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CICLO XXXI

FRICTION MATERIALS FOR BRAKE SYSTEMS:

**ROLE OF THE SINGLE CONSTITUENT PROPERTIES ON THE
TRIBOLOGICAL BEHAVIOUR**

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INTRODUCTION

The aim of each materials scientist is to understand how the history of a material, its processing, influences its structure, and thus materials properties and performance. The understanding of processing-structure-properties relationships is called the materials paradigm¹.

In this thesis, the materials paradigm is relative to the relationships among materials properties and the tribological behaviour, which means the friction and wear features of a material in different conditions: as raw material, in a polymer matrix, or in a composite.

1 – TRIBOLOGY

Tribology is defined as the science and technology of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear.

The word tribology was first reported by Peter Jost (1966) and it is derived from the Greek word “τρίβε ιν” meaning “rubbing” and “λογος” meaning “study of”, so the literal translation would be “the study of rubbing”². Peter Jost coined the word in the eponymous report, which highlighted the cost of friction, wear and corrosion to the UK economy. Since his report, the global impact of friction and wear on energy consumption, economic expenditure and carbon dioxide emissions has attracted major attention. According to some estimates, losses resulting from tribology in the USA amount to about 6% of its gross national product, which means about 420 billion dollars per year³. Approximately one-third of the world’s energy resources in present use appears as friction in one form or another.

In 2017, Kenneth Holmberg and Ali Erdemir⁴ attempted to quantify the impact of tribology worldwide, considering transport, manufacturing, power generation and residential, which are the four main energy consuming sectors. In total, about 23% of the world total energy consumption originates from tribological contacts. The new technologies for friction reduction and wear protection in many fields could potentially reduce the energy losses due to tribological phenomena by 40% in approximately 15 years. On global scale, these savings would amount to 8.7% of the total energy consumption in the long term. Implementing advanced tribological technologies can also reduce CO₂ emissions globally (like 1,460 metric tons of carbon dioxide equivalent), resulting in more than 400,000 million euro cost savings in the short term. Fifty years ago, wear and wear-related failures were a major concern for UK industry and their mitigation was considered the major contributor to potential economic savings. Today, the calculated contribution to cost reduction is about 74% by friction reduction and 26% from better wear protection. Overall, wear appears to be more critical than friction as it may result in catastrophic failures and operational breakdowns that can adversely affect productivity and hence cost. Tribology research ranges from macro to nano scales, in a wide variety of areas. Traditionally, the research fields are the transport and manufacturing sectors, but they have been considerably diversified and can be loosely divided into:

- Classical tribology, concerned with friction and wear in machine elements as well as manufacturing processes
- Biotribology, focused on friction, wear and lubrication in biological systems, like human hip and knee joints
- Green tribology, which aims to minimize the environmental impact of tribological systems along with their entire lifecycle, by reducing tribological losses
- Geotribology, relative to geological systems, such as glaciers and faults

- Nanotribology, field regarding the nanoscopic scale, becoming increasingly important as devices become smaller
- Tribotronics, which aims to integrate active control loops into tribological systems in order to increase machine efficiency and lifetime
- Computational tribology, focused on modelling the behaviour of tribological systems through multiphysics simulations, combining different disciplines
- Space tribology, regarding tribological systems that can operate under the harsh environmental conditions of outer space
- Open system tribology, which studies systems that are exposed to and affected by the natural environment

2 – FRICTION THEORY

Friction is the force resisting the relative motion of solid surfaces, fluid layers, and material elements sliding against each other. When surfaces in contact move relative to each other, the friction between the two surfaces converts kinetic energy into thermal energy, with possibly dramatic consequences.

Friction is not itself a fundamental force, because it arises from a combination of inter-surface adhesion, surface roughness, surface deformation and surface contamination. The complexity of these interactions makes the friction phenomena an example of multivariate system, which necessitates the use of empirical methods for analysis and the development of theory.

The classic laws of sliding friction were discovered by Leonardo da Vinci in 1493⁵, but they remained unknown till 1699 when Guillaume Amontons rediscovered them. He presented the nature of friction through the surface roughness model, based on the supposition that friction corresponds to the work required to lift interlocking asperities over each other during sliding^{6,7}. Based on it, he generated two laws, which can be summarized as the force of friction is directly proportional to the applied load and independent of the geometric (apparent) area of contact. From these laws, the Amontons' formula of frictional force results in:

$$F_f = \mu F_n$$

Where F_f is the frictional force, F_n the normal force and μ the coefficient of friction.

Charles-Augustin de Coulomb (1785) further developed the understanding of friction through investigating the influence of four main factors on friction: the nature of materials in contact and their surface coatings, the extent of the surface area, the normal pressure or load, the length of time that the surfaces remained in contact. He demonstrated that a wide range of materials behave in a manner consistent with the findings of Amontons and developed the so-called third law of friction. This law states that kinetic friction is independent of velocity, but several exceptions were found. Typically, exceptions are found at very low or very high sliding speeds. For instance, at high sliding speeds, the friction level observed can show a gradual decrease as velocity increases.

After other developments, the focus of research during the 20th century has been to understand the physical mechanisms behind friction. Frank Philip Bowden and David Tabor (1950) showed that, at a microscopic level, the actual area of contact between surfaces is a very small fraction of the apparent area⁸. The real area of contact derives from asperities on surfaces and increases with pressure. Due to the reduced area of contact, the applied load is distributed over a few small points, which are under high stress. Thus, even with the lightest loads, the stress at the tips of the asperities is capable of causing the hardest metals to flow plastically. Therefore, the concept of friction based on elastic or reversible deformation processes results not adequate for describing friction.

Bowden and Tabor concluded that metallic asperities undergo plastic flow resulting in the formation of physical junctions between the two bodies. These newly formed junctions were considered the underlying cause of the observed resistance to motion known as friction. Higher loads will force more asperities into contact and thus produce more junctions, increasing the real contact area. To separate two bodies in contact under a given load, a tangential force sufficient to shear all junctions is necessary. Theoretically, if the applied load is large enough and the real area of contact is equal to the apparent area of contact, the friction force would approach the bulk shear properties of the weaker of the two materials, which provides a quantifiable physical limit for frictional processes. In the Bowden and Tabor model, the degree of energy loss is assumed to be the result of plastic deformation of junctions and explains the generation of heat that occurs during sliding motion. An overall conclusion is that friction is a dissipative process requiring constant energy input to continue the relative motion.

Bowden and Tabor also studied abrasion and determined that friction is not limited to adhesive processes, but combines adhesion and abrasive components. Both components are dependent on the load applied to the system, because at higher loads the hard asperities are forced deeper into softer materials increasing the abrasive component of friction.

By the theory of Bowden and Tabor, a formula of friction coefficient can be obtained, starting from the assumption that the real contact area A_r is equal to the ratio between the applied load (L) and the penetration hardness (σ_c) of softer material:

$$A_r = L/\sigma_c$$

This real contact area is formed by all the junctions generated at interface and the force F necessary to shear all of them, which is the frictional force, can be obtained by the formula:

$$F = \tau_c A_r$$

Where τ_c is the yield stress during shear. Combined the two previous formulas in the first Amontons' law, the friction coefficient can be defined as the ratio between the yield stress of shear and the penetration hardness:

$$\mu = \frac{F}{L} = \frac{\tau_c}{\sigma_c}$$

This derivation explains why the friction force is proportional to the load but also why it is independent of the surface area A and of the nature of the surface roughness. Furthermore, it explains why typically μ is about 1 for the sliding of clean surfaces of the same material, due to the fact that the τ_c and σ_c are of similar magnitude and on clean surfaces the friction is practically due just to the adhesive component.

At the start of the 20th century, also study on the atomic-scale origins of friction was developed. Tomlinson proposed a model of friction based on the assumption that the surface was atomically smooth and without any asperity⁹. In this condition, the spacing between the protrusions was represented by the lattice constant. The atoms of the moving body could be in two different positions: between two atoms of the surface or displaced by this position. In the first case, the potential energy is minimized and atoms are stable, while when they are displaced from their equilibrium positions, an unstable configuration is reached until atoms are in a new equilibrium position. The character of atomic-scale friction described is generally named stick-slip¹⁰.

The Frenkel-Kontorova (FK) model is another theory about atomic-scale friction. In this case, the interaction at interface is expressed with sinusoidal periodic potential and the surface atoms are connected by harmonic springs. A weakness of this model is that the connection between the surface atoms and the sliding body is not considered. Thus, a better model is obtained by coupling the two models into the Frenkel-Kontorova-Tomlinson (FKT) model. It describes the effect of commensurability on frictional behaviour. The contribution of each atomic pair to the total frictional

force is maximized in commensurability cases, while in incommensurate ones the contribution of a pair may cancel out among the other pairs, leading to a low frictional force.

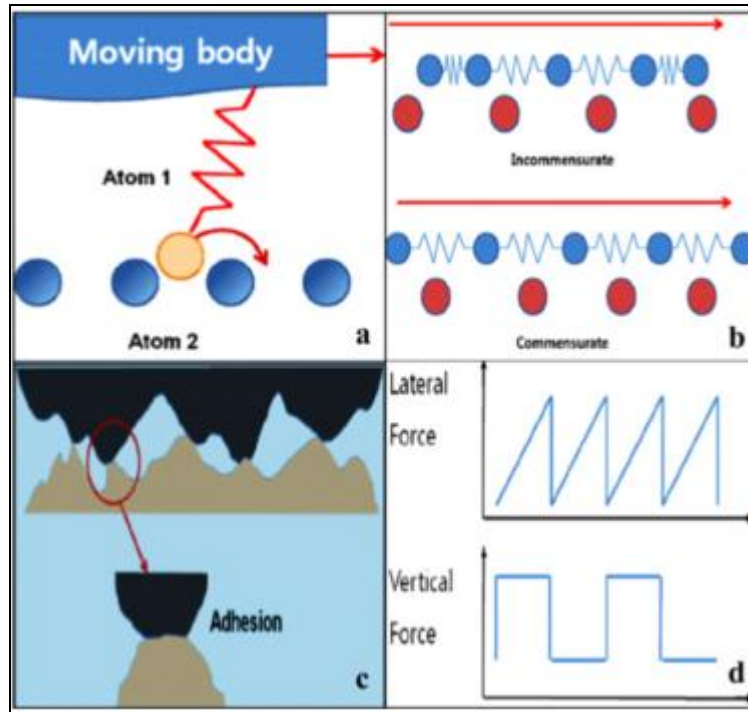


Figure 1: Atomic-scale friction models: a) Tomlinson model; b) Frenkel-Kontorova model; c) Bowden and Tabor model of adhesion; d) Lateral and vertical forces in 2D atomic-scale stick-slip behaviour¹⁰.

According to the Tomlinson model, Xu et al.¹¹ showed that the frequency of the interfacial exciting force is the key factor to energy conversion in a friction process. This force is nearly zero in the equilibrium stage, then it acts on each atom and its effect is integral and uniform. In another stage, especially at the unstable jumping stage, the frequency is very high and the distribution of energy gained by the interfacial atoms is non-uniform. Thus, the excess of energy is transformed to heat and this dissipation of energy is irreversible in a friction process. Subsequent studies showed that the interface atoms excitation increases with increasing applied load¹² and the atomic friction increases logarithmically with the sliding speed¹³. This dependence by velocity is due to thermal activation of the irreversible jumps. Fusco et al.¹⁴ showed that an appreciable velocity dependence of the kinetic friction force in the absence of thermal fluctuations in the stick-slip regime has the form of a power-law.

More studies were performed in order to explain the mechanism of energy dissipation during the friction course and Park et al.¹⁵ introduced three different contributions: phonons, electron-hole pairs, and electronic excitations that decay via emission of electrons or photons. Which process of these excitations represents the best contribution to energy dissipation is still a challenging until now, also because it is affected by several variables, like hardness and surface imperfections.

The adhesion model showed in Figure 1c is the Bowden and Tabor model already explained previously. In this model, the friction comes from the loss of energy due to plastic deformation during relative motion.

3 – WEAR MECHANISMS

Wear is defined as the unwanted removal of solid material from rubbing surfaces. Although its definition is quite simple, the wear process involves several phenomena such as abrasion, corrosion, galling, etc. The problem is complicated because wear is a property of the system, that depends as much on the imposed sliding conditions as on the properties of the materials concerned¹⁶.

Wear is also an important process from an economical point of view, due to the catastrophic consequences, which cause the replacement of the industrial part. However, because of the complicated situation of wear process, any quantitative empirical relation connecting the quantity of wear with the operating parameters such as load, speed and the material constants has been developed to date.

In general, wear is evaluated by the amount of volume lost and the state of the wear surface. The degree of wear is described by wear rate, specific rate or wear coefficient. The wear rate is defined as wear volume per unit distance, while specific wear rate is defined as wear volume per unit distance and unit load¹⁷. Wear coefficient K is defined as the product of specific wear rate and the hardness of the wearing material. In function of the specific wear rate, the distinct type of wear can be identified considering the material nature. For example, for metallic materials in sliding contact, the observed specific wear rates show a wide distribution in the range of 10^{-15} to 10^{-1} mm^3/Nm , depending on materials and friction conditions, as shown in Figure 2.

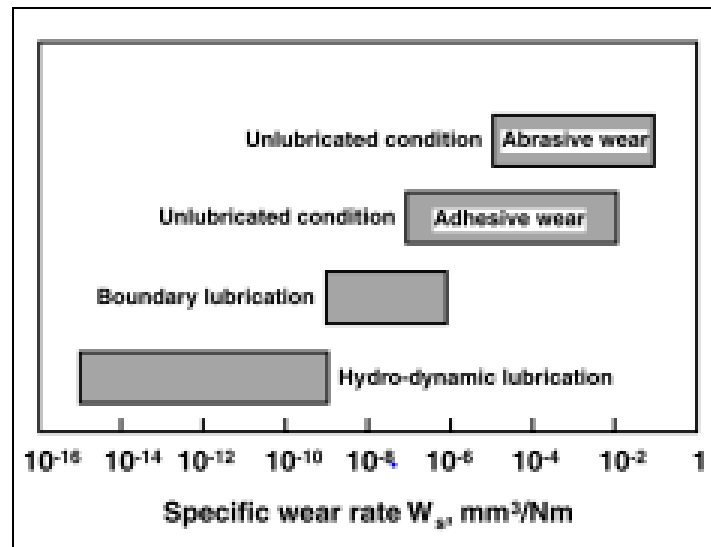


Figure 2: Distribution of specific wear rate of metallic materials in sliding contact under different lubrication conditions¹⁷.

A tribosystem is composed of dynamic, environmental and material parameters, then wear changes drastically even with a small variation in the tribosystem.

The single term wear includes at least four principal quite distinct and independent phenomena, which have in common just their end result of the removal of solid material from the rubbing surfaces. Thus, the following distinct types of wear are generally accepted¹⁷:

- Adhesive or galling wear
- Abrasive and cutting wear
- Surface fatigue
- Corrosive wear
- Thermal wear

Adhesive and abrasive wear modes are generated under plastic contact. In the case of plastic contact between similar materials, the contact interface has adhesive bonding strength and the strong adhesion at the contact interface results in a fracture. In the case of plastic contact between a hard material and a relatively soft one, the harder material penetrates the softer one; thus, the fracture derives from micro-cutting by the indented material thanks to the interlocking contact configuration.

During the running-in state, fatigue fracture is generated after repeated friction cycles. In the case of contact in corrosive media, the tribochemical reaction is accelerated, generating, for example, the oxidative wear of metals in air due to oxygen. Fatigue and corrosive wear can be generated in both plastic and elastic contacts.

Adhesive, abrasive and fatigue wear are generally described as mechanical wear modes, due to the fracture modes, which are fatigue, brittle or ductile fracture generated by mechanically induced strains and stresses. In corrosive wear, the material removal is governed by chemical reactions that are highly activated and accelerated by frictional deformation, frictional heating, micro fracture, and successive removal of reaction products.

The last kind of wear is the thermal one. It happens in two cases: by surface melting caused by frictional heating or by surface cracking caused by thermal stress.

4 – BRAKE PADS

The braking system in an automobile has been considered as one of the key features among the overall performance of the vehicle. The reason for this high interest is its crucial role in various aspects of the total performance such as a stopping distance, pedal feel, induced vibrations and disc wear. Since a single constituent has never been successful for commercial brake friction materials, commercial brake pads are multicomponent composites and important efforts have been given to improve their performance by testing several different formulations.

Asbestos has been used since 1908 when English inventor Herbert Froom came up with a combination of asbestos, brass wire and resins for use as a friction lining¹⁸. Eighty years ago, asbestos fibres start to be used in brake pad formulation, in which act as an ideal component thanks to its outstanding properties, as high heat resistance, mechanical strength, easy manufacture process and low cost. Thus, for several decades, thermosetting phenol formaldehyde resins reinforced with this fibre constitute the basis of brake pads.

Since the 1970s, asbestos had gained widespread acknowledgement as a carcinogen, because its occupational exposure can lead to some lung disease^{19,20}. The asbestos ban in the United States came in 1989¹⁸; thus, the industry has been actively attempting to replace it but it is a very harsh task since no other single material exhibits a similar behaviour in brake pad composites. So in order to solve this issue, other replacement materials have been tested which have at least some of the beneficial properties of asbestos. Therefore, a multitude of different brake pads has sprung on to the market in the post-asbestos brake pad revolution, each with their own unique composition.

4.1 – BRAKING PROCESS

The braking process of any vehicle is the consequence of complex dynamics that depend on many parameters and actors as the vehicle, the road and the driver. It must be easy to stop the vehicle in a quick and reliable way under varying conditions.

The main components, which constitute the brake assembly, are the disc, the calliper and the two pads. The calliper is built up with one or more cylinders and with one piston for each. The pads are located

between the piston and the disc, while they are linked to the calliper by retaining pins, which permit movement of the pads during braking.

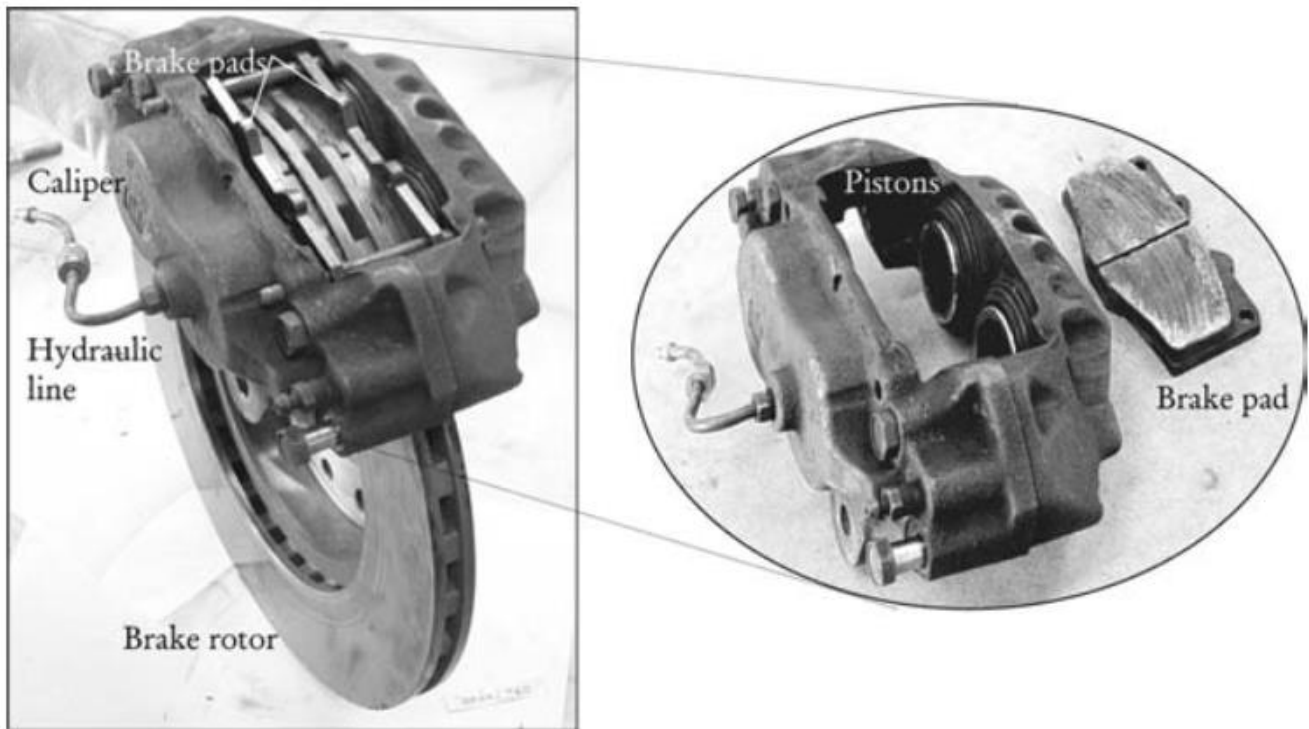


Figure 3: Typical brake calliper and rotor set-up¹⁸.

A movement on the brake pedal forces a piston to move in the master cylinder, which causes a pressure on the liquid ahead of the piston. The liquid is forced under pressure against the calliper moving the pads against the disc. At the end of the braking, after releasing the hydraulic pressure, the calliper pistons come back to their resting position, ready for a new brake application.

Brake pads must maintain a sufficiently high, stable and consistent friction coefficient with the brake disc. Furthermore, pads must not decompose or break down in order to not compromised the friction coefficient at high temperatures^{18,21}.

4.2 – TYPE OF BRAKE PAD

The generic type of friction material commonly used in disc brakes on all classes of modern road vehicles is the “resin-bonded composite” friction material. Within this generic type, three classes are generally considered, namely “non-asbestos organic” (NAO), “low-steel” (LS) and “semi-metallic” (SM). Each class includes many different formulations designed to match the operational duty and requirements specified for particular brakes and vehicles, usually to operate against a cast iron rotor.

NAO friction materials are usually the most expensive, without significant quantities of iron or steel in the formulation. They tend to have lower friction levels, around 0.3-0.4, and superior wear characteristics up to around 220°C. NAO pads are relatively clean in operation and have low noise propensity.

LS friction materials use iron and/or steel in the formulation, which led to higher friction levels than NAO materials, around 0.35-0.5. They have good fade and high-speed performance, but noise

propensity tends to be higher. Respect NAO pads, LS friction materials are not so clean in operation and have lower wear characteristics.

SM friction materials are generally simpler formulations compared with NAO and LS and have a metal content of up to 40% by weight. These friction materials have the lowest cost of the three classes and tend to have low friction levels (0.25-0.35). They show high wear at high speed and low temperatures, while wear and fade performance are better at higher temperatures.

Other generic types of automotive friction materials are specially designed to operate against different rotor materials. Some examples are:

- Sintered: formulated and manufactured using powder metallurgy technology, used in motorcycle disc brake pads
- Ceramic: used for very high-duty applications, they provide stable high friction, but they are expensive and require specialist rotor materials
- Carbon: expensive and sensitive to temperature and humidity, they are carbon fibre composites that operate against a rotor of a similar material, used in F1 racing cars and aircraft

4.3 – BRAKE PAD COMPOSITION

Brake pads typically comprise four categories of materials: reinforcing fibres, binders, fillers and frictional additives.

The purpose of reinforcing fibres is to provide mechanical strength to the friction material. Nowadays, the reinforcing fibres used are of different nature, like glass, aramid, potassium titanate, sepiolite, etc. Glass fibres are suitable as reinforcing fibres thanks to their thermal resilience. Metallic chips or granules are commonly used as reinforcing fibres and examples include steel, brass and copper. A significant advantage of using metal fibres concerns their high thermal conductivities, able to remove heat from the frictional surfaces very quickly. Aramid fibres such as Kevlar fibres are also widely used. They are very light and exhibit excellent thermal stability, with a very good stiffness-weight ratio. Aramid fibres in pulp form have also been utilized in maintaining the uniformity of the brake pad material mixture during the processing of a moulded brake pad. Furthermore, they show superior wear resistance. Potassium titanate fibres are prepared from highly refined, single crystals, but they have the potential to cause mesothelioma, like asbestos. For this reason, they are not commonly used in form of fibres, but with other morphology as filler. Sepiolite is a hydrated magnesium silicate mineral with a fibrous chain-structure. It has excellent sorptive properties in water and is stable at high-temperature. However, sepiolite is a potential health hazard, because it is associated with the development of inflammation in lung and pulmonary interstitial fibrosis. Ceramic fibres are typically made of various metal oxides such as alumina or silicon carbide. With a high thermal resistance, lightweight and high strength, they are very suitable as reinforcing fibres.

The purpose of a binder is to hold the components together and to prevent the brake pads constituents from crumbling apart. The choice of binders is an important issue because a high heat resistance is required. For this reason, epoxy and silicone modified resins would generally be ideal as the binder for most braking applications. However, the most common resin binder used is the phenolic resin, a type of polymer formed by a condensation reaction between phenol and formaldehyde, able to act as a matrix for binding together different substrates.

The fillers in a brake pad are present for improving its manufacturability as well as to reduce the overall cost of the final product. Usually, materials used in a large proportion are named fillers regardless of their effect. For example, metal silicates are used in a large proportion in some formulations and named fillers instead of abrasives. Fillers can be divided into two main classes: organic and inorganic. Typical inorganic fillers include barium sulphate, mica, vermiculite and calcium

carbonate. All of them possess a relatively high melting point, giving heat stability to the brake friction material, at the same time aiding the friction characteristic. Examples of organic fillers are cashew dust and rubber in form of dust. Both have similar properties, usually incorporated into brake pads to reduce brake noises due to their superior viscoelastic characteristics.

The last category is the most complex one because frictional additives are components added to brake pad in order to modify the friction coefficients as well as the wear rates. They are divided into two main categories in function of their effect on friction and wear: lubricants, which decrease both friction and wear, and abrasives, which instead increase friction and wear. The main purpose of a lubricant is to stabilize the friction coefficient during braking, particularly at high temperatures. Commonly used lubricants include graphite and various metal sulphides. A positive effect of abrasives is the removal of iron oxides from the counter face as well as other undesirable surface films formed during braking. A brake pad with higher abrasive content exhibits a greater variation of friction coefficient, resulting in instability. Examples of abrasives are hard particles of metal oxides and silicates, as zirconium oxide and zirconium silicate, aluminium oxide and chromium oxide.

For each category, the comprehension of the influence of single constituents on tribological behaviour of brake pad is still the main problem for manufacturers. This is because friction and wear properties can be affected by morphology, particle size, nature and structure of the material, surface roughness, etc. So, although several studies have been performed about how to select and evaluate the role of the raw material in the friction process²², it has been impossible to obtain a reliable predictive model of friction and wear to date²³. Thus, the selection of the different mixture components and their relative amounts has been largely relied on experience and on trial and error approach.

AIM OF THE WORK

Due to the importance of brake pads as safety devices in the machines, the selection of friction materials to use in a formulation is the most important aspect in brake pads industry. The selection of the different mixture components and their relative amounts has been largely relied on experience. In fact, systematic studies of the friction materials for optimum brake pad performance are difficult to found in literature, due to the system complexity.

Nowadays, thousands of ingredients can be used in brake pad formulation, but most ingredients were selected using a trial and error approach for some specific purposes. A well-known example is the replacement of asbestos, used for over 70 years, which has been obtained with the same trial and error process²⁴⁻²⁶. There are many properties attributable to asbestos, which have an important role both for final product performance and for friction materials manufacture. Unfortunately, a material that possesses all the advantageous properties of asbestos without health risk has been never found. Therefore, to meet the requirements for the safety of driving a vehicle and to be economically competitive in the market, different materials have been selected to replace asbestos and the number of components increased from less than 10 up to 20.

The system complexity generated by this replacement led to different methods in literature, devoted to obtain a systematic study of brake pad formulation: comparison of similar formulation^{25,27,28}, combinatorial approach^{22,29}, chemometrical approach^{30,31}, etc. As reported by C.F. Tang et al.²², several studies have been performed about how to select and evaluate raw materials role in the friction process. However, although many studies have led to clarifying some phenomena occurring at interface in the brake system, it has been impossible to obtain a reliable predictive model of friction and wear to date, as affirmed by M. Renouf et al.²³.

In the past literature on friction, Lancaster was the first (to our knowledge) to suggest the necessity of a complete characterization of each component in order to understand the phenomena occurring in a composite, (in his case environmental effects in composite wear)³². Kato et al.³³ published a first tentative and a new approach regarding the study of raw materials used in brake pad formulation. They focused the attention on the major component of the third body generated at interface, iron oxide Fe_3O_4 , in order to investigate the severe-mild wear transition occurring at metals interface. The most interesting contribution derived from this article is the use of pin-on-disc wear test as method, in which a stationary, loaded pin rubs against a rotating disc. Österle et al.³⁴ applied the same modified pin-on-disc test to determine tribological properties of typical brake pad constituents, focusing the attention on tribolayer characterization. Rodrigues et al.^{35,36} employed this method to investigate the effect of copper particles as an interfacial media on the friction coefficient of steel against steel and on tribofilm formation with powder supply. Unfortunately, this approach cannot explain completely the tribological and physicochemical behaviour of a raw material in a polymer matrix. Furthermore, the literature cited does not consider the selection of a raw material among itself family, for example how to select the correct graphite for a specific formulation.

To overcome these issues, this work is devoted to the understanding of the single constituent effect on the tribological behaviour of brake pad, going through three steps. First, in order to study the influence of material's properties on tribological behaviour, systems of raw materials belonging to the same family were characterized, focusing the attention on the generation of a tribological and physicochemical selection method. Systems of lubricants, abrasives, and fillers were selected in agreement with the industrial partner based on its commercial interest. The materials selected and the characterization methods are fully described in the *Materials and methods* chapter.

Then, the second step is devoted to study the effect of raw material on the tribological behaviour of the composite (polymer matrix). The basic mix is composed of phenol formaldehyde resin, the whole

material binder, and aramid fibres in order to give a sufficient mechanical strength to the sample. An investigation on the basic mix tribological behaviour was done to compare it with mono-filler systems. Basic mix and one filler, which content is equal to 50% v/v, compose them. In the *Materials and methods* chapter, the characterization method applied at the basic mix and mono-filler systems is fully described. The results on raw materials and composites are presented by material type, one chapter for each family.

The third step is aimed at the study of the tribological behaviour of a complete brake pad formulation, in which just one filler at time is changed. For this purpose, a series of carbon materials, widely characterized in the first two parts of the thesis, was selected to build a formulation with approximately 6% v/v of carbon-based filler. Each sample was tested by a dynamometer, an instrument simulating braking at different conditions, used in industry as a preliminary test on new formulations. This test is fully described in *Materials and methods* chapter and led to compare the samples' tribological behaviour and to collect information on wear particles generated during the test. In this way, it is possible to obtain information on the amount and composition of wear particles, responsible to some extent for air pollution^{37,38}.

CAP. 1 - MATERIALS AND METHODS

1.1 – COMMERCIAL POWDERS

As mentioned in the introduction, the ingredients of brake pads are classified in the inorganic filler, metallic or inorganic reinforcing fibre, friction modifiers^{18,39}. The main industrial interest is focused on this last category, which includes lubricants and abrasives. Both affect not only the friction coefficient, but also other important performance properties, like noise, pollution, wear resistance, etc.

Apart from the category, the effect of each constituent on materials properties is often unclear. For this reason, in order to study the influence of material's properties on tribological behaviour, systems of raw materials belonging to the same family were characterized. Systems of lubricants, abrasives and fillers were selected based on the commercial interest of the industrial partner, following these criteria:

- the composition of each material belonging to a family must be the same or at least as more similar as possible
- the number of materials selected for each family must be minimum 5 to consider the study systematic
- each material must show different shape and size respect to the other family materials, in order to investigate the morphology effect

1.1.1 – CARBON MATERIALS

Carbon materials have been extensively studied in optics, electrochemistry, mechanics and tribology for several decades owing to a wide variety of their morphologies, good corrosion resistance, excellent mechanical behaviours and high thermal conductivity⁴⁰. Carbon is polymorphic: it exists in three forms known as diamond, graphite and fullerenes⁴¹. The hybridization of carbon bonds, sp^3 in diamond and sp^2 in graphite, is the main difference. Diamond shows a three-dimensional crystal structure and graphite shows carbon layers stacked in an AB sequence, linked by a weak Van der Waals interaction produced by a delocalized π -orbital. The carbon layers in graphite are known as graphene layers⁴¹.

Graphite is widely used as a solid lubricant in the majority of friction composites^{32,42,43}. Its low friction coefficient is due to the highly anisotropic, layered crystalline structure, which has strong bonding within the basal planes, but weak bonding between them⁴⁴. This characteristic allows the formation of a lubricant layer that ensures a stable friction coefficient.

However, the lubricity of graphite is not an intrinsic property, but derives from the presence of certain gases and vapours in the environment. Water, O_2 and CO_2 could enter into the graphite lattice and reduce the binding strength between basal planes. In absence of these gases, graphite would exhibit high friction and wear behaviour⁴⁵.

The graphite used in brake friction materials can be of natural or synthetic origin, but it cannot be used too liberally in phenolic resins because the bonding strength between graphite and phenolic resin is very weak, leading to low shear strengths. In nature, it is possible to find flake graphite, highly graphitized, and amorphous graphite that contains less carbon depending upon the source. Synthetic one is obtained from calcined petroleum coke by heating to very high temperatures like $3000^\circ C$ ⁴⁶. Graphite content affects the heat conductivity of the pad. A quick heat dissipation is a desirable characteristic, but it could result in a temperature increase of the hydraulic braking fluid: when the temperature reaches its boiling point, failure of the braking application system will occur⁴⁷⁻⁴⁹.

In this project, the tribological properties of a system of carbon materials were investigated: two natural graphite, two synthetic graphite, a graphitized coke, a calcined coke, carbon black and three graphene samples were selected according to ITT formulators input. The description of their physicochemical and tribological properties is reported in Chapter 4.

1.1.2 – TITANATES

Alkali-metal titanates, $A_2Ti_nO_{2n+1}$ ($n = 3-8$), are of great interest for the possible applications as photocatalysts, fuel cell electrolytes and cation exchanger⁵⁰⁻⁵³. Their chemical and physical properties depend on the reactants and the preparation method⁵⁴. Usually, titanium oxide and alkaline carbonate are used as the raw materials to synthesize titanates with different methods, including calcinations, flux growth, melt reaction and slow cooling calcinations^{52,55,56}.

All titanates have a monoclinic structure with almost the same b value. A high alkali-metal content ($n = 3-4$) results in a structure formed by $(Ti_3O_7)^{2-}$ layers held together by alkali-metal ions. They are preferred as cation exchangers and catalysts because of their distinctive intercalation ability and catalytic activity. In the case of low alkali-metal content ($n = 6,7,8$) the structure shows a tunnel shape and exhibits high insulating ability and chemical stability⁵⁷.

Among these materials, potassium hexatitanate $K_2Ti_6O_{13}$ is a good candidate for whisker-reinforced metals and plastics. It has been proved to be a suitable substitute for asbestos, years before their phasing out⁵⁸, and it has the advantage of lower cost with respect to other ceramic whiskers. The addition of potassium hexatitanate in composite formulation showed an increase in thermal and wear resistance, suggesting also its potential as an additive in brake pad formulations⁵⁹⁻⁶¹.

In order to understand the tribological properties of $K_2Ti_6O_{13}$, a system of nine titanates was studied. Each sample showed the same crystallographic structure, with some differences in structure parameters, particle size distribution, and morphological features. In Chapter 5 they are fully described.

1.1.3 – ALUMINA

Alumina is popular for a variety of applications, because of its unique catalytic, adsorption, optical and electronic properties. Regarding them, the control of physicochemical properties of this material is the key topic of ongoing research. Aluminium oxide is widely used in the chemical process industry, due to the variety of surface properties, or in the advanced and traditional ceramic industries, due to the remarkable thermal, mechanical, and chemical properties of the α -alumina structure. Aluminium oxide is also well known as reinforced ingredients in composites, due to its effect of increase mechanical properties of the polymer and non-polymer matrix⁶²⁻⁶⁴.

The first commercial method of aluminium oxide production began in 1887 when Bayer developed a three-step process for converting bauxite into aluminium oxide. The method outlined in Bayer's patents consists in these steps:

- digestion of bauxite in a strong alkaline solution under elevated temperature and pressure
- impurities precipitation and removal, resulting in a highly alkaline solution of aluminium hydroxide
- cooling, with consequent alumina trihydrate precipitation
- filtration, washing and calcination of trihydrate alumina

In this last step of calcination, the particles undergo phase transitions and take on various forms. The most thermodynamically stable is alpha-alumina, which forms when the calcination temperature exceeds 1000°C.

In pads formulations, aluminium oxide is used for its abrasive properties, then belonging to the family of friction modifiers. Typically a commercial friction material contains 1-8 %vol of abrasives, while the size ranges and the type selection is mainly determined by the manufacturer's experience⁶⁴. The purpose of abrasive is to clean the disc surface by removing iron oxides and pyrolyzed film, but the possibility of scratching the disc can lead to some unwanted phenomena, such as unstable friction coefficient, squealing noise, etc. Thus, the selection of a proper kind of abrasive in terms of size, shape and amount is extremely important.

Six alumina samples were selected in this thesis: the main crystallographic phase is α -alumina, with the addition of other crystallographic structures in some samples (considered as impurities). Then, in this system, crystallographic phase is a further variable affecting the friction and wear features.

1.2 – COMPOSITE MATERIALS

As described in the *Aim of the work* section, the second step of this thesis is devoted to study the effect of the raw material on the tribological behaviour of the composite.

The formulation of this composite is 50%vol of polymer matrix, 50%vol of one filler at a time. The so prepared composite are named “mono-filler” and the polymer matrix “basic mix”. In literature, some studies about mono- and multiple-filler composites are present, aimed at investigating the tribological behaviour arising from the possible interactions among all the constituents^{22,29}. Differently, the purpose of this work is to investigate the single effect of a brake pad constituent and to develop a selection method for a family of materials. For this reason, the study was limited to mono-filler composites.

The third step of this thesis is aimed at studying the effect of a single raw material on the tribological behaviour of a complete formulation that is a real brake pad. In order to compare a system of raw materials, a new formulation was developed by ITT formulators. This kind of brake pad is a NAO type (Non-Asbestos Organic pad) in which there is a low content of metallic constituents. The preparation method and the composition of brake pad are reported in section 1.2.3 - *Real Brake Pads*.

1.2.1 – BASIC MIX

The basic mix is composed of phenol formaldehyde resin, the whole material binder, and aramid fibres, providing a sufficient mechanical strength to the sample.

The phenol formaldehyde resin selected in this project (Figure 1.1) is phosphorous and boron modified (as declared from the supplier).

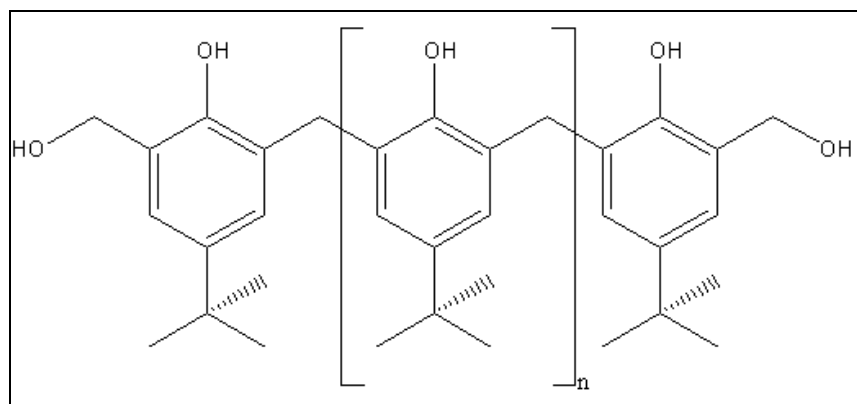


Figure 1.1: Chemical structure of the phenolic resin.

Main data on this raw material (from supplier and ITT characterization) are summarized in Table 1.1.

Table 1.1: Data form for phenolic resin raw material.

Density	Granulometry	Humidity content	Volatile part
1.25 g/cm ³	D50 = 33 μm	2-3 % wt	0-6 % wt

The vast majority of friction material manufacturers around the world universally accepts phenolic resins as the binder of choice. Its prominence derives from the innate benefits and desirable attributes of phenolic resins. Many commercial phenolic resins can be tuned by a number of different modification methods, and either by chemical or physical means, which permits further enhancement of selected properties. Modifiers can be added to improve properties of the final product.

The reactions that produce phenolic resins can be considered as a reaction between phenol and formaldehyde. The products of these reactions are classified as either resole or novolak resins depending on the concentration of each reagent and type of catalyst employed. Nowadays, they are classified also as “one-step” and “two-step” resins respectively: the one-step resole required only heat to cure, but the two-step novolak required additional curing agents and heat to fully cure.

Formaldehyde reacts with phenol through a condensation reaction in the presence of a catalyst to form methylene bridges producing water. Further reactions between the dimeric intermediates will form more bridges, ultimately leading to the formation of a rigid three-dimensional network that gives phenolic resins the desired strength and thermal resistance that makes them ideally suited for use in friction applications.

The resole resin is produced by reacting phenol with an excess of formaldehyde in basic conditions. The resole reaction is referred to as the Lederer-Manasse reaction (Figure 1.2) and begins by adding a suitable base such as sodium hydroxide to a reactor charged with phenol. The base abstracts a hydrogen atom from the hydroxyl portion of phenol, forming water and a negatively charged phenolate ion. This negative charge on the oxygen atom of the phenol molecule alters the electron configuration of the benzene ring and allows formaldehyde to attack the benzene ring, liberating a hydrogen ion and forming a hydroxymethyl group on the ring at the ortho or para position. The phenolate ion then reacts with water, removes a hydrogen atom to convert the phenolate ion into phenol, and reforms basic ions to continue catalysis of subsequent reactions.

Unlike resole resins, novolak resins are produced from an acid catalysed reaction where phenol is used in excess relative to the concentration of formaldehyde (Figure 1.2). Novolak resins are not thermosetting, but are actually thermoplastic in nature, because of the low formaldehyde concentration. Its thermoplastic nature is due to limitations in the number of methylene bridges formed during the reaction, which does not allow the formation of a permanent rigid network.

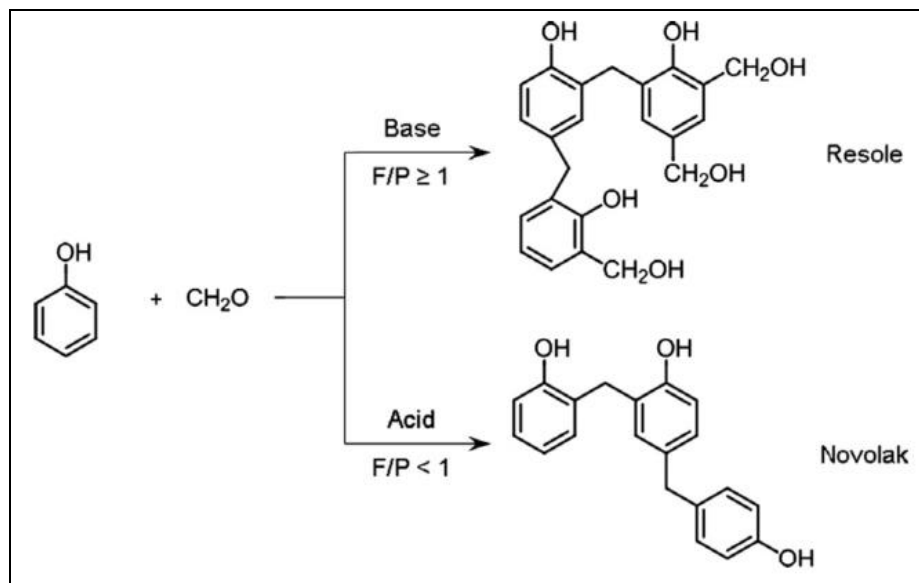


Figure 1.2: Reactions relative on resole and novolak resins⁶⁵.

To convert a novolak resin into a thermosetting resin, an additional ingredient such as hexamethylenetetramine (HMTA) must be used. This additive will promote the formation of additional linkages to form the rigid 3D polymeric network (Figure 1.3). The first step of the curing reaction occurs within a short time (around 2 minutes) at around 150°C. The second reaction is called post-curing process and consists in 3D crosslinks of the structure. Contrary to the first step, this second process takes several hours and occurs at temperature up to 200°C.

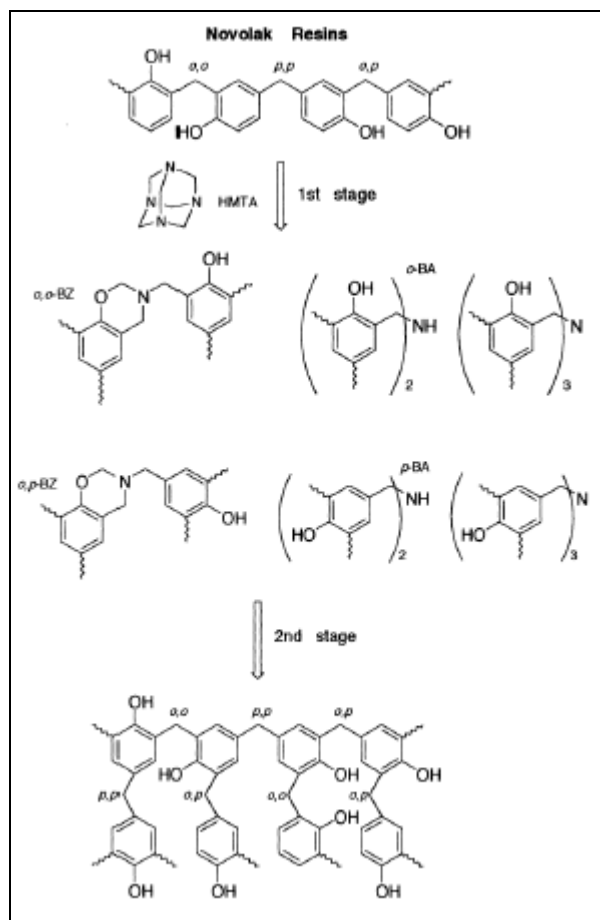


Figure 1.3: Crosslinking reaction of phenolic resin with HMTA⁶⁶.

Traditionally, the success of phenolic resin over other materials is based on its intrinsically superior heat resistance. However, several vehicle platforms have emerged that are exceeding the limits of conventional phenolic resins and their brake systems promote rapid oxidation of the binder during braking. This can lead to a host of potential concerns such as wear and loss of frictional output in the form of brake fade.

The process of oxidation is a critical aspect in wear processes and is a form of chemical wear^{67,68}. The heat of braking generates thermal effects that, when combined with operation in an oxygen-rich atmosphere, lead to thermo-oxidative degradation of the polymeric matrix. A proposed mechanism for the degradation of phenolic polymer systems begins with oxidation of the methylene bridges, which generates peroxide. This can subsequently convert into a carbonyl functional group due to heat, forming the structural analogue of benzophenone. Additional reactions with oxygen at the carbonyl group result in the destruction of the methylene bridges by scission of this carbonyl group. All this process results in the formation of carbon oxides and produces a carbon-rich char structure.

The oxidation process can be affected by a chemical modification, which could improve the oxidation resistance of resin. However, in friction composite other materials can affect the oxidation process also in a negative way. For example, pure metallic additives such as copper or iron have a catalytic effect and accelerate the process of oxidation.

An aramid pulp with a fibrillary structure was selected (Figure 1.4), named Kevlar® fibres. They are the most used fibres belonging to the reinforcing fibres category.

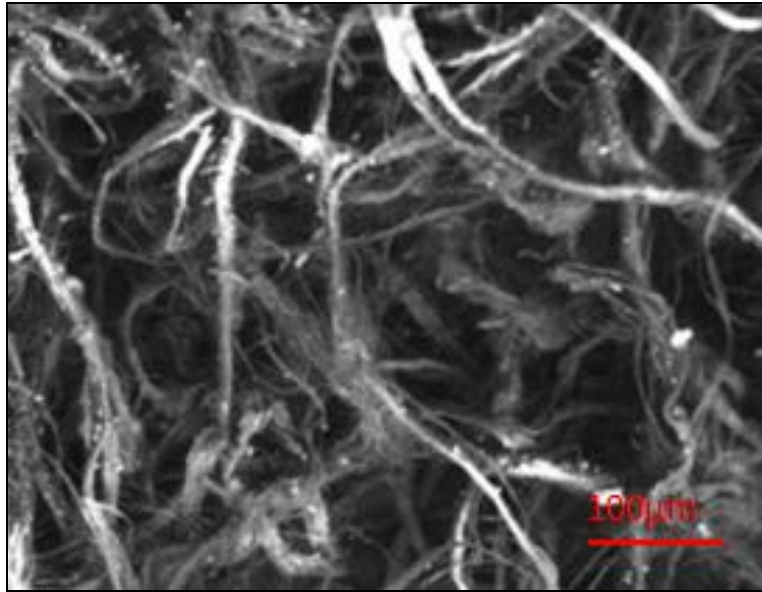


Figure 1.4: SEM picture of aramid fibre (backscattered electrons) supplied by ITT

Table 1.2 summarizes the data on Kevlar® fibres, obtained from supplier ITT.

Table 1.2: Data form for aramid pulp raw material.

Absorbed moisture	5-8%
Density	1.44 g/cm ³
Thermal conductivity	0.04-0.05 W/K*m
Thermal expansion coefficient	-3.5*10 ⁻⁶ 1/K
Tensile strength	2500 MPa
Elongation	2-3%
BET	7-15 m ² /g
Fibre length	0.75-1.30 mm
Granulometry	D50 = 1 mm
Volatile part	4-10% wt

The amount of aramid fibres dispersed in the phenolic resin was 30%wt, corresponding to 27.1%vol. This amount was selected according to the PhD thesis of Eng. Vivier Florence, who investigated the synergetic effects of simplified friction materials (mono- and multiple-filler of eight raw materials)⁶⁶. Also S.K. Sinha and S.K. Biswas studies, dealing with the friction and wear behaviour of phenolic resin and Kevlar® fibres composite, reported this amount as the optimal value^{69,70}.

Due to its crystal structure, Kevlar® presents high anisotropic properties with strong covalent bonds in the fibre direction and a weak bonding (H-bonding) in the transverse direction. It is obtained by the condensation of m- or p-phenylenediamine and isophthalic or terephthalic acids⁷¹ (Figure 1.5).

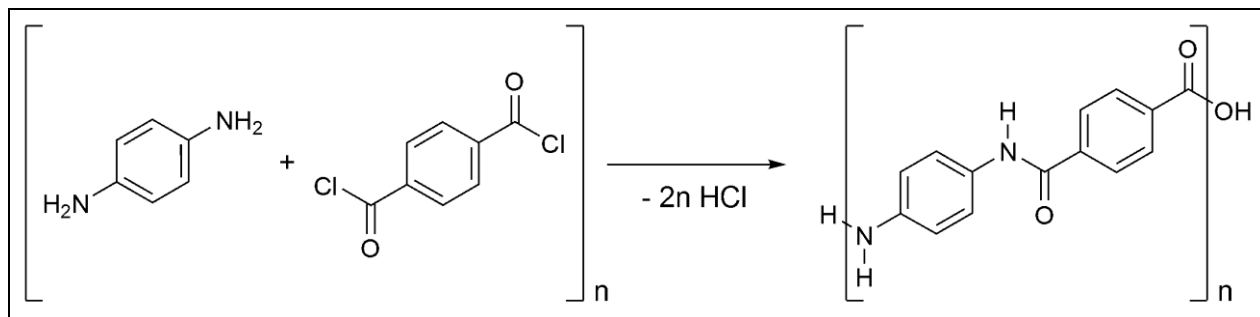


Figure 1.5: Direct synthesis of Kevlar fibres.

Aramid pulp/fibre has attracted interest in friction material field thanks to its ability of filler retention and of improving tribological properties. In fact, according to the literature, aramid fibres lead to a higher friction coefficient in a wide range of temperatures and improve the wear resistance⁷². They exhibit excellent thermal stability and possess a very low weight, which makes them better than their historical concurrent asbestos relative to anti-fade properties⁷³.

The fibres concentration influences remarkably and beneficially all properties of composites, but not linearly⁷⁴. Furthermore, also the aspect ratio of aramid fibres affects tribological and mechanical properties. For example, with an increase in aspect ratio of fibre, the flexural strength of composites generally increased and the compressive strength decreased⁷⁵.

Aramid fibres have a very low weight and exhibit excellent thermal stability. Furthermore, they exhibit better anti-fade properties than their historical concurrent asbestos⁷³.

As thermal properties investigated in a previous study⁶⁶, aramid fibres show a complex depolymerisation, random rupture, hydrolysis, restructuring and other chemical reactions occur for Kevlar fibres in the temperature range 400-600°C.

About the basic mix, its thermal properties were characterized in previous PhD project⁶⁶. The DSC measurement reports an endothermic peak at around 125°C due to water evaporation and the 1st glass transition temperature at 190°C. This T_g value results higher than the value measured on the phenolic cured resin, equal to 140°C, due to the complex 3D network created by aramid fibres. The 3D network contributes to the mechanical integrity and decreases the polymer chains mobility, which significantly increases the glass transition of the basic mix.

As last characterization on the basic mix in the previous study, a wear test was performed using an alumina sphere and applying 10N as load and 0.25 ms⁻¹ as speed. In this condition, the basic mix shows a friction coefficient of 0.32 and a wear constant (K) of 1.18*10⁴ μm³/Nm.

1.2.2 – COMPOSITE PREPARATION

For each specific family, composites were prepared changing one filler at time. As stated before, each composite is made of 50%vol of basic mix and 50%vol of filler. The basic mix is constituted by 72.9%vol of phenolic resin and 27.1%vol of Kevlar® fibres.

In order to get closer to real friction materials, the composites were produced by friction material press used in the prototype area of ITT, using the same protocol set up applied in the PhD project of Eng. Vivier⁶⁶.

For each composite, a blend of 4kg was mixed in an 8L capacity Eirich R02E mixer for 15 minutes. This mixing procedure is necessary to disperse efficiently aramid fibres, then obtaining a homogeneous mixture.

The second step is the pressing phase, using a die of circular shape with 90 mm of diameter. It consists of 5 cycles at 150 kg/cm² as load and 150°C as temperature. Each cycle is divided into 13 minutes of pressing followed by 15 minutes of outgassing. At the end of the cycles, other 60 minutes of pressing are applied. This procedure is necessary to obtain a polymerisation process, also known as press-cure of the phenolic resin. During this step, the condensation reaction of resin occurs and generates water that must be allowed to escape as vapour. For this reason, a moulding cycle is applied, with the outgassing time.

However, the rate of polymerisation is exponentially related to temperature. The processing temperature must be equal to or higher than 250°C to have a rapid cure⁷⁶. However, it is not possible to increase too much the curing temperature because friction material is a poor heat conductor and could be degraded at high temperature. To overcome this issue and complete the polymerisation, a third step was applied. A heating cycle in an oven was set up, with a heating ramp of 15 minutes to rise 160°C of temperature, and 60 minutes at a constant temperature, as reported in Figure 1.6. At the end of the heating cycle, samples were cooled at room temperature.

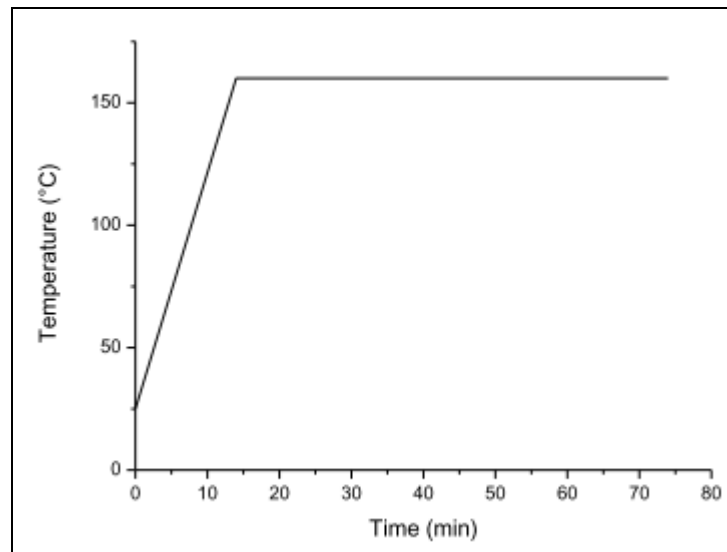


Figure 1.6: Heating cycle in oven applied to samples

In order to test composites by tribometer, all samples were cut into square pieces of 2 cm side. The thickness of each sample is variable, in function of the amount of mixture used during the press-cure procedure by ITT workers. As an average range, the thickness is 7-13 mm.

The tribological characterization is described in section 1.3.4.

1.2.3 – REAL BRAKE PADS

As described in the Introduction, the real brake pads are classified into three categories: metallic, semi-metallic, and non-asbestos organic. However, the general composition is always the same: binder, abrasives, lubricants, fillers, and reinforcing fibres.

In this case, a non-asbestos organic (NAO) formulation was selected, according to the basic mix used for the monocomponent preparation.

The investigation was restricted to carbon family as fillers, which are among the most studied materials for friction applications. Thus, a system of eight formulations was generated and the relative brake pads were produced by ITT with the same industrial lining used for commercial pads. The exact composition

of the pad is omitted for confidentiality reasons. Such omission does not affect at all the aim of the thesis, since the overall composition, except the carbon, can be considered as a material constant.

1.3 – CHARACTERIZATION METHODS

The characterization method is constituted of the following sections: study of morphological and surface properties; investigation of structure and physical features, functional group and amorphous content; tribological characterization.

As described previously, many variables influence the friction and wear phenomena. Tribological behaviour could be considered a multivariate problem and to disentangle its complexity, one variable at time (OVAT) approach is not suitable. Instead, a multivariate study could lead to understand the synergetic effect of variables. For this reason, all the data collected were treated through statistical and chemometrical methods, fully described in section 1.3.3.

1.3.1 – MORPHOLOGICAL AND SURFACE CHARACTERIZATION

Data from literature and industrial formulators affirm that particles having the same nature, but different shape and size, can show different tribological behaviour. Studies about the effect of particle size^{77–79} are not restricted to brake pad application, for which a clear understanding is still missing.

Raw materials widely used in this field present a large size distribution and irregular shape, then a systematic study aimed at correlating the influence on these variables on friction and wear properties is still missing, to the writer knowledge. Since now, few studies have been published on the effect of shape^{80–83}, but regarding materials synthesized and selected for their particular morphology, with a very low distribution.

1.3.1.1 – SCANNING ELECTRON MICROSCOPY

Morphological features were investigated by Scanning Electron Microscopy (SEM), using a ZEISS EVO 50 XVP with LaB₆ source, in high vacuum, collecting secondary electrons (SEs). The potential difference used is equal to 10 keV for all the pictures and the working distance is maintained at 8.5 mm since it is the optimal distance for obtaining information on elemental composition in this instrument. The instrument is equipped with detectors for secondary and backscattered electrons collection and Energy Dispersion Spectroscopy (EDS) probe for elemental analysis. EDS instrument is an INCA of Oxford Instruments, with a 10 mm² sensor.

1.3.1.1.1 – HISTORY OF SCANNING ELECTRON MICROSCOPY

The history of electron microscopy began in 1926 when Busch studied the trajectories of charged particles in axially symmetric electric and magnetic fields⁸⁴. He showed that such fields could act as particle lenses, laying the foundations of geometrical electron optics. Nearly at the same time, de Broglie introduced the concept of corpuscle waves. The wave electron optics began by the association of a frequency and hence a wavelength with charged particles.

The invention of the electron microscope occurred in 1931 by Max Knoll and Ernst Ruska at the Berlin Technische Hochschule. Their work resulted in the construction of the first transmission electron microscope (TEM). This invention finally overcame the barrier to a higher resolution that had been imposed by the limitations of visible light. By the late 1930s electron microscopes with theoretical

resolutions of 10 nm were produced and by 1944 the resolution was further reduced to 2 nm. Knoll built a first scanning microscope (SEM) in 1935, but the first true SEM was described and developed in 1942 by Zworykin, who showed that secondary electrons provided topographic contrast by biasing the collector positively relative to the specimen. He reached a resolution of 50 nm using an electron multiplier tube as a preamplifier of the secondary electrons emission current. The resolution was still considered low in comparison with TEM; however, many scientists and technologists recognised the SEM ability to study surfaces of specimens. This interest leads to an important development of scanning electron microscopy. In particular, Smith in 1956 showed that signal processing could be used to improve micrographs introducing nonlinear signal amplification. He was also the first to insert a stigmator in the SEM to correct lens cylindrical imperfections. In 1960, Everhart and Thornley created a new detector to improve the secondary electron detection with a positively biased grid to collect electrons, a scintillator to convert them to light, and a light-pipe to transfer the light directly to a photomultiplier tube. This detector is commonly known as the Everhart-Thornley detector (ETD). Pease and Nixon, who combined all the improvements in one instrument, made the prototype for the first commercial SEM (developed in 1965) in 1963: the SEM V with three magnetic lenses and an ETD. The SEMs used today are not very different from this first instrument. Their resolution is of the order of 2 nm, while the transmission electron microscope has a resolution of approximately 0.1 nm.

1.3.1.1.2 – THEORY OF SCANNING ELECTRON MICROSCOPY

A scanning electron microscope produces images of a sample by scanning the surface with a focused beam of electrons. In most cases when an incident electron strikes the specimen surface, instead of being bounced off immediately, the energetic electrons penetrate into the sample. In doing so, the primary electron beam produces a region of primary excitation with a size and shape largely dependent upon the beam electron energy, the atomic number and the density of the specimen. The volume and depth of penetration increase with an increase of the beam energy and fall with the increasing specimen atomic number. The use of a high accelerating voltage will result in deep penetration length and a large primary excitation region, but will cause the loss of detailed surface information of the samples.

The electrons interact with atoms in the specimen, producing various signals that contain information about the sample's surface topography and composition. Generally, it is possible to divide these interactions into two major categories: elastic and inelastic interactions.

Elastic scattering results from the deflection of the incident electron by the specimen atomic nucleus or by outer shell electrons of similar energy. In this interaction, there is a negligible energy loss during the collision and a wide-angle directional change of the scattered electron. The so-called back-scattered electrons (BSE) are incident electrons elastically scattered through an angle of more than 90° and provide a useful signal for imaging the sample. Elements with higher atomic numbers have more charges that are positive on the nucleus and as a result, more electrons are back scattered. Because BSEs have a large energy, which prevents them to be absorbed by the sample, the region of the specimen from which BSEs are produced is larger than the SE one. For this reason, the lateral resolution of a BSE image is considerably worse (1.0 µm) than it is for a secondary electron image (10 nm). The detector for BSEs differs from that used for SE because it has a biased Faraday cage not employed to attract the electrons, but biased negatively to repel any SE from reaching the detector. In this way, only those electrons that travel in a straight path from the specimen to the detector go toward forming the back-scattered image.

Inelastic scattering derives from a variety of interactions between the incident electrons and the electrons and atoms of the sample. It results in an energy transfer to the atom and the amount of energy

loss depends on whether the specimen electrons are excited singly or collectively and on the binding energy of the electron to the atom. This leads to the generation of secondary electrons (SE), which are widely used to obtain images or analyse the sample.

They have low energy, so they can only escape from a region within a few nanometres giving topographic information with good resolution. Because of their low energy, they are attracted to a detector carrying some applied bias, in which their energy is converted into photons. They travel into a photomultiplier tube (PMT) which converts the quantum energy of the photons back into electrons. Secondary electrons are used principally for topographic contrast in the SEM and the image is dependent on the amount of the SE that actually reaches the detector. Low voltage incident electrons will generate secondary electrons from the surface region, which will reveal structural information on the sample surface more detailed.

In addition to these signals, a number of other signals are produced when an electron beam strikes a sample, including the emission of characteristic x-rays, Auger electrons, and cathodoluminescence.

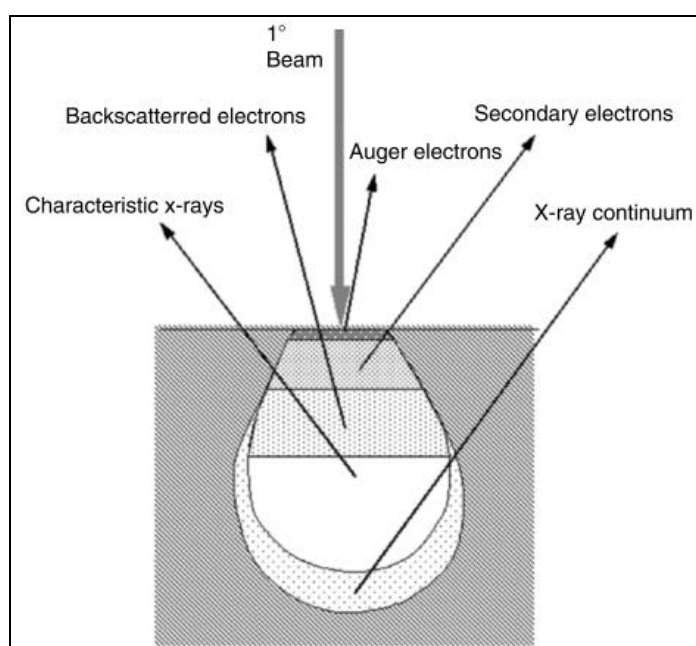


Figure 1.7: Illustration of several signals generated by the electron beam-specimen interaction and the regions from which the signals can be detected, copy by “Fundamentals of scanning electron microscopy” of Zhou and co-workers⁸⁵.

The emission of characteristic x-rays happens when an inner shell electron is displaced by collision with a primary electron and an outer shell electron fall into the inner shell to re-establish the proper charge balance in its orbitals following an ionization event. With the emission of an x-ray photon, the ionized atom returns to ground state. The analysis of characteristic x-rays to provide chemical information is the most widely used micro analytical technique in the SEM. In addition to x-ray peaks, a continuous background is generated through the deceleration of high-energy electrons as they interact with the electron cloud and with the nuclei of atoms in the sample.

Auger electrons are produced following the ionization of an atom by the incident electron beam and the falling back of an outer shell electron to fill an inner shell vacancy. This electron has a characteristic energy and, therefore, can be used to provide chemical information. Auger electrons are emitted only from near the surface due to their low energies, and then they provide useful information on the first surface layer (few nm).

Cathodoluminescence is another mechanism for energy stabilization following beam-specimen interaction, similar to photoluminescence. When external electrons recombine to fill holes, electromagnetic radiations are emitted to release the excess energy for certain materials. The radiations can have infrared, visible, or ultraviolet wavelengths and they could be detected and counted by using a light pipe and photomultiplier similar to the ones utilized by the SE detector.

1.3.1.1.3 – SCANNING ELECTRON MICROSCOPY INSTRUMENT

A general schematic diagram of a scanning electron microscope is shown in Figure 1.8.

SEM system requires that the electron gun produces a stable electron beam with high current, small spot size, adjustable energy and small energy dispersion. SEM based on thermionic emissions is the most diffused instrument. Usually, tungsten or lanthanum hexaboride (LaB_6) cathodes are used. The lanthanum hexaboride has lower work function respect tungsten, and then it provides stronger emission of electrons at the same heating temperature. Therefore, LaB_6 electron guns provide greater brightness and a longer lifetime compared with conventional tungsten guns. The electron emission increases with the filament current, reaching a saturation point, at which there is the most effective electron emission. Then electrons are focused into a tight bundle by the negative accelerating voltage. After this, the electron beam goes through the condenser lenses, which allows converging and collimating the electron beam into a relatively parallel stream. For modern electron microscopes, a second condenser lens is often used to provide additional control on the electron beam. This will diverge below the condenser aperture and this is the reason why there are objective lenses used to focus the electron beam into a probe point at the specimen surface and to supply further demagnification. An appropriate choice of lens demagnification and aperture size leads to a reduction of the diameter of the electron beam on the specimen surface and enhances the image resolution.

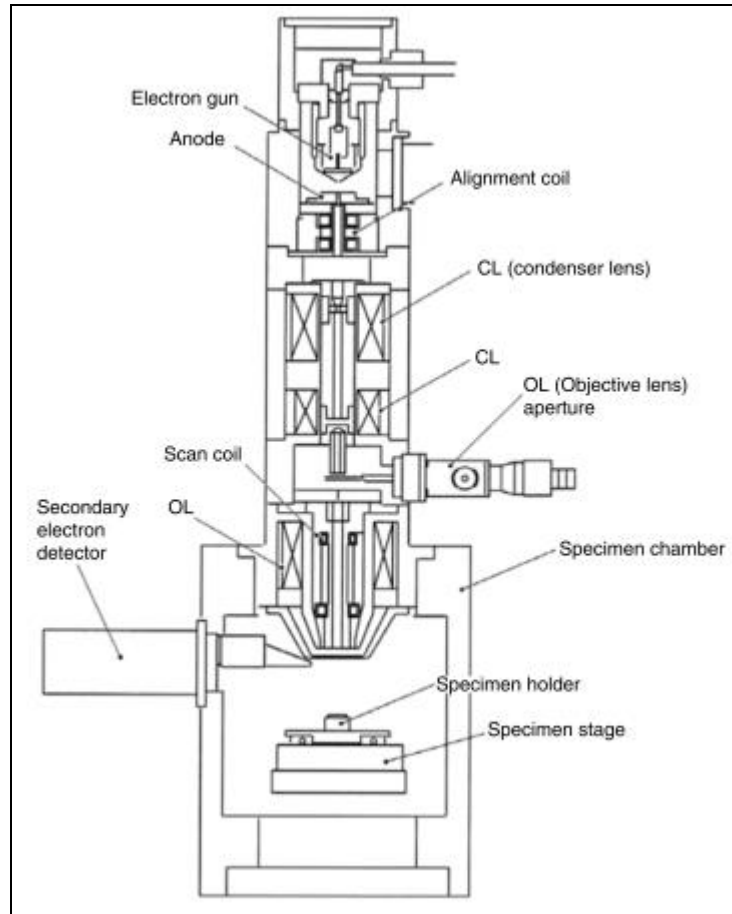


Figure 1.8: Schematic diagram of a scanning electron microscope, copy by “Fundamentals of scanning electron microscopy” of Zhou and co-workers⁸⁵.

An optimum choice of aperture size can also minimize the detrimental effects of aberrations on the probe size. However, there could be a problem related to the lens defects and contamination on the aperture or column. These issues can cause the cross-section of the electron beam profile to vary in shape. Practically, the image will stretch along a different direction at under-focus and over-focus condition. This imperfection on the electromagnetic lens is called astigmatism. For this reason, a series of coils surrounding the electron beam can be used to correct this error and achieve an image with higher resolution: the so-called stigmators. Generally, the astigmatism correction is performed while operating at the increased magnification, which ensures higher quality for images at lower magnification even when there is not a perfect compensation.

The portion of the image that results acceptably in focus is called the depth of field. This is influenced also by the working distance (WD): at short WD, the sample will be scanned with a wide cone of electrons, so the depth of field is little; by contrast, at a longer WD, the depth of field results enhanced due to a narrow cone of the electron beam. A longer WD, however, does not mean a better resolution: if the topography of the specimen is relatively flat, a shorter WD is preferred as the depth of field is less important and higher resolution can be achieved in this way.

The images collected in this work derived from secondary electron detection, based on a scintillator that converts the electron signal into light and then a light pipe to transfer the light to a PMT, which converts the light signal back into an electron signal. Because the amount of light generated by the scintillator depends both on the scintillator material and on the energy of the electrons striking it, a bias of typically 10kV is applied to the scintillator so that every electron strikes it with enough energy to

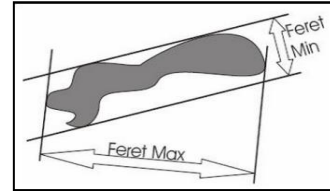
generate a significant flash of light. In this way the conversion of SE to light and then back to an electron signal makes possible to use the PMT, which has a high amplification factor and a logarithmic response. This allows it to process signal covering a large intensity range, is of low noise, responds rapidly, and is low in price.

1.3.1.2 – APPLICATION OF IMAGE-J

The morphological properties were measured by IMAGE-J, a public domain Java image processing and analysis program, able to calculate area and pixel value statistics of user-defined selections, measure distances and angles, already used in literature for particle characterization^{86–88}.

The parameters used in this thesis are defined in the following:

- Area (A)
- Perimeter (P)
- Feret's diameter (F), the longest distance between any two points along the selection boundary, also known as maximum calliper
- Roundness (R), which represents the ratio between the area of one particle and the area of a circle with a diameter equal to the major axis of the same particle
 - $R = 4 * \frac{A}{\pi * [major\ axis]^2}$
- Circularity (C), with a value of 1.0 indicating a perfect circle, while as the value approaches 0.0 it indicates an increasingly elongated shape
 - $C = 4 * \frac{A}{[Perimeter]^2}$
- Aspect Ratio (AR), which is the ratio between major and minor axis of the fitted ellipse relative to the particle
 - $AR = [Major\ axis] / [Minor\ axis]$
- Solidity (S), which is the ratio between the particle area and the convex area
 - $S = A / [Convex\ area]$



On each image analysed, the boundary of particles was selected and the obtain shape and size parameters are the average value of 50 counts as minimum. The measurement was repeated three times.

1.3.1.3 SURFACE INVESTIGATION

The composite samples were observed using an optical microscopy Zeiss Axiolab A1 m, equipped with image analysis software AxioVision SE64 “Material Core Package”. In this way, the surface of composite before and after the tribological test was compared. Images processed with ImageJ software, allowed the measurement of the dimensions of trace and tribofilm.

A more detailed investigation was performed using a 3D profilometer, in particular a Keyence VHX 1000 Digital Microscope. 3D representations of friction and wear trace were obtained, allowing the analysis of the depth of wear trace and the presence of tribofilm in the friction trace.

1.3.2 – STRUCTURE AND PHYSICAL CHARACTERIZATION

The crystallographic structure of powder materials was investigated by X-ray diffraction, in order to evaluate the composition, highlighting the differences among materials of the same family. Raman

spectroscopy was also used to investigate the degree of disorder in the carbon materials, while Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the nature of surface groups. .

1.3.2.1 – X-RAY DIFFRACTION

All the measurements were carried out by using a Philips X'Pert MPD diffractometer, with a copper $K\alpha$ radiation and a solid-state detector. The search of the phases was performed with the Pearson's Crystal Data, while data processing has been performed using OriginPro.

1.3.2.1.1 – HISTORY OF X-RAY DIFFRACTION

Since the discovery of X-rays, the entire society has recognized their importance for daily life. X-rays are employed in structural investigation of organic and inorganic materials, for chemical elemental analysis and biological imaging.

They have been discovered by Wilhelm Röntgen in 1895^{89,90}, awarded of Nobel Prize in the remote 1901. In 1912 Paul Ewald⁹¹ was concerned with a crystalline solid which on the sub-microscopic level consists of a triply periodic and regular arrangement of atoms or molecules. With the help of Max von Laue, they understood that a crystal might serve as a three-dimensional diffraction grating for X-rays. To test this hypothesis, a scattering experiment has been performed by Walter Friedrich and Paul Knipping⁹¹. When a beam of X-rays strikes a crystal, the crystal scatters the incident beam in many different directions and with different intensities. On a photographic plate, these scattered X-rays will blacken the plate where they strike and in this way, the so-called diffraction pattern is obtained. In 1913, Sir William Henry Bragg and Sir William Laurence Bragg determined the first mineral structure from X-ray diffraction, the structure of NaCl. The English physicists Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence θ . In the so-called Bragg's law, λ is the wavelength of the incident beam; n is an integer and d is the distance between atomic layers in a crystal. The Bragg's law formula is: $n\lambda = 2d_{hkl} \sin \theta$. They were awarded of Nobel Prize in Physics in 1915.

The crystal structure determines the directions and intensities of the X-rays scattered by a crystal, so if one knew the crystal structure then one could calculate the diffraction pattern completely. Many years later it turns out that diffraction pattern determine unique crystal and molecular structures.

However, since X-rays are electromagnetic waves, they have a phase as well as intensity, but the phases cannot be measured in diffraction experiment and only the intensities can be directly measured. This issue is known as "phase problem" and it consists in how to deduce the values of the phases knowing just their intensities^{89,91}. In the next 40 years, it therefore came to be generally believed that a procedure for going directly from the measured intensities to crystal structures could not be devised. The phase problem was thought to be unsolvable. It was not until the early 1950s that these conclusions were finally refuted through discovering of special properties of molecular structures and a simple mathematical argument. The special property is atomicity: the electron density function in a crystal takes on large positive values at the atomic position vectors and drops to small values between the atoms. If the attention is focused on position vectors and not on electron density function, it is possible to eliminate the lost phase information from the relationships between crystal structure and diffraction pattern. This elimination results in equations relating the diffraction intensities alone with the atomic position vectors. In this way, there exist relationships between the measured diffraction intensities and the lost phases that may be exploited.

There remains the task of calculating the individual phases respect the abundance of experimentally measured diffraction intensities. The techniques of X-ray crystallography that deduce the individual phases by exploiting intensities and phases are known as direct methods. In 1948 Jerome Karle and Herbert Hauptman started to work on this problem⁸⁹. Their first step was to exploit the non-negativity of the electron density function. Then, during the early 1950s, they introduced the use of the joint probability distribution of several diffraction intensities and the corresponding phases as the central tool in the solution of the phase problem. However, due to the mathematical complexity of these direct methods, few early attempts to apply them were made, until the 1960s, when widespread applications were made using computer programs.

Nowadays, 100,000 molecular structures are known, most determined by the direct methods.

1.3.2.1.2 – THEORY OF X-RAY DIFFRACTION

Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles. The strength with which an atom scatters light is proportional to the number of electrons around the atom. Due to the fact that X-rays wavelength is similar to the distance between atoms, the scattering from them produces a diffraction pattern, which contains information about the atomic arrangement within the crystal. As said in precedent section, the diffraction pattern is a product of the unique crystal structure of a material.

The crystal structure can be defined as the repetition of the basic repeating unit, the unit cell, which contains the maximum symmetry that uniquely defines the crystal structure. The unit cell repeats in all dimensions to fill space and produce the macroscopic grains or crystals of the material. To describe a crystal structure it is necessary to know the shape and size (lattice parameters) of the unit cell. Regarding the shape of the unit cell, symmetry elements are used to define seven different crystal systems: cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, and triclinic. The lattice parameters represent the unit cell dimensions, generally indicated as (a, b, c) the sides and as (α, β, γ) the angles.

Diffraction peaks are associated with planes of atoms, which are identified using Miller indices (hkl). These parallel planes of atoms intersecting the unit cell define directions and distances in the crystal. Miller indices define the reciprocal of the axial intercepts of planes in the unit cell. The distance from the origin to the plane (hkl) is represented by the vector d_{hkl} and it is used in Bragg's law to determine where diffraction peaks will be observed. The vector magnitude is the distance between parallel planes of atoms in the family (hkl). The Bragg's law $n\lambda = 2d_{hkl} \sin \theta$ calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak.

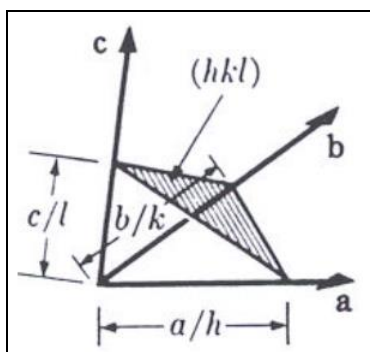


Figure 1.9: general (hkl) planes and correlation with lattice parameters

The intensity I_{hkl} of the diffraction peaks are determined by the arrangement of atoms in the entire crystal. It is proportional to the square of the structure factor F_{hkl} that sums the result of scattering from all of the atoms in the unit cell to form a diffraction peak from the (hkl) planes of atoms. The amplitude of scattered light is determined by the position of atoms in plane and the kind of atoms, because it depends from the number of electrons around the atom.

The lattice parameters can be obtained from X-rays diffraction pattern, knowing the crystal system because for each shape of unit cell the lattice parameters have some important correlations, reported in Table 1.3.

Table 1.3: seven crystal systems - review

CRYSTAL CLASS	AXIS SYSTEM
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$

Once the symmetry of unit cell and the specific atomic planes distance d_{hkl} is known, it is possible to obtain the lattice parameters (a,b,c) using the general formula: $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$.

For cubic lattices in which $a = b = c$, the formula becomes $\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$.

In general, obtaining peak position and intensity it is possible calculate the distance d of specific plane (hkl) and derived the lattice parameters in function of crystal class or system. Furthermore, the peak shape in X-rays diffraction can give more information on material properties. In particular, it is useful to calculate the peak width, generally named Full Width at Half Maximum (FWHM). This measure is important to calculate particle or grain size and residual strain in correlation with peak position.

X-rays diffraction (XRD) is then a useful non-destructive technique applied to identify crystalline phases and orientation, to determine structural properties like grain size, strain, etc., to measure thickness of thin films or multi-layers and to determine atomic arrangement.

The phase's identification is one of the most important uses of XRD, since it is possible to compare the data obtained with known standards. Hanawalt, Rinn and Fevel at the Dow Chemical Company initiated the task of building up a collection of known patterns in 1930s. After this point, several societies increased the number of classified diffraction data and in 1995, the powder diffraction file (generally called PDF) contained nearly 62,000 different diffraction patterns. Hanawalt decided to classify each substance in function of its three strongest lines, considered by relative intensity. The values of two lines are usually sufficient to characterize the pattern of an unknown material. Therefore, to identify a substance by XRD it is necessary to consider number of reflections, peak position and peak splitting due to symmetry effect.

1.3.2.1.3 – X-RAY DIFFRACTOMETER

In Figure 1.10, a schematic diagram of basic principle of XRD is shown. The incident beam is generated in the X-ray Tube, also called Coolidge tube. This X-Rays source is a high vacuum tube containing a tungsten filament cathode and a massive anode, generally constituted by a heavy block of copper, as in the diffractometer used. The electrons, produced by heating the cathode, are accelerated

versus the metallic anode by a potential of 100kV. Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect. Unfortunately, this process is very inefficient, since less than 1% of electric energy is converted in radiation energy. This problem is however overcome by the high sensibility of actual detectors of X-rays.

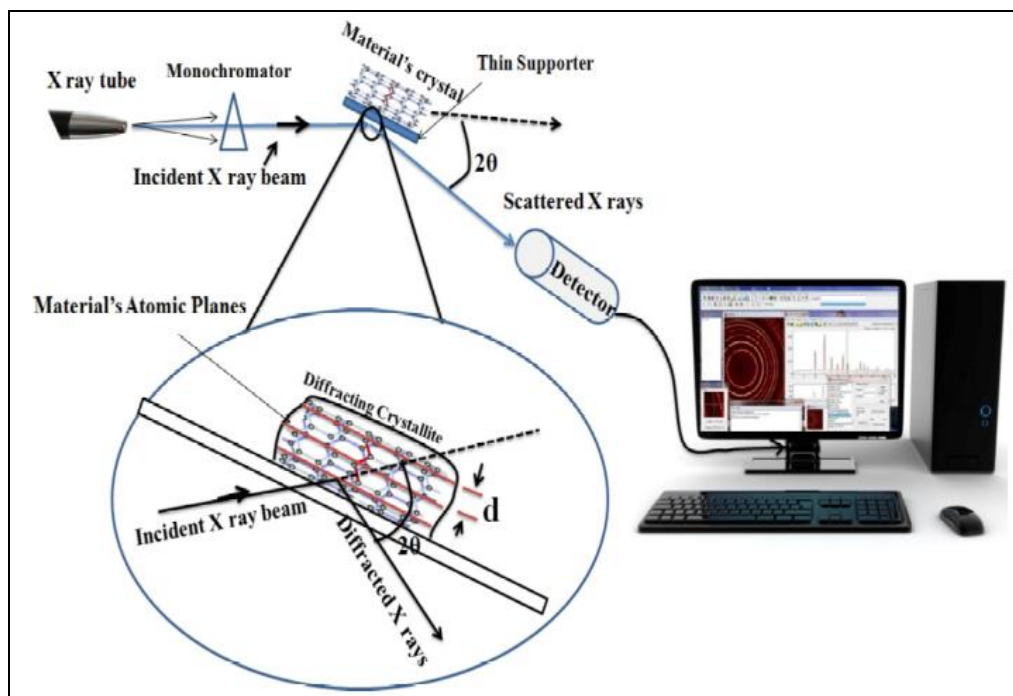


Figure 1.10: Schematic diagram of basic principle of XRD, copy by Rasel Das and co-workers review “Current applications of X-ray powder diffraction”⁹².

The characteristic X-ray emission of copper (Figure 1.11) appears as a continuous spectrum to which a striped spectrum is superimposed. Two emissions at a wavelength of 0.139 nm and 0.154 nm respectively called K_β and K_α (this last used to collect spectra in this work) are visible. In order to irradiate the sample just with K_α radiation, a Nichel filter is generally used. However, the X-ray beam obtained still consists of several characteristic wavelengths of X-rays, and then the presence of a monochromator is required.

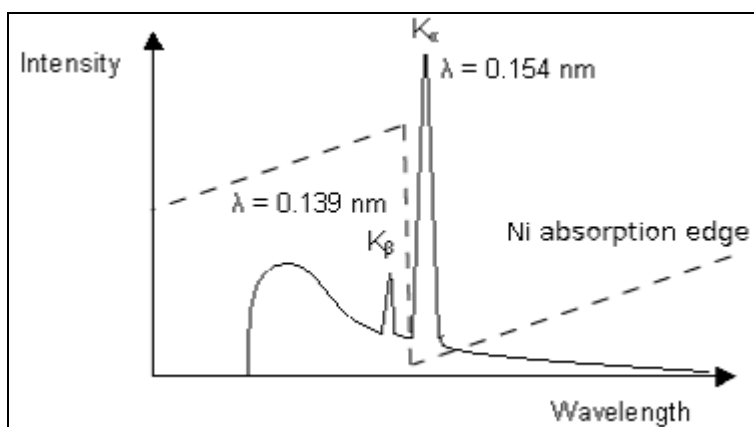


Figure 1.11: X-ray emission spectrum of copper and Nichel absorption edge, copy from <https://www.doitpoms.ac.uk/tlplib/xray-diffraction/production.php?printable=1>

In fact, a doublet of K_{α} will usually be present, identified as $K_{\alpha 1}$ and $K_{\alpha 2}$. Only very expensive optics can remove the $K_{\alpha 2}$ line. The two radiations overlap heavily at low angles and are more separated at high angles. Furthermore, it is possible to find some tungsten lines, which form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source. Then, to remove unwanted wavelengths, the use of a monochromator is necessary.

In the case of powder diffractometers as the one used, the Bragg-Brentano parafocusing geometry is used. In this configuration, a point detector and sample are moved so that the detector is always at 2θ and the sample surface is always at θ with respect to the incident X-ray beam. In the parafocusing arrangement, the incident and diffracted beam slits move on a circle centred on the sample. Divergent X-rays from the source hit the sample at different surface points. During the diffraction process, the X-rays are refocused at the detector slit. This arrangement provides the best combination of intensity, peak shape, and angular resolution for the widest number of samples.

The detector could be of two types: point detector or position sensitive detector. The first kind observes one point of space at a time, making the analysis slow, but compatible with most optics. The position sensitive detectors are of different kind: in this work a solid state real-time multiple semiconductor strips was used, that provides high speed with high resolution.

In the collection of an X-rays powder diffraction pattern, the sample preparation is an important step. First, an ideal powder sample should have many crystallites in random orientations. Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation. Crystallites should be less than 10 μm in size to get good powder statistics. Second, the sample should have a smooth flat surface in order to avoid intensity reduction of low angle peaks. For this reason, the powder was dispersed on a smooth surface, which is a zero background holder (ZBH) that avoids the problem of an amorphous contribution to the diffraction pattern, as happens for glass, by using an off-axis cut single crystal.

1.3.2.2 – RAMAN SPECTROSCOPY

Raman spectra were collected using a Horiba JobinYvon HR800 Raman Spectrometer (Centro Scansetti, Torino), with a CCD detector at -70°C , an optical microscope Olympus BX41 and using as light source a green laser (532 nm) with 250 mW of power. Data processing was performed using OriginPro and will be discussed in the following chapters.

1.3.2.2.1 – RAMAN SPECTROSCOPY HISTORY

Raman spectroscopy was named in the honour of its inventor C.V. Raman, who published this discovery with his co-workers K.S. Krishnan in 1928⁹³ and was awarded of Nobel Prize two years later. It is possible to consider the genesis of Raman spectroscopy as developed in the first quarter of the 20th century, when the Austrian quantum physicist A. Smekal predicted theoretically the scattering of monochromatic radiation with change of frequency⁹⁴. Rayleigh in 1871, Einstein in 1910 and others, had previously investigated the scattering of light by various media but no change of wavelength had been observed. Therefore, Raman and Krishnan were the first who reported experiments on inelastic scattering of radiation. The work immediately following its discovery had been devoted to fundamental studies and during the period 1930-1950 its development occurred slowly. However, only when suitable electronic measuring devices had been developed, advances in Raman spectroscopy occurred.

In the first attempt to improve this technique, the attention had been focused on the experimental problems of Raman spectroscopy: the low intensity of inelastic scattering with respect to the significantly higher intensity of the Rayleigh scattering. This issue gave several restrictions to the

progress of Raman spectroscopy. The inventors used filtered sunlight as a radiation source and detected the Raman lines of some sixty liquids and gases. In 1929 a more definitive spectrum of carbon tetrachloride had been recorded using 435.83 nm mercury excitation⁹⁴. Early experimental work was directed toward improving the radiation sources, starting from mercury lamp. Only in 1960, the invention of the laser resulted in a decisive transformation of the Raman spectra quality⁹⁵. Laser was shortly applied as a monochromatic source, leading to the advantages of focusing onto a very small sample surface and enabling excellent spectra. The capabilities of the laser to provide variable wavelength permitted to avoid the problems of fluorescence and absorption occurring on many samples. During the 1970s, most Raman instrumentation used Ar⁺ lasers with the lines of 488 nm and 514.5 nm. Cd, Kr⁺, He-Ne, and ruby lasers were also widely employed. Optoelectronic devices have progressed significantly in the past decade as a consequence of major achievements in solid-state technology, leading to reliable diode lasers, now available from the visible to the infrared radiation.

1.3.2.2.1 – THEORY OF RAMAN SPECTROSCOPY

Raman spectroscopy is a versatile method for analysis of a wide range of samples and it can be used for both qualitative and quantitative purpose. This technique is considered complementary to infrared spectroscopy.

Raman spectroscopy is a scattering technique based on the so-called Raman Effect: the frequency of a small fraction of scattered radiation is different from frequency of monochromatic incident radiation, due to inelastic scattering derived from the interaction of radiation with vibrating molecules.

When the laser beam strikes at sample surface, it scatters with mostly the same frequency of the incident radiation generating the so-called Rayleigh scattering. Only a small fraction of scattered radiation has a different frequency and derives from two possible situations. First, a part of molecules excited by laser perturbation falls in a higher vibrational energy state respect the fundamental one. In this way, a Stokes Raman scattering is obtained, that means a scattered radiation with lower frequency than incident radiation frequency. Second, molecules already in higher vibrational energy state are excited by laser and then return to fundamental vibrational level (Figure 1.12). In this case, anti-Stokes lines appear due to scattered radiation with higher frequency than incident one. Stokes Raman bands result in more intense bands respect anti-Stokes ones due to the position of the majority of molecules in the fundamental vibrational level at room temperature, so it is more probable that a molecule is excited when it is in the fundamental vibrational level rather than in a higher one. The wavelength of incident radiation affects the Raman scattering, but not the magnitude of Raman shifts. To obtain Raman spectra it is necessary a change in polarizability during molecular vibration, thus in some cases there are no active Raman mode.

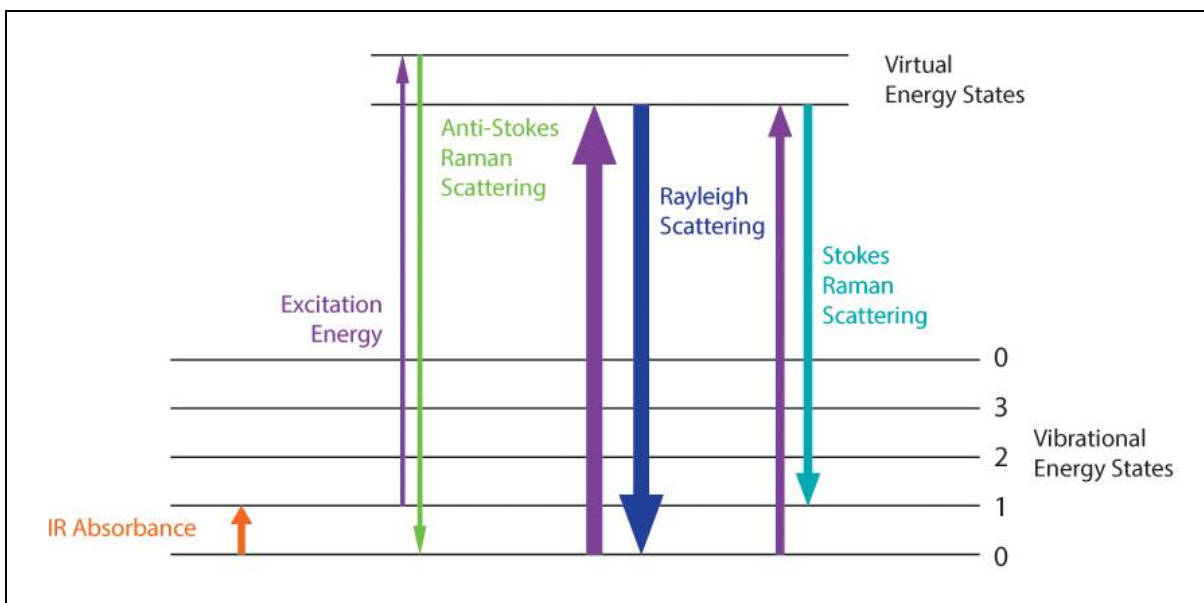


Figure 1.12: Mechanism of Raman Scattering with respect to the vibrational energy states.

1.4.2.2.1 – RAMAN SPECTROPHOTOMETER

Raman spectrophotometers all have the same basic components: a laser source, a filter, a diffraction grating, and a detector.

Nowadays, several different laser sources can be used to excite the target species. Ultraviolet excitation has been particularly successful in obtaining spectra of organic molecules. Generally, a Raman spectrophotometer uses a double monochromator to reduce the spurious radiations that arrive at the detector. Furthermore, usually the double-beam configuration is adopted to eliminate the intensity fluctuations of source.

The filter collects the Raman scattered light (Stokes) and filters out the Raleigh and Anti Stokes light. Then, the diffraction grating bends the Raman shifted light according to wavelength.

The detector records the signal and passes this information to a computer for decoding. In the majority of Raman spectrophotometers, photomultiplier tubes are used as detectors.

1.3.2.3 – FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In this work, Mid-IR spectra were obtained by Fourier transform infrared spectrometer Nicolet 6700 (Thermo USA) using the single reflection ATR (Attenuated Total Reflection) technique using a diamond crystal. Measurements were performed with a resolution of 4 cm^{-1} and 32 scans, in the range $4000\text{--}400\text{ cm}^{-1}$.

1.3.2.3.1 – FTIR HISTORY

Chemical infrared spectroscopy emerged as a science in the 1800 by Sir Friedrich Wilhelm Herschel, who discovered infrared radiation. After this discover, numerous scientists improved the knowledge about the nature of light, as Thomas Young in 1802 demonstrating wave nature of light by using a transmission grating. However, only in 1859 G. Kirchoff and R.W. Bunsen affirmed that elements have both characteristic absorption and emission spectra, lead to important application of spectroscopy as analytical technique.

Firstly, most IR instrumentation was based on prism or grating monochromator. The development of FTIR would have been impossible without the use of the Michelson interferometer. This optical device was invented in 1880 by Albert Abraham Michelson, awarded of Nobel Prize in Physics in 1907 for accurately measuring wavelengths of light using his interferometer. This optical device was not originally designed to perform infrared spectroscopy, but to test the existence of a “luminiferous aether”, a medium through which light waves were thought to propagate. With the famous Michelson-Morley experiment, it has been shown there is no evidence for the existence of this kind of medium. In a sense, this experiment produced the most famous “negative” results in the entire history of science.

The interferometer showed the potential use to obtain spectra and so Dr. Michelson manually measured many interferograms. The problem is the time consuming calculations required to convert an interferogram into a spectrum. Due to this problem, in the early 1940s, chemical infrared spectroscopy was still an immature scientific field. Only with commercial development of the optical null dispersive spectrophotometer, chemical infrared spectroscopy came into widespread use.

In 1949, Peter Fellgett used an interferometer to measure light from celestial bodies and produced the first Fourier transform infrared spectrum. At this point, only a few advanced research groups with access to large and expensive computers used FTIR spectroscopy, due to the long analysis time required (up to 12 hours). For two decades more, FTIR spectrometers had been used to studying problems not solvable with dispersive techniques. Advances in how computers perform mathematical operations were necessary to make FTIR a reality.

In the late 1960s, commercial FTIR spectrometers appeared when microcomputers able to do the Fourier transform became available. J.W. Cooley and J.W. Tukey made the major advance in this area inventing an algorithm that quickly does a Fourier transform. It is known as the “Fast Fourier Transform” (FFT) or “Cooley-Tukey Algorithm”.

Gradually, technology reduced the cost, increased the availability and enhanced the capabilities of FTIR spectroscopy systems.

1.3.2.3.2 – THEORY OF INFRARED SPECTROSCOPY

The infrared radiation is referred to the region of electromagnetic spectrum between visible and microwave regions. In particular, this spectrum part is divided into near infrared (NIR – 13000-4000 cm^{-1}), medium infrared (MIR – 4000-200 cm^{-1}) and far infrared (FIR – 200-10 cm^{-1}). The zone of major interest is often the MIR region.

IR is a vibrational spectroscopy, due to the conversion of radiation energy in vibrational energy. The molecules strike by infrared radiation could vibrate in two fundamentals way: stretching and bending. A stretching vibration is the rhythmic movement of bond axis with increase and decrease of interatomic distance. A bending vibration could be the variation of an angle between two bonds with a common atom or the movement of a group of atoms with respect to the entire molecule. In this last case, there is another subdivision of vibrational mode into vibration in plane and out of plane. The in plane vibrations are called scissoring and rocking, while the out of plane vibrations wagging and twisting.

A vibration is IR active only when there is a change in the molecule’s dipolar moment as a consequence of radiation interaction. In fact, when this condition is satisfied, the molecule produces an oscillating electric field, which makes possible the exchange of energy with electromagnetic waves.

The intensity of a band depends from the value of bond dipolar moment, and then depends from the relative electronegativity of bond atoms. The dipolar moment can be calculated according to the formula $\mu = q * \vec{d}$, where μ is the dipolar moment, q the electric charge and d the vector distance.

To know the frequency at which a functional group would absorb the electromagnetic radiation, one can use Hooke's law. In this case, two linked atoms are considered as a simple harmonic oscillator, in which the frequency depends on atom's mass and bond strength. In fact, the Hooke's law is:

$$\nu_{vibr} = \frac{1}{2\pi c} * \sqrt{\frac{k}{\mu}}$$

In which ν_{vibr} is the vibration frequency, c is the light speed, k is the strength constant, and μ the reduced mass. Then, higher the constant of strength k , higher is the absorbance frequency, while higher the reduced mass and lower is the frequency.

1.3.2.3.3 – FTIR SPECTROMETER

The optical system in an FTIR spectrometer is very simple: the interferometer requires two mirrors, an infrared light source, an infrared detector, and a beam splitter. Last one is the heart of the interferometer and it is essentially a half-silvered mirror, which reflects about half of an incident light beam while simultaneously transmitting the remaining half. One half of this split light beam travels to the interferometer's moving mirror while the other half travels to the interferometer's stationary mirror. The two mirrors reflect both beams back to the beam splitter where each beam is again half reflected and half transmitted. When the two beams return to the beam splitter, an interference pattern or interferogram is generated. This interference pattern varies with the displacement of the moving mirror and yields spectral information.

In this work, Mid-IR spectra were obtained by Fourier transform infrared spectrometer Nicolet 6700 (Thermo USA) using the single reflection ATR (Attenuated Total Reflection) technique using a diamond crystal. Measurements were performed with a resolution of 4 cm^{-1} and 32 scans, in the range $4000\text{--}400\text{ cm}^{-1}$.

ATR enables to examine samples directly in the solid or liquid state. It is based on the property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal, where it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave, which extends into the sample with a penetration depth typically between 0.5 and $2\text{ }\mu\text{m}$. The exact value is determined by the wavelength of light, the angle of incidence, and the indices of refraction for the ATR crystal and the medium being probed.

The evanescent effect only works if the crystal is made of an optical material with a higher refractive index than the sample being studied. Otherwise light is lost to the sample.

1.3.2.4 – PHYSICAL CHARACTERIZATION

The powder density was obtained by x-ray diffraction data. By the calculation of lattice parameters, the unit cell volume was obtained and then the mass of unit cell was divided for it to obtain the theoretical density of powder. For carbon materials, the powder density was measured with a helium pycnometer at the institute ISTEK of Faenza (Italy).

On composite samples, the density was measured using the geometrical volume. Each pad, as described in previous sections, is a disc of 90 mm as diameter and a variable thickness. The pad thickness was measured in five different points obtaining an average value. The volume was then calculated as surface area multiplied for thickness. As second step, the pad was weighted, and then the weight was divided for the calculated volume. In addition, the measurement was repeated on more than one sample and the density is given as average value with relative standard deviation.

On composites, also hardness was measured with Brinell test. The measurement of hardness was performed using a ball of 2.5 mm of diameter, 62,5 Kg as load and 30 s as analysis time for the majority of samples. In total, ten repetitions were made on different point of pad surface in order to verify the homogeneity of this property.

1.3.3 – STATISTICAL AND CHEMOMETRICAL METHODS

As mentioned at the beginning of the section 1.4, in this thesis two kind of approach were used in order to analyse the influence of physico-chemical properties on tribological behaviour of different materials. The first kind is named OVAT, “one variable at time”, which means that just a couple of variables is considered to investigate their correlation. However, this correlation can be considered true just in case all the other possible variables are constant, otherwise the interaction observed becomes impossible to be reproduced in the same way, and then it is not possible to consider it as scientifically true. However, the OVAT approach is useful to understand in what way a variable affects the response investigated and to suggest a scientific explanation of the mechanical, physical, or chemical mechanism. To avoid the construction of many graphs of responses in function of each variable, the Pearson coefficient was calculated for each pair of response – variable and also variable – variable.

The second kind is the Multivariate Approach, in which different variables are considered all together in order to study not only their influence on a particular response, but also their interaction. In this way, it is possible to find if the response investigated is affected by more variables or by the combination of two or more variables. To perform a multivariate analysis is necessary to use the principle of chemometrics, which is the science of extracting information from chemical systems by data-driven means. Chemometrics is inherently interdisciplinary, using methods frequently employed in disciplines such as multivariate statistics, applied mathematics, and computer science.

1.3.3.1 – PEARSON COEFFICIENT

In statistics, the Pearson correlation coefficient (PCC) is a measure of the linear correlation between two variables X and Y. it has a value between +1 and -1, where one is total positive linear correlation, zero is no linear correlation and minus one is total negative linear correlation. Karl Pearson developed it from a related idea introduced by Francis Galton in the 1880s.

As definition, PCC is the covariance of the two variables divided by the product of their standard deviations.

$$PCC = \frac{cov(X,Y)}{\sigma_X \sigma_Y}$$

By the mathematical point of view, this coefficient is symmetric and invariant under separate changes in location and scale in the two variables. Symmetric means that $corr(X,Y) = corr(Y,X)$, while invariant indicates that it is possible to transform both the variables, like X to (a+bX) and Y to (c+dY), where a,b,c and d are constants with b,d>0, without changing the correlation coefficient.

By the geometrical point of view, for centred data, PCC can also be viewed as the cosine of the angle θ between the two observed vectors in N-dimensional space, for N observations of each variable.

1.3.3.2 - CHEMOMETRICS

Chemometrics is applied to solve both descriptive and predictive problems in experimental natural sciences, especially in chemistry. In descriptive applications, properties of chemical systems are modelled in order to learn the underlying relationships and structure of the system. In predictive applications, properties of chemical systems are modelled with the intent of predicting new properties or behaviour of interest.

The field of chemometrics is generally recognized to have emerged in the 1970s as computers became increasingly exploited for scientific investigation. The term “chemometrics” was coined by Svante Wold in a grant application 1971⁹⁶, and the International Chemometrics Society was formed shortly thereafter by Svante Wold and Bruce Kowalski.

In this thesis, the R-based software developed by the Group of Chemometrics of the Division of Analytical Chemistry of the Italian Chemical Society, freely downloadable from the site gruppochemiometria.it, was used to perform chemometrics analysis.

1.3.3.2.1 DESCRIPTIVE APPLICATIONS

As mentioned before, chemometrics can be used in descriptive applications, in which the aim is to learn the underlying relationships and structure of the investigated system. In this kind of chemometrics, two possible approaches can be used.

In the first case, the aim is to describe a system from the point of view of a low number of variables, all of them controllable. To verify the influence of each variable and underlying possible combined effect of them, it is necessary to prepare an Experimental Design before tests. Named also design of experiment (DOE), it is the design of any task that aims to describe or explain the variation of information under set up conditions. In the DOE, the experimental area studied is named experimental domain, while the controlled variables, which can be varied independently and have an impact on the results, are named factors. Different kind of variables can be used in a DOE: quantitative and qualitative variables. The quantitative ones are continuous and independent; they can be adjusted to any value over a specified range or to a specific number of values. The qualitative ones describe non-continuous variation, as type of solvent or catalyst. Factors affect responses, which are the observed variables resulting from changing of independent variables. Another kind of variables is the uncontrolled or background variables, which are not possible to alter. The DOE is constituted by a number of experiments, which aims to describe the variation of a response in function of each variable in their investigated range through the minimum number of experiments. Different possible experimental design can be selected in function of the system investigated. For example, one kind is the Full Factorial Design, in which every level of a factor is investigated at both levels of all the other factors. Thus, for a system with k factors each one of two levels, the number of experiments is 2^k . When all the experiments are performed, the influence of each variable and their possible combinations can be described modelling the experimental results for each response.

In the second case, the analysis regards experiments already obtained, without a prepared DOE. To describe the influence of each variable, usually the Principal Component Analysis technique (PCA) is applied. This technique is a projection method able to extract information from large data sets. It creates “windows” in a multidimensional space and the data are pre-treated in order to obtain variables with equal chance to influence the PCA model. In this multidimensional space, Principal Components can be individuated (PC). Each PC represents a direction of variance and a percentage of system variance is associated to all PCs. The first PC represents the direction of maximum variance in the investigated system, while the second PC is perpendicular to the first. From the combination of two

PCs, a 2D representation can be obtained showing the position of variables or of experiments. In the first case, it is named Loading Plot and the variables are distributed in function of their influence on the two PCs selected. Their relative position gives information on their relationships and the structure of the investigated system. In the second case, the 2D representation is named Scores Plot, which is useful to individuate possible group of experiment or individuate some anomalies in the system. To individuate possible outlier, a diagnostic plot can be obtained including the Q index and the Hotelling's T^2 index. The Q index represents the chi-squared distribution, used to evaluate the goodness of fit of an observed distribution to a theoretical one. When an experiment is out of range respect the Q index, this means that the experiment cannot be collocated in the components space, and then it is an outlier, a possible error. The Hotelling's T^2 index is a generalization of Student's t-statistic that is used in multivariate hypothesis testing. It represents the Mahalanobis distance of an experiment respect the distribution of the other experiments. When a test is out of T^2 , it means that the experiment can be collocated in the same components space as the others, but it is far from them. So in general, by PCA is possible observed the relationships among both independent and dependent variables and the observation on the loading plot can be confirmed by calculating the relative PCC.

1.3.3.2.2 – PREDICTIVE APPLICATIONS

In predictive applications, the aim is to find a model able to predict the investigated response in function of each variable considered. Also in this case, the possible approaches are two. When a DOE is applied to investigate the effect of some factors, at each of them is associated a numerical coefficient. It derives from the analysis of result through Multiple Linear Regression (MLR), which is a regression method using a least squares fit. A separate model for each response investigated can be obtained as different coefficients for each factor. In this way, the influence of a variable can be described and quantified with respect the other parameters. The model obtained need to be validate through two parameters: R^2 and Q^2 . R^2 is the coefficient of determination, which is the proportion of the variance in the dependent variable that is predictable from the independent variable. It provides a measure of how well observed outcomes are replicated by the model, based on the proportion of total variation of outcomes explained by the model. Q^2 is obtained by the cross-validation of the system, which consists in building a model on the remaining data while a part of them is held out. This process is repeated until all the data has been kept out once. In general, to consider acceptable a model R^2 must be equal or higher than 0.8 and Q^2 equal or higher than 0.5. Only in these conditions, the model can be considered stable, interpretable, and useful for predictions.

When the investigation regards a set of data already obtained with a large number of variables, by PCA this number must be reduced until the variables are less than experiments. This is a necessary condition to apply the regression method able to build a predictive model. In this case, the method is the Partial Least Square regression (PLS), which is able to maximize the covariance among variables and responses. This method generates a linear formula of the investigated response in function of the other variables, where each of them is multiplied for a numerical coefficient. By the comparison of these numerical coefficients, it is also possible to evaluate the different influence of each variable and compare it by a quantitative point of view. In addition, in this case the validation of model is through R^2 and Q^2 .

After obtaining a model through MLR or PLS, in order to confirm its validity, more tests are necessary and the experimental result must be in the range of confidence respect the calculated value using the model. In general, the range of confidence is 95%, which means that the experimental and fitted values must not differ more than 5% of their value.

1.3.4 – TRIBOLOGICAL CHARACTERIZATION

In the past literature, the systematic study of brake pad formulation has been based on comparison of similar blends in which just one filler at time or relative amount of some components is changed^{25,47,97,98}. In this approach, the attention was focused on brake pads performance through a tribological characterization mainly constituted by dynamometer tests. Moreover, the comparison among these materials is affected by test kind, conditions applied, formulation of samples, and properties of fillers under studying. These features make the results difficult to regain and largely affected by the interaction of fillers with other components. In this condition, obtaining the own tribological behaviour of each filler is practically impossible. To overcome this problem, Lancaster suggestion has been taken in consideration³². He affirmed that to understand the phenomena occurring in a composite, each constituent has to be characterized as completely as possible.

Regarding the tribological behaviour of raw materials, a test able to give information on the friction properties of powders has to be used. Unfortunately, the kinds of test generally performed on friction materials are not suitable for powders. To overcome this issue, Kato³³ employed a pin-on-disc wear test method in order to study the effects of supplying iron-oxide or iron particles on rubbing steel surfaces. Supply of fine oxide particles on the wear surface accelerates the severe to mild wear transition, thanks to the formation of an oxide layers at interface. This method of analysis inspired more recent studies on the tribological properties of typical brake pad constituents. Österle and co-workers⁹⁹ used a modified pin-on-disc test to characterise some raw materials and several binary and ternary mixtures, in order to simulate the expected third body structure with iron oxide as major constituent. In their opinion, without additional heating stage, pin-on-disc tests are not suitable to simulate the tribological behaviour of real braking conditions, mainly because in the latter case the high-energy input inevitably leads to material modifications at the interface. However, Rodrigues et al. employed this method to investigate the effect of copper particles as an interfacial medium on the friction coefficient of steel against steel and on tribofilm formation with powder supply^{35,36}.

A similar test was employed in this study. More specifically, it was applied to study the phenomena occurring at the interface, trying to improve the basic knowledge about brake pad constituents.

Relative to composites, two kinds of tribological test were applied: pin-on-pad and ball-on-pad test, fully described in next paragraph. In this work, the attention was especially focused on how the filler could change the tribological behaviour of polymer matrix. The basic mix was characterized by the same test and its tribological properties are described in chapter 2.

For the third and last step, regarding the study of the effect of filler in a real formulation, a brake dynamometer test was applied on a real brake pad formulation. Each sample was tested by dynamometer instrument at VŠB – Technical University of Ostrava (Czech Republic) during the period of international mobility, ranging from October 2017 to January 2018. A standard test, called officially ISO-26867:2009(E)¹⁰⁰, and commonly defined Short AK Master, was used. This test, fully described in section 1.4.1, is constituted by twenty parts at different brake conditions, for 166 brakes. It is a suitable test to compare brake pads performance, but it differs from industrial tests, in which there are similar parts with higher number of stops (commonly more than 300).

1.3.4.1 – TRIBOMETER SET UP

A common pin-on-disc CSEM High Temperature Tribometer was used for the friction measurement (Figure 1.13).



Figure 1.13: CSEM High Temperature Tribometer.

Three different configurations were used in order to characterize the tribological behaviour of powders and composites.

The first is a pin-on-disc test, as performed by Kato, Österle and Rodrigues^{34,101,102}, called “powder test” in the following. The contact surfaces are made of 100Cr6 steel, commercial low alloy martensitic chromium steel. The chemical composition of steel, in agreement with the reference normative EN ISO 683-17: 1999¹⁰³, is reported in Table 1.5.

Table 1.5: General chemical composition of steel.

C%	Si%	Mn%	P% max	S% max	Cr%	Mo% max	Al% max	Cu%
0.93-1.05	0.15-0.35	0.25-0.45	0.025	0.015	1.35-1.60	0.10	0.050	0.30

The test consists in a stationary pin pressed against a rotating disc, which is fixed on a support.

The disc is 10 mm thick and has an outer diameter of 55 mm, with a groove of 5 mm width and a depth of 2 mm, in which the powder can be fed continuously, maintaining the contact powder/pin during the whole test. The pin is 17 mm long and 4 mm in diameter.

A normal load, ranging between 1 and 18 N, is applied on the pin, while a rotating speed, ranging between 0.1 and 0.3 ms⁻¹ is applied on the disc. In Figure 1.14, the working powder test is showed and the amount of powder supplied is enough to assured a constant contact powder/steel.



Figure 1.14: “powder test” configuration

The test at 10N and 0.2 ms⁻¹ was considered as “standard test”. This standard test was applied also to the system constituted by steel disc and pin, to evaluate the friction coefficient of steel against steel.

The effect of load and speed on friction coefficient were investigated under the following conditions:

- 5 tests at different load, in the range 3-18N, with constant sliding speed of 0.2 ms^{-1}
- 5 tests at different sliding speed, in the range $0.1\text{-}0.3 \text{ ms}^{-1}$, with constant load of 10N

The tribological tests were performed in a laboratory kept at a temperature ranging between 20 and 25°C .

The roughness of disc groove and pin surface was considered as test condition and measured before and after the test in order to evaluate the effect of this variable.

The friction coefficient obtained corresponds to the average value of the so-called stationary friction. During the test, in function of surface roughness and material nature, friction coefficient is subject to an evolution divided into running-in and stationary period (fully described in Introduction). When the friction coefficient reaches a plateau, this is considered the stationary period and corresponds to equilibrium in the physico-chemical phenomena occurring at interface. The value of friction coefficient is not exactly constant during this phase, but it is subject to fluctuation in function of interface phenomena (relative to roughness or particle nature). To measure this variation of friction value, at each result is associated the standard deviation, generally identified as the amplitude of friction coefficient.

The second configuration is a pin-on-pad test, applied on composites. The test conditions and the characteristics of pin are the same as for pin-on-disc test previously described. Also with this configuration, the test at 10 N and 0.2 ms^{-1} was set up as “standard test”. The experimental difference in test conditions is the radius of pin, which is 5 mm from the centre of sample. For this reason, the angular velocity and the friction trace dimension are different from powder test.

The third configuration is a ball-on-pad test, applied on composites with the same conditions of the “standard test”. In addition, the roughness was measured on pad surface before the test, while after the profile of friction trace was measured to calculate the wear volume as described in section 1.4.4.3. The ball used is of 100Cr6 steel, in order to avoid differences in the chemical interactions among surfaces respect pin-on-pad and powder test.

1.3.4.2 – DYNAMOMETER TEST

Dynamometer test is the second step of characterization generally applied by researchers and manufacturers on brake pads. Preceded by small laboratory tests, like pin-on-disc testing, it could be subscale or full-scale and it is followed by real field tests. All these experiments demonstrate how the tested brake pads perform in a wide range of conditions. Studies dealing with automotive brake wear emissions also use these methods to generate brake wear particles for their subsequent evaluation. Advantage of small testers is typically related to low costs, but also to a considerably higher accuracy of detected physical variables compared to large scale and field tests, which often allows for a better understanding of wear mechanisms.

Dynamometer testing is trying to simulate conditions close to real urban or sub-urban driving. When the dynamometer is equipped with an environmental chamber, wear emissions can be also collected and subsequently evaluated. A schematic of brake dynamometer is presented in Figure 1.15.

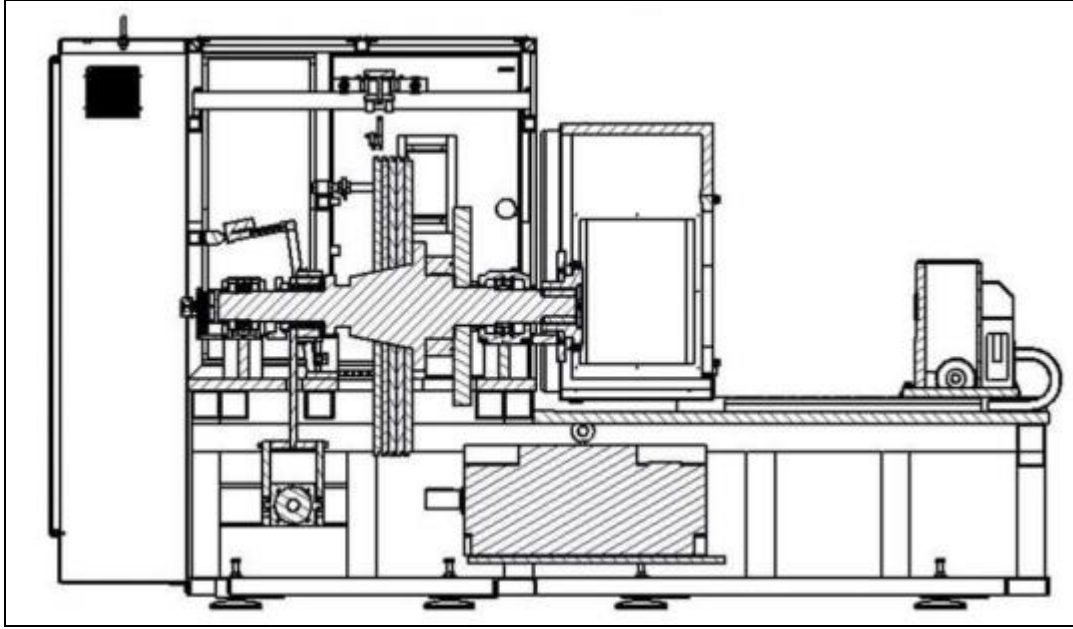


Figure 1.15: Schematic of the brake dynamometer with environmental chamber¹⁰⁴.

In the instrument, the brake rotor is attached to a driven shaft, usually by an electric motor, on which flywheels are mounted to simulate the vehicle inertia and kinetic energy. The brake stator, called also calliper, is mounted to the “tailstock” shaft of the machine, which is free to rotate on bearings and is constrained by a torque arm with a load cell to measure torque. The machine operates by engaging the motor drive to rotate the flywheels and rotor. When the required rotational speed is reached, the drive is disconnected and the brake is used to decelerate the flywheels. Inertia dynamometers are suitable for performance, durability, wear, noise, and vibration brake testing. They may be installed with environmental control chambers, as in the instrument used for this thesis, and many other features to simulate the actual conditions experienced on the vehicle.

A Link full-scale brake dynamometer model M2800 with the Short AK Master test procedure was used for automotive brake dynamometer tests. This experiment is a standard test, identified as ISO 26867:2009(E)¹⁰⁰, constitute by twenty parts for a total of 166 stops. Table 1.6 shows the individual parts of the testing procedure. The main parameters showed in Table 1.6 are initial temperature T_i , initial speed S_i , final speed S_f and applied pressure P .

Table 1.6: List of single parts in the ISO 26867 performance test with relevant test conditions for each part.

N°	SECTION NAME	N° of STOPS	T_i (°C)	S_i (Km/h)	S_f (Km/h)	P (bar)
1	Green Characteristics	10	150	80	30	30
2	Burnish	32	200	80	30	Variable
3	Characteristic Value	5	150	80	30	30
4	Ramp. Application	2	100	50	0	25
5	Cold Characteristic	6	150	80	30	30
6	Low Speed/Pressure	3	150	20	0	10, 20, 30
		3	150	30	0	10, 20, 30
7	Press line	6	150	80	40	10 – 60
8	Speed line	5	150	Inc.	Inc.	30
9	Failed Booster	6	100	100	0	30

10	Motorway Application	1	150	100	0	60
		1	150	175	100	35
11	Low Speed/Pressure	3	150	20	0	10, 20, 30
		3	150	30	0	10, 20, 30
12	Characteristic Recovery	10	150	80	30	30
13	Fade 1	15	Inc.	100	0	a = 0.4 g
14	Hot Performance 500°C	6	500	80	40	Inc.
15	Low Speed/Pressure	3	150	20	0	10, 20, 30
		3	150	30	0	10, 20, 30
16	Characteristic Recovery	10	150	80	30	30
17	Press line	6	150	80	40	10 – 60
18	Fade 2	15	Inc.	100	0	a = 0.4 g
19	Low Speed/Pressure	3	150	20	0	10, 20, 30
		3	150	30	0	10, 20, 30
20	Final Characteristics	6	150	80	30	30

As reported in Table 1.6, there are similar parts as brake conditions. In the ISO 26867:2009(E), each type of part is generally described:

- characteristic part: series of brake application at moderate speed, brake pressure and temperature, in order to assess how the friction level changes as the test progresses; it is also used as stability checks after other sections
- burnish part: series of brake application at varying braking power to condition the friction couple and develop a steady coefficient of friction
- ramp application part: series of brake stops where the brake pressure increases steadily and slowly, in order to assess the friction change with increasing input force
- low speed/pressure part: series of brake stops at low energy and low brake pressure
- pressure line part: series of brake application at moderate energy in order to assess the effect on friction level as a function of increasing input brake pressure
- speed line part: series of brake application at constant input brake pressure and increasing speeds and hence kinetic energy
- failed booster part: series of brake stops in order to assess the torque output while simulating a failed condition when the vacuum or hydraulic assist unit is fully depleted, and when only the driver input load at the brake pedal, brake pedal amplification and master cylinder multiplication factors are used to generate input pressure to the brake corner
- motorway applications part: series of brake application in order to assess the ability of the brake to develop torque at or near highway speeds
- fade part: series of brake stops intended to heat the brake and assess the coefficient of friction sensitivity to the increasing elevated temperatures on the surface of the mating couple
- hot performance part: series of brake application similar to the pressure line but at elevated temperatures, in order to simulate heavy braking or overloaded conditions

Brake dynamometer used has an environmental chamber with wind tunnel simulating corresponding airflow. The chamber was cleaned before each test. The wear debris was collected in two ways: as deposited wear debris, in a collector placed under the friction brake system, constitute by pads, disc,

and calliper; as airborne wear debris using a filter placed at the end of environmental chamber in correspondence of wind tunnel entrance.

The rotor used for each test is of lamellar cast iron type A with a composition principally eutectic. Each lining set (two pads) was run using a resurfaced brake rotor, cleaned after each test with a degreasing agent.

Before and after each test, pictures of pads and rotor surface were collected with a commercial digital photo camera.

1.3.4.3 – MEASURE OF ROUGHNESS AND WEAR

The surface parameters of discs and pads, before and after the test, were measured by a contact profilometer Form Talysurf 120. Analysis was performed with a cut off equal to 0.8 mm and a length of 4 mm. In some tests, also the pin surface was measured, using a cut off equal to 0.25 and a length of 1 mm.

The stylus type is conical, with a radius tip of 2 μm . The tests were performed within an air-conditioned laboratory, where the temperature is kept at 20°C. The instrument was calibrated using a standard calibration block prior to the measurements.

The parameters considered to describe the roughness are R_a , R_{sk} , and R_{ku} .

R_a is the arithmetic average of the absolute values of the profile heights over the evaluation length. It is the most universally used roughness parameter for general quality control.

$$R_a = \frac{1}{l} \int_0^l |y(x)| dx \quad R_a = \frac{1}{n} \sum_{i=1}^n |y_i|$$

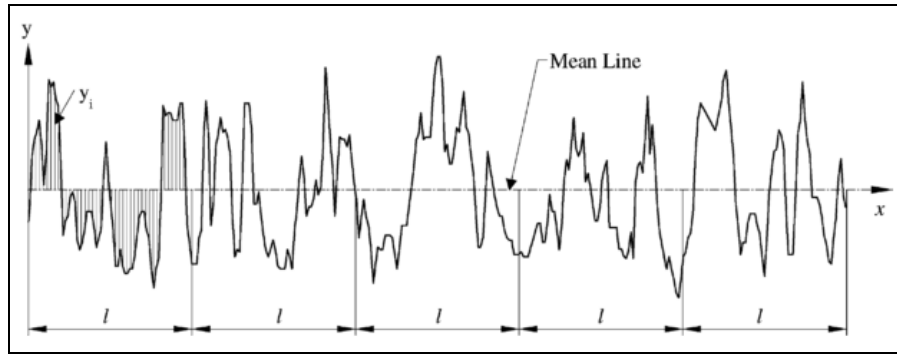


Figure 1.16: Definition of the arithmetic average height (R_a)¹⁰⁵

R_{sk} is named the skewness of a profile, defined as the third central moment of profile amplitude probability density function, measured over the assessment length. It is used as a measure of the asymmetry of the profile about the mean line. A negative skewness indicates that a greater percentage of the profile is above the mean line and a positive value indicates that a greater percentage is below the mean line.

$$R_{sk} = \frac{1}{R_q^3} \int_{-\infty}^{\infty} y^3 p(y) dy \quad R_{sk} = \frac{1}{NR_q^3} (\sum_{i=1}^N Y_i^3)$$

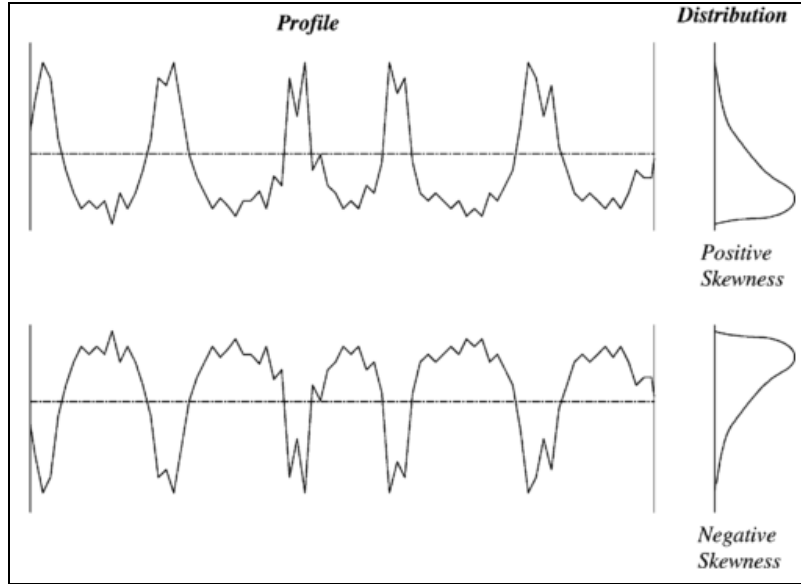


Figure 1.17: Definition of skewness (R_{sk}) and the amplitude distribution curve¹⁰⁵

R_q is the root mean square roughness, also known as RMS. It represents the standard deviation of the distribution of surface heights.

$$R_q = \sqrt{\frac{1}{l} \int_0^l \{y(x)\}^2 dx} \quad R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$$

R_{ku} is the kurtosis coefficient and it is a measure of the peakedness of the profile about the mean line. It is the fourth central moment of profile amplitude probability density function and describes its sharpness. If $R_{ku} < 3$, the distribution curve is said to be platykurtic and has relatively few high peaks and low valleys. If $R_{ku} > 3$, the distribution curve is called leptokurtic and it has relatively many high peaks and low valleys.

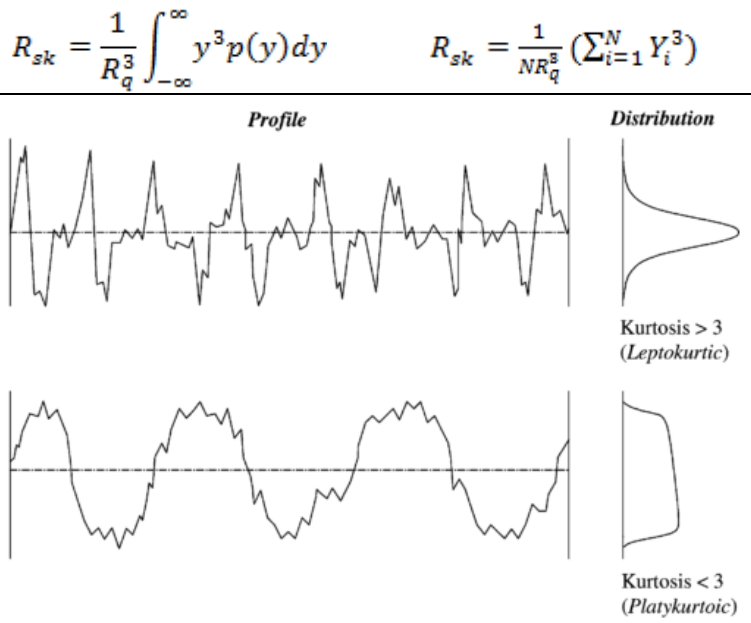


Figure 1.18: Definition of kurtosis (R_{ku}) parameter¹⁰⁵.

In each test of roughness, the measure was repeated three or five times randomly on the surface of disc or pin.

To investigate the significance of roughness parameters, some reproducibility tests were performed on a new disc, with three tests on the same evaluation length. Table 1.7 shows an example of results.

Table 1.7: Roughness parameters of steel disc 1.

STEEL DISC 1	R _a	R _{sk}	R _{ku}
1	0.2802	-1.5003	5.5181
2	0.2873	-1.5282	5.5660
3	0.2949	-1.5301	5.3114
MEDIA	0.2841	-1.3862	5.4652
DEV.STD	0.0073	0.0167	0.1353

By the results shown in previous table, the roughness parameters can be described with 2 significant digits. So, samples with a difference lower than the two significant digits were considered practically identical. However, for disc and pin the profile is not perfectly homogeneous, so a standard deviation was considered with the average roughness profile. In Table 1.8 an example of this feature, measured always on a steel disc:

Table 1.8: Roughness parameters of steel disc 2.

STEEL DISC 2	R _a	R _{sk}	R _{ku}
1	0.6168	-1.2367	5.5476
2	0.4589	-1.0837	4.0718
3	0.6588	-1.0921	6.5192
MEDIA	0.5782	-1.1375	5.3795
DEV.STD	0.1054	0.0860	1.2323

About this last test, considering the previous affirmation that only 2 significant digits can be considered, it is possible to describe the profile of disc 3 as:

$$R_a=0.58\pm0.11 \quad R_{sk}=-1.1\pm0.1 \quad R_{ku}=5.4\pm1.2.$$

The same contact profilometer was used to measure the 2D profile of the wear trace in 10 different zones, in order to obtain an average value of trace depth and section area. Figure 1.19 shows an example of profile.

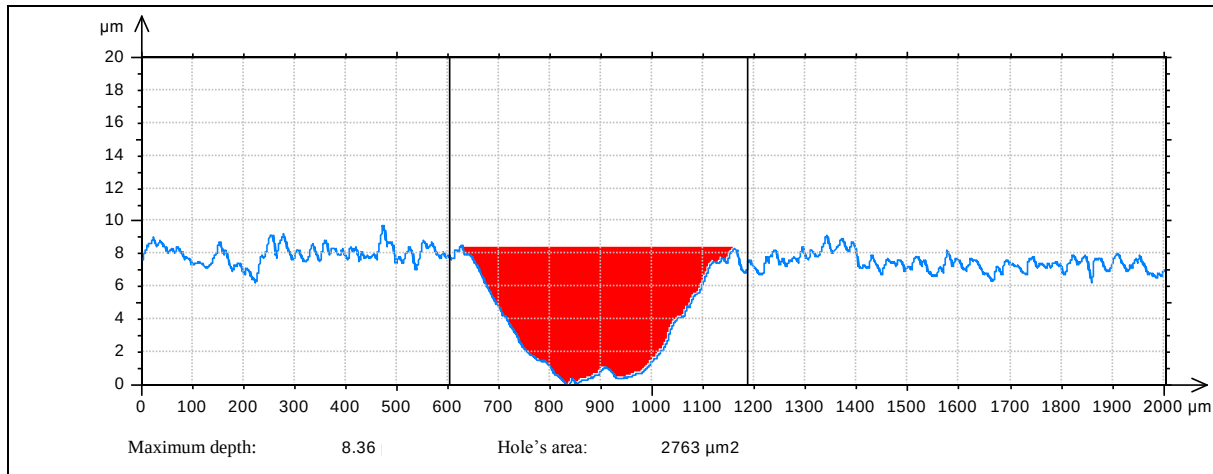


Figure 1.19: example of wear trace measurement.

The elaboration of the profile measurements was done by Talysurf software.

The value of wear volume was calculated as the average area of sections multiplied for trace circumference. Knowing the wear volume, the wear constant K was calculated using the modified Archard's formula¹⁰⁶ generally applied in literature:

$$K = \frac{V}{L * \Delta x}$$

In which V is the wear volume, L the load and Δx the sliding distance. K is defined as the lost wear volume per unit of applied load and sliding distance; the K -value is given in mm^3/Nm . In this thesis, also the original Archard's formula^{16,17} was considered to calculate another wear constant, named K' , in which the total volume of wear debris is proportional to the work done by frictional forces and inversely proportional to the hardness (H) of the softest contacting surface. The resulting formula of volume and K are:

$$V = \frac{KL\Delta x}{H} \quad K = \frac{VH}{L\Delta x}$$

As for dynamometer tests, wear of both pads and rotor was investigated. The rotor thickness was measured in five different points before and after each test, selected along the entire disc in a central position respect the disc part in contact with pads. Moreover, also the mass difference was taking in consideration, measuring the disc weight before and after test. As for pads, the measure of the thickness was collected in four points: one on the left, one on the right and two points respectively over and under the centre of pad. In this way, it is possible to observe the different consumption along the pad surface.

CHAPTER 2 – STEEL FRICTION

2.1 – STEEL 100Cr6

Steel 100Cr6 was selected as material for disc and pin in tribological tests, obtained in agreement with the reference normative EN ISO 683-17:1999¹⁰³. This kind of steel is mainly used for small and medium size bearing components, as also for other machine components that require high tensile strength and high hardness.

The tribological behaviour of steel is the focus of various research activities since the 1980s. A lot of scientists focused their attention on the study of severe-mild wear transition in metallic sliding contact^{33,107–110}. This transition is constituted by an initial severe wear regime, called running in, and a second part with mild wear regime. Severe and mild wear are regarded as adhesive wear and as oxidative wear respectively. During sliding contact of metals, an intensive metallic adhesion occurs with a high wear rate and consequently high friction coefficient. Due to surfaces contact, wear debris particles are formed from metal surfaces and are oxidized by oxygen present in air. The oxidation process requires the metal ions and/or oxygen to penetrate across the barrier layer and combine chemically. This process is usually controlled by diffusion rate of the reactants across the barrier layer, thus the process is very dependent on temperature, due to the exponential relationship between diffusion rates and temperature^{111,112}. When there is sufficient oxide formed on the surface, the formation of the compacted oxide layer is a necessary condition for the transition severe-mild wear^{33,107}. The oxide layer prevents metal loss due to mechanical damage caused by sliding wear¹¹². Wear debris particles play an important role in the establishment of mild wear regime with consequent reduction in friction coefficient.

Recent studies show that an artificial supply of particles on the rubbing surfaces significantly decreases the time to attain mild-wear conditions^{33,101}. Kato published a paper in which he studied the influence of the size of supplied Fe_2O_3 oxide particles on the severe-mild transition³³. He found that the supply of fine oxide particles with diameters of 0.5 μm and less accelerates the severe-mild wear transition, due to the formation of a tribofilm. Furthermore, the tribofilm formation affects also the friction coefficient, which is in the range 0.5-0.6 for particles with diameters of 0.5 μm and less, or higher than 0.8 for particles with diameters of 1 μm . The contact steel against steel leads to a friction of 0.7-0.8, so iron oxide acts as lubricant generating a tribofilm at interface, while as abrasive in the opposite case with consequent no severe-mild wear transition.

In a more recent work, Kato and Komai published a study on tribofilm formation in function of nanometre-sized oxide particles supply on rubbing steel surfaces¹¹³. They observed that the tribofilm is produced by tribosintering of the supplied oxide particles, so the layer formation depends on the sintering rate. Sintering is a process whereby particles bond together at temperatures typically below the melting point, by atomic transport events. In particular, the sintering mechanisms are usually diffusion processes and the kinetics is dominated by the atomic diffusion rate. In this study, Kato and Komai observed a decrease in total wear volume as the oxygen diffusion coefficient in the supplied oxide increases. Thus, an oxide of high diffusion rate allows a tribofilm formation dominated by high sintering rate. As in the previous article, Kato used pin and disc with the same starting roughness in each test, without considering the evolution of surface topography during tribological tests and its possible influence on friction coefficient.

Also Österle and co-workers⁹⁹ did not take in consideration the influence of roughness on friction coefficient. In their work, they studied different powder friction materials using the same test apparatus used by Kato. The aim of this article was to investigate the formation of tribofilm at interface in

function of powder friction materials generally used in brake pad formulation. For example, they compared graphite and iron oxide singularly and mixed.

In all the articles previously cited, the roughness of specimens was modified in order to start from the same value in each test. Literature survey suggests that the starting surface roughness doesn't influence friction coefficient in a large range of applied load¹¹⁴. They consider only the initial wear behaviour, while the wear rate at the steady state was not taken into account, as for example in the Jahanmir and Suh article¹¹⁵.

Studies dealing with the influence of roughness on friction coefficient, considering value before and after friction test, were not found in literature, to the author knowledge. For this reason, in this thesis a set of experiments regarding steel against steel contact was performed to investigate the roughness influence on friction by multivariate approach. This study was divided in three steps. First, the disc roughness was considered as variable keeping constant test conditions and pin starting roughness. This method aims to understand and describe the roughness influence using simple parameters as R_a , R_{sk} and R_{ku} , applying chemometrical approach. In the second step, pin and disc roughness was considered to investigate possible correlations between pin and disc surface evolution, taking in account also the pin wear and debris formation. The last step regards the influence of test conditions in order to verify if roughness is more influent of load and speed or vice versa.

2.2 – STANDARD TEST

The pin-on-disc “standard test” at 10 N and 0.2 ms^{-1} was applied on steel against steel system in order to characterize the tribological behaviour at interface between disc and pin, and to obtain a value of friction coefficient to compare with subsequent tests.

The surface roughness of discs was measured before and after each test (Table 2.1). The discs were selected with similar starting roughness, while the pin surface was modified to reach a value of R_a around $0.40 \mu\text{m}$. These tests aim to verify the reproducibility of the measurement.

The friction coefficient (Table 2.1) is almost the same in all three test. Figure _ shows the first test on disc A (a), which presents a running-in period (b) of less than 100 m as sliding distance. As suggested in literature, during the running-in period, the roughness is subjected to an important change due to the increase in wear. The change in surface roughness leads to reach a stable tribofilm at interface and consequently a stable friction coefficient and wear rate^{99,116,117}. Considering the roughness parameters, the symmetry of profile (R_{sk}) doesn't change significantly, while the increase in R_{ku} value indicates a reduction in the number of asperity, deformed by wear.

Table 2.1: Roughness parameters of discs before (I) and after (F) test.

TEST	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}	COF	AMPL.
A	0.84	-0.31	3.48	0.39	-0.46	4.30	0.61	0.01
B	0.76	-0.45	3.82	0.35	-0.23	4.94	0.60	0.01
C	0.72	-0.03	3.87	0.31	-0.44	4.83	0.59	0.03

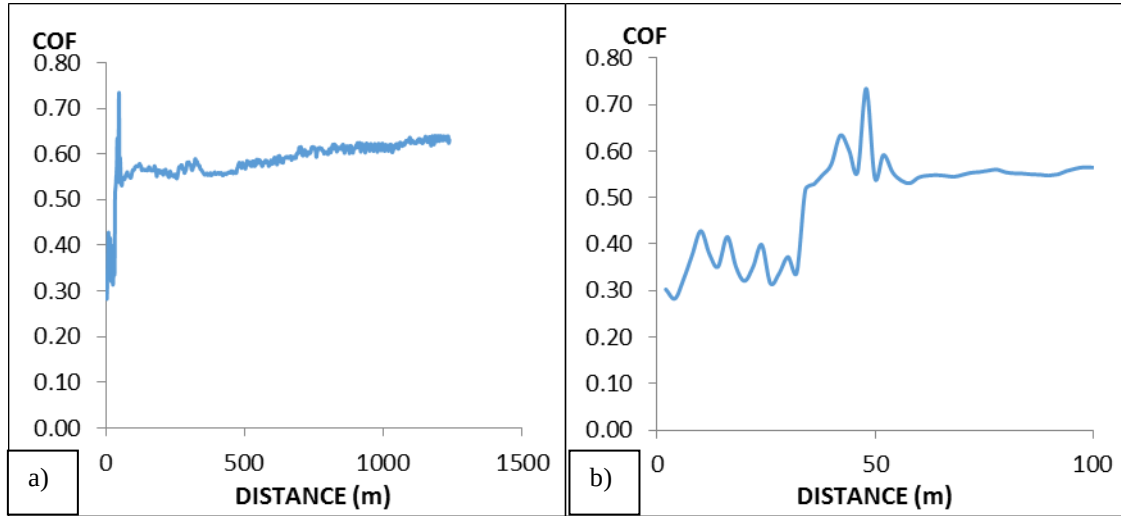


Figure 2.1: a) Friction coefficient evolution of test A in function of sliding distance; b) Zoom on running.-in period of test A in the first 100 m of friction coefficient evolution.

2.2.1 – INFLUENCE OF DISC ROUGHNESS

The influence of roughness parameters was investigated repeating the standard test using a pin with R_a around $0.40 \mu\text{m}$ and changing the disc roughness, in condition of moisture in the range 40-50%. In these tests, the starting roughness was investigated in the range $0.60 - 0.90 \mu\text{m}$, obtaining $0.30 - 0.75 \mu\text{m}$ as range of final roughness. The friction coefficient increases by increasing the final roughness, changing from 0.59 to 0.80. Apart from some tests, the change in R_{sk} is not significant, while R_{ku} increases or decreases depending on the starting value. For R_{kuI} around 4.40-4.60 the change is not significant, while for lower value an increasing is observed. Opposite situation occurs in test F, which starts from R_{kuI} of 5.44 and decreases to 3.19.

Table 2.2: Roughness parameters of disc and relative friction coefficient obtained applying the standard test conditions.

TEST	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}	ΔR_a	ΔR_{ku}	COF	AMPL.
A	0.84	-0.31	3.48	0.39	-0.46	4.30	0.46	0.82	0.61	0.01
B	0.76	-0.45	3.82	0.35	-0.23	4.94	0.41	1.12	0.60	0.01
C	0.72	-0.03	3.87	0.31	-0.44	4.83	0.41	0.96	0.59	0.03
D	0.70	0.27	3.82	0.62	-1.20	5.04	0.08	1.22	0.71	0.01
E	0.61	-0.27	4.46	0.50	-0.30	3.74	0.11	-0.72	0.73	0.01
F	0.82	-0.78	5.44	0.73	-0.25	3.19	0.09	-2.25	0.80	0.01

The Pearson coefficient was measured on each pair of variables, using the 2-tailed test of significance to identify significant correlations. The correlations found are COF – R_{kuI} (0.84), COF- R_{kuF} (-0.73) and COF – R_{aF} (0.90).

The effect of R_{ku} is correlated not only with initial or final value singularly, but also on its changes during friction test. In fact, considering the difference between final and initial value (ΔR_{ku}), the Pearson coefficient with COF results -0.82: the friction coefficient increases if ΔR_{ku} decreases. So

friction coefficient is affected by surface texture as found by Menezes et al. in a different system¹¹⁴, due to the variation of transfer layer which depends on the texture of surfaces.

The results show a linear proportionality between COF and R_aF . This means that starting from different roughness a similar friction coefficient can be obtained if the final roughness is similar. The change in roughness depends on many variables, but results show that roughness decreases and its reduction (ΔR_a) is inversely proportional to friction coefficient (Pearson coefficient = -0.93). The linear proportionality between friction and R_a can be motivated by the deformation of asperities during surfaces relative motion, which increases the asperity plasticity¹¹⁸.

Using the R-based software¹¹⁹, on data matrix reported in Table 2.2 a Principal Component Analysis (PCA) was applied considering 6 components. To explain more than 90% of variance three principal components are necessary (Table 2.3, Figure 2.2). In this study, the values of R_{sk} were not considered due to their Pearson coefficient respect COF, lower than 0.30 and then not influent.

Table 2.3: Percentage of explained variance for each component used in PCA analysis.

PC	1	2	3	4	5	6
% EXPL VAR	59.67	17.99	14.56	6.38	1.40	0.00

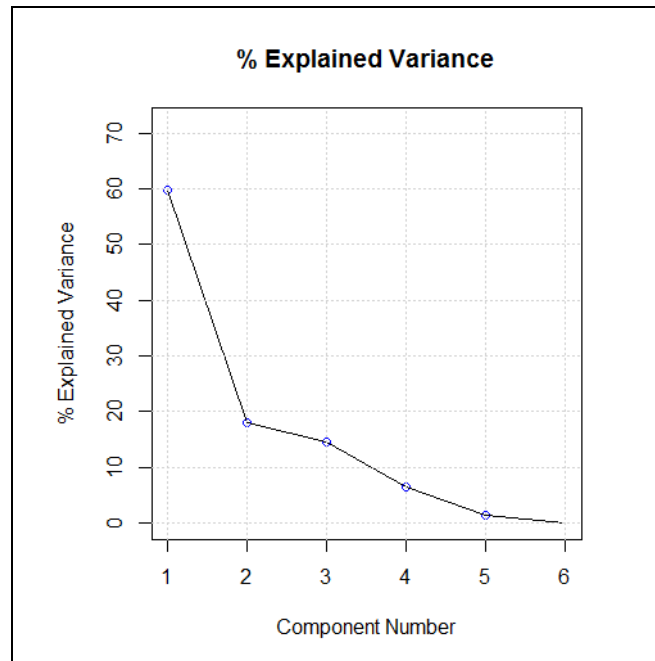


Figure 2.2: Percentage of explained variance in function of component number.

With three principal component and using both Q index and T^2 Hotelling index, the diagnostic plot shows that all the tests are significant, as reported in Figure 2.3.

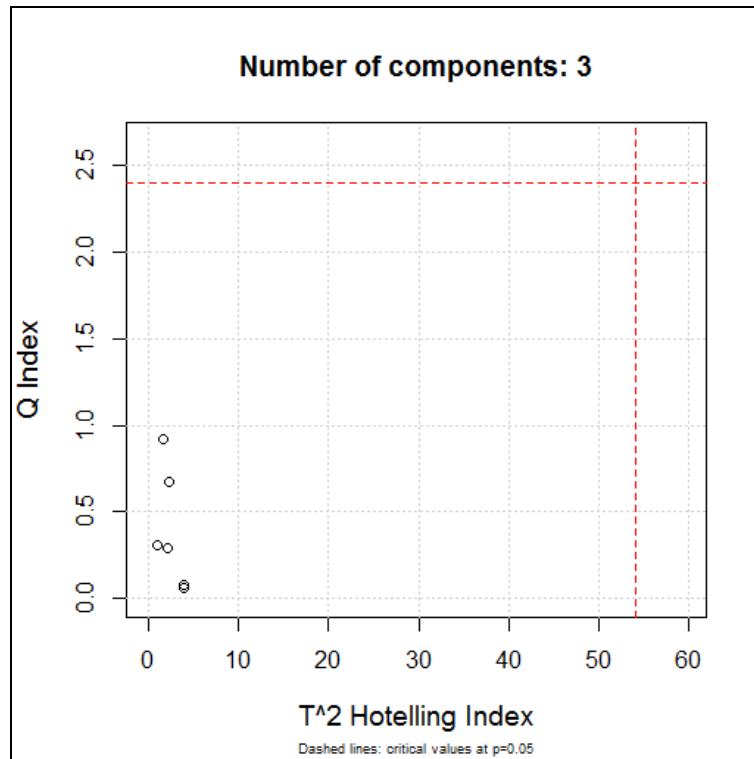


Figure 2.3: Diagnostic plot considering 4 components.

To identify the correlations among variables, it is necessary to observe the loading plot obtained from PCA analysis (Figure 2.4). In this plot, the linear correlation between COF and R_aF is confirmed, whereas other correlations can be observed. First, the standard deviation of COF is not correlated to COF, as confirmed by Pearson coefficient. Respect other variables, the Pearson coefficient results lower than 0.40, so no one of them is linearly correlated with standard deviation of friction. On the other hand, the inverse proportionality of initial and final value of R_{ku} is confirmed by Pearson coefficient, equal to -0.84.

The starting roughness has no linear influence on friction coefficient or on other variables studied in this system.

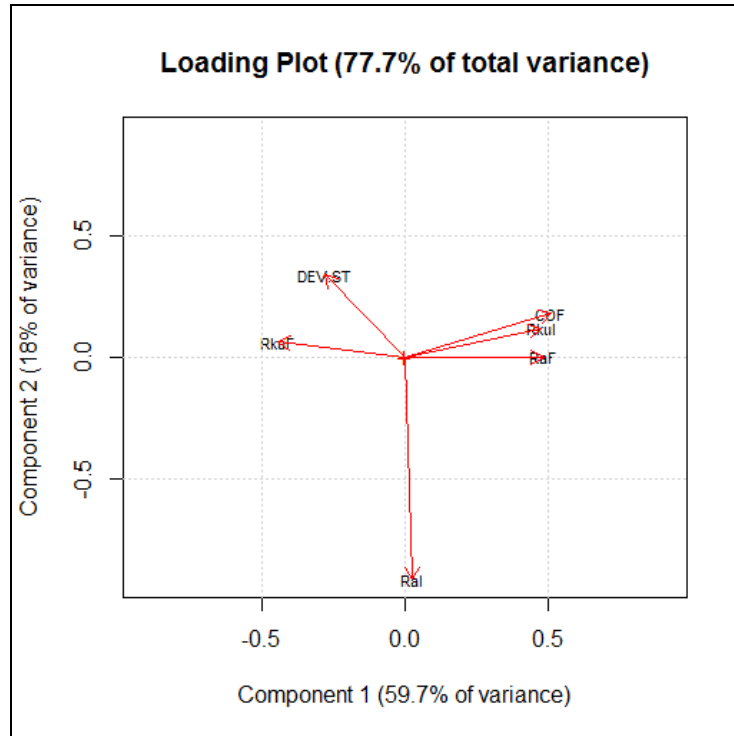


Figure 2.4: Loading plot of component 1 and 2.

The friction amplitude could be omitted at this point, due to the absence of correlations with roughness parameters investigated in this study. For the same reason, R_{aI} could be omitted, but in order to not simplify too much the system, it was considered in next elaborations. Acting in this way and applying a new PCA, two components are enough to explain more than 90% of system variance with all tests significant (Table 2.4).

Table 2.4: Percentage of explained variance for each component used in PCA analysis.

PC	1	2	3	4	5
% EXPL VAR	67.15	20.96	9.31	2.57	0.01

A Partial Least Square regression (PLS) was applied considering COF as response and the other variables as factors. This analysis suggests two components to explain the majority of system variance and gives a formula of friction coefficient in function of initial and final values of both R_a and R_{ku} .

$$2.1 \quad COF = 0.68 - 0.26R_{aI} + 0.30R_{aF} + 0.04R_{kuI} - 0.02R_{kuF}$$

The coefficients obtained from PLS regression show a lower effect of R_{ku} parameters with respect to R_a ones.

By PCA and Pearson coefficient, the starting roughness results not so influent on COF, but in this formula its coefficient is high enough to reconsider its importance. Due to this result, it is possible to consider the different change of roughness occurring during test using the starting roughness as correction factor for final roughness. As discussed before, the starting roughness can be taken into account calculating the reduction of roughness ΔR_a , equal to the difference between R_{aI} and R_{aF} . Another way is the ratio between final and initial R_a (R_{aF}/R_{aI}); the goodness of this correlation with

COF is validated by Pearson coefficient, equal to 0.95, which indicates a linear correlation as reported in Figure 2.5.

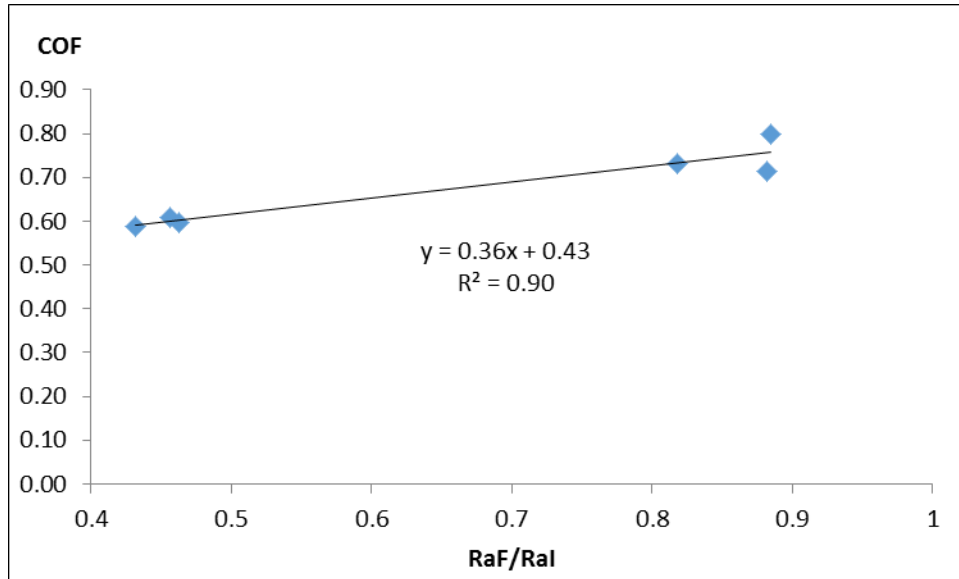


Figure 2.5: Correlation of friction coefficient with the ratio of final and starting Ra value.

The friction coefficient is correlated to the change in roughness parameters more than with each single parameter. In fact, recalculating the PLS regression based on ΔR_{ku} and ΔR_a or R_aF/R_{aI} , the following two equations are obtained:

$$2.2 \quad COF = 0.75 - 0.03 * \Delta R_{ku} - 0.27 * \Delta R_a$$

$$2.3 \quad COF = 0.53 - 0.03 * \Delta R_{ku} + 0.22 \frac{RaF}{RaI}$$

Both equations lead to calculate friction coefficient in function of the change in roughness parameters. To compare the proposed models a comparison of residuals was made. Table 2.5 shows the experimental values of COF and the calculated values obtained from models previously cited.

Table 2.5: Experimental and predicted values of COF

TEST	COF	MOD. 2.1	Δ	MOD. 2.2	Δ	MOD. 2.3	Δ
A	0.61	0.63	0.02	0.65	0.04	0.61	0.00
B	0.60	0.64	0.04	0.67	0.08	0.60	0.00
C	0.59	0.64	0.06	0.67	0.08	0.60	0.01
D	0.71	0.74	0.02	0.76	0.05	0.69	-0.03
E	0.73	0.77	0.04	0.70	-0.03	0.73	0.00
F	0.80	0.84	0.04	0.66	-0.14	0.79	-0.01

In this study, it is possible to consider 0.05 as acceptable level of error relative to models, which represents the maximum difference between fitted and experimental value. As reported in Table 2.5, the model that shows residuals under 0.05 is the number 2.3. This observation suggests that to predict friction coefficient through simple roughness parameters occurs to consider the evolution of R_{ku} (ΔR_{ku})

and the ratio R_aF/R_aI . A model based on single roughness parameters as model 1.1 or on evolution of roughness as model 2.2 is not good enough if the desirable level of prediction is ± 0.05 .

The consideration of residuals is not enough to affirm the validity of a model, for which it is necessary to perform other tests and compare the new experimental results with values forecast using the models. If the difference between them is lower or equal to ± 0.05 , the model can be considered predictive. In this case, other two tests G and H were performed at the same conditions of previous tests. Table 2.6 shows the friction coefficient and roughness parameters obtained.

Table 2.6: Roughness parameters of disc, relative friction coefficient obtained applying the standard test conditions and values obtained by models.

TEST	R_{aI}	R_{kuI}	R_{aF}	R_{kuF}	ΔR_a	ΔR_{ku}	R_{aF}/R_{aI}	COF	AMPL.	2.1	2.2	2.3
G	0.85	4.60	0.45	4.54	0.40	-0.06	0.53	0.69	0.05	0.69	0.64	0.65
H	0.81	4.22	0.55	4.41	0.26	0.19	0.68	0.72	0.02	0.72	0.69	0.67

Results show that all three models are able to predict the friction coefficient in the range of error ± 0.05 . Therefore, the model 2.3 based on ΔR_{ku} and R_{aF}/R_{aI} results the best in terms of both residuals and ability of prediction. However, this model can be assumed valid only in the conditions considered.

Aim of next steps is to individuate models able to predict the friction coefficient in other test conditions.

The first condition considered is the only one that is usually uncontrolled: the moisture. As specify in *Materials and Methods*, all tests were performed in a laboratory kept at a temperature ranging between 20 and 25°C, without control of humidity. For this reason, standard tests were performed in a different period in which the measured moisture was ranging between 70 and 80%. The experimental values result significantly different with respect to predicted values obtained by previous models. Thus moisture affects friction coefficient significantly, decreasing it.

2.2.2 – INFLUENCE OF PIN ROUGHNESS

Three standard tests were performed considering the roughness of both disc and pin, measured before and after each test (Table 2.7), in condition of moisture ranging between 70 and 80%.

Table 2.7: Roughness parameters of discs and pins selected before test.

	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}
DISC 1	0.50	0.65	3.78	0.67	-0.33	3.50
DISC 2	0.81	-0.57	3.95	0.60	-0.78	5.37
DISC 3	1.51	-0.83	4.35	1.01	-1.40	5.95
PIN 1	0.08	-0.09	3.93	0.09	1.90	9.44
PIN 2	0.48	-0.07	3.20	0.48	0.80	3.34
PIN 3	0.50	-0.26	2.86	0.14	0.90	4.18

A black powder was generated at interface and it is probably constituted by iron oxides, reported as the major constituent of wear debris in steel against steel, due to tribooxidation phenomena^{101,120}. All the three pins used show a film on their surface, as reported in Figure 2.6. Thus, the final roughness of pin is not directly related to the topography of metal surface, but to the tribofilm generated at interface.

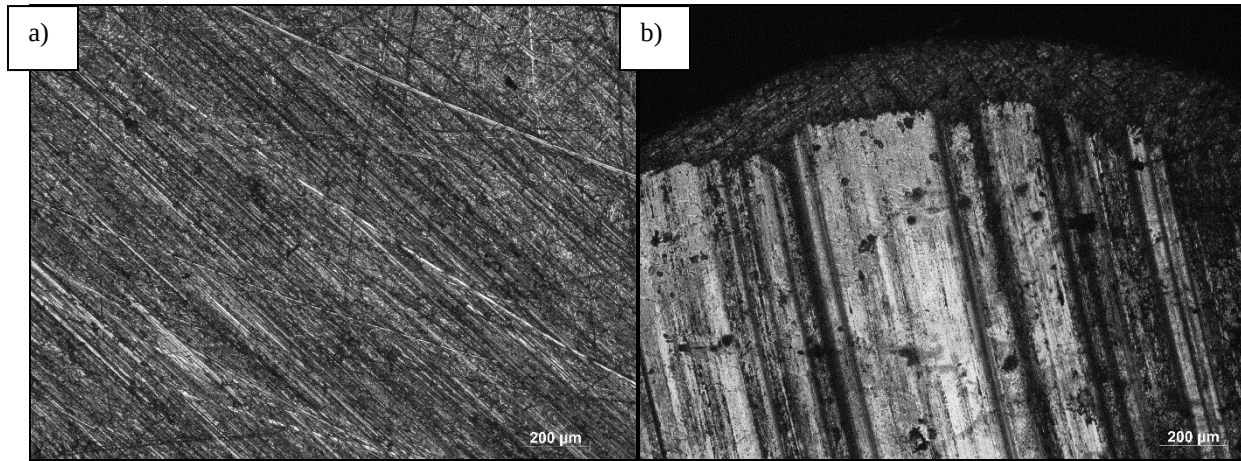


Figure 2.6: Optical microscope images: a) Surface of new pin; b) Example of film on pin surface.

The amount of powder generated and the pin wear linearly increase with COF (Table 2.8).

Table 2.8: Friction coefficient and relative amount of powder collected after test.

	COF	DEBRIS (mg)	PIN WEAR (mg)
DISC – PIN 1	0.63	47	1.6
DISC – PIN 2	0.56	29	0.8
DISC – PIN 3	0.48	22	0.5

The friction coefficient results also in this case inversely proportional to ΔR_{ku} and ΔR_a but directly proportional to $R_a F / R_a I$, (Figure 2.7).

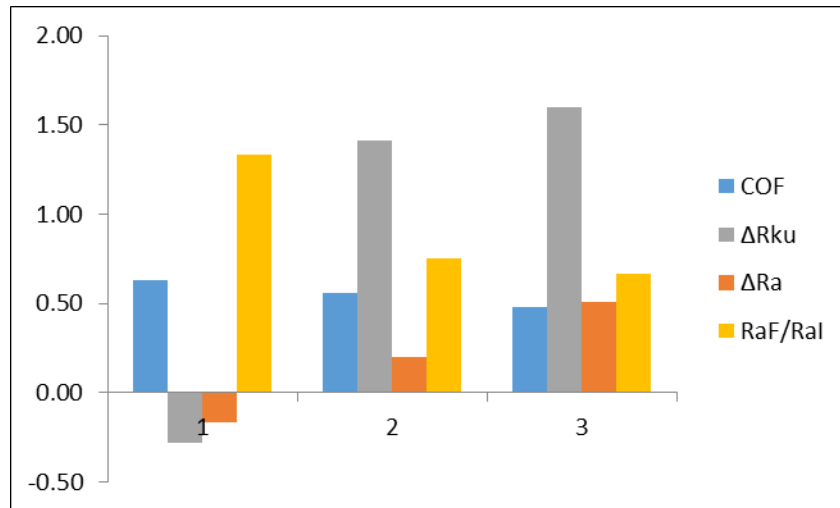


Figure 2.7: Friction coefficient, ΔR_{ku} and ΔR_a relative to standard tests 1,2 and 3.

The influence of pin roughness does not change the correlation of COF with disc roughness previously found; thus the moisture decreases friction coefficient but does not affect the influence of roughness on COF. The wear of pin and the amount of debris generated are proportional to friction coefficient and not to roughness change.

All the considerations described until now are true in the standard test tribological conditions, which are 10N and 0.2ms^{-1} . In order to verify the influence of roughness also in other test conditions, a systematic study was set up changing load and speed.

2.3 – INFLUENCE OF LOAD AND SPEED

Considering test conditions of 10N as load and 0.2ms^{-1} as speed, friction coefficient is correlated mainly with the final roughness of disc, but also with the change in disc roughness parameters R_a and R_{ku} . In these conditions, the pin surface seems not affect significantly friction coefficient. To verify the influence of roughness in a larger range of test conditions, load and speed were changed and their effect compared to roughness one.

Load was considered in the range 5 – 15 N, adding to previous standard test other four tests at the same sliding speed of 0.2 ms^{-1} (two at 5N, two at 15N). In each test, the starting and final roughness of disc and pin were measured and considered as variables. Also in this set of experiments, the friction coefficient is proportional to pin wear and amount of debris (Table 2.9).

Table 2.9: Data obtained at 5N and 15N

LOAD (N)	COF	AMPL.	DEBRIS (mg)	PIN WEAR (mg)
5	0.504	0.027	16	0.0
5	0.522	0.005	21	0.0
15	0.527	0.015	34	0.3
15	0.639	0.019	41	1.1

To understand the effect of load in correlation with roughness parameters, a PCA analysis was applied using seven components in the first step (Table 2.10 and Figure 2.8). The majority of system variance is explained by the first two principal components, but this is not enough to obtain a clear understanding of variables effect. To improve the knowledge on variables influence, parameters explaining the same variance on components must be removed as did before, leaving just significant variables in the system.

Table 2.10: Percentage of explained variance for each component used in PCA analysis.

PC	1	2	3	4	5	6	7
% EXPL VAR	41.72	21.99	15.19	9.73	8.59	2.79	0.00

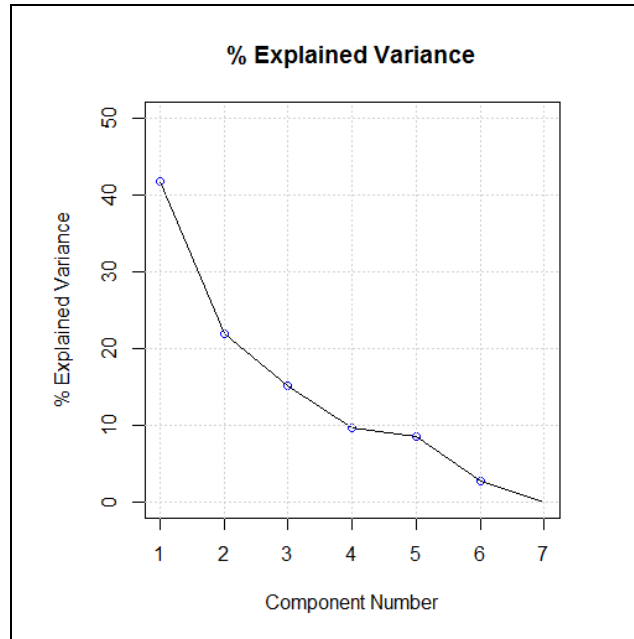


Figure 2.8: Explained variance in percentage in function of component number.

In the loading plot obtained from this PCA (Figure 2.9), it is hard to individuate the correlations among variables. However, some preliminary considerations can be done. ΔR_{ku} and ΔR_a result again inversely proportional to friction coefficient, while $R_a F / R_a I$ is directly proportional to COF. Increasing the load applied, pin wear, and amount of debris increase. Based on these correlations, the system can be simplified deleting disc roughness single parameters and focusing the attention only on pin roughness and friction coefficient.

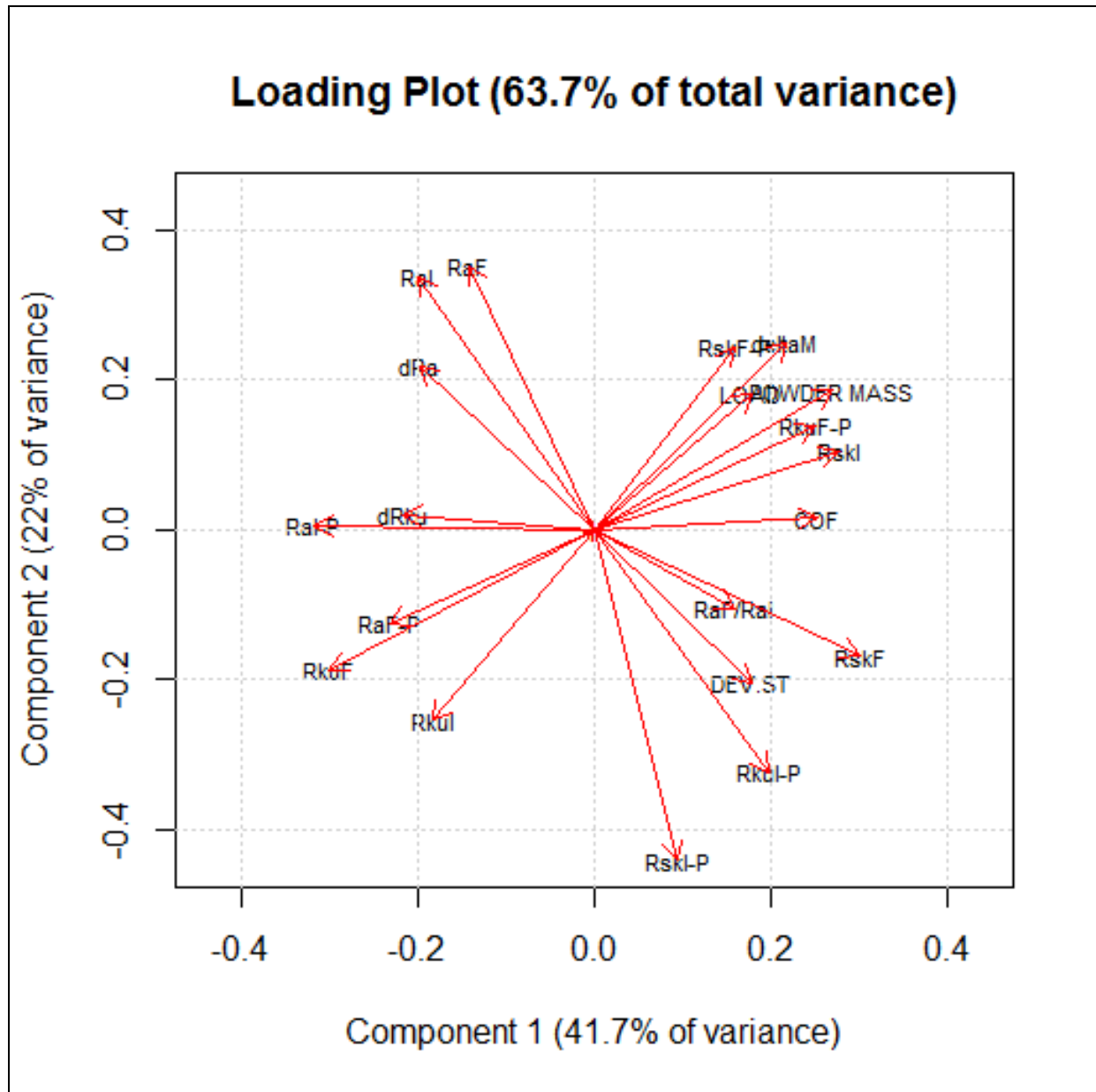
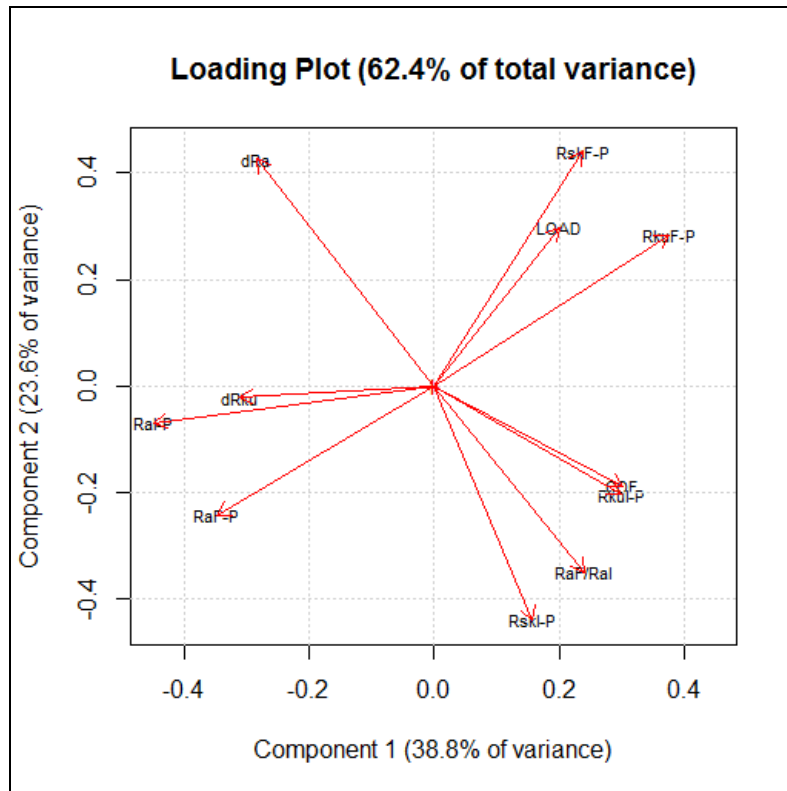


Figure 2.9: Loading plot of component 1 and 2 of PCA analysis.

After a significant reduction of variables, a new PCA analysis focused on COF was applied and the relative loading plot shows the same correlations previously found in the case of disc roughness (Figure 2.10). About pin roughness parameters, no one results linearly correlated with COF considering Pearson coefficient calculation. However, the relative position in loading plot of parameters suggests some kind of correlations. Pin R_{sk} values do not affect friction, while pin R_a seems inversely proportional to COF. To confirm this influence, the difference between initial and final value of pin R_a was calculated with the relative Pearson coefficient with respect to COF. The result shows a similar value as for $COF - \Delta R_a$, but more interesting is the correlation between ΔR_a of disc and pin. The change in roughness of pin is directly proportional to disc change (Pearson coefficient 0.72), so considering disc roughness also the pin roughness change is taken into account.



Then a new PCA was applied considering only disc parameters and load. In this way, the resulting explained variance shows that three components are enough to explain more than 90% of system variance.

Table 2.11: Percentage of explained variance for each component used in PCA analysis.

PC	1	2	3	4	5
% EXPL VAR	52.78	33.82	10.64	1.81	0.95

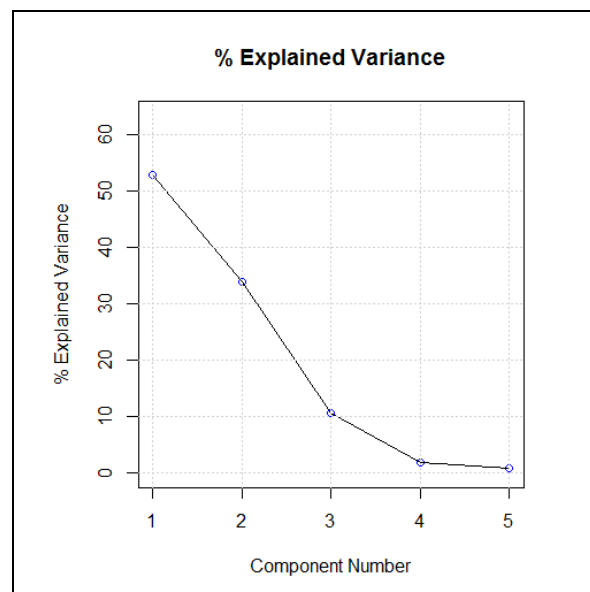


Figure 2.11: Explained variance in function of component number of third PCA analysis.

In this system, friction coefficient can be considered as response, then applying PLS regression analysis, COF in function of disc roughness and load can be obtained.

$$2.4 \quad COF = 0.31 + 0.01 * LOAD + 0.18 * \frac{RaF}{RaI} - 0.01 * \Delta Rku$$

Load shows an influence on friction approximately equal to 1/20 of R_a effect. Also in this case, the residuals between experimental and predicted values are equal or lower to ± 0.05 .

The load increases the friction coefficient due to a higher contact steel-steel. When load increases, the relative increase in real contact area lead to a fragmentation of oxide film generated at interface, which allows metallic contact and does not occur at low load. At low load, the friction coefficient is lower because corresponds to oxide film friction. Otherwise, at higher load, the fragmentation of oxide film allows the instauration of metal-metal regime, in which the adhesive component of friction increases. Consequently, also wear increases (as found in this study).

To validate the entire hypothesis, other tests were performed at 5, 10 and 15 N using 0.4 ms^{-1} as sliding speed. Two tests for each value of load were performed and the pin surface roughness was maintained at $0.40 \text{ }\mu\text{m}$ as starting value. Also in these tests, the friction coefficient results directly proportional to R_aF/R_aI and inversely proportional to ΔR_{ku} and ΔR_a . Applying a PLS regression and considering a level of confidence of ± 0.05 , the resulting formula of COF is:

$$2.5 \quad COF = 0.67 - 0.01 * LOAD + 0.18 * \frac{RaF}{RaI} - 0.02 * \Delta Rku$$

The effect of roughness does not change using 0.4 ms^{-1} as speed, which suggests a predominance of roughness effect on tribological conditions as already found for load. However, two differences with respect the previous case can be observed. The coefficient of ΔR_{ku} doubles, but it remains significantly lower with respect to R_aF/R_aI influence. Furthermore, the effect of load becomes the opposite, maintaining the same coefficient. At 0.4 ms^{-1} the fragmentation of oxide tribofilm is lower with respect tests at 0.2 ms^{-1} , thus the instauration of metal-metal regime is avoided and the resulting friction coefficient is lower. At this point, a system composed by test at 0.2 and 0.4 ms^{-1} can be generated and analysed by PCA. In this last step, only significant parameters were considered (Table 2.12), in order to generate a general formula of COF in function of roughness and tribological conditions. As done before and due to the inversely proportionality of R_aF/R_aI and ΔR_a , in the PCA analysis R_aF/R_aI was considered as parameter to describe the roughness effect instead of ΔR_a .

Table 2.12: Data on tribological test steel against steel

LOAD	SPEED	R_aF/R_aI	ΔR_a	ΔR_{ku}	COF
5	20	1.12	-0.04	1.21	0.50
5	20	0.86	0.08	0.29	0.52
5	40	0.67	0.20	-0.52	0.70
5	40	0.59	0.25	-0.36	0.83
10	20	1.33	-0.17	-0.28	0.63
10	20	0.75	0.20	1.42	0.56
10	20	0.67	0.50	1.60	0.48
10	40	0.31	0.54	0.02	0.62
10	40	0.93	0.03	-1.89	0.81

15	20	0.50	0.32	-0.25	0.53
15	20	0.91	0.04	0.39	0.64
15	40	0.41	0.41	0.70	0.57
15	40	0.56	0.43	2.47	0.62

The PCA model at five components shows that two components are enough to explain more than 70% of system variance (Table 2.13). As expected, roughness parameters affect COF as found before, while load results in general inversely proportional to COF and speed affects directly the friction coefficient. The Pearson coefficient of COF with R_aF/R_aI is practically zero, which suggests a linear correlation with COF through all the range of load, but only at constant speed. Otherwise, in a system in which both load and speed change; the linear correlation is not valid due to speed effect.

Table 2.13: Percentage of explained variance for each component used in PCA analysis.

PC	1	2	3	4	5
% EXPL VAR	42.63	31.87	14.76	8.37	2.37

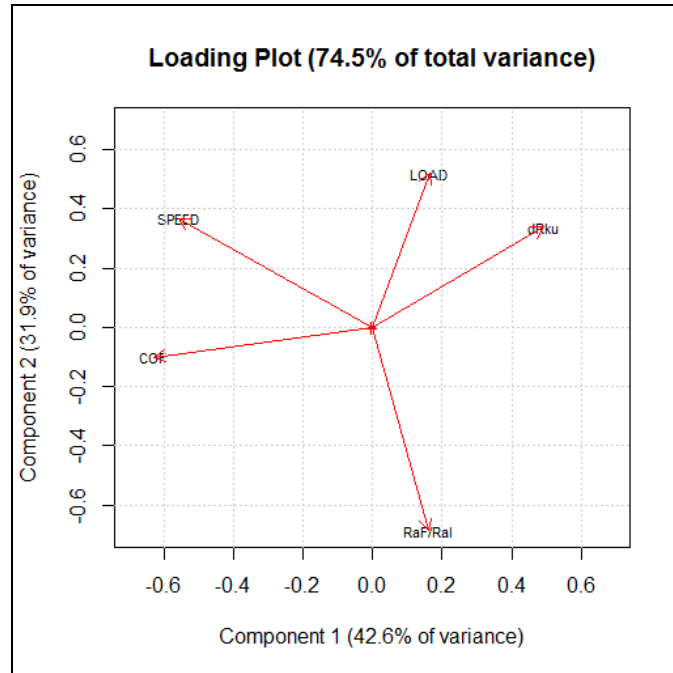


Figure 2.12: Loading plot of PCA analysis on Table 2.12.

PLS regression was applied to investigate the influence of all the variables. With this system, the resulting formula is:

$$2.6 \quad COF = 0.29 - 6.05 * 10^{-4} * LOAD + 8.06 * 10^{-3} * SPEED + 0.14 * \frac{RaF}{RaI} - 0.04 * \Delta Rku$$

The influence of load results the lowest one. Using this formula to calculate values, the residuals are lower than ± 0.1 , so this model is less precise compared to previous ones, probably due to its complexity.

To validate the models found in this third step, three standard tests were performed and the experimental and model values were compared (Table 2.14). Results show that the formula 2.6 is not

able to predict friction coefficient properly, while formula 2.4 is acceptable considering a level of confidence equal to ± 0.1 .

Table 2.14: Tests of validation for models 1.4 and 1.6.

	R _{aI}	R _{aF}	R _{kuI}	R _{kuF}	R _{aF} /R _{aI}	ΔR_a	ΔR_{ku}	COF	COF 2.4	COF 2.6
A	0.80	0.35	5.08	0.17	0.43	0.45	0.17	0.55	0.49	0.50
B	0.67	0.80	3.50	1.42	1.19	-0.13	1.42	0.59	0.61	0.55
C	0.63	0.29	2.85	3.21	0.46	0.34	3.21	0.50	0.46	0.38

2.4 – CONCLUSION

The roughness and test conditions influence were studied in steel against steel system using pin-on-disc test as suggested by Kato³³.

Despite in literature the majority of tribological tests was performed starting from same surface roughness of specimens, in this study the effect of initial and final roughness on friction coefficient was demonstrated.

Friction coefficient is affected by how roughness changes during tribological test and this influence can be quantified through R_{aF}/R_{aI} and ΔR_{ku} as done in formula 2.3.

$$2.3 \quad COF = 0.53 - 0.03 * \Delta R_{ku} + 0.22 \frac{R_{aF}}{R_{aI}}$$

This study also evidenced the importance of operating in conditions as similar as possible, because variables as relative humidity can affect value of friction coefficient, but they do not change the trends of friction with respect to roughness parameters.

Variables that seem not influent on friction in the range investigated are the roughness parameters of pin, both initial and final. A common feature of all tests is the formation of stable tribofilm on pin surface, formed by tribosintering of wear debris generated at interface. The effect of test conditions is not clear because load affects in different way based on speed value, but both load and speed have a very low influence on friction coefficient value if compared to roughness parameters.

A constant correlation found in this study at each load and speed regards the pin wear and amount of wear debris. They linearly increase with friction coefficient.

CHAPTER 3 – POLYMER MATRIX

3.1 – BASIC MIX

The basic mix used in this thesis is composed of phenol formaldehyde resin as binder and aramid fibres, providing a sufficient mechanical strength to the sample.

The data collected on these raw materials from supplier are summarized in Table 3.1.

Table 3.1: Data on raw materials from supplier.

	Phenol formaldehyde resin	Aramid fibers
Density (g/cm ³)	1.25	1.44
Granulometry (μm)	D50 = 33	D50 = 1000
Volatile part (%wt)	0-6	4-10
Thermal conductivity (W/(K.m) at 298K)	0.15	8.05

The selected basic mix is the same already used in a previous PhD thesis, made by Eng. Vivier⁶⁶, in which a full characterization of polymer matrix was done. In Table 3.2, data of previous mechanical characterization are reported and considered as starting point for the characterization made in this thesis.

Table 3.2: Characterization of basic mix in previous study⁶⁶.

Density (g/cm ³)	1.32±0.02
Stiffness value (GPa)	7.08±0.36

3.1.1 – PHENOLIC RESIN

The phenolic resin used in this thesis is phosphorus and boron modified, which means that some P and B particles were added to the powdered neat resin. Furthermore, it is already mixed with 10% of HTMA (hexamethylenetetramine) to promote the formation of additional linkages to form the rigid 3D polymeric network.

DSC, TGA and DTG measurements indicated that the resin heating leads to a material composed of polycondensated novolak oligomers with some aromatic ring bond¹.

3.1.2 – ARAMID FIBRES

Kevlar fibres were selected for the basic mix, in particular an aramid pulp with a fibrillary structure. They are the most used in the reinforcing fibres category and they derive from the condensation of m- or p- phenylenediamine and isophthalic or terephthalic acids¹²¹ (Figure 3.1).

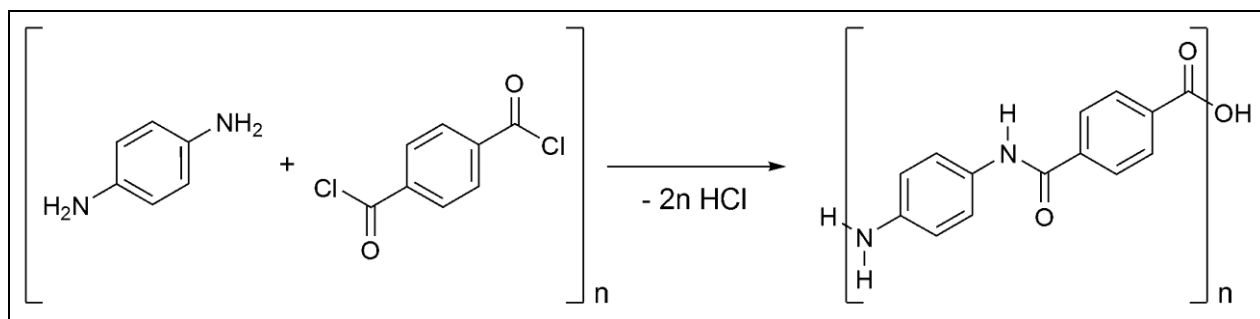


Figure 3.1: Direct synthesis of Kevlar fibres.

Thermal properties indicates that a complex depolymerisation, random rupture, hydrolysis, restructuring and other chemical reactions occur for Kevlar fibres in the temperature range 400-600°C.¹

3.2 – CHARACTERIZATION OF BASIC MIX

Figure 3.2 shows the microstructure of the basic mix: just in some part of pad surface, some Kevlar fibres are visible. More details appear by observing the pad surface with polarized light, since Kevlar fibres are visible.

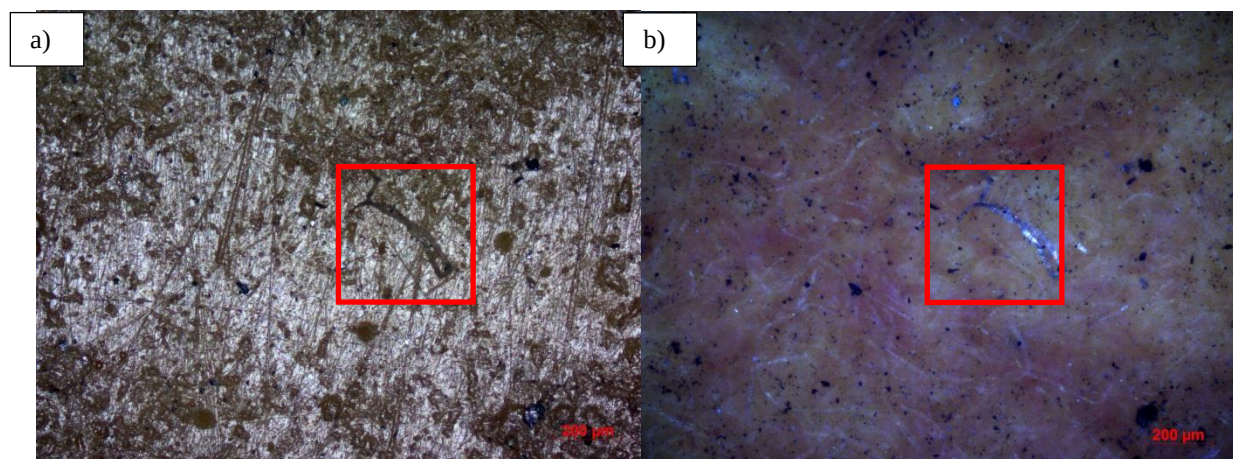


Figure 3.2: Optical microscope image of basic mix pad surface: a) in bright field; b) in polarized light. Kevlar fibre in the red square.

As reported by Vivier, aramid fibres contribute to generate a complex 3D network, which affects positively the mechanical properties of basic mix.

An example of Kevlar fibres influence is the change in hardness of phenol formaldehyde resin. In fact, the resin alone possesses a Brinell hardness of 330 MPa, while Kevlar hardness is around 1.3 GPa¹²², (by nano indentation). The resulting hardness measured on basic mix by Brinell test is equal to 844±59 MPa.

FTIR spectra (Figure 3.4) show the presence of peaks around 3200 cm⁻¹, representing the hydroxyl groups –OH of phenolic resin, while the peaks at 2920 and ~2850 cm⁻¹ derive from carboxylic –OH of Kevlar fibres and methyl groups –CH₃ of phenolic resin respectively.

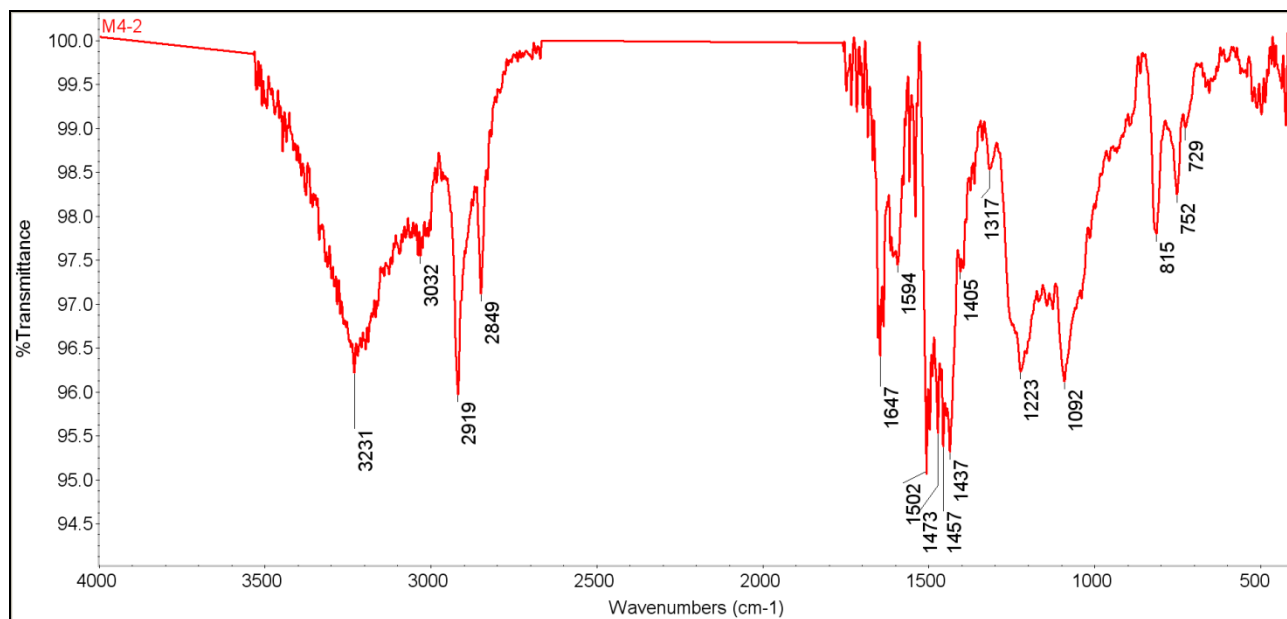


Figure 3.4: FTIR spectra of basic mix, obtained in ATR geometry.

Further information by Raman spectroscopy could not be obtained because of the intense fluorescence using the laser source at 532 nm.

3.3 – TRIBOLOGICAL STANDARD TEST

The pin-on-pad “standard test” at 10 N and 0.2 ms^{-1} was applied on polymer matrix in order to characterize the tribological behaviour at interface between pad and pin, and to obtain the value of friction coefficient to compare with subsequent tests.

The surface roughness of pads was measured before and after each test (Table 3.3), whereas the pin surface was set up at R_a of $0.50 \text{ }\mu\text{m}$.

These tests aim to verify the influence of roughness, as done for steel against steel. The friction coefficient ranges between 0.29 and 0.41 for starting roughness between 0.81 and $1.10 \text{ }\mu\text{m}$. The final roughness shows a wider range than initial roughness, varying from 0.34 to $0.98 \text{ }\mu\text{m}$. The Pearson coefficient, calculated using all the roughness parameters, indicate the absence of a linear correlation between the starting parameters and the COF. All the three final roughness parameters are correlated, especially R_aF and $R_{sk}F$ with a respective Pearson coefficient of -0.79 and -0.88 .

Table 3.3: Roughness parameters of pads before (I) and after (F) test.

TEST	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}	COF	AMPL.
A	1.10	0.79	3.28	0.25	-0.47	4.66	0.41	0.01
B	1.03	0.71	3.50	0.44	0.45	4.03	0.34	0.01
C	0.91	1.00	3.88	0.53	0.27	4.05	0.31	0.00
D	1.16	0.88	4.31	0.98	1.04	3.85	0.29	0.01
E	0.81	1.59	6.33	0.34	0.00	3.33	0.33	0.01

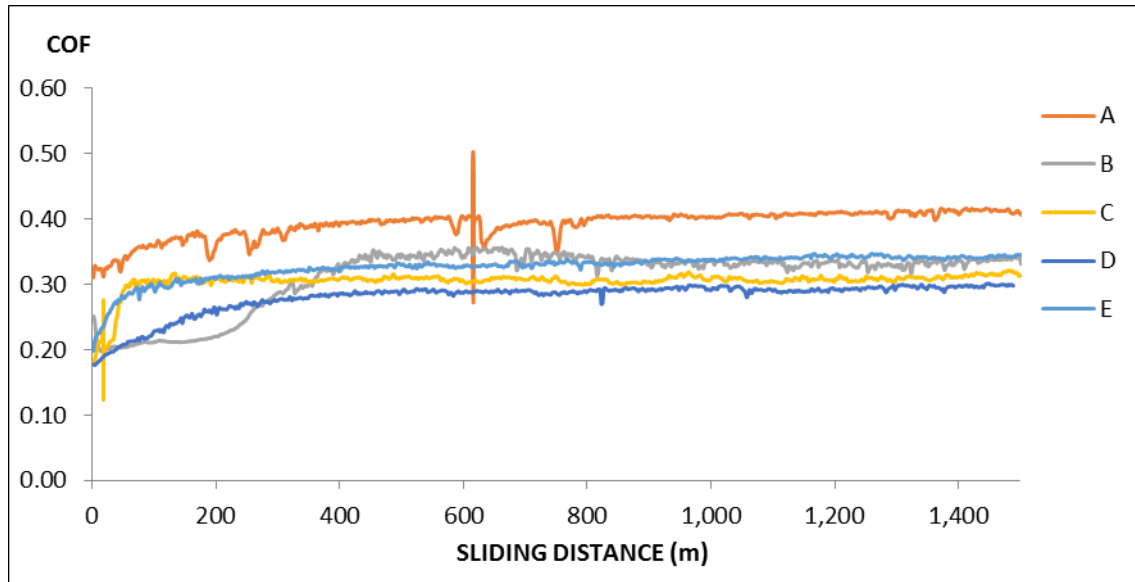


Figure 3.5: Friction coefficient in function of sliding distance obtained in standard tests.

Figure 3.6 shows the linear correlations of COF with R_aF and $R_{sk}F$. The symmetry of profile (R_{sk}) affects friction coefficient linearly and inversely, thus the friction coefficient changes respect not only the surface roughness, but also respect the surface texture. The linear proportionality between R_a and COF derives from the change of real contact area. In fact, when the surface roughness increases, the real contact area decreases which means an increase of pressure at interface. The higher pressure obtained generates a lower friction coefficient¹²³.

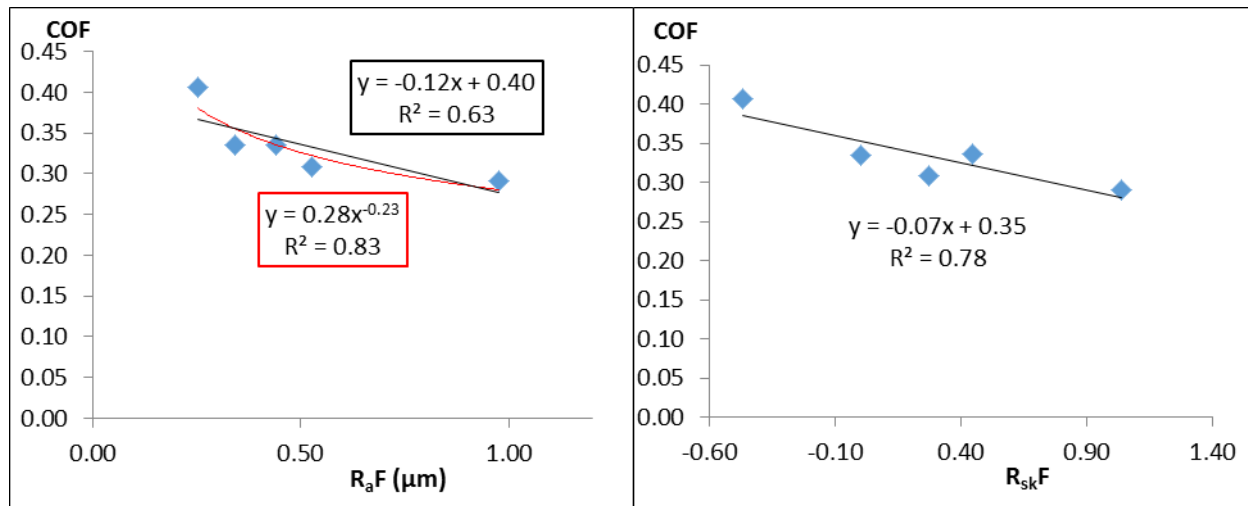


Figure 3.6: Friction coefficient in function of final roughness R_aF and symmetry final parameter $R_{sk}F$.

Figure 3.7 reports a part of trace obtained by tribological test, in which Kevlar fibres are much visible with respect to initial surface, due to consumption of resin, softer than fibres.



Figure 3.7: Optical microscope image in bright field of tribological trace.

In order to better understand the effect of roughness on friction coefficient, also the difference between final and initial value were considered. Among them, only the difference between final and initial R_a results linearly correlated with COF, with a Pearson coefficient of -0.96.

As done in chapter of Steel, the ratio of final and starting R_a was considered and R_{aF}/R_{aI} shows a Pearson coefficient of -0.91. However, to verify the influence of roughness not just in a univariate way, a principal component analysis was applied on this system of five standard tests, taking into account all the single roughness parameters initial and final, the difference between final and initial value of each parameter, and the ratio R_{aF}/R_{aI} . The PCA has five principal components and with just the first two more than 90% of system variance is explained (Table 3.4).

Table 3.4: Explained variance of each principal component.

Principal Component	PC1	PC2	PC3	PC4	PC5
Explained Variance (%)	51.18%	42.89%	3.73%	2.20%	0.00%

From the loading plot obtained (Figure 3.8), no one of the parameters studied results directly proportional to friction coefficient. Only inverse proportionalities are present in the loading plot, relative to final value of R_a and R_{sk} as single parameters and to ΔR_a and R_{aF}/R_{aI} .

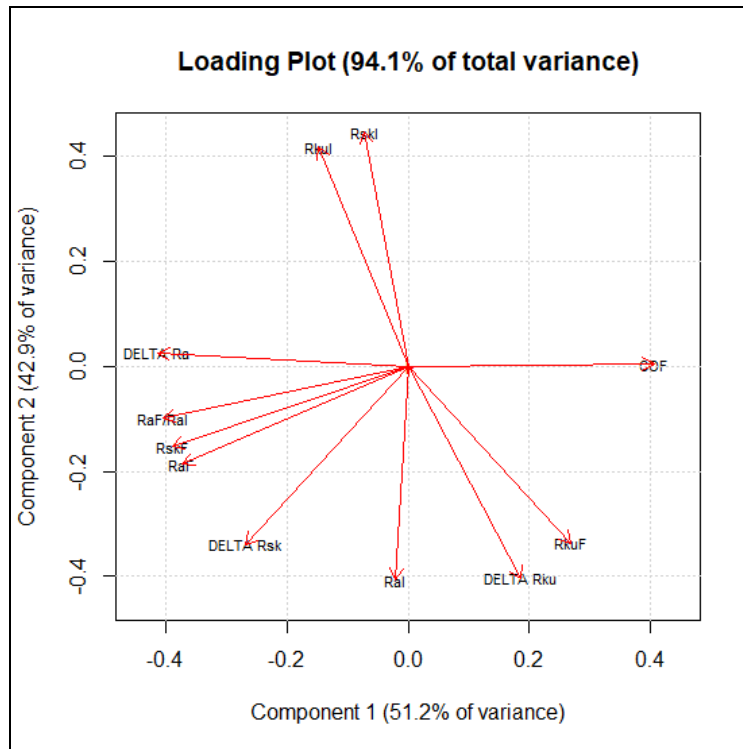


Figure 3.8: Loading plot obtained from PCA analysis.

In particular, the change in roughness is the most linearly proportional to friction coefficient, as already found comparing relative Pearson coefficient. Thus, the multivariate analysis confirmed the possibility to consider a model in which the friction coefficient is calculated in function of ΔR_a or R_aF/R_aI . Figure 3.9 reports the linear correlation of COF with ΔR_a and R_aF/R_aI .

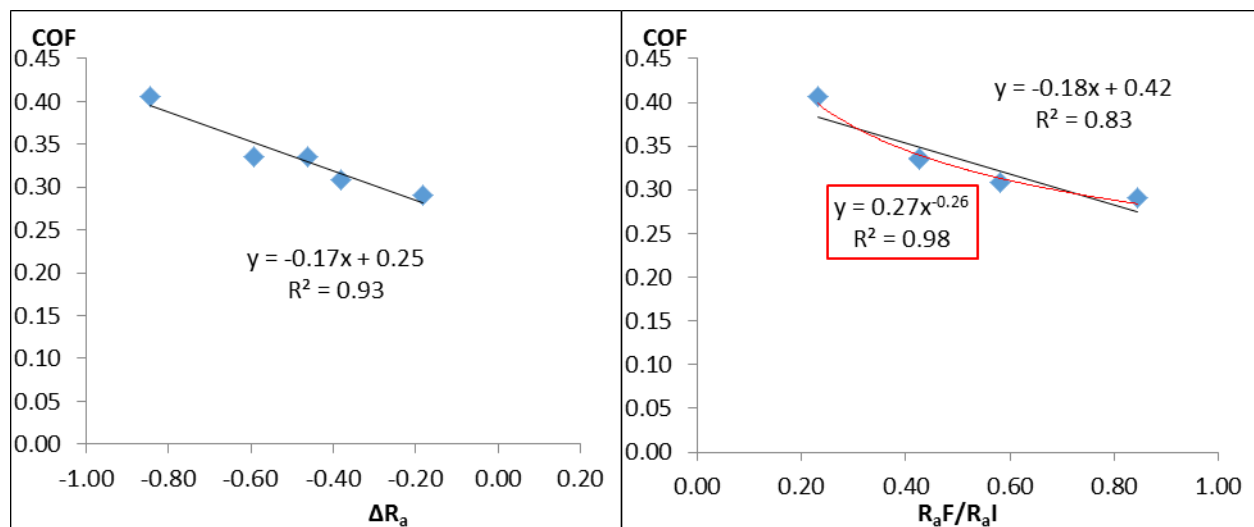


Figure 3.9: Friction coefficient in function of ΔR_a and R_aF/R_aI .

Using the formulas of friction coefficient in function of R_aF/R_aI or ΔR_a it is possible to obtain values, which differs from experimental ones for ± 0.01 .

$$3.1 - COF = -0.17\Delta R_a + 0.25$$

$$3.2 - COF = 0.27 \left(\frac{R_a F}{R_a I} \right)^{-0.26}$$

$$3.3 - COF = -0.18 \frac{R_a F}{R_a I} + 0.42$$

The system obtained can be simplified deleting all the single roughness parameters and taking in account just their evolution and the ratio $R_a F/R_a I$. In this way, two principal components are enough to explain more than 95% of system variance and the ratio $R_a F/R_a I$ and ΔR_a result the parameter more affecting friction coefficient. To quantify their influence, a PLS was done on the system obtaining the formula:

$$3.4 - COF = 0.33 - 7.38 * 10^{-2} \frac{R_a F}{R_a I} - 7.07 * 10^{-2} \Delta R_a - 1.58 * 10^{-2} \Delta R_{sk} + 4.01 * 10^{-3} \Delta R_{ku}$$

Results suggest that ΔR_{ku} is not as influent as the other parameters and can be removed from the system. Another observation is that $R_a F/R_a I$ and ΔR_a show a quite similar coefficient, suggesting an equal influence on friction coefficient. In fact, taking in account just the change in R_a and R_{sk} it is possible to obtain a new formula similar to formula 3.1.

$$3.5 - COF = 0.25 - 0.16 \Delta R_a - 8.53 * 10^{-3} \Delta R_{sk}$$

So in practice the best way to obtain friction coefficient by roughness parameters is to consider the correlation with $R_a F/R_a I$ or ΔR_a .

3.4 – INFLUENCE OF LOAD AND SPEED

Considering test conditions of 10N as load and 0.2 ms^{-1} as speed, friction coefficient is correlated with $R_a F/R_a I$ and ΔR_a . To verify the influence of roughness also in other test conditions, load and speed were changed and their effect compared to roughness one.

Load was considered in the range 5 – 15 N, while speed was changed between 0.1 and 0.3 ms^{-1} and other five tests were performed. Specifically, two of them at 5 N and three at 15 N, changing in each test the speed condition. In this way, considering also the standard tests previously studied, all the tests constitute a full factorial experimental design from load and speed point of view, in which it is possible to investigate possible interactions among variables.

Table 3.5: Tribological tests performed at different load and speed conditions.

	COF	AMPL.	L (N)	S (ms^{-1})	$R_a I$	$R_{sk} I$	$R_{ku} I$	$R_a F$	$R_{sk} F$	$R_{ku} F$	$R_a F/R_a I$	ΔR_a	ΔR_{sk}	ΔR_{ku}
A	0.41	0.01	10	0.2	1.10	0.79	3.28	0.25	-0.47	4.66	0.23	-0.84	-1.26	1.37
B	0.34	0.01	10	0.2	1.03	0.71	3.50	0.44	0.45	4.03	0.43	-0.59	-0.26	0.53
C	0.31	0.00	10	0.2	0.91	1.00	3.88	0.53	0.27	4.05	0.58	-0.38	-0.73	0.16
D	0.29	0.01	10	0.2	1.16	0.88	4.31	0.98	1.04	3.85	0.84	-0.18	0.16	-0.47
E	0.34	0.01	10	0.2	0.81	1.59	6.33	0.34	0.00	3.33	0.43	-0.46	-1.59	-3.00
F	0.34	0.01	15	0.2	0.74	1.26	5.01	0.40	0.20	5.08	0.54	-0.34	-1.05	0.07
G	0.40	0.01	15	0.1	0.75	1.54	7.44	0.21	-0.26	5.44	0.28	-0.54	-1.80	-2.00
H	0.31	0.01	15	0.3	0.83	1.77	7.58	0.23	-0.01	5.83	0.28	-0.60	-1.77	-1.75
I	0.40	0.02	5	0.1	0.91	0.56	2.90	0.35	0.05	3.99	0.38	-0.56	-0.51	1.09
J	0.39	0.01	5	0.3	1.25	0.73	3.35	0.75	0.17	3.86	0.60	-0.50	-0.57	0.51

A PCA was applied on this new system using ten principal components (Table 3.6). All the tests result acceptable by diagnostic test considering the first two principal components (Figure 3.10). The fact that each point results in the graph area delimited by red lines indicates the goodness of tests. If one or more tests were outside of red lines, they must be deleted from the matrix due to their condition of outlier, as explained in *Materials and Methods* section.

Table 3.6: Explained variance of each principal component.

Principal Component	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
Explained Variance (%)	44.97 %	27.40 %	10.28 %	6.69%	5.20%	2.87%	1.77%	0.55%	0.27%	0.00%

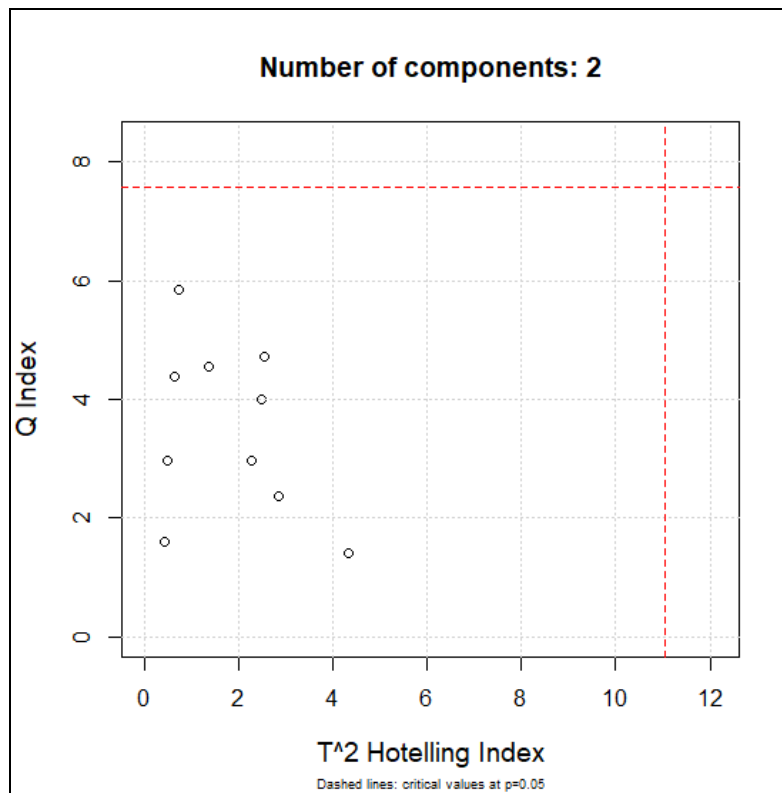


Figure 3.10: Diagnostic plot of experimental system relative to Q index and T^2 Hotelling index.

To describe the influence of each variable it is necessary to consider the loading plot (Figure 3.11), which shows the inverse proportionality between COF and ΔR_a or $R_a F/R_a I$ as already found before. Furthermore, the change in R_{sk} seems to affect no one of the other variables of interest, neither COF neither load and speed, whereas $R_{sk} F$ has a variance similar to $R_a F/R_a I$, suggesting that also in different condition this parameter decreases the friction coefficient. Thus in the range investigated the influence of roughness does not change and a new PCA can be obtained deleting from variables the single roughness parameters, in order to build a new formula including test conditions, and the amplitude, which is practically constant in the range investigated.

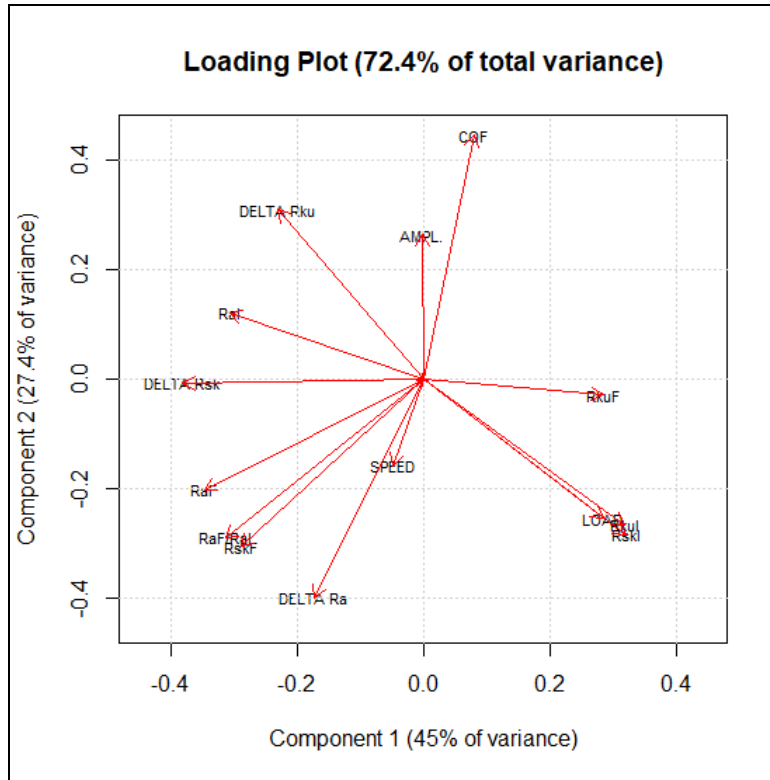


Figure 3.11: Loading plot of PCA on test with load and speed conditions changing.

The new PCA shows again the linear inverse correlation of COF with change in R_a , but in particular an inverse proportionality of COF with speed. This relationship can be observed also in the tests at 15 N performed at three different value of speed, in which the friction coefficient decreases at the increase of speed. This effect can be correlated with a major thickness of the transfer layer obtained at higher speed, which generates a lower friction coefficient¹²⁴. Load results inversely proportional to change in R_{sk} and R_{ku} .

Table 3.7: Explained variance of each principal component.

Principal Component	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Explained Variance (%)	41.43%	31.58%	14.94%	7.46%	3.37%	0.99%	0.22%

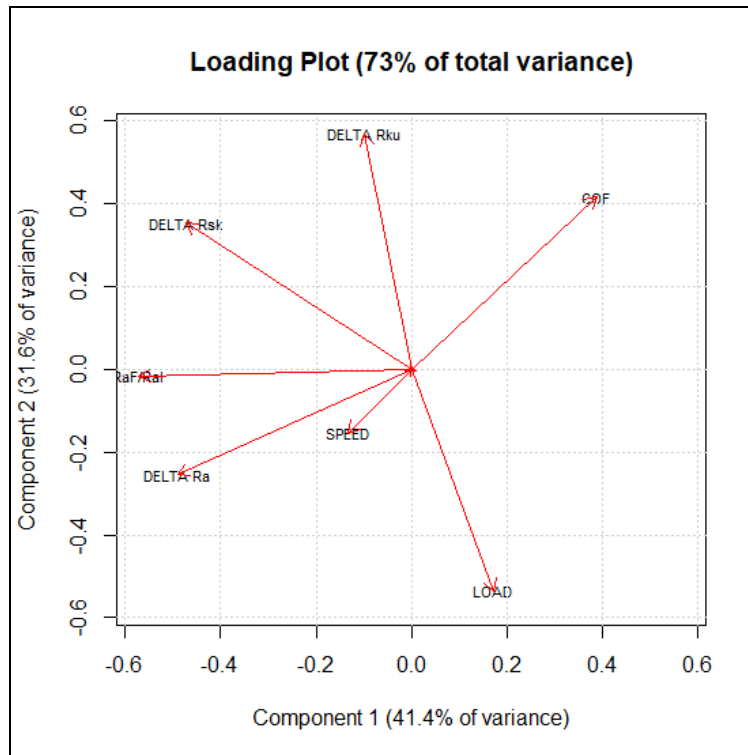


Figure 3.12: Loading plot without single roughness parameters.

Due to the increase in the percentage explained by the third principal component, the loading plots including this component can suggest more information than previously cited one (Figure _). Respect the third component, the first PC shows the inverse proportionality of COF with R_a and R_{sk} change, while load increases friction. However, on the second PC load results inversely proportional to COF, so its effect cannot be described in a single way. It is necessary to reduce the system variables and apply a partial least square regression.

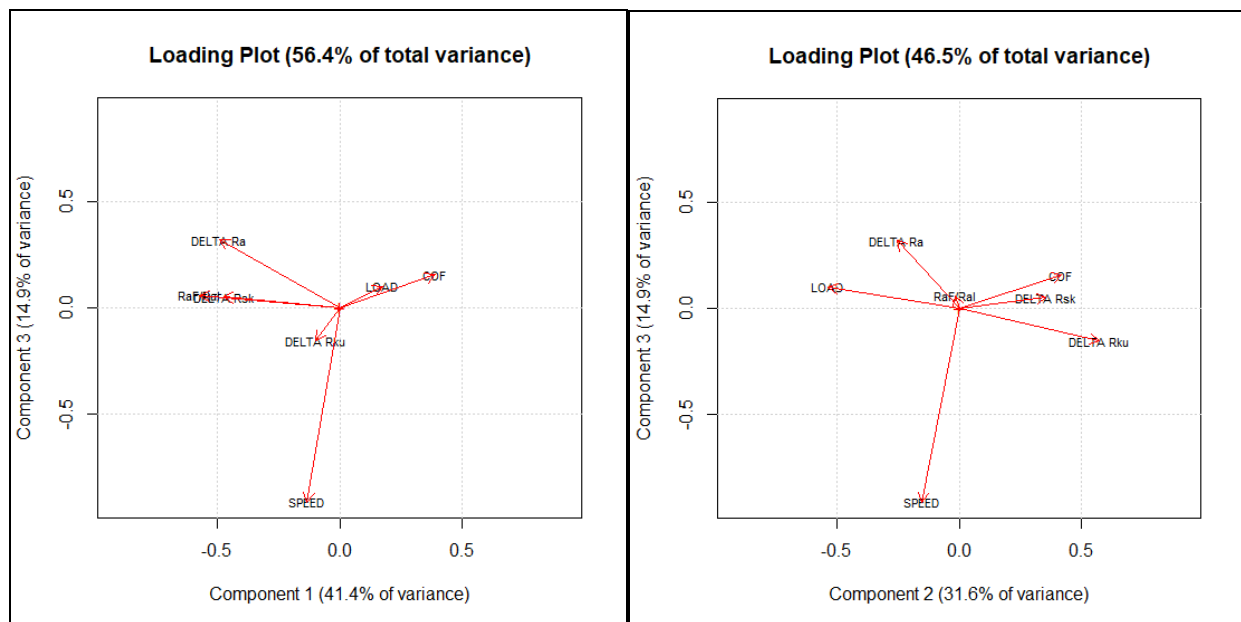


Figure 3.13: Loading plots including principal component 3.

Due to the previous results, ΔR_{ku} and $R_a F/R_a I$ or ΔR_a can be deleted. ΔR_{ku} in each loading plot results not directly correlated with COF, but linearly with test conditions, so considering the change in test conditions the variance due to ΔR_{ku} is considered. $R_a F/R_a I$ has almost the same variance as ΔR_a , so just one of these two parameters should be considered to obtain a correct model. Then, two formula of COF in function of test conditions and roughness parameters were obtained, changing just $R_a F/R_a I$ with ΔR_a .

$$3.6 - COF = 0.35 - 3.42 * 10^{-3} LOAD - 0.23 SPEED - 0.15 \Delta R_a - 1.50 * 10^{-2} \Delta R_{sk}$$

$$3.7 - COF = 0.47 - 3.27 * 10^{-3} LOAD - 0.22 SPEED - 0.12 \frac{R_a F}{R_a I} - 1.43 * 10^{-2} \Delta R_{sk}$$

In order to validate the models obtained, other three tests were performed at 10 N and 0.2 ms⁻¹. In Table 3.8, the roughness parameters are reported, while the comparison between experimental and calculated value is shown in Table 3.9.

Table 3.8: Roughness parameters obtained in the three standard tests.

TEST	R _a I	R _{sk} I	R _{ku} I	R _a F	R _{sk} F	R _{ku} F	R _a F/R _a I	ΔR _a	ΔR _{sk}	ΔR _{ku}
1	1.12	0.85	3.24	0.30	0.52	4.50	0.27	-0.82	-0.33	1.26
2	0.83	0.95	4.12	0.62	0.32	4.02	0.75	-0.21	-0.63	-0.10
3	0.31	-0.14	3.45	0.23	0.05	4.11	0.75	-0.08	0.19	0.67

Table 3.9: Comparison of experimental and calculated value using formulas 3.1-3.7.

TEST	EXPERIMENTAL	3.1	3.2	3.3	3.4	3.5	3.6	3.7
1	0.39	0.39	0.38	0.37	0.38	0.38	0.40	0.37
2	0.32	0.29	0.29	0.29	0.30	0.29	0.31	0.31
3	0.34	0.26	0.29	0.29	0.28	0.26	0.28	0.30

The difference between experimental value and calculated values from each model is lower than ±0.05 in the first two tests. Thus, in the range investigated all the models found are validated and could be used to obtain a predictive value of friction coefficient. In the third test, the starting conditions were changed in order to obtain values out of the range previously investigated. In this case, only the models containing the ratio $R_a F/R_a I$ result acceptable respect to ±0.05 as level of confidence; in particular model 3.2, 3.3 and 3.7, which results the best.

3.5 – WEAR OF POLYMER MIX

The wear of polymer matrix was measured by Vivier using an alumina sphere, 10N as load, 0.25 ms⁻¹ as speed for 100 000 laps. In these conditions, the wear constant K resulted equal to 1.18*10⁻⁵mm³/Nm and the relative friction coefficient was 0.25.

In this thesis, as described in *Materials and Methods* chapter, the wear test is performed using a steel sphere in order to maintain the same chemical interactions between surfaces as in pin-on-pad tests. The conditions of load and speed are 10N and 0.20 ms⁻¹ equal to standard test applied in pin-on-pad configuration.

In this case, the resulting friction coefficient is equal to 0.34 (Figure 3.14), higher than the value obtained with alumina sphere. In the case of metal-polymer contact, Van der Waals interactions and hydrogen bonds generated at interface play an important role in determined the tribological behaviour¹²⁵. Probably the functional groups of pad surfaces interact differently with alumina and steel, generating a different amount of transfer layer. Considering that the contact polymer-polymer generates a low friction coefficient, a thicker and more homogeneous transfer layer could be generate on alumina

sphere, while on steel one it has lower thickness and homogeneity, thus the resulting friction is higher. However, the resulting wear constant K is equal to $1.27 \cdot 10^{-5} \text{mm}^3/\text{Nm}$, so the change in the ball material only affects the value of friction coefficient due to a different adhesion component in the generation of transfer layer. The value of K in the wear test conditions depends much by mechanical phenomena, which don't vary much with the ball material.

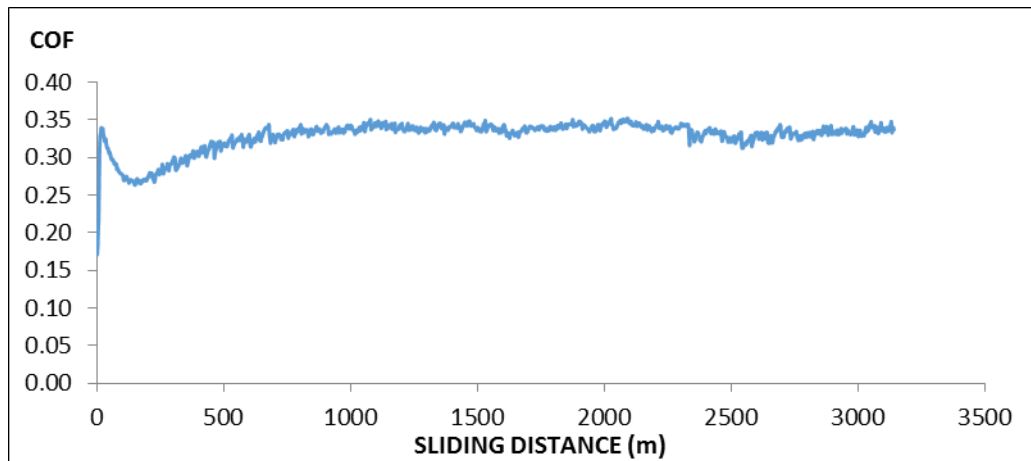


Figure 3.14: Friction coefficient of basic mix during wear test using steel as counterface.

An example of trace depth is reported in Figure 3.15.

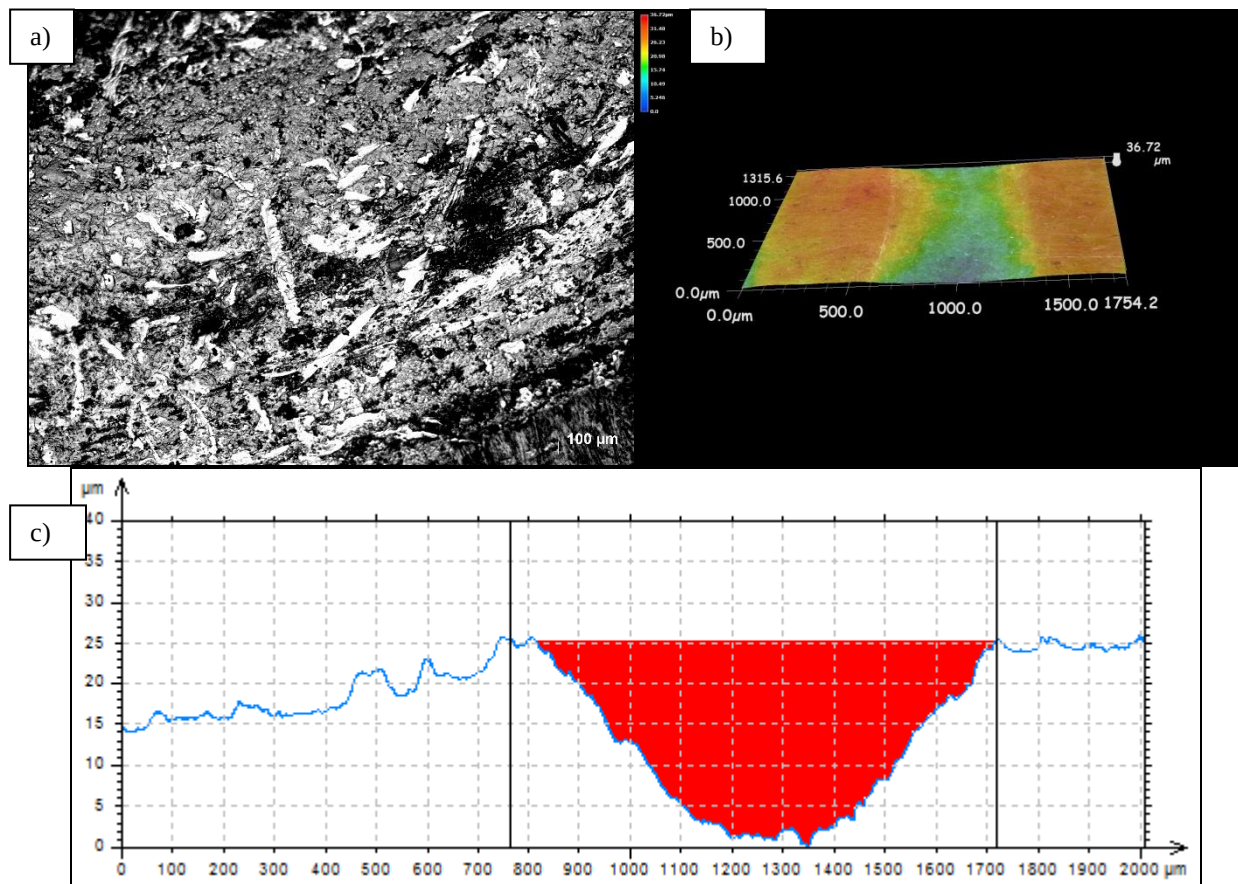


Figure 3.15: Wear trace profile measured by: a) Optical microscope; b) 3D digital microscope : c) contact profilometer.

Kevlar fibres are visible in the wear trace, due to higher wear of phenolic resin. The value of wear constant can be calculated also by Holm-Archard equation^{17,106}, obtaining a dimensionless value of K equal to $1.07 \cdot 10^{-2}$. Theoretically, considering the formula proposed by Gutierrez-Miravete¹²⁶, the real contact area during wear test can be calculated as the ratio between load and basic mix hardness, which results equal to $1.18 \cdot 10^{-8} \text{m}^2$ or $1.18 \cdot 10^{-2} \text{mm}^2$. It would be interesting compare not only the general accepted value of K in literature, but also the value obtained by Holm-Archard equation and investigate the material properties affecting wear phenomena.

3.6 – CONCLUSION

The roughness and test conditions influence were studied in basic mix system using pin-on-pad test. As found for steel against steel system, also in the case of basic mix the friction coefficient results proportional to the change in roughness parameters. Thus, different models were built in order to predict friction coefficient in function of roughness conditions.

The COF results linearly proportional to ΔR_a and $R_a F / R_a I$, which have a higher influence on the value of friction compared to other roughness parameters. When the reduction of R_a is lower, the friction coefficient decreases due to a lower adhesion between surfaces.

The images obtained by optical microscope on pad surface after the test suggest a higher mechanical wear of phenolic resin respect Kevlar fibres, due to their higher hardness.

When also the test conditions change, the influence of speed is of the same order as for ΔR_a and $R_a F / R_a I$, whereas the influence of load is the lowest respect all the other parameters. Thus, in the range studied, an increase in speed reduces the friction coefficient, probably due to a lower wear of phenolic resin, then lower contact with Kevlar fibres.

The wear constant of basic mix results equal to $1.22 \cdot 10^{-5} \text{mm}^3/\text{Nm}$, which is comparable with previous result obtained by Eng. Vivier⁶⁶, indicating a poor effect of the ball material on the wear resistance of the pad.

CHAPTER 4 – CARBON MATERIALS

4.1 – INTRODUCTION

As described in Chapter 1, carbon materials have been extensively studied in several fields thanks to their variety of morphologies and properties like corrosion resistance or high thermal conductivity⁴⁰.

Carbon is polymorphic and exists in three forms, namely diamond, graphite, and fullerenes, in function of the type of carbon bonds⁴¹. The carbon materials used in brake pad formulation, are graphite, graphene, and coke, that are considered solid lubricants, thanks to their low friction coefficient which derives from the layered crystalline structure. Their structure shows strong bonding within the basal planes, but weak bonding between them⁴⁴, which allows the formation of a lubricant layer that ensures a stable friction coefficient. In fact, carbon materials are not used only to decrease friction coefficient but also to stabilize it during brake.

Graphite is a readily available and very effective solid lubricant, which can be found as natural or synthetic form. The natural graphite is typically available as amorphous graphite and in form of flakes. Their lubricating ability can change as a function of the type and concentration of impurities present. The synthetic graphite is typically very pure, obtained from petroleum coke, which is produced during the refinery process. The manufacturing process for synthetic graphite consists in heat treating of amorphous carbon materials at above 2500°C, to allow the reconstructive transformation as sp^2 carbon ring structures that combine and align to form a 3D ordered graphite⁴⁶. The main role of graphite is to reduce and stabilize the friction coefficient during brake, but it also affects the heat dissipation. It must be balanced in order to have a quick heat dissipation at interface and contemporarily to keep the temperature of the hydraulic braking fluid under its boiling point, or failure of the braking application system will occur^{47–49}.

Graphene consists of sp^2 carbon hexagonal network like graphite, but with few layers. The 3D graphite structure corresponds to a stacking of individual graphene layers¹²⁷. Different production methods are available for graphene, based on the type and quality wanted. The first developed method is the mechanical exfoliation process, where multiple layers are peeled from highly ordered pyrolytic graphite and then transferred to the desired substrate. Nowadays, the majority of methods are based on dry mechanical or chemical exfoliation. In recent years, reducing friction and wear-related mechanical failures has gained increased attention, also in brake pad formulation. Graphene has attracted attention as a possible novel lubricant, but its tribological potential remains relatively unexplored¹²⁸. By using an Atomic Force Microscopy (AFM), Li-Yu Lin et al.¹²⁹ observed that despite its low thickness, graphene has relatively high wear resistance and the wear mechanism consists in the breakage of the in-plane bonds between carbon atoms and shear at the interface of the graphene layers. Moreover, graphene has a passivation effect on steel surfaces, which results in low corrosion, wear and friction, confirming that graphene constitutes a new class of lubricant for metal surfaces¹³⁰.

The last category of carbon materials used in brake pad formulation is coke, which is obtained as a byproduct in the refinery process of petroleum. Generally, in brake pad formulation, coke is used in combination with graphite, but until now, its tribological behaviour is not completely disentangled. Petroleum coke (PC) is produced when the bottom part of refinery material is heated to remove the last bit of lower boiling compounds recoverable. This petroleum coke is used to obtain the calcined petroleum coke (CPC) by heat-treating PC to about 1350°C in a rotary kiln. To obtain a graphitized coke a new heat treatment at more than 1800°C is necessary.

The focus of this chapter is to correlate tribological behaviour with material properties studying different type of carbon materials: natural graphite (N), synthetic graphite (S), coke (C), and graphene

(G). All of them are commercially available, used or under testing for brake pad formulation. In next section, their physico-chemical characterization is described and compared with tribological results, using the OVAT and multivariate analysis.

4.2 – MORPHOLOGY OF RAW MATERIALS

Particle size and shape of four graphite, two natural and two synthetic, two cokes, one carbon black sample, and three kind of graphene, were analysed by SEM (Table 4.1).

Table 4.1: Samples and relative description.

SAMPLE	DESCRIPTION
N1	Coarse natural graphite
N2	Fine natural graphite
S1	Coarse synthetic graphite
S2	Fine synthetic graphite
C1	Carbon black
C2	Graphitized coke
C3	Calcined coke
G1	Coarse graphene
G2	Fine graphene A
G3	Fine graphene B

The two natural graphite (N1 and N2 in the following) show a lamellar morphology with a different particle size distribution. N1 sample consists of a coarse natural graphite (Figure 4.1.a), with particle size between 100 and 2000 μm , while the sample N2 is a fine natural graphite (Figure 4.1.b), with particle size lower than 300 μm .

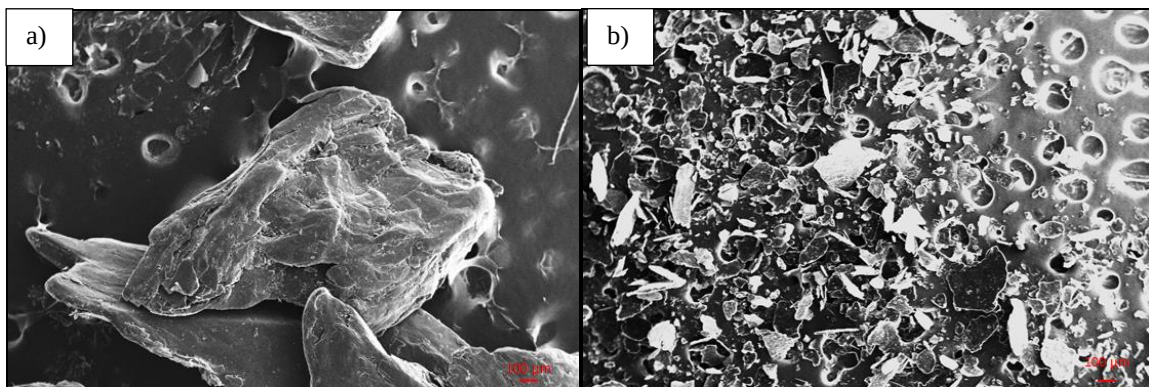


Figure 4.1: Scanning electron microscope images of natural graphite: a) coarse, N1; b) fine, N2.

As described in Materials and Methods chapter, several parameters were investigated to describe the particles morphology. In the case of natural graphite, results are reported in Table 4.2 and show the similar shape and different average size.

Table 4.2: Morphological parameters of natural graphite samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S
N1	182228	931.75	353.38	1.75	0.61	0.70	0.89
N2	5656	275.63	101.10	1.76	0.62	0.69	0.91

The two synthetic graphite (S1 and S2) differ for both particle size and shape, because the finer sample S2 results more elongated with respect to S1, thus S2 shows higher aspect ratio and lower circularity (Table 4.3, Figure 4.2).

Table 4.3: Morphological parameters of synthetic graphite samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S
S1	6774	284.99	101.46	1.73	0.62	0.65	0.88
S2	244	63.01	20.95	1.77	0.63	0.59	0.85

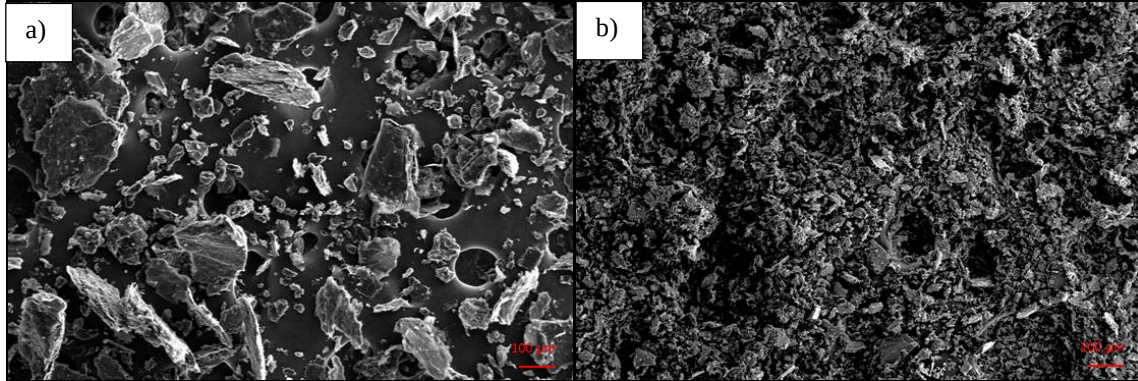


Figure 4.2: Scanning electron microscope images of synthetic graphite: a) coarse, S1; b) fine, S2.

Figure 4.3 shows the particular morphology of carbon black, which is constituted by spherical agglomerates of particles.

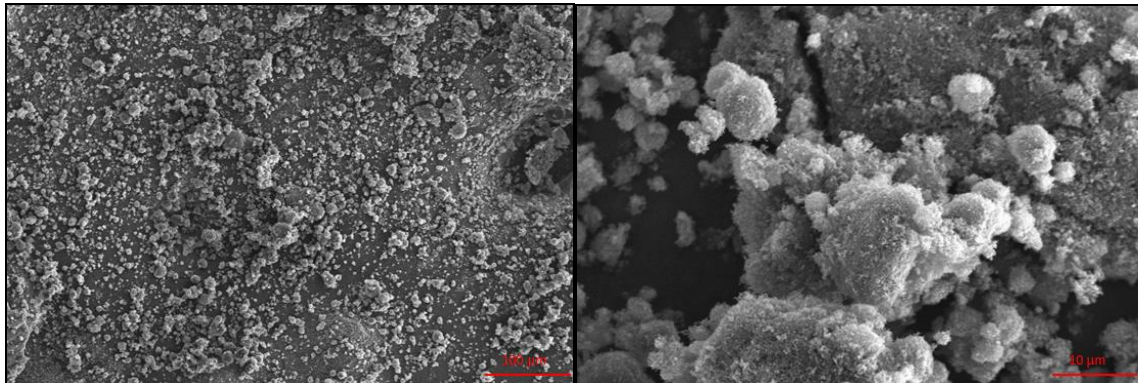


Figure 4.3: Scanning electron microscope images of carbon black at different magnification, C1.

The graphitized coke has a particle size similar to N1 and shows a structure constituted by several lamellae superimposed (Figure 4.4), which derives from the graphitization process. Instead, the calcined coke shows an irregular morphology and a lower average particle size.

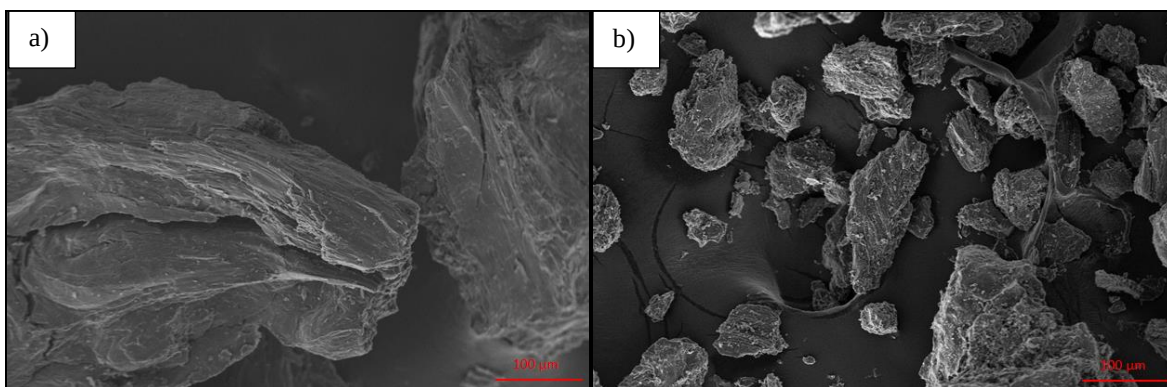


Figure 4.4: Scanning electron microscope images of coke: a) graphitized coke, C2; b) calcined coke, C3.

Table 4.4: Morphological parameters of coke samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S
C1	11.28	18.98	6.80	1.31	0.78	0.42	0.96
C2	84488	965.33	344.37	1.98	0.59	0.63	0.86
C3	13255	432.42	161.33	1.83	0.59	0.69	0.89

The last category of carbon materials analysed in this work concerns three graphene samples. They are constituted by sheets smaller than $10\mu\text{m}$ (Figure 4.5). A more detailed morphological analysis cannot be carried out by SEM.

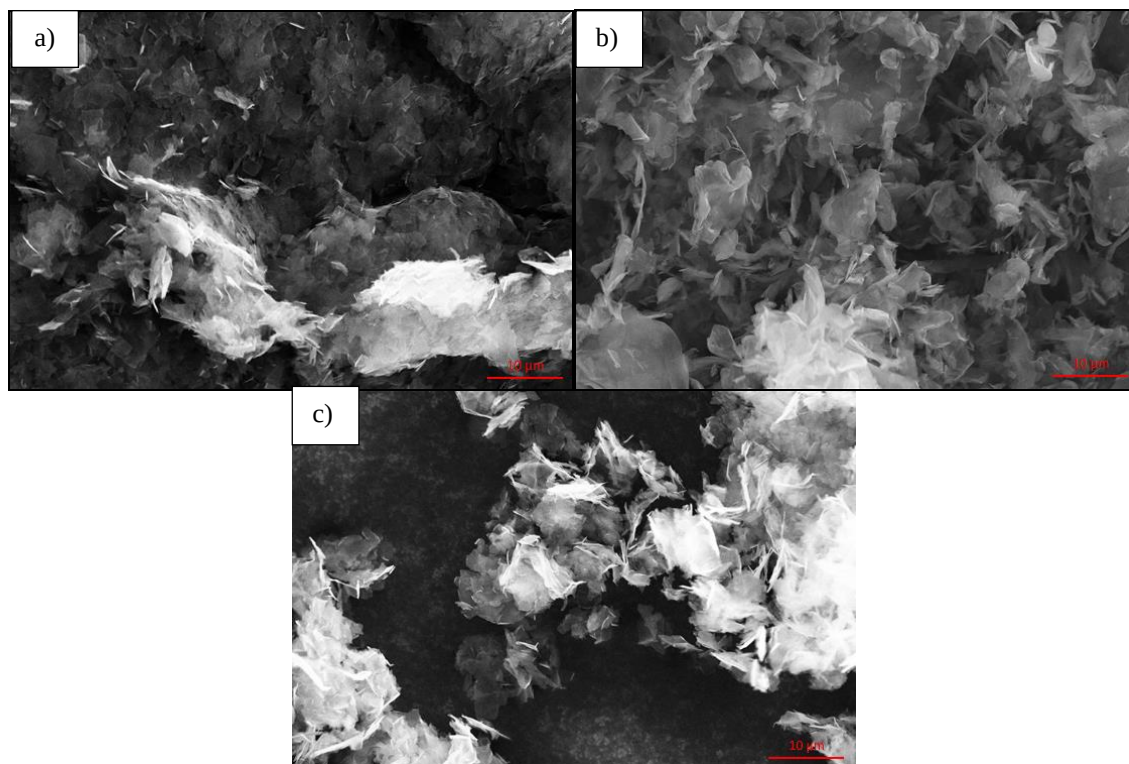


Figure 4.5: Scanning electron microscope images of graphene: a) G1, b) G2, c) G3.

Details on particles size distribution were obtained by granulometric analysis, performed by the industrial partner ITT. Sample G1 shows the highest particle size, with more than 75% of particles

bigger than 1000 μm . The other two graphene G2 and G3 show a similar particle size distribution (Figure 4.6), with respectively 8.3 and 7.7 μm as D50.

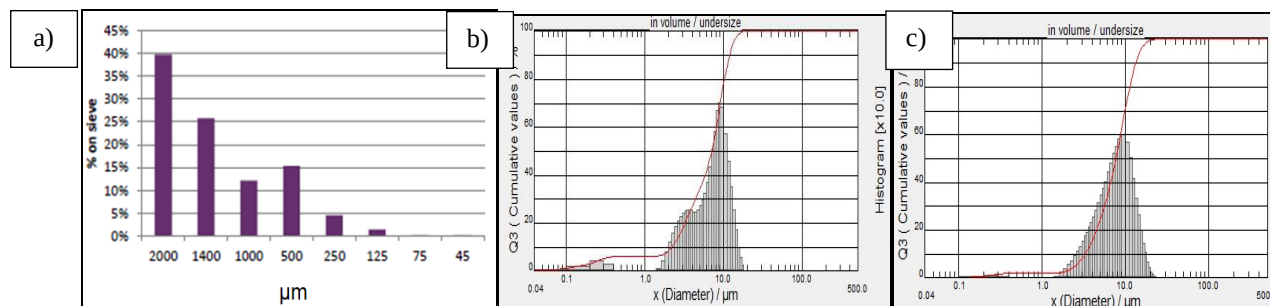


Figure 4.6: Particle size distribution of graphene samples: a) G1, b) G2, c) G3.

4.3 – COMPOSITION AND STRUCTURE

The study of materials composition was performed using EDS as a preliminary analysis to investigate the presence of impurities.

The results obtained on natural graphite N1 and N2 confirm information from the supplier, which highlights a content of C around 97-98 %w and impurity of Al, Fe and Si around 2 %w. Instead, synthetic graphite S1 and S2 show a composition of C at 100%w, as confirmed by the supplier.

In the case of coke family, the composition is quite different, because the only one showing just carbon is the graphitized coke, so it results similar to synthetic graphite for composition. The calcined coke has a content of oxygen around 2%wt, which derives from the production process that allows the presence of oxidized species. The analysis on carbon black highlights the presence of S as impurity around 1%wt.

Sample G1 is constituted only by C, while the other two samples contain less than 1%wt of S.

4.3.1 – X-RAY DIFFRACTION ANALYSIS

The fit of each spectrum was performed using a Lorentzian function to obtain the fit of XRD peaks.

Graphite samples show the typical diffraction pattern of hexagonal graphite, with the most intense peak at around 26°, relative to the diffraction of the [002] plane. In the case of crystalline graphite, the layers are commonly stacked in the AB sequence with a unit cell characterized by the lattice parameters $a = 2.46\text{\AA}$ and $c = 6.71\text{\AA}$ (Figure 4.7d)³.

Considering the entire normalized spectra, significant differences are not visible (Figure 4.7a), whereas different shape and position can be observed by focusing the attention on the main peak [002] (Figure 4.7b) and peaks around 40° (Figure 4.7c). The peak [002] results sharp and intense, with a less intense reflection around 50°. The two peaks relative to diffraction of planes [100] and [101] result broader and less intense than peak [004]. The fine synthetic graphite S2 has the highest peaks [100] and [101], which represent a higher preferred orientation of planes not overlapping with [002]; these features indicate a more disordered structure.

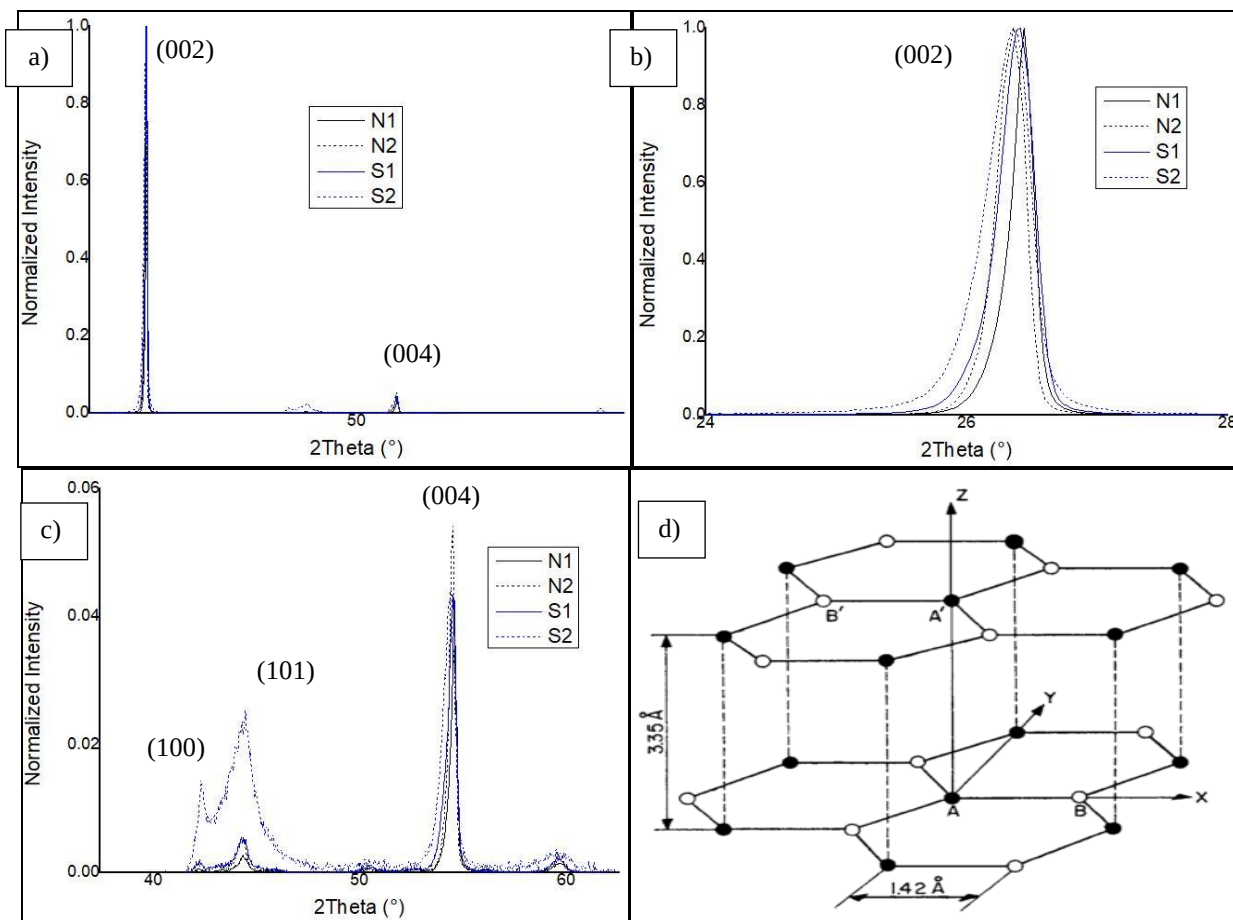


Figure 4.7: X-ray diffraction powder pattern for graphite samples: a) normalized spectra; b) zoom on the peak [002]; c) zoom on peaks around 50°; d) the crystal structure of graphite⁴¹.

The fit of x-ray pattern highlights these differences that suggest dissimilarities in the structure (Table 4.5). The peak [002] position changes among samples at decimal values, while the Full Width at Half Maximum (FWHM) and the peak area (I) results lower for natural graphite with respect to synthetic ones. The resulting differences probably derive from the presence of defects and the crystallite dimension. From data obtained through the fitting of x-ray pattern, other parameters were calculated as the d-spacing, by the Bragg law (4.1), the lattice parameter c, using the crystal geometry equation relative to the hexagonal system (4.2), and the crystallite dimension by the Scherrer equation (4.3). From the formula 4.2, inverse equations can be obtained to calculate the lattice parameters “a” and “c” from respectively the data of peaks [101] and [002]. Furthermore, the ratio L_c/D_{002} gives the average number of aromatic layers stacked on c direction¹³¹.

$$4.1 - d = \frac{\lambda}{2 \sin \theta}$$

$$4.2 - \frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad 4.2.1 - [101] \ a = \sqrt{\frac{4 d^2 c^2}{3(c^2 - d^2)}} \quad 4.2.2 - [002] \ c = d/2$$

$$4.3 - L = \frac{0.9 \lambda}{FWHM * \cos \theta} \quad 4.3.1 - N \text{ (layers)} = L_c / D_{002}$$

The results show a decreasing crystallite dimension on c axis (Table 4.5), from natural graphite to the graphitized coke, probably derived from the synthesis process of sample S1, S2 and C2. In fact, the data relative to C2 are reported together with graphite results due to its similarity as x-ray diffraction

pattern, especially to S2 one. The d-spacing and c values do not show significant differences, while more significant is the difference in terms of L_c , indicating a different number of stacked aromatic layers, suggesting a much more ordered structure on c direction for natural graphite than for other samples.

Table 4.5: Normalized data of x-ray pattern fitting relative to peak 002 of graphite samples.

SAMPLE	PEAK [002]	I [002]	FWHM [002]	D-SPACING (Å)	c (Å)	L_c (nm)	N layers
N1	26.42	0.22	0.20	3.371	6.741	90.67	269
N2	26.34	0.28	0.23	3.381	6.762	74.17	219
S1	26.38	0.35	0.28	3.376	6.751	60.44	179
S2	26.32	0.43	0.36	3.383	6.767	47.99	142
C2	26.24	0.44	0.37	3.393	6.787	44.33	131

The coke samples are completely different from graphite ones, apart for the aforementioned graphitized coke C2. This sample shows an x-ray pattern very similar to that of synthetic graphite S2, which confirms the appropriate result of the graphitization process (Table 4.5, Figure 4.8). The main difference is the peak position, which derives from a higher d-spacing and lattice parameters for coke with respect to graphite.

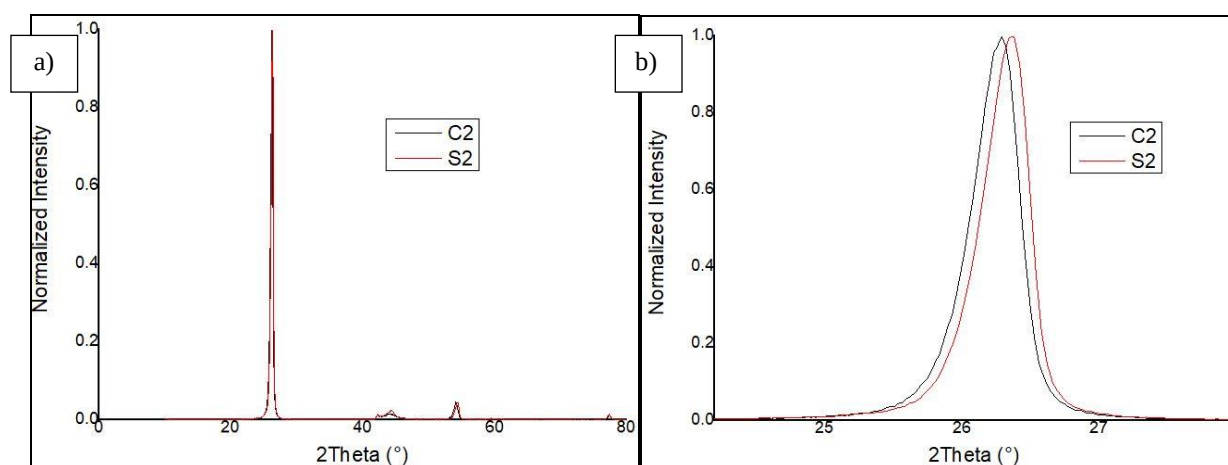


Figure 4.8: X-ray diffraction powder pattern for graphite S2 and graphitized coke C2: a) normalized spectra; b) zoom on the peak [002] around $2\theta = 26^\circ$.

The other two cokes are completely different as x-ray diffraction pattern due to a high content of amorphous carbon. Figure 4.9 shows the resulting spectra and the resulting fit data are reported in Table 4.6.

Table 4.6: Normalized data of x-ray pattern fitting relative to peak 002 of coke samples.

SAMPLE	PEAK (002)	I (002)	FWHM (002)	D-SPACING (Å)	c (Å)	L_c (nm)	N layers
C1	24.29	8.54	5.54	3.661	7.323	2.93	8
C3	25.43	3.15	3.13	3.500	6.999	5.20	15

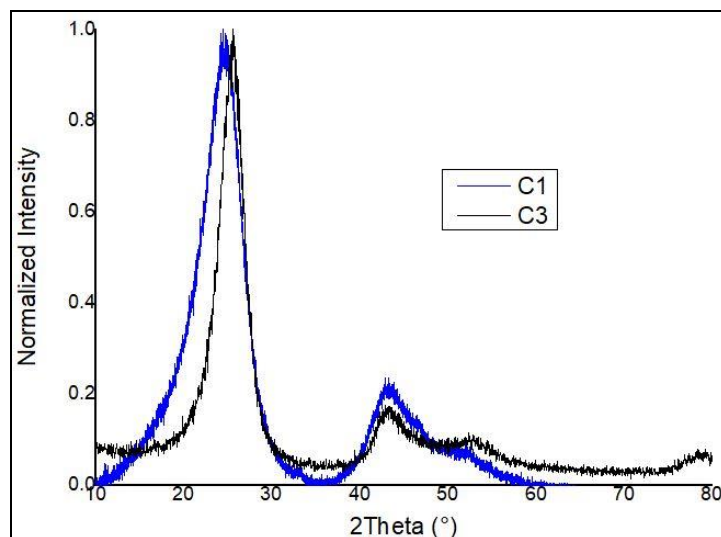


Figure 4.9: X-ray diffraction powder pattern for carbon black C1 and calcined coke C3.

The graphene samples show very similar x-ray diffraction patterns, and then fit results are about the same. Figure 4.10a shows the comparison of their patterns and Figure 4.10b highlights the similitude in the main peak relative to the plane [002] diffraction. As for synthetic graphite and graphitized coke, the three graphene show low and broad peaks relative to the diffraction of planes [100] and [101]. The similar d-spacing and lattice parameter c obtained for plane [002] (Table 4.7) indicates a similar structure, as can be seen also from L_c and N values.

Table 4.7: Normalized data of x-ray pattern fitting relative to peak 002 of graphene samples.

SAMPLE	PEAK (002)	I (002)	FWHM (002)	D-SPACING (Å)	c (Å)	L_c (nm)	N layers
G1	26.35	0.78	0.47	3.380	6.759	34.72	103
G2	26.32	0.77	0.47	3.383	6.767	33.99	100
G3	26.34	0.79	0.47	3.381	6.762	33.99	101

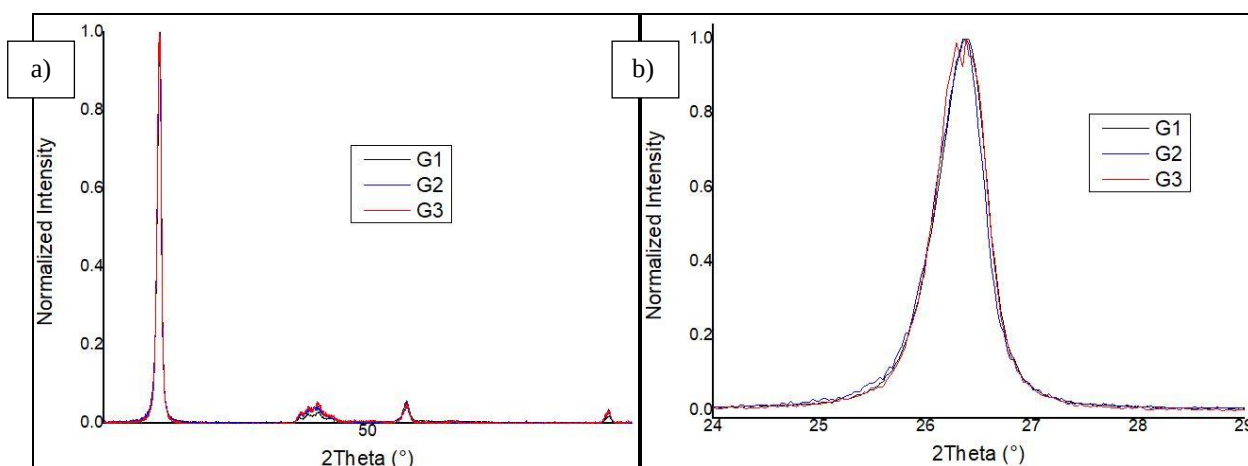


Figure 4.10: X-ray diffraction powder pattern for graphite S2 and graphitized coke C2: a) normalized spectra; b) zoom on the peak [002].

Based on the discussed results, the carbon materials can be divided into two groups: i) one constituted by graphitized coke, graphite, and graphene samples, ii) the second one contains carbon black and

calcined coke. Although other more detailed differences can be found among the first group, the two cokes show a completely different structure due to the amorphous carbon content respect all the other samples.

To investigate and verify the possible division of carbon materials system based on x-ray diffraction analysis, all data (summarized in Table 4.8) were used as starting matrix for Principal Component Analysis. Applying a PCA with eight components the 100% of the system variance can be explained. The loading and score plot (Figure 4.11a and b), highlight the diversity of carbon black and calcined coke with respect to all the other samples (black circle in Figure 4.11b). Using the loading plot as a reference, they differ from others for the shape of peaks (002) and (004), which are comparable as effect, thus for following analysis it can be considered just the main peak (002). Furthermore, the two peaks (002) and (004) show a linear proportionality for each parameter, comparing the Pearson coefficient calculated on pair of respective parameters. A further division between the other samples is observable, i.e. the difference in L_c value and peak (101). The graphitized coke can be considered as synthetic graphite.

Table 4.8: Matrix of x-ray diffraction data collected on carbon materials.

SAMPLE	PEAK (002) (°)	I (002)	FWHM (002)	D (002)	L _c (nm)	N Layers	PEAK (101) (°)	I (101)	FWHM (101)	D (101)	L (101)	PEAK (004) (°)	I (004)	FWHM (004)	a (Å)	c (Å)
N1	26.43	0.28	0.18	3.37	90.67	269.09	44.34	0.01	3.07	2.04	0.49	54.55	0.02	0.31	2.47	6.74
N2	26.34	0.36	0.22	3.38	74.17	219.39	44.25	0.01	1.06	2.05	1.41	54.47	0.03	0.30	2.48	6.76
S1	26.38	0.44	0.27	3.38	60.44	179.04	44.22	0.02	2.82	2.05	0.53	54.47	0.03	0.46	2.48	6.75
S2	26.33	0.56	0.34	3.38	47.99	141.90	44.27	0.06	1.70	2.04	0.88	54.33	0.05	0.64	2.48	6.76
C1	24.29	8.54	5.54	3.66	2.93	8.01	43.57	1.41	4.27	2.08	0.35	50.72	1.37	9.62	2.50	7.32
C2	26.24	0.44	0.37	3.39	44.33	130.64	44.19	0.06	2.36	2.05	0.63	54.14	0.05	0.68	2.48	6.79
C3	25.43	3.15	3.13	3.50	5.20	14.87	43.58	0.65	3.39	2.08	0.44	51.84	0.68	7.15	2.51	7.00
G1	26.35	0.78	0.47	3.38	34.72	102.73	44.17	0.08	2.38	2.05	0.63	54.37	0.06	0.77	2.48	6.76
G2	26.33	0.78	0.48	3.38	33.99	100.51	43.99	0.16	2.48	2.06	0.60	54.36	0.06	0.76	2.49	6.76
G3	26.34	0.80	0.48	3.38	33.99	100.55	44.07	0.16	2.25	2.05	0.66	54.39	0.05	0.68	2.49	6.76

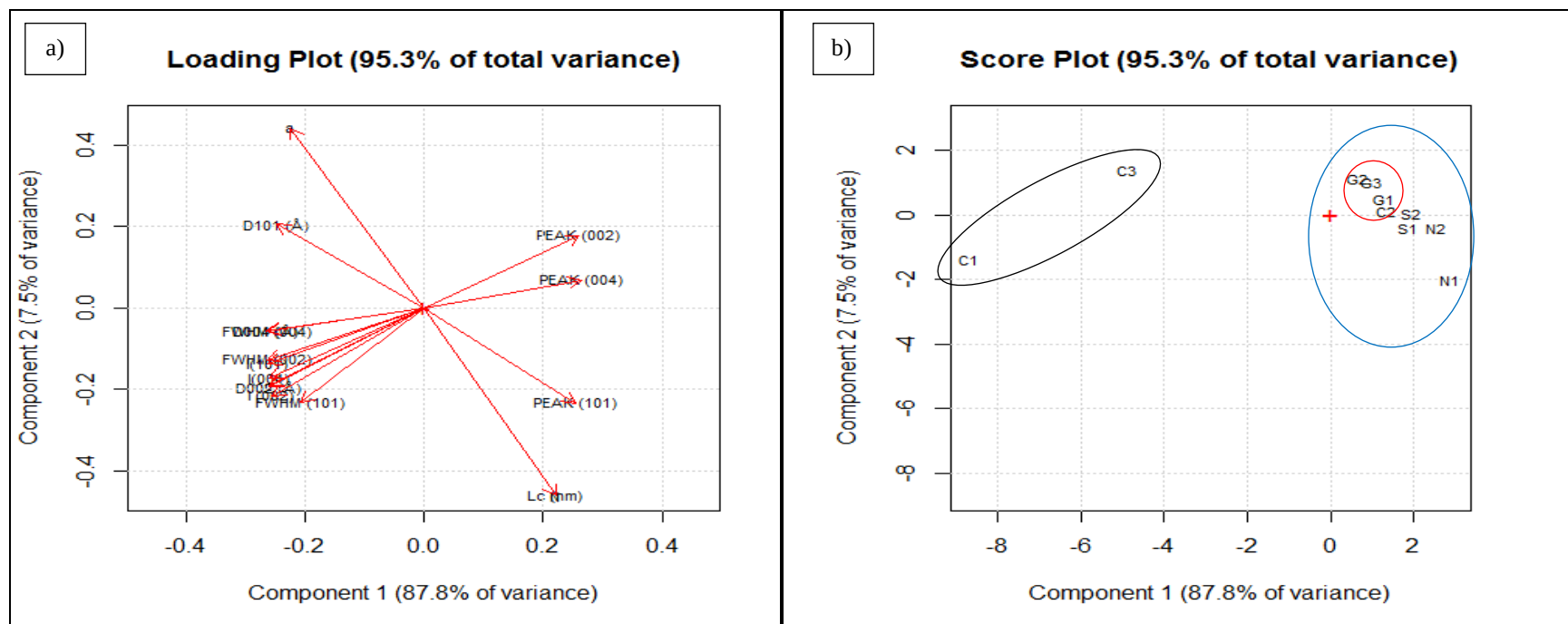


Figure 4.11: Principal Component Analysis of data matrix on x-ray diffraction: a) loading plot; b) score plot

4.3.2 – RAMAN SPECTROSCOPY

The fit of spectra was performed applying a Lorentzian equation, as suggested by previous studies¹³². Graphite single-crystal has vibrational modes $2E_{2g}$, $2B_{2g}$, E_{1u} , and A_{2u} , of which only the $2E_{2g}$ modes are Raman active^{133–135}. The main peak derived from this vibrational mode is located at 1581 cm^{-1} and it is named band G, but when the graphite analysed is not completely crystalline, other two bands are visible at around 1360 and 1620 cm^{-1} , named respectively band D and D'. Above 2000 cm^{-1} , other four distinct second-order peaks at around 2440 , 2730 (2D), 2940 and 3240 cm^{-1} (2D') can be detected. The band 2D and 2D' are overtones of first-order peaks, respectively of D and D' band. The other two bands derive both from kind of combination: the peak around 2440 derives from a combination of TO and LA mode, while peak around 2940 is a combination of band D and G^{136,137}. In general, the most important bands are D and G, considered respectively the disorder and order band. The G peak is due to the stretching of all pairs of sp^2 atoms in both rings and chains, corresponding to an ideal lattice vibration mode (E_{2g} symmetry). The D peak is due to the breathing modes of sp^2 atoms in the ring, corresponding to a graphitic lattice vibration mode with A_{1g} symmetry^{138,139}. Usually in graphite samples the D peak is lower than G, but when defects are present in the structure the intensity of D band increases and also D' band can be visible as shoulder of G one. In amorphous carbon samples, the D band exceeds G one due to the higher disorder, and both peaks are broader. The graphene shows sharp G peak; the band 2D is 4 times higher than G for graphene monolayers¹⁴⁰. The shape and relative intensity of band 2D with respect to band G depends on the number of layers that constitute the sample, and generally with more than 10 layers it is possible to consider the sample as graphite¹⁴¹.

All the aforementioned peaks are reported in Figure 4.12a as example. Figure 4.12 reports the five Raman spectra collected for both the two natural graphite. Sample N1 (Figure 4.12a) shows five spectra slightly different, suggesting a non-perfect homogeneity among particles. Instead, Figure 4.12b shows five overlapped spectra of sample N2, which has a major homogeneity respect N1. To qualitative and quantitative considered the Raman spectra of carbon materials, an average spectrum was calculated for each sample.

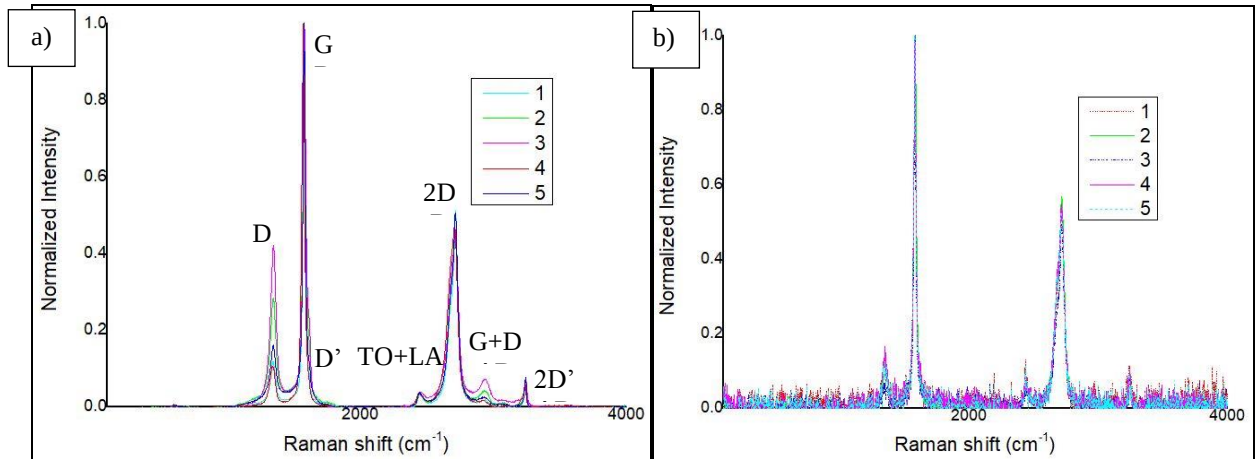


Figure 4.12: Normalized Raman spectra of natural graphite: a) N1; b) N2.

Figure 4.13 shows the Raman spectra collected for the graphite samples (Figure 4.12a) and the graphene samples (Figure 4.12b). For all of them the peak G results sharp and shows intensity roughly equal to double of peak 2D one.

The main difference among graphite concerns the intensity of peak D and the shape of peak 2D, which qualitatively suggests a difference in the amount of defects and number of layers overlapped inside the structure. Graphene samples differ mainly on the relative intensity of peak D, then on the degree of organization.

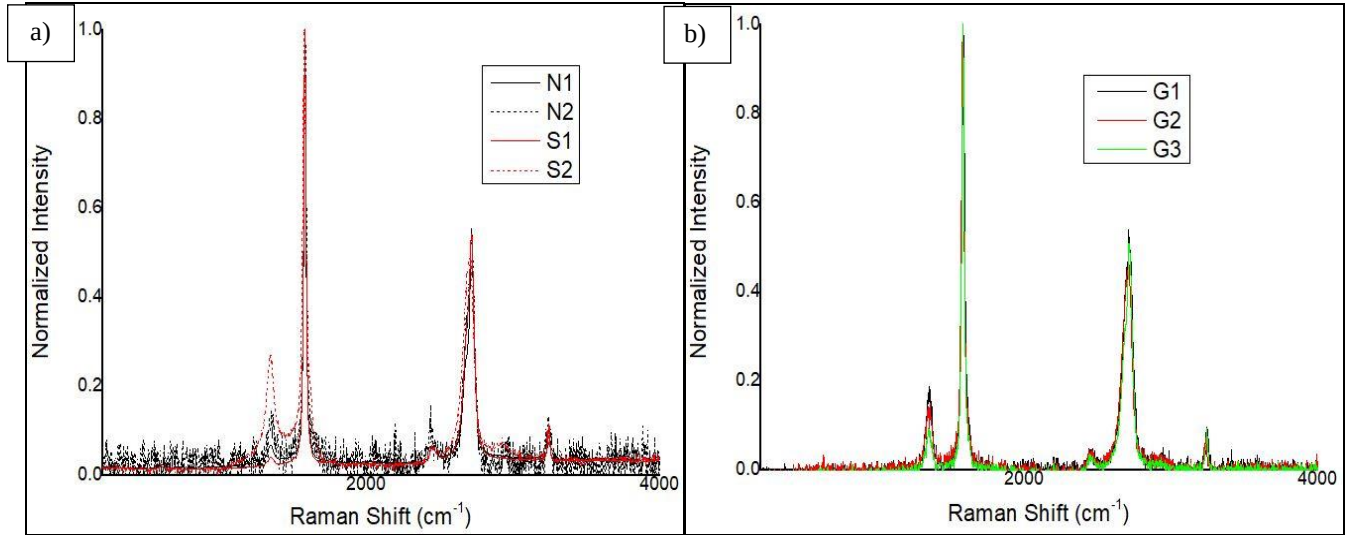


Figure 4.13: Raman spectra of : a) graphite; b) graphene.

Figure 4.14 reports the Raman spectra of coke samples, of which the graphitized coke C2 results significantly different to the others, but similar as peak shape to graphite and graphene Raman profile. The coke C1 and C3 show broader peaks at major wavenumber respect C2, due to the high amorphous carbon content. In fact, considering the values ACC, they show a percentage of amorphous content higher than 60%, while all the other samples are fewer than 45%.

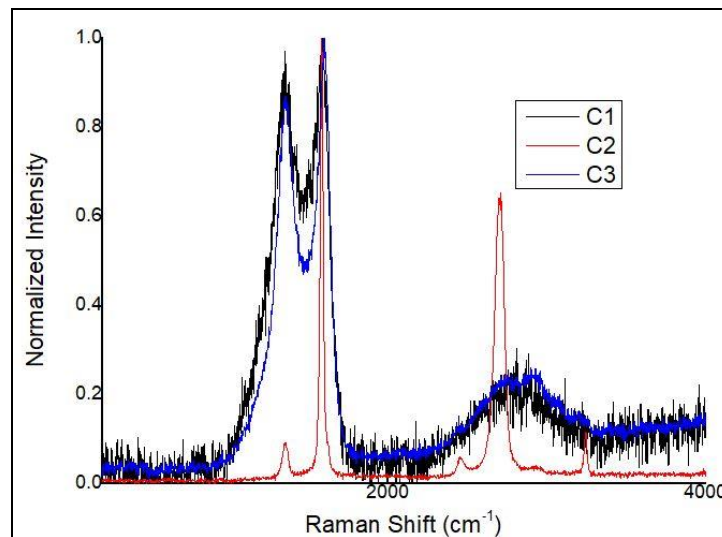


Figure 4.14: Raman spectra of coke samples.

The fit of spectrum performed using Lorentz formula allows to quantitatively investigate the position and the shape of each band, focusing the attention on the ratio $I(D)/I(G)$, considered linear proportional to the sp^3 content¹⁴². Also the width of the G band is correlated to sp^3 content, as shown by Cui et al.¹⁴³, through a logarithmic correlation. Furthermore, the ratio $I(D)/I(G)$ is considered inversely proportional

to the in-plane crystallite dimension $L_a^{138,144,145}$, although several studies disagree with this proportionality^{146,147}, originally named Tuinstra and Koenig equation (4.4). This formula was obtained considering that the D band intensity scales with the perimeter of the crystallite, while the G band intensity is proportional to the crystallite area¹⁴⁸.

Another equation useful for this study was published by Beyssac et al.¹⁴⁹. They used the ratio reported in formula 4.5 as parameter to describe the degree of organization, thus it can be considered as an indicator of the amorphous carbon content (ACC), as done by Cuesta et al.¹⁵⁰. This ratio contains the peak area of D, D' and G bands, where D and D' represent the defects in the structure, while G is relative to the organized structure.

$$4.4 - \frac{I(D)}{I(G)} = \frac{4.4}{L_a(nm)}$$

$$4.5 - ACC = \frac{I_D}{I_D + I_{D'} + I_G}$$

Tables 4.9 and 4.10 show all the data collected from Raman spectra by their fit, respectively concerning the first and second order peaks.

Table 4.9: Matrix of first-order Raman spectroscopy data collected on carbon materials.

SAMPLE	PEAK D	FWHM D	I (D)	PEAK G	FWHM G	I (G)	I(D)/ I(G)	I(D)/ (I(D)+I(G))	L _a (nm)
N1	1346	66.80	14.99	1579	22.47	35.15	0.43	0.30	10.32
N2	1352	48.38	7.12	1583	20.81	32.80	0.22	0.18	20.27
S1	1348	61.85	4.57	1579	19.33	30.99	0.15	0.13	29.85
S2	1348	76.94	34.71	1579	31.09	46.99	0.74	0.42	5.96
C1	1353	230.38	308.79	1579	101.71	130.37	2.37	0.70	1.86
C2	1349	49.34	17.34	1582	25.53	40.28	0.43	0.30	10.22
C3	1360	192.72	249.55	1589	94.49	135.43	1.84	0.65	2.39
G1	1351	42.62	15.43	1583	22.88	35.89	0.43	0.30	10.24
G2	1349	52.70	11.97	1580	22.44	35.61	0.34	0.25	13.09
G3	1348	45.93	9.77	1580	20.69	33.14	0.29	0.23	14.93

Table 4.10: Matrix of second-order Raman spectroscopy data collected on carbon materials.

SAMPLE	PEAK TO+LA	FWHM TO+LA	I TO+LA	PEAK 2D ₁	FWHM 2D ₁	I 2D ₁	PEAK 2D ₂	FWHM 2D ₂	I 2D ₂	PEAK G+D	FWHM G+D	I G+D	PEAK 2D'	FWHM 2D'	I 2D'
N1	2451.89	46.18	4.45	2674.29	46.83	21.01	2716.99	35.86	51.40	3088.92	1185.20	54.55	3243.09	13.91	3.27
N2	2439.88	53.88	12.78	2682.44	53.71	38.86	2719.15	38.15	49.39	2954.89	30.54	3.72	3243.05	34.09	9.26
S1	2453.19	53.58	5.44	2680.63	56.71	36.61	2717.36	37.70	50.82	2935.89	48.52	0.56	3242.55	16.24	4.28
S2	2448.84	57.33	6.60	2681.51	70.74	73.63	2712.83	42.52	38.10	2924.64	87.71	7.62	3234.33	26.05	5.72
C1	2441.23	26.98	5.15	2575.70	144.70	43.75	2731.99	224.88	131.10	2914.19	357.38	246.97	3241.77	44.13	4.83
C2	2456.59	53.79	5.41	2690.74	53.68	65.73	2718.15	36.63	31.04	2941.17	61.09	2.00	3243.31	21.26	5.21
C3	2439.71	48.44	9.30	2575.16	158.58	50.91	2709.95	218.86	202.68	2921.57	304.76	387.85	3202.94	80.33	16.21
G1	2452.88	37.56	3.91	2687.88	60.00	53.68	2721.27	38.00	43.54	2937.81	80.50	6.20	3244.21	23.50	5.96
G2	2450.85	45.43	5.06	2684.55	63.11	56.02	2717.53	39.99	43.32	2935.02	69.58	3.32	3240.21	24.27	5.84
G3	2452.56	48.57	4.94	2681.91	64.11	56.35	2715.43	39.44	44.22	2935.63	66.95	4.02	3237.15	20.79	5.34

Based on first order spectrum, the attention was focused on the ratio $I(D)/I(G)$, the width of peak G and the in-plane crystallite dimension L_a . As reported previously, both $I(D)/I(G)$ and FWHM G are correlated with the sp^3 fraction in different way. Due to the linear correlation between $I(D)/I(G)$ and the sp^3 fraction, plotting the ratio $I(D)/I(G)$ in function of FWHM G the expected graph would show a logarithmic correlation, confirmed in Figure 4.15. The calcined coke and carbon black have the highest sp^3 content that represents their amorphous carbon content, while the graphitized coke can be considered as graphite and graphene samples also by Raman data, as already observed from x-ray diffraction analysis.

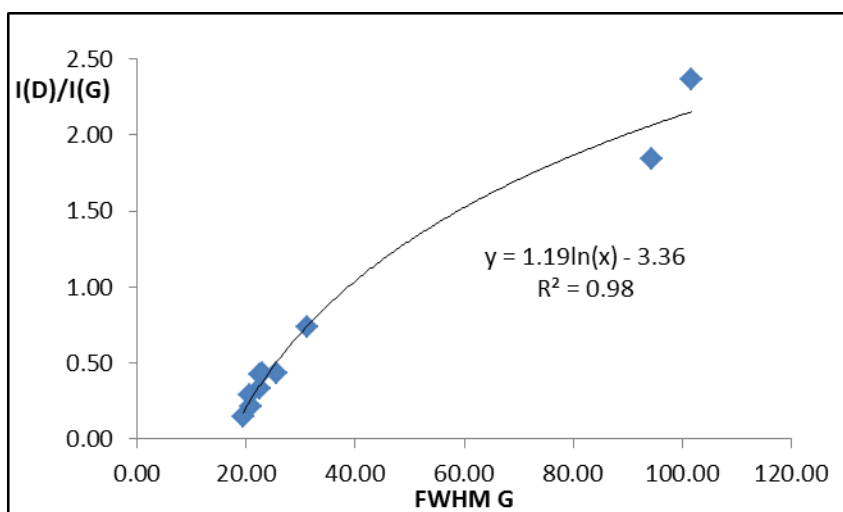


Figure 4.15: Correlation of ratio $I(D)/I(G)$ with FWHM G for all samples.

The ratio $I(D)/I(G)$ is also directly proportional to $1/L_a$ based on Tuinstra and Koenig formula¹³⁸, but this correlation is not always true¹⁴⁷. However, it can be used to have a general comparison of in-plane crystallite dimension among the carbon system. Results show a range of crystallite dimension of 1-30 nm, where the two cokes C1 and C2 have the lowest value of L_a and the synthetic graphite S1 the highest.

Considering the second order Raman spectrum, the attention was focused on the shape and intensity of peak 2D, due to its correlation with the number of layers overlapped. Based on both intensity and width, for the components fitted, the coke C1 and C3 result significantly different from the others, which are roughly similar, especially the three graphene.

Applying a PCA analysis on the overall data obtained from Raman spectra, the resulting score plot highlights the significant difference of samples C1 and C3 respect all the others (Figure 4.16a), which are slightly similar. The resulting loading plot is too complicate to understand what variables mainly affect the differences among samples. Thus, based on previous observations on Raman spectra, the system can be simplified considering the shape of peaks D, G and 2D, together with ratio $I(D)/I(G)$ and in-plane crystallite dimension L_a . Figure 4.16b reports the resulting biplot (loading and score plot together), where two components explained practically the overall variance of the system (98.8%). The PC1 is mainly dominated by ratio $I(D)/I(G)$ and less by shape of peaks, while the PC2 depends on L_a . Thus, it is possible to differentiate the samples first of all based on the ratio $I(D)/I(G)$, which means on the degree of organization, and as second step based on the in-plane crystallite dimension. The graphene samples result similar respect each other, and slightly different from graphite due to the L_a value.

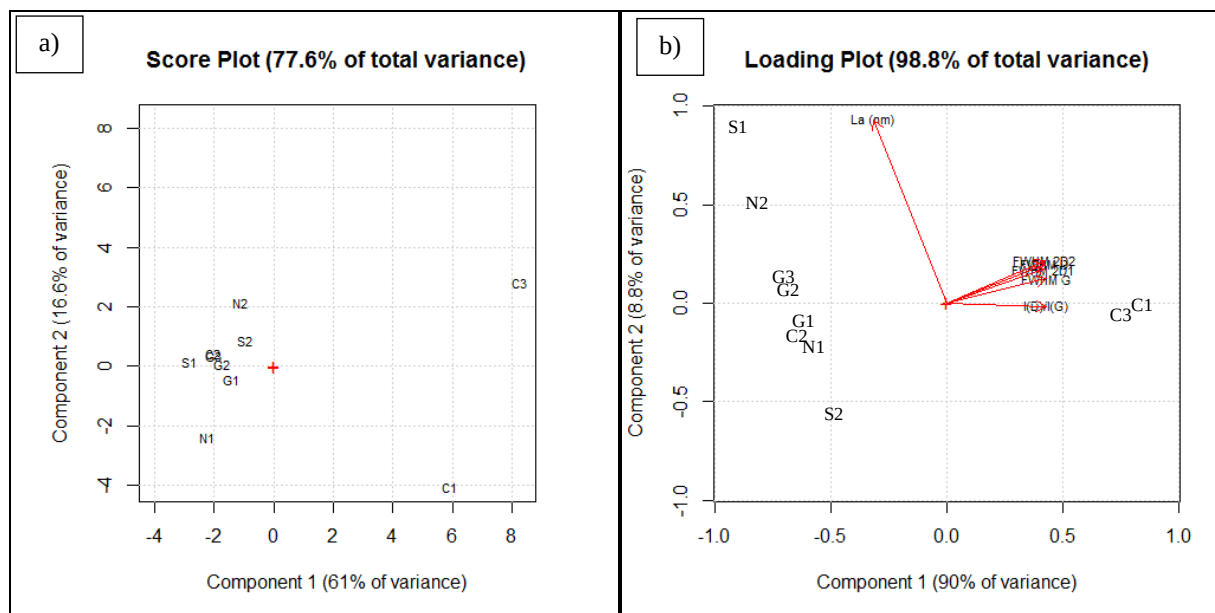


Figure 4.16: a) Score plot of PCA on all Raman parameters; b) Loading plot of data on Raman spectra.

4.3.3 – DENSITY

The density was measured on graphite and coke samples (Figure 4.17). Density values for graphite are in agreement with literature data¹³¹, equal to 2.26 g/cm³. All the three coke show a lower density with respect to graphite, that probably derives from the large amorphous carbon content in the case of C1 and C3, while for C2 can be a consequence of the graphitization process, which transformed the structure in ordered stacked layers, but with several pores respect graphite samples.

The Pearson coefficient was calculated for density using each structural parameter derived from x-ray diffraction and Raman spectroscopy. No one of them results linearly correlated with density, suggesting a complete different nature and meaning of this macroscopic parameter.

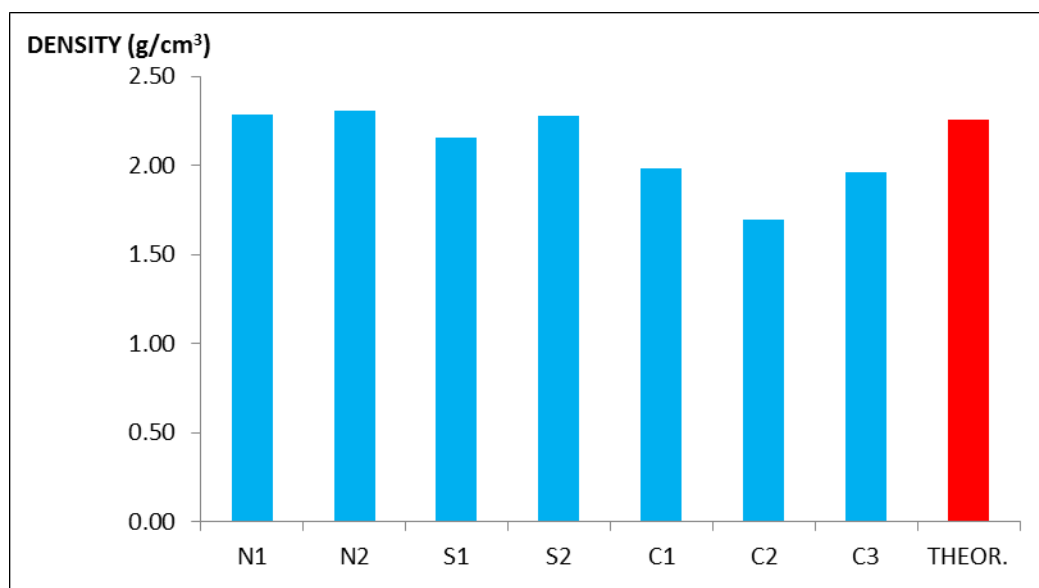


Figure 4.17: Density of raw materials obtained by helium pycnometer.

4.4 – TRIBOLOGY OF POWDERS

The friction coefficient of each carbon materials was measured by tribometer at standard condition of 10 N as load and 0.2 ms^{-1} as speed. Figure 4.18a shows the comparison of friction coefficient with the value of friction amplitude as error bar. This parameter is calculated as the standard deviation of friction coefficient evolution during sliding in the steady state⁹⁹.

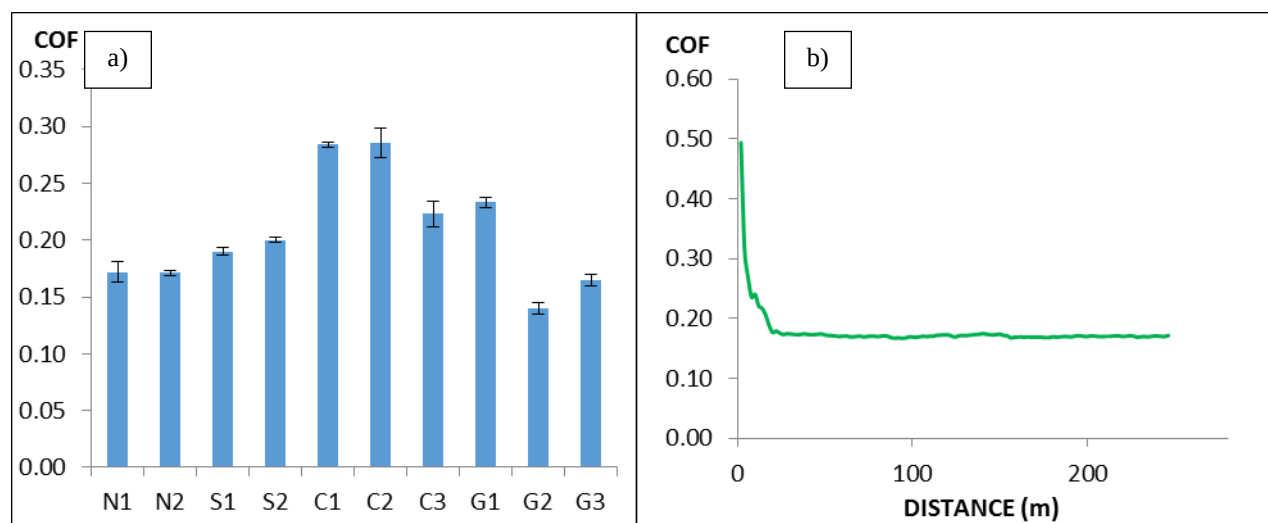


Figure 4.18: a) Comparison of friction coefficient values for all samples; b) friction behaviour as a function of distance for N2.

The typical evolution of the friction coefficient as a function of the sliding distance is reported in Figure 4.18b. The decrease of the COF, observed for all the materials, is attributed to increase of particle density at interface, thus preventing the steel-steel contact. In the case of graphite samples, the formation of a stable tribofilm was observed on the steel surface. Whereas, for the graphitized coke, a little amount of tribofilm was observed, but it was not enough stable because when the rest of powder was removed, tribofilm was taken off simultaneously. The same phenomenon occurred in the case of graphene samples, while for the other two coke no layers were observed on the disc surface. However, in all the samples the run-in period is quick and after 50 meters or less the friction coefficient reaches a stable value, considered its steady state, with a very low amplitude.

Some reproducibility tests were performed in order to evaluate the possible influence of disc roughness, but the difference in friction coefficient was in the range 0.01-0.02, which does not represent a significant influence of surface topography on carbon friction. The roughness of disc and pin was measured after removal of powder and tribofilm, but probably the surface topography of tribofilm can result influent on friction behaviour. Unfortunately, it was not possible to measure roughness on tribofilm, due to its fragility.

4.4.1 – INFLUENCE OF MORPHOLOGY AND DENSITY

The friction coefficient is considered as the result of several variables combined together; thus in this and next sections the aim is to correlate the friction behaviour with macro and micro features of the material itself, using chemometrical and statistical method.

As macroscopic feature, the morphology parameters and density (D) were considered. A matrix of these variables was generated and a descriptive statistical method was applied to calculate the Pearson coefficient.

The data analysed concern graphite and coke samples (Table 4.9), which show a wide range of particle size and shape. Table 4.10 reports the correlation coefficients with its significance (Sig) calculated through the 2-tailed test. The asterisked values are the only significant correlation factors and it is possible to establish if the proportionality is linear or not, direct or inverse, based on the Pearson value. Friction coefficient results inversely proportional to the material density, then a denser structure generates a lower friction. Thus, the friction coefficient can be considered directly proportional to material porosity, which has opposite trend respect density. A material with higher porosity would not allow the formation of a stable tribofilm and it consequently generates a higher friction coefficient. The difference in density can also explain why the graphitized coke shows a higher friction with respect to graphite samples though it has a similar structure at atomic scale. Experimentally, the effect of density can be observed considering the absence of a stable tribofilm for graphitized coke, which causes the higher COF.

The amplitude of friction is linearly proportional to particle size represented as perimeter or Feret's diameter, since they are linearly correlated (Pearson coefficient = 1.00). From a physical point of view, the friction amplitude can be affected by Feret's diameter because at interface the continuous succession of particles with different size causes an oscillation of interface distance between pin and disc, in function of number and size of particles present in some instants. Thus, it is reasonable that the average particle size affects the average deviation of friction from its steady state value. Higher the Feret's diameter, wider the particle size distribution and consequently higher the amplitude of COF.

In the industrial field of brake pad, the morphological parameters are supposed to affect friction coefficient due to several experience in comparing similar materials with different shape and size. From this first comparison, this supposition seems to be wrong, because the particle size affects just amplitude and COF does not depend on any morphological parameters. However, by x-ray diffraction and Raman spectroscopy, the samples C1 and C3 result as outlier of the carbon materials system analysed. Thus, it can be supposed that to observe the morphology influence, it is necessary to compare materials with similar structure, which means in general that to compare a macroscopic property the micro and atomic characteristics must be as much similar as possible. From this point of view, a systematic group of samples with similar structure features is composed by graphite and graphitized coke. In this subgroup, the friction coefficient and amplitude correlations with density and Feret's diameter respectively do not change, but new proportionalities are evident. The amplitude is inversely proportional (Pearson coefficient = -0.95) to particle roundness R, which can be interpreted as a lower change in the distance between pin and disc due to the easier rolling motion at interface of spherical-like particles. Furthermore, the aspect ratio AR is linearly proportional to friction coefficient, which means that elongated particles increase the interface friction. This influence can be explained considering the powder sliding against the pin as a system subjected to uniaxial compression. In this hypothesis, oblong particles form stronger 3D structure under compression as found by Wiacek et al.⁸⁰. The formation of a compact structure at interface reduces the possibility of sliding plans, then reducing the lubricant action.

Table 4.9: Data matrix on morphological and density results.

SAMPLE	COF	AMPL.	D	A	P	F	AR	R	C	S
N1	0.172	0.009	2.28	182228.80	931.75	353.38	1.75	0.61	0.70	0.89
N2	0.171	0.002	2.30	5656.50	275.63	101.10	1.76	0.62	0.69	0.91
S1	0.190	0.003	2.16	6774.33	284.99	101.46	1.73	0.62	0.65	0.88
S2	0.200	0.002	2.28	243.98	63.01	20.95	1.77	0.63	0.59	0.85
C1	0.284	0.002	1.99	11.28	18.98	6.80	1.31	0.78	0.42	0.96
C2	0.285	0.013	1.70	84488.02	965.33	344.37	1.98	0.59	0.63	0.86

C3	0.223	0.011	1.96	13255.15	432.42	161.33	1.83	0.59	0.69	0.89
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Table 4.10: Matrix of Pearson coefficient obtained by matrix reported in Table 4.9.

		COF	AMPL.	D	A	P	F	AR	R	C	S
COF	Pearson	1.00	0.31	-0.88*	-0.15	0.03	0.01	-0.23	0.45	-0.68	0.23
	Sig.	--	0.50	0.01	0.74	0.95	0.99	0.63	0.31	0.10	0.62
AMPL.	Pearson	0.31	1.00	-0.64	0.58	0.85*	0.84*	0.62	-0.56	0.42	-0.37
	Sig.	0.50	--	0.12	0.17	0.02	0.02	0.13	0.19	0.34	0.41
D	Pearson	-0.88*	-0.64	1.00	0.01	-0.35	-0.32	-0.18	-0.02	0.26	0.04
	Sig.	0.01	0.12	--	0.99	0.44	0.49	0.70	0.97	0.57	0.93
A	Pearson	-0.15	0.58	0.01	1.00	0.86*	0.88*	0.30	-0.33	0.39	-0.18
	Sig.	0.74	0.17	0.99	--	0.01	0.01	0.51	0.47	0.39	0.70
P	Pearson	0.03	0.85*	-0.35	0.86*	1.00	1.00*	0.63	-0.59	0.55	-0.38
	Sig.	0.95	0.02	0.44	0.01	--	0.00	0.13	0.16	0.20	0.39
F	Pearson	0.01	0.84*	-0.32	0.88*	1.00*	1.00	0.61	-0.59	0.55	-0.37
	Sig.	0.99	0.02	0.49	0.01	0.00	--	0.14	0.17	0.20	0.42
AR	Pearson	-0.23	0.62	-0.18	0.30	0.63	0.61	1.00	-0.96*	0.79*	-0.86*
	Sig.	0.63	0.13	0.70	0.51	0.13	0.14	--	0.00	0.03	0.01
R	Pearson	0.45	-0.56	-0.02	-0.33	-0.59	-0.59	-0.96*	1.00	-0.92*	0.81*
	Sig.	0.31	0.19	0.97	0.47	0.16	0.17	0.00	--	0.00	0.03
C	Pearson	-0.68	0.42	0.26	0.39	0.55	0.55	0.79*	-0.92*	1.00	-0.57
	Sig.	0.10	0.34	0.57	0.39	0.20	0.20	0.03	0.00	--	0.18
S	Pearson	0.23	-0.37	0.04	-0.18	-0.38	-0.37	-0.86*	0.81*	-0.57	1.00
	Sig.	0.62	0.41	0.93	0.70	0.39	0.42	0.01	0.03	0.18	--

As previously reported, also the particle size is considered an important feature affecting friction coefficient in brake pad. In this system, the size affects the friction amplitude, but not directly the COF, probably for the same reason as the morphology influence is not observable among materials with a different structure. Then, it is necessary to compare materials with similar structure and shape in order to observe the influence of particle size. Moreover, samples with a sharp particle size distribution are better for comparison.

For the aforementioned reason, the two natural graphite N1 and N2 were selected for the study of size influence. They show similar structure features by x-ray diffraction and Raman spectroscopy and similar shape, while their particle size distribution is quite different. The first sample has a particle size ranging between approximately 100 and 2000 μm , while N2 shows the range 50-300 μm . Thus, both of them were sifted with the purpose to obtain different fractions of powders with a less wide particle size distribution. Each sifted fraction was analysed through the standard test at 10N and 0.2 ms^{-1} , after which a portion of powder near the pin was collected and analysed by optical microscope to measure the final particle size after the tribological test. The results show that COF increases as the particle size decreases when the starting size is above 250 μm , while under this value the trend is opposite. To explain the different trend, the final particle dimension must be considered. The results show that the fractions under or around 250 μm do not change their average size significantly during the test, while the fractions above 250 μm suffer a decrease in particle size, becoming similar to lower fractions. In particular, higher the starting dimension, lower the size of particles at interface. This is the reason why friction coefficient results specular with respect to fractions under and above 250 μm . Horng et al.¹⁵¹

explained in their paper that lower the particle size, lower the friction coefficient because of the higher particle density at interface. Thus, the higher number of particles between pin and disc causes a higher lubrication.

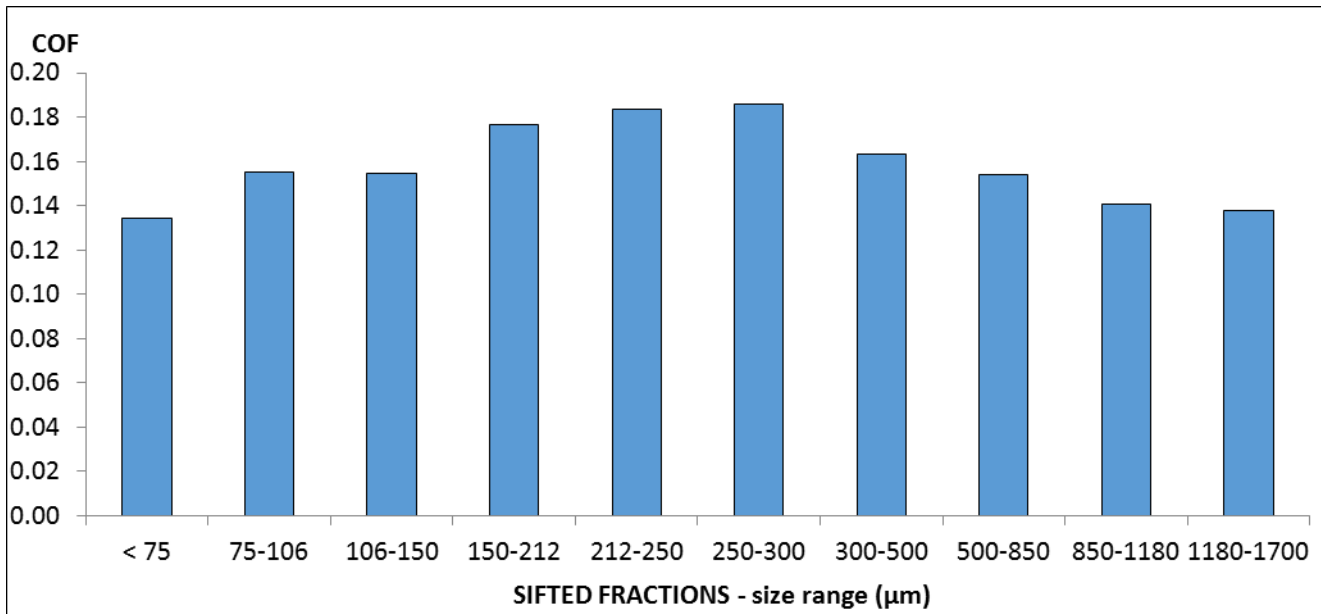


Figure 4.19: Friction coefficient of standard test relative to sifted fraction of natural graphite.

The same conclusion formulated by Horng et al. and verified in the previous tests on sifted graphite fraction can be applied in the comparison of graphene tribological behaviour. The three samples show different particle size distribution, as shown by granulometry analysis, from which G1 results the graphene with the highest average particle size. Thus, the density of the particles at interface in the case of this sample would be lower than the other two graphene, which show similar D50 size. However, samples G2 and G3 have a different average friction coefficient that becomes equal after 500 m as sliding distance. G3 needs of a higher distance to reach the steady state, but this difference does not seem to derive from particle size distribution.

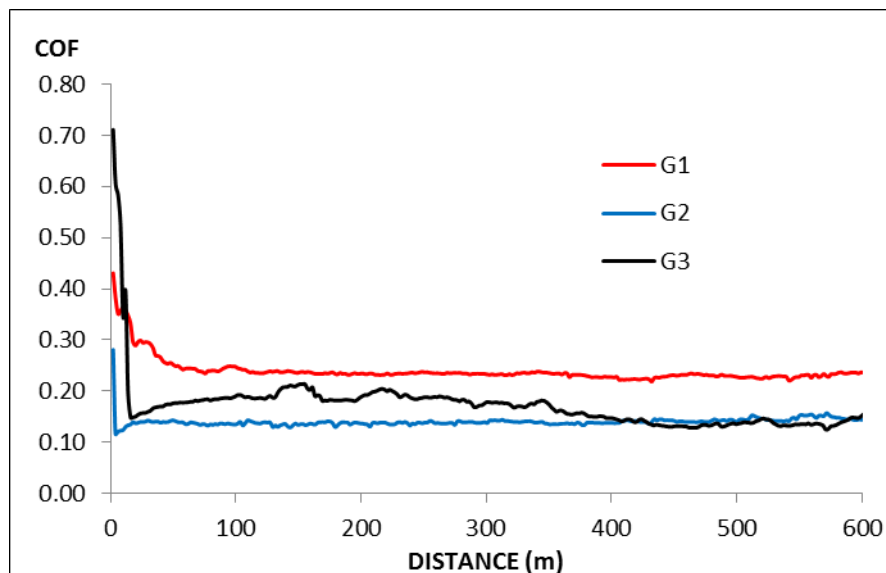


Figure 4.20: Comparison of friction coefficient behaviour in function of distance for graphene samples.

4.4.2 – INFLUENCE OF STRUCTURAL FEATURES

Based on the amorphous carbon content, the coke C1 and C3 result as outlier respect the group made by C2, graphite and graphene samples.

Considering all the samples, the calculated Pearson coefficient between friction and the overall structural parameters does not show any linear proportionality (Pearson coefficient > 0.9), both in case of x-ray diffraction and Raman spectroscopy. Thus, just structural features cannot describe the carbon materials system, because the friction behaviour is the result of several variables at the same time. As described in the section 4.4.1, density, shape and size of particles affect the tribological behaviour and, in some cases, to observe the effect of a single parameter is necessary to select materials with the other parameters as much similar as possible (example: effect of particle size for natural graphite). This observation highlights the fact that each parameter has a different weight in affecting friction coefficient. Therefore, from previous section, results show that the shape affects friction more than particle size, whereas size influences the amplitude of COF. This is the reason why x-ray diffraction and Raman data do not give any linear correlation with friction among the entire system.

Raman data show some significant Pearson coefficient around 0.80 that can be considered as non-linear correlation with COF. It is affected by the amount of disorder in the structure, because it depends on the full width at half maximum of peaks D, G, 2D₁, and 2D₂. Each of them represents the disorder associated with the structure feature, in particular D and G derive from in-plane defects, while the two 2D components from out-of-plane defects. Results suggest that the formation of tribofilm at interface depends on the amount of disorder due to both in-plane and out-of-plane defects. Furthermore, friction is proportional to the ratio $I(D)/I(G)$ and the amorphous carbon content calculated as $I(D)/(I(D)+I(G))$, but at the same time these two parameters are correlated with the FWHM values of each peak previously considered. Thus, the ratio $I(D)/I(G)$ can be used as parameter to establish approximately the amount of defects in the structure, which is directly proportional to friction coefficient.

In the case of x-ray diffraction, no one of the parameters considered results significantly correlated with friction, if considering the whole carbon system. With the purpose to limit the attention to samples with similar morphology and density, the analysis was restricted to the four graphite that differ only for particle size distribution, which mainly affects the amplitude of COF. The friction behaviour of graphite results affected by the full width at half maximum of peak (002). The correlation with FWHM (002) confirms what previously found by Raman data, because the full width at half maximum is affected also by the amount of disorder. However, this parameter is strongly correlated with the crystallite dimension obtained by Scherrer equation (4.3), as confirmed by statistical analysis (Pearson coefficient $L_c - \text{FWHM (002)} = -0.98$), which can be considered a quantitative parameter of the out-of-plane order. Instead, the crystallite dimension results not significantly correlated with friction, suggesting that the tribological behaviour can be described as the combination of amount of defects in-plane and out-of-plane. If this conclusion is true, there must be a correlation between the crystallite dimension and the full width at half maximum of Raman peaks 2D. Figure 4.21 shows that, when the order on c axis is poor, broad peaks are observed around 2700 cm^{-1} in Raman spectra, while a sharper peak is obtained for high order on c axis. The reason why the stacking order affects friction coefficient is probably correlated with the formation of tribofilm, because a structure with high order on c axis generates a stable and thick layer at interface when subjected to compression. Instead, when the stacking order is poor, the planes easily slide on each other without allowing the formation of a thick layer with higher lubricant effect. By this conclusion, all the experimental observations are confirmed: the coke C1 and C3 do not form tribofilm due to their poor stacking order and high amount of amorphous content, while all the other samples generate a stable tribofilm in different amount. In fact, considering just L_c , also the graphitized coke C2 should show a tribofilm at interface and a friction

coefficient slightly higher than synthetic graphite S2, but its COF is equal to 0.284, significantly higher than S2 one and the amount of layer at interface is very poor. The reason for this difference must be sought in the lower density and higher porosity of sample C2 respect graphite, features that do not allow the formation of tribofilm.

The influence of crystallite dimension on friction behaviour can be used also to explain the friction of graphene samples. As suggested in section 4.4.1, their COF depends on the different particle size distribution, but at the same time, the influence of disorder must be considered. By Raman data, all the samples result affected by amount of defects, but in the case of graphene the values of FWHM of both Raman and x-ray diffraction peaks previously considered are similar, as shown in Figure 4.21. Thus, considering their similar amount of defects in-plane and out-of-plane, the effect of particle size becomes dominant on the friction behaviour, confirming the previous hypothesis.

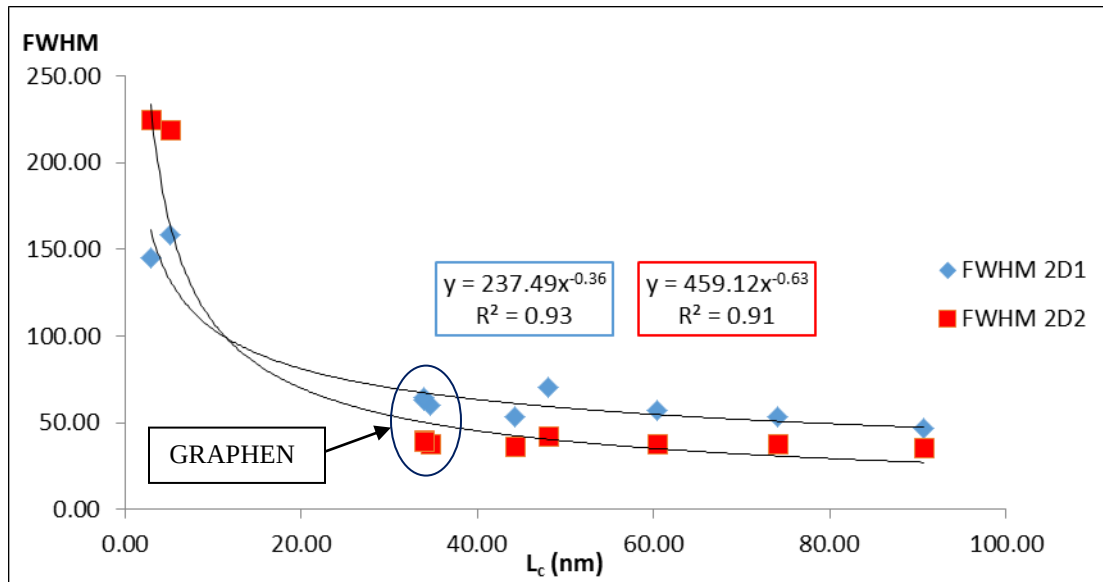


Figure 4.21: Correlation of FWHM of Raman peaks 2D with L_c obtained by x-ray diffraction.

In the case of graphite, the tribofilm resulted enough to be collected and analysed by Raman spectroscopy in order to investigate the possible change in defects quantity and its correlation with friction. Results show that the ratio $I(D)/I(G)$ increases for all samples apart from S2, while the full width at half maximum of peaks 2D does not change significantly. Thus, the tribofilm generated at interface shows a higher number of in-plane defects that can derive from the sintering process as finite size boundaries, while the stacking order remains almost the same. This experimental result suggests a higher influence of stacking order respect in-plane defects on friction behaviour.

4.4.3 – INFLUENCE OF TRIBOLOGICAL CONDITIONS

The tribological phenomena are affected by several variables and in previous sections the complexity of this behaviour was partially disentangled restrictively to carbon materials. However, from a macroscopic point of view, also the test conditions affect the development of friction, then other experiments were set up in order to study the influence of load and speed on graphite and coke samples.

As first step, the two variables were considered in an OVAT approach (One Variable At Time). Load was changed in the range 3 – 18 N, while speed in the range 0.10 – 0.30 ms⁻¹. Figure 4.22 shows the variation of COF in function of speed and load for the synthetic graphite S2as example. The increase of

load affects non-linearly the friction coefficient that decreases following a power function. This inverse correlation is quite in agreement with the published results of Bowden, who reported in his review that friction coefficient is proportional to $\text{Load}^{-1/3}$ for non-metallic materials⁸. Instead, the sliding speed does not affect COF in the range investigated.

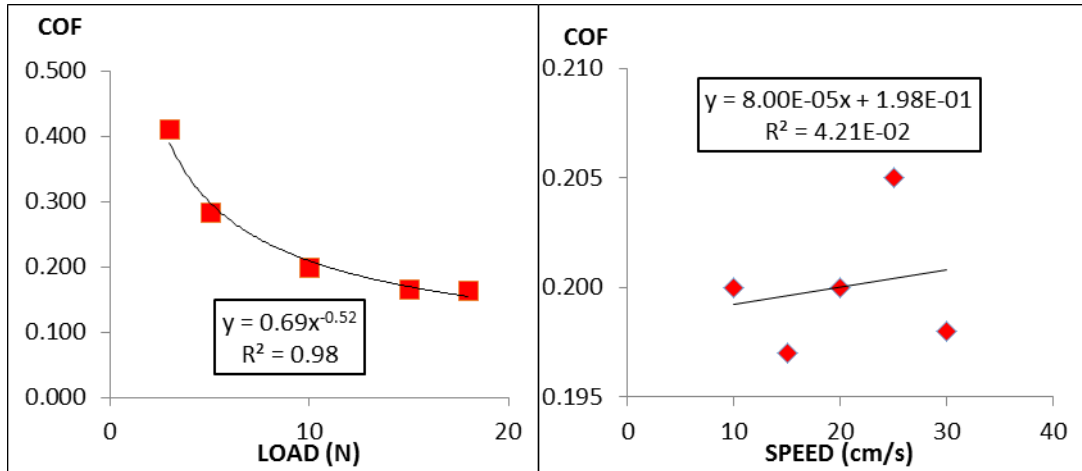


Figure 4.22: Variation of COF in function of load and speed for sample S2.

The correlation of COF with load can be expressed in two forms: a power function between them or a linear correlation of COF with the reciprocal of load.

$$4.6 - \mu = b_0 \text{Load}^\alpha$$

$$4.7 - \mu = \frac{a}{\text{Load}} + b$$

The numerical parameters obtained for each sample are summarized in Table 4.11. By statistical analysis, all the factors result proportional each other, but they show different influences from morphological and structural parameters. Although b is correlated to the other factors, it does not show any significant proportionality with previous characterization, then to better understand the influence of load from a chemico-physical point of view, formula 4.6 seems to be more significant. In fact, b_0 and α show interesting correlation with structural and morphological features.

The factor α is directly proportional to FWHM of both peaks (002) and (004), following the correlation of friction with in-plane and stacking order. Moreover, it has a direct proportionality also with the ratio $I(D)/I(G)$, which is relative to the amount of in-plane defects, and with particle roundness. Thus, α tends to zero for materials with high amount of defects and in the case of particles with spherical shape, then friction coefficient becomes equal to b_0 .

The factor b_0 can be considered as the friction obtained at load of 1 N or for spherical amorphous particles. It results inversely proportional to FWHM (002) and directly to aspect ratio. Considering b_0 as a possible value of friction coefficient, the inverse correlation with full width at half maximum of peak 002 disagrees with previous discussion on structural influence. Moreover, it does not show any significant correlation with FWHM (004) and $I(D)/I(G)$, then this factor is not affected by structural features as α . Instead, the correlation with aspect ratio follows the previous considerations on morphological influence and confirms the dependence of load effect on packaging of particles at interface.

Table 4.11: Comparison of numerical parameters obtained for formula 4.6 and 4.7.

SAMPLE	b_0	α	a	b
N1	0.57	-0.45	0.67	0.14
N2	0.56	-0.48	0.79	0.09
S1	0.54	-0.43	0.70	0.12
S2	0.68	-0.51	0.90	0.11
C1	0.41	-0.16	0.31	0.25
C2	0.64	-0.36	0.72	0.21
C3	0.55	-0.39	0.66	0.15

4.5 – CHARACTERIZATION OF MONOCOMPONENT PADS

Composites based on carbon materials were produced in order to investigate the influence of morphological and structural features not only on powder friction, but also on pad tribological behaviour. Thus, for selected carbon materials previously characterized, a monocomponent pad was obtained that is constituted by 50%vol of basic mix and 50%vol of carbon powder.

Based on the previous characterization, the four graphite and the graphitized coke C2 were selected as filler for monocomponent pad, due to their likeness in structural features. In next section, all the samples have the same name as powder ones.

This part of thesis is devoted to understand how each single carbon materials affects the tribological behaviour of the basic mix and what kind of properties should be considered in order to select the appropriate solid lubricant.

4.5.1 – PHYSICAL CHARACTERIZATION

Powder size and shape are unchanged when added to the basic mix (Figure 4.23). Therefore, for further comparison the morphological data obtained for powders would be considered also for pads.

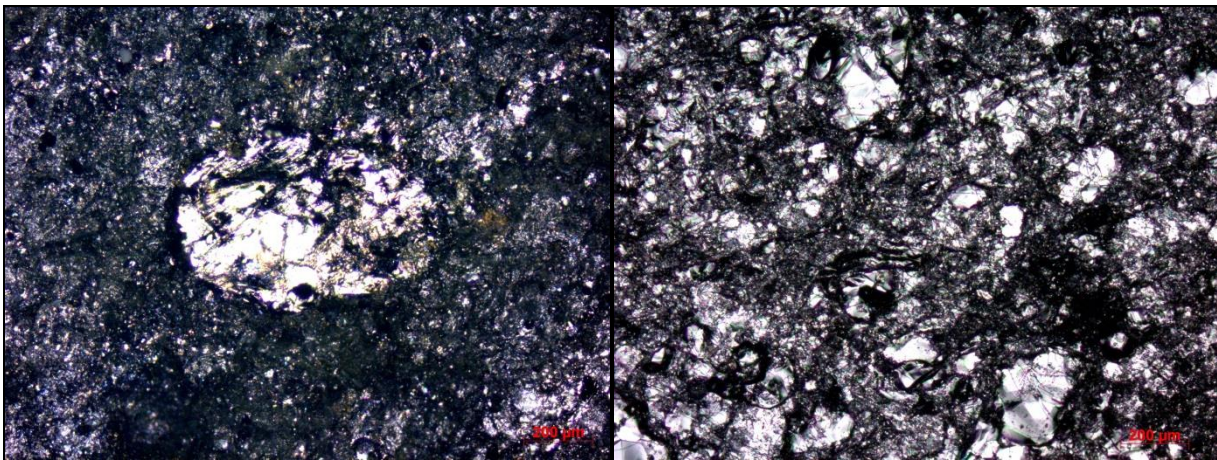


Figure 4.23: Optical images of pad surfaces for sample N1 and N2.

A first influence of carbon filler can be investigated through the measurement of pad density by geometrical volume. Table 4.12 reports the value of measured and theoretical density (last one obtained using the theoretical densities of each component). Apart from N1 and C2, all the calculated densities are comparable with the theoretical ones. Comparing the results obtained with the density of basic mix, all the composites show a higher value, as expected because of the higher density of powder materials.

In order to understand what kind of material property affects the resulting density of pads, the Pearson coefficient was calculated between pad density and each structural and morphological parameter previously considered. Note that no one of structural factors affects significantly the pad density, and then the influence of degree of organization and of structural dimensions is negligible regarding the bulk density of monocomponent samples. Instead, the particle morphology affects linearly this parameter because it depends on particle aspect ratio and roundness. The pad density increases due to a decrease in aspect ratio or an increase in roundness, which means that more the particle shape is spherical, higher is the final density of pad. Consequently, it can be supposed that spherical particles have a major interaction with the basic mix, decreasing the pad porosity.

Table 4.12: Density of carbon based pad.

SAMPLE	DENSITY (g/cm ³)	THEORETICAL DENSITY (g/cm ³)	POWDER DENSITY (g/cm ³)
MATRIX	1.32	1.30	-
N1	1.53	1.66	2.28
N2	1.64	1.66	2.30
S1	1.61	1.62	2.16
S2	1.63	1.66	2.28
C2	1.36	1.47	1.70

A second macroscopic property affected by the filler is the pad hardness, measured by Brinell test. In literature, the reported hardness of graphite ranges from 50 to 90 MPa¹⁵², significantly lower than that of the basic mix value. Thus, the carbon based pads show a lower hardness than matrix (Figure 4.24), because the presence of the filler interrupts the 3D network of Kevlar fibres and polymer chains. Moreover, the hardness values are linearly proportional to the FWHM of peaks 2D₁ and 2D₂, then this mechanical property is inversely correlated with the stacking order of carbon powders.

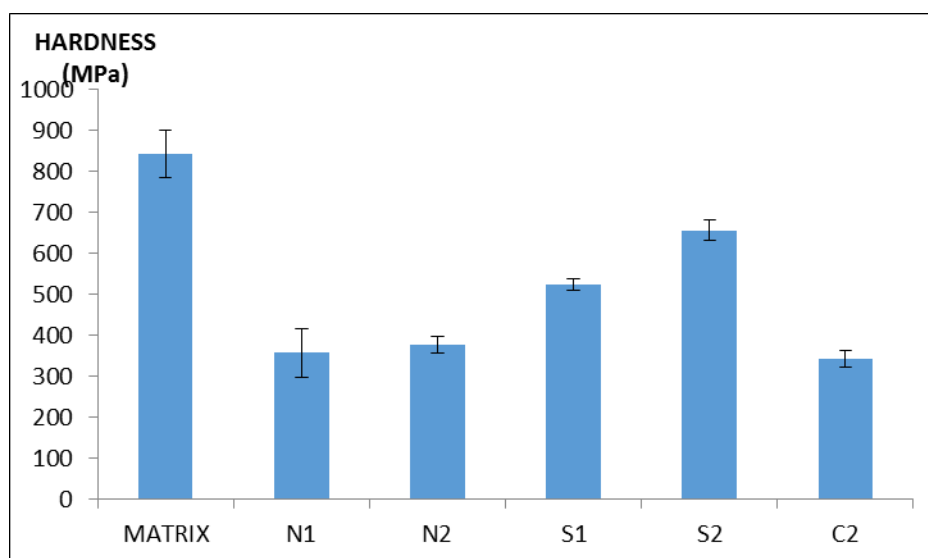


Figure 4.24: Comparison of hardness values obtained by Brinell test.

4.5.2 – INFLUENCE OF ROUGHNESS IN PIN-ON-PAD TEST

Before studying the tribological behaviour of monocomponent pads, the attention was focused on the influence of roughness in pin-on-pad test, due to the correlation of friction coefficient with the ratio R_aF/R_aI found for both steel and polymer matrix. Moreover, on the pad the evolution of roughness and friction coefficient was studied to investigate the tribological conditions needed to rise the friction steady state. Figure 4.25 shows the evolution of both roughness and friction coefficient of monocomponent pad N1. The standard test applied (R) was interrupted at increasing time intervals, in order to measure the surface roughness and obtain its evolution during test. Results show that roughness changes significantly in the first 60-70 minutes of test, during which friction coefficient decreases. After this run-in period, both roughness and friction reach a stable value, suggesting a correlation between the final surface topography and COF, as already supposed and observed for steel and polymer matrix.

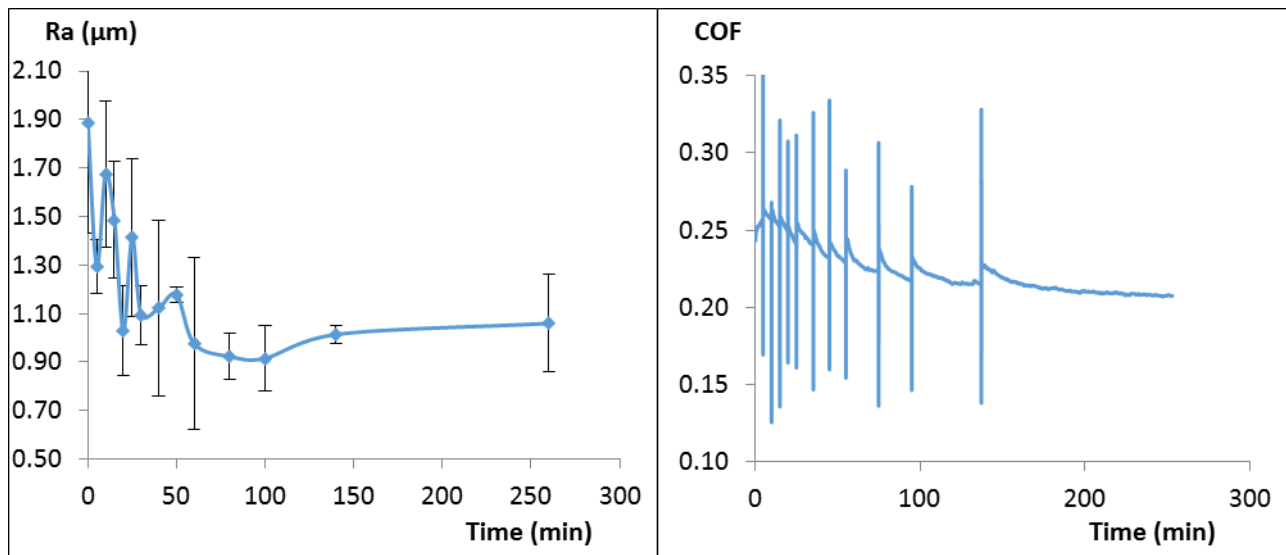


Figure 4.25: Evolution of roughness and friction in function of time during test R.

Following this experimental observation, other eight standard tests were applied on pad N1 in order to investigate the influence of roughness parameters (Table 4.13). As done for steel against steel and polymer matrix, both final and initial factors were considered. Moreover, the ratio R_aF/R_aI and the differences between final and initial value of each parameter were used to investigate the roughness influence. By Pearson coefficient, COF results linearly proportional to $R_{sk}F$ and ΔR_{sk} , that indicates an influence on friction of surface texture as found for steel, probably due to the variation of transfer layer¹⁵³. As further confirmation, $R_{ku}F$ is inversely proportional to friction and it shows an inverse linear proportionality with $R_{sk}F$ (Pearson coefficient = -0.94). Thus, friction can be described as a function of surface texture variation through skewness or kurtosis final parameter. Compared to the previous systems studied, there is no linear or significant proportionality between friction and R_a based parameters. This is probably due to a higher influence of the transfer layer formation, arising from the presence of graphite as filler that generates a stable tribofilm under compression. Furthermore, R_a affects friction indirectly, because it is directly correlated with $R_{sk}F$, then with respect the polymer matrix in carbon based pad the dominant mechanism is the formation of tribofilm at interface, which mainly depends on surface texture.

Table 4.13: Standard test on N1 pads and relative surface roughness parameters.

N1	COF	AMPL.	R _a I	R _{sk} I	R _{ku} I	R _a F	R _{sk} F	R _{ku} F	R _a F/R _a I	ΔR _a	ΔR _{sk}	ΔR _{ku}
A	0.190	0.001	0.95	-0.51	8.20	0.29	-2.01	12.18	0.30	-0.67	-1.50	3.98
B	0.209	0.009	0.55	-0.13	3.67	0.31	-1.10	7.02	0.56	-0.25	-0.98	3.35
C	0.217	0.007	0.47	-0.22	5.96	0.42	-1.87	11.68	0.89	-0.05	-1.65	5.72
D	0.231	0.006	0.92	-0.19	3.26	1.03	-0.71	5.68	1.12	0.11	-0.53	2.41
E	0.217	0.001	3.34	1.66	8.20	1.37	0.08	5.60	0.41	-1.97	-1.58	-2.60
F	0.252	0.004	1.90	-0.70	3.57	1.38	0.43	3.19	0.73	-0.52	1.13	-0.39
G	0.208	0.005	3.50	0.39	3.10	1.22	-0.83	9.16	0.35	-2.28	-1.22	6.06
H	0.229	0.002	1.86	0.08	3.71	1.15	0.00	3.92	0.62	-0.71	-0.09	0.20

To further verify the results obtained by Pearson coefficient, a PCA was applied (Table 4.13). Figure 4.26 shows the relative loading plot, in which all the previous considerations are confirmed. The friction coefficient variance coincides with ΔR_{sk} one and it is inversely proportional to R_{ku}F. The PCA highlights also the correlation of R_aF and R_{sk}F, which suggests a higher influence of surface texture with an important contribution from the final roughness. As shown in Figure 4.25, the final roughness does not change significantly after run-in period, which is the necessary condition to have a steady state friction coefficient; on the contrary, both R_{sk} and R_{ku} are subjected to a continuous change during test (Figure 4.27). This variation is probably correlated with the continuous formation of tribofilm at interface due to wear mechanisms occurring at interface.

Given the previous conclusions, three parameters were considered in order to obtain a formula of friction coefficient in function of roughness, in particular the ratio R_aF/R_aI and the variation of surface texture factors (ΔR_{sk} and ΔR_{ku}). From the PLS applied, two formulas were obtained:

$$4.8 - COF = 0.216 + 0.026 \frac{R_{aF}}{R_{aI}} + 0.011 \Delta R_{sk} - 0.002 \Delta R_{ku}$$

$$4.9 - COF = 0.215 + 0.024 \frac{R_{aF}}{R_{aI}} + 0.014 \Delta R_{sk}$$

The equation 4.8 highlights that the kurtosis evolution has the lowest influence on friction coefficient and considering its correlation with R_aF and R_{sk}F by the loading plot, it can be removed from the regression, obtaining equation 4.9.

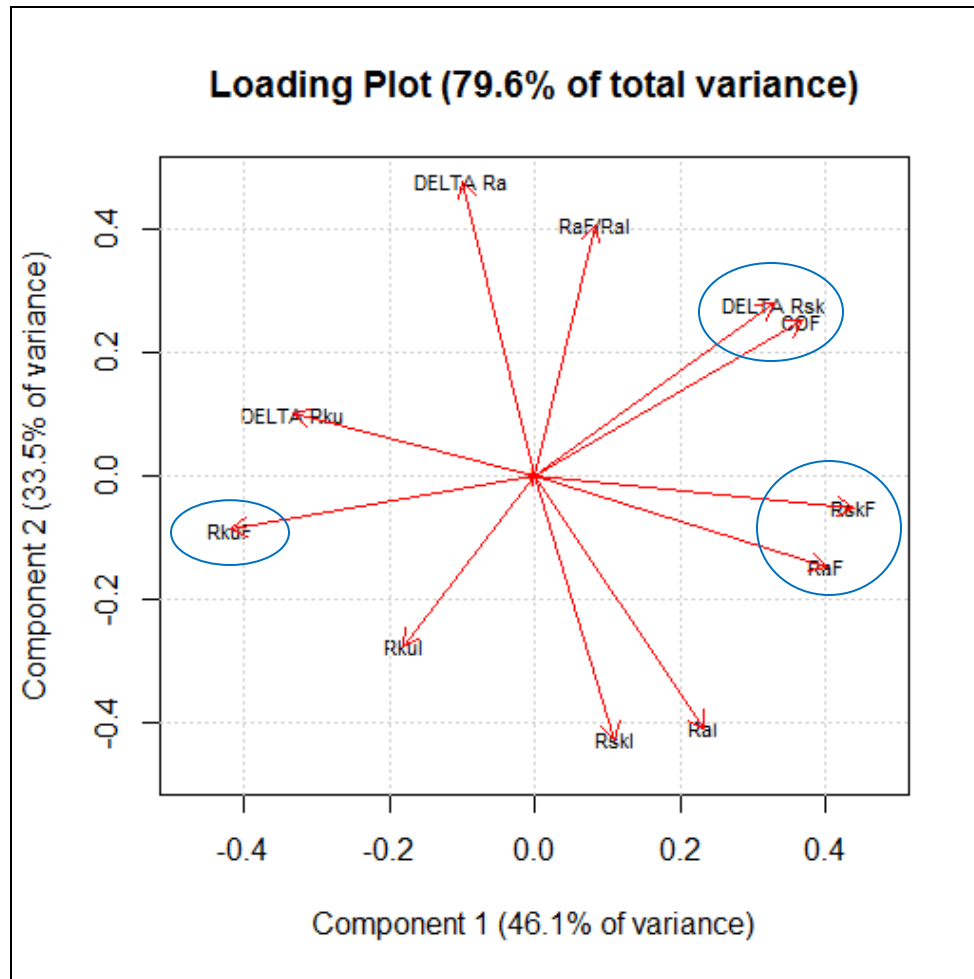


Figure 4.26: Loading plot of PCA on roughness data relative to pad N1.

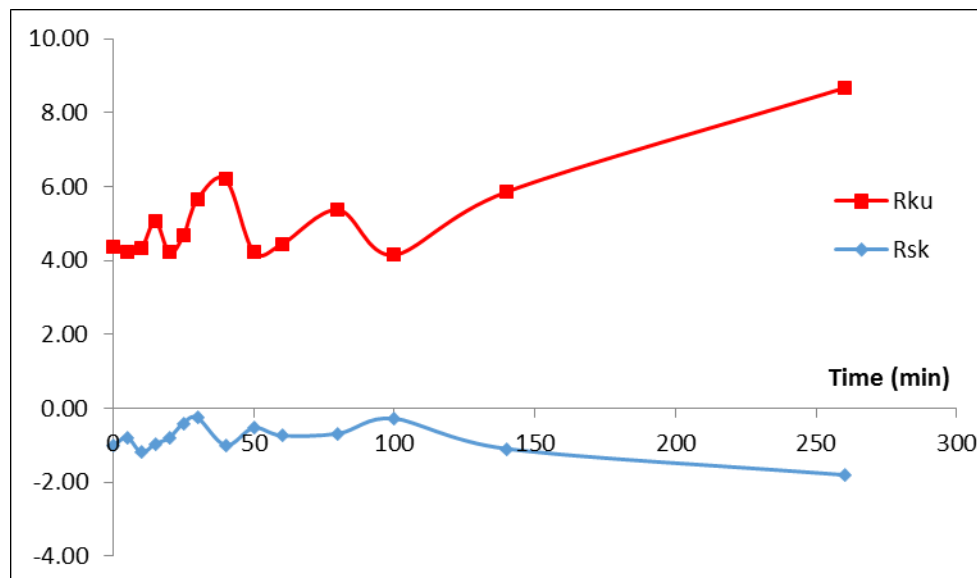


Figure 4.27: Variation of texture parameters in function of time during test R.

The difference with respect to the studies on influence of roughness for steel and polymer matrix derives from the wider range of roughness investigated for N1 pad. In fact, the starting roughness was studied in the range 0.5-3.5 μm , while the 0.5-1.5 μm range was used in previous investigations. Thus, the resulting correlations with surface texture as dominant factor in determining the friction value are true in this wider range, while for lower range the influence of R_a parameters is more evident. This conclusion can be verified considering just the first four test of Table 4.13, where the starting roughness is lower than 1 μm . In this condition, the friction coefficient is directly linear proportional to the ratio R_{aF}/R_{aI} (Figure 4.28). The trend observed is opposite respect the matrix one, which means that at equal starting roughness the friction coefficient increases linearly with final roughness, due to a lower real contact area. On the contrary, for a final roughness near zero, COF becomes approximatively equal to the powder friction coefficient (for N1 0.172), suggesting the formation at interface of a complete contact graphite-graphite with maximum real contact area.

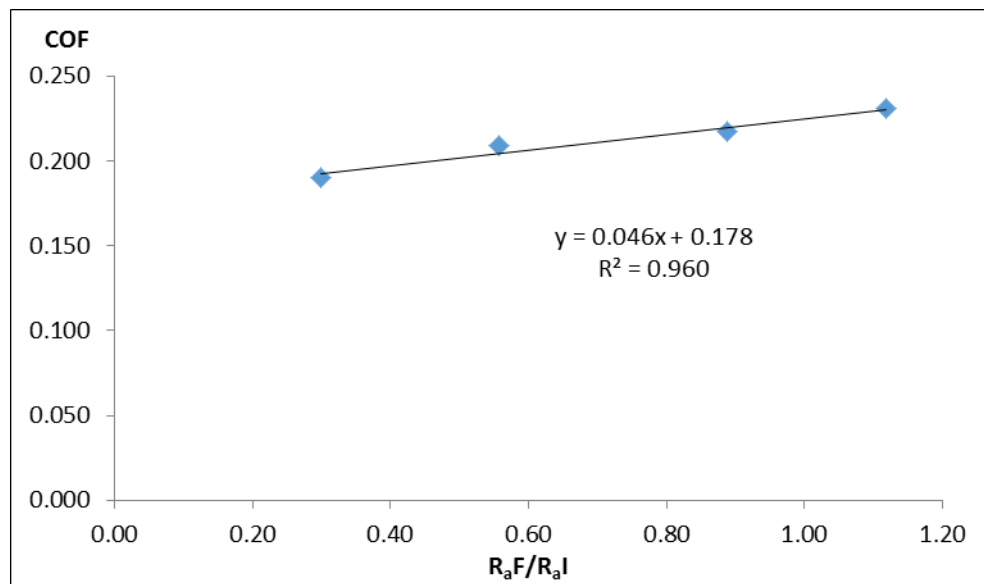


Figure 4.28: Friction coefficient in function of the ratio R_{aF}/R_{aI} for test with starting roughness under 1 μm .

This preliminary study demonstrates one more time that friction coefficient depends mainly on final roughness parameters. Considering the test with starting roughness under 1 μm , in a range of R_{aF}/R_{aI} 0.3-1.2 the friction coefficient varies between 0.190 and 0.231, with an average value of 0.212 and a standard deviation of 0.017, equivalent to ~8% of friction value. Thus, results suggest that for starting roughness under or around 1 μm , a standard deviation of ~0.02 can be associated with the experimental value.

On sample N2, other two standard tests were performed in order to verify the previous conclusion. The surface roughness of pads was modified to obtain a similar starting roughness and compare friction in function of the ratio R_{aF}/R_{aI} . Table 4.14 shows the results that confirm the linear proportionality of COF and R_{aF}/R_{aI} . Moreover, the standard deviation associated with COF values is 0.011, equal to ~4% of average COF value, which confirms that an error of 0.02 is an acceptable fluctuation to take in account for the friction coefficient obtained.

Table 4.14: Standard tests on sample N2 with similar starting roughness.

COF	AMPL.	R_{aI}	R_{aF}	R_{aF}/R_{aI}
0.246	0.009	0.78	0.29	0.37
0.261	0.003	0.77	0.33	0.43

For each test previously reported, also the wear was calculated as difference between initial and final mass and results show that the loss of mass is always ≤ 0.01 g without a particular correlation with the friction behaviour. Thus, in further analysis the wear relative to pin-on-pad test was not considered. Due to all the conclusions found in this section, further tests on carbon samples were performed with a starting roughness around or under $1\mu\text{m}$ and the resulting friction coefficient was compared considering 0.02 as the possible range of variation. For this reason, the friction coefficient of pads is expressed with only two significant decimal digits instead of three as for powders.

4.5.3 – INFLUENCE OF LOAD AND SPEED ON PIN-ON-PAD TEST

To study the influence of test conditions, other test at different load and speed were performed and then analysed together with standard test at starting roughness around or lower than $1\mu\text{m}$. As found before, in this range of starting roughness, the friction coefficient is directly proportional to the ratio R_{aF}/R_{aI} , while in general it is also directly proportional to the variation of R_{sk} . For these reasons, from Table 4.15 both the parameters aforementioned were calculated and analysed in a PCA. The principal component analysis explains all the system variance by seven components and by loading plot the friction coefficient results directly proportional to load, R_{sk} and R_{aF} . In order to simplify the system, all the single parameters of roughness can be removed and only their variation can be considered.

Table 4.15: Data matrix for the study of load and speed influence.

N1	COF	AMPL	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}	LOAD (N)	SPEED (ms^{-1})
A	0.190	0.001	0.95	-0.51	8.20	0.29	-2.01	7.31	10	0.20
B	0.209	0.009	0.55	-0.13	3.67	0.31	-1.10	7.02	10	0.20
C	0.217	0.007	0.47	-0.22	5.96	0.42	-1.87	11.68	10	0.20
D	0.231	0.006	0.92	-0.19	3.26	1.03	-0.71	5.68	10	0.20
I	0.263	0.012	0.98	1.72	6.55	0.54	-0.74	4.91	15	0.30
J	0.223	0.008	1.13	0.60	4.40	0.79	-0.83	3.31	15	0.10
K	0.237	0.005	0.93	-1.20	8.65	0.54	-1.43	7.59	5	0.10
L	0.273	0.005	1.04	-0.94	4.02	0.60	-0.99	7.08	5	0.30

After this step, the resulting loading plot (Figure 4.29) shows a direct correlation of friction coefficient with the ratio R_{aF}/R_{aI} , as previously found, and with the sliding speed. Instead, load results inversely proportional to the change in surface texture represented by R_{sk} . It seems that also changing the test conditions, the roughness ratio affects friction coefficient, while the influence of surface texture can be reduced to the only variation of R_{sk} , affected by the change of load. However, considering just the comparison between test J-K and I-L, which have same speed and different load, the COF slightly decreases at higher load.

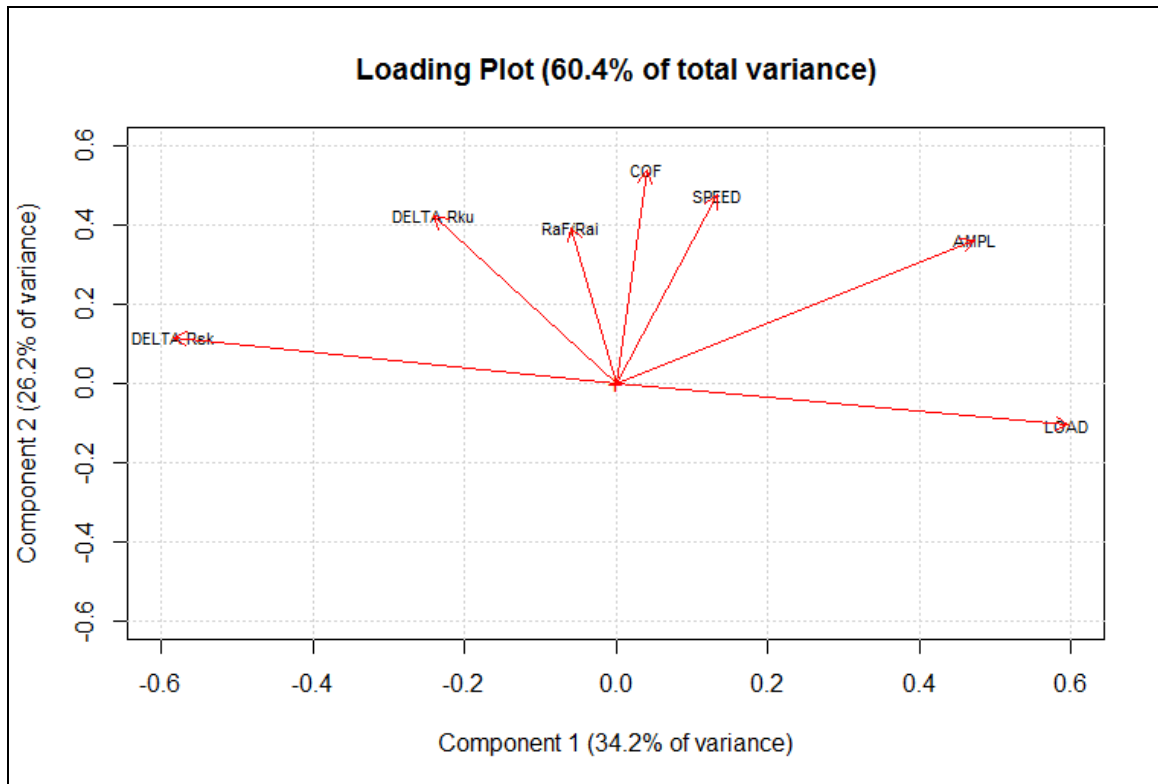


Figure 4.29: Loading plot of PCA on load and speed influence.

4.5.4 – COMPARISON OF PIN-ON-PAD TESTS

Based on previous results, the standard test was applied on all samples modifying the initial roughness in order to start with $R_a \leq 1\mu\text{m}$. Figure 4.30 shows the comparison of results among samples and with the theoretical value of friction relative to sample N1 at the same roughness conditions. This value was calculated using the formula $COF = 0.046 \frac{R_a F}{R_a I} + 0.178$ reported in Figure 4.28.

All samples have higher friction than N1, then natural graphite N1 results the solid lubricant with the highest effect as filler in the polymer matrix. Note that this consideration can be considered true only in the range of conditions in which tests were performed (room temperature, load, speed, etc...).

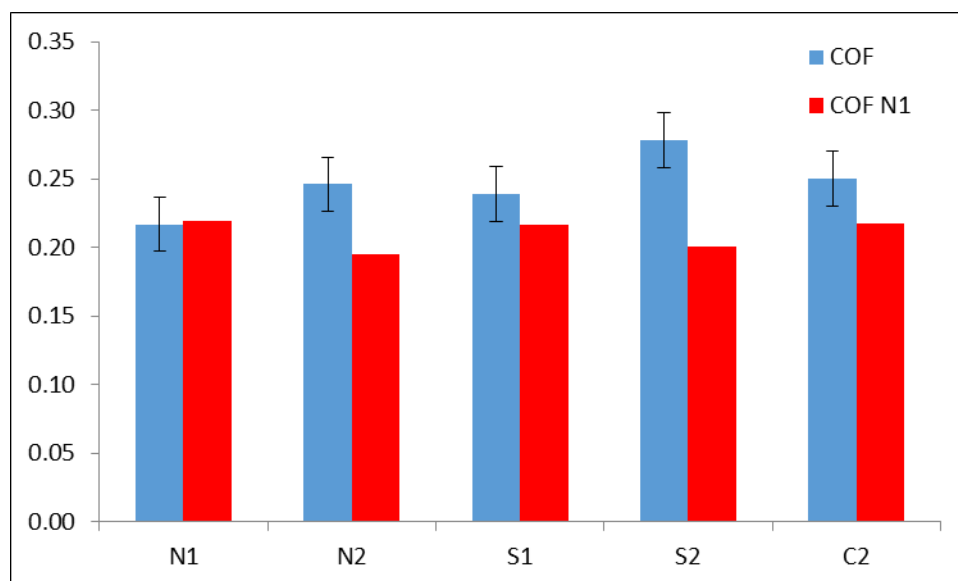


Figure 4.30: Comparison of friction coefficient for carbon based pads.

To better understand the correlation between material properties and its tribological behaviour, the Pearson coefficient was calculated considering all the structural and morphological parameters found by chemico-physical characterization of powders and pads. This technique highlights three significant correlations of friction coefficient, respectively with the peak (002) intensity (Pearson coefficient 0.92) and the full width at half maximum of bands 2D₁ and 2D₂ (Pearson coefficient 0.93 and 0.89 respectively). No proportionality was found with macroscopic properties as pad density or hardness, but the width of bands 2D directly affects the composite hardness, and then it can be considered as correlated with friction. Moreover, morphological features result negligible respect friction, probably due to their incorporation in the 3D structure of phenolic resin and Kevlar fibres, while in pin-on-disc test their morphology affects friction as a consequence of the rolling movements of particles at interface.

To disentangle the complexity of structural influence on pad friction, it is necessary to analyse the physical meaning of each correlation. Considering the peak (002) intensity, this parameter is affected by the crystallite dimension as dominant factor and by the amount of disorder. In fact, it shows a direct linear correlation with the FWHM 2D₁ and 2D₂, which are representative of the stacking order. Thus, the contemporary correlation of COF with these three structural features highlights the influence of the carbon stacking order not only on powder friction, but also on the tribological behaviour of carbon based composites.

4.5.5 – INFLUENCE OF ROUGHNESS ON BALL-ON-PAD TEST

A ball-on-pad test was performed for each sample in order to measure its wear resistance. The tribological conditions set up were the same as for pin-on-pad, in order to compare the friction behaviour in function of the different instrumental configuration. However, based on previous studies on the effect of roughness and due to the lack in literature, to the author best knowledge, of a study on influence of roughness in ball-on-pad test, some experiments were performed on sample N2 (Table 4.16). The sliding distance was set up at two values in order to verify that K is independent from the sliding distance and to observe if the correlations with friction and roughness are the same. Two different wear constant were calculated, based on the formula usually used in literature and the original Archard's equation^{16,17,106}, as described in chapter *Materials and Methods*.

By Pearson coefficient, friction and wear constant are not correlated and show different proportionality with the parameters reported in Table 4.16. Considering the friction coefficient, it results inversely proportional to the max depth of wear track and to the wear volume (Pearson coefficient -0.91 and -0.88 respectively). Thus, the friction behaviour is strongly correlated to the amount of debris generated at interface. Moreover, it results also directly proportional to R_{kuI} (Pearson coefficient 0.87) probably due to the ploughing mechanism at interface. The wear constant, conversely, does not depend by surface texture, but by the starting roughness with a linear proportionality (Pearson coefficient 0.97). Results suggest that a more regular profile with low R_a should have a higher wear resistance respect an irregular surface, probably due to a different dominant mechanism of wear. In fact, it can be supposed that for low R_a the wear mechanism is mainly composed by adhesion and fracture, consequently the removed volume is low. On the contrary, for high R_a the abrasion phenomena become dominant respect adhesion and the consequent fracture causes a high wear volume.

Considering all the data obtained, in the range 0.6-5.6 μm of starting roughness, the wear constant K shows an average value of $3.75 \cdot 10^{-4} \text{ mm}^3/\text{Nm}$ with a standard deviation of $2.63 \cdot 10^{-4} \text{ mm}^3/\text{Nm}$. Thus, it is impossible to consider this average value as enough objectives to be compared with the wear of other carbon based composite. Due to the previous restriction for pin-on-pad of roughness influence in a range with an upper limit around 1 μm , the three tests with a similar starting roughness were considered to calculate an average value of K and the relative standard deviation in order to use it as error for the wear comparison among the carbon system. For the aforementioned tests, the average value is equal to $1.84 \cdot 10^{-4} \text{ mm}^3/\text{Nm}$, with a standard deviation of $3.25 \cdot 10^{-5} \text{ mm}^3/\text{Nm}$, equivalent to about 18% of the average wear constant. Thus, this parameter has a higher dispersion with respect to the pin-on-pad friction coefficient and especially respect the relative COF obtained by wear test. The average value of data in Table 4.16 is equal to 0.197 with a standard deviation of 0.006, corresponding to an uncertainty of around 3%. Thus, in order to compare all the carbon based composite in terms of wear behaviour, the starting surface roughness was reduced at value $\leq 1 \mu\text{m}$ and all the other test conditions were kept constant.

Table 4.16: Data on wear test of samples of carbon composite with natural graphite N2.

COF	MAX DEPTH (μm)	VOLUME (mm^3)	DISTANCE (m)	K ($10^{-4} \text{ mm}^3/\text{Nm}$)	K' (10^{-4})	R_aI	R_{skI}	R_{kuI}
0.197	155.28	6.49	3000	2.16	0.77	1.22	-0.79	5.84
0.195	137.37	5.51	3000	1.84	0.66	0.64	0.04	3.27
0.192	262.64	14.3	3000	4.77	1.71	2.11	0.11	4.43
0.206	76.5	2.27	1500	1.51	0.54	0.80	-0.05	7.41
0.189	255.35	12.7	1500	8.47	3.03	5.66	-0.83	3.75
0.200	141.12	5.6	1500	3.73	1.34	2.75	-1.46	6.56

4.5.6 – COMPARISON OF BALL-ON-PAD TESTS

Table 4.17 shows the data of wear test of all samples performed at 10 N and 0.20 ms^{-1} with a sliding distance of 3000 m. All samples show a lower friction coefficient with respect to the polymer matrix, while the wear constant has a wide dispersion and can be lower or higher than matrix one. Note that K and K' of carbon based composite show the same trend in which the S2 sample shows the higher wear resistance, but their comparison with the matrix is different. In particular, considering K , the samples S2 and C2 generate a lower wear volume at same load and sliding distance with respect to matrix, while all the others loose a higher amount of material. Instead, K' shows that also sample N1 has a higher wear resistance than matrix, probably due to its lower hardness and supposing abrasion as the

main wear mechanism. Considering the previous study of roughness influence, all the carbon based composite were tested in a supposed condition of wear due to adhesion and fracture. An experimental observation that supports this mechanism is the inverse correlation between the friction coefficient of pads and the density of carbon fillers (Pearson coefficient -0.88). This result suggests that at interface the generated debris, mainly constituted by carbon filler, dominates the friction behaviour and then the resulting friction coefficient has the same correlation previously found on powders analysis.

Furthermore, considering just the graphite based composite, also solidity results inversely proportional to friction coefficient (Pearson coefficient -0.97) which means that friction is higher if particles have an irregular shape, probably due to a different influence on the formation of stable tribofilm at interface.

Figure 4.30 reports the comparison of K' values with the theoretical standard deviation equal to 18% of K' calculated value. This wear constant is linearly proportional to the other one, and then all the possible correlations are true for both. Considering all the data obtained, both wear and chemico-physical characterization of powders and pads, no one of the factor investigated results proportional to K or K' . Instead, removing the graphitized coke C2 from this matrix, the wear constants result inversely proportional to the full width at half maximum of Raman band D and directly proportional to band G position. These two linear correlations suggest an influence of composite resistance to the in-plane disorder of carbon fillers, because FWHM D represents the amount of in-plane defects¹³⁷ and the band G position is inversely proportional to sp^3 fraction¹⁴⁵. From a chemico-physical point of view, these correlations highlight that the presence of heteroatoms, grain boundaries, vacancies or sp^3 bond allow the formation of a bulk structure more resistant to wear with respect to graphite with a high degree of organization. All defects represent active points of interaction among phenolic resin, Kevlar fibres, and graphite particles, which increase the wear resistance of composite. Note that this kind of correlation becomes evident just comparing graphite samples, which mainly differ from the graphitized coke in density. To observe the influence of structural in-plane disorder on the wear resistance derived from bulk network, samples with similar density must be compared.

Table 4.17: Data on wear test of all carbon based composites.

SAMPLE	COF	MAX DEPTH (μm)	VOLUME (mm^3)	H (MPa)	K ($10^{-5} \text{ mm}^3/\text{Nm}$)	K' (10^{-5})
MATRIX	0.337	23.69	0.38	844	1.27	1.07
N1	0.211	35.77	0.50	378	1.65	0.62
N2	0.195	137.37	5.51	358	18.37	6.58
S1	0.216	65.69	1.76	525	5.87	3.08
S2	0.226	12.23	0.15	657	0.51	0.34
C2	0.254	8.4	0.11	343	0.38	0.13

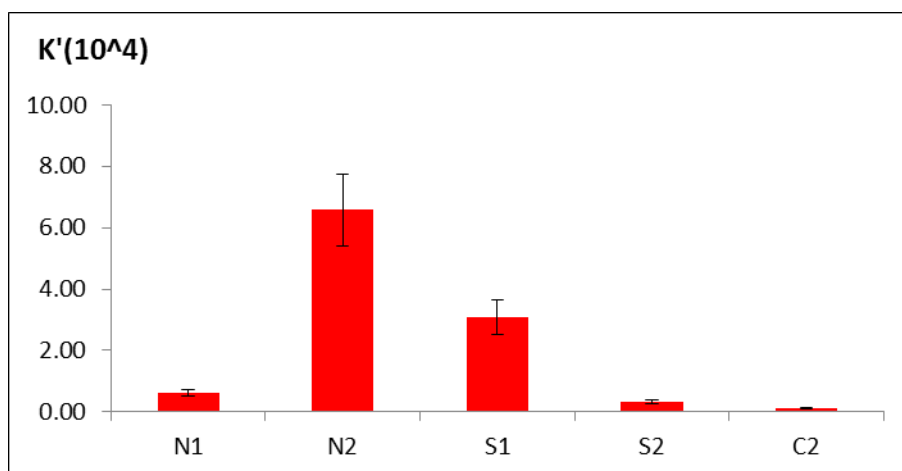


Figure 4.31: Comparison of K' obtained for carbon based composites with relative error of ~18%.

4.6 – TRIBOLOGY OF INDUSTRIAL BRAKE PADS

The tribological characterization of industrial brake pads was made at VSB – University of Ostrava, using a Link full-scale brake dynamometer and applying the test ISO 26867, as reported in chapter *Materials and Methods*.

Five prototypes of non-asbestos organic (NAO) brake pads were designed with the general formulation containing organic fibres, resin, fillers, abrasives and lubricants. The samples were kindly provided by ITT friction technologies industry. As done for monocomponent carbon based composite, also for the prototype brake pads one single carbon material was introduced in the formulation at 6%vol, while all the other components are the same as content and type.

The exact composition of the pad is omitted for confidentiality reasons. Such omission does not affect at all the aim of obtaining a comparison of carbon effect in a complete brake pad, since the overall composition, except the carbon, can be considered as a material constant.

On each formulation, as routine industrial test, the compressibility was measured and expressed as percentage of pad compression, considering the minimum, maximum and average value, reported in Table 4.18. All the formulations concerning graphite filler show similar compressibility, while the graphitized coke C2 shows a higher compressibility. Thus, the resulting 3D network of pad C2 is the softest and this difference is comparable with the different density of graphite (around 2.26 g/cm³) and graphitized coke (1.70 g/cm³).

Table 4.18: Compressibility of pads expressed in percentage.

SAMPLE	CMPX RT (%)		
	MIN	MED	MAX
N1	0.68	0.71	0.73
N2	0.71	0.75	0.79
S1	0.74	0.81	0.85
S2	0.71	0.74	0.76
C2	1.43	1.51	1.54

4.6.1 – WEAR OF BRAKE PADS

As reported in chapter *Materials and Methods*, the wear of pad and rotor was measured for each test. For the three different kind of wear measurement, the number of significant digits depends on the instrumentation used for the measure. The debris wear indicated as dish represents the particles collected in the environmental chamber after test under the brake system, while the filter wear is relative to the debris collected as airborne dust.

Table 4.19: Wear data obtained from dynamometer tests.

SAMPLE	PAD MASS WEAR (g)			PAD THICKNESS WEAR (mm)			DEBRIS WEAR	
	IN	OUT	ROTOR	IN	OUT	ROTOR	DISH (g)	FILTER (mg)
N1	11.8	11.1	1.8	1.057	0.787	0.009	1.15198	3.07
N2	11.0	10.4	4.4	0.790	0.742	0.006	0.90887	2.32
S1	9.3	10.0	0.8	0.625	0.548	0.002	0.70347	2.33
S2	12.9	11.5	4.3	0.964	0.871	0.007	0.97712	0.46
C2	8.5	10.2	1.0	0.482	0.707	0.004	1.03543	0.17

In the previous data matrix, the pad loss of mass is linearly proportional to the difference in thickness for both in and out pads, while for rotor this correlation is not verified. This is probably due to possible localized abrasion and fracture of disc, and then the average thickness does not reflect this wear. No one of the factors investigated results proportional to the amount of airborne dust, that derives not only from mechanical mechanism, but also from chemical reaction at interface producing micro and nanoparticles. Instead, the non-airborne dust amount is proportional to the thickness reduction of rotor and both in and out pads for the samples containing graphite, not for the one with the graphitized coke. At the same time, the amount of non-airborne dust for graphite pads is inversely proportional to pad compressibility. Higher the percentage of thickness reduction under compression, lower the amount of debris generated, probably due to a lower contribution of abrasive wear at interface and a higher one of ploughing friction.

4.6.2 – COMPARISON OF AVERAGE FRICTION BEHAVIOUR

Considering the entire test, with all sections, an average friction value can be obtained from its cumulative frequency respect each brake done. Figure 4.32 shows the friction distribution for all the sections and for brakes at low speed and low pressure relative to sample N1. Table 4.20 shows that all samples have a similar average friction for both cases, then as generic assumption, it can be concluded that the selected carbon materials do not affect significantly the friction distribution among dynamometer test. Thus, a general correlation of pad and material properties cannot be obtained considering the overall sections.

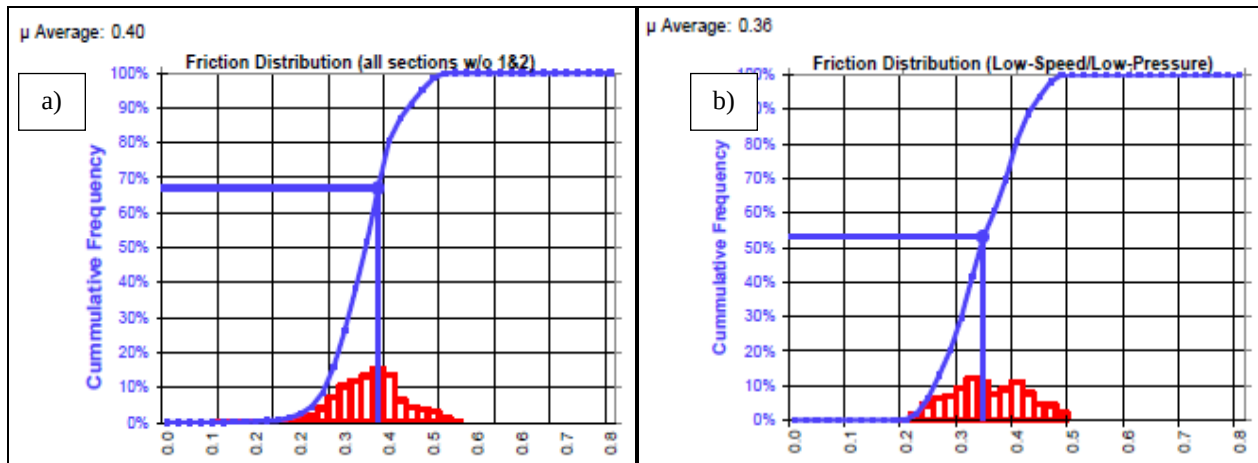


Figure 4.32: Friction distribution for dynamometer test on N1 relative to: a) all sections; b) low speed and low pressure sections.

Table 4.20: Average value of friction for all sections and low speed-pressure sections.

SAMPLE	Average COF (all sections)	Average COF (low speed-pressure)
N1	0.40	0.36
N2	0.39	0.35
S1	0.39	0.35
S2	0.38	0.35
C2	0.39	0.34

Figure 4.33 shows the friction coefficient evolution through the entire test sections, where it can be observed a general decrease of COF along the test. Respect the optimal range of friction variation, which is 0.4-0.5 for a real brake pad, all the samples show a lower friction in several sections, then they cannot be considered as optimal formulations. This is generally well known in the field of pad formulation, where a combination of carbon materials is used to obtain a better performance. From Figure 4.33, as first observation, the graphitized coke C2 shows a different behaviour mainly in the central sections, but in the others, it shows a similar COF as graphite samples. All samples show a decrease of friction in correspondence to fade sections, in which the temperature reaches values higher than 600°C. The lower COF can derive from burning process at interface with a consequent formation of carbon layers or a high amount of debris with a consequent lubrication effect.

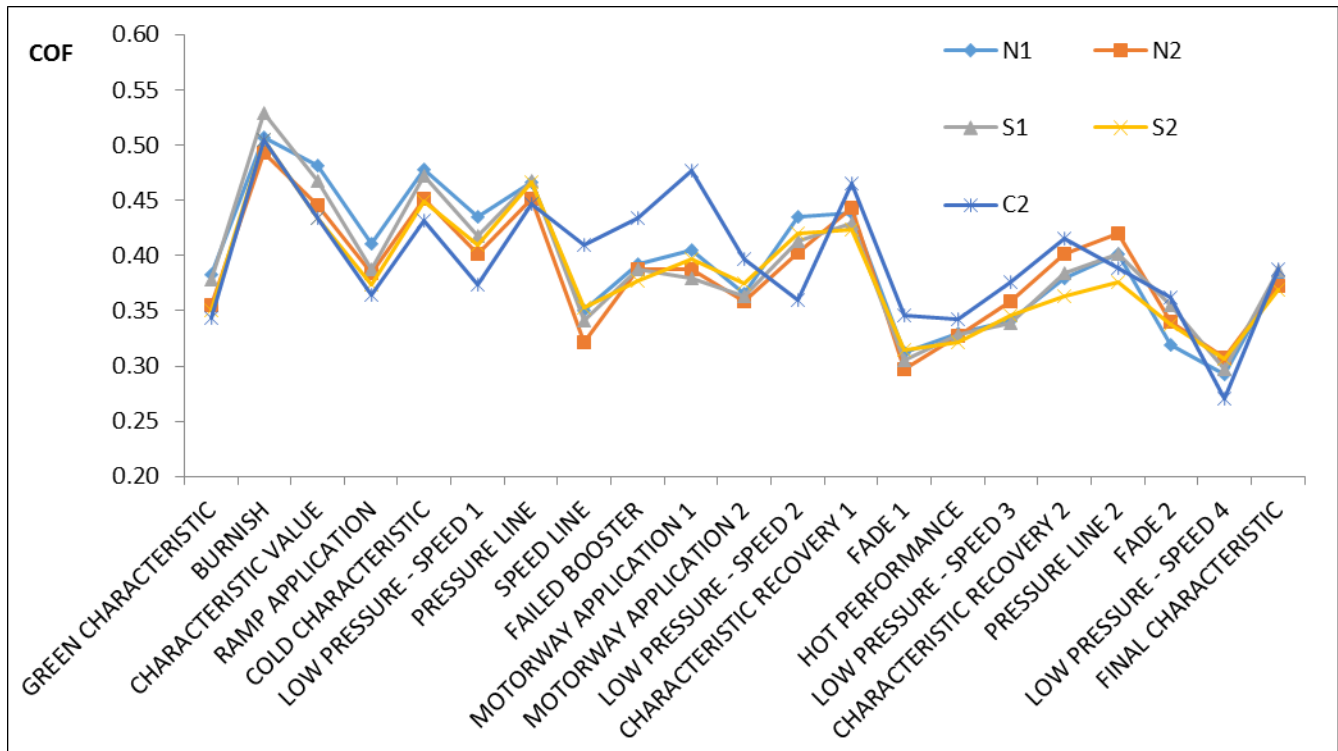


Figure 4.33: Friction coefficient evolution among test sections.

For all the sections in which each brake was done at same test conditions, only the data of last brake are considered, while for sections in which one or more test condition changes all the data are considered together in order to verify the influence of conditions on friction coefficient. A more detailed investigation is reported in next paragraphs.

4.6.3 – LOW SPEED AND LOW PRESSURE SECTIONS

The low speed and low pressure section (LPS) is repeated among test four times, in which three test at 20 Km/h and three at 30 Km/h are done changing the pressure at 10, 20 and 30 bar. Comparing the different friction obtained, it can be observed that in the first two LPS sections the friction linearly increases with the applied pressure. In the other two LPS parts, the COF results independent from pressure, due probably to a stable layer on pad surfaces derived from the fade sections, in which the temperature reaches values higher than 500°C. Thus all the phenomena previously occurred at interface generate a new surface that is not affected by pressure at the conditions of LPS.

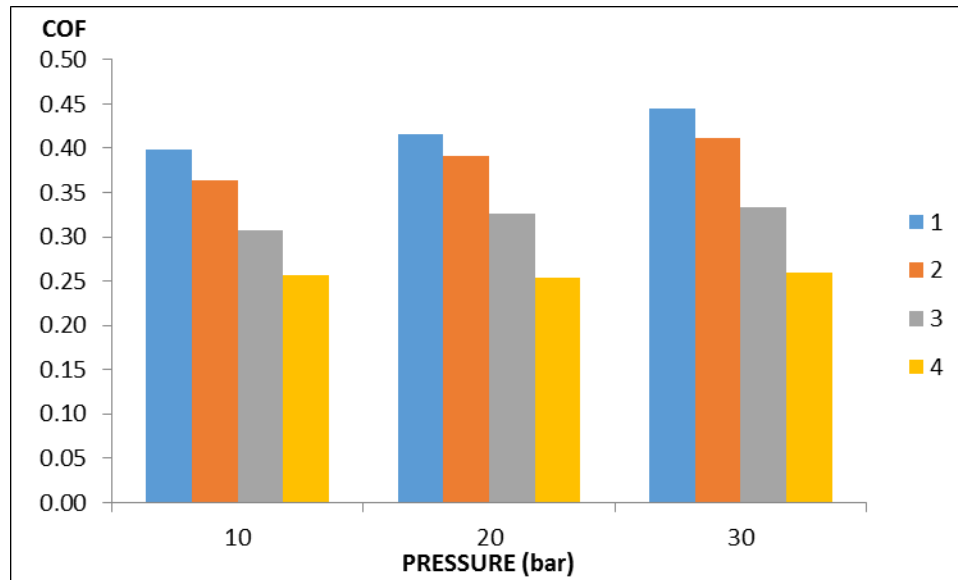


Figure 4.34: Comparison of friction coefficient for LPS sections at 20 Km/h relative to pad N1.

Thus, the average value of the last LPS section can be considered as the result of the stable interface layer generated among the test and observed possible influences of carbon fillers on it. Table 4.21 shows the comparison of final friction value at both sliding speed of 20 and 30 Km/h.

In order to investigate the possible correlations among the friction behaviour of brake pads and the material properties of carbon powders or carbon based composites, the obtained friction coefficient was compared with the data of chemico-physical characterization of powders and monocomponent composites.

At 20 Km/h in the range 10-30 bar, the COF results inversely proportional to the particle size of carbon (Pearson coefficient -0.95) and directly proportional to particle roundness and composite hardness (Pearson coefficient 0.89 for both the correlations). The influence of size is probably correlated with a higher contact at interface for bigger particles, because also if there could be a higher number of little particles at interface the contact with bigger particles allow the disruption of a higher portion of carbon planes and the formation of a more stable tribofilm. The effect of roundness can be associated to the formation of tribofilm as consequence of debris compression. Probably, the carbon particles at interface as debris are compressed to generate tribofilm and it is easier to constrict an irregular particle rather than a spherical one. The influence of hardness is correlated to the roundness influence, because a harder structure generates a lower amount of debris and consequently less tribofilm with an increase in friction coefficient, regardless of particles shape.

At 30 Km/h the tribological phenomena are slightly different from the previous case. All the COF values are higher, which suggests a direct proportionality of speed, as previously found for monocomponent composites. However, respect the previous correlations, in this case only the direct proportionality with roundness is significant. Thus, particles with a spherical shape decrease the formation of a stable tribofilm as previously supposed. In this second case, the friction coefficient results inversely proportional to the pad compressibility, which is inversely affected by the powder and monocomponent pad density.

Table 4.21: Average friction values and relative standard deviation for last LPS section.

SAMPLE	20 Km/h		30 Km/h	
	COF	DEV.ST	COF	DEV.ST
N1	0.257	0.003	0.290	0.003

N2	0.264	0.016	0.297	0.010
S1	0.269	0.006	0.295	0.002
S2	0.273	0.005	0.305	0.002
C2	0.255	0.005	0.274	0.007

4.6.4 – COMPARISON OF FRICTION AND MATERIAL PROPERTIES

Through statistical investigation, it was highlighted that in the first six sections, from the green characteristic to the first low pressure and speed part, no one of the material and pad properties affects the tribological behaviour. Thus, the low differences among samples have not explanation by chemico-physical point of view. Probably there are factors not considered in this thesis, which allow explaining the different behaviour, but from the obtained data, it can be supposed that this first part of the entire test is mainly dominated by the formation at interface of a stable layer and by the change in the surface topography.

This hypothesis is further supported by the correlations found in next sections. In fact, from the pressure line to the final characteristic, the majority of sections show a direct and linear proportionality between friction coefficient and the pad compressibility. This trend is interrupted in the sections characteristic recovery 1 and 2, fade 2 and final characteristic. From this point of view and observing the friction evolution along the test, it can be supposed that after the first pressure line at interface there is a stable and homogeneous tribofilm that allows the decrease of friction for the speed line. In the following sections, this tribofilm is subjected to different conditions that cause its partial wear with a consequent increase in the general friction coefficient. In the characteristic recovery section, the tribofilm probably has a lower thickness and homogeneity with a consequent higher friction, while in the fade section due to the high temperature reached and the consequent burning process at interface the new layer generated decreases again the friction. At the same time, the value of COF results linearly proportional to the compressibility, then this evidence can be associated with a better contact between pad and disc, besides the tribofilm obtained.

From the aforementioned correlations, it can be concluded that on the general performance of the entire pad, the difference among the carbon materials selected is negligible. However, in several sections the friction coefficient depends linearly by the pad compressibility, which in turn depends by the carbon powder density and morphology. Thus, the slight differences among the carbon based brake pads analysed derive mainly by the carbon powder density and the particle morphology.

4.7 – CONCLUSION

A system of several carbon materials of different nature was investigated by chemico-physical and tribological characterization.

The friction behaviour of carbon powders mainly depends on density, morphology and the degree of organization, considering both in-plane and out-of-plane defects. When all these variables are similar, then the direct effect of particle size on COF can be observed and at the same time, the friction is mainly dominated by the stacking order of carbon structure. Consequently, higher the amount of aromatic planes overlapped, lower the friction coefficient obtained due to a thicker and more homogeneous tribofilm at interface.

When the carbon materials are incorporated in a polymer matrix, they affect the pad density through their morphology and the hardness with their stacking order, due to a different interaction between carbon particles and the polymer matrix. This feature is responsible also for the friction behaviour, where the degree of organization on c axis direction affects directly the formation of a stable tribofilm

at interface, with a consequent decrease of COF. Thus, in general the friction behaviour of a carbon material, as powder or incorporated in a polymer matrix, depends on the stacking order on c axis direction.

In the case of real brake pads, the difference among carbon materials is negligible considering the overall performance, but in several conditions, it can be observed a different COF based on the pad compressibility. Thus, due to the correlation of compressibility with the powder density and particle morphology, it can be affirmed that a carbon material with elongated particles and low density increases the compressibility of pad with a consequent increase in the friction coefficient.

Considering the wear behaviour of monocomponent pads, the wear constant is affected by the degree of organization because a higher amount of defects allows a better interaction between filler and matrix forming a stronger 3D structure. Thus, the wear resistance is directly proportional to the amount of defects in the carbon structure. Instead, the friction behaviour is inversely proportional to the powder density, which is also correlated with the compressibility of real pads as previously cited.

Note that also the amount of non-airborne dust is inversely correlated with the compressibility. Thus, it can be concluded that a brake pad with higher compressibility generates less non-airborne dust, which is a desirable property, but at the same time the friction coefficient would be higher.

CHAPTER 5 – TITANATES

5.1 – INTRODUCTION

Alkali-metal titanates $A_2Ti_nO_{2n+1}$ ($n = 3-8$) are used as photocatalysts, electrolytes in fuel cell and as cation exchanger⁵⁰⁻⁵³. Based on the reactants and the preparation method, they have different chemical and physical properties⁵⁴. Several different methods are used to synthesize titanates, including calcinations, flux growth, melt reaction and slow cooling calcinations^{52,55,56}. Usually, as raw materials for the synthesis, titanium oxide and alkaline carbonate are used. Due to the several methods of synthesis and the wide range of applications, titanates are used in a wide range of morphologies, from the more common whisker shape to the nanowires^{55,154,155}, nanorods^{52,156,157} and nanoribbons¹⁵⁸.

Titanates can be divided in two categories: high alkali metal content and low alkali-metal content. The first category ($n = 3-4$) results in a structure formed by $(Ti_3O_7)^{2-}$ layers held together by alkali-metal ions, which is a preferential feature in order to use it as cation exchangers and catalysts. In the second category ($n = 6,7,8$), the structure shows a tunnel shape and exhibits high insulating ability and chemical stability⁵⁷. In both the kind of titanates, the structure is monoclinic with almost the same b value.

Among these materials, potassium hexatitanate $K_2Ti_6O_{13}$ is a good candidate for whisker-reinforced metals and plastics. It has been proved to be a suitable substitute for asbestos, years before their phasing out⁵⁸, and it has the advantage of lower cost with respect to other ceramic whiskers. Furthermore, in the last 30 years, several patents have been deposited on the use of non-whisker-like titanates in the brake pads formulation, in order to prevent the generation of micro or nanofibers during brake. The addition of potassium hexatitanate in composite formulation showed an increase in thermal and wear resistance, suggesting also its potential as additive in brake pad formulations⁵⁹⁻⁶¹. Moreover, it shows two opposite effect in friction composite because it acts as abrasive for the counterface and as solid lubricant, due to a reduction of the overall friction coefficient.

The focus of this chapter is to correlate tribological behaviour with material properties, studying potassium hexatitanate samples with different shape and size, comparing in particular a whisker-like sample with others not in form of fibres. All of them are commercially available, used or under testing for brake pad formulation. In next section, their physico-chemical characterization is described and compared with tribological results, using the OVAT and multivariate analysis.

5.2 – MORPHOLOGY OF RAW MATERIALS

Nine samples were selected for this study, in particular one of them has a whisker-like shape and is used as reference, due to the necessity of replace it with a hexatitanate with different shape but similar or better tribological properties.

Figure 5.1 shows the scanning electron microscope image of the sample T1, which has a whisker-like shape. This kind of titanate has a high aspect ratio and particle size, but the correct size of fibres is difficult to be defined by SEM analysis, due to their aggregation and overlapping. Thus, the industrial partner performed a granulometric analysis in order to analyse the particle size distribution, reported in Table 5.1 as average diameter of different percentage sections.

Table 5.1: Morphological parameters of natural graphite samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S	D10% (μm)	D50% (μm)	D90% (μm)
T1	1513.51	203.99	91.48	5.33	0.23	0.41	0.82	5.29	19.12	48.98

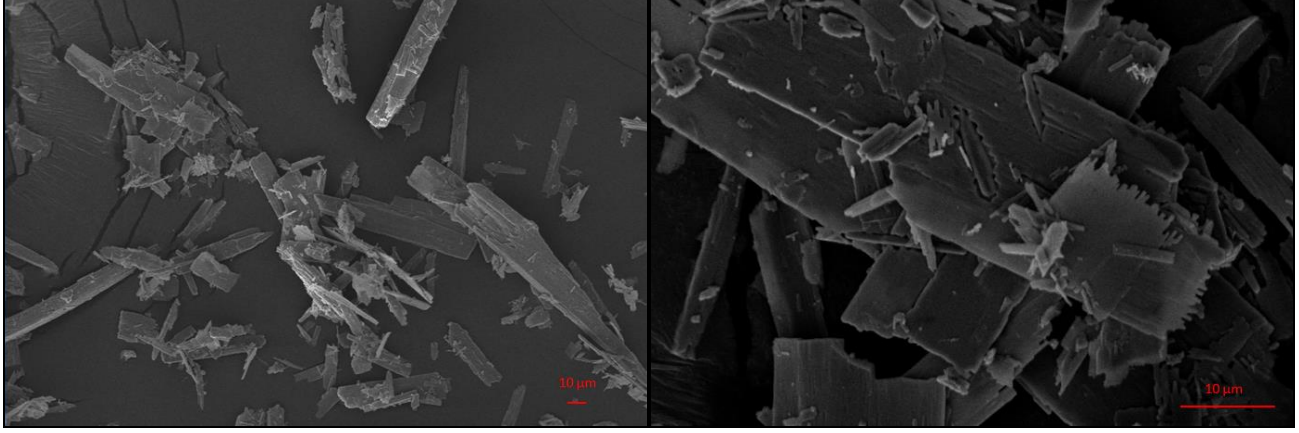


Figure 5.1: Scanning electron microscope images of whisker-like sample T1 at different magnification.

For the aforementioned reason, other eight potassium hexatitanate were selected with a non-whisker-like shape (Figure 5.1 a-h). The parameters obtained by morphological and granulometric analysis are reported in Table 5.2.

Figure 5.1 a-d shows four samples with a gravel shape, slightly irregular, where sample T4 has the less wide size distribution, as shown by granulometric results. The average particle size measured by Feret's diameter is similar to the D50% value or slightly higher for samples T2-T5.

Sample T6 (Figure 5.2 e) has a rod-like shape, which generates aggregates that causes a wider size distribution. The resulting Feret's diameter is in agreement with granulometric results, in which the sample is subjected to a previous ultrasonic bath in order to separate the aggregated particles. The granulometric results suggest that particles are not strongly bonded in the aggregates, because the average size is quite lower than the aggregates dimension. Sample T7 (Figure 5.2 f) shows spherical-like particles not aggregated and with the sharpest particle size distribution. Instead, sample T8 (Figure 5.2 g) shows spherical-like particles strongly aggregated together, as attested by the granulometric results in which the D50% is noticeably different by the average size obtained as Feret's diameter, suggesting that the ultrasonic bath applied before the granulometric test was not able to completely separate the aggregated particles. The last sample, T9 (Figure 5.2 h), has a plate-like shape and a low average particle size, and it has a lower aspect ratio and higher roundness, similar to samples T7 and T8.

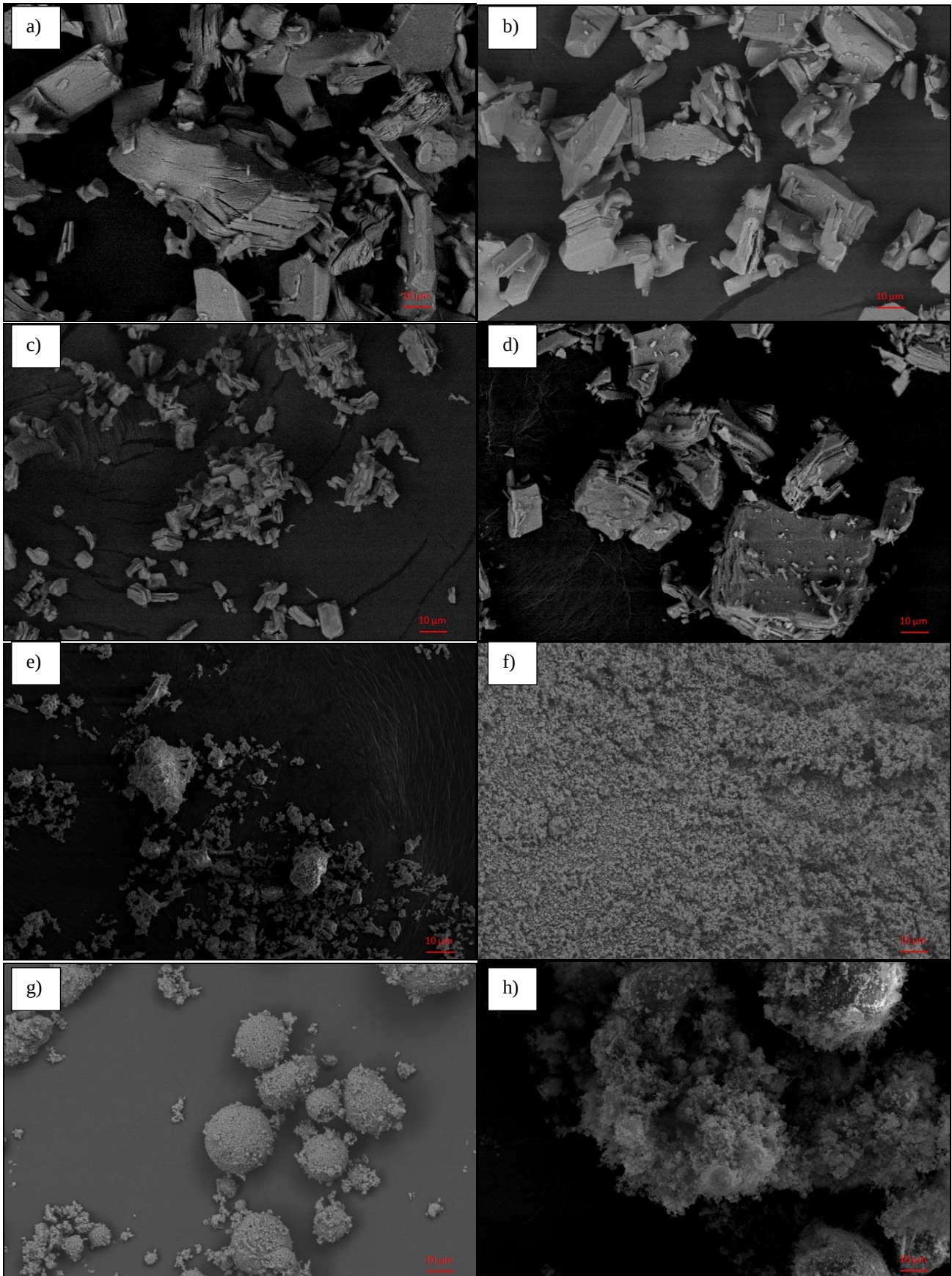


Figure 5.2: Scanning electron microscope images of potassium hexatitanate samples: a) T2; b) T3; c) T4; d) T5; e) T6; f) T7; g) T8; h) T9.

Table 5.2: Morphological and granulometric parameters of non-whisker-like samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S	D10% (μm)	D50% (μm)	D90% (μm)
T2	582.87	96.84	38.20	2.24	0.51	0.70	0.91	9.20	28.41	59.07
T3	139.63	46.36	18.23	2.26	0.51	0.66	0.90	8.98	22.00	47.97
T4	34.54	22.61	8.50	1.79	0.62	0.74	0.91	1.91	8.11	16.44
T5	190.92	52.22	19.75	1.95	0.56	0.69	0.89	4.67	27.44	58.08
T6	1.56	4.49	1.78	2.43	0.52	0.66	0.89	0.65	4.33	26.60
T7	0.83	3.38	1.26	1.45	0.72	0.83	0.91	0.21	0.83	2.11
T8	49.97	13.70	4.81	1.41	0.74	0.84	0.95	4.21	31.99	56.11
T9	0.87	3.32	1.23	1.54	0.71	0.82	0.94	0.51	2.77	30.41

5.3 – COMPOSITION AND STRUCTURE

The study of materials composition was performed using EDS (Electron Dispersive Spectroscopy) as a preliminary analysis to investigate the presence of impurities. All the samples show a similar spectrum in which the identified elements are O, Ti and K, with the C of the adhesive support. The relative percentage for all samples shows a ratio Ti:K equal to 3:1, which confirms the general formula $\text{K}_2\text{Ti}_6\text{O}_{13}$.

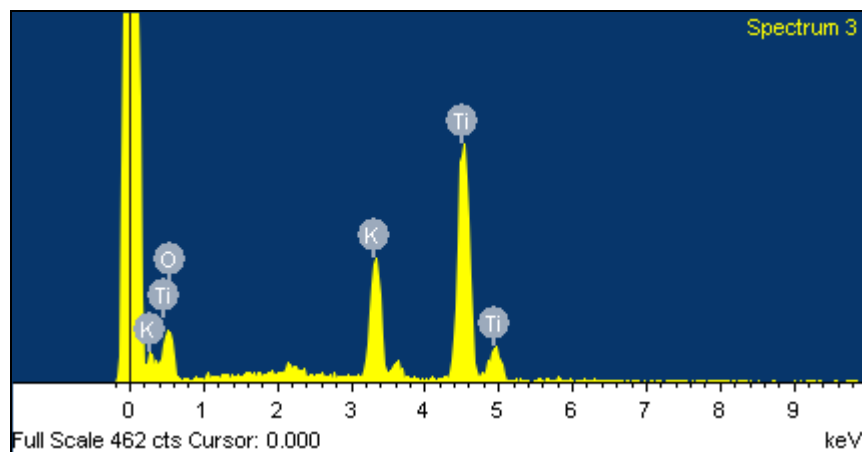


Figure 5.3: Electron dispersive spectrum of sample T7 as example.

5.3.1 – X-RAY DIFFRACTION ANALYSIS

All the samples show a monoclinic structure, generally indicated as mS42, and the space group is C2/m. The unit cell shows as lattice parameters the values a 15.582 Å, b 3.82 Å, c 9.13 Å and β 99.764°, as reported by Cid-Dresdner and Buerger¹⁵⁹. Figure 5.4 reports the general structure of a potassium hexatitanate $\text{K}_2\text{Ti}_6\text{O}_{13}$.

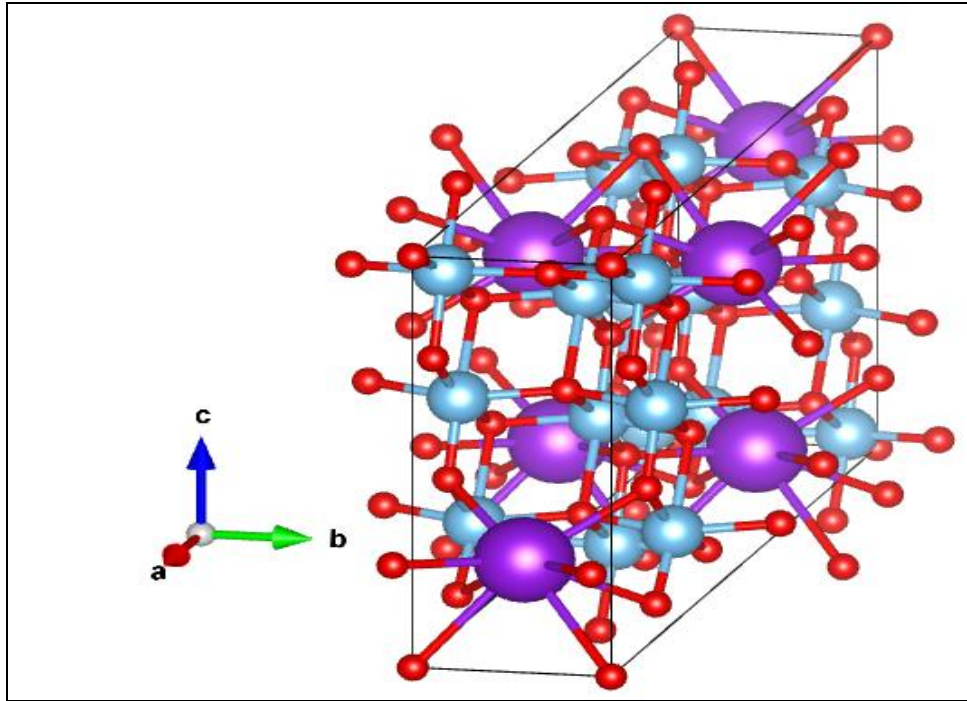


Figure 5.4: Structure of potassium hexatitanate, obtained by Vesta software; K violet spheres, Ti light blue spheres, O red spheres.

Figure 5.5 shows the x-ray diffraction spectra of samples T1-T3. They show an x-ray diffraction pattern very similar, where T1 results preferentially oriented on the direction [001], due to the higher intensity of generic peaks (h00) and (h0l) respect to the reference spectrum and the other samples pattern. For example, in Figure 5.5b the peak (401) is significantly higher for T1, while peak (110) results depressed. This difference can be observed on several other peaks, and in particular Figure 5.5b highlights the presence in sample T1 of a peak around 27.5°, named as R (110), which indicates the presence of rutile as impurity, which main peak is exactly at 27.38°. Probably, T1 was synthesized starting from rutile titania.

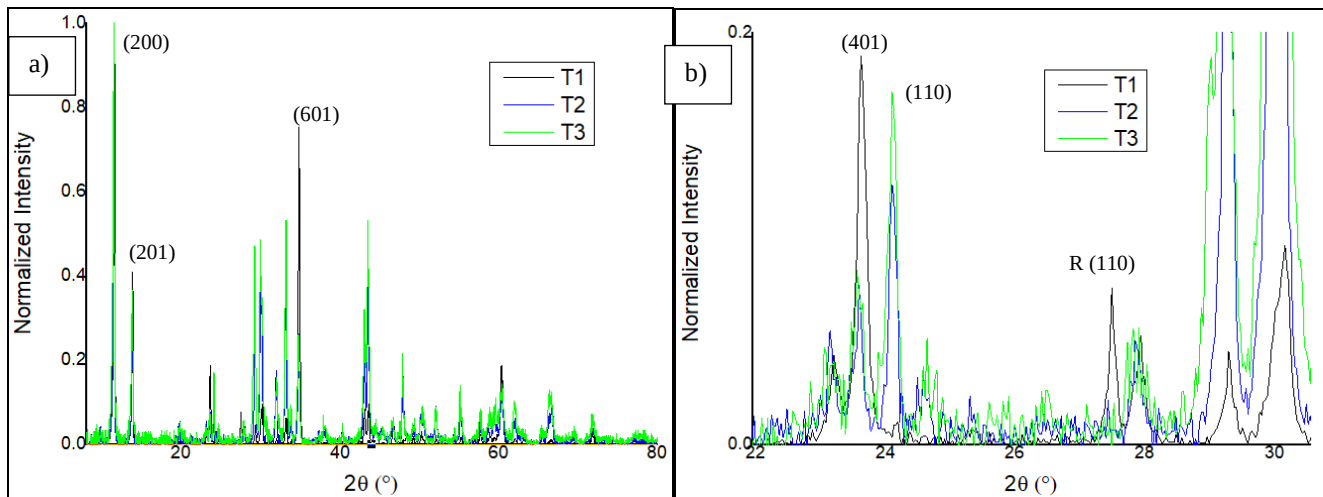


Figure 5.5: X-ray diffraction spectra of samples T1,T2, and T3: a) comparison of entire spectrum; b) zoom on range 22-30°.

In addition, the sample T6 shows a similar diffraction pattern with respect to the aforementioned samples. However, it shows different preferential orientation, due to the higher relative intensity of several peaks (hk0) and (h0l), as shown in Figure 5.6a. The orientation observed probably derives from the synthesis process used to obtain the rod-like shape¹⁶⁰. Furthermore, Figure 5.6b highlights the presence of rutile as impurity in sample T6.

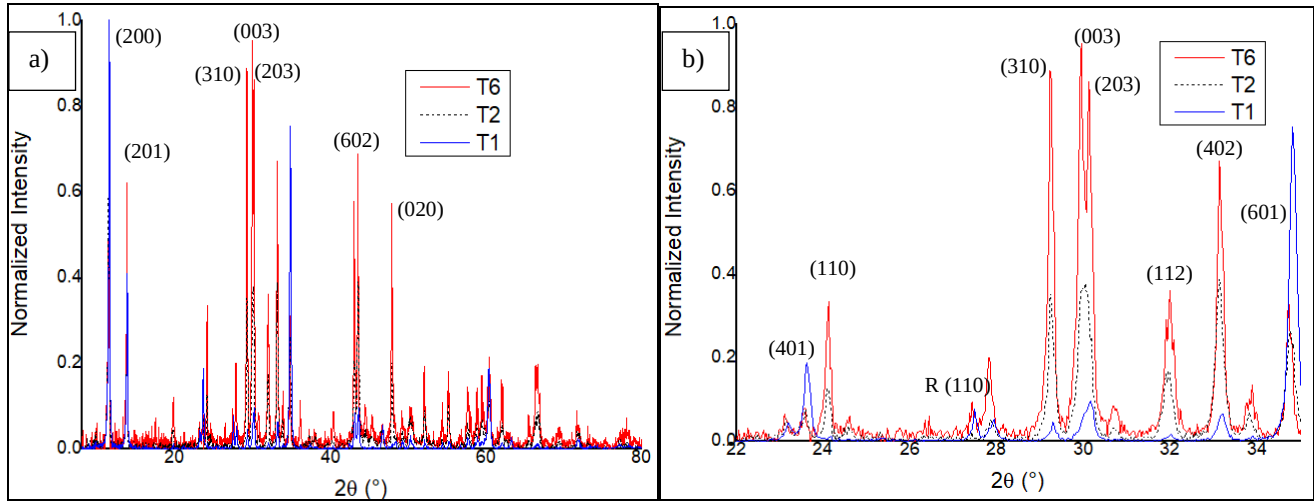


Figure 5.6: X-ray diffraction spectra of samples T1, T2, and T6: a) comparison of entire spectrum; b) zoom on range 22-35°.

Samples T4 and T5 show a significant different pattern with respect to the previous samples (Figure 5.7), due to the different main peak around 48° relative to the diffraction of plane (020). Note that sample T5 shows higher relative intensity for peaks (h0l), while for all the other kind of directions it has peaks less intense (Figure 5.7a). The focus in the range 20-30° (Figure 5.7b) highlights the previous consideration and shows the presence in both samples of anatase as impurity (A). Comparing the two patterns, sample T5 has a significant amount of anatase with respect to sample T4.

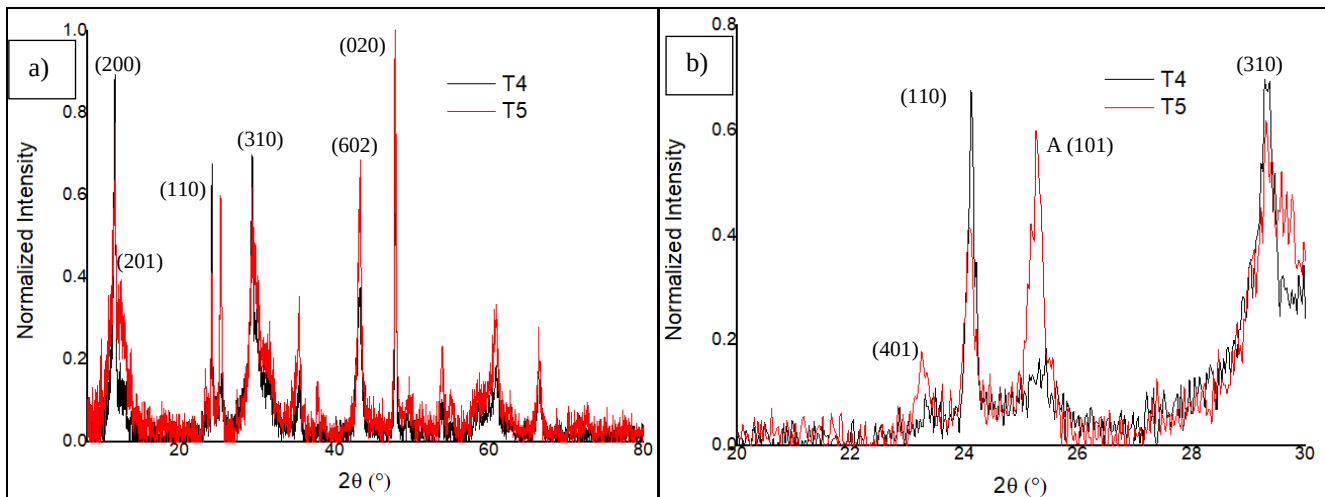


Figure 5.7: X-ray diffraction spectra of samples T4 and T5: a) entire spectrum; b) zoom on range 20-30°.

T7, T8 and T9 samples show similar patterns that differ only for some relative peak intensity (Figure 5.8). The main peaks are relative to diffraction of planes (310), (203) and (020). In particular, the higher peaks are (hk0) and (h0l) like, as for sample T6. However, they do not show the presence of rutile or anatase as impurities.

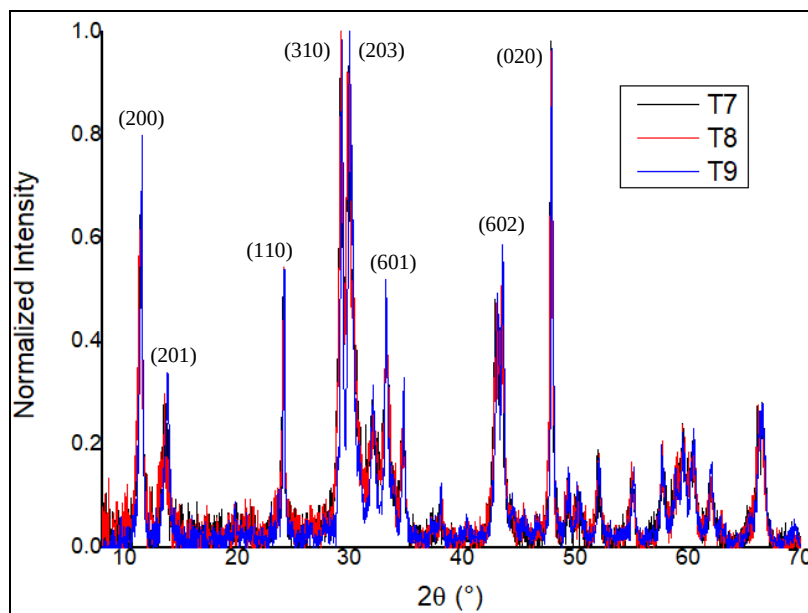


Figure 5.8: X-ray diffraction spectra of samples T7, T8 and T9.

By the fitting of spectra, the peak position, its full width at half maximum and its intensity (area) were calculated and the data of the peaks with significant differences are reported in Table 5.3. The interplanar distance was obtained for all the three peaks by Bragg law (5.1) and by peak (200) and (020) the crystallite dimension was calculated on a and b direction respectively, using the Scherrer equation (5.2).

$$5.1 - d = \frac{\lambda}{2 \sin \theta}$$

$$5.2 - L = \frac{0.9\lambda}{FWHM \cdot \cos \theta}$$

Results show a wide range of crystallite dimension on both “a” and “b” directions. Sample T5 shows the highest value of FWHM for each peak considered, which means it has the lowest crystallite dimension in all the directions. This probably derives from the presence of anatase as impurity in the structure. In addition, sample T4 shows higher FWHM for some peaks, but less than T5, then it can be supposed a different degree of organization in these two samples containing different amount of anatase. Note that all samples show the same D_{110} and D_{020} , apart from T1 that has a higher interplanar distance on b direction. Moreover, results show slightly different crystallite dimension along b direction.

Table 5.3: Data of x-ray diffraction fit.

SAMPLE	$2\theta_{200}$ (°)	FWHM (200)	I (200)	D_{200} (Å)	L_a (nm)	N_a	$2\theta_{201}$ (°)	FWHM (201)	I (201)	D_{201} (Å)
T1	11.54	0.16	0.26	7.66	50.54	66	13.84	0.16	0.10	6.39
T2	11.50	0.13	0.21	7.69	59.14	77	13.81	0.13	0.07	6.41
T3	11.46	0.20	0.32	7.72	39.14	51	13.78	0.20	0.11	6.42
T4	11.54	0.35	0.44	7.66	22.88	30	12.68	0.80	0.11	6.98
T5	11.47	0.84	0.62	7.71	9.53	12	12.57	1.52	0.48	7.04
T6	11.49	0.10	0.16	7.70	76.77	100	13.81	0.11	0.10	6.41

T7	11.42	0.35	0.33	7.74	22.88	30	13.62	0.45	0.14	6.50
T8	11.41	0.41	0.40	7.75	19.42	25	13.54	0.64	0.19	6.53
T9	11.51	0.24	0.28	7.68	32.86	43	13.80	0.38	0.19	6.41

SAMPLE	$2\theta_{110}$ (°)	FWHM (110)	I (110)	D_{110} (Å)	$2\theta_{020}$ (°)	FWHM (020)	I (020)	D_{020} (Å)	L_b (nm)	N_b
T1	X	X	X	X	46.73	0.22	0.02	1.94	38.63	199
T2	24.11	0.12	0.02	3.69	47.91	0.22	0.06	1.90	39.16	206
T3	24.11	0.15	0.04	3.69	47.88	0.21	0.07	1.90	41.19	217
T4	24.12	0.13	0.13	3.69	47.87	0.19	0.27	1.90	45.74	241
T5	24.09	0.17	0.10	3.69	47.83	0.27	0.35	1.90	32.19	169
T6	24.11	0.12	0.06	3.69	47.88	0.20	0.15	1.90	43.90	231
T7	24.09	0.20	0.15	3.69	47.84	0.24	0.33	1.90	36.82	194
T8	24.11	0.23	0.18	3.69	47.85	0.24	0.35	1.90	36.06	190
T9	24.17	0.16	0.13	3.68	47.93	0.21	0.29	1.90	42.00	221

Lattice parameters of each sample, calculated by XRD, are reported in Table 5.4. Comparing the results with the published values for a crystalline potassium hexatitanate, no samples are significantly different from the reference structure, but some slight differences can be observed. Sample T1 slightly differs on “a” and “c” values, while it has a significant lower value of b. Samples T4 has a lower value of a, while T5 has a significant lower value of a and higher of c. Thus, with respect to the unit cell, the samples showing significant differences are T1, which has a whisker-like shape, and T4-T5, which contain anatase as impurity.

Table 5.4: Lattice parameters obtained by x-ray diffraction.

SAMPLE	a (Å)	b (Å)	c (Å)	β (°)
T1	15.56	3.76	9.09	99.76
T2	15.57	3.80	9.12	99.72
T3	15.57	3.80	9.11	99.66
T4	15.53	3.80	9.12	99.66
T5	15.41	3.80	9.16	98.70
T6	15.60	3.80	9.11	99.78
T7	15.62	3.80	9.14	99.90
T8	15.61	3.80	9.11	99.60
T9	15.56	3.80	9.10	99.74

To further understand the influence of each x-ray diffraction parameters and the relative difference among the samples, a principal component analysis (PCA) was applied using Table 5.4 as data matrix. Eight principal components are necessary to describe the 100% of system variance and three of them to compare all the samples. For this reason, the score plots of Figure 5.9 highlight the differences among the samples comparing the PC1 with both PC2 and PC3.

In Figure 5.9a the samples appear divided into a main group and two outliers, T1 and T5, which are significantly different from the others; T1 due to its preferential orientation and T5 due to the content of anatase. By Figure 5.9b, the division of titanates system is even more detailed, because the component 3 mainly concerns the d-spacing of planes (200) and (201), and the crystallite dimension L_b ,

while component 1 the L_a and the full width at half maximum of several peaks, then also the crystallite dimension on directions different from “a” and “b” axis. Thus, samples are dispersed along a general direction, highlighted by the red arrow in Figure 5.9b, with a higher component on PC1 that mainly derives from the different crystallite dimension on an axis and other directions. At the same time, the perpendicular direction respect the red arrow mainly concerns the d-spacing of planes (200) and (201), where samples T4 and T5 have the structure with the major interplanar distance along (200) and (201), probably due to the presence of anatase. By score plot, also samples T7 and T8 are slightly different due to their low L_a value, though sample T5 has the lowest crystallite dimension.

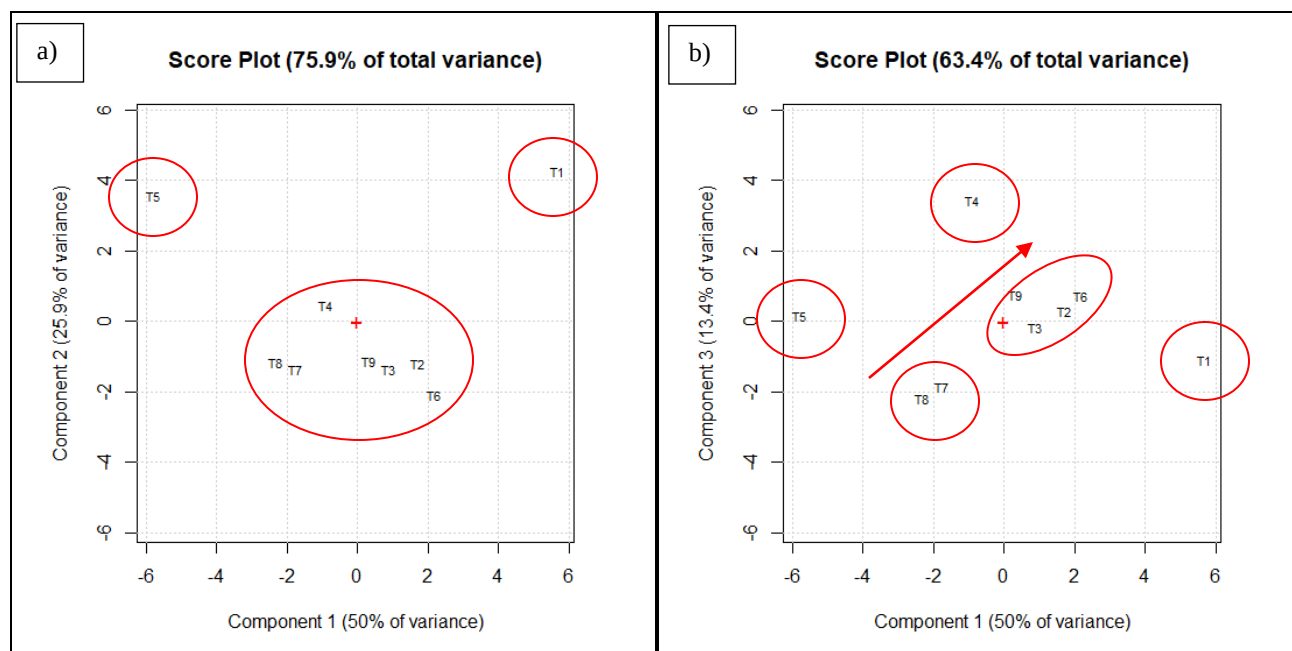


Figure 5.9: Score plot of PC1 respect: a) PC2; b) PC3.

5.3.2 – RAMAN SPECTROSCOPY

All the samples show the main peak around 145 cm^{-1} , which is similar to both rutile and anatase peak (144 and 147 cm^{-1} respectively). In the case of rutile, the peak derives from B_{1g} vibrational mode and it does not represent the most intense peak, while for anatase it is the main peak and derives from E_g vibrational mode¹⁶¹. Thus, the main peak of titanate samples can be associated with the E_g vibrational mode of anatase, but it shows a lower frequency.

In literature a complete attribution of potassium hexatitanate peaks, it is not reported, to our knowledge. For example, Lee et al.¹⁶² reported that the peak around 280 cm^{-1} is relative to the vibration of Ti-O-K bonds, while the peak around 445 cm^{-1} concerns the Ti-O bending vibration involving three-fold oxygen coordination. Su et al.¹⁶³ published a study of Raman spectroscopy of silico-titanates in which the peak in the range $600\text{--}650\text{ cm}^{-1}$ is attributed to the stretching of Ti-O bonds in the octahedral TiO_6 . Instead, the peak around 750 cm^{-1} concerns the Ti-O-Ti stretching in the corner-shared TiO_6 chains. Figure 5.10 shows the Raman spectrum of sample T1, which is in agreement with the spectra reported in literature^{164,165}. By x-ray diffraction, this sample contains a little amount of rutile, which can be identified in the Raman spectrum by the shoulder of peak around 650 cm^{-1} because the A_{1g} vibration mode of rutile is located at 612 cm^{-1} ¹⁶¹. Titanate peaks cover the other possible signals of rutile.

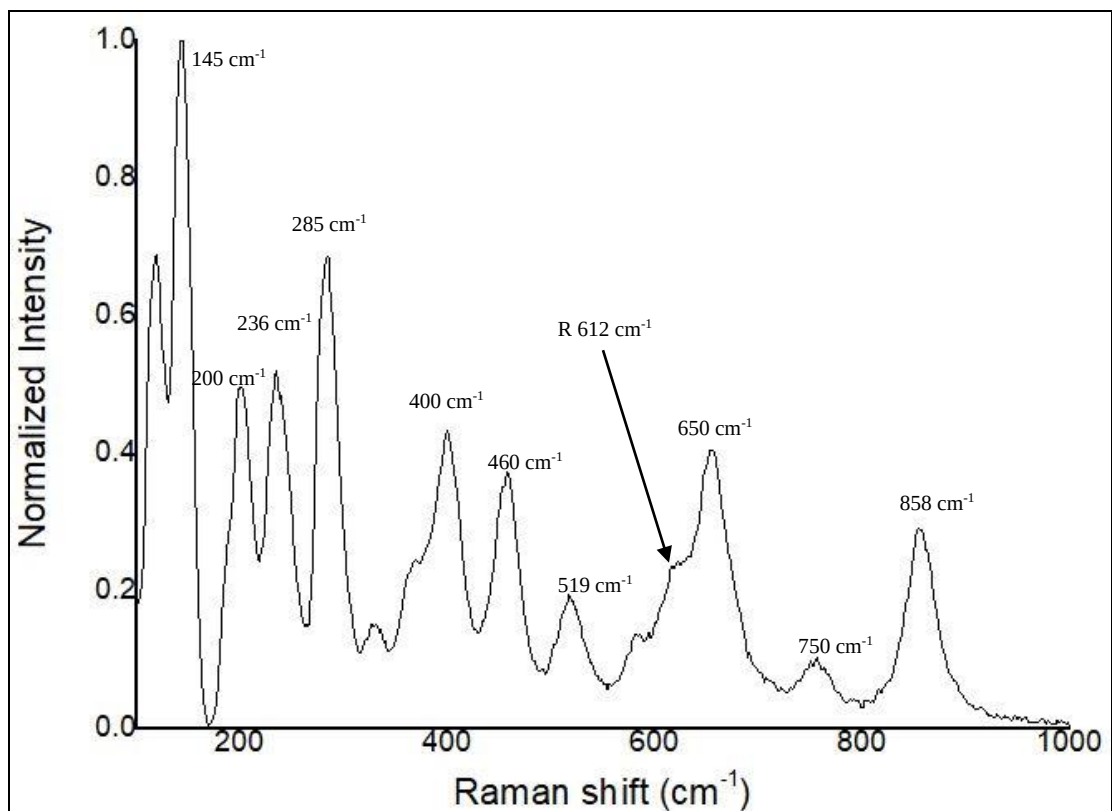


Figure 5.10: Raman spectrum of sample T1 and relative main peaks.

The spectral pattern of all the samples appears similar to T1, although some differences in the peak position are visible (Figure 5.11). The only two samples significantly different from the others are titanate A4 and A5 (Figure 5.12), probably due to the presence of anatase.

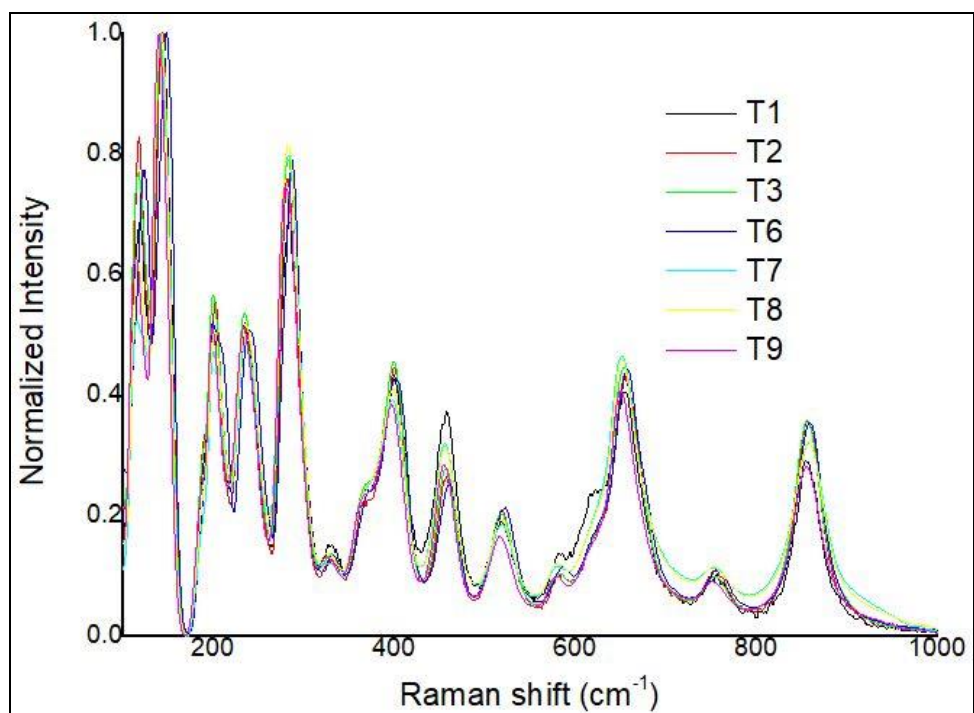


Figure 5.11: Raman spectra of all samples, a part T4 and T5.

The influence of anatase on Raman signals is observable considering the full width at half maximum of peaks, because samples T4 and T5 show some broader peaks respect all the other samples. In particular, the peak around 400 cm^{-1} , corresponding to B_{1g} of anatase, has a FWHM that is almost twice the one of other samples. Furthermore, T4 and T5 peaks do not match with the other samples. They show a peak around 920 cm^{-1} which is not present in the other samples and it can be ascribed to the Ti-O stretching involving non-binding oxygen¹⁶². Instead, they do not show the stretching in corner-shared TiO_6 chains at around 750 cm^{-1} .

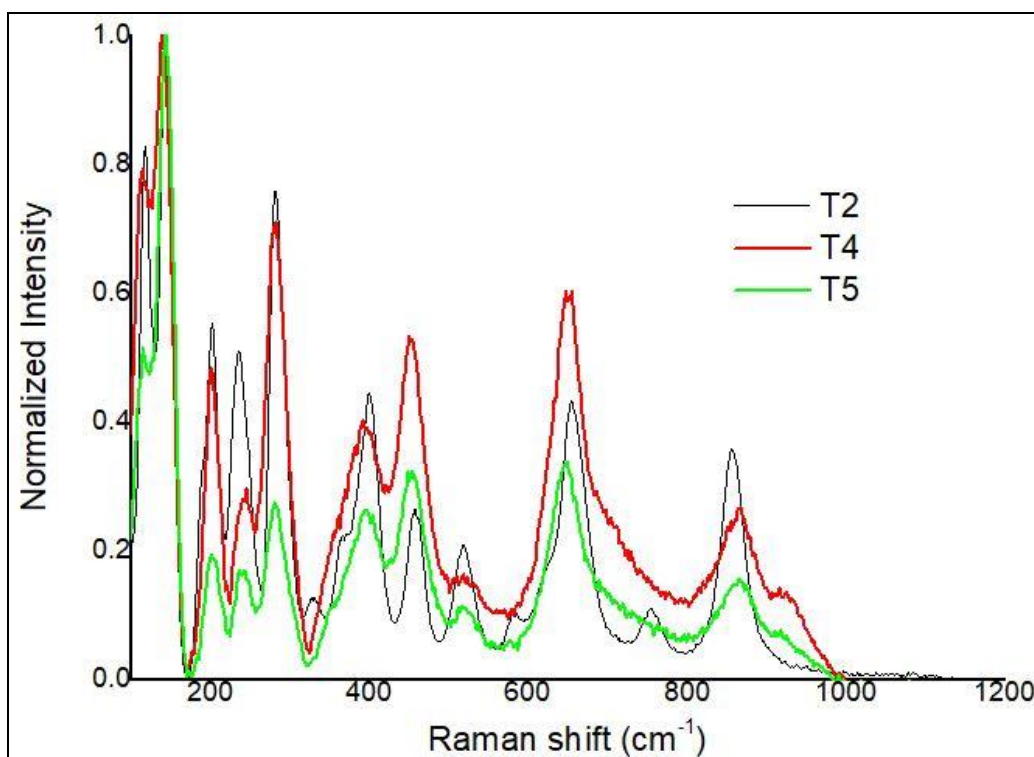


Figure 5.12: Comparison of Raman spectra of samples T2, T4 and T5.

Table 5.5 reports the data obtained by the fit of each spectrum. The peaks were named with a capital letter in order of increasing frequency.

Table 5.5: Matrix of Raman spectroscopy data collected on titanates.

	A	FWHM A	I A	B	FWHM B	I B	C	FWHM C	I C	D	FWHM D	I D
T1	117.78	13.98	9.83	144.51	16.55	26.72	202.21	14.64	7.44	236.66	22.14	11.04
T2	119.90	19.62	22.46	145.83	14.51	21.97	202.16	17.45	13.42	237.89	20.23	15.09
T3	117.29	18.20	19.79	143.18	16.82	26.00	200.81	16.38	13.42	235.88	22.71	17.79
T4	114.68	25.45	27.69	141.74	20.43	30.09	201.66	12.04	6.77	243.42	18.73	4.88
T5	115.85	21.48	15.51	143.08	19.38	29.61	203.30	14.49	4.67	240.37	25.28	7.15
T6	118.17	20.04	22.83	144.86	16.83	26.96	201.61	19.80	18.24	238.66	24.68	21.35
T7	117.18	17.02	11.33	142.49	18.15	28.92	202.35	15.26	9.66	236.79	23.02	15.85
T8	115.73	15.37	13.12	141.53	16.41	25.95	200.93	14.98	10.50	235.58	22.26	15.85
T9	115.19	15.54	13.97	141.14	16.08	25.40	200.11	15.37	10.98	234.57	21.76	16.01

	E	FWHM E	I E	F	FWHM F	I F	G	FWHM G	I G	H	FWHM H	I H	J	FWHM J	I J
T1	284.16	21.42	16.51	399.94	29.24	12.41	458.50	25.67	7.97	519.20	26.94	4.96	652.29	44.29	20.18
T2	285.41	19.74	23.36	400.93	25.07	15.35	459.56	18.90	6.67	519.79	24.31	7.17	657.64	37.09	23.62
T3	284.26	22.57	28.93	399.87	27.31	17.83	457.75	22.97	9.71	518.71	29.09	9.04	654.52	44.47	31.11
T4	282.23	25.59	31.71	390.23	47.31	27.46	451.92	43.57	43.00	525.19	43.05	5.98	648.86	47.96	37.35
T5	282.82	31.85	16.55	394.45	47.33	18.59	454.05	41.29	22.28	516.45	27.86	4.88	650.82	74.44	38.30
T6	285.06	23.18	29.49	399.88	29.38	18.73	458.22	22.65	8.66	518.99	26.97	7.97	655.82	41.30	26.29
T7	284.54	24.55	32.13	399.02	28.84	15.59	457.10	26.69	12.95	519.32	28.15	7.15	652.23	49.47	35.70
T8	283.31	22.61	27.24	398.30	26.92	14.21	456.35	23.16	9.67	518.25	27.48	6.47	652.30	46.12	28.90
T9	282.78	22.46	26.78	397.70	26.84	14.56	456.06	22.68	9.62	517.49	26.48	6.11	651.75	44.74	27.68

Figure 5.12 shows the loading and score plot obtained by PCA, in which the samples T4 and T5 show a significant difference with respect to the other samples. Instead, the whisker-like titanate T1 is slightly similar to other titanates, suggesting that it mainly differs for its preferential orientation. By the loading plot (Figure 5.12a), it is possible to observe a correlation among FWHM of peaks B-F-G (blue circle) and E-J (green circle). The first three peaks are correlated with the content of anatase or rutile and derive from similar vibrational mode. Peaks E and J concern just the titanate structure, because they are correlated respectively with the Ti-O-K vibration and the Ti-O stretching of octahedral TiO_6 . Considering the values of FWHM reported in Table 5.5, samples T4 and T5 show a large FWHM for both peaks F and G, due to the presence of anatase inside the structure. However, only in sample T5 anatase seems to significantly affect the titanate structure, because in peaks E and J the FWHM is different just for sample T5, especially for peak J. This suggests a higher content of anatase in sample T5, as already suggested by x-ray diffraction pattern where the peak at around 25° is more intense for T5 respect T4 (Figure 5.7b).

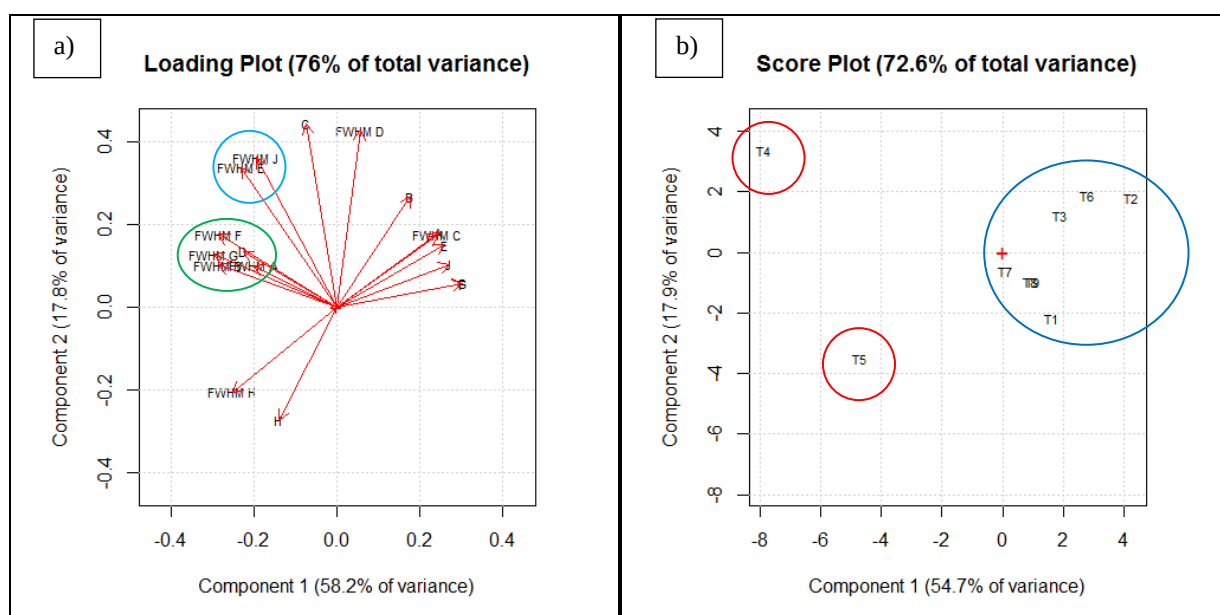


Figure 5.12: PCA results on Raman spectra data: a) Loading plot; b) Score plot.

5.3.3 – INFRARED SPECTROSCOPY

The FTIR spectra obtained are in agreement with those reported in literature^{166,167}, showing similar peaks in the range $400\text{--}1000\text{ cm}^{-1}$, while some differences can be observed in the range $1000\text{--}4000\text{ cm}^{-1}$.

Figure 5.13 reports the spectra of four samples in the range $400\text{--}1800\text{ cm}^{-1}$, while only sample T6 shows signals at higher wavenumber, in particular a low peak around 3400 cm^{-1} . The peaks between 400 and 800 cm^{-1} are generally attributed to the O-Ti-O bending and to the Ti-O stretching in the TiO_6 octahedral groups. In sample T1, the significant difference of intensity for peaks under 600 cm^{-1} is probably correlated with the preferential orientation observed by x-ray diffraction, which allows a lower bending vibrational mode. Moreover, this sample shows a peak around 1110 cm^{-1} which was not exactly identified, but it can be associated with the rutile content of sample T1. All the samples show also a common peak around 933 cm^{-1} which is expected for Ti=O group¹⁶⁶. This result agrees well with the Raman signals in the range $800\text{--}900\text{ cm}^{-1}$, also expected for Ti=O vibrational mode¹⁶³. The main difference is relative to peaks around 1380 and 1630 cm^{-1} of sample T6, together with the low peak around 3400 cm^{-1} aforementioned. This peak is generally attributed to the stretching of hydroxyl group adsorbed on the titanate, as also found for titanium oxide¹⁶⁸, and indicates the presence of adsorbed water molecules. This result is further confirmed by the peak at around 1630 cm^{-1} , which is relative to the bending of adsorbed water molecules¹⁶⁷. These signals

suggest the presence of adsorbed water between titanate layers, but the presence of a peak around 1380 cm^{-1} confirms also the presence of rutile observed by x-ray diffraction. In fact, the stretching of Ti-O bonds generates a signal around 1380 cm^{-1} , as found for sample T6. Thus, the water molecules could be adsorbed between titanate layers or on the particles of titanium oxide.

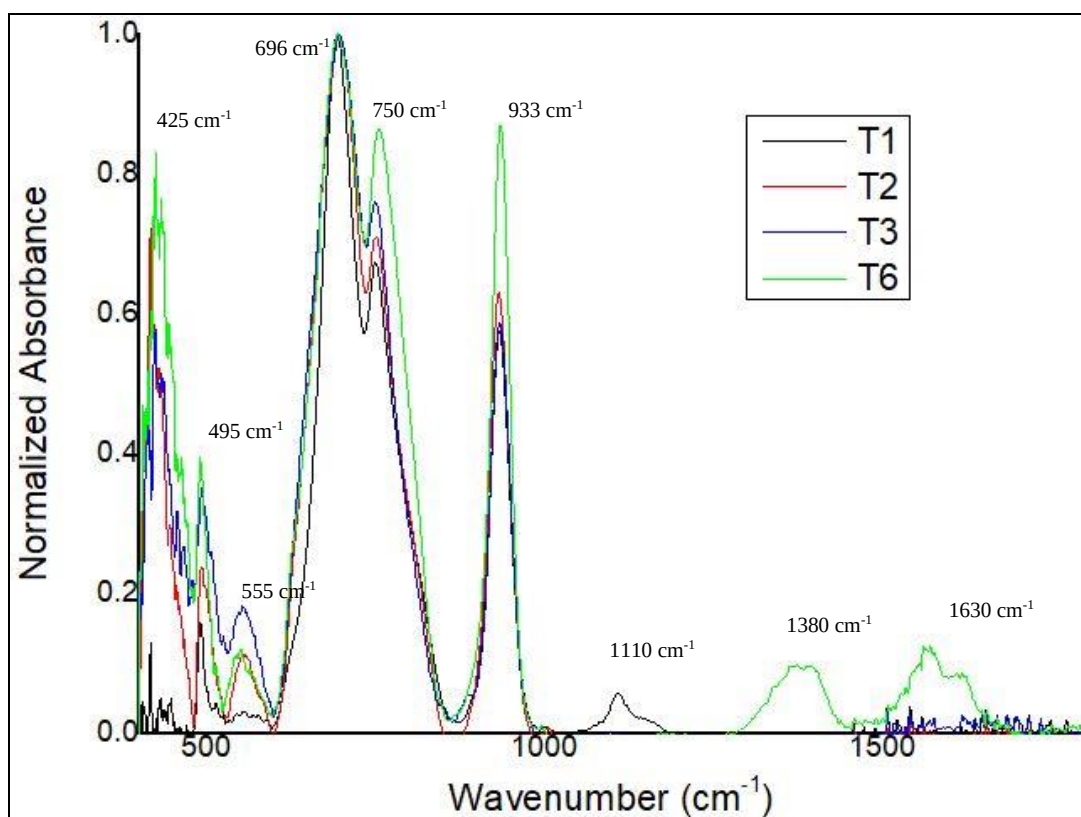


Figure 5.13: FTIR spectra of four samples, showed as normalized absorbance.

Samples T4 and T5 show spectra different from the previous samples, characterized by a broad peak around 700 cm^{-1} due to the Ti-O stretching of TiO_6 octahedral group and the peak around 930 cm^{-1} relative to Ti=O . Sample T4, as already found for T1, has a broad and low intense peak around 1110 cm^{-1} , probably due to the presence of anatase as impurity. Moreover, it shows a broad peak around 3400 cm^{-1} due to adsorbed water molecules. Sample T5 shows more intense peaks that can be correlated with the content of anatase, especially the peak at around 1380 cm^{-1} which is relative to the stretching modes of Ti-O bonds in titanium oxide¹⁶⁸. However, it does not show the peak at 1630 cm^{-1} relative to bending of adsorbed water molecules and also above 3000 cm^{-1} is not present a significant signal relative to the presence of hydroxyl groups. Thus, in both samples, anatase is present as found by x-ray diffraction, but adsorbed water molecules are present only in sample T4, while sample T5 has been probably calcined after the synthesis process.

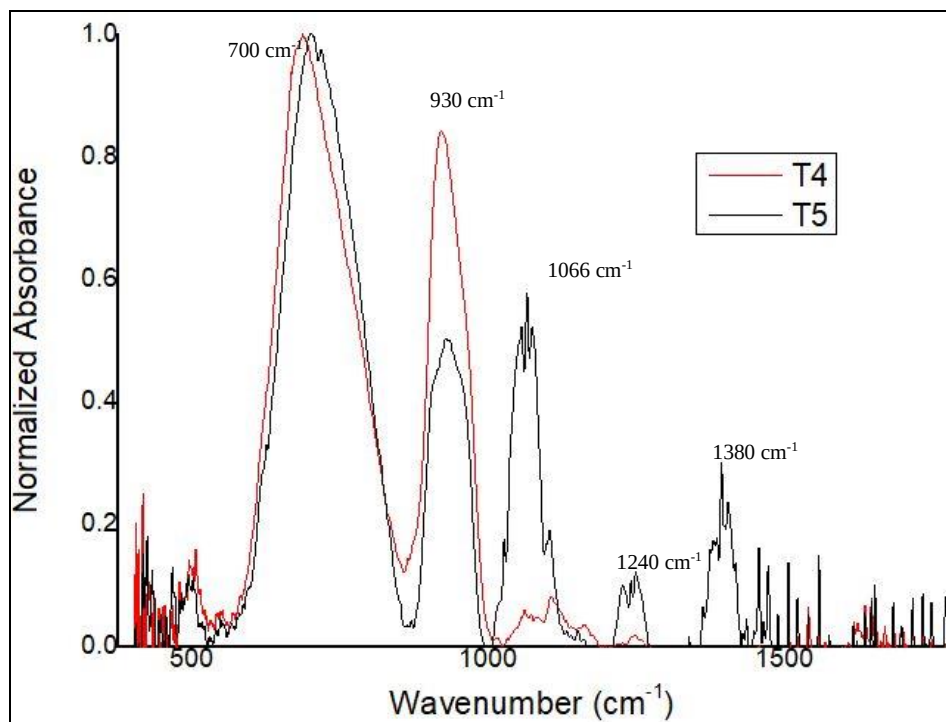


Figure 5.14: FTIR spectra of samples T4 and T5, showed as normalized absorbance.

The last three samples show similar spectra as samples T1-T3 in the region 400-1000 cm^{-1} , but they present a signal relative to Ti-O vibrational modes typical of anatase (peak 1380 cm^{-1}) and peaks of adsorbed water molecules (1630 and 3400 cm^{-1}). However, by x-ray diffraction it was not identified the presence of rutile or anatase, maybe because of the low amount.

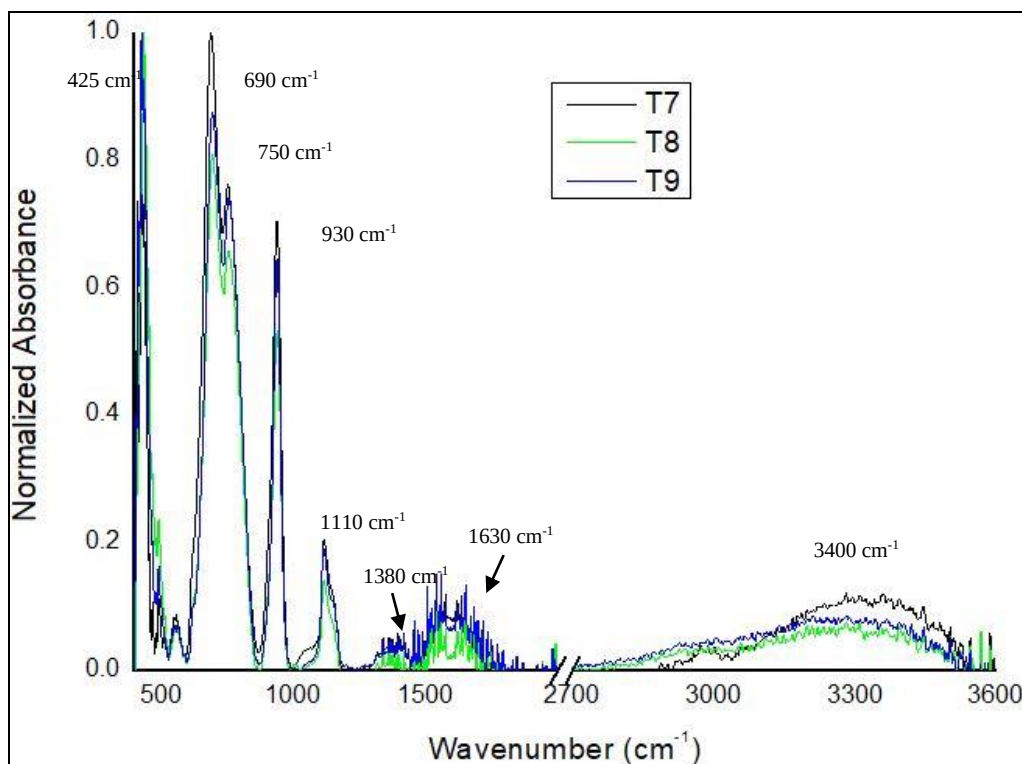


Figure 5.14: FTIR spectra of samples T7, T8 and T9, showed as normalized absorbance in the two ranges 400-1800 and 2700-3600 cm^{-1} .

5.3.4 – DENSITY

The density of potassium hexatitanate samples can be obtained by lattice parameters, derived from x-ray diffraction. Dresdner et al.¹⁵⁹ studied the crystal structure of potassium hexatitanate deriving its density by the calculated lattice parameters (3.582 g/cm³), which is close to the observed value of 3.58 g/cm³. Thus, the theoretical density obtained by lattice parameters can be considered as a good approximation of the real density. Table 5.6 shows the lattice parameters, the cell volume and the obtained density. Each sample shows a density similar to the Dresdner et al. published value and the unique sample that is slightly different is T1, the whisker-like titanate.

Table 5.6: Lattice parameters and relative volume cell and powder density calculated.

SAMPLE	a	b	c	β	V cella (Å ³)	DENSITY (g/cm ³)
T1	15.56	3.76	9.09	99.76	523.73	3.64
T2	15.57	3.80	9.12	99.72	531.54	3.58
T3	15.57	3.80	9.11	99.66	531.22	3.58
T4	15.53	3.80	9.12	99.66	530.58	3.59
T5	15.41	3.80	9.16	98.70	530.22	3.59
T6	15.60	3.80	9.11	99.78	532.17	3.58
T7	15.62	3.80	9.14	99.90	534.43	3.56
T8	15.61	3.80	9.11	99.60	532.82	3.57
T9	15.56	3.80	9.10	99.74	529.63	3.60

The obtained value of density results correlate by Pearson coefficient analysis with some morphological parameters, but deleting the sample T1 from this analysis, no one of the morphological parameters is significantly correlated with density. Instead, the density is in both cases inversely proportional to D_{200} , and then if this interplanar distance increases, the density decreases. Comparing just the sample with potassium hexatitanate (no T4 and T5) the correlation with D_{200} becomes more linear and it is observable an inverse correlation with D_{110} .

5.4 – TRIBOLOGY OF POWDERS

Figure 5.13 displays the friction coefficient values with the value of friction amplitude as error bar. This parameter is calculated as the standard deviation of friction coefficient evolution during sliding in the steady state⁹⁹.

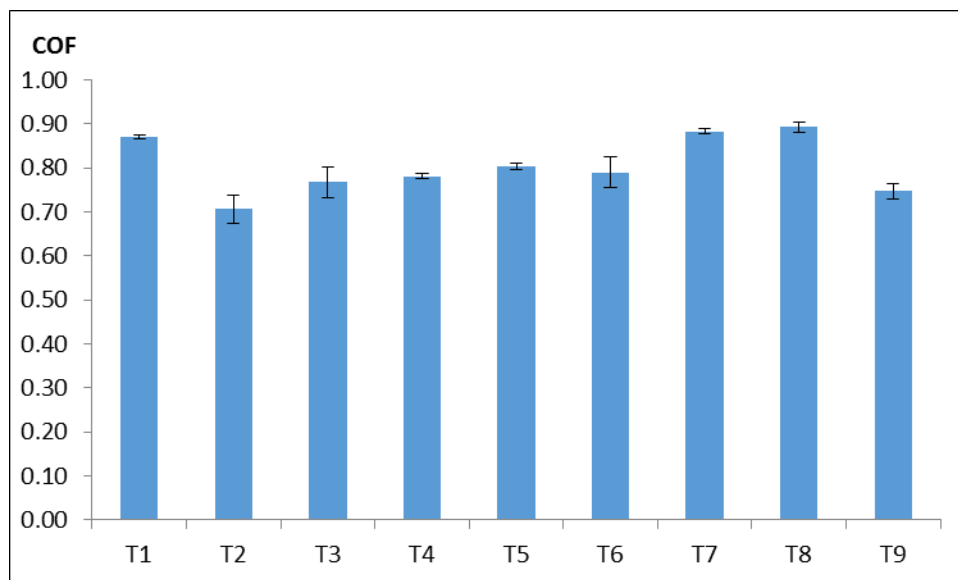


Figure 5.13: Comparison of friction coefficient values for all samples.

All the potassium hexatitanate samples show a friction similar or higher than steel against steel friction. Osterle et al.⁹⁹ reported a friction around 0.7 for the $K_2Ti_6O_{13}$; furthermore, for ceramic materials like titanate the same authors observed a high fluctuation of COF.

In some of the samples analysed, the amplitude of friction is higher than 0.01, which is probably correlated with a strong adhesion at interface. Experimentally, it was observed a compact layer of particles at interface in all the tests performed, but not as stable as the carbon materials one. The compression of particles at interface generates a layer of titanate, which is composed by aggregated particles and not by sintered ones as in the case of carbon materials. Another experimental evidence is the change of colour for all the powders analysed, from the general white colour of titanates to light grey, probably due to the abrasion of steel surfaces and consequent formation of iron oxide, which is black, as already observed in steel against steel tests. In the pin-on-disc test steel-steel without powder, a layer of iron oxide covers the surface of pin, whereas in the case of titanates no layers on the pin surface are visible.

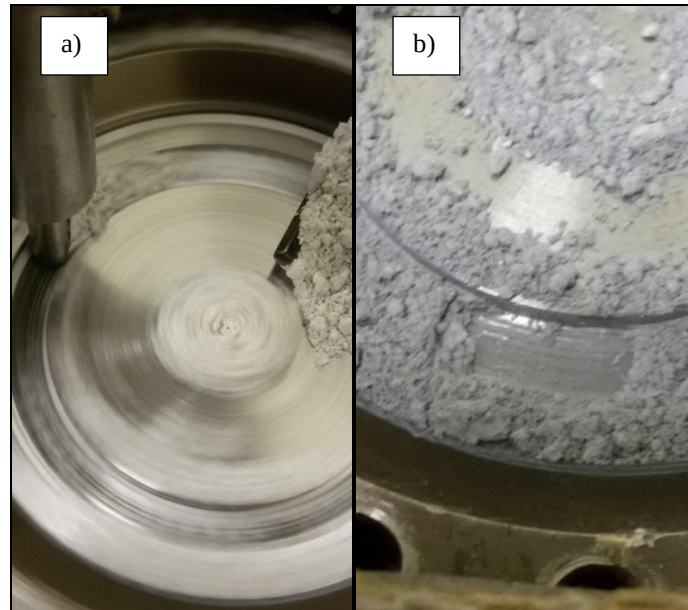


Figure 5.14: Pin on disc test for sample T9: a) at the beginning of test; b) after test.

Some reproducibility tests were performed in order to evaluate the possible influence of disc roughness, selecting three discs with different starting roughness and pin with R_a of $0.50\ \mu\text{m}$. Table 5.6 shows the starting and final roughness of disc with the relative average friction coefficient obtained. Results show a difference in COF lower than 0.02, which does not represent a significant influence of surface topography on titanate friction. Note that the final value of roughness is practically the same and, as found before, this parameter has a dominant influence on the friction behaviour, which seems not affected by the evolution of roughness. However, Figure 5.15 highlights some differences in the friction evolution for the three reproducibility tests. Test A shows a continuous increase of friction till a plateau after 400-500 m as sliding distance, while the other two tests show an immediate increase of friction in the first 100 m with a subsequent stabilization at the same average value after 400-500 m. Thus the starting roughness seems to affect the run-in period, because at high R_{aI} values the friction starts around 0.6-0.7, which is the range for steel contact, probably due to the large amount of asperities at interface, while for low R_{aI} values the contact at interface is immediately constituted by steel against titanate with a consequent increase of friction.

Table 5.6: Roughness parameters of disc used in reproducibility tests.

TEST	$R_{aI}\ (\mu\text{m})$	$R_{aF}\ (\mu\text{m})$	COF
A	0.791	0.604	0.789
B	0.301	0.598	0.795
C	0.165	0.584	0.803

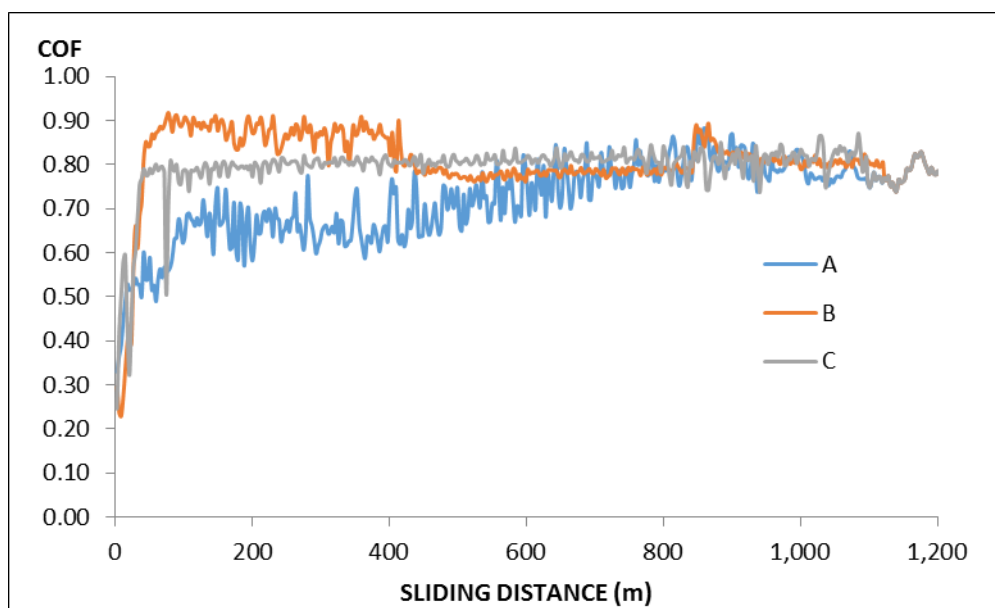


Figure 5.15: Comparison of friction evolution during test of sample T6.

5.4.1 – INFLUENCE OF MORPHOLOGY

A matrix of all the morphological parameters was generated with the aim to calculate the Pearson coefficient, by applying statistical method, as for carbon materials.

The data analysed concern all the potassium hexatitanate samples (Table 5.7), which show a wide range of particle size and shape.

The friction coefficient of powders does not depend on any morphological parameters; instead the particles solidity appears directly or inversely proportional to the other morphological parameters. In particular, it is linearly proportional to roundness (Pearson coefficient 0.93) and inversely proportional to aspect ratio (Pearson coefficient -0.92), as expected because solidity is 1 for spherical particles which have $AR=1$ and $R=1$. Thus, solidity can be considered as the parameter which summarizes the influence of AR and R.

Based on this observation and comparing just the samples with similar solidity (samples T2-T7) an inverse proportionality between COF and Feret's diameter can be found, then lower the particle size higher the friction at interface. This result agrees with the concept suggested by Horng et al.¹⁵¹ relative to a direct dependence of friction by particle density at interface. In the case of titanates, higher the number of particles at interface, higher the friction coefficient due to an increase in the abrasion and adhesion phenomena with steel surfaces. Note that the correlation improves removing the samples T4 and T5, which contain anatase as shown by previous structural characterization. Among this group of six samples, the titanates with more elongated particles show a significant high fluctuation of friction at the steady state, because their amplitude is higher than 0.03. Instead, samples with $AR < 2$ have amplitude lower than 0.01, suggesting a different compaction at interface in function of particle shape. The correlation shows a good R^2 if T4 and T5, containing anatase, are not considered Figure 5.16). As found in the case of carbon materials, the aspect ratio affects the friction behaviour due to the different packaging process at interface with a consequent formation of strong structures⁸⁰, which in this case increase the COF fluctuation.

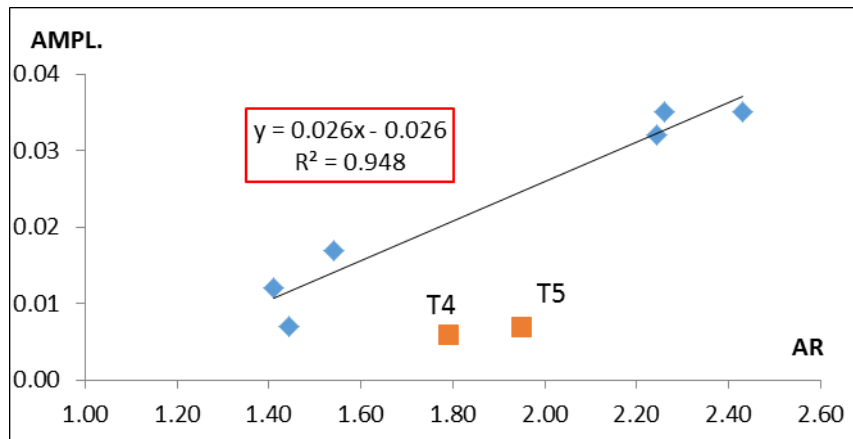


Figure 5.16: Correlation of amplitude with the particle aspect ratio.

Table 5.7: Data matrix on morphological parameters. (A area, P perimeter, F Feret's diameter, AR aspect ratio, R roundness, C circularity, S solidity).

SAMPLE	COF	AMPL	A	P	F	AR	R	C	S	D10%	D50%	D90%
T1	0.870	0.005	1513.51	203.99	91.48	5.33	0.23	0.41	0.82	5.29	19.12	48.98
T2	0.706	0.032	582.87	96.84	38.20	2.24	0.51	0.70	0.91	9.20	28.41	59.07
T3	0.768	0.035	139.63	46.36	18.23	2.26	0.51	0.66	0.90	8.98	22.00	47.97
T4	0.781	0.006	34.54	22.61	8.50	1.79	0.62	0.74	0.91	1.91	8.11	16.44
T5	0.804	0.007	190.92	52.22	19.75	1.95	0.56	0.69	0.89	4.67	27.44	58.08
T6	0.790	0.035	1.56	4.49	1.78	2.43	0.52	0.66	0.89	0.65	4.33	26.60
T7	0.883	0.007	0.83	3.38	1.26	1.45	0.72	0.83	0.91	0.21	0.83	2.11
T8	0.892	0.012	49.97	13.70	4.81	1.41	0.74	0.84	0.95	4.21	31.99	56.11
T9	0.747	0.017	0.87	3.32	1.23	1.54	0.71	0.82	0.94	0.51	2.77	30.41

5.4.2 – INFLUENCE OF STRUCTURAL FEATURES

The main difference, in terms of structural features, concern the preferential orientation of sample T1, and the presence of anatase in samples T4 and T5.

Raman and FTIR features do not show any significant correlation with the tribological behaviour, then only the information obtained by x-ray diffraction are useful for obtaining a correlation with friction properties of the titanates.

Considering all the samples, the only significant correlation deals with friction and the full width at half maximum of peak [110] (Pearson coefficient 0.86), which is not present in the pattern of sample T1 due to its preferential orientation. Thus, the only significant correlation does not concern T1, which appears as outlier, probably because of the pronounced preferential orientation.

Figure 5.17 shows the 3D representation of plane [110] of potassium hexatitanate, which highlights the presence of a hole among potassium atoms (violet spheres). This configuration is the reason why titanates are considered tunnel-like, from a structural point of view, and used to intercalate ions^{55,167}. The full width at half maximum is inversely proportional to the crystallite dimension on the considered direction, which can give an idea of the length of the tunnel-like structure.

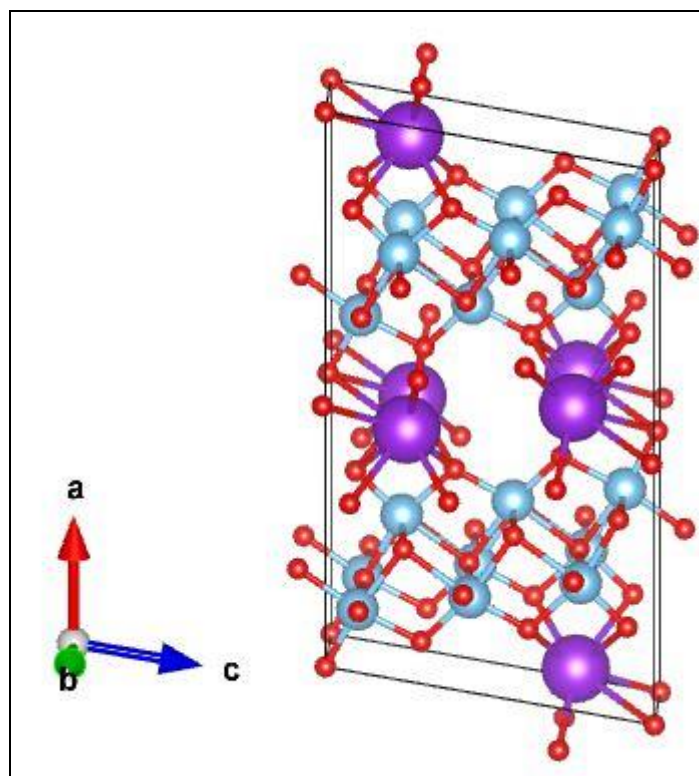


Figure 5.17: 3D representation of plane [110] obtained by Vesta software; K violet spheres, Ti light blue spheres, O red spheres.

Considering all the samples except T1, friction shows other correlations with structural parameters, in particular it is directly proportional to the interplanar distance of plane [200] and [020] (Pearson coefficient respectively 0.79 and 0.77). However, the d-spacing relative to plane [020] is practically the same for all the samples considered (Table 5.4), then only the D_{200} changes significantly. Observing the 3D representations (Figure 5.18), it can be supposed that friction directly depends on the distance between the galleries constituted by potassium atoms in both the directions along “a” and “b” axis. The interplanar distance along “a” axis is also inversely proportional to the crystallite dimension on [110] direction. Based on these results, it can be supposed that the friction increases for titanates with crystallites of lower dimension on [110] direction and with a major interplanar distance on [200] direction. Assuming that the decrease of friction is due to a larger amount of iron oxide mixed with titanate, it seems that titanates with the previous features (lower L_{110} and higher D_{200}) generates less abrasion of steel surfaces.

Considering also the previous correlation between powder density and D_{200} , it can be affirmed that friction increases not linearly, if the density decreases. This is a correlation similar to the one found for carbon materials, but the possible explanation is different. At lower density, the layer generated at interface has a higher compressibility, thanks to the higher interplanar distance on [200] direction, and it partially abrades the counterface, but the main contact is steel-titanate. At higher density and lower D_{200} the layer generated at interface is only partially compressible and it abrades significantly the counterface, with a consequent contact of steel with a mix of titanate and iron oxide, which generates a lower friction.

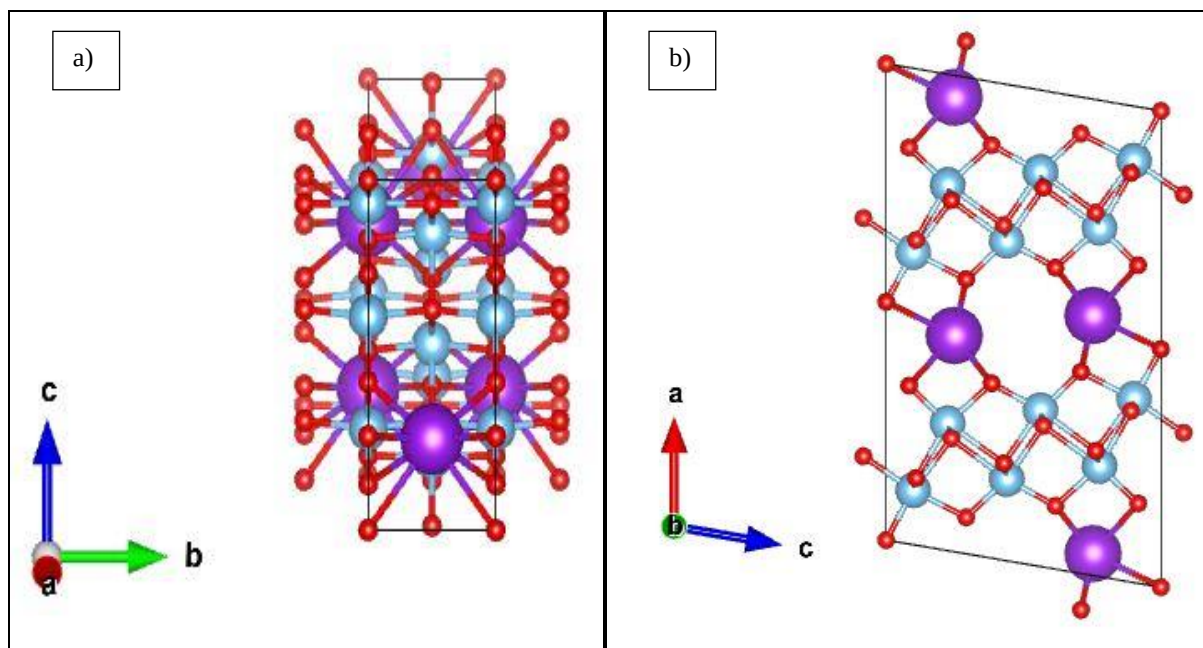


Figure 5.18: 3D representation of plane a) [200] and b) [020] obtained by Vesta software; K violet spheres, Ti light blue spheres, O red spheres.

5.4.3 – INFLUENCE OF TRIBOLOGICAL CONDITIONS

To investigate the influence of load and speed applied, the two variables were considered in an OVAT approach (One Variable At Time) on two samples, T1 and T6, in order to investigate a possible different behaviour correlated with the whisker-like shape of T1. Load was changed in the range 3 – 13 N, while speed in the range 0.10 – 0.30 ms⁻¹. Figure 5.19 shows the variation of COF in function of speed and load for the sample T1 as example. The increase of load affects non-linearly the friction coefficient that decreases following a power function. This inverse correlation is quite in agreement with the published results of Bowden, who reported in his review that friction coefficient is proportional to Load^{-1/3} for non-metallic materials⁸. Instead, the sliding speed does not affect COF in the range investigated. Thus, titanate samples show a similar correlation of COF with load and speed as found for carbon materials. This is probably due to the formation in both cases of a layer at interface that results mainly affected by the compression force, with a relative variation of COF in the range 0.85-1.15 for an applied load ranging between 3 and 13 N. It was not possible to explore a wider range of load due to the strong adhesion at interface that made impossible a continuous motion of disc. In both the samples, the sliding speed does not show any correlation with friction, which shows a variation of 0.01 in the range 0.1-0.3 ms⁻¹ of sliding speed.

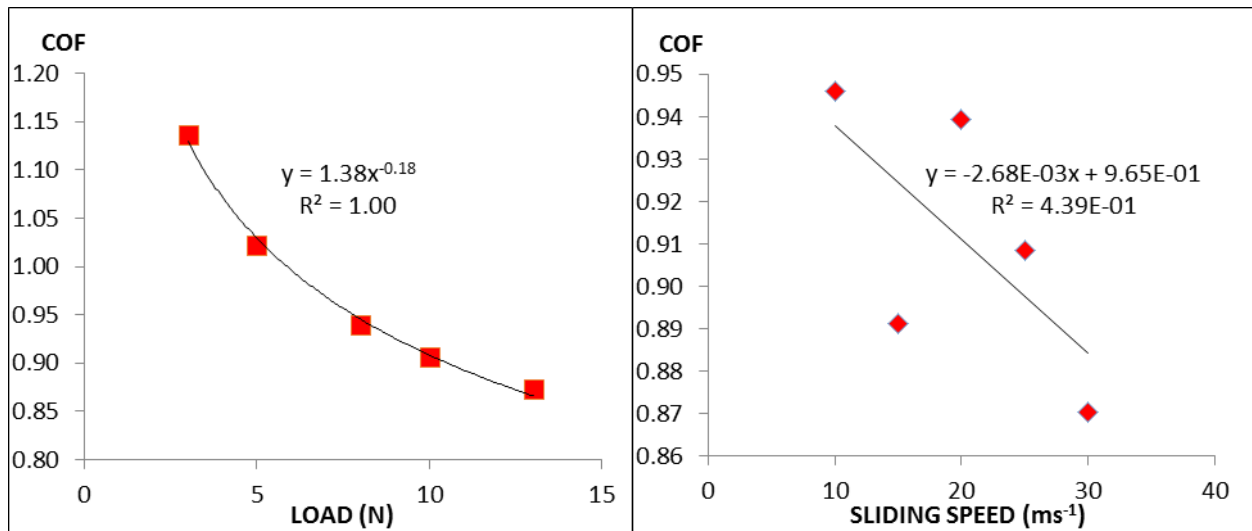


Figure 5.19: Variation of COF in function of load and speed for sample T1.

5.5 – CHARACTERIZATION OF MONOCOMPONENT PADS

All the samples previously described were used to produce composites based on potassium hexatitanate in order to investigate their influence on the tribological behaviour of the polymer matrix. As for carbon materials, each pad is constituted by 50%wt of basic mix and 50%wt of titanate powder.

5.5.1 – PHYSICAL CHARACTERIZATION

Titanates dispersed in the matrix keep the original size and shape of the starting powders, as visible in Figure 5.20.

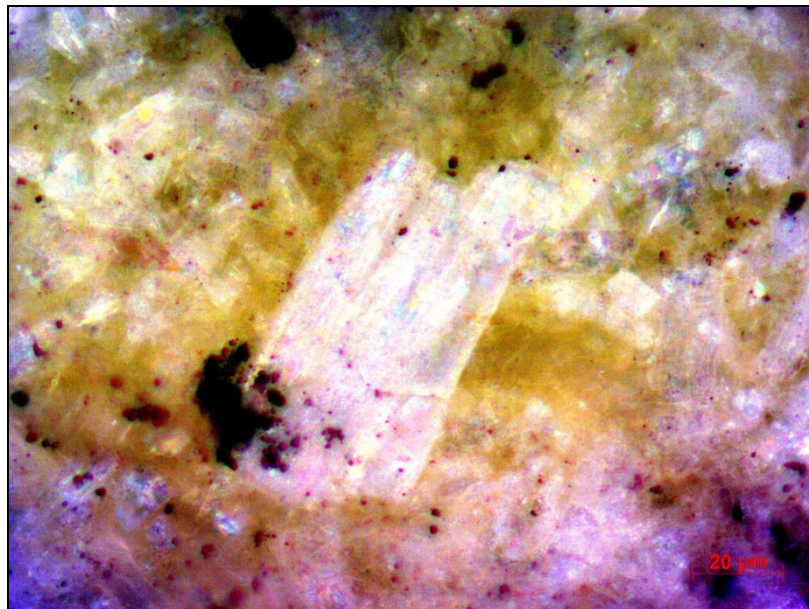


Figure 5.20: Optical microscope image obtained on T1 based pad in polarized light.

Therefore, for further comparison the morphological data obtained for powders would be considered also for pads. A general difference observed on pad surfaces concerns the formation of particles aggregates in the polymer matrix for titanate samples with high particle size. Figure 5.20

shows a comparison of pad with T1 (Figure 5.20 a) and T2 (Figure 5.20 b) powders, where the presence of aggregates is visible, while there is no evidence of aggregation phenomena in sample T6 (Figure 5.20c). Considering the particle size distribution of titanate fillers (Table 5.8), it can be observed that smaller particles are better distributed among the polymer matrix.

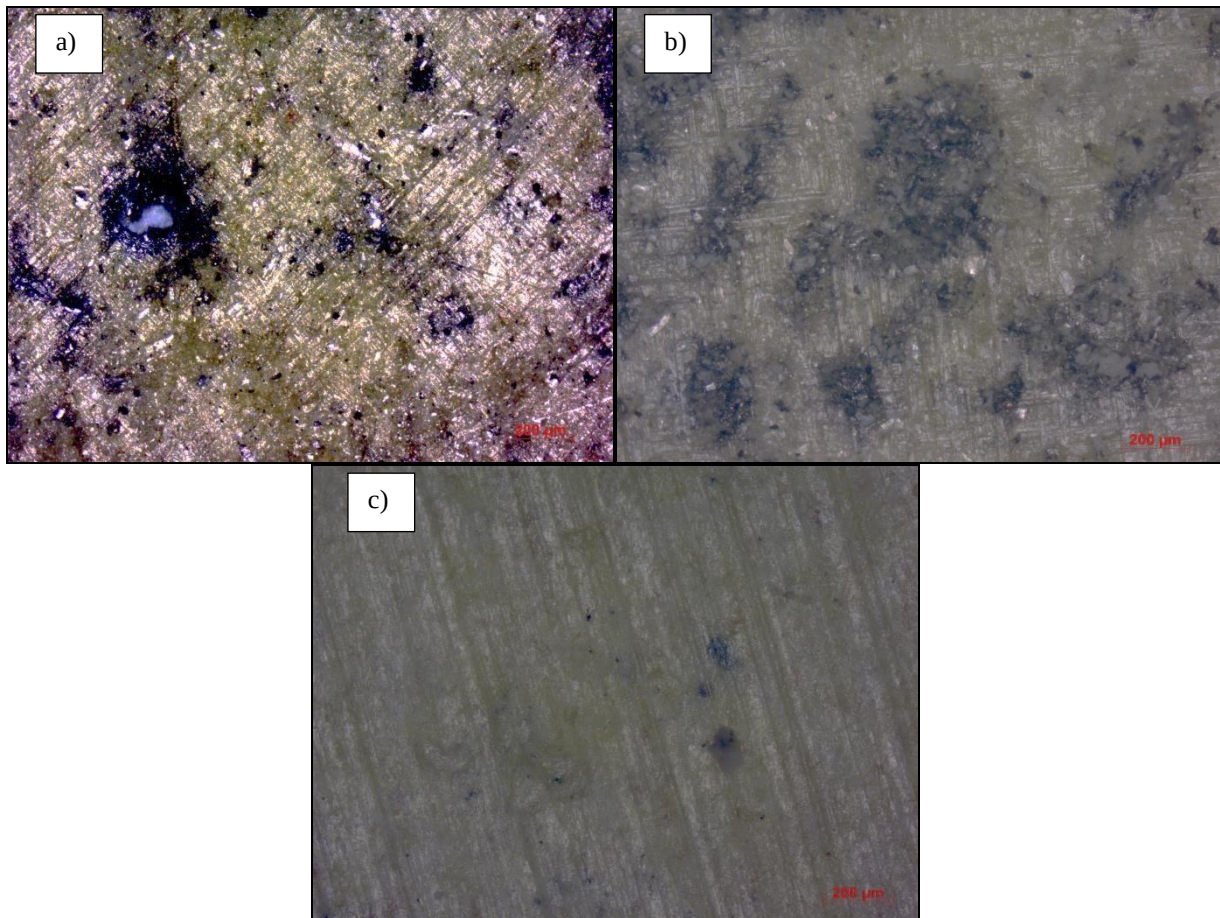


Figure 5.20: Optical images of pad surfaces for samples: a) T1; b) T2; c) T3.

Table 5.8: Particle size distribution of samples T1, T2 and T6.

SAMPLE	D10 (μm)	D50 (μm)	D90 (μm)
T1	5.29	19.12	48.98
T2	9.20	28.41	59.07
T6	0.65	4.33	26.60

Table 5.9 shows the value of all the samples density, calculated using the geometrical volume, and the theoretical pad density, obtained using the titanate volume fraction, calculated from x-ray diffraction. Comparing the results obtained with the density of basic mix, all the composites show a higher value, as expected, based on the higher density of titanates. The calculated pad density is quite in agreement with the theoretical value and it is inversely proportional to the powder theoretical density. This correlation is true for all the samples apart from T1, the whisker-like titanate, which has a higher density for both powder and pad.

Table 5.9: Density of titanate-based pad.

SAMPLE	GEOMETRICAL PAD DENSITY (g/cm ³)	THEORETICAL PAD DENSITY (FROM XRD DATA) (g/cm ³)	THEORETICAL POWDER DENSITY (FROM XRD DATA) (g/cm ³)	TITANATE VOLUME (%)
T1	1.85	1.92	3.64	26.36
T2	1.84	1.91	3.58	26.65
T3	1.82	1.91	3.59	26.61
T4	1.82	1.91	3.59	26.60
T5	1.80	1.91	3.58	26.67
T6	1.81	1.91	3.58	26.64
T7	1.86	1.91	3.56	26.75
T8	1.81	1.92	3.57	26.70
T9	1.75	1.91	3.60	26.58
MATRIX	1.32	1.30	X	X

A second macroscopic property affected by the filler is the pad hardness, measured by Brinell test. In literature, the reported hardness of titanate is in the range 3-4 Mohs hardness^{58,61} and generally the potassium hexatitanate slightly increases the hardness of a polymer⁵⁹. The pad hardness is similar to the basic mix hardness for all the samples, except T7-T9, which most significant difference is in the standard deviation (Figure 5.21).

Two parameters appear inversely proportional to the pad hardness: roundness and lattice parameter “a”.

The roundness decreases the hardness probably due to a different network in the bulk of pad, based on a lower interaction with the basic mix. Instead, roundness increases the standard deviation, suggesting a negative influence on the dispersion among the basic mix with a consequent inhomogeneity of this mechanical property.

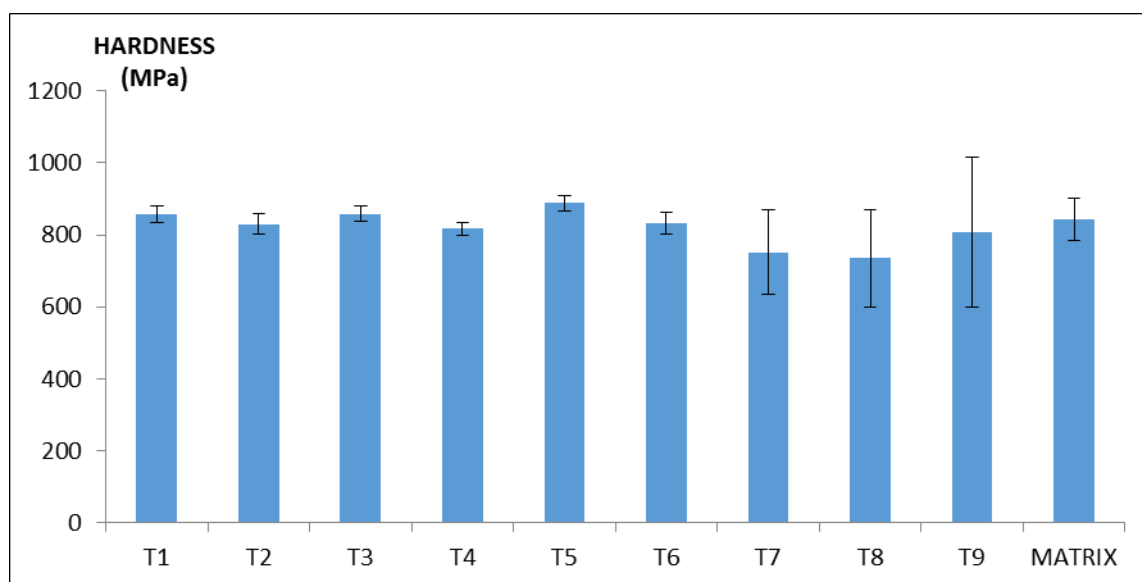


Figure 5.21: Comparison of hardness values obtained by Brinell test.

The inverse proportionality with the lattice parameters “a” indicates a direct effect on the resistance to compression of the cell structure. Figure 5.22 highlights the titanate structure long a axis, in order to visualize the possible effect of a compression along any directions. For a unit cell with lower

length on “a” the hardness increases probably due to the less possible compression of the gallery, which has a circular shape. Instead, at higher value of a, the unit cell results elongated and can be compressed with a consequent decrease in titanate hardness, then of the overall composite.

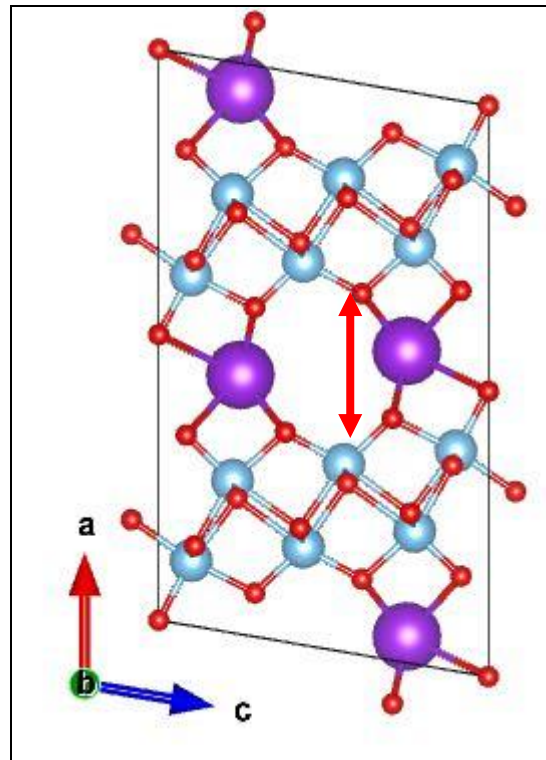


Figure 5.22: 3D representation of titanate structure.

Removing from the data matrix analysed the sample T1, due to its significant different morphology and structure, it can be observed an increase in the Pearson coefficient relative to previous correlations. Furthermore, the hardness depends also on aspect ratio and solidity. This means that hardness increases for elongated particles with a non-spherical shape, while at the same time the inhomogeneity of this mechanical properties decreases, due to a better dispersion of particles across the 3D network of basic mix.

5.5.2 – INFLUENCE OF ROUGHNESS IN PIN-ON-PAD TEST

As done in previous chapters, the influence of roughness for pin-on-pad test was investigated. For this purpose, five standard tests were applied on pad T2. Table 5.10 shows the roughness parameters and friction coefficients. The starting roughness was modified in order to be in the range 0.4-0.6 and to observe the fluctuation of friction in this narrow range. As done for the other systems, both final and initial factors were considered together with the ratio R_{aF}/R_{aI} and the differences between final and initial value of each parameter.

Table 5.10: Standard test on T2 pads and relative surface roughness parameters.

T2	COF	DEV.ST	R_{aI}	R_{skI}	R_{kuI}	R_{aF}	R_{skF}	R_{kuF}	R_{aF}/R_{aI}	ΔR_a	ΔR_{sk}	ΔR_{ku}
A	0.572	0.004	0.50	0.38	4.57	0.40	-0.43	13.08	0.80	-0.10	-0.81	8.51
B	0.302	0.004	0.54	1.92	12.17	0.17	-0.05	3.65	0.31	-0.37	-1.97	-8.52
C	0.31	0.008	0.56	0.26	4.44	0.21	0.21	3.61	0.38	-0.35	-0.05	-0.83
D	0.563	0.007	0.48	1.14	6.89	0.50	0.27	10.95	1.03	0.02	-0.87	4.06
E	0.497	0.015	0.42	0.09	3.74	0.37	-0.58	9.69	0.87	-0.06	-0.66	5.96

Figure 5.23 shows two images of tribological trace, where it is possible to observe the formation of a significant amount of layer at interface. It does not result homogeneous, as found for carbon based pad, but it covers the majority of trace surface. The image obtained in polarized light (Figure 5.23b) highlights the overlap of titanate on the surface, reducing the contact basic mix – pin and suggesting a tribological behaviour dominated by the contact of titanate with steel of pin.

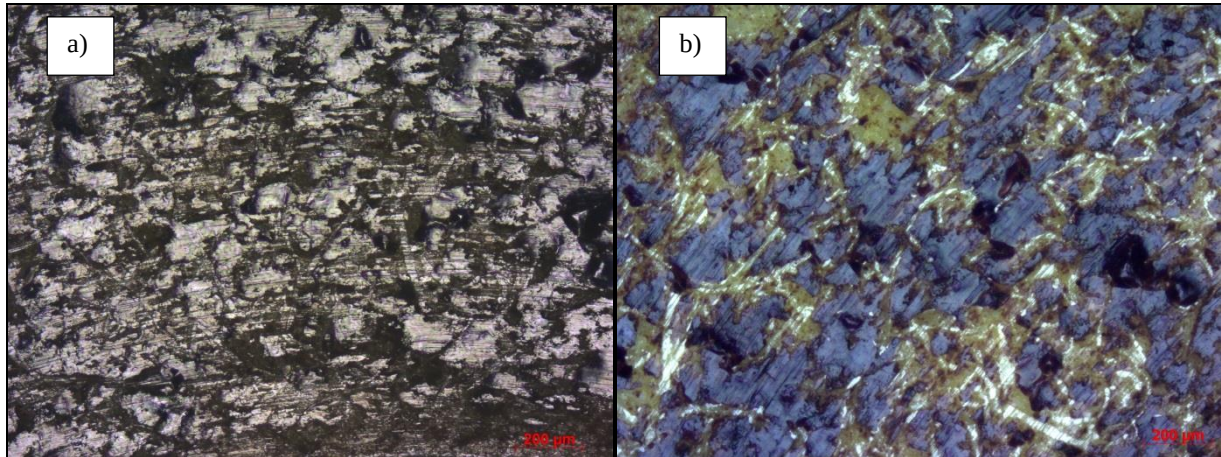


Figure 5.23: Optical images of tribological trace for sample T2 after test A obtained in: a) light field; b) polarized light.

Pearson coefficient indicates a linear proportionality of COF to $R_{ku}F$ and R_aF , indicating an influence of the final surface roughness and texture on friction, as already found for carbon based pads, probably because of the variation of the layer generated at interface¹⁵³. Although the starting roughness was modified to have a narrow range, the final roughness ranges between 0.17 and 0.50, which represents a wide fluctuation. The linear proportionality with friction can be motivated by the deformation of asperities during surfaces in relative motion, which increases the asperity plasticity¹¹⁸. In the case of titanate, this change generates a higher friction at interface, due to a dominant contact of steel with titanate layer. Consequently, the increase of friction in function of $R_{ku}F$ can be explained by the deformation of asperities during the tribological test. An increase in $R_{ku}F$ means a decrease in the asperities density at interface with a consequent lower real area of contact and higher friction. This hypothesis suggests that the tribological behaviour of titanate-based pads is similar to both basic mix and carbon based pads. In the basic mix, the friction mainly depends on the final roughness, and its variation can be described using the ratio R_aF/R_aI , which means a dominant effect of the final real area of contact with respect to the surface texture. In the carbon based pads, the dominant mechanism is the formation of tribofilm at interface, which mainly depends on the surface texture. In the case of titanate, both the mechanisms are present because at interface a non-homogeneous tribofilm is generated, with consequent contact of pin against this layer and at the same time the deformation of its asperities is a dominant factor for friction coefficient. This synergetic effect of surface roughness and texture derives from a linear proportionality between the final values of R_a and R_{ku} , probably observed in this case thanks to the narrow range of starting roughness investigated. However, the resulting friction has an average value of 0.45 with a standard deviation of 0.13, showing that the combined effect previous defined makes wider the COF fluctuation, respect the case of carbon where the average friction was 0.21 with standard deviation of 0.02 for an even wider range of starting roughness respect this case. To further verify the results obtained by Pearson coefficient, a PCA was applied on data shown in Table 5.10. Figure 5.24 shows the relative loading plot, in which all the previous considerations are confirmed. The friction coefficient variance coincides with R_aF/R_aI , ΔR_a and the final values of R_a and R_{ku} (light blue circle in Figure 5.23a), while it results inversely proportional to R_aI . The PCA

highlights a possible correlation between the COF fluctuation and ΔR_{sk} , but it is not supported by the relative Pearson coefficient, which is lower than 0.5. Based on this PCA, some parameters can be removed in order to analyse the influence of R_a and R_{ku} , focusing the attention also on what kind of parameter better explains the COF variance. Reducing the data matrix, the resulting loading plot shows that the main parameters affecting the COF are ΔR_a or $R_a F/R_a I$ and $R_{ku} F$ (green circle in Figure 5.23b). In order to compare this investigation with the previous ones, the ratio $R_a F/R_a I$ was selected together with $R_{ku} F$ to obtain a formula of COF in function of roughness parameters. Thus, a partial least square regression (PLS) was applied obtaining the formula 5.3, which shows a dominant influence of ratio $R_a F/R_a I$ on the COF value. The fluctuation associated to the COF obtained by formula 5.3 is equal to ± 0.02 .

$$5.3 - COF = 0.173 + 0.211 \frac{R_a F}{R_a I} + 0.016 R_{ku} F$$

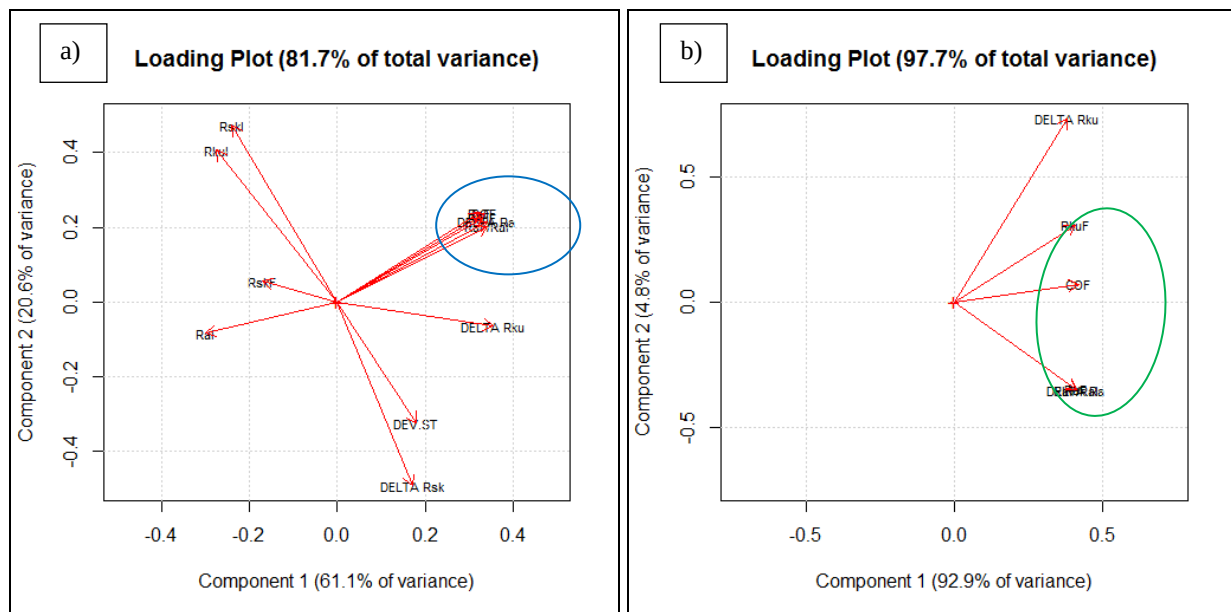


Figure 5.24: Loading plot of the two PCA (a and b) applied on roughness data relative to pad T2.

In order to verify the validity of equation 5.3, another standard test was applied on sample T2 and the experimental and calculated frictions were compared (Table 5.11). The difference between experimental and calculated value is 0.010, lower than the fluctuation of PLS formula 5.3, confirming its validity in the prediction of the friction coefficient in the range investigated.

Table 5.11: Test F on sample T2.

T2	COF	DEV.ST	$R_{ku} F$	$R_a F/R_a I$	COF CALC.	Δ
F	0.526	0.007	8.25	0.92	0.516	0.010

To further confirm the previous correlation between friction and roughness, other two tests were performed on sample T1, which is the most significant different titanate analysed. Table 5.11 shows the parameters relative to test G and H performed on T1, and the resulting friction values with respect to the previous correlation of linear proportionality with $R_a F/R_a I$ and $R_{ku} F$. Thus, the roughness parameters must be considered in order to correctly compare the samples analysed, also due to the wider fluctuation of COF for titanate based pads respect carbon based pads.

Table 5.11: Test F on sample T2.

T1	COF	DEV.ST	R _a I	R _{sk} I	R _{ku} I	R _a F	R _{sk} F	R _{ku} F	R _a F/R _a I
G	0.465	0.015	0.47	-0.08	5.47	0.21	0.65	6.81	0.45
H	0.515	0.022	0.58	-0.65	6.58	0.29	-0.84	10.50	0.51

5.5.3 – COMPARISON OF PIN-ON-PAD TESTS

Based on previous results, the standard test was applied on all the samples modifying the initial roughness in order to start with R_a in the range 0.4-0.5 μm . Figure 5.25 shows the comparison between experimental results and the theoretical value of friction relative to sample T2 at the same roughness conditions, calculated by equation 5.3. The values relative to sample T2 must be considered affected by a fluctuation of 0.02 due to the previous model, then the sample T8 can be considered similar as tribological behaviour to sample T2. In order to compare the titanate samples, the difference between their friction and the calculated one using sample T2 must be considered. Based on this comparison, the samples ranking is: $T7 < T4 < T2 < T8 < T1 < T9 < T6 < T3 < T5$. This order is quite different from the one observed for powder titanates, then probably different material properties affect the tribological behaviour of pads.

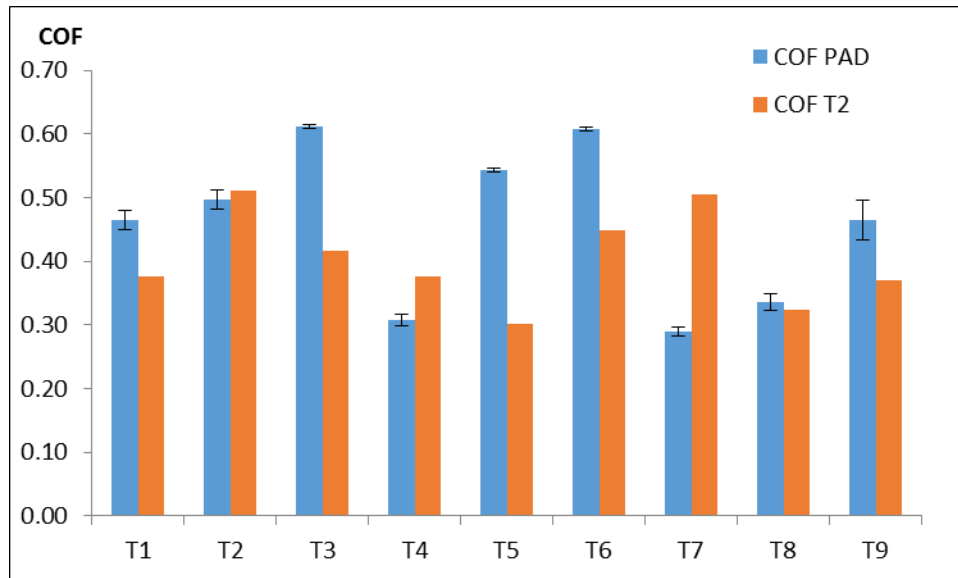


Figure 5.25: Comparison of friction coefficient for titanate based pads.

The Pearson coefficient was calculated considering all the structural and morphological parameters found by chemico-physical characterization of powders and pads. The results highlight a direct proportionality between friction and hardness of composites (Pearson coefficient 0.74), and at the same time the COF fluctuation is directly correlated with the inhomogeneity of pad hardness (Pearson coefficient 0.72). Furthermore, removing from the data matrix the sample T1, the friction of composites results correlated also with particle aspect ratio and roundness. Thus, the shape of particles directly affects the friction of titanate-based pad because it changes the composite hardness. Then, to reduce the friction of the composite, a titanate with elongated particles should be used as filler, while it must be considered that replacing the whisker-like sample with a titanate of spherical-like shape the resulting friction and hardness of the composite would be significantly lower.

5.5.4 – INFLUENCE OF ROUGHNESS ON WEAR BALL-ON-PAD TEST

Based on previous studies on the effect of roughness in ball-on-pad test for carbon based composite, some experiments were performed on sample T1 (Table 5.12). The starting roughness was reduced at value $\leq 1 \mu\text{m}$ to measure the wear constant K fluctuation in a narrow range of roughness. Results show similar values for both the wear constants, K and K', which have a standard deviation of 0.03 ($10^{-4} \text{ mm}^3/\text{Nm}$). Thus, starting from roughness $\leq 1 \mu\text{m}$, the difference in wear constant is negligible and all the composites can be compared without considering the roughness.

Considering the friction coefficient, it results directly proportional to the max depth of wear track and to the wear volume (Pearson coefficient 0.96 and 0.94 respectively). Thus, it can be supposed that the friction behaviour can be correlated to the amount of debris generated at interface, as already found for carbon materials. Moreover, another similarity with carbon based pads is the direct proportionality between COF and R_{kuI} , probably due to the ploughing mechanism at interface. The wear constant, conversely, does not depend on surface texture, but on the starting roughness, with a direct proportionality (Pearson coefficient 0.84). However, as affirmed before, the fluctuation of wear constant in function of starting roughness can be neglected and the resulting K value can be considered as affected by an error of ± 0.03 ($10^{-4} \text{ mm}^3/\text{Nm}$).

Table 5.12: Data on wear test of T1.

COF	MAX DEPTH (μm)	VOLUME (mm^3)	DISTANCE (m)	K ($10^{-4} \text{ mm}^3/\text{Nm}$)	K' (10^4)	R _{aI}	R _{skI}	R _{kuI}
0.405	65.18	1.77	1500	1.18	1.01	0.68	0.43	4.01
0.428	84.66	2.53	2250	1.12	0.97	0.61	0.82	5.30
0.436	104.31	3.56	3000	1.19	1.02	0.81	-0.33	5.63

5.5.5 – COMPARISON OF BALL-ON-PAD TESTS

Table 5.13 shows the data on wear test of all samples performed at 10 N and 0.20 ms^{-1} with a sliding distance of 1500 m.

All samples show a higher friction coefficient with respect to the polymer matrix, apart from the sample T8, while the wear constant has a wide dispersion and can be similar or significantly higher than matrix one. Considering both the wear constants, the samples can be ranked as follow: T3 < T1 < T2 < T5 < T4 < T8 < T9 < T6 < T7. Thus, the majority of samples shows a higher wear resistance with respect to the T1 sample.

Table 5.13: Data on wear test of all carbon based composites.

SAMPLE	COF	MAX DEPTH (μm)	VOLUME (mm^3)	H (MPa)	K ($10^{-5} \text{ mm}^3/\text{Nm}$)	K' (10^{-5})
MATRIX	0.337	23.69	0.38	844	1.27	1.07
T1	0.405	65.18	1.77	858	11.80	10.13
T2	0.442	52.95	1.82	829	12.10	10.03
T3	0.469	81.82	2.40	858	16.00	13.73
T4	0.462	61.30	1.58	816	10.53	8.60
T5	0.471	63.90	1.68	888	11.20	9.94
T6	0.352	14.58	0.26	831	1.70	1.41
T7	0.403	15.42	0.21	751	1.40	1.05
T8	0.296	29.45	0.53	736	3.53	2.60
T9	0.366	18.68	0.28	807	1.87	1.51

The friction coefficient and the relative wear constant are directly correlated with the pad hardness, then a softer material shows lower friction and higher wear resistance. Supposing that the friction behaviour is dominated by the amount of debris generated, as found for carbon, a softer material loses less volume with a consequent COF more similar to basic mix friction. This is probably due to the poor amount of titanate at interface, that behaves as an abrasive. This observation is supported by the optical analysis of wear trace, done by 3D optical microscope and shown in Figure 5.26. Comparing the samples T2 and T8, in the first, the amount of titanate at interface is significantly higher than the one of T8. In fact, it is possible to observe a rough surface for sample T2 (Figure 5.26a), while the trace of sample T8 seems smooth, without the inhomogeneous titanate layer usually generated and observed in this study.

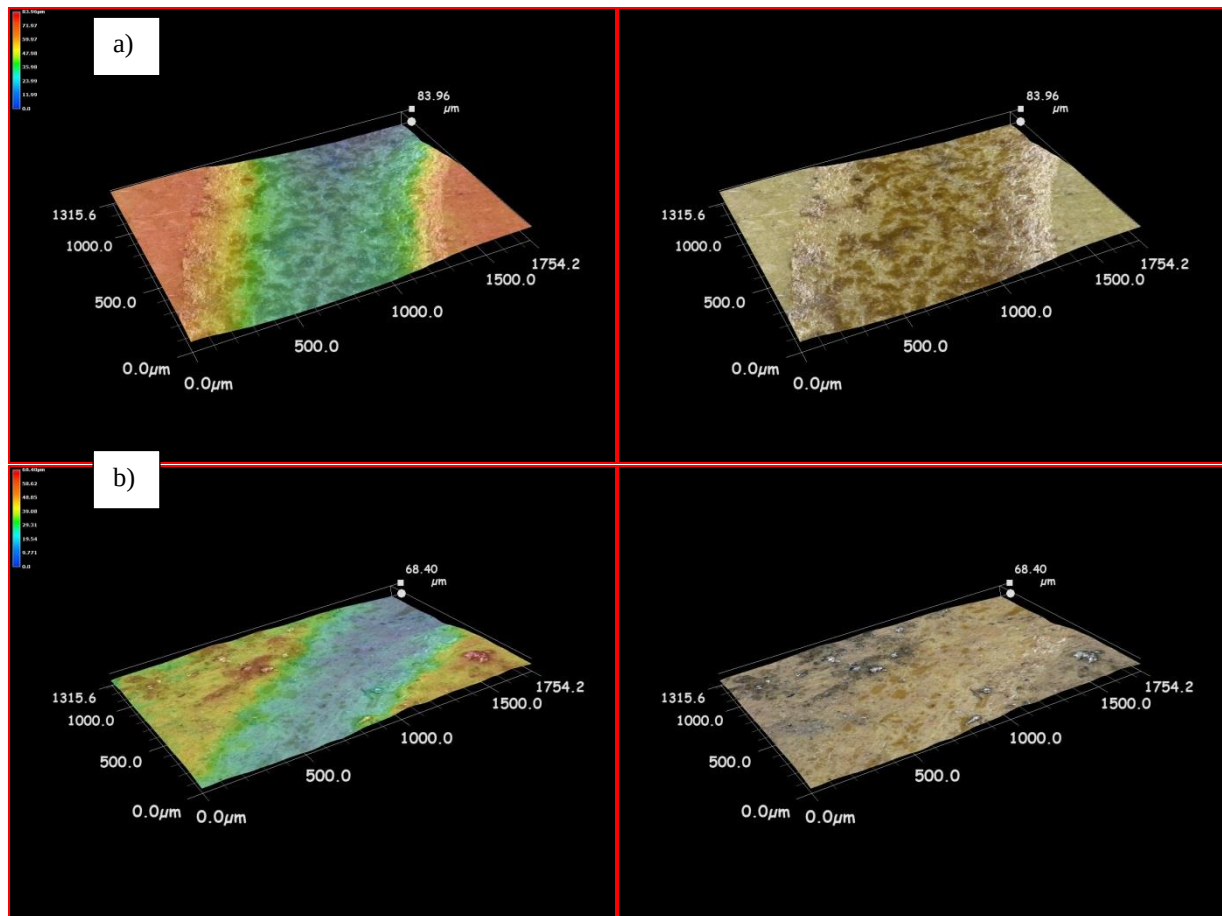


Figure 5.26: Comparison of wear trace by 3D optical microscope: a) sample T2; b) sample T8.

Figure 5.27 shows the comparison of K' wear constant values. Note that the last four samples are significantly different from the others, since they show a lower K' , then a higher wear resistance. By the statistical analysis, no one of morphological or structural features can give an explanation of this difference except for the correlation with the hardness. However, considering the data obtained by FTIR, some qualitative correlations can be supposed. The first three samples, which contain just potassium hexatitanate and no significant amount of other impurities, have the lowest wear resistance and highest hardness. Samples T4 and T5, which contain anatase, are slightly different from the previous ones, while the four samples in which is possible to observe the bending and stretching signal of hydroxyl groups show the highest wear resistance and lowest hardness. Based on this observation, it can be supposed that the interaction among titanate particles and basic mix concerns the non-binding oxygen on the particles surface. Due to the presence of adsorbed water between titanate layers or on the particles surface, the coordination with the phenolic resin and

Kevlar fibres is significantly reduced, with a consequent decrease of hardness, wear constant and friction.

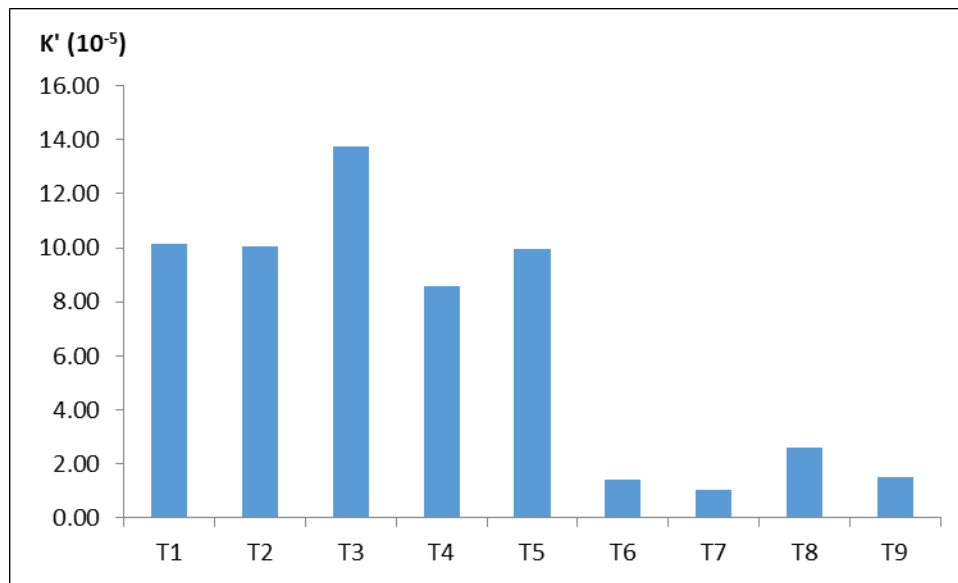


Figure 5.27: Comparison of K' obtained for titanate based composites.

5.6 – CONCLUSION

A system of nine potassium hexatitanate of different size and shape was investigated by chemico-physical and tribological characterization.

The friction behaviour of titanate powders mainly depends on the crystalline structure and on the ability to abrade the steel counterface, generating iron oxide. The friction coefficient increases if the width of peak [110] increases, which means a lower crystallite dimension on the direction [110].

This direction corresponds to the galleries which gives the well-known tunnel-like structure of titanate materials. Thus, lower the length of these galleries higher the friction coefficient. Moreover, the friction is directly proportional to the interplanar distance along [200] direction, then the crystalline structure can be subjected to a higher compression. Results suggest that this higher compressibility reduces the abrasion of steel, with a consequent less amount of iron oxide at interface and a higher friction. The morphology does not show significant correlations with friction, while its amplitude is directly proportional to the aspect ratio. Thus, for elongated particles the friction coefficient shows a major fluctuation. Comparing samples with similar shape, it is possible to observe also an inverse proportionality between COF and particle size, due to an increase in the particle density at interface and a major contact steel-titanate.

When the titanate materials are incorporated in a polymer matrix, they increase the pad density with respect to the value of the basic mix and they change the hardness, in an amount depending on their particles shape, probably because of a different interaction between titanate particles and the polymer matrix. The hardness increases if the roundness decreases, and this feature is responsible also for the friction behaviour, because the COF is directly proportional to the hardness. For all the samples except the whisker-like titanate, the hardness is correlated with the roundness and aspect ratio of particles, and then the resulting friction can be considered as affected by particles shape through its influence on the pad hardness.

Also the wear constant K depends on hardness and the hardest mono-component pad shows the highest wear constant, then the lowest wear resistance. Thus, a titanate with spherical-like shape would decrease the hardness of pad and increase its wear resistance.

CHAPTER 6 – ALUMINA

6.1 – INTRODUCTION

Alumina is a ceramic material known since the XIX century and it is a raw material for the ceramic industry. Henri Sainte-Claire Deville performed the first commercial extraction of alumina (Al_2O_3) in 1854, while Karl Josef Bayer invented the process for the preparation of pure Al_2O_3 , known as the Bayer Process, in 1888¹⁶⁹. This invention allowed a significant reduction of cost for the extraction of metallic aluminium. Bayer discovered that $\text{Al}(\text{OH})_3$ precipitated from alkaline solution (sodium hydroxide as example) was crystalline, easy to filter and free from impurities. By calcination of the aluminium hydroxide, the pure Al_2O_3 is obtained. The thermodynamic stable form of alumina is the α -alumina, but several other forms are possible, generally named transitional alumina¹⁷⁰. They have wide applications in catalysis and adsorption technologies, as the Claus process¹⁷¹ for the production of sulphur from H_2S in the refineries or the refining of Fischer Tropsch syncrude¹⁷². The formation of transitional alumina occurs between the thermal dehydroxilation of the aluminium hydroxides (300°C - 600°C) and the crystallization into α - Al_2O_3 at 1100°C ¹⁷³.

Pure alumina is also used as biomaterial since the early 1970s, especially in the arthroplasty of the hip, one of the most successful surgeries¹⁷⁴.

In the tribological field, alumina is known as strong abrasive, which slightly increases the friction of composites and significantly improves their wear resistance. Gregory Sawyer et al.¹⁷⁵ used alumina nanoparticles as filler for PTFE (polytetrafluoroethylene) which is a widely used solid lubricant. They observed an increase of friction, with respect to the unfilled samples, and a monotonic increase of the wear resistance by increasing the filler concentration from 0 to 20%wt. In another study, the tensile strength, flexural strength, impact energy and hardness of PMMA (polymethylmethacrylate) based nanocomposites were gradually improved by increasing the volume fraction of the nanoparticles¹⁷⁶. At the same time, the friction coefficient and weight loss were both reduced by increasing the concentration of alumina nanoparticles. Almaslow et al.⁶³ observed a similar behaviour also in semi-metallic brake friction materials, but the major system complexity and multiple variables affecting the tribological behaviour allow a constant friction only until 30% as volume fraction.

The focus of this chapter is the correlation of the tribological behaviour with material properties studying alumina raw materials with different size and shape. All of them are commercially available, used or under testing for brake pad formulation. In next section, their physico-chemical characterization is described and compared with tribological results, using the OVAT and multivariate analysis.

6.2 – MORPHOLOGY OF RAW MATERIALS

Six alumina raw materials were selected for this study (Table 6.1).

Table 6.1: Samples and relative description.

SAMPLE	DESCRIPTION
A1	Ellipsoidal alumina
A2	Irregular plate like alumina1
A3	Irregular plate like alumina2
A4	Plate-like alumina
A5	Flakes alumina
A6	Coarse alumina

Their particle size and shape were analysed by SEM. The representative images of all the samples are shown in Figure 6.1. Sample A6 can be displayed in Figure 6.1f at different magnification because of its particle size, significantly higher than that of other samples.

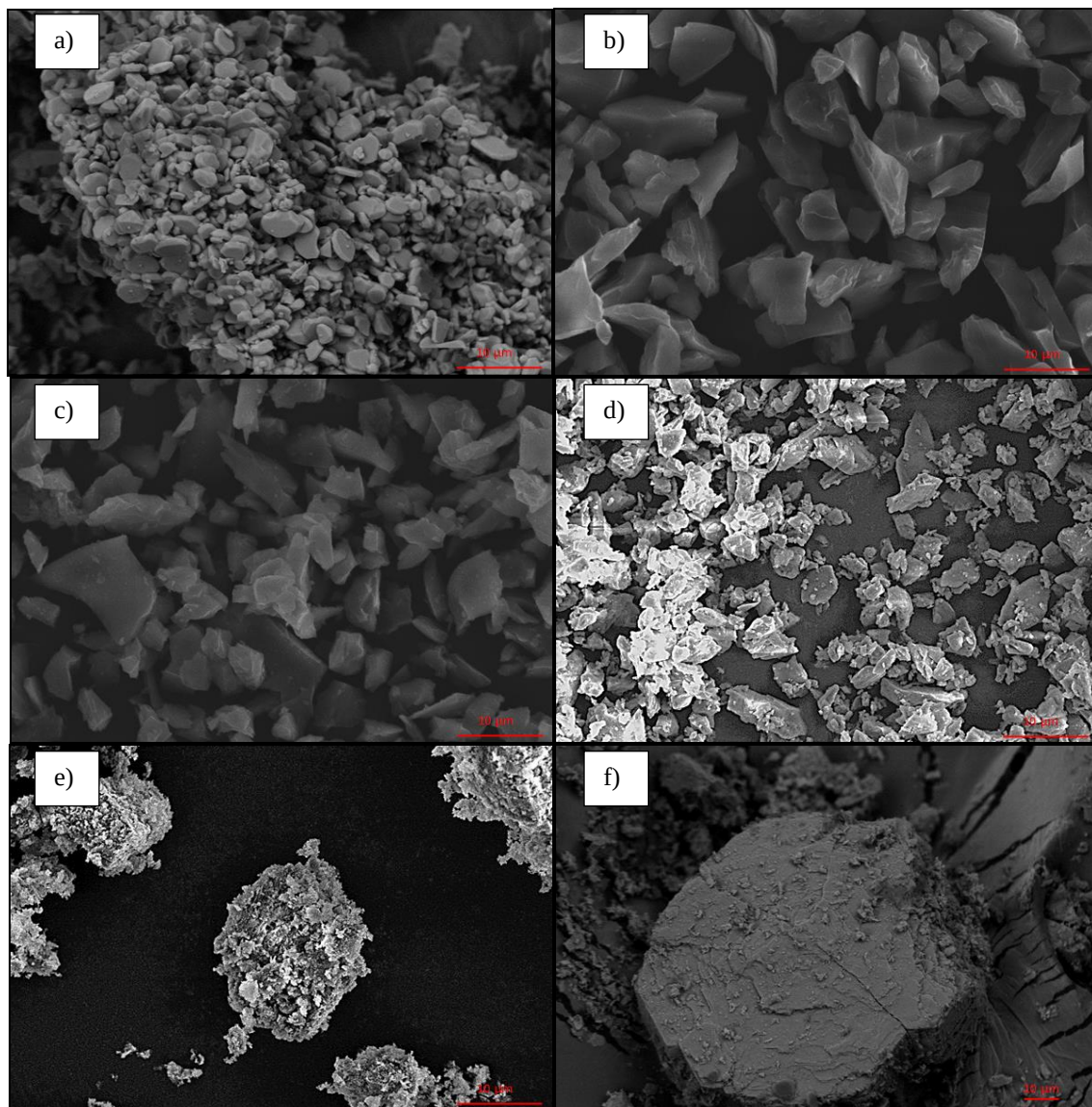


Figure 6.1: Scanning electron microscope images of alumina samples: a) A1; b) A2; c) A3; d) A4; e) A5; f) A6.

As described in Materials and Methods chapter, several parameters were investigated to describe the particles morphology. In the case of alumina samples, which main parameters are summarised in Table 6.2, the particle size distribution is narrower with respect to the previous systems. The Feret's diameter is comparable with the D50 resulting from granulometric analysis. All the samples show a slightly elongated shape and a wide range of roundness, while the solidity is similar among samples. The alumina A5 and A6 show the widest range of particle size distribution, with the difference that A6 is constituted by particle of different size, while A5 shows flake-like particles, which generate aggregates, and the adhesion forces are strong enough to extend the particle size distribution, as found by granulometric analysis.

Table 6.2: Morphological parameters of natural graphite samples.

SAMPLE	A (μm^2)	P (μm)	F (μm)	AR	R	C	S	D10% (μm)	D50% (μm)	D90% (μm)
A1	5.27	8.39	3.09	1.45	0.72	0.86	0.95	1.15	6.50	25.50
A2	70.43	34.55	13.94	2.25	0.53	0.68	0.91	3.10	10.79	18.95
A3	30.22	21.44	8.30	1.80	0.61	0.74	0.91	1.94	6.24	12.37
A4	9.17	11.13	4.27	1.80	0.62	0.74	0.92	0.47	3.27	6.69
A5	314.14	56.62	20.39	1.49	0.70	0.75	0.91	2.19	37.10	84.61
A6	609.76	64.17	22.97	1.54	0.69	0.81	0.93	2.72	29.82	67.94

6.3 – COMPOSITION AND STRUCTURE

The study of materials composition was performed using EDS as a preliminary analysis to investigate the presence of impurities, but in all the samples results show the presence of just oxygen and aluminium. Thus, the samples do not show the presence of any impurity over the 1%wt of content

6.3.1 – X-RAY DIFFRACTION ANALYSIS

Alumina is known as mineral with the name of corundum and it has a hexagonal (rhombohedral) crystal system constituted of aluminium atoms, each surrounded by six oxygen atoms. This structure can be visualized as layers of hexagonal close-packed oxygen atoms with small Al atoms in two-thirds of the octahedrally coordinated holes between the oxygen atoms^{177,178} (Figure 6.2). 12 aluminium atoms and 18 oxygen atoms constitute the unit cell. Its dimensions are: $a = b = 4.7588 \text{ \AA}$ and $c = 12.992 \text{ \AA}$ ¹⁷⁹.

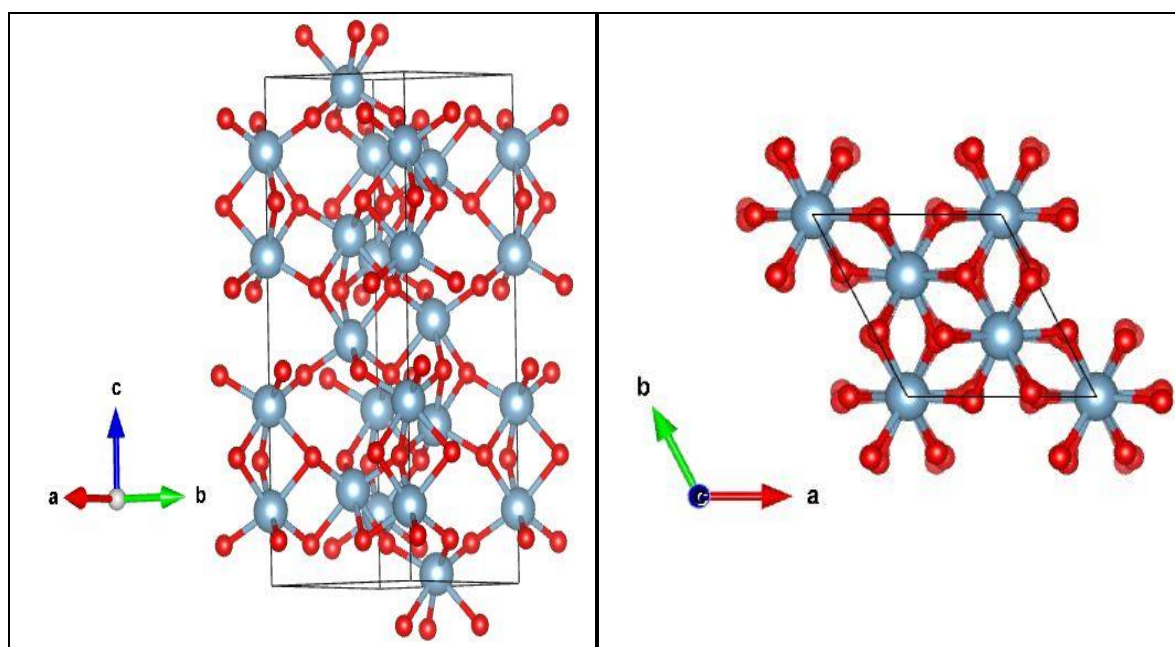


Figure 6.2: Corundum structure obtained by Vesta software.

On the samples analysed, the main peak in the x-ray diffraction pattern concerns the reflection of plane [104], but also the peaks [113] and [116] have a high relative intensity, as reported by Feret et al.¹⁷⁸. All the samples show a similar pattern (Figure 6.3), with no significant differences in the

number of signals, except sample A4, which shows a poor intense peak around 27°, attributable to rutile impurity.

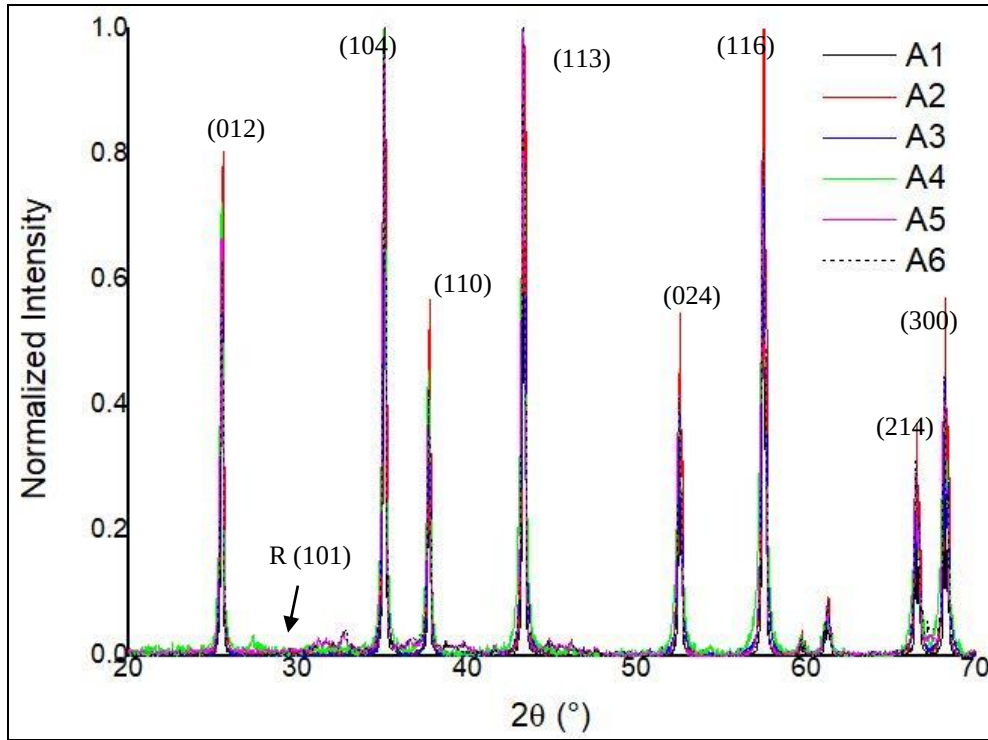


Figure 6.3: X-ray diffraction powder pattern for alumina samples.

The fit of x-ray pattern was performed using a Lorentzian function. The interplanar spacing, lattice parameters and crystallite dimension were calculated using formulas 6.1-6.3 respectively.

$$6.1 - d = \frac{\lambda}{2 \sin \theta}$$

$$6.2 - \frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

$$6.2.1 - [300] \ a = 2d\sqrt{3}$$

$$6.2.2 - [104]c = 4 \sqrt{\frac{3d^2 a^2}{(3a^2 - 4d^2)}}$$

$$6.3 - L = \frac{0.9\lambda}{FWHM \cdot \cos \theta}$$

Table 6.3 shows the results of pattern fitting for the three more intense peaks, concerning the reflection of plane [104] [113] and [116]. Results do not show any significant difference among samples in terms of peak position or interplanar distance, while the intensity and width of peaks are slightly different.

Table 6.3: Normalized data of x-ray pattern fitting relative to the main peaks [104], [113] and [116] of alumina samples.

SAMPLE	PEAK (104)	FWHM (104)	I (104)	D (Å) (104)	PEAK (113)	FWHM (113)	I (113)	D (Å) (113)	PEAK (116)	FWHM (116)	I (116)	D (Å) (116)
A1	35.11	0.13	0.20	2.554	43.32	0.13	0.18	2.087	57.46	0.15	0.19	1.602
A2	35.16	0.18	0.27	2.550	43.37	0.22	0.35	2.085	57.52	0.23	0.32	1.601
A3	35.13	0.17	0.25	2.552	43.34	0.21	0.31	2.086	57.49	0.26	0.29	1.602
A4	35.09	0.22	0.35	2.555	43.29	0.27	0.41	2.088	57.44	0.35	0.38	1.603
A5	35.08	0.17	0.28	2.556	43.28	0.19	0.31	2.089	57.44	0.24	0.30	1.603
A6	35.11	0.17	0.27	2.554	43.32	0.18	0.30	2.087	57.47	0.23	0.29	1.602

The same situation can be observed on other three peaks, relative to reflection of plane [012], [110] and [300] (Table 6.4).

Table 6.4: Normalized data of x-ray pattern fitting relative to peaks [012], [110] and [300].

SAMPLE	PEAK (012)	FWHM (012)	I (012)	D (Å) (012)	PEAK (110)	FWHM (110)	I (110)	D (Å) (110)	PEAK (300)	FWHM (300)	I (300)	D (Å) (300)
A1	25.54	0.11	0.11	3.485	37.74	0.13	0.07	2.382	68.17	0.15	0.08	1.374
A2	25.58	0.15	0.19	3.479	37.78	0.15	0.13	2.379	68.23	0.27	0.20	1.373
A3	25.55	0.14	0.16	3.483	37.76	0.18	0.11	2.380	68.21	0.30	0.17	1.374
A4	25.52	0.19	0.23	3.488	37.72	0.23	0.17	2.383	68.14	0.40	0.24	1.375
A5	25.51	0.16	0.17	3.489	37.71	0.18	0.12	2.383	68.15	0.27	0.18	1.375
A6	25.53	0.15	0.16	3.486	37.73	0.19	0.12	2.382	68.18	0.27	0.18	1.374

Using data of peaks [104] and [300], the lattice parameters and the crystallite dimension along a direction were calculated. Furthermore, the lattice parameters allowed the calculi of the cell volume and then the theoretical density of each sample could be obtained. Data shown in Table 6.5 are in agreement with the values reported in literature¹⁷⁸.

Table 6.5: Structural parameters obtained for alumina samples.

SAMPLE	a (Å)	c (Å)	V (Å ³)	Theoretical Density	L _a (nm)
A1	4.7613	13.0110	255.44	3.977	652.51
A2	4.7576	12.9882	254.60	3.990	355.38
A3	4.7588	13.0036	255.03	3.983	316.64
A4	4.7631	13.0195	255.81	3.971	237.97
A5	4.7625	13.0264	255.88	3.970	357.87
A6	4.7607	13.0121	255.40	3.978	348.82

All parameters were used as starting matrix for Principal Component Analysis. Based on the relative position of each variable in the loading plot, some of them were removed to simplify the system.

Figure 6.4 shows the loading and score plot obtained considering as variables the width and intensity of peaks [104] and [300], together with their interplanar distance. Furthermore, the lattice parameters and the crystallite dimension were considered in the PCA. The score plot (Figure 6.4b) highlights that samples A1 and A4 are significantly different from the others, mainly in terms of crystallite dimension. A4 contains rutile as impurity and shows the lowest crystallite dimension along one direction. A1 has a narrow peak relative to plane [300], significantly different with respect to the other samples, due to its high crystallite dimension L_a. The other four samples differ each other along one direction that can be mainly attributed to lattice parameters and interplanar distances. Moreover, the loading plot (Figure 6.4a) highlights an inverse correlation between D₃₀₀ and the theoretical density obtained from lattice parameters.

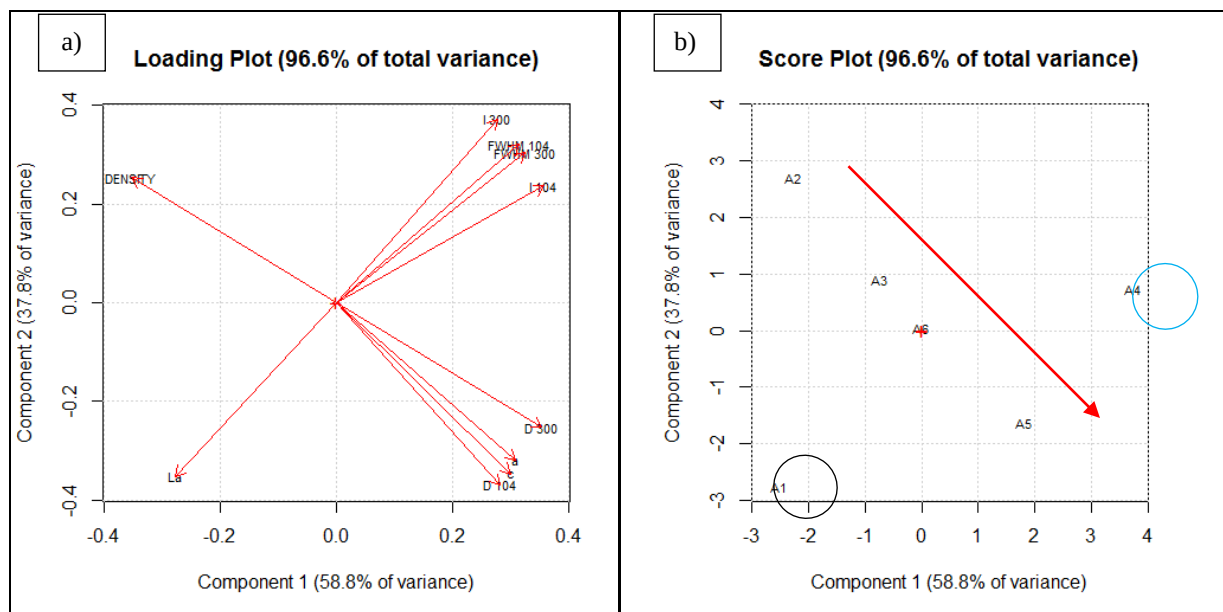


Figure 6.4: Principal Component Analysis of data matrix on x-ray diffraction: a) loading plot; b) score plot.

6.3.2 – RAMAN SPECTROSCOPY

Alumina has a structure constituted by aluminum atoms octahedrally coordinated with two layers of oxygen atoms. The irreducible representations¹⁸⁰ for the vibrational modes in the crystal are:

$$2A_{1g}+2A_{1u}+3A_{2g}+2A_{2u}+5E_g+4E_u$$

Since the unit cell has a centre of symmetry, all vibrations that are Raman allowed are infrared forbidden and vice versa. In particular, vibrations with symmetry A_{1g} and E_g are Raman active and infrared inactive while the A_{2u} and E_u vibrations are infrared active and Raman inactive. The other vibrations are inactive in both cases.

In literature, the Raman bands reported are seven, collocated respectively at 378, 418, 432, 451, 578, 645 and 751 cm^{-1} . The bands at 418 and 645 cm^{-1} are relative to A_{1g} vibration, in particular the first band represents an equal vibration on “a” and “c” axis, while the second one concerns a vibration parallel to “c” axis. Among the E_g vibrations, three of them can be assigned to the internal Al_2O_3 vibrations with a major movement on plane xy (ab), and they are the bands at 451, 578 and 751 cm^{-1} . Instead, the bands at 378 and 432 cm^{-1} correspond to vibrations of perimeter molecules in the crystal^{179,180}.

Figure 6.5 shows the Raman spectrum collected for sample A5, as example. The bands position are in agreement with the data reported in literature, apart from band at 477 cm^{-1} , which attribution is not clear. In addition, sample A1 shows a similar spectrum as A5, but with different relative intensity of bands. Due to the weak intensity of Raman signals for the other samples, comparable with noise in large extent, a complete characterization and further comparison of Raman spectra is not possible.

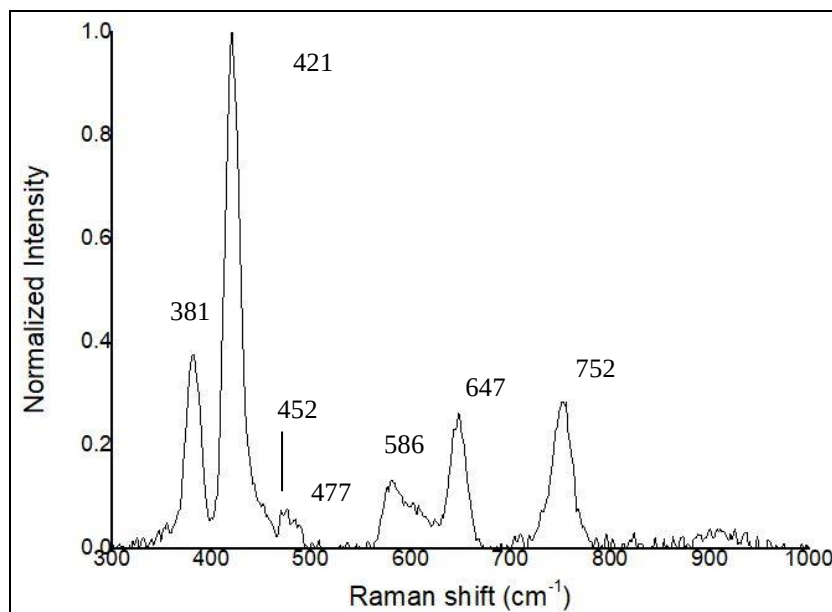


Figure 6.5: Raman spectrum of sample A5 reported as example.

6.3.3 – INFRARED SPECTROSCOPY

The IR active modes belong to the stretching of Al-O bonds. In the hexagonal structure of alumina, with the Al atoms octahedrally coordinated with six oxygen atoms, the IR active vibrations are the A_{2u} and E_u modes¹⁸⁰.

Figure 6.6 shows the IR spectra obtained for all alumina samples in the region 400-1600 cm^{-1} , while the region above is not reported due to the absence of signals. A5 and A6 samples have the main peak up-shifted with respect to all the others. Furthermore, sample A5 is the only one with signals above 1000 cm^{-1} .

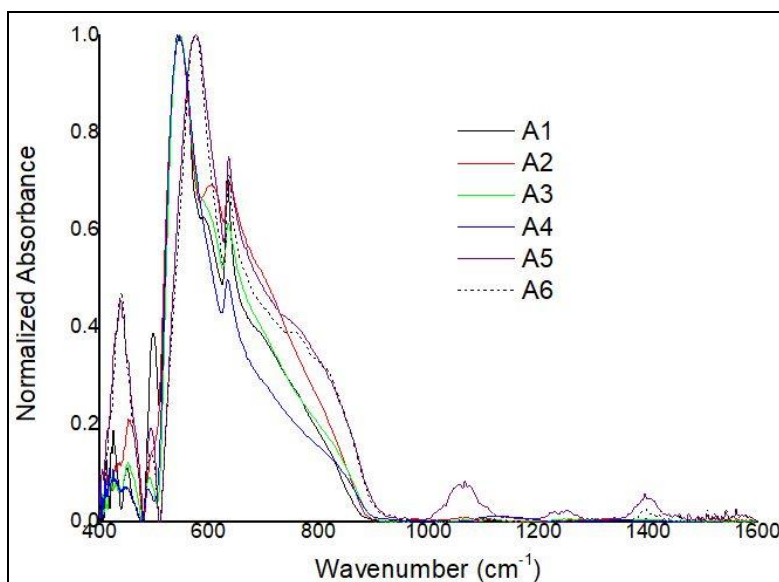


Figure 6.6: IR spectra of alumina samples in the region 400-1600 cm^{-1}

Figure 6.7 shows the spectra of sample A5 and A6 only the bands are located at the same positions of those reported by Boumaza et al.¹⁸¹, concerning α -alumina samples. The signal at 442 cm^{-1} is relative to the AlO_6 stretching modes, while the peak at 496 cm^{-1} can be attributed to the stretching

of AlO_4 ¹⁸². Thus, comparing also the x-ray diffraction data with literature, it is possible to suppose that samples A5 and A6 are $\alpha\text{-Al}_2\text{O}_3$.

The other signals are relative to stretching of AlO_6 (575 and 636 cm^{-1}), while the shoulder at 751 cm^{-1} can be assigned to AlO_4 . The sample A5 shows a band at 1064 cm^{-1} , which can be attributed to the symmetric and asymmetric bending of AlOH reported for boehmite (AlOOH)¹⁸¹, while the band at 1394 cm^{-1} can be ascribed to vibration of $\text{Al}=\text{O}$ ¹⁸³. The boehmite is commonly used as starting material to obtain the different alumina phases by heating boehmite powder in ambient atmosphere at the appropriate temperature¹⁸¹. Thus, it can be supposed that sample A5 was synthesized by boehmite and the reaction was not complete.

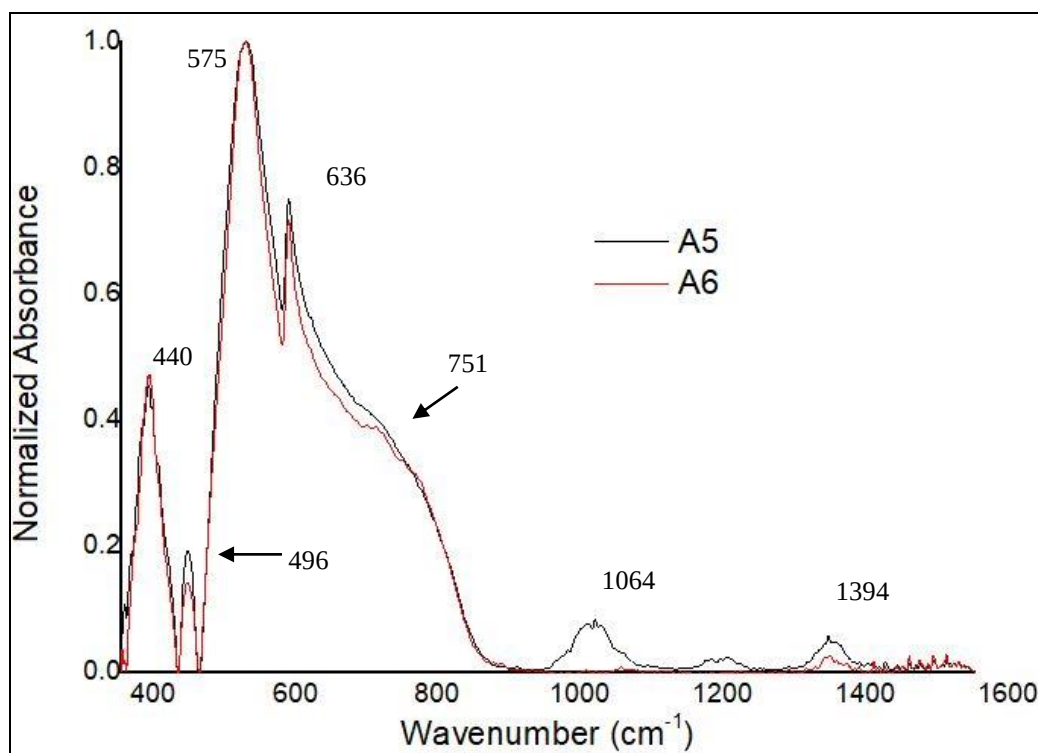


Figure 6.7: IR spectra of samples A5 and A6 in the region 400-16000 cm^{-1} .

Figure 6.8 shows the IR spectra of the other four alumina samples, which result quite similar each other in terms of peak positions. The main peak is downshifted with respect to previous samples. This probably derives from the different interplanar distance for several planes calculated by x-ray diffraction data. As reported for previous samples, the signals in the range 400-700 cm^{-1} are relative to stretching modes of bonds Al-O in both AlO_6 and AlO_4 . No significant differences can be observed in sample A4, in spite of the presence of rutile as impurity.

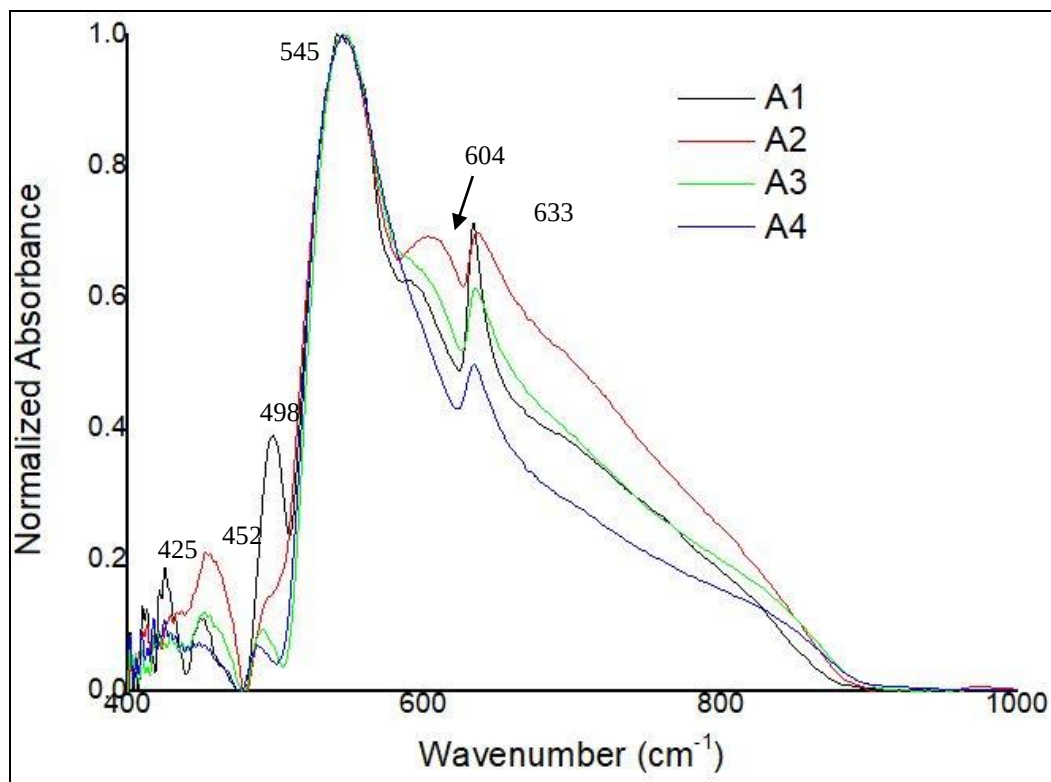


Figure 6.8: IR spectra of alumina samples A1-A4 in region 400-1000 cm^{-1} .

Infrared spectroscopy highlights a structural difference among samples, which is not correlated with significant differences in the x-ray diffraction data. Thus, it can be supposed that samples A1-A4 contains β -alumina, which is the only crystal phase with almost identical interplanar distance of α - Al_2O_3 , but it has a slight internal distortion in the structure¹⁷⁸.

6.4 – TRIBOLOGY OF POWDERS

Figure 6.9 shows the comparison of friction coefficient with the value of friction amplitude as error bar.

This parameter is calculated as the standard deviation of friction coefficient evolution during sliding in the steady state⁹⁹. All samples show an amplitude higher than 0.01, except sample A1 which has a stable friction coefficient at the steady state. The values of COF are similar or slightly lower with respect to the friction of steel against steel (~ 0.7). The observed change of colour of the powder during the tests, from white to grey, suggests the formation of iron oxide, probably due to the abrasion of steel surfaces, as confirmed by EDS analysis on the samples after tribological test. Thus, as found for titanates, also in this case the different amount of steel abrasion affects the general friction of alumina because the iron oxide reduces the overall COF.

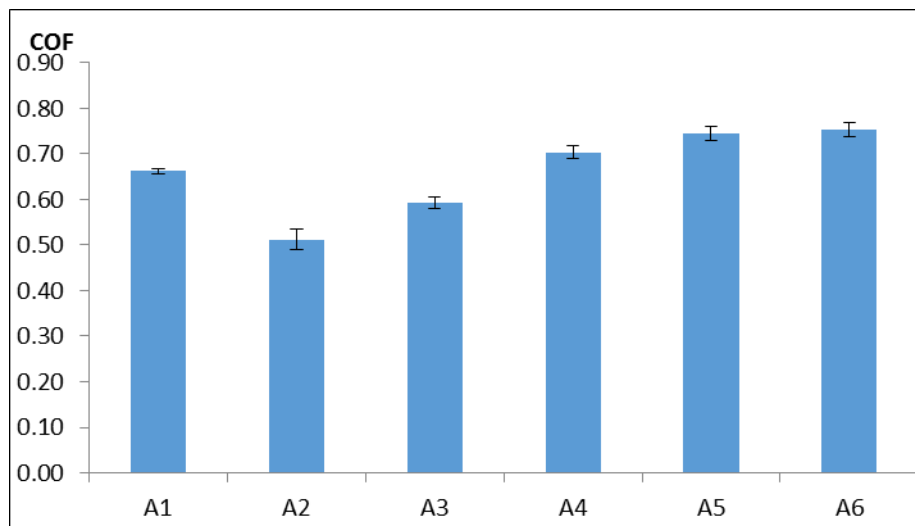


Figure 6.9: Comparison of friction coefficient values for all alumina samples.

6.4.1 – INFLUENCE OF MORPHOLOGY

The friction coefficient of alumina samples results affected by the particle aspect ratio (AR), which is inversely proportional to COF. The Pearson coefficient of this correlation is -0.83, but plotting COF in function of AR (Figure 6.10) the resulting graph does not show a linear inverse correlation.

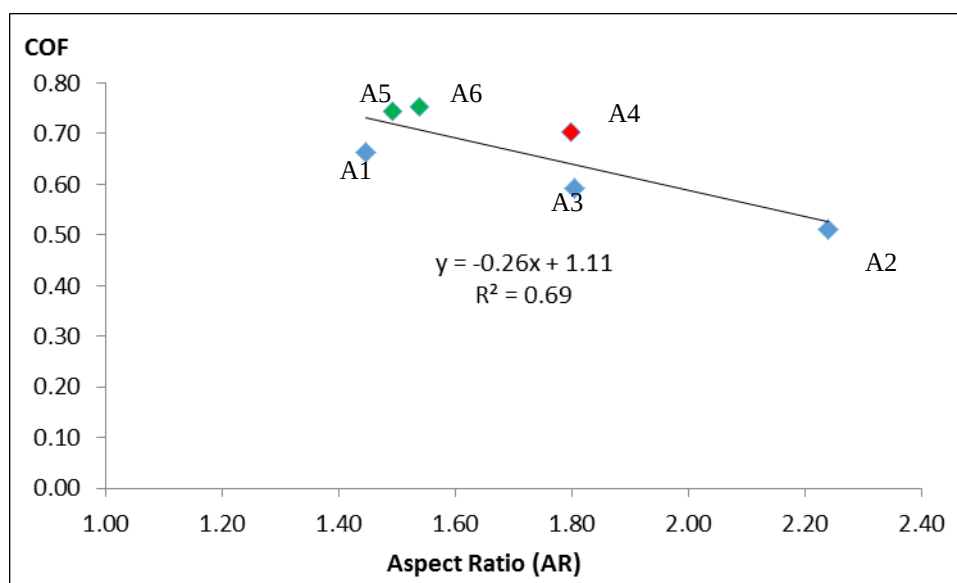


Figure 6.10: Plot of friction coefficient in function of particles aspect ratio.

A5 and A6 samples, constituted by α - Al_2O_3 , show the highest friction coefficient, followed by A4, which belong to the A1-A3 group in terms of structural features, as suggested from IR-spectra. However, A4 differs from the other three powders for the presence of rutile, which can be the reason of a major friction in spite of an aspect ratio similar to sample A3. In the case of A1-A3 samples, all probably containing β - Al_2O_3 , an inverse linear proportionality between COF and AR can be observed (Figure 6.11a). For the same three samples, a linear inverse influence of the average particle size can also be observed (Figure 6.11b).

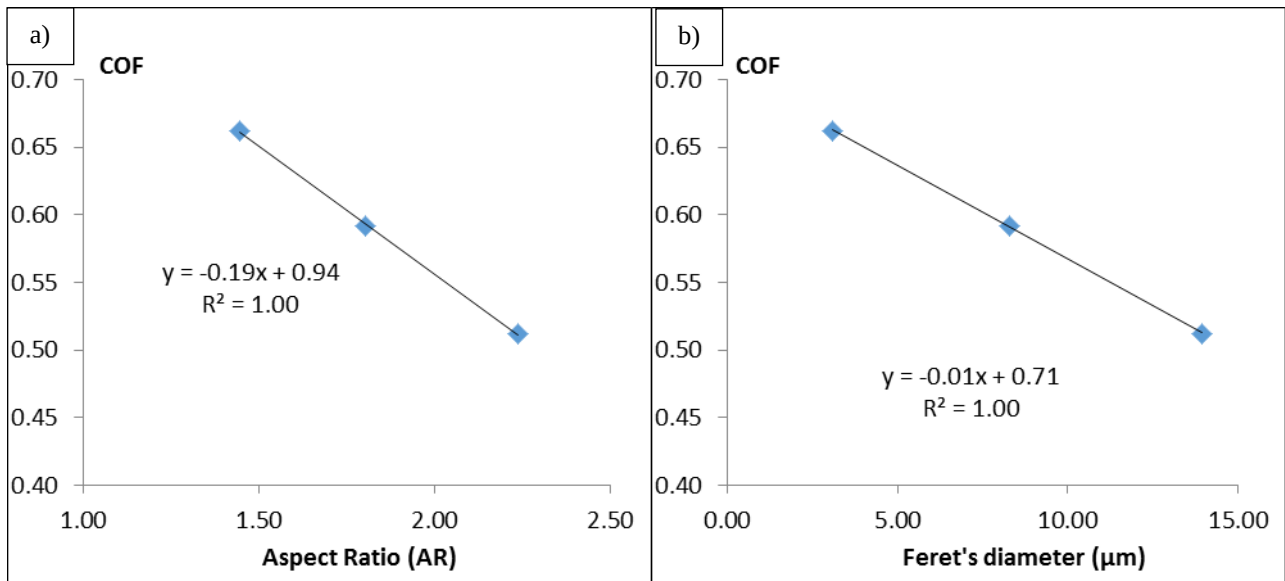


Figure 6.11: Friction coefficient of samples A1-A3 as a function of: a) aspect ratio AR; b) Feret's diameter F.

Assuming that friction decreases by increasing the content of iron oxide derived from abrasion, (as done for titanate), in alumina samples the friction coefficient decreases with the particle size and aspect ratio, probably because an elongated and bigger particle abrades the steel counterface more than a spherical particle.

Note that for samples A1-A3, the friction amplitude is directly proportional to particle size and AR, while inversely proportional to particle roundness. Thus, when the abrasion increases, the stability of steady state friction decreases. Figure 6.12 displays the friction coefficient amplitude as a function of aspect ratio and roundness.

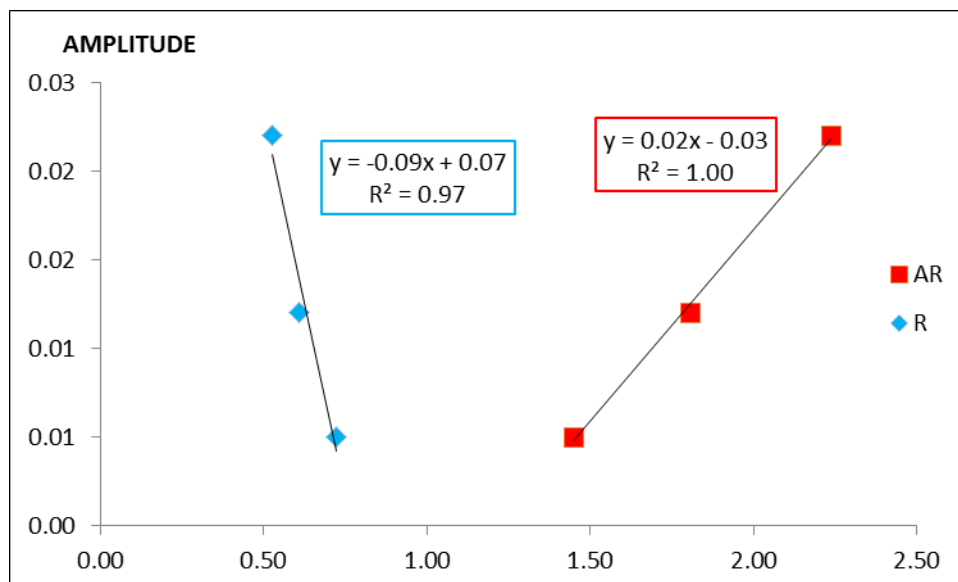


Figure 6.12: Friction coefficient amplitude as a function of aspect ratio and roundness.

The similar friction coefficient of samples A5 and A6 confirms the previous considerations, because they have practically the same particle shape and size, then the friction behaviour and relative abrasion mechanism must be similar. The only different sample is A4, probably due to the presence of rutile as impurity.

6.4.2 – INFLUENCE OF STRUCTURAL FEATURES

As observed in the previous section, the structure plays an important role in define the friction behaviour. Morphology results influence on friction only comparing samples with similar structural properties. Thus, it can be expected that some structural features have a dominant influence on friction behaviour for alumina samples.

Calculating the Pearson coefficient of structural parameters and friction (or its amplitude), results show a direct proportionality of the interplanar distance on friction coefficient. Furthermore, also the lattice parameters and the derived unit cell volume are directly proportional to COF. Supposing the dependence of friction on the amount of iron oxide generated by steel abrasion, results suggest that an alumina with a larger unit cell and interplanar distance less abrades the counterface. This probably derives from the higher compressibility of structure, as suggested for titanate samples in chapter 5.

Figure 6.11 reports the friction coefficient in function of unit cell volume. Figure 6.11a highlights that sample A6 results an outlier, although its presence does not affect the significance of the proportionality. Removing from the graph both A5 and A6, due to their similar structure and IR spectral pattern, the friction coefficient results linearly proportional to the unit cell volume. In particular, sample A4, which resulted an outlier based on its morphology, shows a higher friction with respect to A1-A3 due to its major unit cell volume.

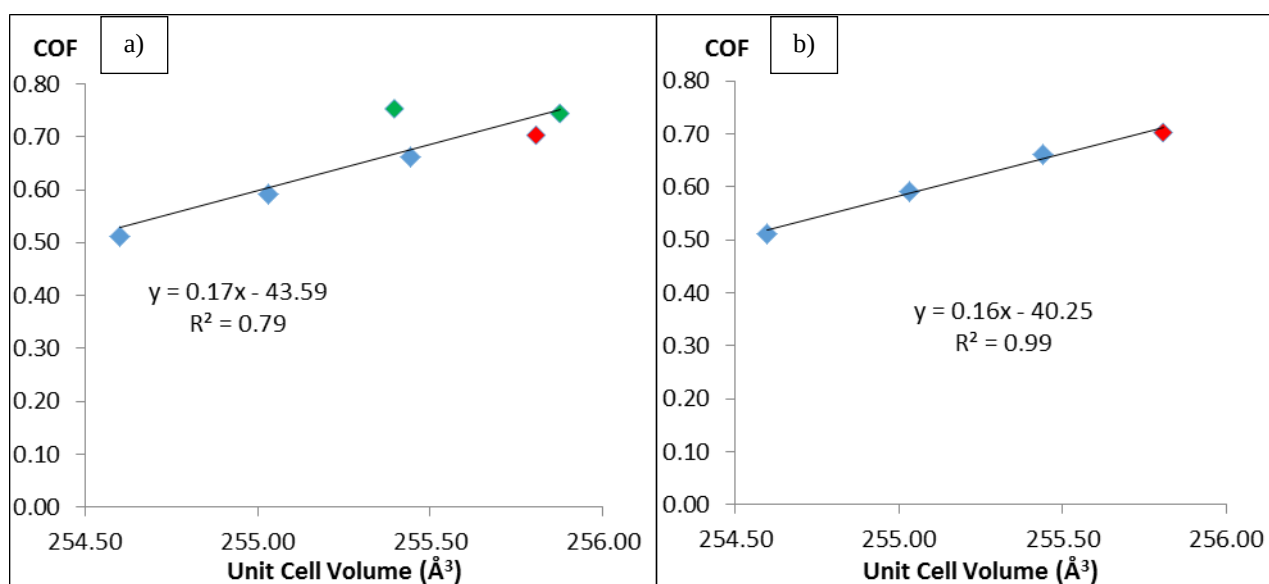


Figure 6.11: Friction coefficient in function of unit cell volume: a) all sample; b) samples A1-A4.

Considering that the unit cell volume is inversely proportional to the theoretical density, it can be affirmed that also friction is inversely correlated with the powder density. Thus, an alumina sample with a more compacted structure and consequently a higher density generates a lower friction coefficient in pin-on-disc test due to the major abrasion of steel counterface.

6.4.3 – INFLUENCE OF TRIBOLOGICAL CONDITIONS

The influence of tribological conditions was investigated in an OVAT approach (One Variable At Time). Load was changed in the range 3 – 18 N, while speed in the range 0.10 – 0.30 ms⁻¹.

Figure 6.12 shows the variation of COF in function of load and speed for the alumina A4. This sample was selected to investigate the tribological conditions influence due to the industrial interest on it.

The increase of load (Figure 6.12a) linearly affects the friction coefficient. Considering that at higher load the real contact area increase, it can be supposed that at interface the contact steel-alumina increases. Furthermore, supposing that friction decreases with the iron oxide generated by abrasion, at higher load it can be supposed that the abrasive effect of alumina is less, probably due to a less motion freedom of particles at interface.

The increase of speed (Figure 6.12b) causes an increase of friction through a logarithmic correlation. In addition, at higher speed value the abrasion of counterface is lower and the relative friction increases.

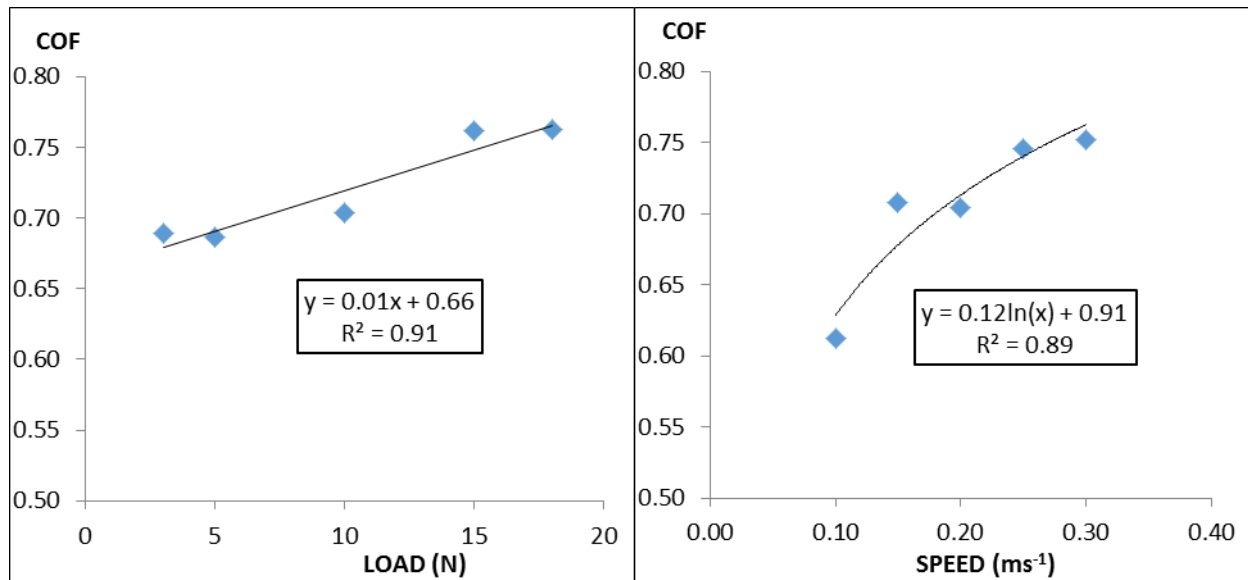


Figure 6.12: Variation of COF in function of load and speed for sample S2.

6.5 – CHARACTERIZATION OF MONOCOMPONENT PADS

Composites were produced using 50%wt of basic mix and 50%wt of alumina powder. All the previous analysed samples were selected as filler for monocomponent pad.

6.5.1 – PHYSICAL CHARACTERIZATION

Powder size and shape are unchanged when added to the basic mix (Figure 6.13). Therefore, for further comparison the morphological data obtained for powders would be considered also for pads.

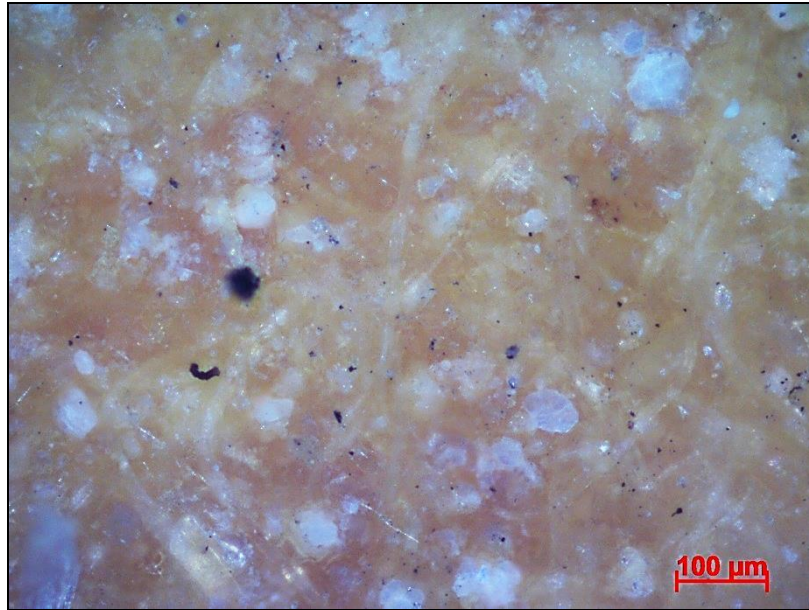


Figure 6.13: Optical images of pad surfaces for sample A6 in polarized light.

A first influence of alumina filler can be investigated through the measurement of pad density by geometrical volume. Table 6.6 reports the value of measured and theoretical pad density, obtained using the density of alumina calculated from x-ray diffraction data. The resulting pad density is quite similar to the theoretical one.

Table 6.6: Density of alumina based pad.

SAMPLE	DENSITY (g/cm ³)	THEORETICAL PAD DENSITY (g/cm ³)	POWDER DENSITY (FROM XRD) (g/cm ³)	ALUMINA VOLUME FRACTION (%)
MATRIX	1.32	1.30	-	-
A1	1.88	1.96	3.977	24.66
A2	1.83	1.96	3.990	24.60
A3	1.87	1.96	3.983	24.63
A4	1.90	1.96	3.971	24.68
A5	1.92	1.96	3.970	24.69
A6	1.92	1.96	3.978	24.65

A second macroscopic property affected by the filler is the pad hardness, measured by Brinell test. In literature, the reported Mohs hardness of aluminum oxide is 9, because alumina is the second hardest materials after diamond¹⁷⁷. Figure 6.14 shows the value of hardness measured for alumina

based pads. Only samples A4 and A5 are significant harder than the matrix, while all the other samples are roughly similar. A5 results also the most inhomogeneous sample in terms of hardness. The hardness results linearly proportional to the unit cell volume (Pearson coefficient 0.92), which suggests that alumina with a unit cell with higher interplanar distance generates a composite with a higher hardness.

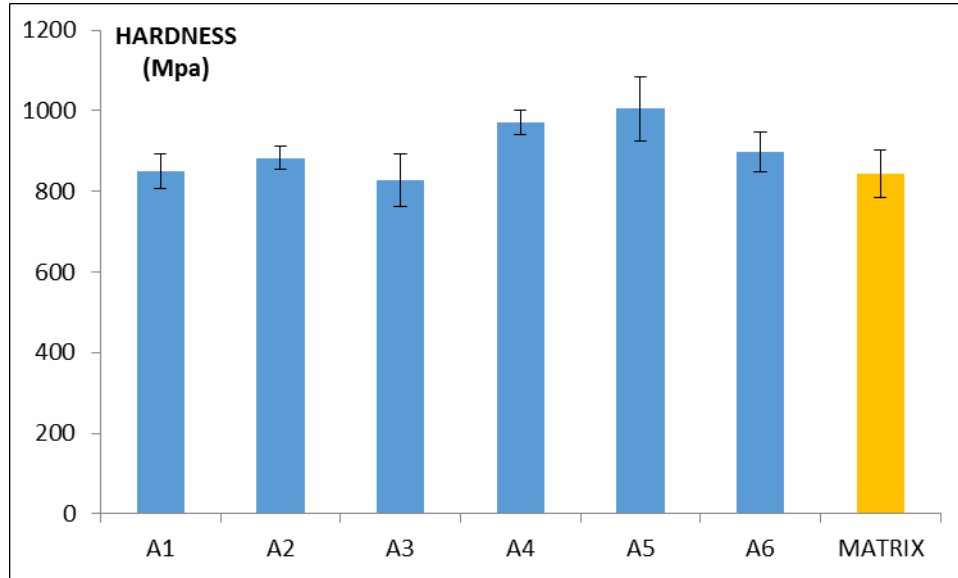


Figure 6.14: Comparison of hardness values obtained by Brinell test.

6.5.2 – INFLUENCE OF ROUGHNESS IN PIN-ON-PAD TEST

Due to the correlation of friction coefficient with the ratio R_aF/R_aI found for all the system previously studied, the pad with A5 as filler was selected in order to verify the correlation of friction with R_aF/R_aI also in the alumina based pad. Three tests at 10N and 0.2 ms^{-1} were performed, measuring the roughness before and after the tribological test. Table 6.7 shows the values obtained for both roughness and friction. The starting roughness were modified in order to have a similar value of R_a , in particular lower than $1\mu\text{m}$ to correctly compare the results with the previous analysed system.

Table 6.7: Tribological tests applied on A5 pad and relative measured roughness and friction.

TEST	$R_{aI} (\mu\text{m})$	R_{skI}	R_{kuI}	$R_{aF} (\mu\text{m})$	R_{skF}	R_{kuF}	R_{aF}/R_{aI}	COF	AMPL.
A	0.43	0.07	6.71	0.47	0.12	4.42	1.09	0.610	0.011
B	0.50	-1.48	11.73	0.52	0.15	5.25	1.06	0.606	0.009
C	0.43	-1.72	18.70	0.49	0.28	4.94	1.16	0.689	0.016

Figure 6.15 shows a comparison between friction and ratio R_aF/R_aI obtained for the three tests performed and highlights that COF increases with the roughness ratio. This general correlation can be summarized in the formula 6.4. Instead, other possible correlations with roughness parameters are not present.

$$6.4 - COF = 0.82 \frac{R_{aF}}{R_{aI}} - 0.27$$

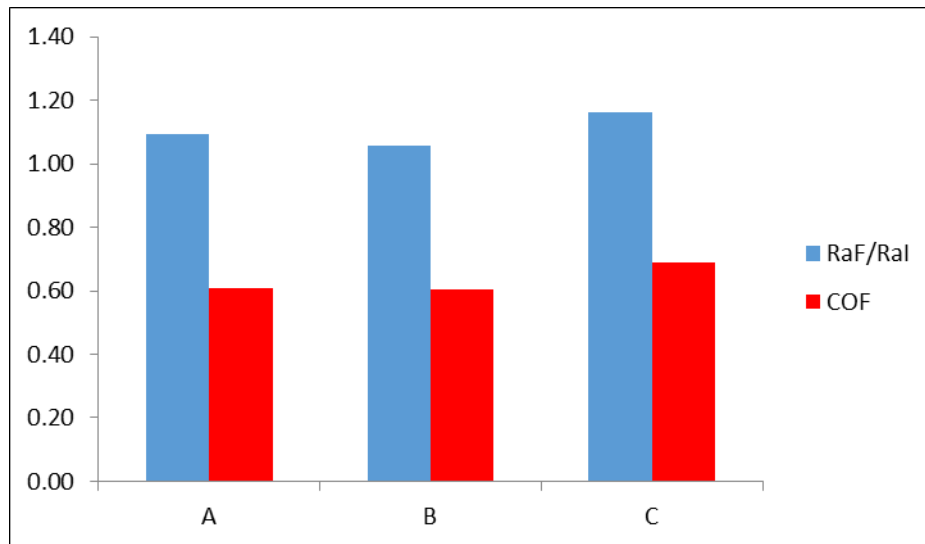


Figure 6.15: Comparison of ratio R_aF/R_{aI} and friction coefficient of tests on A5 sample.

6.5.3 – COMPARISON OF PIN-ON-PAD TESTS

Based on previous results, the standard test was applied on all samples modifying the initial roughness in order to start with $R_a \leq 1\mu\text{m}$. Figure 6.16 shows the comparison of results among samples and with the relative powder friction found before. Results highlight a friction higher than basic mix one and generally over 0.5. The two samples A5 and A6, which already showed the highest friction in pin-on-disc test, cause a major increase also of the COF of basic mix.

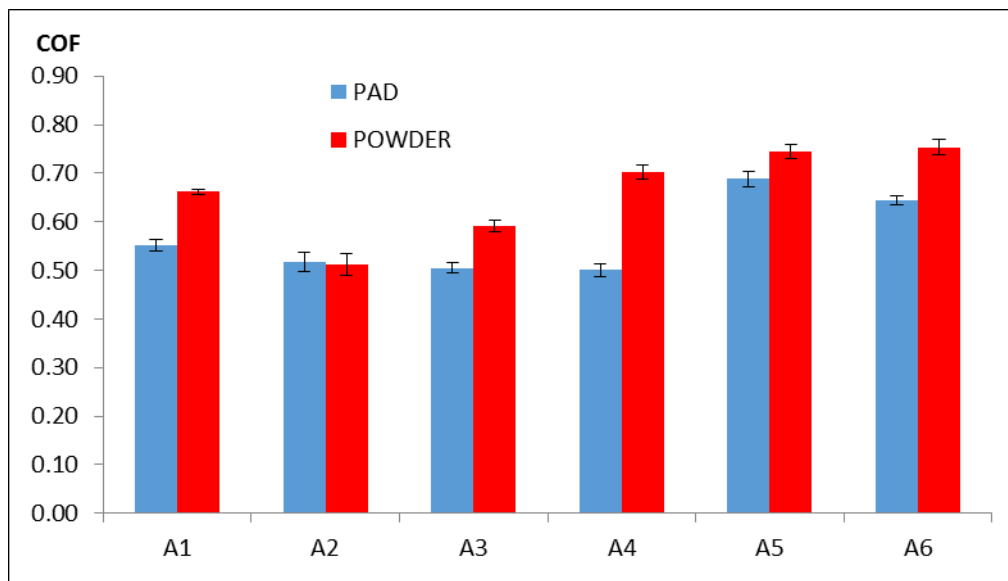


Figure 6.16: Comparison of pad and powder friction coefficient for alumina samples.

The friction coefficient obtained in pin-on-pad test is linearly proportional to the particle size (Pearson coefficient 0.97), which represents an opposite trend respect the one found for powder samples. In pin-on-disc test, the particle size is supposed to be directly correlated with the abrasion of steel surface and consequent generation of iron oxide, which decreases the friction coefficient. In the alumina-based pads, the trend is opposite and can be observed on the overall system. Figure 6.17 shows the comparison between samples A1 and A5 in the tribological trace. Sample A1 shows a more homogeneous layer, which is probably constituted by iron oxide, alumina and basic mix. Sample A5 shows an irregular layer, but with the same constituents. This surface inhomogeneity

suggests that a big particle size does not allow the generation of a stable layer and consequently the irregular profile reduces the contact area between pad and pin surfaces, with a consequent increase of pressure. Results show an increase of friction due to this inhomogeneous surface. Instead, for low particle size, a stable layer is generated at interface, and then the friction decreases due to a major real contact area. In both cases, the friction generated is higher respect the basic mix one.

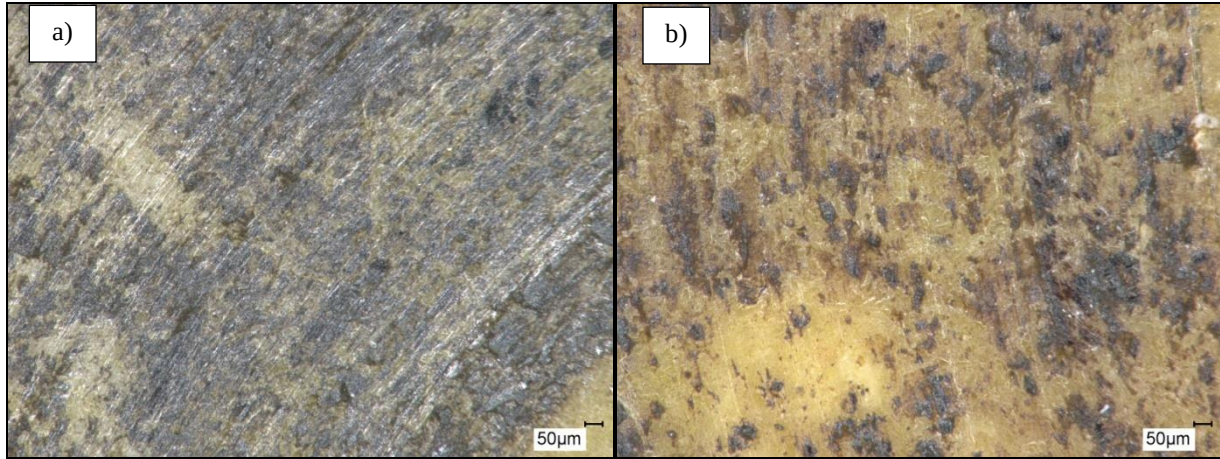


Figure 6.17: Optical microscope images: a) sample A1; b) sample A5.

6.5.4 – INFLUENCE OF ROUGHNESS ON WEAR BALL-ON-PAD TEST

Three tests were applied on sample A5, modifying the starting roughness in order to have three different values of R_aI and to investigate the influence of roughness on friction and wear behaviour of wear ball-on-pad test. The tribological conditions were the same for all the three tests (10N, 0.20 ms^{-1} , 1500 m). In all the tests performed, the steel ball used as counterface was abraded with a consequent wear of ball and formation of iron oxide at interface. Probably due to this wear mechanism, the roughness does not show any correlation with the wear constant obtained. The resulting average K is 1.79 ($10^{-5} mm^3/Nm$) with a standard deviation of 0.70 ($10^{-5} mm^3/Nm$).

Table 6.8: Data on wear test of sample A5.

COF	MAX DEPTH (μm)	VOLUME (mm^3)	DISTANCE (m)	K ($10^{-5} mm^3/Nm$)	R_aI	R_{skI}	R_{kuI}
0.493	12.01	2.56	1500	2.49	0.32	0.15	6.94
0.443	12.58	1.84	1500	1.82	0.50	-2.96	18.58
0.477	8.71	0.69	1500	1.04	0.29	-0.08	2.46

6.5.5 – COMPARISON OF BALL-ON-PAD TESTS

Table 6.9 shows the data of wear test of all samples performed at 10 N and 0.20 ms^{-1} with a sliding distance of 1500 m. All samples show a higher friction coefficient and wear constant with respect to the polymer matrix. The only significant correlation among wear results and the previous chemico-physical characterization is relative to the wear constant and the pad density. K and K' are directly proportional to the pad density (Pearson coefficient 0.82), then an increase of density causes a lower wear resistance.

Table 6.9: Data on wear test of all alumina based composites.

SAMPLE	COF	MAX DEPTH (μm)	VOLUME (mm^3)	H (MPa)	K ($10^{-5} \text{ mm}^3/\text{Nm}$)	K' (10^{-5})
MATRIX	0.337	23.69	0.38	844	1.27	1.07
A1	0.478	19.80	0.47	851	3.13	2.54
A2	0.581	23.51	0.79	883	5.27	4.44
A3	0.464	29.46	1.08	827	7.20	5.97
A4	0.424	23.36	0.68	971	4.53	4.20
A5	0.493	12.01	0.39	1005	2.60	2.49
A6	0.483	21.76	0.44	899	2.93	2.51

6.6 – CONCLUSION

A system of six alumina samples of different shape and size was investigated by chemico-physical and tribological characterization.

The tribological behaviour of samples in form of powder or pad is affected by the unit cell volume, which highlights the dominant influence of structural features with respect to morphology or other macroscopic features. Considering morphology, results show a partial influence of aspect ratio on samples with similar structural properties for powder and a direct influence of particle size on the pad friction behaviour.

Instead, no significant correlations were found for the wear properties of alumina based composites, apart from an influence of the pad density on the wear constant. It was observed a significant abrasion of the counterface during wear tests, with a consequent formation of iron oxide at interface. Thus, for further analysis, it could be advantageous to use an alumina ball instead of steel, in order to reduce the wear of counterface and enhance the abrasion of pad.

CONCLUSION

In the brake pad formulation, the selection of the different mixture components and their relative amounts has been largely relied on experience, leading to a trial and error approach. Thus, the aim of this thesis is to understand the single constituent effect on the friction and wear of brake pad, in order to obtain a systematic selection method for raw friction materials.

Three systems of commercially available raw materials were investigated to understand the correlation between their tribological behaviour and their morphological and structural features.

Systems of lubricants, abrasives and fillers were selected in agreement with the industrial partner, based on its primary interest. The raw materials were investigated in three different situations: as powder, to study their own frictional behaviour; as filler of a basic mix, constituted by phenol formaldehyde resin and aramid fibres, with the aim to study the influence of a single constituent in the matrix usually employed in the real application; as ingredient of a real brake pad formulation, to observe the influence of raw material on a complex formulation.

The first system selected concerns ten carbon materials, in particular four graphite, three graphene and three cokes. Structural characterization combined with a chemometrical approach, allowed to identify calcined coke and carbon black as outlier with respect to the other materials, due to their amorphous carbon content, higher than 60%. The friction behaviour of the all other samples mainly depends on the formation of a stable layer at interface, generally named tribofilm.

Carbon materials in form of powders show a friction affected by density and morphology. Indeed, friction coefficient is inversely proportional to the material density, because a denser structure generates a more stable layer at interface, with a consequent major lubricant effect. In addition, the particle aspect ratio affects friction, because elongated particles generate a too compact structure at interface that reduces the possibility of sliding plans, then hindering the lubricant action. The friction amplitude, that is the friction fluctuation in the steady state, increases as a function of the particle size. The reason for this phenomenon lies in the continuous succession of particles with different size, that cause a slight oscillation of the distance between pin and disc, then increasing the amplitude as a function of the number and size of particles present at a particular instant at interface. For samples with similar density and morphology, more insight about the influence of the structural properties can be obtained. Indeed, the friction is affected by the stacking order of carbon structure: higher the number of aromatic planes overlapped, lower the friction coefficient, thanks to a thicker and more homogeneous tribofilm at interface.

When the carbon materials are incorporated in the polymer matrix, the density of pad become higher than the basic mix one and it is affected by the morphology of carbon materials. The pad density increases for spherical particles, probably due to a major interaction with the basic mix, that decrease the pad porosity. Instead, the hardness is inversely proportional to the stacking order of carbon materials, probably because of different particles compressibility. This feature is responsible also for the friction behaviour, where the degree of organization along the “c” axis directly affects the formation of a stable tribofilm at interface, with a consequent COF decrease. Thus, in general, the friction behaviour of a carbon material, as powder or incorporated in a polymer matrix, depends on the stacking order along the “c” axis. The wear resistance also appears affected by the degree of organization, since it increases with the amount of defects present in the carbon structure. Instead, the friction behaviour during wear test is inversely proportional to the powder density, according to the outcomes on the powder samples.

In the case of real brake pads, the powder density and the particle morphology of carbon materials affect the compressibility of the entire composite. Elongated and less dense particles increase the compressibility of pad, with a consequent increase in the friction coefficient. Furthermore, also the amount of non-airborne dust is inversely correlated with the compressibility. Thus, it can be

concluded that a brake pad with higher compressibility generates less non-airborne dust, which is a desirable property, but at the same time, the friction coefficient becomes higher.

The second system concerns a whisker-like potassium hexatitanate, used as reference, and other eight samples with different shape and size. Titanate is considered a good candidate to replace asbestos, but its whisker morphology shows the same health problems observed for asbestos fibres. Thus, it is mandatory to replace the whisker-like potassium hexatitanate with another having different shape, but similar or better tribological properties.

The friction behaviour of titanate powders is dominated by the formation of iron oxide at interface, coming from the abrasion of the steel counterface. The abrasive ability of titanate seems to be inversely correlated with the structural compressibility, because friction coefficient is inversely proportional to the crystallite dimension along the direction (110) and directly proportional to the interplanar distance along (200) direction. The direction (110) corresponds to the galleries, lending the well-known tunnel-like structure of titanate materials. Thus, lower the length of these galleries higher the friction coefficient. Instead, the morphology affects the friction amplitude: in particular, elongated particles cause a major fluctuation of the friction coefficient.

When the titanate samples are incorporated in a polymer matrix, they increase the pad density with respect to the value of the basic mix and they change the hardness, in an amount depending on their particles shape, probably because of a different interaction between titanate particles and the polymer matrix. The hardness increases if the roundness decreases, and this feature is responsible also for the friction behaviour, because the COF is directly proportional to the hardness. For all the samples except the whisker-like titanate, the hardness is correlated with the roundness and aspect ratio of particles, and then the resulting friction can be considered as affected by particles shape through its influence on the pad hardness.

In addition, the wear constant K depends on hardness and the hardest mono-component pad shows the highest wear constant, then the lowest wear resistance. Thus, a titanate with spherical-like shape would decrease the hardness and friction coefficient of pad, while it would increase its wear resistance.

The third system is constituted by six alumina samples, with different shape and size. Results show some differences in the structural features and the presence of rutile in one sample as impurity. Although these differences, the tribological behaviour is affected by the unit cell volume for both powder and mono-component pad. This result highlights the dominant influence of structural features with respect to morphological characteristics. Similarly to titanate samples, also in the case of alumina ones the friction is affected by the presence of iron oxide, derived from the abrasion of steel counterface. Results suggest that alumina with a lower unit cell volume has a higher abrasive effect on the steel counterface, with a consequent decrease in friction coefficient.

No significant correlations between alumina composites properties and wear resistance, apart from an influence of the pad density on the wear constant. All the composites produced a significant abrasion of the steel ball, which debris was observed on all the tests in large extent. The poor resistance of the steel against the alumina composites did not allow highlighting differences dependent on the intrinsic composites features.

Overall, it can be concluded that friction materials of the same family can be classified based on their morphological and structural features. Indeed, significant correlations between tribological and material properties were found. The comprehension of the main features affecting the friction and wear properties results in the possibility to make a preliminary selection of the raw materials based on the desired tribological behaviour.

The characterization method set up can be applied on several other families of friction materials and the investigation can be extended to other applications, different from brake pads.

BIBLIOGRAPHY

- 1 M. I. Pech-Canul and F. Kongoli, The modified central paradigm of materials science and engineering in the extraction and development of new and recycled materials, *Trans. Institutions Min. Metall. Sect. C Miner. Process. Extr. Metall.*, 2016, **125**, 238–241.
- 2 B. Bhushan, *INTRODUCTION TO TRIBOLOGY*, 2013.
- 3 B. N. J. Persson, Sliding friction, 2000, 101–162.
- 4 K. Holmberg and A. Erdemir, Influence of tribology on global energy consumption, costs and emissions, *Friction*, 2017, **5**, 263–284.
- 5 I. M. Hutchings, Leonardo da Vinci's studies of friction, *Wear*, 2016, **360–361**, 51–66.
- 6 R. L. Cox and S. of Automotive Engineers, *Engineered Tribological Composites: The Art of Friction Material Development*, SAE International, 2012.
- 7 M. Hirano, Atomistics of friction, *Surf. Sci. Rep.*, 2006, **60**, 159–201.
- 8 F. P. Bowden, A review of the friction of solids, *Wear*, 1958, **1**, 333–346.
- 9 V. L. Popov and J. A. T. Gray, Prandtl-Tomlinson model: History and applications in friction, plasticity, and nanotechnologies, *ZAMM Zeitschrift für Angew. Math. und Mech.*, 2012, **92**, 683–708.
- 10 J. Nian, Y. Si and Z. Guo, Advances in atomic-scale tribological mechanisms of solid interfaces, *Tribol. Int.*, 2016, **94**, 1–13.
- 11 Z. Xu and P. Huang, Study on the energy dissipation mechanism of atomic-scale friction with composite oscillator model, *Wear*, 2007, **262**, 972–977.
- 12 J. A. Harrison, C. T. White, R. J. Colton and D. W. Brenner, Investigation of the atomic-scale friction and energy dissipation in diamond using molecular dynamics, *Thin Solid Films*, 1995, **260**, 205–211.
- 13 E. Gnecco, R. Bennewitz, T. Gyalog, C. Loppacher, M. Bammerlin, E. Meyer and H.-J. Güntherodt, Velocity Dependence of Atomic Friction, *Phys. Rev. Lett.*, 2000, **84**, 1172–1175.
- 14 C. Fusco and A. Fasolino, Velocity dependence of atomic-scale friction: A comparative study of the one- and two-dimensional Tomlinson model, *Phys. Rev. B*, 2005, **71**, 45413.
- 15 J. Y. Park and M. Salmeron, Fundamental Aspects of Energy Dissipation in Friction, *Chem. Rev.*, 2014, **114**, 677–711.
- 16 J. K. Lancaster, Material-specific wear mechanisms: relevance to wear modelling, *Wear*, 1990, **141**, 159–183.
- 17 K. Kato and K. Adachi, Wear Mechanisms, *Mod. Tribol. Handbook. Vol 1*, 2001, 28.
- 18 D. Chan and G. W. Stachowiak, Review of automotive brake friction materials, *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, 2005, **218**, 953–966.
- 19 R. Begin, Asbestos-related diseases, *Eur. Respir. Monogr.*, 1999, **4**, 158–177.
- 20 A. N. Rohl, A. M. Langer, M. S. Wolff and I. Weisman, Asbestos exposure during brake lining maintenance and repair, *Environ. Res.*, 1976, **12**, 110–128.
- 21 J. R. Laguna-Camacho, G. Juárez-Morales, C. Calderón-Ramón, V. Velázquez-Martínez, I. Hernández-Romero, J. V. Méndez-Méndez and M. Vite-Torres, A study of the wear mechanisms of disk and shoe brake pads, *Eng. Fail. Anal.*, 2015, **56**, 348–359.
- 22 C. F. Tang and Y. Lu, Combinatorial Screening of Ingredients for Steel Wool Based Semimetallic and Aramid Pulp Based Nonasbestos Organic Brake Materials, *J. Reinf. Plast. Compos.*, 2004, **23**, 51–63.
- 23 M. Renouf, F. Massi, N. Fillot and A. Saulot, Numerical tribology of a dry contact, *Tribol. Int.*, 2011, **44**, 834–844.
- 24 P. M. T. Trends, Eliminating asbestos from brake pads, *Met. Powder Rep.*, 1992, **47**, 12–14.
- 25 V. S. Aigbodio, U. Akadike, S. B. Hassan, F. Asuke and J. O. Agunsoye, Development of asbestos - free brake pad using bagasse, *Tribol. Ind.*, 2010, **32**, 12–18.

- 26 R. L. Williams and J. L. Muhlbaier, Asbestos brake emissions, *Environ. Res.*, 1982, **29**, 70–82.
- 27 M. C. Lagel, L. Hai, A. Pizzi, M. C. Basso, L. Delmotte, S. Abdalla, A. Zahed and F. M. Al-Marzouki, Automotive brake pads made with a bioresin matrix, *Ind. Crops Prod.*, 2016, **85**, 372–381.
- 28 R. Yun, P. Filip and Y. Lu, Performance and evaluation of eco-friendly brake friction materials, *Tribol. Int.*, 2010, **43**, 2010–2019.
- 29 Y. Lu, A combinatorial approach for automotive friction materials: Effects of ingredients on friction performance, *Compos. Sci. Technol.*, 2006, **66**, 591–598.
- 30 G. Drava, R. Leardi, A. Portesani and E. Sales, Application of chemometrics to the production of friction materials: Analysis of previous data and search of new formulations, *Chemom. Intell. Lab. Syst.*, 1996, **32**, 245–255.
- 31 T. Kato and H. Soutome, Friction material design for brake pads using database, *Tribol. Trans.*, , DOI:10.1080/10402000108982437.
- 32 J. K. Lancaster, A review of the influence of environmental humidity and water on friction, lubrication and wear, *Tribol. Int.*, 1990, **23**, 371–389.
- 33 H. Kato, Severe-mild wear transition by supply of oxide particles on sliding surface, *Wear*, 2003, **255**, 426–429.
- 34 W. Österle, C. Deutsch, T. Gradt, G. Orts-Gil, T. Schneider and a. I. Dmitriev, Tribological screening tests for the selection of raw materials for automotive brake pad formulations, *Tribol. Int.*, 2014, **73**, 148–155.
- 35 A. C. P. Rodrigues, T. Yonamine, E. Albertin, A. Sinatora and C. R. F. Azevedo, Effect of Cu particles as an interfacial media addition on the friction coefficient and interface microstructure during (steel/steel) pin on disc tribotest, *Wear*, 2015, **330–331**, 70–78.
- 36 A. C. P. Rodrigues, W. Österle, T. Gradt and C. R. F. Azevedo, Impact of copper nanoparticles on tribofilm formation determined by pin-on-disc tests with powder supply: Addition of artificial third body consisting of Fe₃O₄, Cu and graphite, *Tribol. Int.*, 2017, **110**, 103–112.
- 37 J. Kukutschová, P. Moravec, V. Tomášek, V. Matějka, J. Smolík, J. Schwarz, J. Seidlerová, K. Šafářová and P. Filip, On airborne nano/micro-sized wear particles released from low-metallic automotive brakes, *Environ. Pollut.*, 2011, **159**, 998–1006.
- 38 K. Malachova, J. Kukutschova, Z. Rybkova, H. Sezimova, D. Placha, K. Cabanova and P. Filip, Toxicity and mutagenicity of low-metallic automotive brake pad materials, *Ecotoxicol. Environ. Saf.*, 2016, **131**, 37–44.
- 39 S. C. Tung and M. L. McMillan, Automotive tribology overview of current advances and challenges for the future, *Tribol. Int.*, 2004, **37**, 517–536.
- 40 Carbon nanomaterials in tribology, *Carbon N. Y.*, 2017, **119**, 150–171.
- 41 D. D. L. Chung, *J. Mater. Sci.*, 2002, **37**, 1475–1489.
- 42 R. Radhika, N. Kumar, R. Pandian, T. R. Ravindran, S. Dash and A. K. Tyagi, Structural transformation and friction behavior in turbostratic graphite sliding against Si₃N₄, SiC and Al₂O₃ balls, *Surf. Coatings Technol.*, 2014, **253**, 300–306.
- 43 J. J. Tang, K. Liu, Q. Z. Yang, Y. H. Wang, P. Zhang, Y. Wang, L. Zhao, Q. Q. Fu, Z. H. Han and Y. Bai, The influence of size and distribution of graphite on the friction and wear behavior of Ni-graphite coatings, *Surf. Coatings Technol.*, 2014, **252**, 48–55.
- 44 B. K. Yen, B. E. Schwickert and M. F. Toney, Origin of low-friction behavior in graphite investigated by surface x-ray diffraction, *Appl. Phys. Lett.*, 2004, **84**, 4702–4704.
- 45 N. Kumar, S. Dash, A. K. Tyagi and B. Raj, Super low to high friction of turbostratic graphite under various atmospheric test conditions, *Tribol. Int.*, 2011, **44**, 1969–1978.
- 46 G. Nicholson, *Facts about Friction: A Friction Material Manual Almost All You Need to Know about Manufacturing*, Gedoran, 1995.

- 47 N. Aranganathan and J. Bijwe, Special grade of graphite in NAO friction materials for possible replacement of copper, *Wear*, 2015, **330**, 515–523.
- 48 M. Dienwiebel, N. Pradeep, G. S. Verhoeven, H. W. Zandbergen and J. W. M. Frenken, Model experiments of superlubricity of graphite, *Surf. Sci.*, 2005, **576**, 197–211.
- 49 Y. M. Abdel-Rahim and S. M. Darwish, Generalized braking characteristics of friction pad synthetic graphite composites, *Tribol. Int.*, 2010, **43**, 838–843.
- 50 L. R. Prado, N. S. de Resende, R. S. Silva, S. M. S. Egues and G. R. Salazar-Banda, Influence of the synthesis method on the preparation of barium titanate nanoparticles, *Chem. Eng. Process. Process Intensif.*, 2015, **103**, 12–20.
- 51 H. Naghib-Zadeh, C. Glitzky, W. Oesterle and T. Rabe, Low temperature sintering of barium titanate based ceramics with high dielectric constant for LTCC applications, *J. Eur. Ceram. Soc.*, 2011, **31**, 589–596.
- 52 M. Sasani Ghamsari, S. Rahim, S. Radiman and J. Hasani, Novel method for synthesis of potassium titanate (K₂TiO₂(OH)) nanorods, *Mater. Lett.*, 2012, **85**, 81–83.
- 53 L. T. O, H. Schneider, P. Maire and P. Novák, Electrochimica Acta Electrochemical and spectroscopic characterization of lithium titanate spinel, *Electrochim. Acta*, 2011, **56**, 9324–9328.
- 54 X. D. Meng, D. Z. Wang, J. H. Liu and S. Y. Zhang, Preparation and characterization of sodium titanate nanowires from brookite nanocrystallites, *Mater. Res. Bull.*, 2004, **39**, 2163–2170.
- 55 B. L. Wang, Q. Chen, J. Hu, H. Li, Y. F. Hu and L. M. Peng, Synthesis and characterization of large scale potassium titanate nanowires with good Li-intercalation performance, *Chem. Phys. Lett.*, 2005, **406**, 95–100.
- 56 X. Meng, D. Wang, J. Liu, B. Lin and Z. Fu, Effects of titania different phases on the microstructure and properties of K₂Ti₆O₁₃ nanowires, *Solid State Commun.*, 2006, **137**, 146–149.
- 57 G.L.Li, G.H.Wang and J.M.Hong, SYNTHESIS OF K₂Ti₆O₁₃ WHISKERS BY THE METHOD OF CALCINATION OF KF AND TiO₂ MIXTURES, *Mater. Res. Bull.*, 1999, **34**, 2341–2349.
- 58 M. L. Halberstadt, J. A. Mansfield and S. K. Rhee, EFFECTS OF POTASSIUM TITANATE, 1978, **46**, 109–126.
- 59 G. Y. Xie, G. S. Zhuang, G. X. Sui and R. Yang, Tribological behavior of PEEK / PTFE composites reinforced with potassium titanate whiskers, *Wear*, 2010, **268**, 424–430.
- 60 Y. C. Kim, M. H. Cho, S. J. Kim and H. Jang, The effect of phenolic resin, potassium titanate, and CNSL on the tribological properties of brake friction materials, *Wear*, 2008, **264**, 204–210.
- 61 W. Huaiyuan, Z. Yanji, F. Xin and L. Xiaohua, The effect of self-assembly modified potassium titanate whiskers on the friction and wear behaviors of PEEK composites, *Wear*, 2010, **269**, 139–144.
- 62 F. Ahmad, S. H. J. Lo, M. Aslam and A. Haziq, Tribology Behaviour of Alumina Particles Reinforced Aluminium Matrix Composites and Brake Disc Materials, *Procedia Eng.*, 2013, **68**, 674–680.
- 63 A. Almaslow, M. J. J. Ghazali, R. J. J. Talib, C. T. T. Ratnam and C. H. H. Azhari, Effects of epoxidized natural rubber–alumina nanoparticles (ENRAN) composites in semi-metallic brake friction materials, *Wear*, 2013, **302**, 1392–1396.
- 64 J. Bijwe, N. Aranganathan, S. Sharma, N. Dureja and R. Kumar, Nano-abrasives in friction materials-influence on tribological properties, *Wear*, 2012, **296**, 693–701.
- 65 L. Pilato, Phenolic resins: 100 Years and still going strong, *React. Funct. Polym.*, 2013, **73**, 270–277.
- 66 F. Vivier, 2016.

- 67 P. Cai, Y. Wang, T. Wang and Q. Wang, Effect of resins on thermal, mechanical and tribological properties of friction materials, *Tribol. Int.*, 2015, **87**, 1–10.
- 68 W. M. Jackson and R. T. Conley, High temperature oxidative degradation of phenol–formaldehyde polycondensates, *J. Appl. Polym. Sci.*, , DOI:10.1002/app.1964.070080516.
- 69 S. K. Sinha and S. K. Biswas, Friction and wear behaviour of continuous fibre as cast Kevlar-phenolic resin composite, *J. Mater. Sci.*, 1992, **27**, 3085–3091.
- 70 S. K. Sinha and S. K. Biswas, Effect of sliding speed on friction and wear of uni-directional aramid fibre-phenolic resin composite, *J. Mater. Sci.*, 1995, **30**, 2430–2437.
- 71 *US Pat. 4446203* 1984, 1984.
- 72 M. C. Andrews, D. Lu and R. J. Young, Compressive properties of aramid fibers., *Polymer (Guildf)*., 1997, **38**, 2379–2388.
- 73 *US Pat. 5965658* 1999, 1999.
- 74 N. Aranganathan, V. Mahale and J. Bijwe, Effects of aramid fiber concentration on the friction and wear characteristics of non-asbestos organic friction composites using standardized braking tests, *Wear*, 2016, **354–355**, 69–77.
- 75 P. Cai, Z. Li, T. Wang and Q. Wang, Effect of aspect ratios of aramid fiber on mechanical and tribological behaviors of friction materials, *Tribol. Int.*, 2015, **92**, 109–116.
- 76 A. J. Day, *Braking of Road Vehicles*, Elsevier Science, 2014.
- 77 K. H. Cho, H. Jang, Y. S. Hong, S. J. Kim, R. H. Basch and J. W. Fash, The size effect of zircon particles on the friction characteristics of brake lining materials, *Wear*, 2008, **264**, 291–297.
- 78 R. K. Gunda and S. K. Reddy Narala, Tribological Studies to Analyze the Effect of Solid Lubricant Particle Size on Friction and Wear Behaviour of Hard Material, *Surf. Coatings Technol.*, , DOI:10.1016/j.surfcoat.2016.06.092.
- 79 Y. Xie and B. Bhushan, Effects of particle size, polishing pad and contact pressure in free abrasive polishing, *Wear*, 1996, **200**, 281–295.
- 80 J. Wiacek, M. Molenda, J. Horabik and J. Y. Ooi, Influence of grain shape and intergranular friction on material behavior in uniaxial compression: Experimental and DEM modeling, *Powder Technol.*, 2012, **217**, 435–442.
- 81 J. P. Giltrow and A. J. Groszek, The effect of particle shape on abrasiveness of lamellar solids, *Wear*, 1969, **13**, 317–329.
- 82 P. Yan, J. Zhang, Q. Fang, Y. Zhang and J. Fan, 3D numerical modelling of solid particles with randomness in shape considering convexity and concavity, *Powder Technol.*, 2016, **301**, 131–140.
- 83 Y. Yang, J. F. Wang and Y. M. Cheng, Quantified evaluation of particle shape effects from micro-to-macro scales for non-convex grains, *Particuology*, 2015, **25**, 23–35.
- 84 A. Bogner, P.-H. Jouneau, G. Thollet, D. Basset and C. Gauthier, A history of scanning electron microscopy developments: Towards “wet-STEM” imaging, *Micron*, 2007, **38**, 390–401.
- 85 W. Zhou, R. P. Apkarian and Z. L. Wang, Fundamentals of Scanning Electron Microscopy, *Scanning Microsc. Nanotechnol.*, 2007, 1–40.
- 86 E. C. Crawford and J. K. Mortensen, An ImageJ plugin for the rapid morphological characterization of separated particles and an initial application to placer gold analysis, *Comput. Geosci.*, 2009, **35**, 347–359.
- 87 C. Igathinathane, L. O. Pordesimo, E. P. Columbus, W. D. Batchelor and S. R. Methuku, Shape identification and particles size distribution from basic shape parameters using ImageJ, *Comput. Electron. Agric.*, 2008, **63**, 168–182.
- 88 C. Igathinathane, L. O. Pordesimo, E. P. Columbus, W. D. Batchelor and S. Sokhansanj, Sieveless particle size distribution analysis of particulate materials through computer vision, *Comput. Electron. Agric.*, 2009, **66**, 147–158.

- 89 H. A. Hauptman, Science of Crystal Structures, 2015, 19–23.
- 90 W. C. Rontgen, On a new kind of rays.
- 91 V. Krastev and G. K. Exner, 100 years of X-ray diffraction: From Röntgen's discovery to top-of-the-art synchrotron source applications, *Bulg. Chem. Commun.*, 2013, **45**, 411–417.
- 92 M. Eaqub Ali, R. Das and S. Bee Abd Hamid, Current Applications of X-Ray Powder Diffraction- a Review, *Rev. Adv. Mater. Sci.*, 2014, **38**, 95–109.
- 93 G. S. Bumbrah and R. M. Sharma, Raman spectroscopy – Basic principle, instrumentation and selected applications for the characterization of drugs of abuse, *Egypt. J. Forensic Sci.*, 2016, **6**, 209–215.
- 94 Javier Laserna, An Introduction to Raman Spectroscopy: Introduction and Basic Principles, <http://www.spectroscopynow.com/details/education/sepspec1882education/An-Introduction-to-Raman-Spectroscopy-Introduction-and-Basic-Principles.html?tzcheck=1,1,1,1,1,1,1,1,1,1&&tzcheck=1>.
- 95 T. H. Maiman, Solid state laser and iraser studies, *Solid. State. Electron.*, 1962, **4**, 236–249.
- 96 S. Wold, Chemometrics; what do we mean with it, and what do we want from it?, *Chemom. Intell. Lab. Syst.*, 1995, **30**, 109–115.
- 97 M. H. Cho, J. Ju, S. J. Kim and H. Jang, Tribological properties of solid lubricants (graphite, Sb₂S₃, MoS₂) for automotive brake friction materials, *Wear*, 2006, **260**, 855–860.
- 98 D. Kolluri, A. K. Ghosh and J. Bijwe, Analysis of load-speed sensitivity of friction composites based on various synthetic graphites, *Wear*, 2009, **266**, 266–274.
- 99 W. Österle, C. Deutsch, T. Gradt, G. Orts-Gil, T. Schneider and a. I. Dmitriev, Tribological screening tests for the selection of raw materials for automotive brake pad formulations, *Tribol. Int.*, 2014, **73**, 148–155.
- 100 *Int. Organ. Stand.*, 2009, 2009, 1–8.
- 101 H. Kato, Effects of supply of fine oxide particles onto rubbing steel surfaces on severe-mild wear transition and oxide film formation, *Tribol. Int.*, 2008, **41**, 735–742.
- 102 A. C. P. Rodrigues, T. Yonamine, E. Albertin, A. Sinatora and C. R. F. Azevedo, Effect of Cu particles as an interfacial media addition on the friction coefficient and interface microstructure during (steel/steel) pin on disc tribotest, *Wear*, 2015, **330–331**, 70–78.
- 103 *Int. Organ. Stand.*, 1999, 1999.
- 104 www.linkeng.com, 2.
- 105 E. S. Gadelmawla, M. M. Koura, T. M. A. Maksoud, I. M. Elewa and H. H. Soliman, Roughness parameters, *J. Mater. Process. Technol.*, 2002, **123**, 133–145.
- 106 J. F. Archard, Contact and rubbing of flat surfaces, *J. Appl. Phys.*, 1953, **24**, 981–988.
- 107 A. Iwabuchi, K. Hori and H. Kubosawa, The effect of oxide particles supplied at the interface before sliding on the severe-mild wear transition, *Wear*, 1988, **128**, 123–137.
- 108 A. Iwabuchi, H. Kubosawa and K. Hori, The dependence of the transition from severe to mild wear on load and surface roughness when the oxide particles are supplied before sliding, *Wear*, 1990, **139**, 319–333.
- 109 S. Q. Wang, L. Wang, Y. T. Zhao, Y. Sun and Z. R. Yang, Mild-to-severe wear transition and transition region of oxidative wear in steels, *Wear*, 2013, **306**, 311–320.
- 110 K. Hiratsuka and K. Muramoto, Role of wear particles in severe-mild wear transition, *Wear*, 2005, **259**, 467–476.
- 111 F. H. Stott, Developments in Understanding the Mechanisms of Growth of Protective Scales on High-Temperature Alloys, 1992, **325**, 311–325.
- 112 F. H. Stott, The role of oxidation in the wear of alloys, *Tribol. Int.*, 1998, **31**, 61–71.
- 113 H. Kato and K. Komai, Tribofilm formation and mild wear by tribo-sintering of nanometer-sized oxide particles on rubbing steel surfaces, *Wear*, 2007, **262**, 36–41.
- 114 P. L. Menezes, Kishore and S. V. Kailas, Influence of surface texture and roughness parameters on friction and transfer layer formation during sliding of aluminium pin on steel

- plate, *Wear*, 2009, **267**, 1534–1549.
- 115 S. Jahanmir and N. P. Suh, Surface topography and integrity effects on sliding wear, *Wear*, 1977, **44**, 87–99.
- 116 N. Fillot, I. Iordanoff and Y. Berthier, Wear modeling and the third body concept, *Wear*, 2007, **262**, 949–957.
- 117 L. Liu, C. Yang and Y. Sheng, Wear model based on real-time surface roughness and its effect on lubrication regimes, *Tribol. Int.*, 2018, **126**, 16–20.
- 118 M. L. Rahaman, L. Zhang, M. Liu and W. Liu, Surface roughness effect on the friction and wear of bulk metallic glasses, *Wear*, 2015, **332–333**, 1231–1237.
- 119 R core team, R: A language and environment for statistical computing., *R Found. Stat. Comput. Vienna, Austria.*, 2017, R Foundation for Statistical Computing.
- 120 I. Velkavrh, F. Ausserer, S. Klien, J. Brenner, P. Forêt and A. Diem, The effect of gaseous atmospheres on friction and wear of steel–steel contacts, *Tribol. Int.*, 2014, **79**, 99–110.
- 121 A. Mariani, O. Monticelli, S. Fiori and S. Russo, Relevance of purification procedures in the direct synthesis of poly(p-phenyleneterephthalamide) from its dimer, *E-Polymers*, , DOI:10.1515/epoly.2003.3.1.766.
- 122 J. A. Bencomo-Cisneros, A. Tejeda-Ochoa, J. A. García-Estrada, C. A. Herrera-Ramírez, A. Hurtado-Macías, R. Martínez-Sánchez and J. M. Herrera-Ramírez, Characterization of Kevlar-29 fibers by tensile tests and nanoindentation, *J. Alloys Compd.*, 2012, **536**, S456–S459.
- 123 R. Elleuch, K. Elleuch, H. Ben Abdelounis and H. Zahouani, Surface roughness effect on friction behaviour of elastomeric material, *Mater. Sci. Eng. A*, 2007, **465**, 8–12.
- 124 S. Bahadur, The development of transfer layers and their role in polymer tribology, *Wear*, 2000, **245**, 92–99.
- 125 N. K. Myshkin, M. I. Petrokovets and A. V. Kovalev, Tribology of polymers: Adhesion, friction, wear, and mass-transfer, *Tribol. Int.*, 2005, **38**, 910–921.
- 126 E. Gutierrez-Miravete, Friction, Wear and Lubrication of Materials, 2013, 1–13.
- 127 L. M. Malard, M. A. Pimenta, G. Dresselhaus and M. S. Dresselhaus, Raman spectroscopy in graphene, *Phys. Rep.*, 2009, **473**, 51–87.
- 128 D. Berman, A. Erdemir and A. V. Sumant, Graphene: A new emerging lubricant, *Mater. Today*, 2014, **17**, 31–42.
- 129 L. Y. Lin, D. E. Kim, W. K. Kim and S. C. Jun, Friction and wear characteristics of multi-layer graphene films investigated by atomic force microscopy, *Surf. Coatings Technol.*, 2011, **205**, 4864–4869.
- 130 D. Berman, A. Erdemir and A. V. Sumant, Few layer graphene to reduce wear and friction on sliding steel surfaces, *Carbon N. Y.*, 2013, **54**, 454–459.
- 131 S. Rodrigues, M. Marques, I. Suárez-Ruiz, I. Camean, D. Flores and B. Kwiecinska, Microstructural investigations of natural and synthetic graphites and semi-graphites, *Int. J. Coal Geol.*, 2013, **111**, 67–79.
- 132 K. Angoni, Remarks on the structure of carbon materials on the basis of Raman spectra, *Carbon N. Y.*, 1993, **31**, 537–547.
- 133 Y. Kawashima and G. Katagiri, Fundamentals, Overtones, and Combinations in the Raman-Spectrum of Graphite, *Phys. Rev. B*, 1995, **52**, 10053–10059.
- 134 M. Nakamizo and H. Honda, Raman Spectra of Ground Natural Graphite, *Carbon N. Y.*, 1978, **16**, 281–283.
- 135 M. Nakamizo, R. Kammereck and P. L. Walker, Laser raman studies on carbons, *Carbon N. Y.*, 1974, **12**, 259–267.
- 136 E. B. Barros, A. G. Souza Filho, H. Son and M. S. Dresselhaus, G' band Raman lineshape analysis in graphitic foams, *Vib. Spectrosc.*, 2007, **45**, 122–127.
- 137 A. Zaida, E. Bar-Ziv, L. R. Radovic and Y. J. Lee, Further development of Raman

- Microprobe spectroscopy for characterization of char reactivity, *Proc. Combust. Inst.*, 2007, **31 II**, 1881–1887.
- 138 F. Tuinstra and L. Koenig, Raman Spectrum of Graphite, *J. Chem. Phys.*, 1970, **53**, 1126–1130.
- 139 C. Casiraghi, F. Piazza, A. C. Ferrari, D. Grambole and J. Robertson, Bonding in hydrogenated diamond-like carbon by Raman spectroscopy, *Diam. Relat. Mater.*, 2005, **14**, 1098–1102.
- 140 A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, Raman spectrum of graphene and graphene layers, *Phys. Rev. Lett.*, 2006, **97**, 1–4.
- 141 M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio and R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1276–1291.
- 142 B. . Tay, X. Shi, H. . Tan, H. . Yang and Z. Sun, Raman studies of tetrahedral amorphous carbon films deposited by filtered cathodic vacuum arc, *Surf. Coatings Technol.*, 1998, **105**, 155–158.
- 143 W. G. Cui, Q. B. Lai, L. Zhang and F. M. Wang, Quantitative measurements of sp³ content in DLC films with Raman spectroscopy, *Surf. Coatings Technol.*, 2010, **205**, 1995–1999.
- 144 S. Prawer, K. W. Nugent, Y. Lifshitz, G. D. Lempert, E. Grossman, J. Kulik, I. Avigal and R. Kalish, Systematic variation of the Raman spectra of DLC films as a function of sp²:sp³ composition, *Diam. Relat. Mater.*, 1996, **5**, 433–438.
- 145 S. Zhang, X. T. Zeng, H. Xie and P. Hing, A phenomenological approach for the Id/Ig ratio and sp³ fraction of magnetron sputtered a-C films, *Surf. Coatings Technol.*, 2000, **123**, 256–260.
- 146 P. Mallet-Ladeira, P. Puech, C. Toulouse, M. Cazayous, N. Ratel-Ramond, P. Weisbecker, G. L. Vignoles and M. Monthieux, A Raman study to obtain crystallite size of carbon materials: A better alternative to the Tuinstra-Koenig law, *Carbon N. Y.*, 2014, **80**, 629–639.
- 147 L. Nikiel and P. W. Jagodzinski, Raman spectroscopic characterization of graphites: A re-evaluation of spectra/structure correlation, *Carbon N. Y.*, 1993, **31**, 1313–1317.
- 148 J. Ribeiro-Soares, M. E. Oliveros, C. Garin, M. V. David, L. G. P. Martins, C. A. Almeida, E. H. Martins-Ferreira, K. Takai, T. Enoki, R. Magalhães-Paniago, A. Malachias, A. Jorio, B. S. Archanjo, C. A. Achete and L. G. Cançado, Structural analysis of polycrystalline graphene systems by Raman spectroscopy, *Carbon N. Y.*, 2015, **95**, 646–652.
- 149 O. Beyssac, B. Goffé, J. P. Petitet, E. Froigneux, M. Moreau and J. N. Rouzaud, On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2003, **59**, 2267–2276.
- 150 A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martínez-Alonso and J. M. D. Tascón, Raman microprobe studies on carbon materials, *Carbon N. Y.*, 1994, **32**, 1523–1532.
- 151 J. H. Horng, C. C. Wei, H. J. Tsai and B. C. Shiu, A study of surface friction and particle friction between rough surfaces, *Wear*, 2009, **267**, 1257–1263.
- 152 N. Kumar, A. T. Kozakov, T. R. Ravindran, S. Dash and A. K. Tyagi, Load dependent friction coefficient of crystalline graphite and anomalous behavior of wear dimension, *Tribol. Int.*, 2015, **88**, 280–289.
- 153 P. L. Menezes, Kishore, S. V. Kailas and M. R. Lovell, Friction and transfer layer formation in polymer-steel tribo-system: Role of surface texture and roughness parameters, *Wear*, 2011, **271**, 2213–2221.
- 154 B. L. Wang, Q. Chen, R. H. Wang and L. M. Peng, Synthesis and characterization of K₂Ti₆O₁₃ nanowires, *Chem. Phys. Lett.*, 2003, **376**, 726–731.
- 155 J. Yang, J. Chen, J. Zhang, Y. Wang and Z. Zhang, Microwave-assisted synthesis of potassium titanate nanowires, *Mater. Lett.*, 2006, **60**, 3015–3017.

- 156 S. O. Kang, H. S. Jang, Y. Il Kim, K. B. Kim and M. J. Jung, Study on the growth of potassium titanate nanostructures prepared by sol-gel-calcination process, *Mater. Lett.*, 2007, **61**, 473–477.
- 157 J. Li, Y. C. Zhang and M. Zhang, Low temperature preparation and optical properties of K₂Ti₆O₁₃, *Mater. Lett.*, 2012, **79**, 136–138.
- 158 L. Xu and L. Cheng, Environmentally friendly growth of single-crystalline K₂Ti₆O₁₃ nanoribbons from KCl flux, *Mater. Charact.*, 2010, **61**, 245–248.
- 159 H. Cid-Dresdner and M. J. Buerger, The crystal structure of potassium hexatitanate K₂Ti₆O₁₃, 1962, **117**, 411–430.
- 160 M. Inada, N. Enomoto, K. Hayashi, J. Hojo and S. Komarneni, Facile synthesis of nanorods of tetragonal barium titanate using ethylene glycol, *Ceram. Int.*, 2015, **41**, 5581–5587.
- 161 U. Balachandran, N. G. Eror and R. Mammone, Raman Spectra of Titanium Dioxide, 1982, **282**, 276–282.
- 162 S. Lee, C. Lee, D. Kim, J.-P. Locquet and J. Seo, Preparation and Photocatalytic Activity of Potassium- Incorporated Titanium Oxide Nanostructures Produced by the Wet Corrosion Process Using Various Titanium Alloys, *Nanomaterials*, 2015, **5**, 1397–1417.
- 163 Y. Su, M. Lou Balmer and B. C. Bunker, Raman Spectroscopic Studies of Silicotitanates, 2000, 8160–8169.
- 164 Q. Wang, Z. Guo and J. S. Chung, Formation and structural characterization of potassium titanates and the potassium ion exchange property, *Mater. Res. Bull.*, 2009, **44**, 1973–1977.
- 165 Q. H. Qian, X. F. Zhou, Y. Y. Hu, C. Liu, X. Feng and X. H. Lu, Preparation of smooth potassium hexatitanate nanofilms by sol-gel method, *J. Mater. Sci.*, 2007, **42**, 8222–8229.
- 166 R. Yahya, A. Hassan and Z. Aiyub, Structural studies of Potassium Hexatitanates prepared under Hydrothermal and Solid State conditions, *Mater. Sci. Forum*, 2006, **517**, 222–226.
- 167 S. Sehati and M. H. Entezari, Ultrasound facilitates the synthesis of potassium hexatitanate and co-intercalation with PbS-CdS nanoparticles, *Ultrason. Sonochem.*, 2016, **32**, 348–356.
- 168 A. León, P. Reuquen, C. Garín, R. Segura, P. Vargas, P. Zapata and P. Orihuela, FTIR and Raman Characterization of TiO₂ Nanoparticles Coated with Polyethylene Glycol as Carrier for 2-Methoxyestradiol, *Appl. Sci.*, 2017, **7**, 49.
- 169 F. Habashi, A short history of hydrometallurgy, *Hydrometallurgy*, 2005, **79**, 15–22.
- 170 G. Busca, The surface of transitional aluminas: A critical review, *Catal. Today*, 2014, **226**, 2–13.
- 171 H. Ghahraloud, M. Farsi and M. R. Rahimpour, Modeling and optimization of an industrial Claus process: Thermal and catalytic section, *J. Taiwan Inst. Chem. Eng.*, 2017, **76**, 1–9.
- 172 A. de Klerk, Hydroprocessing peculiarities of Fischer-Tropsch syncrude, *Catal. Today*, 2008, **130**, 439–445.
- 173 P. K. Kiyohara and H. S. Santos, Structure, Surface Area and Morphology of Aluminas from thermal decomposition of Al(OH)(CH₃COO)₂ Crystals, *An. Acad. Bras. Ci.*, 2000, **72**.
- 174 C. Piconi, 1.5 Alumina, *Compr. Biomater. II*, 2017, 92–121.
- 175 W. Gregoy Sawyer, K. D. Freudenberg, P. Bhimaraj and L. S. Schadler, A study on the friction and wear behavior of PTFE filled with acid treated nano-attapulgite, *Wear*, 2003, **254**, 573–580.
- 176 H. Aghajani Derazkola and A. Simchi, Effects of alumina nanoparticles on the microstructure, strength and wear resistance of poly(methyl methacrylate)-based nanocomposites prepared by friction stir processing, *J. Mech. Behav. Biomed. Mater.*, 2018, **79**, 246–253.
- 177 Joseph Hyde Pratt, *CORUNDUM and Its occurrence and distribution in the united states*, 1906.
- 178 F. R. Feret, D. Roy and C. Boulanger, Determination of alpha and beta alumina in ceramic alumina by X-ray diffraction, *Spectrochim. acta, Part B At. Spectrosc.*, 2000, **55**, 1051–1061.

- 179 M. Kadleikova, J. Breza and M. Vesely, Raman spectra of synthetic sapphire,
Microelectronics J., 2001, **32**, 955–958.
- 180 S. P. S. Porto and R. S. Krishnan, Raman effect of corundum, *J. Chem. Phys.*, 1967, **47**,
1009–1012.
- 181 A. Boumaza, L. Favaro, J. Lédion, G. Sattonnay, J. B. Brubach, P. Berthet, A. M. Huntz, P.
Roy and R. Tétot, Transition alumina phases induced by heat treatment of boehmite: An X-
ray diffraction and infrared spectroscopy study, *J. Solid State Chem.*, 2009, **182**, 1171–1176.
- 182 V. P. Ivanov and L. V. Sapronova, Infrared absorption spectra of aluminum oxide in the
gamma-modification with addition of ferric oxide, 1975, **20**, 536–538.
- 183 D. C. L. Vasconcelos, E. H. M. Nunes and W. L. Vasconcelos, AES and FTIR
characterization of sol-gel alumina films, *J. Non. Cryst. Solids*, 2012, **358**, 1374–1379.

