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Development of materials and processes for energy efficiency improvement and the mitigation of climate change effects

Coordinatore:

Chiar.mo Prof Giovanni Maestri

Tutori:

Chiar.mo Prof. Paolo Pelagatti

Dott.ssa Marcella Balordi

Dottorando: Alessandro Casali

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In memory of Lorenzo.



If beautiful things live in our memories, they live forever.

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SYMBOLS AND ABBREVIATIONS

H_{melting}	Snowflake melting height (km)
T_{max}	Temperature in the inversion zone (°C)
$H_{\text{subfreezing}}$	Height at which supercooled droplets are formed (km)
T_{surface}	Ground temperature (°C)
γ	Water content fraction in the snowflakes (-)
α	Melting ratio (-)
m_w	Mass of hot water (g)
$C_{p,w}$	Specific heat capacity (J/K)
T_1	Initial temperatures of the mixture (°C)
T_2	Final temperatures of the mixture (°C)
m_{sn}	Mass of snow (g)
L_f	Latent heat (J)
T_0	Freezing temperature of ice (°C)
M_T	Mass of the empty container (g)
M_1	Total mass (g)
T_1	Initial temperature (°C)
M_2	Final mass (g)
T_2	Final temperature (°C)
m_w	Mass of hot water (g)
m_{sn}	Mass of the snow (g)
M	Mass of ice and snow (g)
t	Time (s)
F	Mass flux density of the impinging particles (kg/m ² s)
A	Effective cross-sectional area of the object (m ²)
α_1	Collision efficiency (-)
α_2	Coalescence efficiency (-)
α_3	Accretion efficiency (-)

T_g	Glass transition temperature (°C)
T_m	Melting temperature (°C)
F_e	Force applied (N)
k	Spring constant (-)
x	Elongation of an elastic body (mm)
E	Young's modulus (Pa)
σ	Shear stress (Pa)
ε	Axial strain (%)
T	Temperature (°C)
p	Pressure (Pa)
dA	Helmholtz energy variation (J)
dU	Internal energy variation (J)
dS	Entropy variation (J/K)
ν	Poisson's ratio (-)
V	Volume (m ³)
W	Work (J)
F	Generic Force (N)
K	Bulk modulus (Pa)
G/μ	Shear modulus (Pa)
H_a	Hardness Shore A (-)
a	Generic length (mm)
h	Thickness (mm)
σ_s	Critical Shear Stress (kPa)
W_a	Work of Adhesion (J/m ²)
L	Distance (mm)
S	Surface energy (mN/m)
E^*	Apparent Young's modulus (Pa)
Λ	Constant (-)
Θ/ θ	Static contact angle (°)

γ_{SV}	Solid-Air tension, Surface energy (mN/m)
γ_{SL}	Solid-Liquid tension (mN/m)
γ_{LV}	Liquid-Air tension (mN/m)
CAH	Contact angle hysteresis (°)
θ_{adv}	Advancing contact angle (°)
θ_{rec}	Receding contact angle (°)
RO	Roll-off angle (°)
r	Roughness factor (-)
f_s	Fraction of solid (-)
τ_{ice}	Ice adhesion strength (Pa)
F_{max}	Maximum force (N)
δ	Costant (-)
γ_w	Costant (-)
m_{ref}	Mass of snow accumulated on the reference (g)
m_{sam}	Mass of snow present on the coated sample (g)
Δt_{det}	Temporal difference (s)
E^0	Standard reduction potential (eV)
A:B	Part A : Part B ratio
AC	Accelerated aging chamber (test)
ACSR	Aluminium-conductor steel-reinforced
AFM	Atomic Force Microscopy
AFM	Atomic force microscopy
Al	Aluminium
ARF	Adhesion reduction factor
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
CAT	Centrifuge adhesion test
CS/cs	Cold spraying (Cold sprayed surface)

D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
DC	Direct current voltage
EPDM	Ethylene-propylene diene monomer rubber
FS/fs	Flame spraying (Flame sprayed surface)
FT-IR	Fourier transform infrared spectroscopy
HDPE	High-density polyethylene
LBL	Layer-by-layer technique
LDPE	Low-density polyethylene
LNA	Artificial snow laboratory
LV	Liquid-Air interface
LWC	Liquid Water Content
MDPE	Medium density polyethylene
MTEOS	Methyltriethoxysilane
NPs	Nanoparticles
PDMS	Polydimethylsiloxane
PE	Polyethylene
PP	Polypropylene
PST	Phase shifter transformer
PTSLIPS	Phase-Transition slippery liquid infused porous surface
ROP	Ring opening polymerization
s	Smooth surface
S _a	Mean roughness
SAM	Molecular self-assembly
sb	Sand-blasted surface
SCA/CA	Static contact angle
SEM	Scanning electron microscopy

SFR	Snow reduction factor
SHP	Superhydrophobic (surface)
SL	Solid-Liquid interface
SLIPS	Slippery liquid infused porous surface
S_q	Root Mean Square roughness
SRF_{avg}	Average snow reduction factor
SRF_{max}	Maximum snow reduction factor
SV	Solid-Air interface
TEOS	Tetraethyl Orthosilicate
TMOS	Tetramethyl Orthosilicate
TPEs	Thermoplastic elastomers
ttx	Thermal treatment x
UV	Ultraviolet
xgg	x days
YM	Young's modulus

1. Introduction

1.1 Context and motivation

The phenomenon of atmospheric icing is a significant issue for electrical grid infrastructure, particularly for conductors and guard ropes, which are exposed to variable weather conditions. The formation of ice and the accumulation of snow on the network components can lead to overloading of the structures, with the risk of breakage and failure. This not only incurs high costs for damage restoration but also causes significant disruptions for the population by depriving them of access to electricity. With the progressive climate change, the frequency and intensity of extreme weather events, such as snowstorms and ice storms, have become more unpredictable, increasing the risk of damage to the electrical grids. Despite the importance of this phenomenon, current structures are not always adequately prepared to address the challenges posed by atmospheric icing. The difficulty in predicting such events and the limited knowledge regarding optimal solutions to protect energy infrastructure make it necessary to conduct thorough research on new materials and anti-icing solutions. The adoption of innovative materials could significantly improve the resilience of electrical grids, reducing maintenance costs and the risk of failures.

1.2 Research objectives

The main objective of this research is to explore and develop effective solutions to counteract the phenomenon of atmospheric icing, focusing on the use of materials and technologies that do not require additional energy sources but instead rely on the intrinsic chemical and physical properties of the materials themselves. Specifically, this research focuses on the analysis and design of passive anti-icing materials capable of preventing the accumulation of snow and ice on critical electrical grid components, such as conductors and guard ropes. Various types of materials and their properties will be examined to identify solutions that can be applied in a simple and cost-effective manner to improve the reliability of the electrical grid. In this context, the research will delve into the use of solutions based on elastomers, superhydrophobic and slippery surfaces, exploring how their chemical-physical characteristics can be utilized to reduce ice accumulation and enhance the resistance of electrical infrastructures in extreme environments.

2. Atmospheric icing

Nature exhibits its force in fascinating and unpredictable ways, and one of the most challenging examples is the phenomenon of *atmospheric icing*¹⁻³. This term encompasses all processes leading to the formation of ice and snow on exposed surfaces. Although ice and snow may seem harmless, their accumulation poses a complex and dangerous challenge, with significant impacts on infrastructure, transportation, and energy systems⁴⁻⁶.

The understanding of atmospheric icing could allow us to better manage its consequences, reduce its impact on our lives and infrastructures, and anticipate and predict the phenomenon to enhance the safety and resilience of exposed structures, ensuring operational continuity in strategic sectors such as energy field. Atmospheric icing on power lines components is a well-known problem worldwide and is considered a phenomenon that primarily affects polar regions, the mountains of Central Europe, Asia, and North America^{7,8}. However, it can also occur in areas with higher average temperatures, such as the Alpine and Apennine regions of Italy, where the problem is particularly related to the accumulation of wet snow⁹⁻¹¹. An additional factor that may exacerbate the issue of atmospheric icing is the progressive climate change, which increases the likelihood of such events occurring in regions where they were previously never recorded, catching structures unprepared and impacting those not suited to withstand such phenomena. Some events occurred between Emilia-Romagna and Lombardy in 2015, where the accumulation of wet snow on electrical components caused failures in the lines, leaving 450,000 users without power for several days. A similar event occurred in 2017 between Marche and Abruzzo, where 300,000 users were left without electricity.

Addressing the issue of atmospheric icing on electrical system requires considerations of various types of ice accumulation, depending on numerous parameters such as temperature, humidity, and wind speed^{12,13}. Predicting the type of ice formation is not always straightforward, like the construction of reliable models that can accurately describe the development of the phenomenon^{14,15}. For all these reasons, atmospheric icing represents a challenge that should not be underestimated. The following paragraphs will explore the key aspects of this process, starting with the mechanisms of ice and snow formation and moving on its effects on structures and systems. Environmental factors influencing ice and snow growth and their variations under different climatic conditions will be also analysed. The occurrence of these events underscores the need for effective and lasting solutions to prevent and mitigate atmospheric icing on electrical system components

2.1 Ice and snow accretions

A first step in addressing the icing phenomenon is to analyse the different types of accretion, which can be divided into two main categories: *in-cloud icing* and *precipitation icing*¹⁶. In-cloud icing occurs when supercooled water droplets remain in the liquid state within clouds, even at temperatures below 0°C. Upon impact with surfaces, these droplets freeze instantly, leading to ice formation. The most important parameters influencing the type of accretion are the droplet size, wind speed, which affects the impact velocity on surfaces, and air temperature¹⁷. In general, there are three main types of ice: hard rime, soft rime, and glaze ice (Fig. 1).

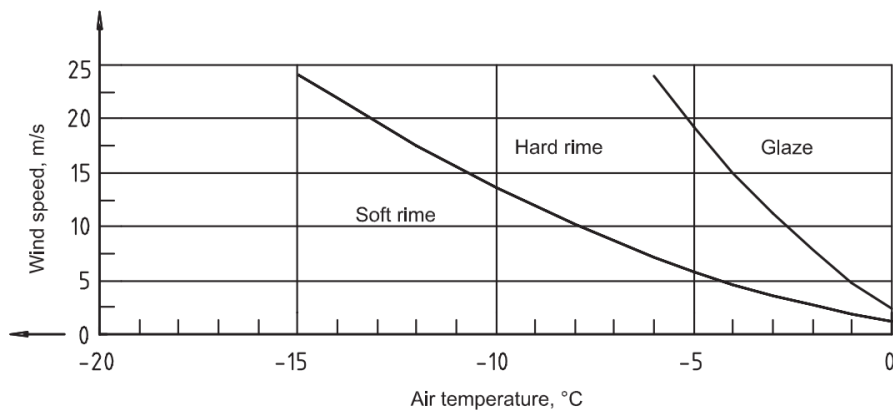


Fig. 1 Different types of in-cloud icing in function of wind speed and air temperature¹⁷

When water droplets are micrometric in size, the accretion is characterized by the inclusion of air bubbles in the ice, a phenomenon known as *rime ice* (Fig. 2). This type of ice appears granular and forms in a temperature range from -2°C to -15°C. Its density varies depending on the impact velocity and droplet size: if the density ranges between 300 and 700 kg/m³, the accretion is considered hard, with strong adhesion to surfaces. Conversely, the accretion is termed soft when it has a lighter structure like frost, with a density below 300 kg/m³ and lower adhesion to the substrate. When the droplets range from 10 to 100 micrometres, the ice develops without trapping air bubbles, resulting in a more compact, smooth, and transparent form. This type of accretion, known as glaze ice (Fig. 2), forms at temperatures typically between 0°C and -5°C with wind speeds higher than 20 m/s, and has a high density, usually around 900 kg/m³. Its high density makes it extremely adhesive to surfaces and difficult to remove, representing one of the most problematic forms of icing for infrastructures

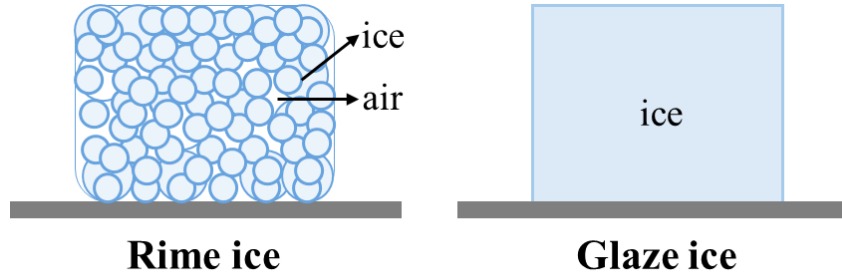


Fig. 2 Schematic representation of rime ice (left) and glaze ice (right). The first one has a sponge-like structure with trapped air inside the structure. The second one has a compact and transparent structure without trapped air bubble.

The precipitation icing phenomenon¹² is caused by the passage of snow through atmospheric layers characterized by thermal inversion (Fig. 3). When snowflakes are at a height from the ground where the temperature is above 0°C (H_{melting} , where H = height), they begin to melt, accumulating water inside their structure. If the temperature in this inversion zone is sufficiently high (T_{max}), normally around $+2^{\circ}\text{C}$, the snowflakes almost completely melt, incorporating a large amount of water, and take on a hybrid form like small water droplets. When these droplets fall towards the ground, they encounter a zone characterized by a sudden drop in temperature ($H_{\text{subfreezing}}$) and transform into supercooled droplets. Upon impact with the ground, on cold surfaces (T_{surface}), these droplets freeze quickly, leading to the formation of *wet snow*, characterized by a density that can reach up to 800 kg/m^3 and a liquid water content that can exceed 40% relative to the total mass.

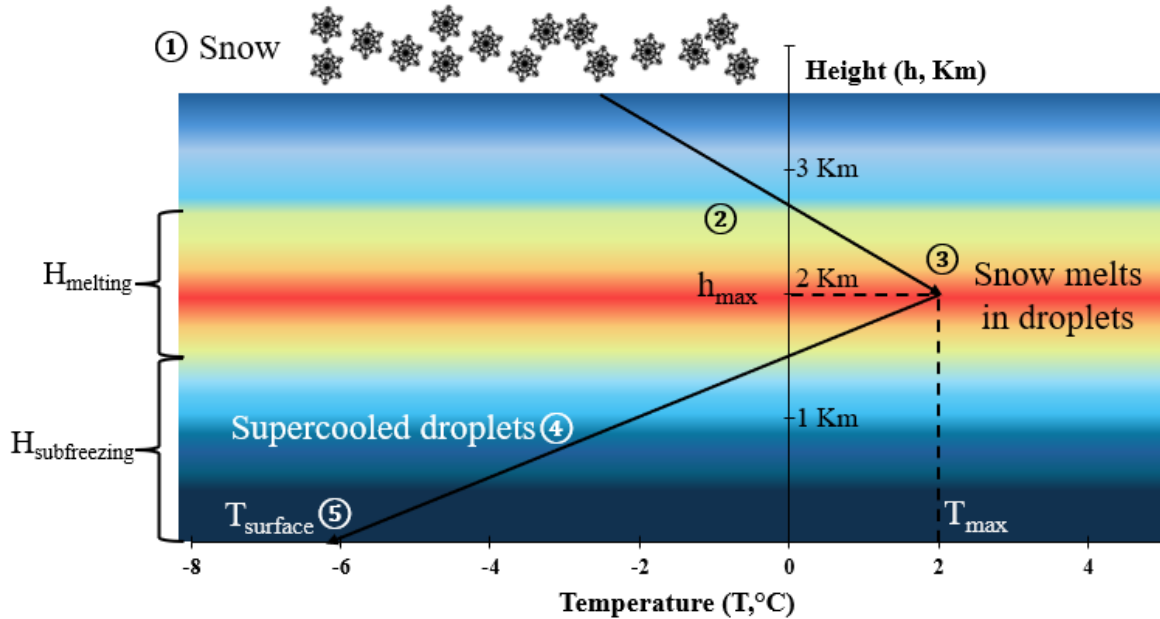


Fig. 3 Precipitation icing as a function of height (H) and temperature (T). Following the black arrows, snow (1) begins to melt as it reaches the melting layer (2), where the temperature increases. When the temperature exceeds 0°C (3), the snow melts into small droplets. These droplets, when moving through a colder layer, become supercooled (4) and can freeze upon impacting cold surfaces at ground level forming wet snow (5).

The presence of a high residual water content significantly increases the adhesion of wet snow to surfaces. This contribution depends on the meteorological conditions during the event and can be quantified through the calculation of the Liquid Water Content (LWC)^{16,18}. In general, LWC is defined as the ratio of the mass of liquid water present in the snow or ice accretion to the total mass of the accretion

$$LWC = \frac{M_{water}}{M_{tot}} * 100$$

In the specific case of *wet snow*, the LWC is the sum of several contributions that account for water initially present in the snowflakes before the melting process begins and the one deriving from the snowflakes melting, transforming a portion of the ice into liquid water. It is defined as

$$LWC = \alpha(1 - \gamma) + \gamma$$

where γ is the initial water content in the snowflakes already present before impact with the surface, α is the melting ratio, indicating how much water is released by the melting of the snow, and $(1 - \gamma)$ represents the remaining solid fraction in the snowflakes after passing through the thermal inversion zone. There are different practical methods based on this relationship that allow calculating the various contributions involved in the LWC calculation¹⁹⁻²¹. Among them, the calorimetric method is applicable both for laboratory and field measurements²². In this process, a sample of snow is mixed with hot water inside a thermally isolated container, and the difference between the initial temperature of the water and the final temperature of the mixture allows the determination of LWC. The in-depth procedure for calculating LWC by calorimetric method is presented in the experimental part.

One final important aspect to consider is that, if the precipitation is not subject to thermal inversion, the water does not accumulate inside the snowflakes during the accretion, and it is referred to as *dry snow*, with a density not exceeding 100 kg/m³ and poor adhesion to surfaces.

2.2 Growth mechanisms and impact on power lines

Atmospheric icing is a complex phenomenon, characterized by dynamics that vary depending on environmental conditions but are also influenced by the type of surfaces involved. Different materials are subjected to this phenomenon, and depending on their chemical-physical characteristics, shape, and size, they may exhibit different behaviours when interacting with ice and snow. This thesis project focuses on studying the effect of atmospheric icing on electrical system components, particularly *conductors* and *ground wires*²³ (Fig. 4).

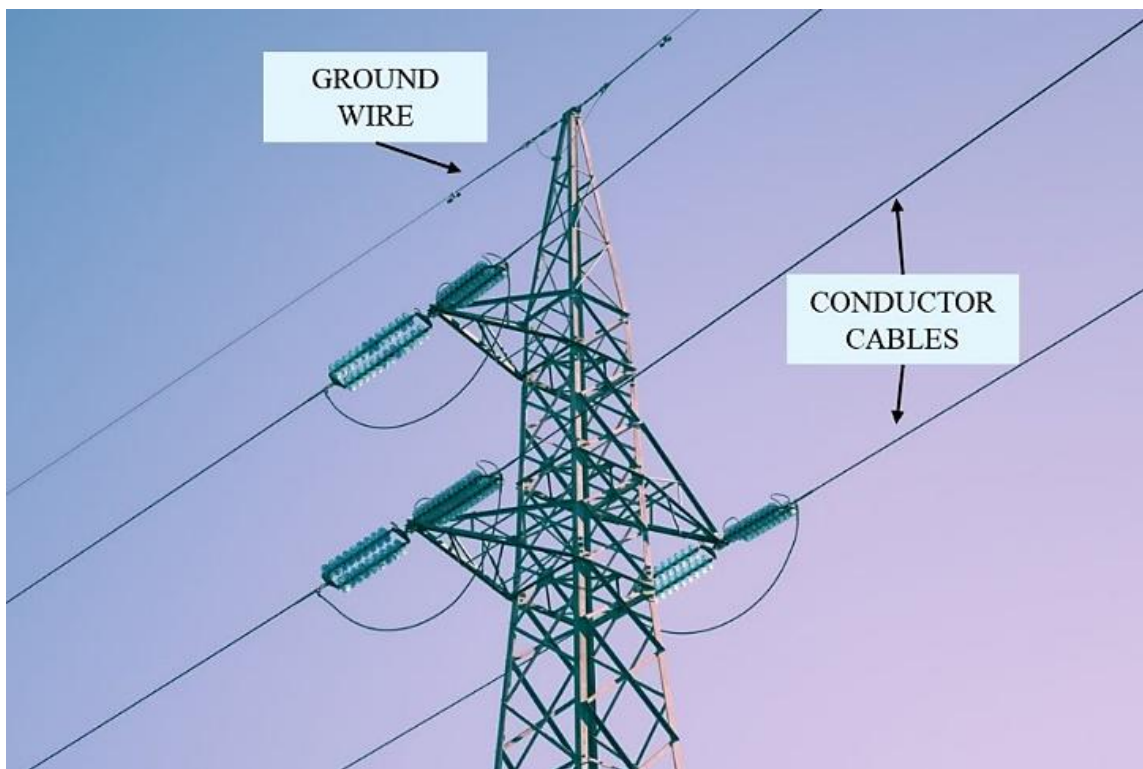


Fig. 4 Electrical pylon with conductor cables and ground wires highlighted

Both components are made mainly of aluminum alloys with a stainless steel reinforcement core, like for example Anticorodal 6082 (Al6082), an aluminium-magnesium-silicon alloy known for its excellent mechanical properties and high resistance to corrosion^{24,25}. Both the conductor cables and the guard ropes consist of individual filaments twisted together. The conductor cables are thicker (Fig. 5, left), while the guard ropes, which are thinner, can incorporate optical fibres for data transmission (Fig. 5, right).



Fig. 5 A conductor cable (left). A ground wire with glass fiber core (right).

The mechanism of ice and snow growth on electrical system components is represented by the *basic equation for ice accretion* described in the International Organization for Standardization (ISO) standard for icing of structures (ISO 2001)^{12,16,26}, in which the icing rate is expressed as the change in mass of ice and snow over time:

$$\frac{dM}{dt} = \alpha_1 \alpha_2 \alpha_3 F A$$

F is the mass flux density of the impinging particles, A is the effective cross-sectional area of the object, while the factors α_1 , α_2 , and α_3 represent, the collision efficiency, the coalescence efficiency and the accretion efficiency, respectively. The collision efficiency (α_1) is a parameter that describes the actual impact of the particles on the surface, and it usually takes values lower than 1 due to the deflection of smaller particles under the effect of the air streamlines (Fig. 6).

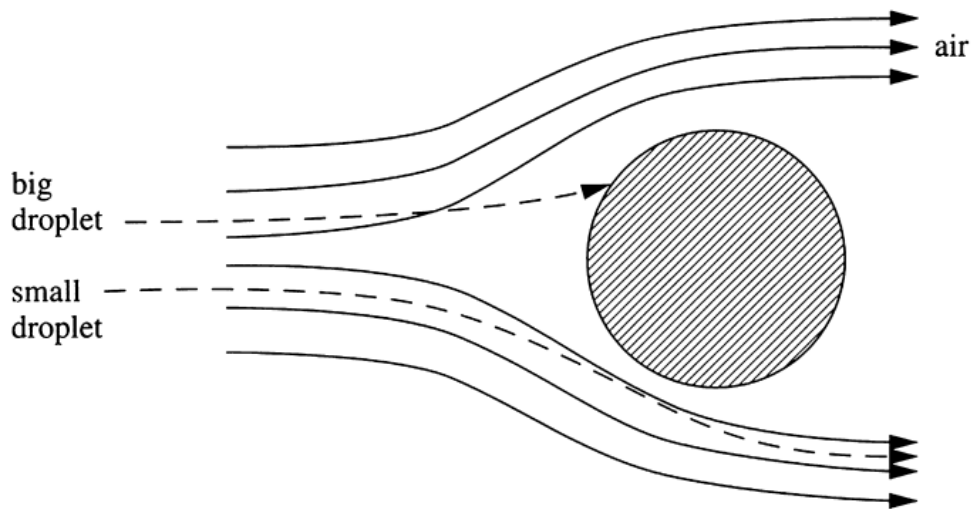


Fig. 6 Deflection of smallest particles due to air streamlines. It causes a loss in collision efficiency²⁶.

The coalescence efficiency (α_2) represents the ratio between the number of particles that stick to the surface and the total amount of particles that hit it. This factor accounts for the particles that, upon impacting the surface, are deflected or repelled from it. The accretion efficiency (α_3), on the other hand, measures how effectively the particles that stick to a surface contribute to the formation of ice. If the efficiency is lower than 1, it means that not all the liquid particles that adhere to the surface freeze, because the amount of heat generated by the accretion process is insufficient to freeze them completely. This results in the formation of a liquid layer on the metallic surface (Fig. 7), with freezing occurring beneath this layer, leading to wet growth^{16,26}. This process leads to the formation of glaze ice or wet snow depending on the atmospheric conditions discussed in the previous section.

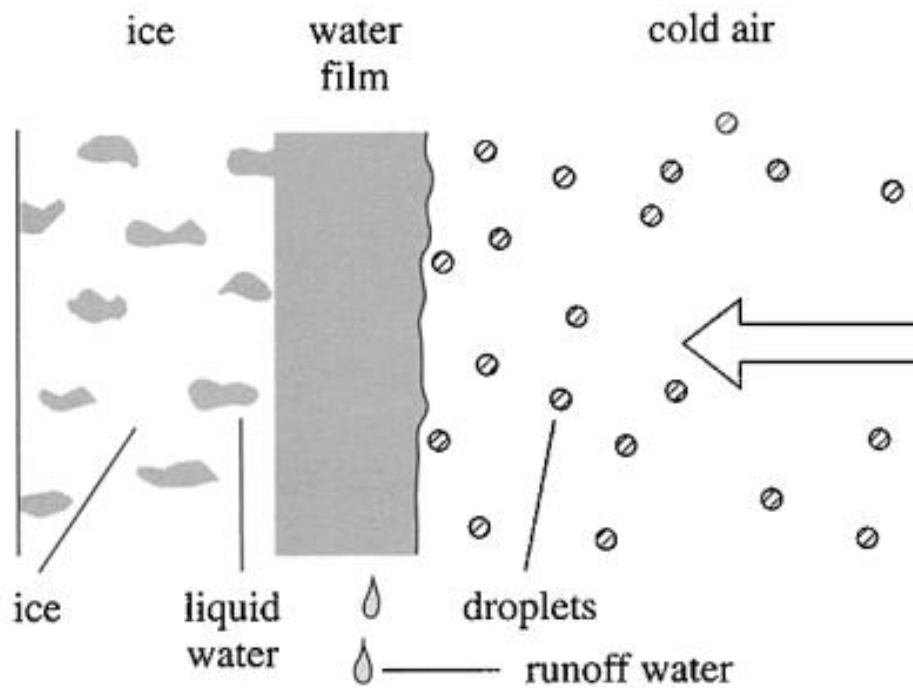


Fig. 7 Wet growth²⁶.

When the efficiency is high there is not formation of any liquid layer and the process is called dry growth (Fig. 8), which leads to the formation of rime ice.

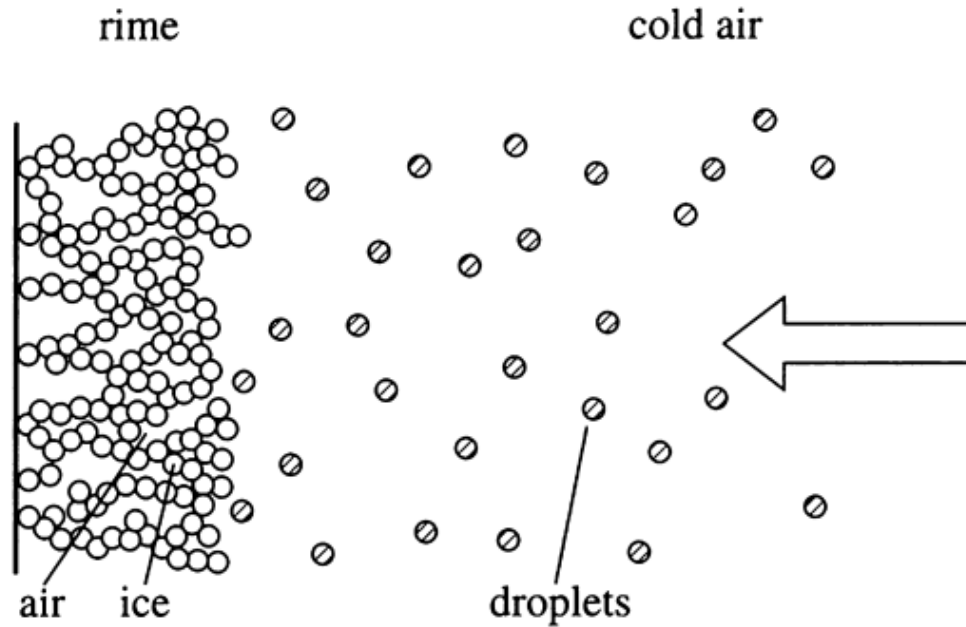


Fig. 8 Dry growth²⁶.

To understand the actual mechanism of ice and snow growth, it is essential to consider the configuration of the entire structure. The movements of suspended cables induced by wind (Fig. 9) influence the process of ice and snow formation^{16,27,28}.

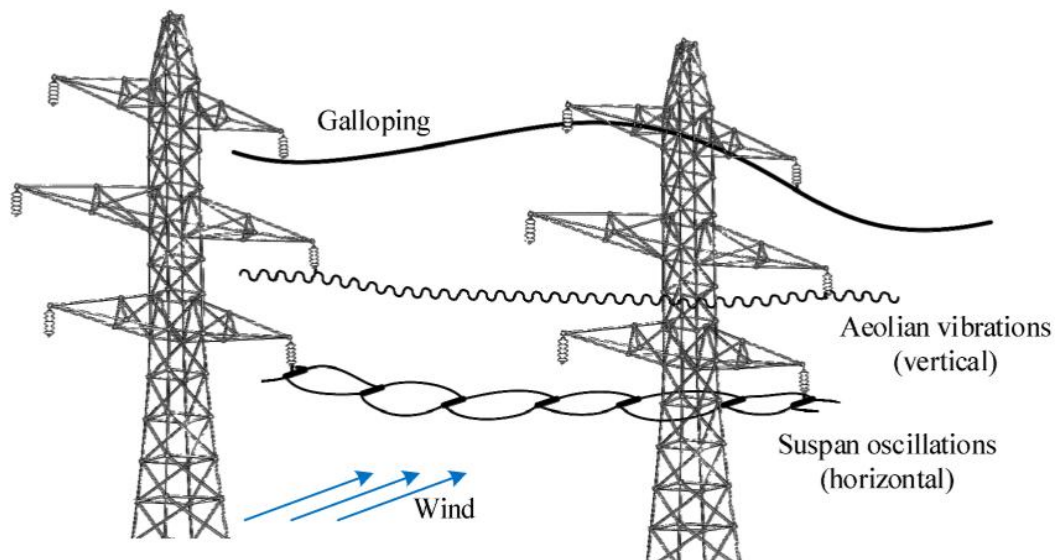


Fig. 9 A schematic representation of typical wind-induced vibrations. A low torsional rigidity of wires contributes to these movements²⁹.

Galloping and aeolian vibrations are vertical movements caused by wind force: aeolian movement occurs mainly when the wind has a relatively low speed (around 4-8 m/s), and the movement of the cables manifests as small oscillations, while galloping occurs when the cable undergoes large and irregular oscillations, generated by stronger and more turbulent winds or by

the presence of ice and snow accumulations, which further intensify the oscillations and increase the likelihood of subsequent galloping events. Suspension oscillations, on the other hand, are horizontal oscillations of the cables also due to the wind force. Meteorological conditions are variable and often change rapidly, making it impossible to estimate which of these movements is more prevalent or more influential in the growth of ice on the surfaces due to the sudden change in wind intensity or direction. However, the combination of these oscillations contributes to the creation of a rotational movement that promotes the formation of the *sleeve*^{30–32} (Fig. 10 and Fig. 11).



Fig. 10 Example of sleeves grown on conductor cables. Clockwise: rime ice (top left), glaze ice (top right) and wet snow (bottom).

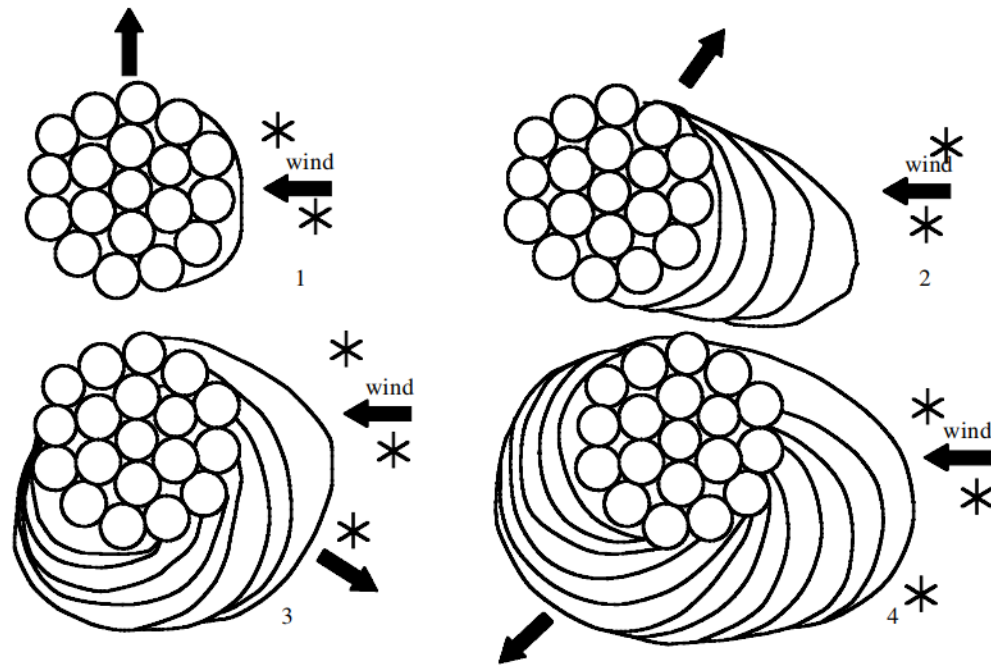


Fig. 11 Ice or snow tends to accumulate in the upwind area creating an initial layer around the conductor, after which the conductor begins to turn favouring the accumulation of additional layers. The continuous movement of the conductor around its axis promotes accumulation that eventually leads to the formation of the sleeve. This model is also applicable to guard ropes, which are more affected by accretion as they are subjected to greater torque being smaller in diameter than conductors³¹

The following chapters will review several anti-icing solutions that could be adopted to address and solve this problem efficiently and sustainably. These solutions include both active strategies, requiring extra energy sources, and passive strategies, focusing on methods that directly mitigate ice and snow accumulation, and approaches that modify surface properties, such as polymeric, superhydrophobic, or slippery coatings. Special attention will be given to the development of surface modifications designed to reduce adhesion, prevent ice nucleation, and promote easy removal, ensuring that these strategies are not only effective but also environmentally and economically sustainable in the context of real-world applications.

3. Strategies against atmospheric icing

Atmospheric icing represents a critical challenge to the resilience and efficiency of electrical system components. To address this issue, two primary approaches have emerged^{16,33,34}: preventing and mitigating ice formation through *anti-icing techniques*, or actively removing ice accretions with *de-icing techniques*. These strategies involve the use of different types of approaches that are divided into *active* and *passive* solutions^{35,36}. Active solutions rely on additional energy sources or external intervention, while passive solutions leverage materials or surface treatments designed to counteract ice and snow formation using their inherent chemical and physical properties.

Let's begin by looking at what current anti-icing solutions are: both active and passive strategies can be employed for ice and snow prevention and mitigation. Among active approaches there is the *ice electrolysis system*³⁷, which functions by applying a direct current (DC) voltage between a grid electrode and a conductive coating applied to the conductor (Fig. 12). The process involves the electrolysis of water molecules within the ice, generating gas bubbles at the ice-conductor interface, which disrupt the ice structure and create micro-cracks, helping to lift the ice away from the surface. One challenge associated with this technique is the installation of the axial grid-electrode, which must be electrically insulated from the conductor itself by a dielectric layer.

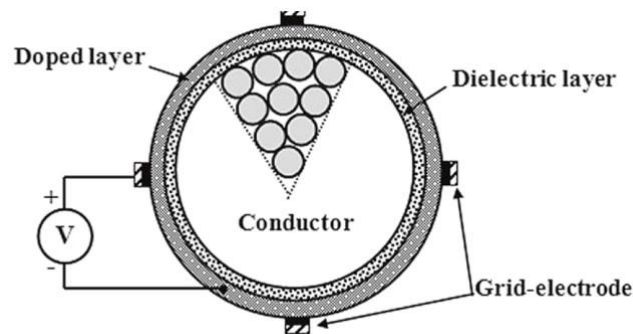


Fig. 12 Simplified scheme of Ice electrolysis system³⁷.

The *pulse electro-thermal de-icer*^{37,38} works in a similar way but relies on the application of a pulsed current to a conductive coating to generate heat at the ice-surface interface. Also, in this case it is necessary to insulate the conductor with a dielectric layer, but compared to the previous technique, much lower powers are required. Another similar technique, shown in the CIGRE technical brochures³⁵, is based on the use of *LC-spiral rods*, a ferromagnetic coating wrapped around the conductor that absorbs energy from the alternating magnetic field generated by the current, releasing heat on the one hand through the phenomenon of hysteresis, and thanks to the

presence of eddy currents that are generated in the ferromagnetic material. One of the advantages of this device is its ability to generate a relatively large amount of heat energy during the winter and a small amount in the summer. These approaches are extremely interesting from an engineering point of view, but very often they are complex to implement, without considering the energy sources necessary for their operation. For the removal of ice and snow from surfaces, active methods based on the *Joule effect* are employed^{37,39}. This effect, which generates heat because of the resistance of the material to the passage of electric current, is intrinsic and always present in conductors. However, the amount of heat produced is not enough to counteract the accumulation of ice or snow. To reach temperatures high enough to favour the melting of the ice, it is necessary to temporarily increase the intensity of the current. The *load shifting method*^{37,40} is a strategy that consists of redistributing the load of electrical energy, transferring or reducing the load to less critical lines or circuits, to convey a greater flow of current in the line subject to the risk of icing. In this way, the increase in current triggers sufficient heating of the conductor to facilitate the melting of accumulated snow or ice, improving reliability and safety of exposed lines. If service interruption or redistribution is problematic, then the *on-load network method*^{41,42} can be applied, which uses a phase shifter transformer (PST) to regulate the flow of power in the transmission lines, generating enough heat to melt the ice without interfering with the wider power grid. The *reduced voltage short-circuit method*^{37,43} is a technique in which heat is generated via a controlled short circuit. The principle behind this technique is that the short circuit created produces a high-intensity current that generates a high amount of heat due to the Joule effect. However, for the practical implementation of this technique, additional equipment, such as switches and protection systems, must be installed to ensure safety during the application of the high current. The *DC current method*^{37,44}, on the other hand, is a particularly advantageous technique for long-distance transmission lines with large diameter conductors. The method is based on the principle that direct current eliminates reactive losses allowing for greater efficiency in energy transmission, minimizing energy losses and improving heating efficiency. These methods are ineffective in protecting guard ropes as it is not possible to directly exploit the Joule effect. For this reason, when the problem arises on the guard ropes, they are isolated from the pylons to prevent the heat produced from being dispersed to the ground or other parts of the network, and then electrical current is supplied through a voltage transformer that allows the Joule effect to be exploited again. Finally, *mechanical methods*^{45,46} involve the physical removal of ice through scraping or by providing vibrations and shock waves. Historically, human intervention was necessary to mechanically remove ice, today thanks to the help of specific devices is possible

to perform these operations in a safer and more effective way^{47,48}. Passive solutions, on the other hand, offer an innovative and potentially more sustainable approach to tackling the ice problem. They exploit the chemical and physical properties of materials and surfaces, without the need for additional energy sources. Surfaces or materials of this type are also called *ice-phobic* and will be discussed in more detail in the following section. Other passive methods involve the use of snow rings⁴⁹ or anti-torsion systems³⁷ to create discontinuity in the growth of the sleeve, decreasing the compactness of the structure and favouring its removal.

3.1 Passive solutions

To date, there is no specific class of materials that can be universally defined as anti-icing, and this is due to the variety of sectors in which it is necessary to face the phenomenon of atmospheric icing. In theory, any material that can reduce or prevent the accumulation of ice or snow could potentially be used as an anti-icing, if it meets the requirements of the application context. The main approaches for the creation of anti-icing surfaces involve the use of *polymeric coatings*^{50,51}, the creation of *superhydrophobic surfaces*^{52,53} or *slippery surfaces*^{54,55}. Polymers represent an important solution, thanks to a wide range of materials with adaptable properties, which can be exploited and modulated to reduce the adhesion of ice and snow. Elastomers are interesting and silicones such as polydimethylsiloxane offer an excellent solution for anti-icing applications. The functionalization of surfaces is another important strategy to obtain anti-icing properties, thanks to the possibility of directly treating the substrates of interest without going through complex synthesis steps. Slippery surfaces, for example, reduce adhesion thanks to a low friction coefficient guaranteed by the infusion of lubricants, while superhydrophobic surfaces use their high water-repellent capacity to inhibit the formation of ice and snow. Each of these approaches has advantages and limitations, and the choice of the most suitable material depends heavily on the context of use and specific performance requirements.

3.1.1 Elastomeric materials

Elastomers, commonly known as rubbers, are *viscoelastic thermoset* polymers with low *glass transition temperature* (T_g) capable of undergoing reversible deformations, allowing them to change size and shape without compromising their chemical or physical properties or causing cracking of the material. This characteristic, known as *elasticity*, is influenced by both the polymer's chemical structure and its thermodynamic behaviour⁵⁶.

At the molecular level, reversible elasticity requires that the polymer chains exhibit a high degree of mobility. However, it is equally essential to fix these chains at specific points via *cross-linking* step⁵⁷ to ensure that the material can return to its original state after deformation (Fig. 13). Typically, this involves starting with a prepolymer containing reactive sites that can form cross-linking nodes, which are critical to maintaining the reversible structural integrity of the material. Alternatively, elastomers with intrinsic elastic properties can be synthesized and subsequently enhanced through a cross-linking process to further improve their performance characteristics^{58,59}.

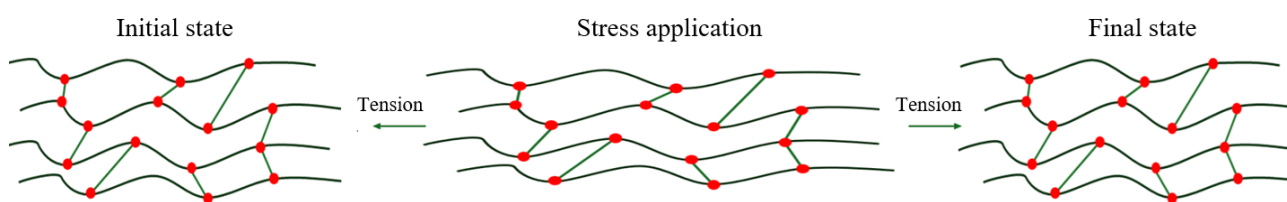


Fig. 13 Simplified representation of reversible deformation of elastomers subjected to tension. In black the elastomer polymer chains, in red the cross-linking nodes.

Crosslinking is therefore essential to obtain high-performance elastomeric materials. In general, this process involves the creation of a three-dimensional network through *chemical* or *physical mechanisms*. Chemical crosslinking is based on the formation of strong, permanent covalent bonds between polymer chains, whereas physical crosslinking relies on weaker intermolecular interactions, such as *Van der Waals forces*, *dipole interactions*, *hydrogen bonds*, or *ionic associations*, which often result in a reversible network⁶⁰ (Fig. 14). The chains can combine autonomously during the polymerization process to form branches with reactive pendants that can interact with other growing chains, or it is necessary to use a *cross-linking agent*⁶¹ that allows bridges to be created among the chains.

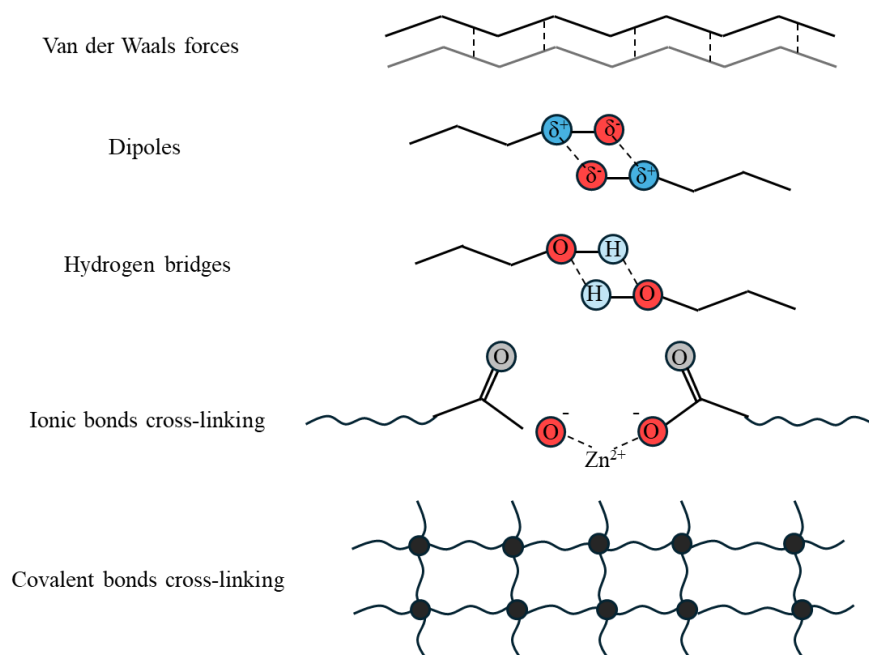


Fig. 14 Cross-linking types.

Within the class of elastomers, the process known as *vulcanization*^{62,63} refers to the historical high temperature cross-linking reaction of natural rubber (polyisoprene) with sulphur⁶⁴ (Fig. 15), during which sulphide bridges are formed between the chains.

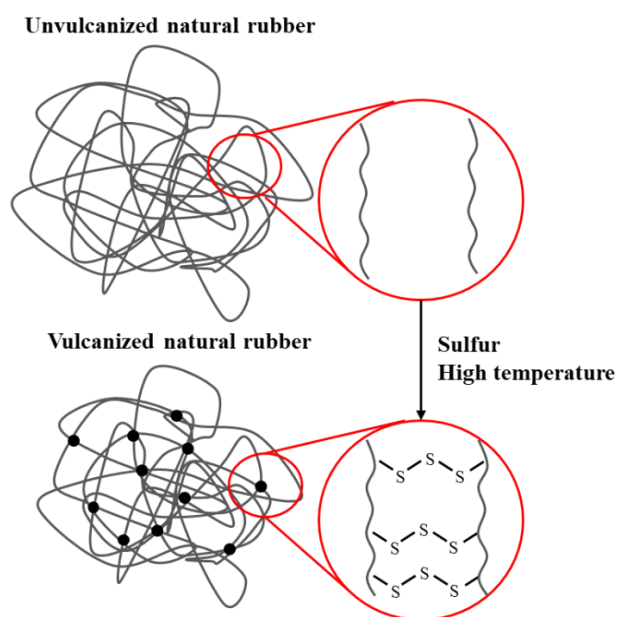


Fig. 15 Diagram illustrating the process of vulcanization, the first cross-linking reaction discovered by Goodyear in the first half of the 19th century⁶⁵.

Although polyisoprene and other elastomers such as polybutadiene already exhibit good elastic behaviour, vulcanization significantly increases their mechanical strength. Today, the term is used to refer to the cross-linking process of elastomers in general.

There are different vulcanization methods that depend on the mechanism and chemistry of the functional groups involved and can be divided into two macro-groups^{51,66}:

- *Condensation cross-linking*, in which two functional groups react by usually eliminating a molecule of water or alcohol. In these cases, it is necessary to use cross-linking agents with functional groups suitable for inducing a condensation reaction between the polymer chains; on the contrary, it is rarer to find materials that can cross-link autonomously during the polymerization, while maintaining an elastic behaviour. For example, cross-linking of silicones can occur through the reaction of silanol groups ($-\text{Si}-\text{OH}$) with crosslinkers containing alcohol groups such as alkylsilanes ($\text{RSi}(\text{OEt})_3$) or tri- and tetraalkoxysilanes (e.g. TEOS, $\text{Si}(\text{OEt})_4$) forming siloxane bonds ($-\text{Si}-\text{O}-\text{Si}-$) with the elimination of ethanol as a by-product⁶⁷. These reactions are usually catalysed by acids, bases, or tin-based catalysts⁶⁸. A more detailed description is presented in section 10.1 concerning the chemistry of polydimethylsiloxane

- *Addition cross-linking* in which functional groups react by forming bridges between polymer chains without by-products. Addition vulcanization processes normally involve the formation of *radicals* using UV radiation, high temperatures, or *initiators* such as peroxides^{69,70}. They are capable of cross-linking saturated elastomers, such as ethylene-propylene diene monomer rubber (EPDM)⁵⁹. The radical mechanism has some limitations due to the possible presence of antioxidant species which, by reacting with the radicals generated, can block the reaction, reducing the efficiency of cross-linking. The cross-linking of polydimethylsiloxane (PDMS) can be carried out using *organometallic complexes* (Fig. 4) by conducting the *hydrosilylation* reaction between a $\text{C}=\text{C}$ vinyl group and the $\text{Si}-\text{H}$ bond through platinum-based catalysts⁷¹. A strategy that allows less drastic conditions to be used, although it normally involves expensive catalysts. A more detailed description is presented in section 10.1 concerning the chemistry of polydimethylsiloxane. Another approach involves the use of *resin*, mainly used in the vulcanization of unsaturated rubbers, such as butyl rubber, where high thermal resistance and durability are required⁷². Compared to other cross-linking methods, this process requires higher temperatures, is generally slower and requires the use of catalysts to be activated⁵⁷.

Dynamic vulcanization is a process in which an elastomer is cross-linked to form micrometer-sized domains dispersed within a molten, non-vulcanizable thermoplastic matrix. This process produces thermoplastic elastomers (TPEs), hybrid materials that combine the elasticity and resilience of elastomers with the ease of processability characteristic of thermoplastics⁷³. Unlike traditional elastomers, in which cross-linking points are created via permanent chemical bonds, cross-linking points in TPEs are generally the result of physical interactions such as hydrogen bonds, π - π interactions, crystallinity, and micro phase separation. A typical example is mixtures

of ethylene-propylene-diene monomer (EPDM) and polypropylene (PP), which can be dynamically vulcanized using a system based on sulphur, zinc oxide, stearic acid, tetramethyl disulfide, and benzothiazil disulfide⁷⁴. TPEs present an innovative solution, as their physical cross-linking enables them to exhibit elastomer-like behaviour at room temperature while retaining the ability to be remolded like traditional thermoplastics when heated above their glass transition temperature (T_g) or melting temperature (T_m). This unique combination of properties makes TPEs particularly versatile, especially in the context of material recycling and reuse⁷⁵. Cross-linking is the crucial step in the preparation and optimization of elastomer properties and strongly influences the chemical nature of the polymer, as well as the mechanical, thermal and chemical properties of the final material. To optimize the process and achieve the desired properties, *additives* such as accelerators, retardants, fillers and plasticizers are often used^{58,76,77}. These additives allow to precisely control cross-linking conditions, modulate reaction times and adapt the process to industrial scale up, while ensuring the improvement and consolidation of material properties. In this way, elastomeric materials can be developed with the desired properties, while ensuring efficiency on a production scale. It is important to emphasize again that the vulcanization step must be carefully controlled to achieve an optimal degree of cross-linking. If the cross-linking is too high, it can severely restrict the mobility of the polymer chains, compromising the material's elasticity.

3.1.1.1 Thermodynamic and mechanical properties of elastomers

Elastomers have a three-dimensional network structure formed by long polymer chains interconnected through cross-linking nodes. But how do they behave under stress? The key lies in their amorphous nature: the polymer chains of an elastomer are long, flexible and arranged in a disordered and intertwined manner, forming a structure called *statistical coil conformation*⁷⁸ (Fig. 16)

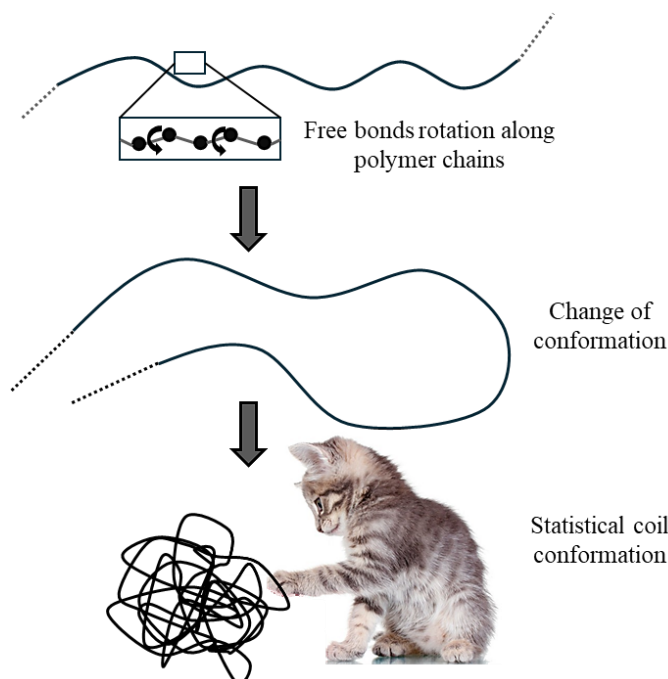


Fig. 16 When polymer chains reach a very high number of units, due to the free rotation around the bonds along the chain, they tend to adopt different conformations, eventually folding back on themselves to form a statistical coil.

The chains inside the statistical coil do not move as a single unit, but rather distinct segments of each chain move cooperatively, influencing each other. These *cooperative segmental motions*⁷⁹ are fundamental for the elastic behaviour of the material, as they allow the polymer chains to respond to external stresses by redistributing it throughout the network. For these cooperative motions, there must be *free volume*⁸⁰ in the material, space between the polymer chains that allows the segments to move and rotate around the chemical bonds, thus changing their spatial conformation and responding elastically to stresses. When one segment of a chain moves, the other neighbours on the same chain or adjacent chains also move in a coordinated manner, especially in regions adjacent to the crosslinking nodes. The cooperative segmental motions depend on temperature: below the glass transition temperature (T_g), the polymer segments are "frozen", and the material becomes rigid, while above the T_g the increase in thermal energy activates the segmental motions, giving the material its characteristic elasticity. It is important to note that in elastomers translational movement cannot occur easily, the presence of cross-linking

nodes prevents the polymer chains from sliding freely over each other, limiting the *permanent deformation* of the material (*creep*)⁸¹. Recoverable creep refers to the portion of the creep strain that can be reversed when the load is removed. This type of behaviour is not considered elastic in the classical sense of the term, because elasticity implies an immediate and reversible deformation that depends on a thermodynamic equilibrium, while this deformation is time-dependent, so it is a *kinetic phenomenon*.

To treat elastomers from a thermodynamic point of view, we must first start from Hook's law:

$$F_e = -kx \quad (1)$$

It describes the behaviour of a spring subjected to constant stress and states that the elongation suffered by an elastic body (x) is directly proportional to the force applied to it (F_e). Similarly, it is possible to apply this principle to explain the behaviour of materials subjected to stress by defining the *Young's modulus* (E) as the ratio between the stress applied to the object (σ) and the resulting axial strain (ϵ) in the linear elastic region of the material, which can be obtained as the slope of the stress-elongation curve^{82,83} (Fig. 17)

$$E = \frac{\sigma}{\epsilon} \quad (2)$$

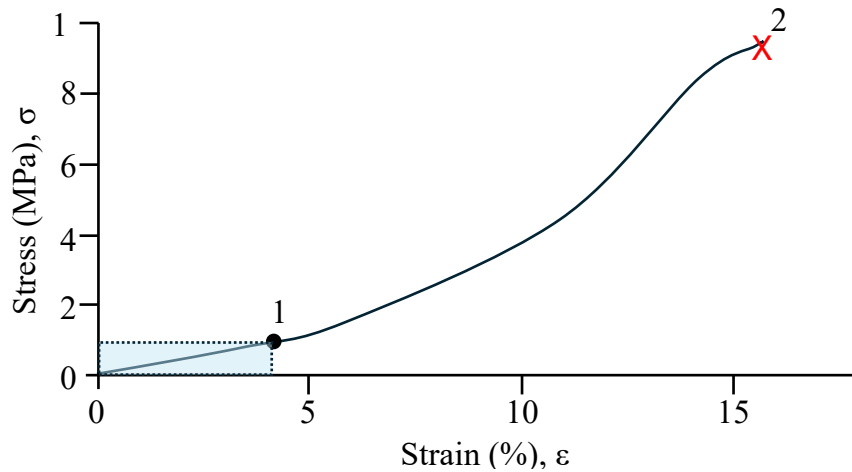


Fig. 17 Example of elastomeric polymer stress-strain curve. It exhibits a linear elastic behaviour for strains up to 50% (1). Above this strain, it exhibits non-linear stress-strain behaviours to a final fracture strain of 165% (2).

It is important to note that Young's modulus describes a generic property of all solid materials, but for elastomers, it directly defines elasticity and is therefore one of the most important parameters featuring this class of polymers. Modulus E follows Hook's law only if the elastomer is ideal and the answer is linear: any real material, also elastomers, will end up yielding a *plastic deformation* (Fig. 17 point 1), until it breaks when stretched with a huge force or for a very large distance, arriving to *fracture* (Fig. 17 point 2). However, all solid materials exhibit almost linear

behaviour for small deformations or stresses⁸⁴. If the range in which Hooke's law holds is large enough compared to the typical stress expected to be applied to the material, the material is said to be linear. Otherwise, if the typical stress that is applied is outside linearity, the material is said to be non-linear. Materials such as rubber are considered non-linear, but when the stress or strains applied is inside the linear response, they can be considered linear material, and they follow the Hook law. Normally, elastomers present extended linear range compared to other materials, and this enables them to better withstand stress compared to other classes of materials. Nevertheless, if the applied stress surpasses a certain threshold, they will still fail and lose their ability to behave in a linear and reversible manner.

Elastomers deviate from linearity at high extents due to the stretching of the chains, the tension generated around the cross-linking nodes, and the orientation of the elongated molecular segments. At low extensions, the initial unwinding of macromolecules is hindered by the tension present in the hank of cross-linked chains. At high compressions, elastomers reach a compressibility limit due to the chains being too close together or a drastic decrease in free volume^{79,80}. From an entropy point of view, an elastomer subjected to elongation passes from a state of maximum disorder, in which the polymer chains are entangled, to a state in which the chains tend to orient and align under the action of the applied force. Once the stress is removed, the material quickly returns to its initial state, as the system turns from a condition of low entropy to one of maximum entropy⁷⁹. The free energy for the change in length of a constant volume elastomer ($P\Delta V = 0$, assuming the Poisson ratio = 0.5) is the Helmholtz free energy (A) which depends on the internal energy (U) and entropy (S):

$$dA = dU - TdS$$

while the work (W) done on the system depends on the elongation (L)

$$W = FdL$$

The change in entropy with length is obtained from Maxwell's equation⁷⁹

$$\left(\frac{dS}{dL}\right)_T = \left(\frac{-dF}{dT}\right)_L \quad (3)$$

When an elastomer is stretched by the application of a constant force and then heated, it tends to contract, reducing its length. When stretching an elastomer, an increase in the temperature of the material is observed. This behaviour can be explained in thermodynamic terms: the action of the

force and the consequent variation in length (FdL) involve a variation in entropy that regulates the elasticity of the material like an engine.

In addition to Young's modulus (E), there are other modulus deriving from Hook's law that describe the stiffness of materials: the *bulk modulus* K^{85} describes the response of the material to uniform hydrostatic pressure, the *shear modulus* G^{86} describes the response of the material to a shear stress.

These modules are not independent of each other and for isotropic materials they are correlated with each other by the equation:

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \quad (4) \quad \text{where } \nu \text{ is the Poisson coefficient}^{87}$$

From an application point of view, properties such as *hardness*⁸⁶ (H) play a key role in characterizing elastomer performance. Hardness provides indications of the material's resistance to local stress or penetration, representing a property related to elastic modulus, but influenced by factors such as cross-linking density and polymer chemical composition. The *Shore A (Ha) scale*, which complies with ASTM D2240⁸⁸, is commonly used to measure the hardness of elastomers. An empirical relationship, developed by Gent^{89,90}, allows to correlate the values obtained with the Shore A scale to the Young's modulus, offering a practical method to estimate the latter starting from hardness measurements.

$$E = \frac{0,0981(56 + 7,62336Ha)}{0,137505(254 - 2,54Ha)} \quad (5)$$

In summary, the elastic behaviour of these materials is the result of a synergy between the molecular structure, the degree of cross-linking and thermodynamic phenomena. Mechanical modulus and features allow these properties to be quantified and described, and their understanding is essential to fully exploit the potential of elastomers in technological applications such as the field of anti-icing materials.

3.1.1.2 Anti-icing mechanism of elastomers

Chaudhury and Kim⁹¹ presented a model that can be used to describe the mechanism of ice detachment from elastomeric surfaces. Consider an object of finite dimensions (a) placed on a polymer surface of a given thickness (h) subjected to a shear force (F) (Fig. 18).

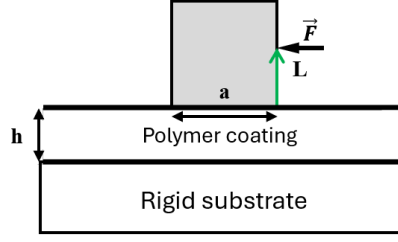


Fig. 18 Shear force applied to a cubic object adhered to a generic polymer surface. F is the shear force. L the height to which the shear stress is applied. h is the thickness of the coating. a is the side of the cube.

When the force is applied to the ice-polymer interface, we expect to see the object to slide on the elastomeric film if its modulus is greater than that of the static shear force. The static shear force represents the amount of force required to slide an object across a surface and is influenced by the chemical composition and roughness of the surface. However, since the force is applied to the height L (Fig. 18) from the surface of the coating, an external torque is generated and consequently the detachment mechanism will no longer depend solely on surface interactions, but also on how the material reacts by responding to the applied stress. If we consider the polymer coating as *completely confined* (Fig. 19, left) all deformations are limited and the stress inside the film is hydrostatically distributed, with no possibility for the material to exhibit local deformations or instability. An interface is created with the surface on which there is maximum torsional stress at the point where the moment is calculated, while maximum compression is expected at the opposite interface limit. In this case it is possible to develop a model⁹¹ that allows to derive the *critical shear stress* σ_s^* as

$$\sigma_s^* \sim \left(\frac{a^2}{hL} \right) \sqrt{\frac{W_a \mu}{h}} \quad (6)$$

where a is the discharge of the object, h the thickness of the polymer coating, W_a the adhesion work, L the distance of the point of application of the force from the surface, and μ the shear modulus. However, this relationship can be used in general to treat polymeric films, but in the case of elastomers we must consider the film as *free from confinement* (Fig. 19, right). This means that the film is no longer rigidly constrained and can undergo non-uniform and localized deformations such as the formation of "spikes" and "bubbles" in the film. These elastic instabilities create more flexible areas in the film that favor detachment from the surface, reducing adhesive strength and altering the separation mechanism compared to the fully confined case.

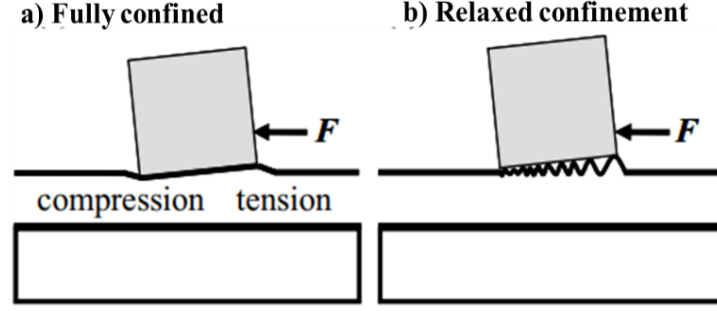


Fig. 19 When applied shear force generates a torque, materials respond differently when fully confined or free from confinement. In the first case we will have maximum torsion at the point of force application and maximum compression at the opposite side (classical polymer). In the second case the material responds by deforming locally and creating instabilities that help the object detach from the surface (elastomers).

The expression now becomes

$$\sigma_s^* \sim \left(\frac{a}{L}\right) \sqrt{\frac{W_a \mu}{h}} \quad (7)$$

In both cases there is a relationship with the shear module, so the detachment depends on the nature of the material and its mechanical characteristics. In addition, there is a proportionality with the *adhesion work* (W_a), defined as the work necessary to separate two phases in contact with each other and bring them to an infinite distance. In other words, it represents the amount of energy required to break the chemical or physical interactions between the surfaces that form an interface. In this case the shear stress no longer depends only on the characteristics of the material, but also on the object that is in contact with it. In fact, ice or snow on the surface will tend to establish some chemical interactions such as hydrogen bonds, or physical interactions due to the roughness and defects present on the surface. Finally, in the confined case, there is a stronger dependence on the thickness ($h^{-1.5}$) than in the case of the second scenario ($h^{-0.5}$).

Another approach⁹² based on fracture mechanics allows to derive the *adhesion strength of ice* as

$$\tau_c = \sqrt{\frac{E^* S}{\pi a \Lambda}} \quad (8)$$

where S is the surface energy, E^* is the apparent Young's modulus, a is the length of the fracture and Λ is a dimensionless constant determined by the geometric configuration of the fracture. Through engineering models based on fracture mechanics, it is possible to define which quantities come into play in the mechanism of interaction and detachment of ice from surfaces, where in the case of elastomeric coatings the mechanical properties and the surface chemical composition that regulates interactions at the interface play a fundamental role^{93,94}. A fundamental phenomenon observed during the detachment of ice from the surface is the formation and

propagation of bubbles along the interface, which contributes decisively to the reduction of adhesion⁹⁵. This reduction in adhesion derives from the combination of two factors (Fig. 20): the elastic instability triggered by the sliding of ice on the surface, which triggers the *formation of bubbles* generally similar in size to the thickness of the film, and their *propagation* along the interface. Propagation is featured by surprisingly high speeds, up to 1000 times higher than the sliding speed of the sample itself. The bubbles represent a local tension relaxation mechanism, which allows the elastomeric film to better adapt to the deformations imposed during the detachment process.

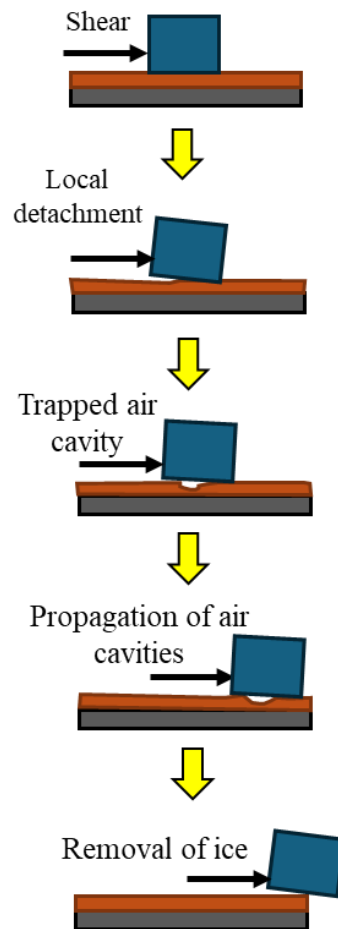


Fig. 20 Mechanism of ice detachment from elastomeric surfaces. The mechanism involves several steps: local ice detachment, air bubble formation and entrapment, air bubble propagation until ice detachment.

3.1.2 Superhydrophobic surfaces

Interfacial chemistry is the study of chemical-physical phenomena that occur at the interface between two phases, for example between a liquid and a solid. This branch of chemistry actively deals with the *functionalization* of surfaces, a technique that aims to modify the surface chemical composition by incorporating elements or functional groups that interact at the interface with the external environment by modifying the final properties of the material^{96,97}. An interesting surface property is *hydrophobicity*⁹⁸, i.e. the characteristic of a material to promote the sliding and repulsion of water from the surface, keeping it dry. This property was observed for the first time in nature, where some plants have adapted and evolved to create surfaces that can stay dry or channel water where it is most advantageous. The leaves of the lotus flower take advantage of their low affinity with water to keep themselves clean: water droplets slide quickly on the surface, taking dirt with them thanks to the high surface hydrophobicity⁹⁹ (Fig. 21). This characteristic has attracted the attention of scientists and researchers who have studied the principles that regulate this property to be able to reproduce the behaviour observed in nature and artificially produce materials that guarantee water repellence¹⁰⁰.



Fig. 21 Loto flower leaf.

The firsts to study in detail the interaction of liquids with surfaces were T. Young and P. S. de Laplace^{101–103} proposing a model in which a liquid is in contact with a perfectly polished ideal solid: three interfaces are created *solid-liquid (SL)*, *solid-air (SV)* and *liquid-air (LV)* and by balancing the *surface tension* (γ) along the direction of a hypothetical horizontal motion, the *Young-Laplace equation* is obtained (Fig. 22):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (9)$$

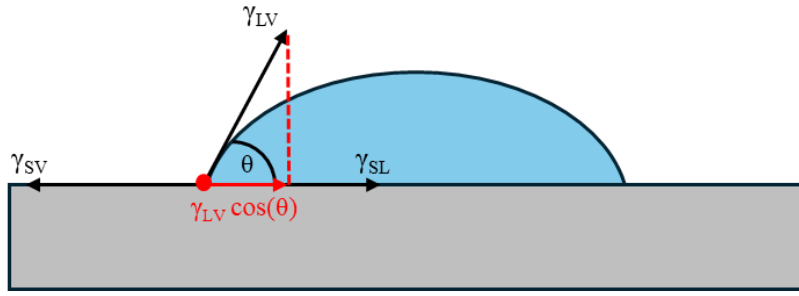


Fig. 22 Young-Laplace model. γ indicates the surface tension and the subscript letters indicate the phases involved at the interface. S = solid, V = air and L = liquid (water). θ is the static contact angle generated between the solid-liquid interface and the liquid-vapor interface at the (red) point of coexistence of all three phases.

where θ is the static contact angle (SCA or CA), one of the parameters that describes in a general way how liquids interact with solid surfaces, indicating in our case the degree of hydrophobicity considering water as liquid. The concept of surface tension is very important and as can be seen from the Young-Laplace equation (9) the value of the contact angle depends on it. Take the liquid-air interface for example (Fig. 23): the forces of attraction acting between molecules of the same type are called *cohesive forces* while those existing between molecules of different types at the interface are called *adhesive forces*.

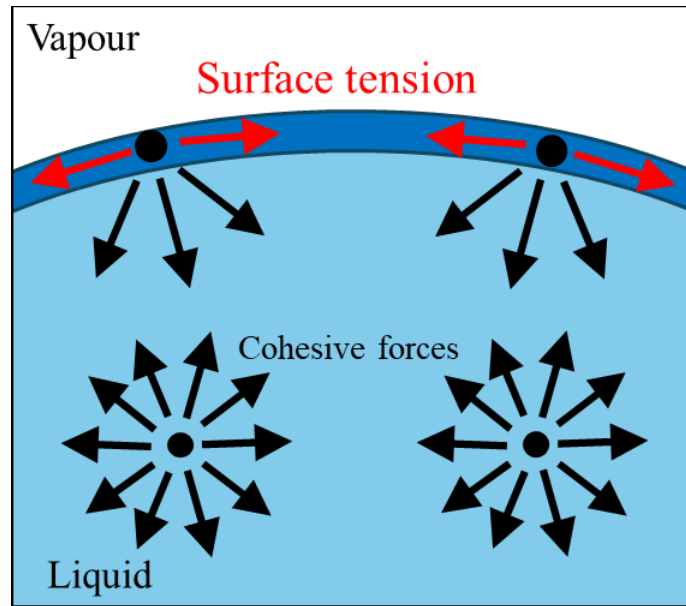


Fig. 23 Liquid-air interface. There are two main mechanisms at play: one is an inward force on the surface molecules that causes the liquid to contract. The second is a surface force of cohesion between molecules (red arrows). This tangential force per unit length is generally referred to as surface tension.

In this case, the internal molecules are equally stressed in all directions by other molecules, so that the resultant of the cohesive forces is zero. In the surface layer, on the other hand, there are molecules whose stresses are not equally distributed in all directions. This happens because the resultant of the cohesive forces of the liquid is not compensated on the surface by the adhesive forces of the molecules in the gas phase. Consequently, the sum of all the stresses acting on each

molecule present on the surface is not zero but is directed towards the inside of the liquid and the surface force of cohesion between the molecules is nothing more than the surface tension of the liquid. Water, due to the relatively high attraction between molecules thanks to hydrogen bonds, has a high surface tension of 72.8 mN/m at room temperature. From a chemical point of view, therefore, both cohesive and adhesive forces result in *intermolecular bonds*, and the stronger these interactions are, the higher the attraction to the inside, which is why water tends to contract into droplets when it is in contact with air. Another way of looking at surface tension is in terms of energy: it is defined as a force per unit of length (N/m) and in physical terms it is equivalent to define it as an energy per unit area (the Joule is N x m, so the unit of measurement is the same). Returning to the model presented in Fig. 23, a molecule in contact with others is in a lower energy state than when isolated. The internal molecules have many other molecules around them, but the boundary molecules lack neighbours compared to the internal ones and therefore have a higher energy: for the liquid to minimize its energy state, the number of boundary molecules with higher energy must be reduced and this translates into a minimization of the surface area (Fig. 24).

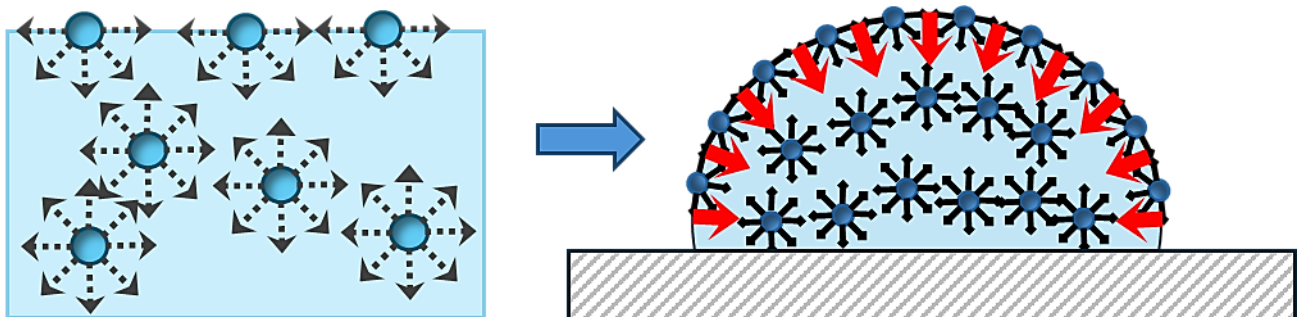


Fig. 24 The boundary molecules have a higher energy; to minimize their number the surface area must be reduced.

The term *surface energy* is more general and applicable to solid materials and indicates the extent to which they allow a liquid substance to adhere to their surface. This is because in a solid, unlike a liquid, the molecular motions are practically absent and the only way to minimize the surface energy is to interact outwards through adhesive forces.

As mentioned before, the value of the contact angle is directly proportional to the surface stresses and through the Young-Laplace equation (9) we can analyse three boundary cases (Fig. 25): in case **A** the difference between the surface energy of the solid (γ_{SV}) and the solid-liquid surface tension (γ_{SL}) is much greater than the surface tension of the liquid

$$(\gamma_{SV} - \gamma_{SL}) \gg \gamma_{LV} \quad \theta \rightarrow 0^\circ$$

The contact angle is close to zero and indicates complete adhesion of the liquid to the surface. In this situation, the surface energy is very high, and the system evolves towards a situation of

greater stability by allowing water to wet the surface increasing the solid-liquid interface. In case **B**, on the other hand, we are on the border between hydrophilicity and hydrophobicity, the contact angle tends to 90°

$$\gamma_{SV} = \gamma_{SL} \quad \theta = 90^\circ$$

Finally, case **C** describes a situation of superhydrophobicity in which the surface energy of the solid is very low so that the system does not need to stabilize from an energy point of view and tends to minimize the surface area in contact with liquid.

$$(\gamma_{SL} - \gamma_{SV}) \gg \gamma_{LV} \quad \theta \rightarrow 180^\circ$$

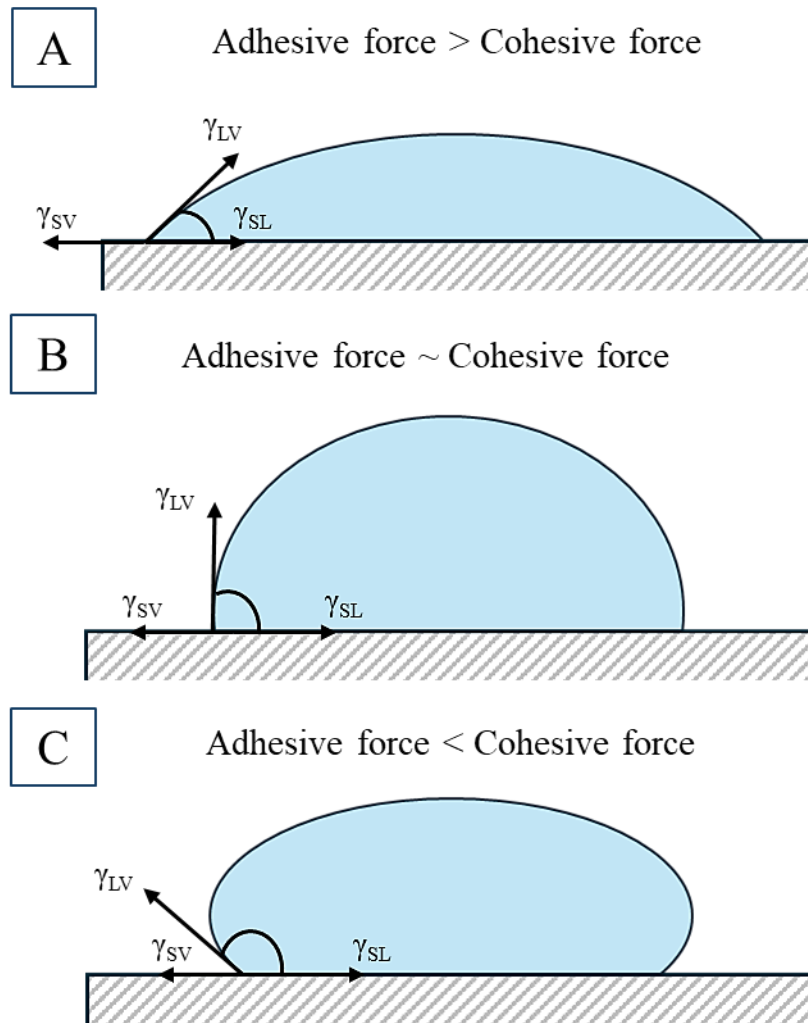


Fig. 25 The three limit cases that can be obtained from the Young-Laplace equation (9).

In conclusion, we can say that the different degrees of hydrophobicity depend on the relationship between the surface energy of the solid and the surface tension of the water and to reach a condition of superhydrophobicity in general Dupre's rule must apply^{104,105}:

"If the surface energy of the solid is less than the surface tension of the liquid, then the liquid does not adhere to its surface."

We analysed the energy aspects that regulate the hydrophobicity of surfaces. However, the Young-Laplace model is valid for describing an ideal and static situation, in which a drop is placed on the surface, while we know that it is also able to move and slide. Therefore, the other fundamental aspect to be taken into consideration to define a superhydrophobic character is the *dynamic behaviour* of the liquid on the surface of the material: we define the *contact angle hysteresis* (CAH) as the difference between the *advancing contact angle* (θ_{adv}) and *receding contact angle* (θ_{rec}), observable when the surface of the material is tilted^{106,107} (Fig. 26).

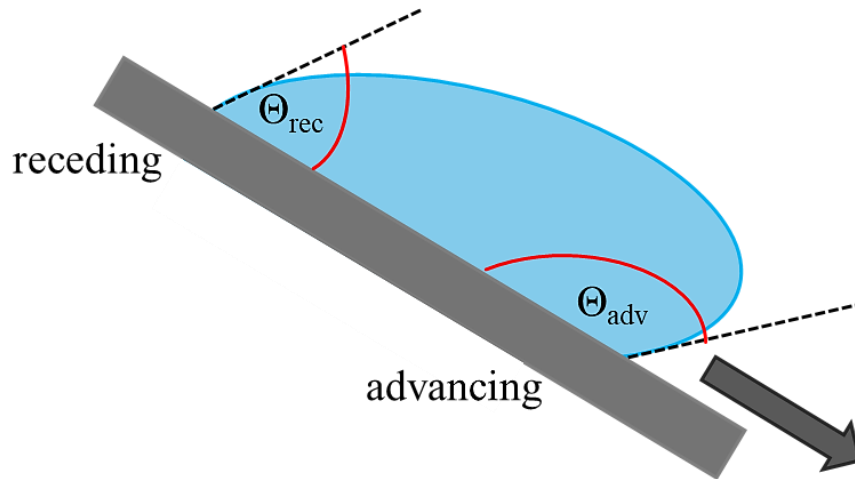


Fig. 26 Contact angle hysteresis (CAH) defined by the difference between θ_{adv} and θ_{rec} .

Hysteresis is not only related to surface energy although it depends on the value assumed by the contact angle as the drop slides from the surface, but strongly depends on the *surface roughness*^{108,109} in terms of morphology at the micrometric and nanometric level. This is because the Young-Laplace model is valid for ideally smooth surfaces that do not consider the presence of defects or roughness. We can identify two different models that describe these surfaces: the Wenzel¹¹⁰ model and the Cassie-Baxter model¹¹¹. In the first case, the water on the surface penetrates the roughness: Wenzel noticed that the roughness increases the surface area of the solid and consequently the solid-liquid interface (Fig. 27).

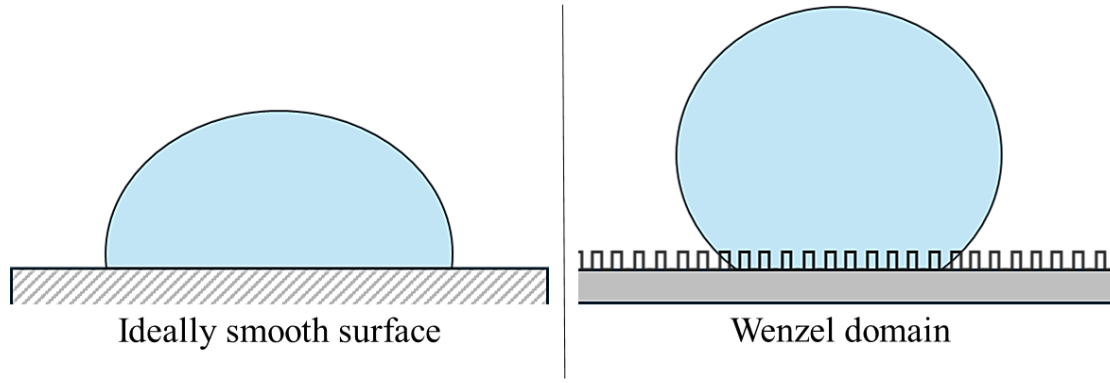


Fig. 27 Unlike a perfectly smooth surface (left), the presence of roughness changes the solid-liquid interface by increasing the contact of the liquid (right).

If a surface had low surface energy, the increase in surface area would enhance its hydrophobic character because the liquid would have to develop a much wider and unstable interface with the solid if the contact angle were kept unchanged. For this reason, there is an increase in the contact angle due to the solid which minimizes the solid-liquid interface due to the addition of "extra" surface. The key parameter is the *roughness factor* r , defined as the ratio of the actual contact area to the apparent contact area that falls in the domain of the Young-Laplace equation (9) which now becomes

$$\cos \theta' = r \cos \theta \quad (10)$$

where θ' is the effective static contact angle and r is the roughness ratio. The higher the r -value, the higher the roughness and the value of the effective contact angle. Contrary to common assumptions, this type of model does not guarantee a superhydrophobic surface¹¹². The presence of water within the surface roughness increases contact angle hysteresis when the surface is tilted, causing the drop to roll unevenly as water becomes trapped in the microstructures. As the drop advances, it interacts with the surface while part of the liquid remains obstructed, leading to greater resistance to movement. This causes a phenomenon called *pinning*¹¹³ which involves a decrease in the recession contact angle and a consequent increase in hysteresis. Therefore, according to this model, high contact angles can be achieved, but not a dynamic behaviour that guarantees superhydrophobicity (Fig. 28)

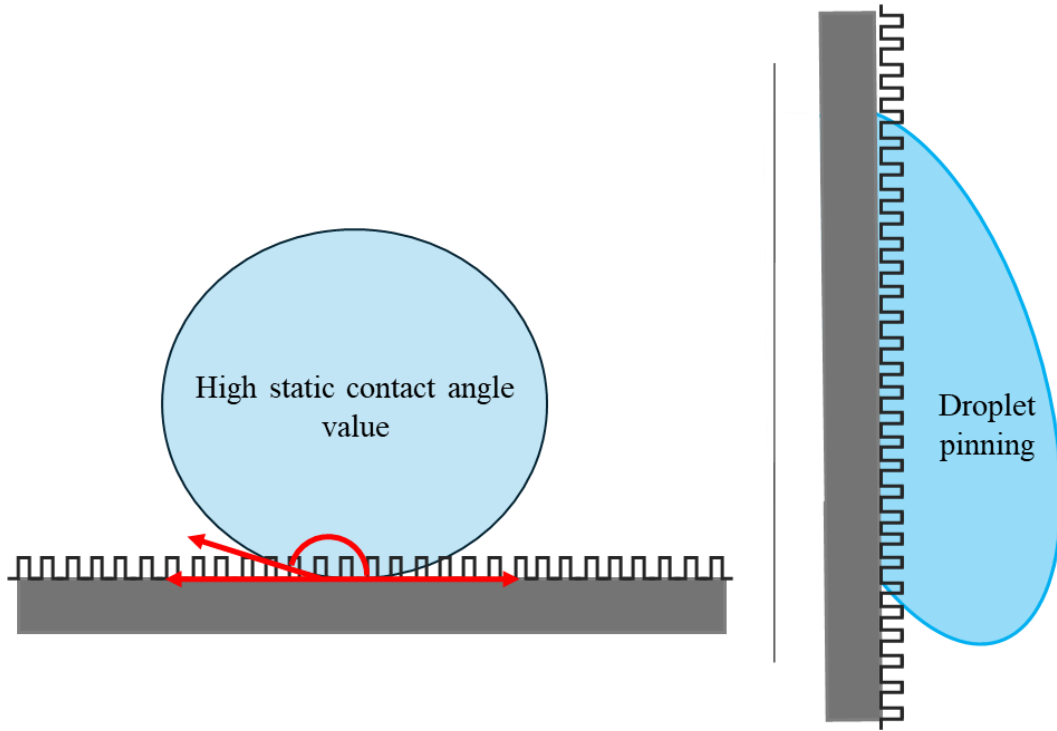


Fig. 28 Wenzel model. The presence of roughness and the consequent increase in the surface area of the solid allow high contact angles (left), but high hysteresis (right) due to the presence of liquid stuck in the roughness when the droplet moves. The recession contact angle is approximately half of the static equivalent.

In the Cassie-Baxter model, on the other hand, water does not penetrate the surface defects, and the liquid is in a situation of minor contact with respect to perfectly smooth surface (Fig. 29). According to literature¹¹⁴ the Young-Laplace equation (9) now depends on two contributions:

$$\cos \theta' = f_1 \cos \theta_1 - f_2 \quad (11)$$

where f_1 is defined as the ratio of the effective contact area between the droplet and the surface of the material to the projected contact area of the droplet, with θ_1 as the contact angle considering the material surface as smooth. The actual contact area accounts for surface irregularities and roughness, which reduce the effective area in contact with the drop compared to the projected area, which is based on an idealized, smooth surface. Similarly, f_2 is defined in an analogous way, but considering air as the material, where $\theta_2=180^\circ$ (i.e. $\cos \theta_2 = -1$). The greater the surface roughness, the more air is trapped between the roughness features, reducing the solid-liquid contact area. As a result, the parameter f_1 tends to 0, reflecting the minimal solid contact, while f_2 tends to 1, as the air occupies a larger portion of the contact area. This leads to an apparent contact angle approaching 180° (i.e. $\cos \theta' = -1$). This situation also facilitates the dynamic behavior of the drop, since the air wedged between the roughness creates a sort of repulsion facilitating the rolling of the drop from the surface.

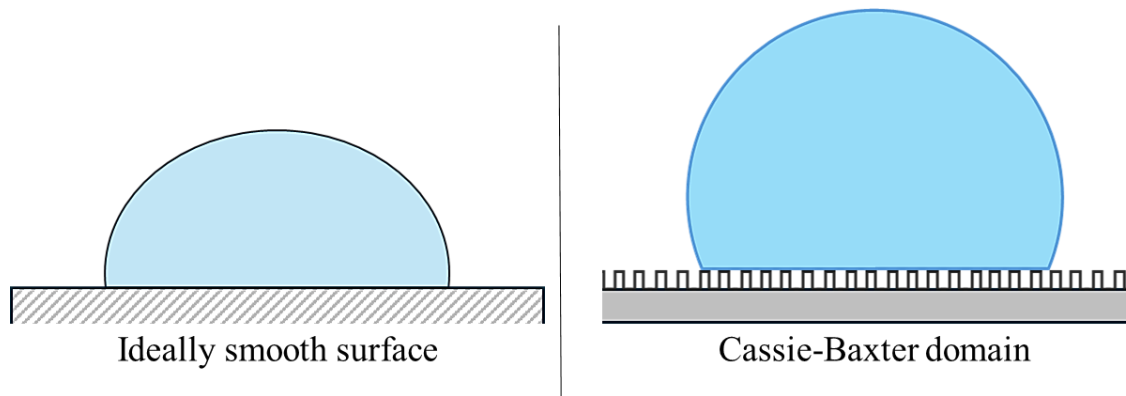


Fig. 29 Cassie-Baxter model. Air is trapped between the roughness and water cannot penetrate inside the roughness. This decreases the solid-liquid interface ensuring a high contact angles and low hysteresis.

Therefore, to obtain superhydrophobic surfaces it is necessary to choose materials with a low surface energy that guarantee high static contact angles, but at the same time it is essential to control the surface morphology by ensuring to reach and stabilize a Cassie-Baxter type regime^{115,116}. Based on the value assumed by the static contact angle (SCA), contact angle hysteresis (CAH) and roll-off angle (RO) we can define the following ranges of hydrophobicity¹¹⁷ (Tab. 1 Hydrophobicity ranges as a function of static contact angle (SCA), contact angle hysteresis (CAH) and roll-off angle (RO).Tab. 1):

Category	Static Contact Angle range (SCA)	Contact angle Hysteresis (CAH)	Roll-off angle (RO)	Description
Hydrophobic surface	90° - 150°	> 15°	> 15°	Water forms droplets but can adhere to the surface.
Superhydrophobic surface	≥ 150°	< 5°	< 5°	The water forms almost spherical droplets and slides off easily

Tab. 1 Hydrophobicity ranges as a function of static contact angle (SCA), contact angle hysteresis (CAH) and roll-off angle (RO).

3.1.2.1 Synthesis and fabrication of superhydrophobic surfaces

Superhydrophobic materials are widely used across various sectors, and as a result, there is no universal methodology for preparing such surfaces. Their fabrication typically requires two main steps: the creation of micro/nano-hierarchical structures and the reduction of surface energy. The synthesis methods can be broadly categorized into *physical* and *chemical* approaches^{118,119}.

Physical methods are primarily used to modify surface morphology by creating controlled roughness through techniques such as *lithography*¹²⁰. This approach allows for the precise control

of the shape and size of surface roughness, effectively creating detailed 'patterns' on the surface (Fig. 30). In general, lithographic methods are expensive and require sophisticated equipment.

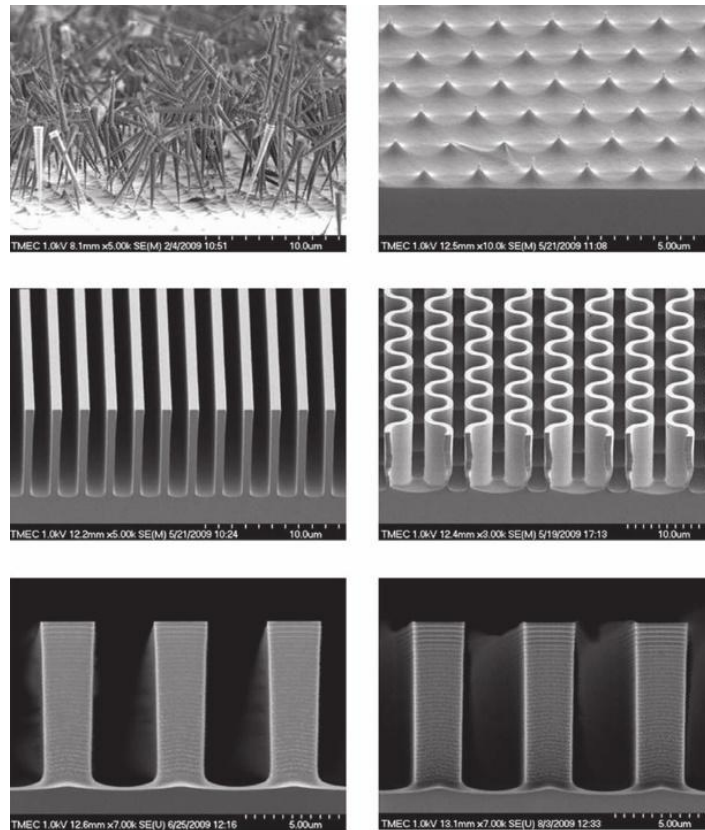


Fig. 30 Lithography patterns examples¹²¹.

Plasma treatment^{122,123} is a technique used to modify polymeric or metal surfaces, creating controlled micro- and nanostructures. Using a high-energy ionized gas, the surface of the material is etched, altering its roughness and, in some cases, even the surface energy. Plasma treatment offers significant advantages, including accuracy of structures, automation, and low material consumption. However, it has some limitations, such as the complexity of the process and the need to control different operating parameters, aspects that negatively impact on its reproducibility. In addition, the gases used can be toxic, and plasma radiation could cause damage to the treated surfaces. The *spray coating techniques*^{124,125} are versatile and relatively simple methods of imparting superhydrophobicity to a wide range of surfaces by creating micro- and nano roughness. It consists of the application of metal, polymer or nanoparticle powders using a spray gun. The materials can be preheated and melted by electric or chemical means or sprayed maintaining low temperatures. This approach allows not only to induce roughness, but to directly create coatings on the substrates of interest. This technique offers some advantages such as ease and speed of execution and reduced costs, making it suitable for a wide range of industrial

applications. However, spray coating has limitations such as material waste due to over-spraying and high gas resource consumption. In addition, it is difficult to obtain extremely thin coatings. Chemical processes are primarily used to reduce surface energy by introducing specific functional groups, but they can also be employed to create surface roughness. Etching^{126,127} offers a simple and effective way to modify the substrate's roughness without the need for complex methodologies. Traditionally, chemical etching involves the use of strongly acidic or basic solutions to etch and scratch the surface of materials, particularly metal surfaces, creating hierarchical structures^{128,129}. This method is widely appreciated for its simplicity, as it requires minimal equipment and provides good selectivity. However, achieving precise control over the morphology—particularly at the nanoscale—remains difficult. The resulting structures depend heavily on parameters such as etchant concentration, temperature, reaction time, and the intrinsic properties of the substrate, such as its grain structure or crystallinity. For instance, higher etchant concentrations or longer reaction times can lead to over-etching, resulting in a loss of desired micro/nano-hierarchical structures. Moreover, chemical etching is sensitive to substrate contamination and competitive side reactions

Despite these limitations¹³⁰, chemical etching remains a quick and versatile method for roughness creation, particularly when combined with subsequent functionalization steps. The chemical functionalization of surfaces is a widely studied approach for reducing surface energy and improving hydrophobic properties. This process often involves interface reactions, like grafting of hydrophobic agents such as silanes, long- alkyl chain compounds, or nanoparticles, which are chemically anchored to the surface via condensation reaction^{131–133} (Fig. 31). This chemical approach can also be extended to the synthesis and functionalization of nanoparticles. Nanoparticles can be tailored with hydrophobic groups and subsequently deposited onto surfaces to create hierarchical structures. These structures can be stabilized through the incorporation of polymer matrices, ensuring durability and improving mechanical properties: the combination of nanoparticles and grafting chemistry allows for the creation of surfaces with enhanced roughness and hydrophobic performance^{134–137}. The use of condensation reactions for grafting hydrophobic agents is particularly advantageous due to its simplicity, efficiency, and versatility. This method not only provides a robust coating but also allows for fine-tuning of surface properties leading to promising anti-icing materials.

Other methods involve the use of *molecular self-assembly* (SAM)^{138,139} and *layer-by-layer technique*¹⁴⁰ (LBL).

However, in the case of superhydrophobic surfaces, the presence of roughness does not translate in an easier nucleation, owing to the low surface energy of the material. According to classical nucleation theory, a larger contact angle on the solid surface implies a higher free energy barrier for the formation of ice nuclei, and a consequent reduction in the nucleation rate. However, this theory is not sufficient to understand the relationship between surface properties and their impact on ice growth and detachment at the molecular level¹⁴⁵. Further analysis of other properties such as wettability, morphology, and chemical composition needs to be investigated. From a macroscopic point of view, based on the theory of heat conduction, superhydrophobic coatings with a wrinkled microstructure facilitate the formation of *air pockets* that act as thermal insulators between the surface of the solid and water¹⁴⁶. L. Makkonen¹⁴⁷ refers to the model presented by Young-Laplace in which a solid drop of water is deposited on a smooth, chemically homogeneous surface, ideally without defects and deformations. It is possible to define the adhesion work necessary to detach the frozen drop from the surface, which will depend on the surface tensions of the system components, based on eq. 12

$$W_a = \gamma_s + \gamma_i - \gamma_{s,i}, (12)$$

where γ is the surface tension, while the subscripts "s" and "i" stand for solid and ice. By introducing the surface tension of the solid (γ_s) obtained from the Young-Laplace equation (9), eq. 12 turns into eq. 13

$$W_a = \gamma_i + \gamma_w \cos\theta + (\gamma_{s,w} - \gamma_{s,i}), (13)$$

where "w" refers to water. Considering the surface tension of ice and water approximately the same ($\gamma_i = \gamma_w$), as well as the respective surface tension at the solid interfaces, the relation becomes

$$W_a \approx \gamma_w(1 + \cos\theta), (14)$$

Let us now consider *ice adhesion strength* expressed as the maximum force ($F_{\max}$) per unit area (A), which corresponds to a pressure

$$\tau_{ice} = \frac{F_{\max}}{A}, (15)$$

The adhesion work can be expressed as a function of the adhesion force of the ice by eq. 16

$$W_a = \tau_{ice} A \delta, (16)$$

where δ is the measurement of the removal distance between ice and surface. In this way you can get

$$\tau_{ice}A\delta \approx \gamma_w(1 + \cos\theta)$$

$$\tau_{ice} \approx \frac{\gamma_w}{A\delta}(1 + \cos\theta) \quad (17)$$

Golovin¹⁴⁸, Meuler¹⁴⁹ and He¹⁵⁰ tried to find a correlation between this model and experimental data. Unfortunately, the results do not always fit well, and this suggests that wettability alone is not sufficient to understand anti-icing properties. The detachment mechanism depends in fact on a combination of factors, either micro and macroscopic, such as the ice crystal structure and substrate morphology¹⁵¹, the possible creation of a liquid layer on the ice surface¹⁴⁷ and the "substrate-ice" thermal contraction following the lowering of the temperature¹⁴⁵.

Building upon these findings, Sarkari¹⁵² investigates how surface wettability and topography influence ice adhesion strength. By analysing 37 coatings with varying micro- and nanostructured topographies, the study examines the role of surface roughness and morphology in determining anti-icing properties. The results indicate that wettability alone is not sufficient to explain ice adhesion behaviour. Instead, a combination of factors—such as surface architecture, ice-substrate interactions at different scales, and thermal contraction effects—plays a critical role. The research highlights inconsistencies in previous studies and underscores the need for precise methodologies and a deeper understanding of ice adhesion mechanisms to develop more effective ice-phobic surface.

As discussed in Chapter 2, atmospheric icing phenomena predominantly occur through precipitation. In cloud environments, water exists as liquid droplets that, upon impact with a surface, induce wetting and form a thin water layer, which may subsequently undergo phase transition to ice. The freezing dynamics are governed by multiple factors, including ambient temperature, surface energy, and the residence time of the liquid phase on the substrate. Superhydrophobic surfaces are engineered to mitigate ice accretion by minimizing the contact time of impinging water droplets. Their low surface energy and nanoscale roughness induce rapid droplet rebound (Fig. 32), thereby preventing the formation of a continuous water film, which is a precursor to icing¹¹⁸.



Fig. 32 Photograms of an impacting water droplet on a superhydrophobic surface.

However, in the case of supercooled droplets—where water remains in a metastable liquid state below its freezing point—impact can trigger immediate crystallization due to the energy dissipated upon collision. Under these conditions, the efficacy of superhydrophobicity is significantly compromised, as the freezing timescale can be comparable to or even shorter than the impact duration, preventing complete droplet detachment prior to solidification.

This underscores the complexity of adhesion and detachment mechanisms in icing conditions, which necessitate a multidisciplinary approach integrating theoretical modelling, experimental investigations, and materials engineering¹⁵³. A comprehensive understanding of these processes is essential for the rational design and fabrication of advanced anti-icing coatings with enhanced performance under extreme environmental conditions.

3.1.3 Slippery liquid infused porous surfaces (SLIPS)

The urge to concretely address the atmospheric icing leads to a continuous study and development of innovative solutions and recently a new biomimetic approach has been proposed to obtain anti-icing surfaces: *slippery liquid infused porous surfaces (SLIPS)*^{154,155} are once again born taking inspiration from the plant world, more precisely from the carnivorous plant *Nepenthes alata* (Fig. 33) which has developed a slippery surface layer that allows it to capture its prey more easily. Differently from lotus flower (Section 3.2.1), this species does not exploit the surface roughness to ensure a superhydrophobic behaviour, but they produce a repellent lubricating fluid that diffuses inside the spaces present in the microstructure, forming a covering film (Fig. 33)¹⁵⁶.

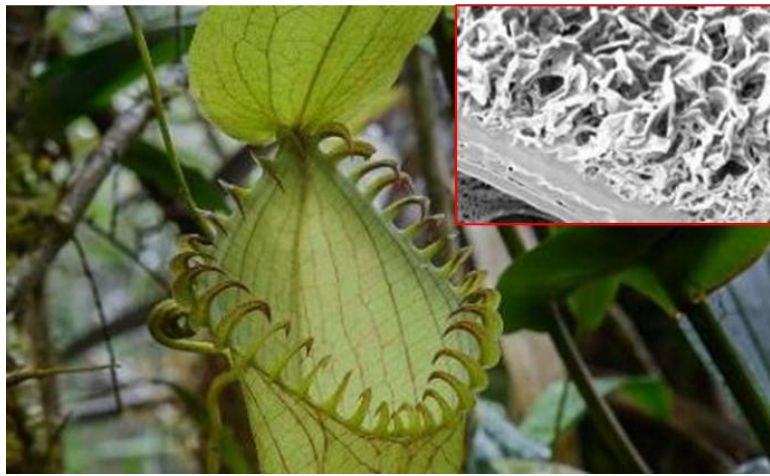


Fig. 33 *Nepenthes alata*. SEM image of the plant inside rough surface where the lubricating liquid is anchored, which creates a stable and repellent surface layer¹⁵⁷.

Inspired by this organism, SLIPS are slippery synthetic surfaces made up of an infused lubricant locked inside a micro/nano porous structure that creates a continuous, resistant and omniphobic layer (Fig. 34).

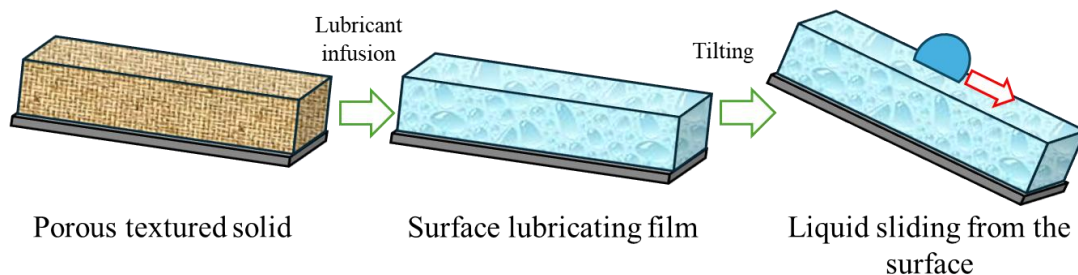


Fig. 34 Scheme for creating a SLIPS. Omniphobicity is the property of a material to repel both polar and non-polar liquids from its surface¹⁵⁴.

SLIPS are characterized by very low contact angle hysteresis and roll-off, proving that liquids tend to slip and leave the substrate easily, although they may normally have much lower static

contact angle values than superhydrophobic surfaces, even at the limit of the hydrophobicity range¹⁵⁸. There are three key aspects to consider when designing a slippery surface¹⁵⁹: (1) the lubricating fluid must penetrate, wet, and adhere firmly to the textures; (2) the surface must preferably be wet by the lubricating fluid rather than the liquid to be rejected; and (3)) the lubricant and the fluid to be repelled must be immiscible to each other. While the creation of surface roughness can be achieved through the methods involved for the SHP, the real challenge to obtain SLIPS is therefore the choice of the most suitable lubricant¹⁶⁰. In the literature there are several examples of lubricating liquids that can be used to create slippery surfaces, but one of the main problems remains the high cost¹⁶¹. For this reason, much attention has been given to natural lubricants such as vegetable or animal oils¹⁶². However, the remarkable repellent properties of SLIPS can be compromised because of the loss of cohesion due to mechanical surface damages, evaporation or diffusion phenomena on other surfaces¹⁵⁶.

To better understand the anti-icing behaviour of SLIPS let's see a comparison with the ice growth model on water-repellent surfaces^{158,163} (Fig. 35).

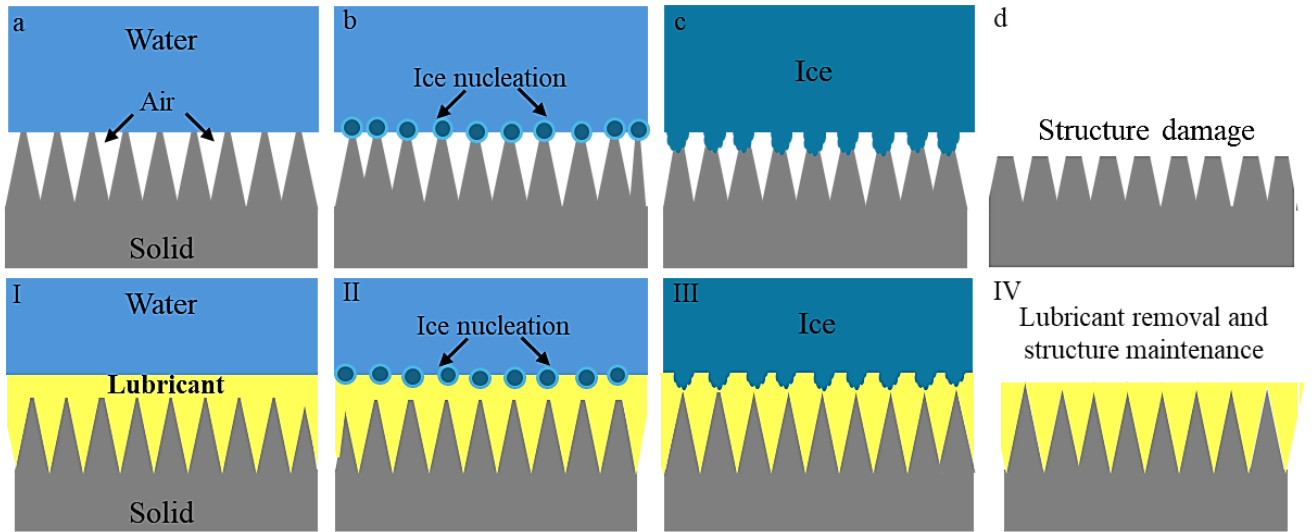


Fig. 35 Mechanism of growth on superhydrophobic substrate (a-d) and mechanism of ice growth on SLIPS (I-IV).

In a condition of superhydrophobicity promoted by a Cassie-Baxter-type regime (Fig. 35 a), we know that water does not penetrate inside the rough structure and when the temperature drops, ice begins to nucleate on spikes of the roughness (Fig. 35 b) and proceeds to partially fill the cavities (Fig. 35 c). When ice detaches from the surface can provoke changes in surface morphology leading, after repeated freezing/defreezing cycles, to a loss of the superhydrophobic and ice phobic properties (Fig. 35 d). Hence, it is not difficult to understand the enormous potential of SLIPS as an anti-icing coating, first because the presence of an external slippery layer

favours poor adhesion and easy removal of ice from the surface. Secondly, the presence of the lubricant inside the roughness (Fig. 35 I) prevents ice growth from directly involving the underlying structure, favouring *homogeneous nucleation* along the entire ice-lubricant interface (Fig. 35 II) which guarantees greater resistance to consecutive freezing/defreezing cycles with the removal of the lubricant layer instead of the damage of the structure (Fig. 35 III and IV). In fact, these types of surfaces are potentially able to promote immediate self-repair through the intervention of the fluid present in the underlying substrate. Even more interesting is the ability of SLIPS to inhibit ice growth even in high humidity conditions thanks to the ability to remove condensed water droplets from the surface before they solidify¹⁵⁵.

4. Development and study of anti-icing elastomeric materials

In the present research, PDMS was prepared using two common commercial formulations: Sylgard184¹⁶⁴ and Sylgard186¹⁶⁵ produced by Dow®. Both are sold as a two-component kit consisting of a prepolymer (A) and a curing agent (B). These formulations are designed for various applications and are therefore required to reach specific properties. For this reason, it is recommended to use a specific A:B mixing ratio of 10:1 and follow the specific curing conditions for both.

PDMS, with its unique chemical and physical properties, is an ideal material for anti-icing applications, combining durability, flexibility, and low surface energy. Commercial formulations such as Sylgard 184 and Sylgard 186 allow for easy application, and their ability to control crosslinking conditions makes them particularly suitable for studying material properties, ensuring reproducible results. In the following sections, the characterization processes of the materials obtained with Sylgard184 and Sylgard186 will be discussed in detail, aiming to identify optimal conditions to develop materials with superior anti-icing performance for practical applications in the energy sector.

4.1 Sylgard184 vs Sylgard186

The starting point for analysing PDMS as an anti-icing coating is to compare the two commercial formulations, Sylgard 184 and Sylgard 186, with the aim of determining which of them yields the most functional and scalable coatings. The choice to use a commercial kit is advantageous as it eliminates the potential variables associated with polymerization and cross-linking processes, which, as discussed in the previous chapter, are critical for producing a reproducible material with specific properties. The cross-linking mechanism employed in these two formulations is hydrosilylation. Specifically, Part B of both formulations contains the Si-H functional group, as indicated on the bottle label. Through IR spectroscopy, the comparison between spectra of Part A and Part B for Sylgard184 (Fig. A8) and Sylgard186 (Fig. A9) is presented in Appendix (see section 10.2 Supporting Materials). Dow® recommends mixing the two components A:B in a 10:1 ratio for both formulations and reports a working time of 90 minutes at 25°C, after which the mixture becomes increasingly difficult to process and apply. The 10:1 mixture of Sylgard 184 and Sylgard 186 show significantly different viscosities (Tab. 2): at time zero, the 10:1 mixture of Sylgard 184 has a viscosity of 2499 cP, which nearly doubles after 90 minutes. In comparison, the viscosity of the 10:1 Sylgard 186 mixture starts at 95000 cP and rises to 122000 cP after 90 minutes.

Formulation	Viscosity 0 min (cP)	Viscosity 30 min (cP)	Viscosity 90 min (cP)	Viscosity 180 min (cP)
Sylgard 184 10:1	2499	2699	4499	6899
Sylgard 186 10:1	95000	105000	122000	150000

Tab. 2 Viscosity measurements conducted with rotor speed of 5 RPM. 90 minutes is the working time at 25°C for both formulations.

To better understand these values, it is useful to compare them with some common substances. For example, water has a viscosity of just 1 cP, while wildflower honey exhibits a viscosity of approximately 2000–3000 cP at room temperature. This comparison highlights that the 10:1 mixture prepared with Sylgard 184 has a consistency like wildflower honey. In contrast, the 10:1 mixture of Sylgard 186 exhibits a viscosity 30–40 times higher than that of Sylgard 184, making it more challenging to work with. High viscosity complicates achieving a uniform mixture and makes the degassing phase more difficult, requiring longer treatment times or more stringent vacuum conditions. These practical aspects must be carefully considered when selecting the formulation, particularly in applications where workability and handling are critical to ensuring process efficiency and reproducibility. Starting from Sylgard184 and Sylgard186 in ratio (A:B)

10:1, coatings with different thickness were prepared on Al6082 50x50mm plates through tape casting method, following the conditions specified in Tab. 3 and reported in detail in Experimental section.

Formulation	Ratio A:B	Temperature (°C)	Time (min)	Range 1 (μm)	Range 2 (μm)	Range 3 (μm)
Sylgard184	10:1	100	35	0-200	300-600	750-950
Sylgard186	10:1	100	35	0-200	300-600	750-950

Tab. 3 Conditions used for the preparation of PDMS-based coatings with Sylgard 184 and Sylgard 186 formulations.

To have a full characterization of the coatings, FTIR, wettability, hardness and shear stress measurements were performed. In both cases, FT-IR spectroscopy (Fig. 36) shows the characteristic peaks of PDMS. No unexpected peaks were detected. The IR results are found to be not dependent on the coating thickness.

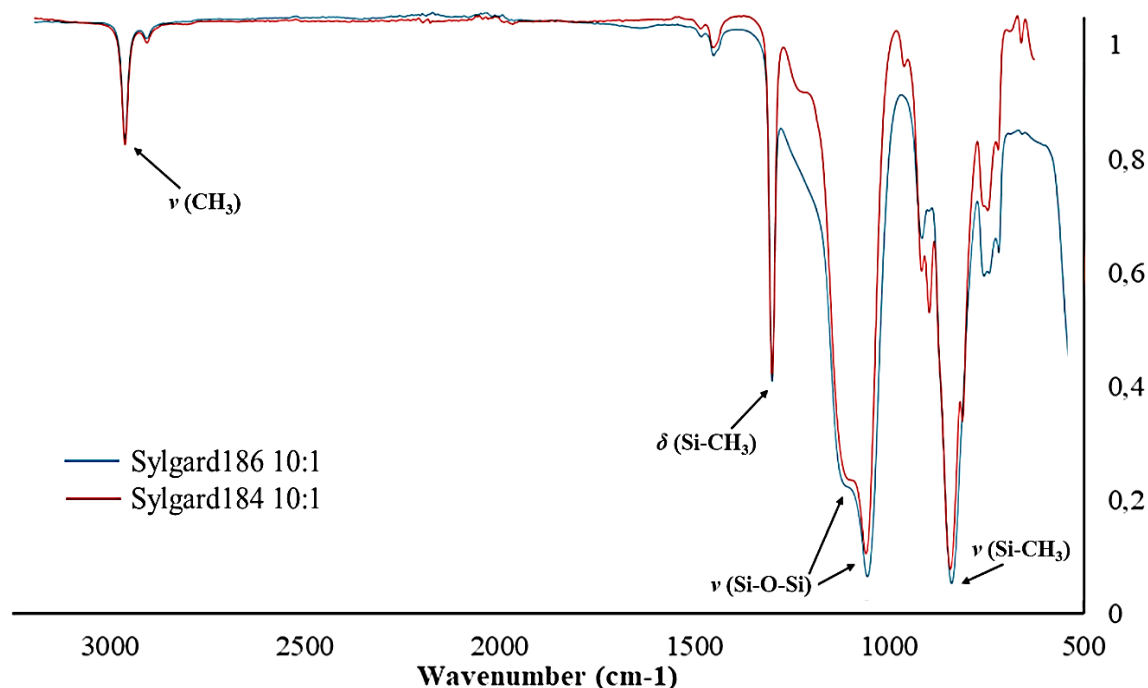


Fig. 36 IR spectrum of PDMS prepared using Sylgard184 and Sylgard186 in 10:1 ratio. We can observe the asymmetric stretching of the methyl groups (2962 cm^{-1}), along with signals corresponding to the stretching of the Si-CH₃ bond (788 cm^{-1}) and bending of the C-H bonds (1258 cm^{-1}), as well as the Si-O-Si stretching ($1010\text{-}1061\text{ cm}^{-1}$) for both formulations.

The materials were then characterized through wettability measurements, including static contact angle (SCA), roll-off angle (RO), and contact angle hysteresis (CAH) (Fig. 37). The surface energy was calculated for both formulations with OWRK model (see Experimental section), yielding a value of $26.1 \pm 0.3\text{ mN/m}$ for Sylgard 184 and $25.4 \pm 3.1\text{ mN/m}$ for Sylgard 186. Again, there is no effect of the thickness on the wettability results as expected.

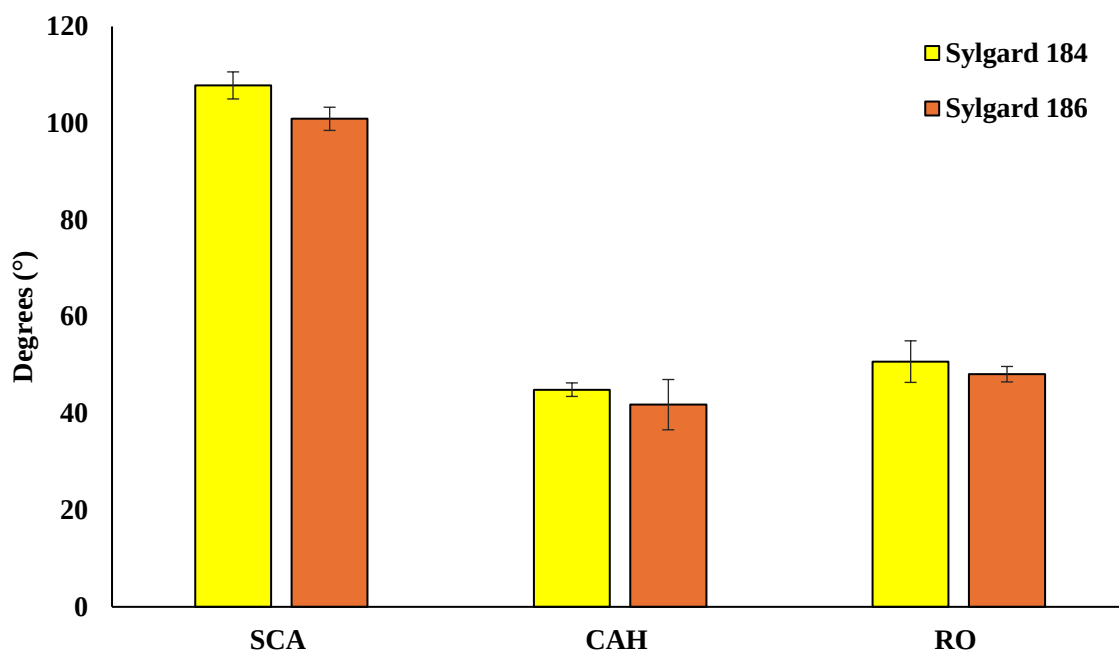


Fig. 37 Wettability data regarding Al6082 coated with Sylgard186 and Sylgard184 shows typical hydrophobic static contact angle (SCA), hysteresis (CAH) and roll-off angle (RO) values (measured values for range 3 thickness are presented).

The mechanical properties were assessed using Shore A hardness measurements following the ASTM D2240 protocol (as reported in detail in Experimental section): Sylgard 186 at a 10:1 ratio showed a hardness value of 30.2 ± 0.9 , while Sylgard 184 exhibited a value of 47.7 ± 1.2 .

Anti-icing measurements were conducted via a push-test to evaluate the shear stress required to detach the ice from the surface of the coatings (see the Experimental section for details on the setup). The Adhesion Reduction Factor^{166,167} (ARF) was also calculated as the ratio between the reference shear stress value of the uncoated Al6082 and the sample shear stress value. This parameter is very important because it describes how many times a material can reduce the adhesion of ice from its surface compared to the reference material. The shear stress measurements and ARF values are presented in Fig. 38.

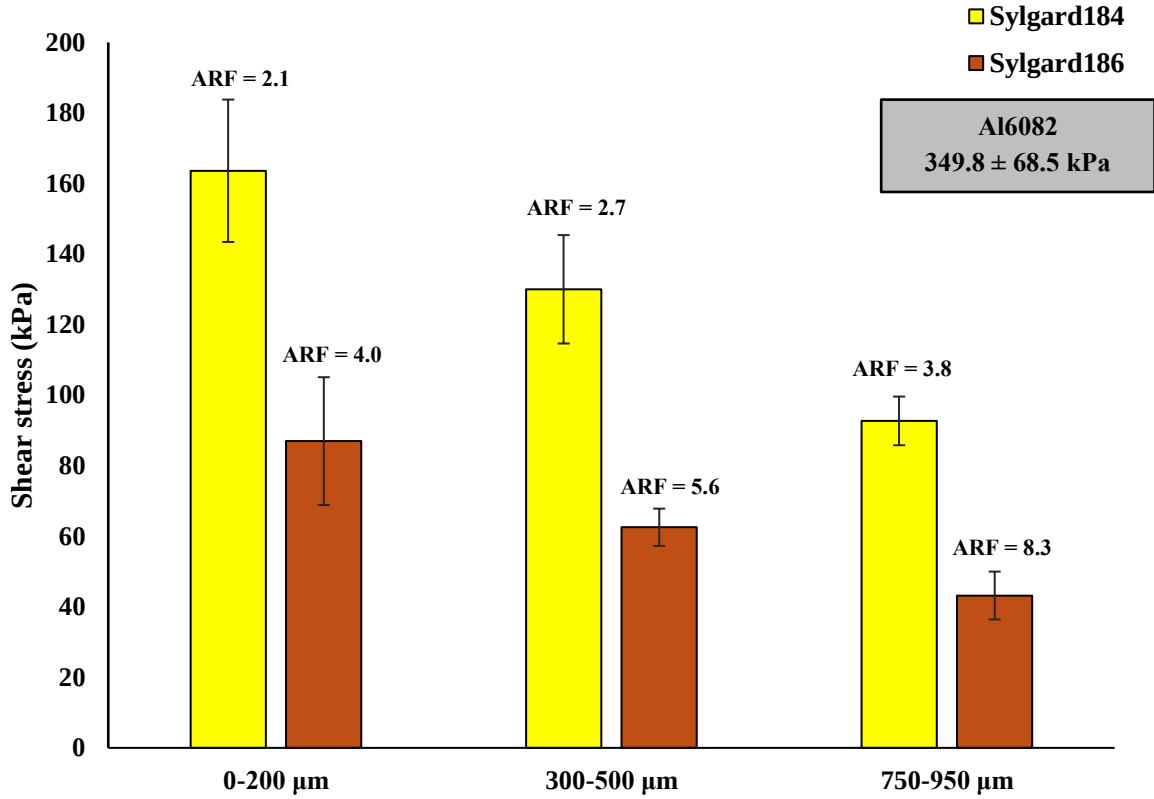


Fig. 38 Shear stress measurements and ARF values for Sylgard184 10:1 and Sylgard186 10:1 prepared with different thickness. The upper and lower limits of the three different thickness ranges were reported. Range 1: 0-200μm. Range 2: 300-500 μm. Range 3: 750 -950 μm.

In this case, coating thickness is a significant parameter that influences the anti-icing properties for both formulations, as expected from the model discussed in Chapter 3 (Equation 6). Sylgard 186 shows consistently lower shear stress values across all thickness ranges, suggesting that, despite the chemical similarity of the coating surfaces, the materials respond differently to mechanical stresses due to their distinct elastic behaviour. By examining Equation (6) (Chapter 3), it is evident that, for a given thickness and considering that the work of adhesion is dependent on the surface energies involved, the only parameter that can affect the shear stress value is the shear modulus (μ). This is directly proportional to the Young's modulus (E) through the Poisson's ratio (ν) (which for PDMS is 0.5), as in equation (4). The Young's modulus is correlated with the Shore A hardness (H_a) as described by Equation (5):

$$E = \frac{0,0981(56 + 7,62336H_a)}{0,137505(254 - 2,54H_a)} \quad (5)$$

Using Gent's equation, it is possible to derive the Young's modulus values for both formulations and subsequently compare them with those obtained through Atomic Force Microscopy (AFM) measures (Tab. 4):

Formulation	Hardness (H _a)	Young's Modulus from Shore A (MPa)	Young's modulus from AFM (MPa)	Approximation error (%)	Percentage difference (%)
Sylgard184 10:1	47,7	2,25	2,47	9,3	8,7
Sylgard186 10:1	30,2	1,15	1,24	7,5	7,1

Tab. 4 Young's modulus values derived from Shore A hardness values through Gent's equation compared with values obtained through AFM. The approximate error was calculated assuming the value measured by AFM as the exact reference; the percentage difference allows for a comparison of the values on equal terms.

The approximate error was calculated by assuming the Young's modulus (YM) value obtained via AFM as the exact reference, while the percentage difference allows for a comparison of the values on equal terms. For Sylgard 184, a difference of 9% is observed between the value determined via AFM and the one calculated from the hardness value (H_a) using Gent's formula, while for Sylgard 186, the difference is approximately 7%. It is important to highlight that, since the shear stress formula directly depends on the Young's modulus, it would not be possible to make a direct comparison using only hardness values. However, the results demonstrate that the Young's modulus calculated from H_a aligns closely with the value obtained experimentally via AFM. This validates the use of Shore A hardness values for reliably comparing the mechanical properties of the two formulations. This also confirms the correlation between hardness and shear stress, with the latter being, at equal thickness, approximatively twofold higher for Sylgard 186 than Sylgard 184. This makes Sylgard 186 a more effective formulation for anti-icing applications. It is important to note that both formulations exhibit significantly higher anti-icing properties compared to the untreated Anticorodal surface, with all the determined ARF values above 2. A summary of the collected data is presented in Table 5.

	Sylgard 184 10:1	Sylgard 186 10:1
SCA (°)	107.8 ± 2.8	1009 ± 2.4
CAH (°)	44.9 ± 1.4	41.8 ± 5.2
RO (°)	50.7 ± 4.3	48.1 ± 1.6
Surface energies (mN/m)	26.1 ± 0.3	25.4 ± 3.1
Hardness Shore A	47.7 ± 1.2	30.2 ± 0.9
Viscosity (cP)	4499	12200
Shear stress (kPa) RANGE 1 (0-200µm)	163.6 ± 20.2	87.0 ± 18.1
ARF RANGE 1 (0-200µm)	2.1	4
Shear stress (kPa) RANGE 2 (300-500µm)	130 ± 15.4	62.5 ± 5.3
ARF RANGE 2 (300-500µm)	2.7	5.6
Shear stress (kPa) RANGE 3 (750-950µm)	92.7 ± 6.9	42.3 ± 6.8
ARF RANGE 3 (750-950µm)	3.8	8.3

Tab. 5 Summary of the properties of PDMS prepared with the two formulations Sylgard184 and Sylgard186.

4.1.1 Ice detachment cycles and aging in outdoor environments

From an industrial application perspective, it is crucial to evaluate the durability of materials over time and their behaviour when exposed to real-world conditions, that can be enormously different from those of a lab-environment. These consider the contaminant that can be present in rainwater able to promote the creation of particulate matter (PM), also known as aerosol. These are mixture of solid particles and liquid droplets found in the atmosphere¹⁶⁸, which may accumulate on surfaces, compromising the coating's integrity and accelerating aging. Pollutants like NO_x and SO_x can react with water, leading to the formation of acidic species that can cause material degradation¹⁶⁸. Additionally, the UV components of solar radiation can interact with materials, altering their chemical structure and promoting degradation reactions^{60,51}.

For these reasons, it is essential to evaluate the performances of anti-icing materials under real operating conditions. In this section, the two formulations, Sylgard 184 and Sylgard 186, are evaluated in terms of durability by subjecting them to repeated ice detachment tests and aging in outdoor environments. Based on the results from the previous section, the coatings were prepared with a thickness comprised in the Range 3 (750-950 µm), maintaining an A:B ratio equal to 10:1, and a curing treatment at 100°C for 35 minutes.

4.1.1.1 Ice detachment cycles

The samples, subjected to a cycle of 20 shear stress tests, were stored inside the laboratory, in a dryer. The samples were not washed after each test and during each test, ice was grown in the same spot on the surface of the elastomeric coatings. The results of these tests are presented in Fig. 39.

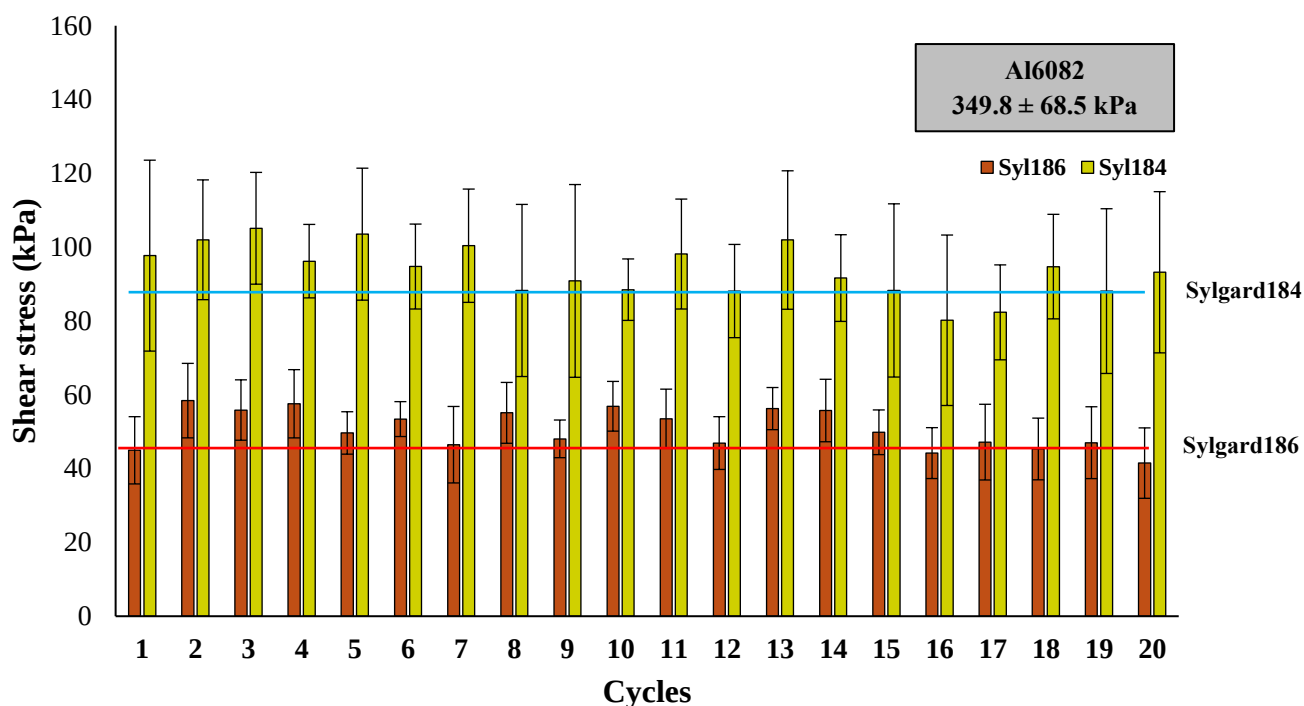


Fig. 39 Results of repeated shear stress test for Sylgard184 and Sylgard 186. Blue and red lines are Sylgard184 and Sylgard 186 values measured before cycles, respectively.

For both formulations, the shear stress value (and consequently the ARF value) fluctuates around the value obtained in the previous section showing great durability in terms of anti-icing properties towards several tests.

To assess any potential surface degradation, IR spectra were collected for both formulations after 20 cycles and compared with the spectra gathered from samples before testing (Fig. A10 and Fig. A11), showing diagnostic peaks of PDMS without the appearance of abnormal signals, also indicating that the surfaces were not contaminated or underwent chemical degradation during the test. Additionally, the wettability measurements (Tab. 6) confirm the surface integrity of the coatings, maintaining values consistent with those obtained prior to the test.

	Sylgard 184 before cycles	Sylgard 184 XX cycles	Sylgard 186 before cycles	Sylgard 186 XX cycles
SCA (°)	107.8 ± 2.8	105.3 ± 1.3	100,9 ± 2.4	105.9 ± 0.8
CAH (°)	44.9 ± 1.4	47.7 ± 2.2	41.8 ± 5.2	47.8 ± 2.1
RO (°)	50.7 ± 4.3	49.1 ± 3.2	48.1 ± 1.6	52.3 ± 1.8

Tab. 6 Comparison of wettability measurements for Sylgard 184 and Sylgard 186 in 10:1 ratio before and after after shear stress cycles.

4.1.1.2 Outdoor aging tests

Outdoor aging tests were conducted to evaluate the material's response to environmental exposure. The focus was to investigate the impact of UV radiation and atmospheric agents, particularly the effect of potential accumulation of atmospheric contaminants on the anti-icing properties of the surfaces. Human caused organic aerosol has a complex composition; its sources include fuel combustion from automobiles, power plants, wood burning, industrial processes, and diesel-powered engines. These fine particles are also formed in the atmosphere when gases such as sulphur dioxide, nitrogen oxides, and volatile organic compounds are transformed in the air by chemical reactions. It is challenging to determine the exact origin of this particulate matter, and even more difficult to establish its precise composition. These powders are often sub-micrometric in size, and when they deposit on surfaces, they may go unnoticed due to interference from the surface itself or because they are present in quantities too small to be detected by current techniques¹⁶⁸.

The samples Sylgard184 10:1 and Sylgard186 10:1 was exposed outdoors for 90 days (Sylgard 186 from 5/10/22 to 4/1/23; Sylgard 184 from 28/10/22 to 28/1/23) and assessed every 30 days from the initial exposure. After the external exposure the samples are prone to forming a stable layer of surface condensation (Fig. 40), that can promote the accumulation of atmospheric contaminants, which may alter the surface properties of the materials.

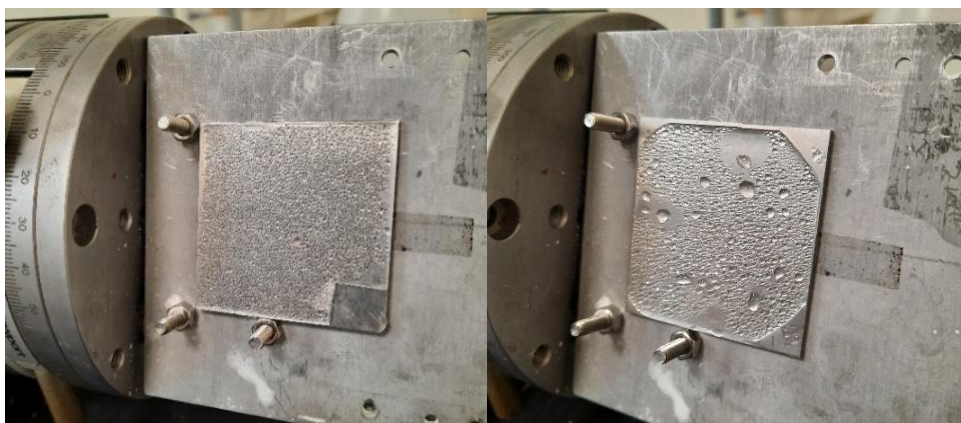


Fig. 40 On the left Sylgard186 10:1, on the right Sylgard184 10:1. Both samples show a stable condensation layer formed by small water droplets. The small droplets don't run away from the surface even with a tilt table inclination of 90°C.

The possible effect of contaminant accumulation on the anti-icing properties of the surfaces was investigated, leaving the exposed samples unwashed before characterization. For characterization, the samples were placed in an oven at 40°C for 5 hours to facilitate the slow evaporation of the water droplets present on the surface. Upon examining the Sylgard 184 and Sylgard 186 samples exposed to the external environment for 30- and 60-days following oven treatment, no visible or significant differences were observed compared to the cleaned, unexposed coatings. After 90 days, a layer of particulate matter was observed on the surface (Fig. 41).

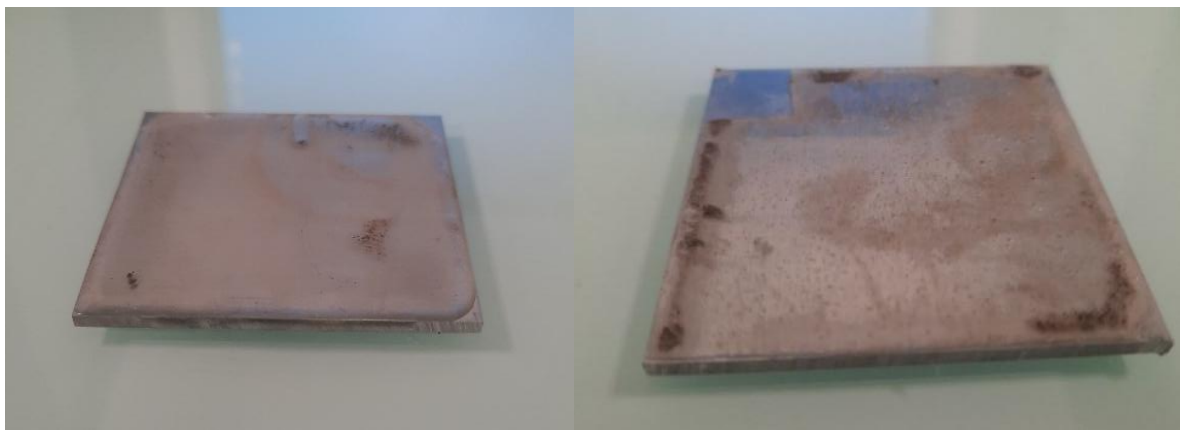


Fig. 41 On the left Sylgard184 10:1 aged outdoors for 90 days before anti-icing measurement. On the right Sylgard 186 10:1 aged outdoors for 90 days before the anti-icing measurement. A dust layer of is visible on the top of the surface for both formulations.

The shear stress measurements are presented in Fig. 42.

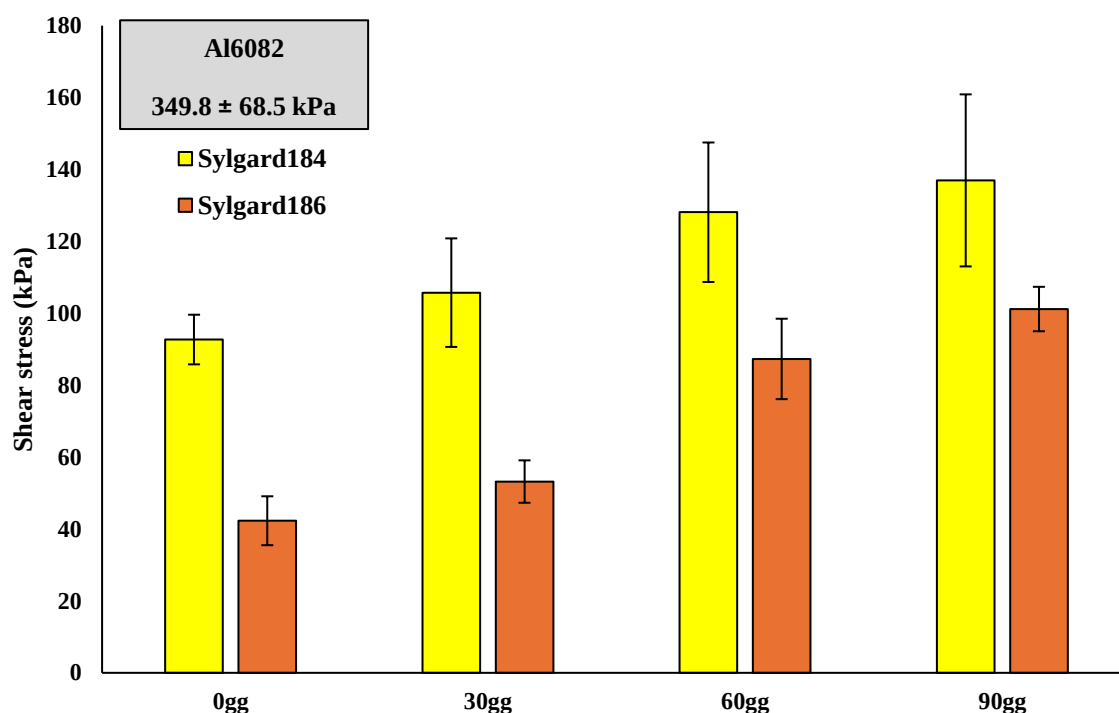


Fig. 42 Shear stress values for Sylgard184 and Sylgard186 after outdoor aging without sample cleaning. The aim is to evaluate the possible effect of contaminants on anti-icing properties.

For both formulations, an increase in shear stress over time can be observed. In the case of Sylgard 184, the increase is gradual, but considering the standard deviations, no significant differences are detected between 0 and 30 days. However, starting from 60 days, the shear stress value rises and remains stable up to 90 days of aging. For Sylgard 186, on the other hand, the increase is not gradual; the anti-icing properties are maintained up to 30 days of aging, after which there is a rise in shear stress that again stabilizes until 90 days of external exposure. After anti-icing measurements on samples aged for 90 days, we can observe the removal of the dust layer from the surfaces of both formulations (Fig. 43). Although the dust layer is not strongly adhered to the surface it has a negative effect on the anti-icing properties of the coating. The wettability measurements are shown in Fig. 44 and Fig. 45.

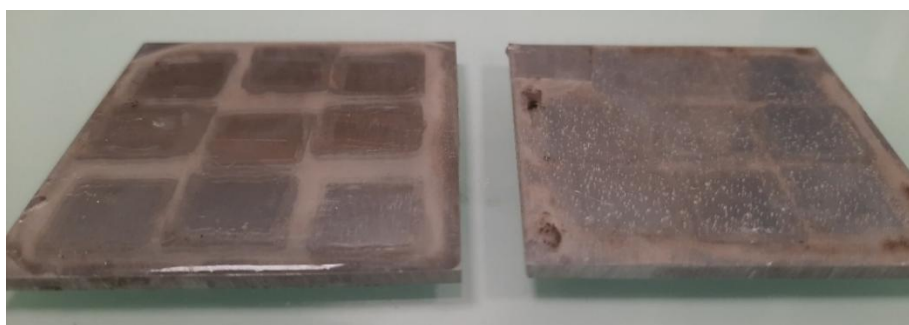


Fig. 43 On the left the Sylgard184 outdoor exposed for 90 days after anti-icing measurements. On the right Sylgard186 outdoor exposed for 90 days after anti-icing measurements. The particulate layer is easily removed by the ice.

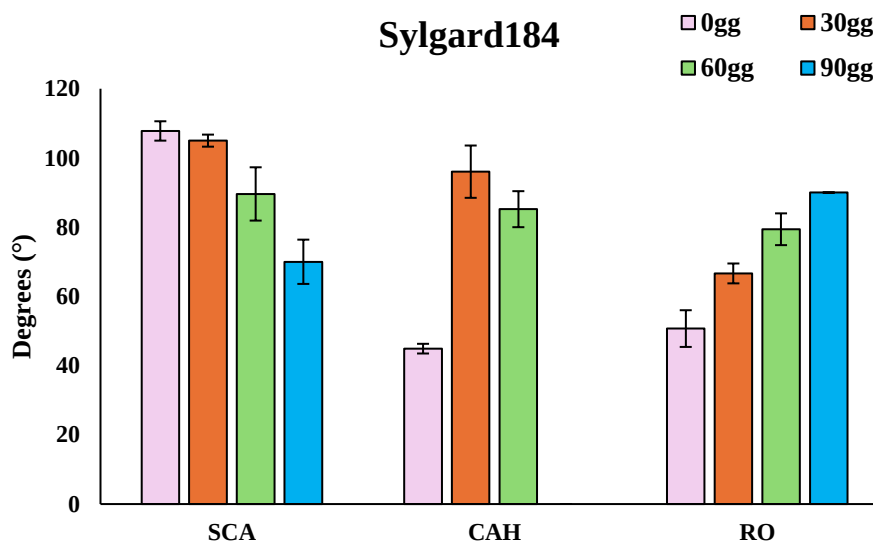


Fig. 44 Wettability measurement for Sylgard186. No CAH and RO could be measured with tilting table method for samples aged 90 days.

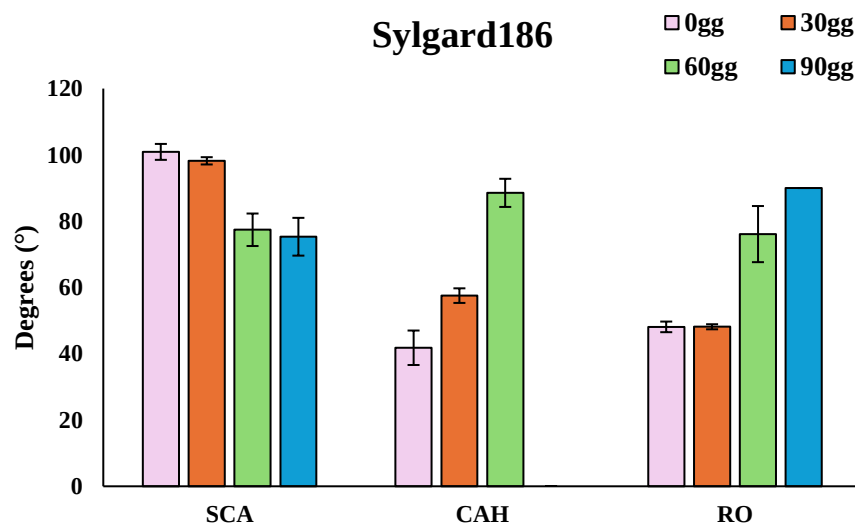


Fig. 45 Wettability measurement for Sylgard186. No CAH and RO could be measured with tilting table method for samples aged 90 days.

For both formulations, a deterioration of the properties over time can be observed, with a decrease in the static contact angle starting from day 60, and an increase in CAH and RO already after 30 days of aging. Fig. 46 shows the movement of a drop on the surface of a 30-day-aged Sylgard 184 10:1 sample, where an evident drop pinning phenomenon is already evident. The drop begins to move at RO values around 55°, but it remains pinned and only starts sliding off the surface at approximately 65°. Similarly, for the 30-day-aged Sylgard 186 10:1, the drop pinning phenomenon is observable on the surface, although less pronounced compared to Sylgard 184 (Fig. 47)



Fig. 46 Droplet pinning on Sylgard184 10:1 surface aged for 30 days. As we can see from the picture, the droplet leaves a path during the movement (red arrows) showing his interlocking on the surface due to dust or impurities present on it.

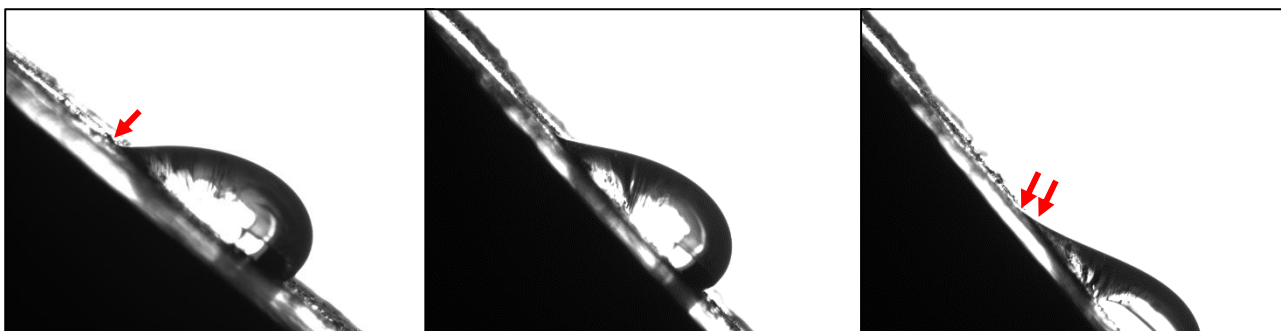


Fig. 47 Droplet pinning on Sylgard186 10:1 surface aged for 30 days. In this case the pinning is less pronounced resulting in a lower RO value compared to Sylgard184

Even though visually only the coatings aged outdoors for 90 days show a significant accumulation of particulate matter, both a degradation in the anti-icing properties and in the surface, wettability can be observed starting from 30 days of exposure for Sylgard 184 and from 60 days of exposure for Sylgard 186. FTIR-ATR spectra of the samples exposed to outdoor conditions for different durations were collected and compared for each formulation. For Sylgard 184 (Fig. 48), the following characteristic peaks of PDMS were identified: the asymmetric stretching of the methyl groups (2963 cm^{-1}), the stretching of the Si-CH₃ bond (785 cm^{-1}), the bending of the C-H bonds (1259 cm^{-1}), and the Si-O-Si stretching ($1010\text{-}1061\text{ cm}^{-1}$). These peaks were observed consistently from day zero through 90 days of outdoor exposure. Starting from 30 days of exposure, a broad signal around 3360 cm^{-1} and a peak around 1620 cm^{-1} , indicative of residual water presence, appeared. After 90 days, these signals grew in intensity. Similarly, for Sylgard 186, characteristic peaks of PDMS were identified (Fig. 49). For samples exposed for 60 days (60gg) and 90 days (90gg), a broad signal around $3300\text{-}3400\text{ cm}^{-1}$ and a signal around 1640 cm^{-1} due to residual water appeared.

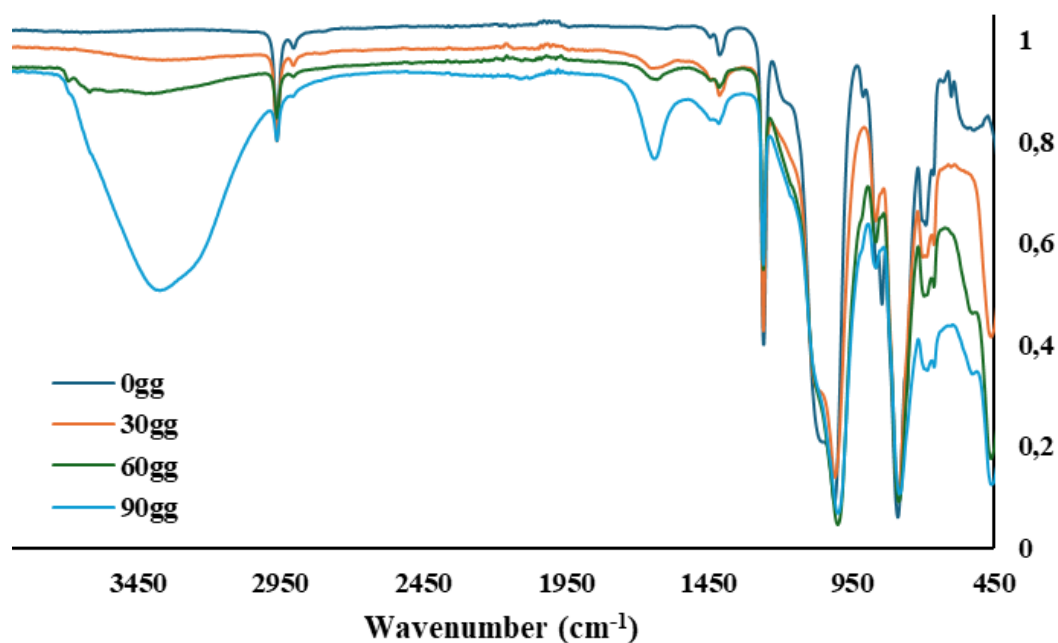


Fig. 48 Comparison between Sylgard 184 10:1 unexposed and exposed to outdoor conditions for 30 (30gg), 60 (60gg), and 90 days (90gg). For 90 days outdoor aging sample, the 3360 cm⁻¹ signal tends in part to overlap and masks the signal related to PDMS methyl groups.

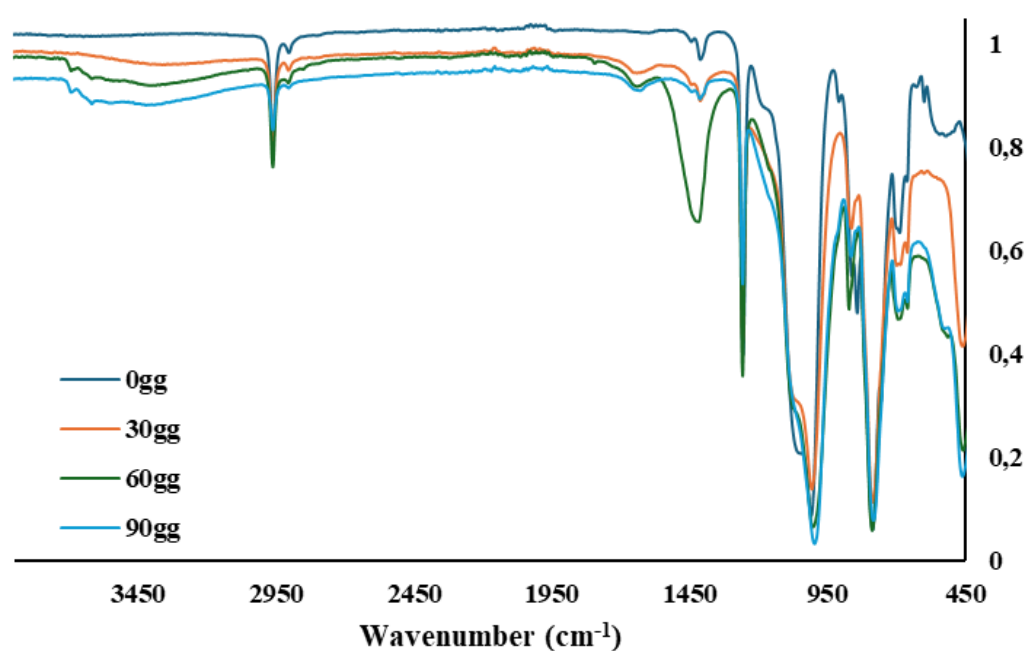


Fig. 49 Comparison between Sylgard 186 10:1 unexposed and exposed to outdoor conditions for 30 (30gg), 60 (60gg), and 90 days (90gg).

Although no significant particulate deposition is visually observed for the samples exposed for 30 days (30gg) and 60 days (60gg), infrared spectroscopy reveals the presence of trace amounts of water, likely due to the condensation of atmospheric aerosol containing particulate matter. An effect on the anti-icing properties and wettability of the coatings is evident when exposed to outdoor conditions, likely due to the accumulation of fine particles and water traces on the

surface. To isolate the possible effect of solar radiation of the PDMS coatings a set of samples, specifically prepared for this purpose

To isolate the solar radiative effects and eliminate the influence of any potential surface contaminants, a set of samples, specifically prepared for this purpose, were aged and then cleaned using water and ethanol after each exposure period and dried in the oven at 40°C for 5 hours and 24h at room temperature before conducting the characterizations. Ice adhesion measurements are presented in Fig. 50.

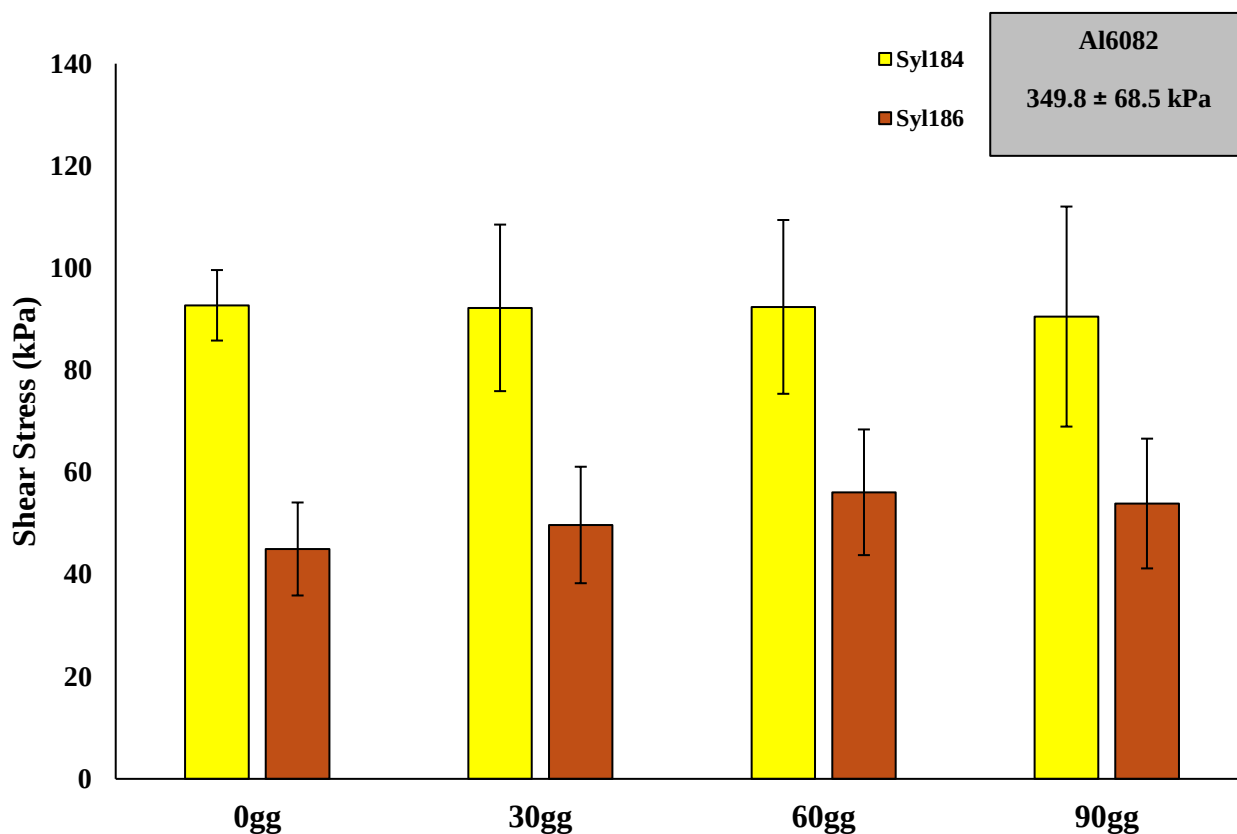


Fig. 50 Anti-icing measurements for the evaluation of UV radiation effect.

The shear stress values for Sylgard 186 show a slight increase over the 90-day aging period, but they remain within the standard deviation range. Sylgard 184 does not exhibit a noticeable deterioration in anti-icing properties, although an increase in standard deviation is observed after 30 days. Wettability measurements for both formulations are presented in Fig. 51 and Fig. 52.

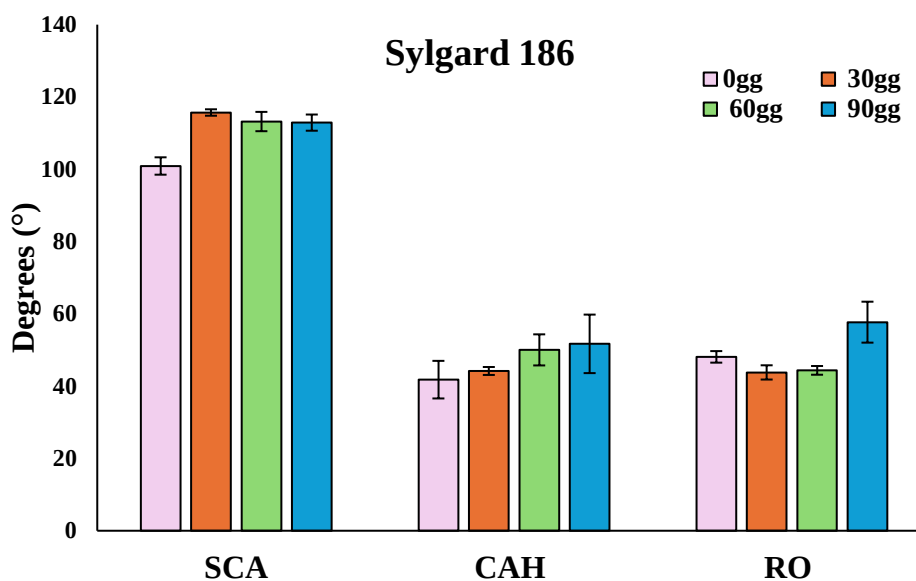


Fig. 51 Sylgard 186 wettability measurements after outdoor aging.

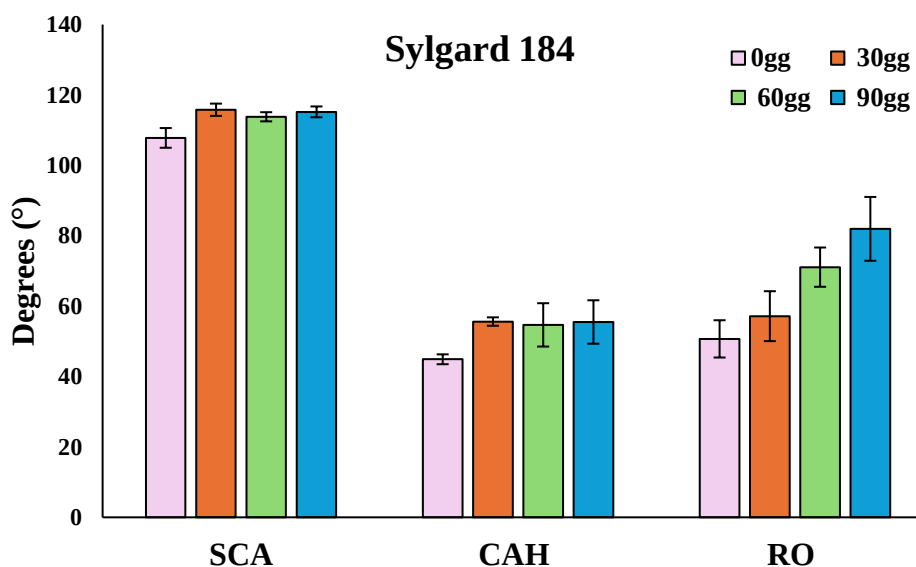


Fig. 52 Sylgard 184 wettability measurements after outdoor aging.

For Sylgard 186, the static contact angle values begin to increase after 30 days of aging. The CAH values rise and stabilize after 60 days, although, considering the standard deviation, a clear difference cannot be asserted. The RO values remain consistent up to 60 days, while at 90 days, an increase in the tilt angle and standard deviation is observed. For Sylgard 184, the static contact angle increases after 30 days of aging, and a rise in hysteresis can also be seen starting from 30 days, stabilizing up to 90 days of aging. The RO undergoes a gradual and significant increase over the 90-day period, accompanied by high standard deviations.

The samples were monitored using IR spectroscopy (Fig. A12 and Fig. A13). For both formulations, no abnormal peaks were observed, but the characteristic peaks of PDMS were

clearly visible. This suggests that the samples did not undergo chemical degradation due to UV radiation at the surface level.

Overall, both formulations performed well under ice detachment cycles, maintaining their properties for 20 consecutive tests without showing signs of surface degradation. The samples did not suffer degradation due to UV radiation during outdoor aging, preserving both their anti-icing properties and chemical surface integrity. However, an increase in the static contact angle and a deterioration of dynamic properties were observed for both formulations. Despite the washing phase, it is possible that dust or contaminants remained on the surface, creating sites where water droplets could become trapped and fail to roll off.

Nevertheless, the two formulations, Sylgard 184 and Sylgard 186, demonstrated excellent performance when subjected to repeated stress or outdoor exposure, confirming the significant potential of PDMS for large-scale anti-icing applications.

4.2 Variation of prepolymer-crosslinking agent ratio

We have examined the properties of Sylgard 184 and Sylgard 186 following the guidelines provided in the technical sheets, maintaining a standard prepolymer (A)/cross-linker (B) ratio of 10:1. However, by adjusting the A:B ratio, it is possible to influence the cross-linking degree within the polymer matrix, leading to changes in the mechanical properties of the PDMS and its anti-icing behaviour. In this section, we will explore how variations in the prepolymer to cross-linker ratio impact the performance of the coatings, evaluating the anti-icing properties under different conditions. This approach allows for a deeper understanding of how changes in composition can significantly affect the overall material behaviour. Samples were prepared for both formulations by varying the ratios from 1:1 to 30:1, cross-linking them at 100°C for 35min, and maintaining a thickness in the range 3 (750-950 μm) (see the Experimental section details on samples preparation). Fig. 53 shows the shear stress measurements for both formulations by varying the A:B ratio and in Tab. 7 are reported the corresponding ARF values.

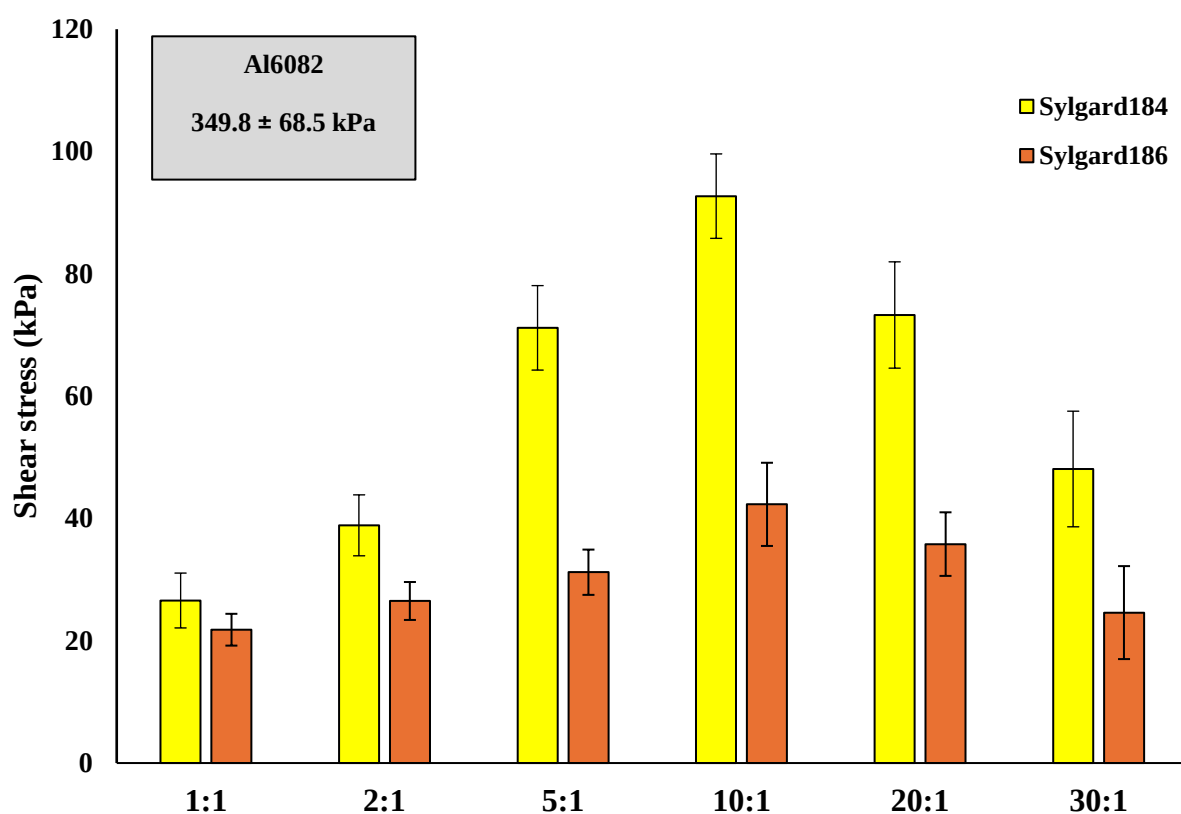


Fig. 53 Shear stress values for Sylgard186 (orange) and Sylgard184 (yellow) in function of the A:B ratio.

Formulation	A:B ratio	ARF
Sylgard186	1:1	16
	2:1	13.2
	5:1	11.2
	10:1	8.3
	20:1	9.8
	30:1	14.2
Sylgard184	1:1	13.1
	2:1	9.0
	5:1	4.9
	10:1	3.8
	20:1	4.8
	30:1	7.3

Tab. 7 Adhesion reduction factor (ARF) values for samples prepared from Sylgard184 and Sylgard186 by varying the A:B ratio.

For both formulations, a pyramidal trend can be observed with the highest shear stress value found for the standard 10:1 ratio. Considering the equation describing the mechanism of ice detachment from the surface (6):

$$\sigma_s^* \sim \sqrt{\frac{W_a \mu}{h}} \quad (6)$$

where shear modulus μ is defined as

$$\mu = \frac{E}{2(1 + \nu)}, \quad (4)$$

The samples were prepared with the same thickness and therefore we can omit in this case the effect of the variable h in the denominator. The critical shear stress value is directly proportional to the shear modulus μ , correlated to Young's modulus E through the Poisson coefficient (ν in equation 4, for PDMS it is constant and equal to 0.5 for PDMS) and to the adhesion work (W_a), which depends on the contributions of surface energies to the interface. It is possible that these two contributions influence the shear stress value of the samples prepared in different ratios, or that their combined effect is responsible of the observed shear stress trend. As discussed in section 3.2.1, the variation of the prepolymer-to-crosslinking agent ratio directly affects the degree of crosslinking and the material's elasticity. Increasing the amount of crosslinking agent leads to a higher density of crosslinked sites between polymer chains, resulting in an increased network structure and reduced elasticity, as the material becomes more rigid. Conversely, reducing the amount of crosslinking agent allows for greater chain mobility, resulting in a lower degree of crosslinking, which enhances the material elasticity due to fewer crosslinking points within the

polymer network. Hardness measurements were then conducted to evaluate a possible effect of the A:B ratio on the flexibility of the coatings (Fig. 54).

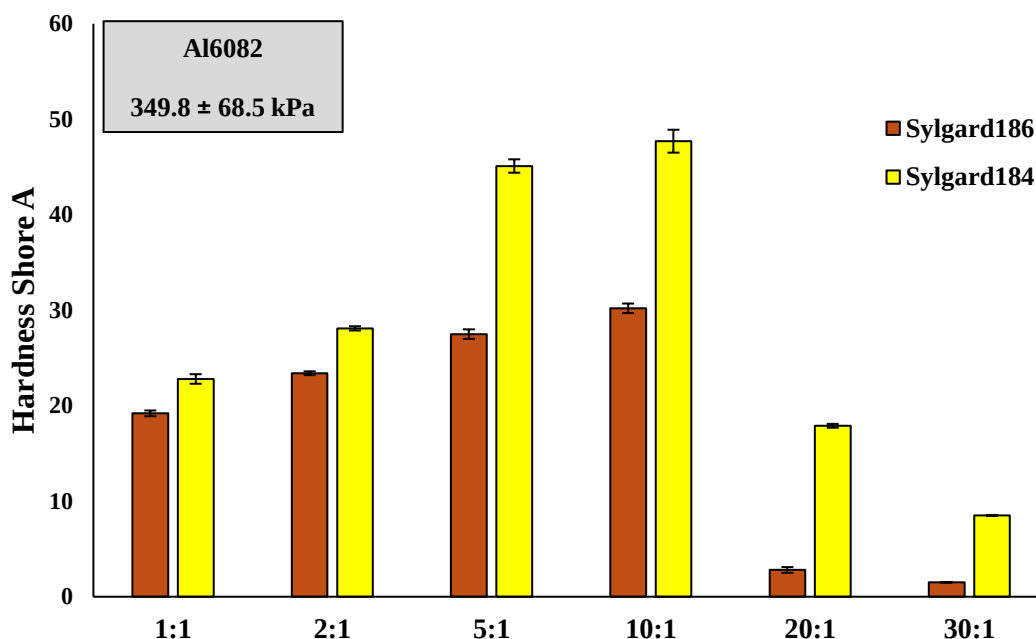


Fig. 54 Hardness Shore A measurements for Sylgard184 and Sylgard186 prepared in different ratio.

In general, the Sylgard186 formulation shows lower hardness than Sylgard184, as inferable from Tab. 8.

Formulation	1:1	2:1	5:1	10:1	20:1	30:1
Sylgard184	22.8 ± 0.5	28.1 ± 0.2	45.1 ± 0.7	47.7 ± 1.2	17.9 ± 0.2	8.5 ± 0.1
Sylgard186	19.2 ± 0.3	23.4 ± 0.2	27.5 ± 0.5	30.2 ± 0.5	2.8 ± 0.3	1.5 ± 0.1

Tab. 8 Hardness values for Sylgard184 and Sylgard186 prepared with different A:B ratios.

Shore A hardness values do not directly describe the elasticity of a material but can be correlated to Young's modulus (YM) through the Gent equation, as discussed in the section on elastomeric materials (Paragraph 3.1.1). In Paragraph 4.1.1, concerning the comparison between the Sylgard184 and Sylgard186 formulations, the Gent equation was applied, and the YM values derived from hardness measurements were consistent with those obtained directly through AFM measurements. This suggests that Shore A hardness values can be reliably used to compare the elasticity of different samples. However, this equation is valid for hardness values comprised between 20 and 80, where a good correlation is found¹⁶⁹. Below or above these values, it is possible that the equation does not provide reliable results. The hardness values obtained with Sylgard184 for the ratio 1:1, 20:1, and 30:1 and with Sylgard186 with the ratio 20:1 and 30:1, are below the threshold for the use of the Gent equation (Tab. 8). To assess the correlation between the Shore A hardness and Young's modulus (YM), YM measurements were taken using AFM on

the samples corresponding to the lowest hardness Shore A value to verify with the softness materials the validity of the Gent equation. The comparison is presented in Tab. 9.

Formulation	Hardness (H _a)	YM Gent equation (MPa)	YM AFM (MPa)	Approximation error (%)	Percentage difference (%)
Sylgard184 20:1	17.9	0.66	0.71	7.3	7.2
Sylgard184 30:1	2.8	0.37	0.31	17.6	17.9
Sylgard186 20:1	8.5	0.22	0.22	0.9	0.7
Sylgard186 30:1	1.5	0.19	0.18	5.4	7.7

Tab. 9 Comparison between Young modulus calculated by Gent equation and measured by AFM. The approximate error was calculated assuming the value measured by AFM as the exact reference; the percentage difference allows for a comparison of the values on equal terms.

Although considering the possible limitations deriving from the use of the Gent equation, we were positively surprised to find a good correlation between the YM values found with the two different approaches. Here, we have considered that the observed trend is indicative of a correlation between the hardness and the shear stress, allowing the use of the hardness value to directly compare the different formulations, also with those corresponding to a 10:1 ratio, for which the YM was inferred from Gent equation.

What we expected for both formulations were that the samples corresponding to 5:1, 2:1, and 1:1 ratio showed an increased hardness with respect to the formulations deriving from a 10:1 ratio. However, both for Sylgard186 and Sylgard184, the hardness decreases as the A:B ratio decreases. As can be inferred from Fig. 54, no significant differences were observed among the formulation corresponding to 10:1 and 5:1 ratio. For Sylgard186, the reduction in hardness occurs more gradually as the A:B ratio decreases, while for Sylgard184, a significant difference in hardness is observed when moving from 5:1 to the 2:1 ratio. The formulations corresponding to 20:1 and 30:1 ratio showed a lower hardness with respect to the formulations deriving from a 10:1 ratio, with Sylgard186 showing significantly lower values than Sylgard184. The pyramidal trend is again maintained and aligns with the shear stress values observed in Fig. 53. However, in Fig. 54 and Tab. 8, it is possible to observe that for both formulations, the materials deriving from the highest A:B ratios (20:1 and 30:1) show hardness values lower than those found for the materials deriving from lower A:B ratios (1:1 and 2:1). Differently, looking at Fig. 53, it can be noted that the same trend is not maintained for shear stress values. This suggests that flexibility alone is not sufficient to reach a shear stress value lower than that of more rigid samples. It is therefore

necessary to evaluate the contribution coming from the surface to understand what really influences the shear stress value. In this direction, a series of wettability measurements were conducted for both formulations, and the relative results are depicted in Fig. 55 and Fig. 56.

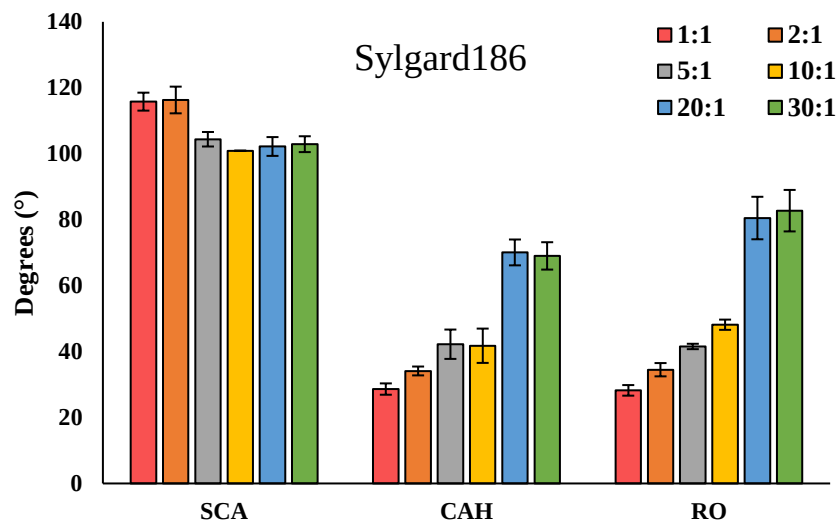


Fig. 55 Wettability measurements for Sylgard186 corresponding to different A:B ratio.

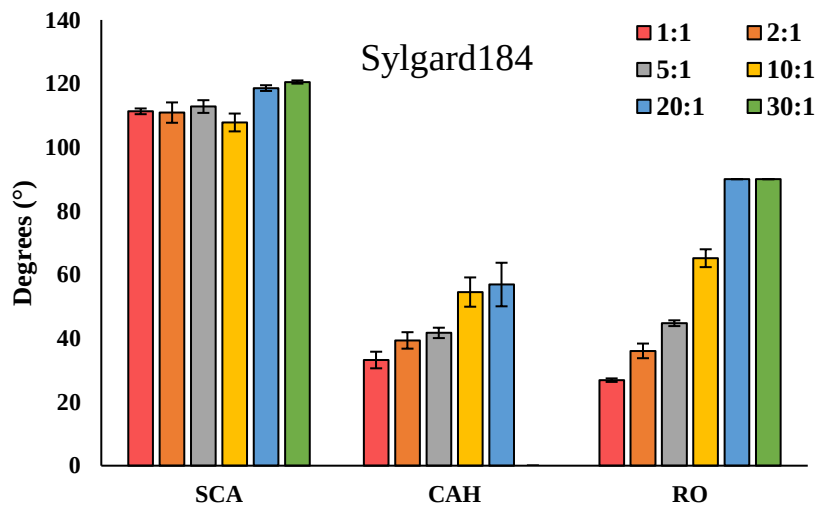


Fig. 56 Wettability measurements for Sylgard184 corresponding to different A:B ratio.

The results of the wettability measurements are similar for both formulations. The static contact angle (SCA) increases both for the "low ratios" (5:1, 2:1, and 1:1) and the "high ratios" (20:1 and 30:1) relative to the standard 10:1 ratio. For Sylgard186, the increase in SCA for the 1:1 and 2:1 ratio is more marked compared to Sylgard184. For both formulations, hysteresis (CAH) and roll-off angle (RO) gradually decrease as the A:B ratio decreases, while for coatings prepared with a "high ratio," the CAH increases, being absent when the roll-off angle reaches 90°, as in the case of Sylgard184 prepared with a 30:1 ratio. The SCA analysis confirms the pyramidal trend observed for both Sylgard184 and Sylgard186 and suggests that there may have been a variation in surface energy with changes in the A:B ratio, which altered the contribution of work of

adhesion and favoured a reduction in shear stress compared to the standard 10:1 ratio. However, it is important to consider that the increase in SCA observed for the 20:1 and 30:1 ratio may, at least partially, be attributed to the high elasticity of the substrate. As demonstrated by Bonaccorso¹⁷⁰, the deformation of soft elastomeric surfaces under the influence of the droplet's surface tension can lead to an overestimation of the apparent contact angle. This effect becomes particularly relevant for highly elastic formulations, such as those prepared with elevated base-to-curing agent ratios, where the increased compliance of the material enhances the distortion at the three-phase contact line. Thus, the measured SCA for the 20:1 and 30:1 sample depends also on the elasticity of the material's surface. It is also known that "dynamic wettability" depends not only on the surface energies involved but also on the surface appearance. The fact that a decrease in the A:B ratio results in a reduction in hardness and an improvement in dynamic properties for both formulations, suggests that some unreacted part B may remain inside the elastomeric matrix, which, similarly to the effect of a liquid filler^{171,172}, reduces the hardness of the material. This might also migrate on the surface of the material to create a quasi-liquid layer^{173,174}, which favours greater surface sliding. This last aspect could explain why the shear stress values of the "high ratio" are higher than those obtained with the "low ratio", despite the hardness of the samples prepared with 20:1 and 30:1 ratio is generally lower for both formulations. In this study, the PDMS coatings were tested without undergoing a solvent-washing step after crosslinking to remove all non-crosslinked molecules from the substrates. This choice was made to ensure that the samples remained in their as-prepared state, closely reflecting real-world applications where PDMS would like to be employed without additional treatments or preparation step. Washing with solvents such as tetrahydrofuran (THF) is known to remove unreacted oligomeric species¹⁷⁵, but the use of solvents can also alter the microstructure of the polymer network and potentially affect its mechanical and surface properties¹⁷⁶. In addition, oligomers and unreacted species present in the polymer matrix may continue to migrate to the surface over time; therefore, washing does not ensure the complete removal of these low molecular weight molecules.

FTIR spectroscopy can be used to highlight chemical differences on the surface between the coatings prepared with "low ratio" and "high ratio" compared to the standard 10:1. For Sylgard184, the comparison between the IR spectra of the 20:1, 30:1, and 10:1 ratios is shown in Fig. 57, and the comparison between the 1:1, 2:1, 5:1, and 10:1 ratios is shown in Fig. 58. For Sylgard the comparison between the IR spectra of the 20:1, 30:1, and 10:1 ratios is shown in Fig. 59, and the comparison between the 1:1, 2:1, 5:1, and 10:1 ratios is shown in Fig. 60.

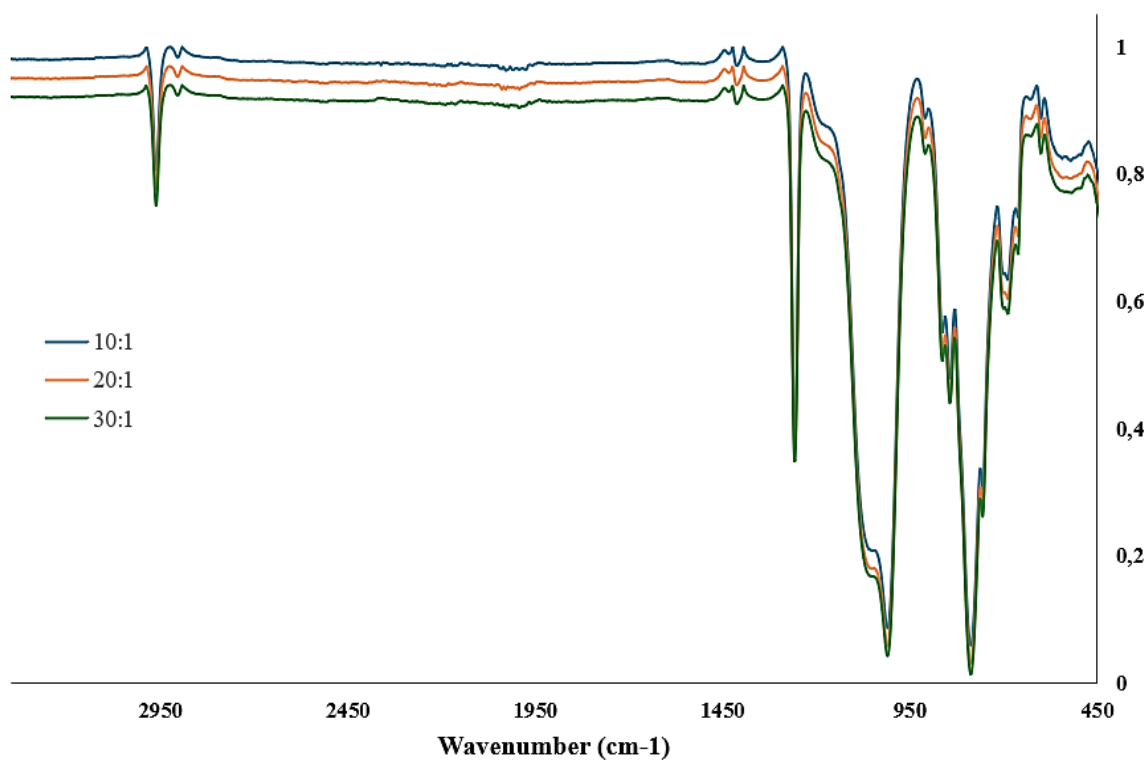


Fig. 57 Comparison of IR spectra of Sylgard184 formulations prepared in 10:1, 20:1 and 30:1 ratio.

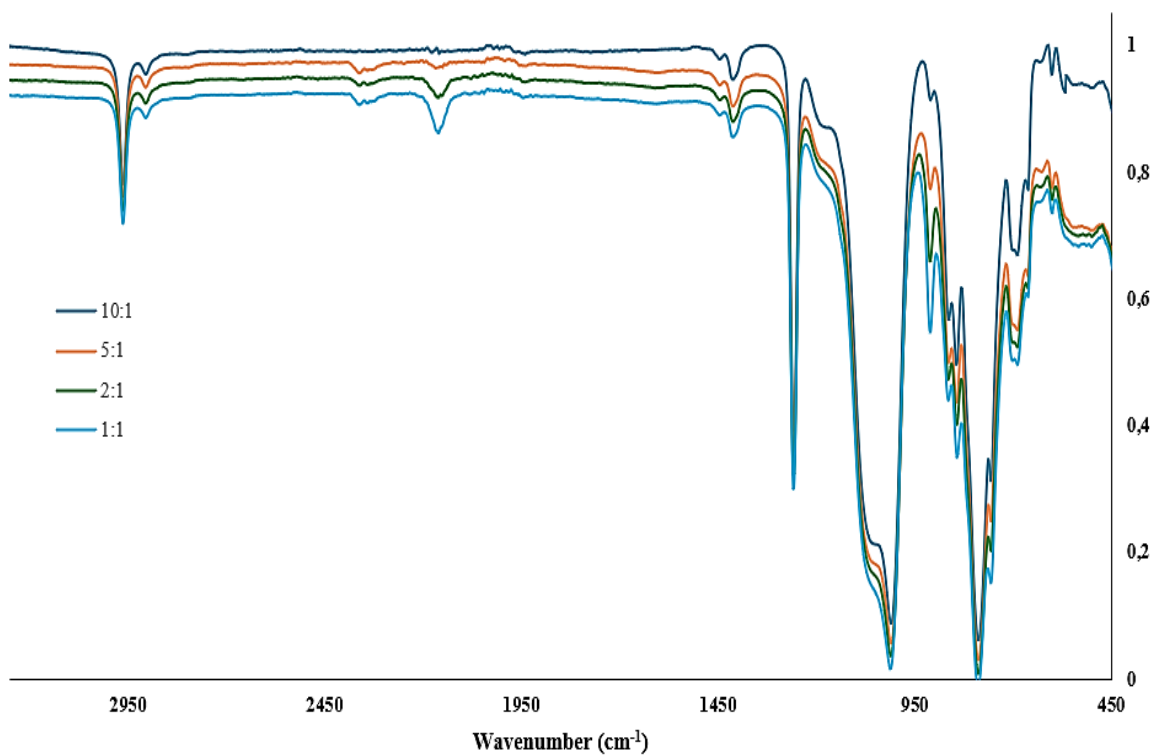


Fig. 58 Comparison of IR spectra of Sylgard184 formulations prepared in 1:1, 2:1, 5:1 and 10:1 ratio.

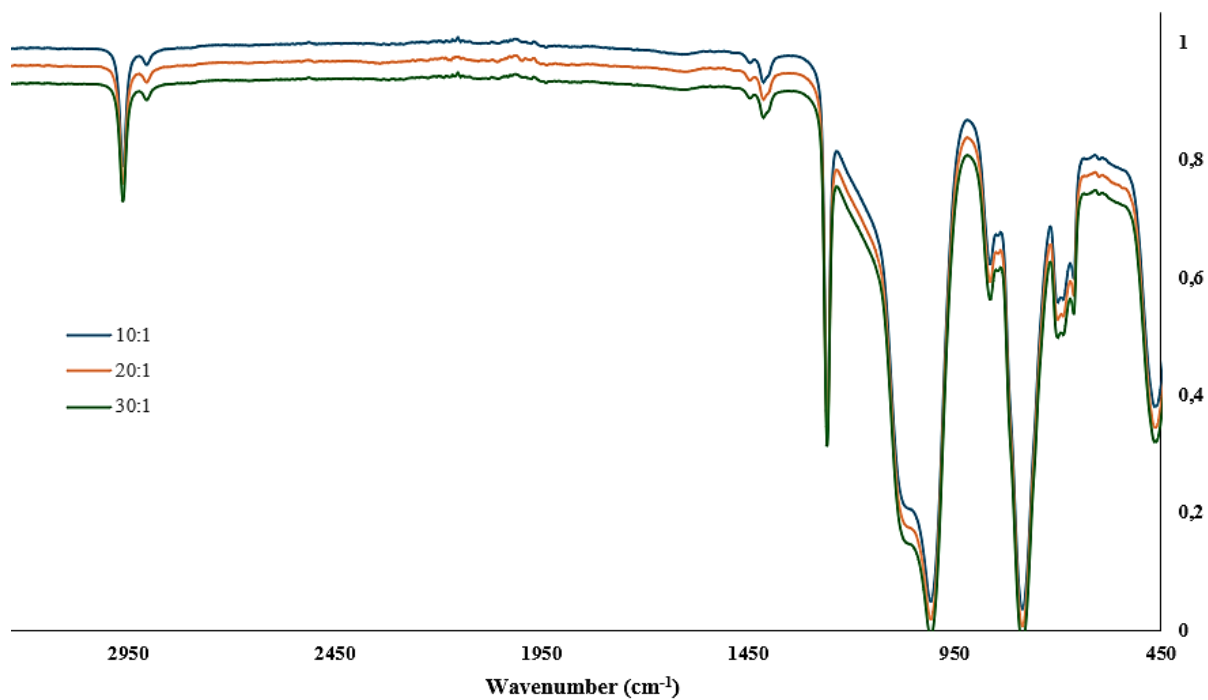


Fig. 59 Comparison of IR spectra for Sylgard186 formulation prepared in 10:1, 20:1 and 30:1 ratio.

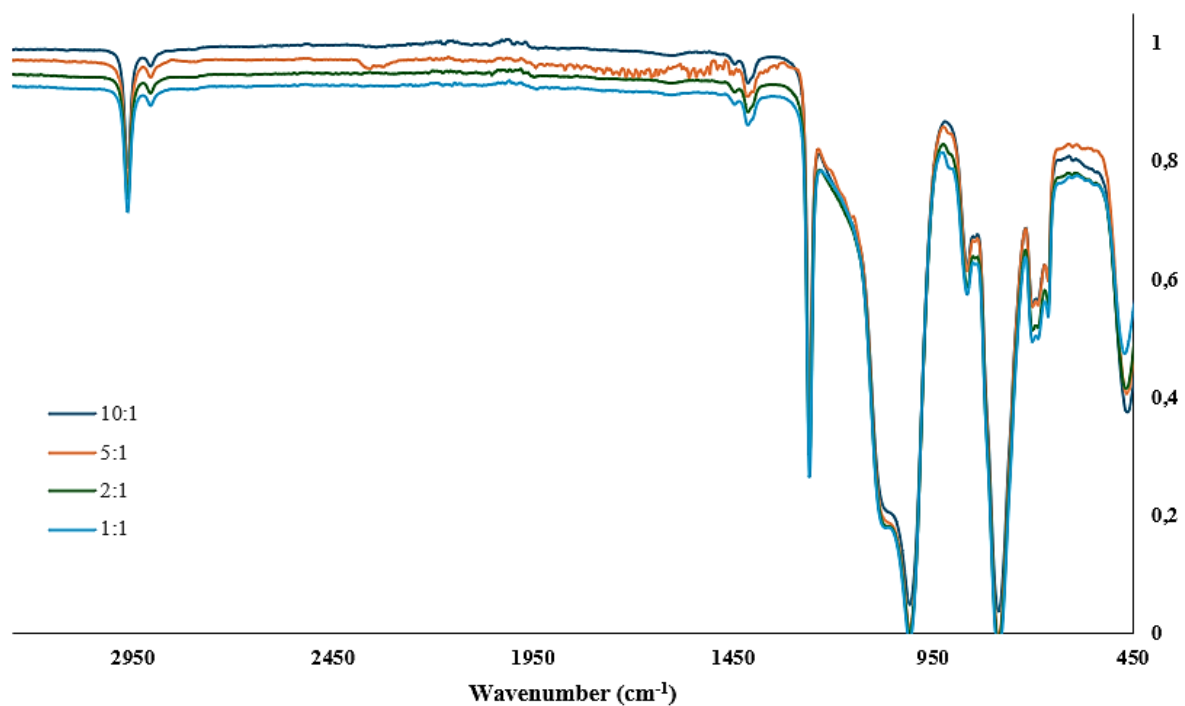


Fig. 60 Comparison of IR spectra for Sylgard186 formulation prepared in 1:1, 2:1, 5:1 and 10:1 ratio.

First, the typical PDMS profile can be recognized for both prepared formulations by varying the A:B ratio. Fig. 57 clearly indicates the absence of significative differences between the different samples. However, from the spectra in Fig. 58, the appearance of the signal corresponding to the stretching of the Si-H bond in the region $2200\text{-}2100\text{ cm}^{-1}$ becomes evident from 5:1 ratio up to 1:1 ratio.

In the case of Sylgard184, the FTIR spectroscopy indicates that the presence of a larger amount of part B could change the properties at the surface level. In fact, although the materials corresponding to 20:1 and 30:1 ratio show lower hardness with respect to the materials corresponding to "low ratios" (1:1 and 2:1), the latter generally have a lower shear stress. However, this hypothesis is not confirmed through IR spectroscopy for the Sylgard186 (Fig. 59 and Fig. 60): the comparison between the different ratios does not show significative differences, and the Si-H stretching peak is not visible.

For both formulations, an excess of part B makes the elastomer softer, as the unreacted part B remains embedded within the crosslinked structure, acting as a liquid filler.

The formation of a "quasi-liquid layer" due to the migration of unreacted species to the surface is not confirmed for the Sylgard186 formulation using IR investigation. Instead, it is more likely that the excess of part B is simply easier to detect through IR spectroscopy in Sylgard184 compared to Sylgard186.

This excess of part B likely contributes to a higher degree of crosslinking in the polymer, thereby reducing the adhesiveness typically observed in poorly crosslinked elastomers. As reported in literature^{177,178}, in the case of a partially crosslinked polymer, the rearrangement of terminal and distal chain segments gives rise to freely protruding ends and loops at the interface. It has been found that these segments have a large effect on adhesion hysteresis in the case of polymer–polymer adhesion and can also influence water mobility. For both formulations, in the case of the 20:1 and 30:1 ratio, where the PDMS crosslinking is reduced, the movement of water is likely hindered by a higher density of free chain segments on the surface.

This increased surface friction could also influence the anti-icing behaviour of the coating. Sylgard184 and Sylgard186 perform better when prepared with an excess of crosslinking agent, which increases the degree of crosslinking, reduces adhesiveness, and remains as a liquid filler within the matrix. This contributes to a reduction in hardness and an improvement in the anti-icing properties of the material.

However, despite these initial advantages, these formulations do not exhibit satisfactory durability over time. In fact, after several weeks, the materials tend to form cracks and fragment,

compromising their long-term effectiveness. For Sylgard184 prepared in the 1:1 ratio (Fig. 61 top left) and 2:1 ratio (Fig. 61 top right), crack formation on the surface of the coating is observable after 7 and 14 days, respectively. After the appearance of the cracks, anti-icing measurements were compromised by the fragility of the coatings (Fig. 61 bottom).

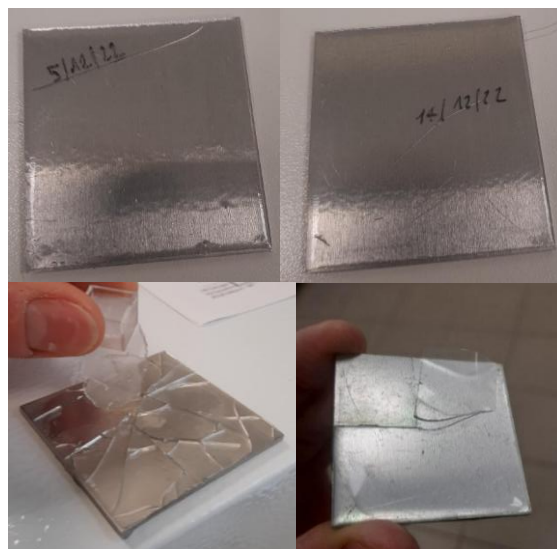


Fig. 61 Top-left: Sylgard184 (1:1 ratio) shows a crack after one week from its preparation. Top-right: Sylgard184 (2:1 ratio) shows a crack 14 days after its preparation. Bottom-left: Sylgard184 (1:1 ratio) fragmented after a shear stress measurement. Bottom-right: Sylgard184 (2:1 ratio) cracked after ice detachment from the surface.

It is possible that the presence of an excess of part B within the crosslinked structure of the coating initially improves durability, but the presence of volatile components creates tension in the structure that tends to fragment after solvent evaporation. For Sylgard186, however, the issue for low formulations is mainly related to the non-uniformity of the coating (Fig. 62).



Fig. 62 Sylgard186 samples show non-uniformity of coating with the presence of parts that are not properly cross-linked creating defects. Left Sylgard186 in 1:1 ratio. Right Sylgard186 in 2:1 ratio.

The study of the Sylgard184 and Sylgard186 formulations prepared by varying the A:B ratio reveals that for both formulations the 10:1 ratio shows worse performance respect to the other ratio studied, with a pyramidal trend that partly reflects the elastic behaviour and partly the surface behaviour of the coatings. Sylgard186 outperforms Sylgard184 for all tested ratios. The excess

of crosslinking agent leads to reduce hardness and adhesiveness but, at the same time, leads to increased material fragility. Considering these results, an in-depth analysis of the correlation between the variation of crosslinking conditions, the maturation of the materials over time, and their anti-icing properties is essential. In the next paragraph, the work will be focused on Sylgard184 with A:B ratios corresponding to 5:1, 10:1, 20:1, and 30:1. They in fact represent the ratios that best maintained properties over time, allowing for a quick and more efficient study. We will further investigate the long-term performance of the materials, aimed at selecting those showing the best performance in terms of durability and resistance to icing conditions.

4.3 Effects of curing treatment on the anti-icing properties of PDMS

As discussed in the previous paragraph, it is possible to modulate the properties of PDMS by varying the prepolymer/crosslinker ratio (A:B). However, it is important to consider that other parameters can also influence the final properties of the elastomer, such as temperature and curing time¹⁷⁹. Furthermore, durability is a crucial aspect in the design of anti-icing materials and can be affected by variations in the synthesis process. Most studies focus on optimizing only one of these experimental parameters^{180,181}, and investigations that address all these factors simultaneously are rare¹⁸², especially in the context of preparing ice phobic surfaces. Based on this, the aim of this section is to analyse how the experimental parameters adopted during the crosslinking process affect the behaviour and durability of PDMS as an anti-icing coating¹⁸³. While Sylgard186 performs better in all the cases studied so far, Sylgard184 was chosen for this study due to its higher workability, making the study more straightforward from an operational point of view. The 5:1, 10:1, 20:1, and 30:1 ratio were selected for their optimal balance between anti-icing properties and durability, while the 1:1 and 2:1 ratio were discarded due to the rapid degradation of the coatings. Up to nine different curing conditions were tested, varying the temperature from 25 °C to 200 °C and the curing time from 35 minutes to 48 hours. The starting point was the study of the effect of curing temperature on the properties of the 10:1 ratio (the standard ratio). The curing temperature and time (ttx) were varied from 25°C for 48 hours (tt1) to 100°C for 35 minutes (tt2, the same used in the previous paragraph, kept as reference) and finally 200°C for 18 minutes (tt9). The times were adjusted to each chosen temperature to ensure proper crosslinking of the material. Wettability measurements are presented in Fig. 63.

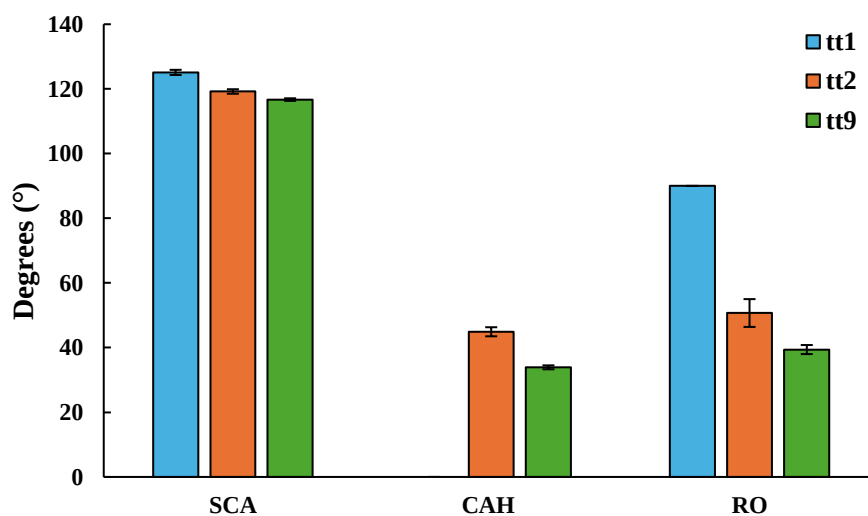


Fig. 63 Wettability measurements for Sylgard184 tt1, tt2 and tt9. No hysteresis (CAH) is present for Sylgard184 10:1 tt1. SCA = static contact angle, CAH = contact angle hysteresis, RO = roll-off angle

The increase in temperature from tt1 to tt9 slightly reduces the static contact angle (SCA), while a more significant decrease is observed for hysteresis (CAH) and roll-off angle (RO).

For tt1, RO is 90° and CAH is absent. It is unlikely that the temperature has altered the chemical composition of the surface; rather, it may have optimized the crosslinking phase and allowed the coating to achieve its final properties.

This hypothesis is confirmed by FTIR spectroscopy conducted on Sylgard184 10:1 tt1, tt2, and tt9 samples (Fig. A14) from which you can observe the characteristic peaks of PDMS. No abnormal peaks and signals related to Si-H were found in each spectrum.

Shore A hardness measurements and shear stress measurements were conducted, and the values shown in Fig. 64.

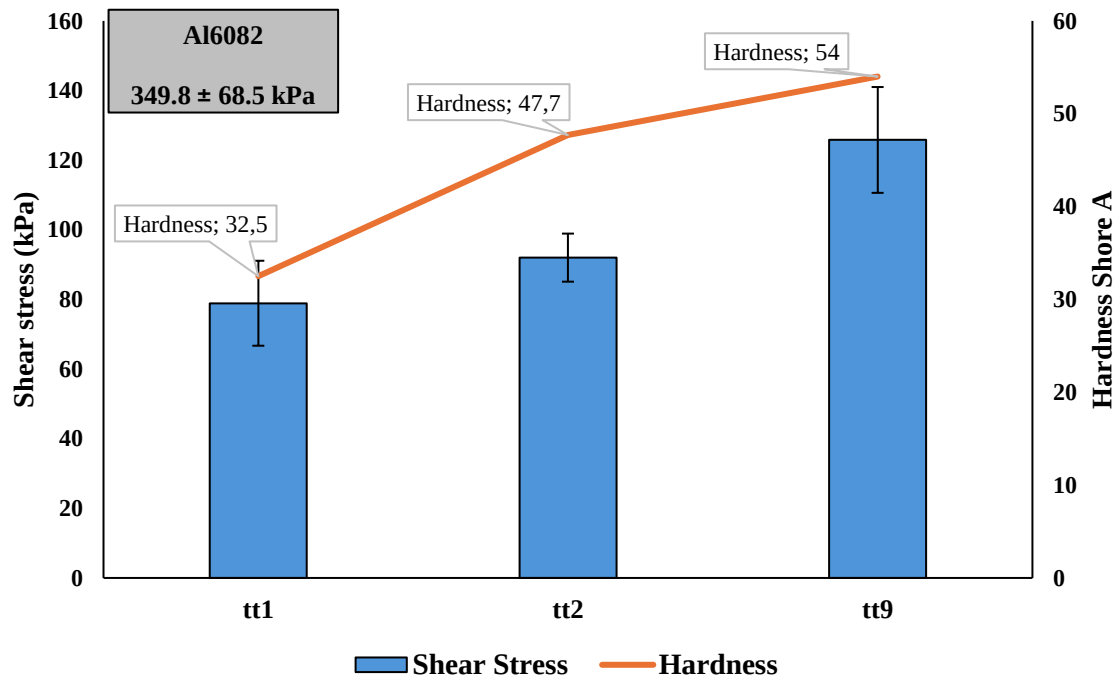


Fig. 64 Shear stress and hardness values for Sylgard 10:1 tt1, tt2 and tt9. Shear stress values: tt1 = 78.9 ± 12.2 kPa; tt2 = 92 ± 6.9 kPa; tt9 = 125.8 ± 15.2 kPa.

We observe the relationship between hardness data and shear stress values: the tt1 sample, despite having a hardness approximately 15 units lower than tt2, has a slightly lower shear stress value, although it remains within the standard deviation range. The tt9 sample, on the other hand, has a hardness approximately 6.5 units higher, but the shear stress value is much higher than that of the sample prepared at 100°C. We again consider the shear stress equation (6), where the thickness h is constant for each sample (we omitted that)

$$\sigma_s^* \sim W_a \mu \quad (6)$$

The work of adhesion (W_a) depends on the contributions of the surface energies: FTIR spectroscopy reveals no significant chemical differences between the thermal treatments studied, and the static contact angle (SCA) values are slightly different, but all oscillate around 120° (Fig. 63). Therefore, the contribution of work of adhesion (W_a) does not appear to be the main factor influencing anti-icing properties. Regarding contact angle hysteresis (CAH) and roll-off angle (RO) (Fig. 63), it is observed that the surface of the sample prepared with tt1 treatment shows higher surface friction compared to the surfaces of the tt2 and tt9 samples, like what was observed with the 20:1 and 30:1 ratio of Sylgard184 and Sylgard186 formulations (section 4.2). This suggests that the crosslinking phase is not fully completed for the tt1 sample, and that the coating may require more time to reach the final properties typical of Sylgard184 10:1 tt2. In contrast, the tt9 treatment shows lower hysteresis (CAH) and roll-off angle (RO) values (Fig. 63), indicating reduced surface friction. This suggests that the high temperature allowed the material to complete the crosslinking phase, achieving its final properties. Therefore, in the case of the tt1 sample, the contribution of hardness is not sufficient to counteract the effect of surface adhesiveness, preventing the expected shear stress values from being reached. In contrast, for the tt9 sample, the temperature ensures complete crosslinking, but at the same time increases the hardness, which in this case has a greater weight on the anti-icing properties than the reduction in surface friction. These results suggest that the tt2 treatment provides a good balance between hardness and surface adhesiveness.

However, this treatment might not allow the material to reach the desired final properties. Therefore, it was decided to extend the curing time while maintaining the temperature at 100°C to explore the effect of this variable on the final properties of the coatings. New thermal treatments were introduced, named tt3 (1h), tt4 (3h), tt5 (6h), tt6 (9h), tt7 (12h), and tt8 (24h). The study was also extended to the 5:1, 20:1, and 30:1 ratio. A summary of the thermal treatments (ttx) used is provided in Tab. 10.

Thermal treatment (ttx)	Temperature ($^\circ\text{C}$)	Time (h)
tt3	100	1
tt4	100	3
tt5	100	6
tt6	100	9
tt7	100	12
tt8	100	24

Tab. 10 The coatings were prepared using Sylgard184 and following the conditions reported, varying the ratio between 5:1, 10:1, 20:1 and 30:1 on Anticorodal 50mmx50mm surfaces, using thickness between 750-900 μm . No tt1 and tt9 were used for this purpose.

The wettability measurements were carried out on all ratios (A:B) prepared with the different heat treatments (ttx) and shown in Fig. 65.

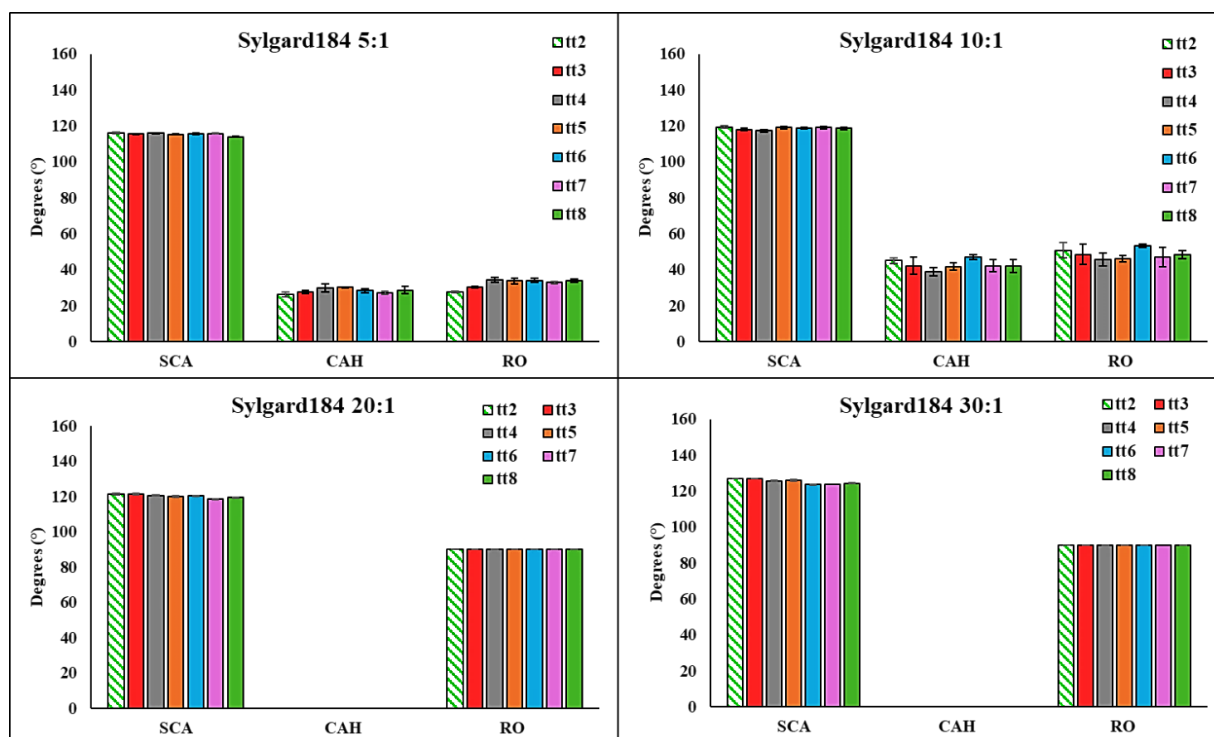


Fig. 65 Wettability measurement for Sylgard184 in ratio 5:1, 10:1, 20:1 and 30:1 prepared using different thermal treatments (ttx). Thermal treatment 2 (tt2, 100°C - 35min) is reported as comparison. SCA = static contact angle, CAH = contact angle hysteresis, RO = roll-off angle.

For each ratio, the variation in curing time from 1h (tt3) to 24h (tt8) does not lead to significant differences in static contact angle (SCA), hysteresis (CAH), and roll-off angle (RO) compared to tt2 (35min). Comparing the results across the different ratios confirms the findings of the previous section: for each ratio, SCA ranges from 115° to 125°, with the 5:1 ratio performing better in terms of CAH and RO compared to the 10:1, 20:1, and 30:1 ratio for each ttx. For the "high ratios" (20:1 and 30:1), it was expected that the extended treatment at 100°C could help reduce adhesiveness, but for each ttx, RO tends to 90° and CAH is absent.

The coatings were also analysed using FTIR spectroscopy to investigate any chemical changes at the surface level following the extension of the curing time. For each ratio and thermal treatment (ttx), the typical signals related to PDMS and already found in previous paragraphs are recognizable. For each individual ratio, the extension of curing time does not lead to significant chemical changes at the surface: for the 5:1 ratio, the Si-H stretching peak (2150 cm⁻¹), already found for tt2 (Fig. A15), is still visible after 24h (tt8) of treatment. For the 10:1 (Fig. A16), 20:1 (Fig. A17), and 30:1 (Fig. A18) ratios, no differences are observed between tt2 and tt8. This

confirms that extending the curing time does not cause significant changes to the material at the surface level.

Shore A hardness measurements were performed on samples prepared with different ratios and thermal treatments, with the results shown in Fig. 66.

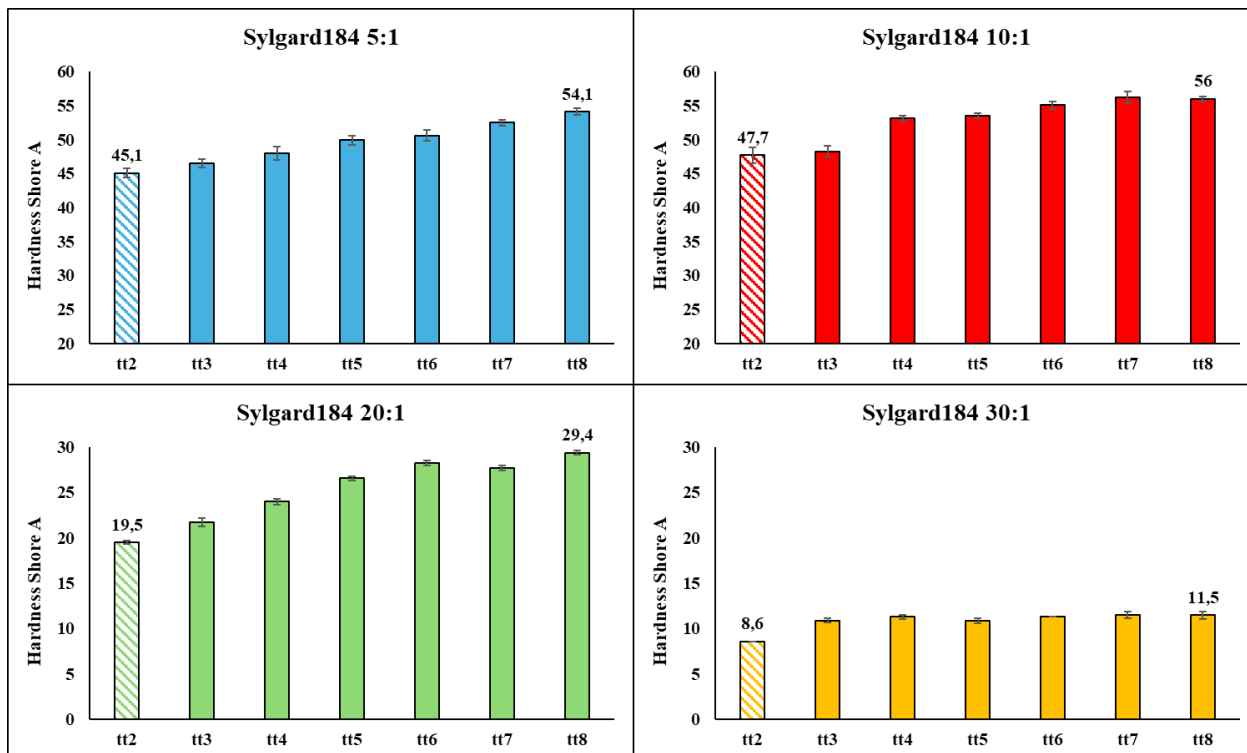


Fig. 66 Hardness measurements for Sylgard184 in different ratio and thermal treatment(tt_x). For each ratio, tt₂ hardness measurement is reported as comparison.

Hardness values are reported to facilitate the discussion. In general, for each ratio, increasing the treatment time up to 24h leads to an increase in hardness. For Sylgard184 samples at 5:1, 10:1, and 20:1 ratio, a hardness increase of about 10 units is observed from tt₂ to tt₈. The 10:1 ratio reaches a hardness value ($H_a = 56$) after 24h of treatment (tt₈), like the sample prepared with tt₉ ($H_a = 54$, Fig.77). The 30:1 ratio, however, shows the smallest increase, with only 3 units higher. We now look at how this reflects on the anti-icing properties of the coating. Shear stress measurements for all ratios prepared with the different ttx are shown in Fig. 67. In general, shear stress values follow the trend of hardness (Fig. 66), increasing as the curing time is extended from tt₂ to tt₈. For the 5:1 ratio, shear stress increases by about 20 kPa from tt₂ to tt₈, remaining within the standard deviation range. The 10:1 ratio shows the largest increase in shear stress from tt₂ (92.9 kPa) to tt₈ (129.4 kPa). This reflects the increase in hardness achieved by prolonging the curing time (Fig. 66). The 20:1 ratio experiences a significant increase in shear stress from tt₂ (69.9 kPa) to tt₈ (95 kPa). In this case, the combined effect of increased hardness and maintained surface adhesiveness, even after prolonged thermal treatment, results in a deterioration of the

anti-icing properties. The 30:1 ratio shows the smallest increase in shear stress from tt2 (51.6 kPa) to tt8 (67.5 kPa). Although it shows high surface friction, it maintains a low hardness value from tt2 (8.6) to tt8 (11.5), providing greater flexibility to the coating and better retention of anti-icing properties.

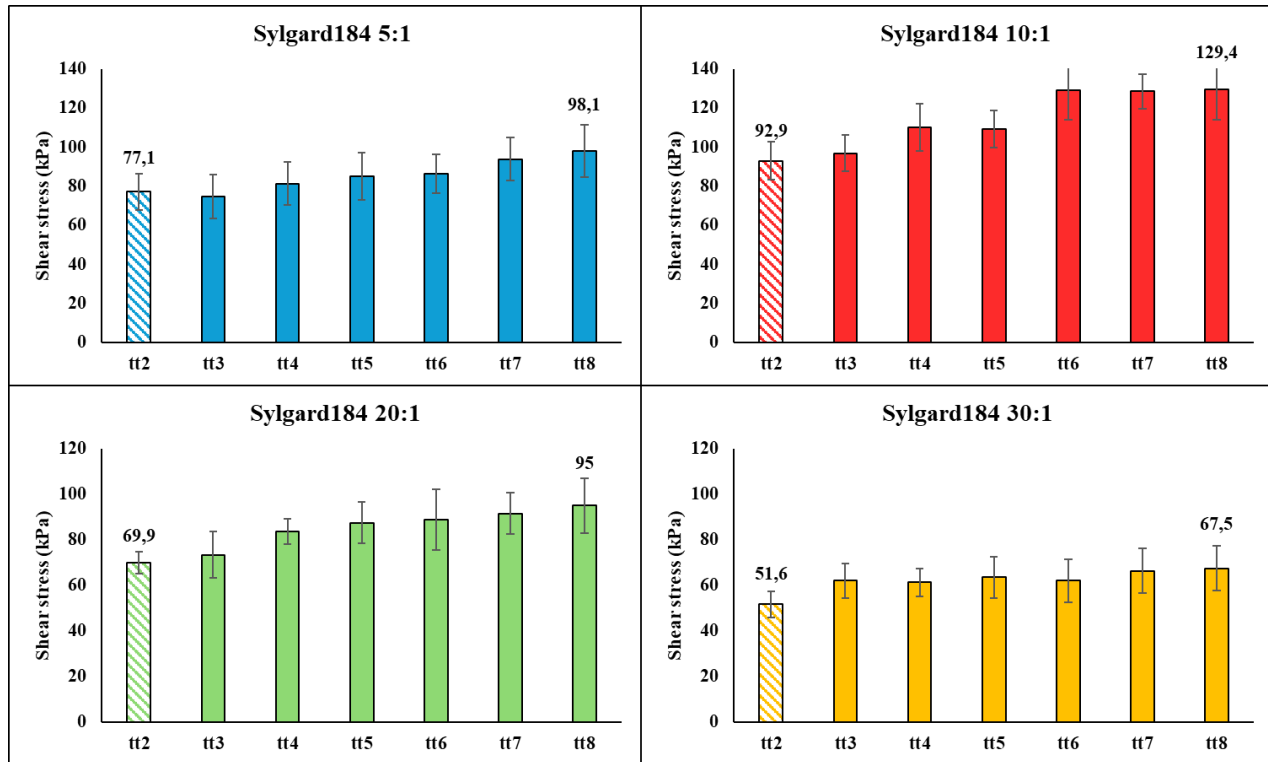


Fig. 67 Shear measurements for Sylgard184 in different ratio and different heat treatment. Al6082 reference shear stress value is 349.8 ± 68.5 kPa.

These results suggest that extending the curing time has a greater impact on the mechanical properties of the coatings than on their surface properties. The wettability of the coatings does not change with the extension of curing time to 24h (tt8), nor does the chemical composition at the surface level. The increase in shear stress from tt2 to tt8 is instead attributed to the increase in hardness, which proves to be a sensitive parameter to variations in the curing conditions. Surface friction also plays an important role in determining the anti-icing properties of the coatings. For high ratios Sylgard184 20:1 ttx and 30:1 ttx, high adhesiveness is attributed to an excess of prepolymer (part A) compared to crosslinker (part B). Despite the extended curing time, this adhesiveness cannot be significantly reduced. This aspect should be considered in the design of elastomeric anti-icing surfaces, as it does not depend on the surface energy of the chosen material but solely on the crosslinking stage.

We evaluated the effect of varying the curing time, extending it up to 24 hours, and observed that this results in changes in the properties, particularly in the mechanical characteristics of the

coatings. Once the curing process is complete, it is possible that the materials continue to age, further consolidating their properties until reaching their final characteristics. To examine this phenomenon, in the following section, the coatings were monitored over time for up to 60 days, and they were subjected to accelerated aging chamber treatments to simulate more prolonged aging. Throughout the process, wettability measurements, FTIR spectroscopy, hardness, and shear stress were performed, and the properties were compared to those of freshly crosslinked materials to assess whether further modifications occur or if the materials remain stable over time.

4.4 Effect of aging on the anti-icing properties of PDMS

Understanding the materials behaviour over time is crucial for determining its applicability in real-world scenarios. Indeed, for a material, it is important not only that it demonstrates good initial performance, but that it retains these properties over an extended period. The ability to mature and the durability over time are key factors in selecting materials for specific applications, as they must meet efficiency and longevity requirements, ensuring consistent protection over time. In this section, the effect of aging on the anti-icing properties and durability of Polydimethylsiloxane (PDMS) will be studied. The samples selected for this study were prepared as detailed in the experimental section, using the Sylgard184 formulation with ratios of 5:1, 10:1, 20:1, and 30:1, and crosslinked at 100°C, varying the curing time from 35 minutes (tt2) to 12 hours (tt7) (Tab. 11).

Thermal treatment (tx)	Temperature (°C)	Time (h)
tt2	100	0.6 (35min)
tt3	100	1
tt4	100	3
tt5	100	6
tt6	100	9
tt7	100	12

Tab. 11 The coatings were prepared following the conditions reported, varying the ratio between 5:1, 10:1, 20:1 and 30:1 on Anticorodal 50mmx50mm surfaces, using thickness between 750-900 µm.

The tt8 (24h) treatment was excluded to simplify the sample preparation phase and because, from an applicative standpoint, a 24-hour treatment is not easily feasible. However, the tt7 (12h) thermal treatment was retained to assess the effect of aging on long-term thermal treatments.

To understand how the material behaves over time, two different tests were used.

A group of samples for each selected ratio (A:B) and each thermal treatment (tx) was monitored from the initial point (0 days) for 60 days at room temperature (60gg.), during which measurements were made using IR spectroscopy, wettability, Shore A hardness, and shear stress. These samples were stored in a desiccator and protected from potential sources of contamination to carefully analyse how the material's properties evolve over time.

Another group of samples, prepared with the chosen ratios (A:B) and each thermal treatment (tx), was subjected to treatments in accelerated aging chambers (AC, see Experimental part for details) to simulate outdoor exposure conditions and reproduce a more prolonged and stressed aging. Briefly, this test consists of four different stages: Stage A lasts 24 hours and includes thermal cycling from -30°C to +80°C, Stage B lasts 71 hours and includes UV radiation exposure, while

Stages C and D last 23 hours each and include wide-spectrum lamp irradiation and demineralized water spraying. This test aims to replicate real environmental conditions and to simulate exposure conditions that may occur over a much longer period. After the test, measurements were made using IR spectroscopy, wettability, Shore A hardness, and shear stress, and the data were compared with those obtained at the initial point (0 days) and after the 60-day aging period (60gg).

The wettability measurements conducted on the samples prepared with different ratios (A:B) and varying crosslinking conditions (ttx) and for convenience and clarity, comparisons between the wettability measurements of the tt2 (35min) and tt7 (12h) treatments, measured at 0 days of aging (0gg), after 60 days of controlled aging (60gg), and after accelerated aging chamber (AC) exposure (Fig. 68), are shown.

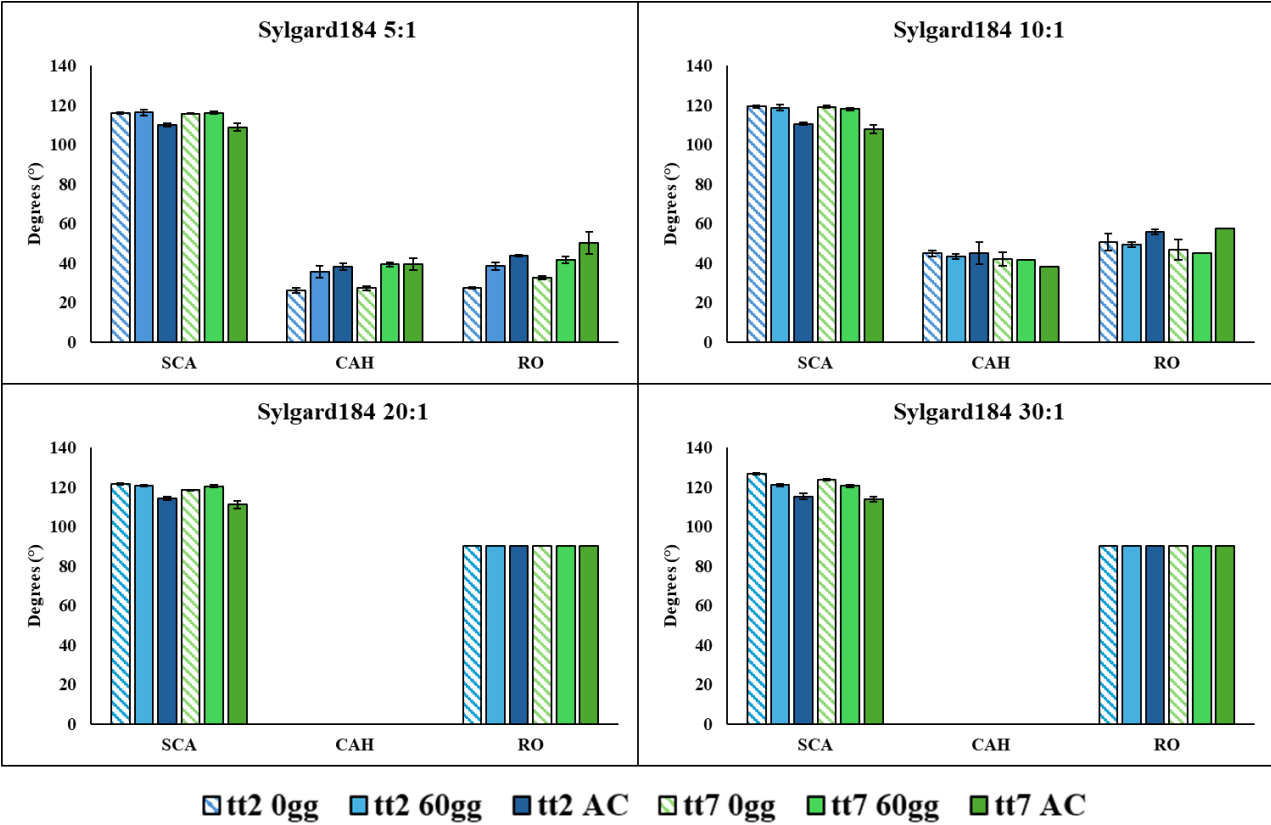


Fig. 68 Wettability measurements for Sylgard184 at different A:B ratios. For clarity, the comparison between the less intense treatment (tt2 0gg, 35min) and the more intense treatment (tt7 0gg, 12h), monitored over 60 days of aging (60gg) and after the accelerated aging (AC) is reported. SCA = static contact angle, CAH = contact angle hysteresis, RO = roll-off angle.

For the 5:1 ratio tt2 (35min), the aging after 60 days (60gg) and in the accelerated aging chamber (AC) does not result in substantial differences in terms of static contact angle (SCA), with values oscillating between 115° and 120°. The most noticeable changes are observed in the dynamic

properties, with an increase in hysteresis (CAH) and roll-off angle (RO). For the 5:1 ratio tt7 (12h), no significant changes in the SCA are observed after 60 days of aging (60gg) and in the AC, similarly to what is observed for the tt2 (35min) treatment, but in both cases, an increase in CAH and RO is observed after both aging tests (60gg and AC). For the 10:1 ratio tt2 (35min), there are no significant differences in terms of SCA after the two aging phases (60gg and AC), with stable values in the 115°–120° range. The CAH value remains unchanged after both aging tests (60gg and AC). A slight increase in the RO is observed after aging in the AC. For the 10:1 ratio tt7 (12h), the contact angle values are maintained after 60 days (60gg) of aging and after the AC, as well as the CAH value. Again, a slight increase in the RO is seen after aging in the AC. The 20:1 ratio tt2 (35min) and tt7 (12h) exhibit nearly identical behaviour, with the SCA maintained after 60gg of aging and a slight decrease after AC. CAH is absent, and the RO remains at 90° for both thermal treatments (tt2 and tt7) after both the 60gg aging and the AC tests. The 30:1 ratio prepared with the tt2 (35min) and tt7 (12h) treatments shows a slight decrease in the SCA below 120° from 60 days of aging (60gg) to AC exposure. The RO remains at 90° for both thermal treatments (tt2 and tt7) after both aging tests (60gg and AC). The surfaces of the coatings were investigated through IR spectroscopy. In each collected spectrum, the diagnostic PDMS signals can be identified. No unexpected signals appear after 60 days of aging (60gg) and after the accelerated aging chamber (AC) are observed. For each ratio, the spectrums are reported in Supporting materials (Fig. A19 - Fig. A26). The presence of water on the surface can compromise the wettability of the material, reducing the SCA and promoting the phenomenon of droplet pinning on the surface, thus increasing the RO and CAH. This justifies the slight and systematic deterioration in wettability of the coatings after the accelerated aging chamber test (AC) as observed in Fig. 68. Shore A hardness measurements were carried out on samples prepared with different ratios (A:B) and thermal treatments (ttx), and the results, compared at zero time (0gg), after 60 days (60gg), and after accelerated aging chamber (AC), are reported in Fig. 69

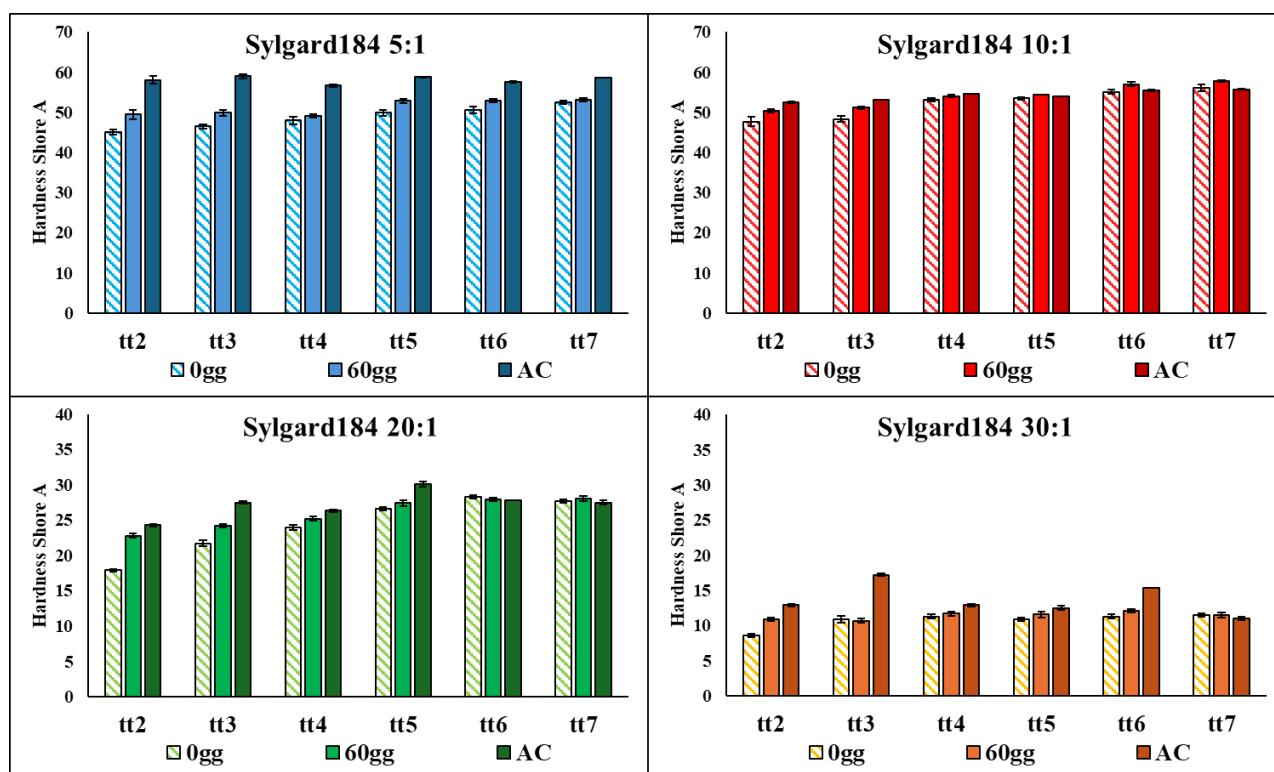


Fig. 69 Hardness Shore A measurements for Sylgard184 at different A:B ratios and thermal treatment (ttx). For each ttx, the comparison of hardness value at time zero (0gg), after 60 days of aging (60gg) and after accelerated aging (AC) is reported.

For Sylgard184 5:1, an increase in hardness is observed after 60 days of aging (60gg) for the thermal treatments tt2 (35min) and tt3 (1h). From treatment tt4 (3h) to tt7 (12h), no significant differences are observed between the hardness value at zero time (0gg) and after 60 days (60gg). The treatment in the accelerated aging chamber (AC) results in an increase in hardness for all treatments (ttx), which stabilizes around a value of 60. These results suggest that coatings prepared using the less intense thermal treatments (tt2 and tt3) mature over time, reaching a stable hardness value after 60 days of aging, like that observed for the other ratios. However, the accelerated aging test suggests that the materials, even after 60 days of aging still change.

For Sylgard184 10:1, the treatments tt2 and tt3 are the most sensitive to the aging phases, with their hardness values increasing after 60 days of aging (60gg) and after accelerated aging (AC). Hardness values remain stable from treatment tt4 (3h) to tt7 (12h) from zero time (0gg) and after both aging tests (60gg and AC). Again, coatings prepared using the less intense thermal treatments (tt2 and tt3) do not reach their final mechanical properties, but maturation over time is observed, with hardness values reaching those observed from treatment tt4 (3h) to tt7 (12h).

Sylgard184 20:1 shows a similar behaviour to the previous ratios, but in this case, the hardness value remains stable for the more intense treatments tt6 (9h) and tt7 (12h) from zero time (0gg) to 60 days (60gg) and after accelerated aging (AC). For the remaining thermal treatments (from

tt2 to tt5), the hardness value increases after 60 days of aging (60gg) and after accelerated aging (AC).

For Sylgard184 30:1, only the thermal treatment tt2 shows maturation, with an increase in hardness after 60 days (60gg) and after accelerated aging. For the other treatments (from tt3 to tt7), the hardness value remains constant, although two anomalous values are observed at tt3 and tt6. The 30:1 ratio seems to consolidate and better maintain mechanical properties, keeping a relatively low hardness value. Shear stress measurements were conducted on the samples with different ratios (A:B) and thermal treatments (ttx), compared at zero time (0gg) and after the aging tests (60gg and AC), and are shown in Fig. 70.

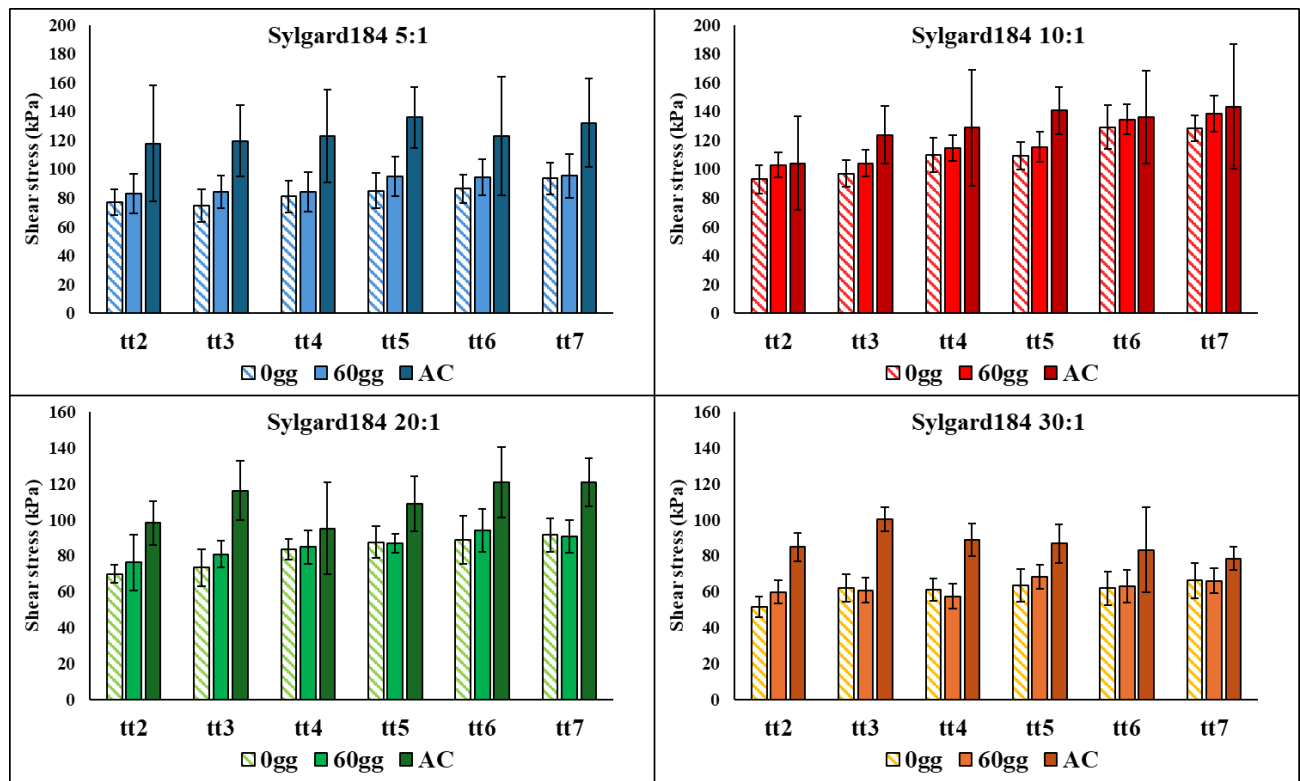


Fig. 70 Shear stress measurements for Sylgard184 at different A:B ratios and thermal treatment (ttx). For each ttx, the comparison of shear stress value at time zero (0gg), after 60 days of aging (60gg) and after accelerated aging (AC) is reported. Al6082 reference shear stress value is 349.8 ± 68.5 kPa.

For Sylgard184 5:1, the shear stress values for all thermal treatments (ttx) at time 0 (0gg) and after 60 days of aging (60gg) are similar, oscillating around 80 kPa, while after accelerated aging (AC), the shear stress values increase significantly, reflecting the trend of hardness observed in Fig.

69.

For Sylgard184 10:1, the shear stress values for all thermal treatments (ttx) are similar at time 0 (0gg) and after 60 days of ambient aging (60gg). After accelerated aging (AC), the shear stress

values do not follow a precise trend and do not align with the trend of the hardness values observed previously in Fig. 69.

For Sylgard184 20:1, the shear stress values between 0 days (0gg) and 60 days (60gg) show a slight increase for tt2 and tt3 and remain stable for the remaining thermal treatments (from tt4 to tt7). After accelerated aging (AC), the shear stress values rise, approaching 120 kPa for tt3 (1h), tt6 (9h), and tt7 (12h). Clearly, these values do not reflect what was observed when analysing the hardness values in Fig. 69.

For Sylgard184 30:1 tt2, the shear stress value shows a slight increase from time 0 (0gg) to 60 days of aging (60gg), while for the remaining thermal treatments, the value remains stable, following the trend of the hardness observed in Fig. 69. After accelerated aging (AC), the shear stress values increase and stabilize around 80 kPa for nearly all thermal treatments (ttx), except for tt3, which shows the greatest increase in shear stress, reaching close to 100 kPa.

In all cases, for each ratio (A:B) and thermal treatment (ttx), the shear stress values at time 0 (0gg) and after 60 days (60gg) remain stable, or for the less intensive treatments (tt2 and tt3), they show a slight increase, in line with the trend of hardness. After accelerated aging (AC), the shear stress values do not follow a clear and comparable trend with the hardness and generally undergo a significant increase. This can be explained by the fact that samples subjected to the stress of accelerated aging show traces of water on the surface, which may contribute to deteriorating the coating's properties by promoting greater ice adhesion on the surface.

For each A:B ratio of the Sylgard184 formulation, the samples that performed best were selected, considering the trade-off between the duration of the thermal treatment, maturation, and the variation of the anti-icing properties of the coatings over time. For the 5:1, 10:1, and 20:1 ratio, the tt2 treatments were selected, while for the 30:1 ratio, the tt3 treatment was chosen (Tab. 12).

Ratio (A:B)	Thermal treatment (ttx)	Temperature (°C)	Time	Shear stress (kPa)	ARF
5:1	tt2	100	35min	77.1 ± 9.2	4.5
10:1	tt2	100	35min	92.9 ± 9.7	3.8
20:1	tt2	100	35min	69.9 ± 4.9	5
30:1	tt3	100	1h	60.3 ± 5.8	6

Tab. 12 Selected sample for each A:B ratio

The shorter-duration thermal treatments (tt2 and tt3) show a slight variation in anti-icing properties after 60 days of aging for all A:B ratios. However, despite this initial variation, these treatments achieve, over time (60 days), the shear stress values obtained with the longer-duration treatments. Therefore, considering the trade-off between thermal treatment duration, maturation, and the variation of properties over time, these treatments ultimately prove to be the most effective in ensuring the best anti-icing properties. Among them, the sample that performs best is Sylgard184 30:1 tt3, which exhibits a shear stress value approximately 6 times lower than the untreated Anticorodal substrate.

5. Test in Artificial Snow Laboratory

PDMS has proven to be a particularly suitable material to reduce ice adhesion on surfaces however the performance evaluation presented so far presents some limitations, related to various aspects.

The first limitation is associated with the complexity of the atmospheric icing phenomenon, which, as illustrated in Chapter 2, can manifest through different types of ice growth depending on meteorological conditions, and in particular, the way in which water or ice particles impact the surfaces. In the laboratory, anti-icing measurements are performed by simulating the formation of ice on the coatings using moulds, leading to the generation of a type of ice closely resembling "glaze ice" (see Experimental section). However, in Italy, atmospheric icing phenomena are primarily related to snow accumulation, in particular "wet snow," making it crucial to study the response of materials to this type of growth.

Another limitation concerns the substrate as materials are usually tested on flat surfaces, while on electrical lines, ice and snow accumulation occurs through the formation of sleeves on conductors and/or guard wires.

To fully understand how coatings react to "wet snow" on conductors and guard wires, it is thus necessary to develop methods that allow for the direct simulation of snow formation on the material surfaces¹¹.

In 2022, the new "Artificial Snow Laboratory" (LNA, Fig. 71left) was inaugurated at the Piacenza headquarters of RSE s.p.a., an advanced facility designed to simulate snowfall conditions in controlled environments. This laboratory allows for the recreation of snowfall phenomena by precisely adjusting parameters such as temperature, humidity, wind speed, and liquid water content (LWC), thereby creating ideal conditions for testing materials in realistic environmental scenario. The primary application of the LNA is the evaluation of the anti-snow properties of the developed coatings, which are applied to segments of conductor cables and guard wires. These samples are exposed to snow flows within a refrigerated chamber, which allows for the replication of natural snow accumulation conditions on the materials^{18,184} (Fig. 71right)



Fig. 71 Artificial snow laboratory located at RSE in Piacenza (Italy)

The laboratory is set up in a container approximately 12 meters in length, equipped with a refrigerated area of about 10 m², dedicated to snow production. Snow is generated by an innovative machine, positioned at a height of approximately 1.8 meters, consisting of a steel drum whose temperature can reach -10 °C. The water is pre-chilled and collected in a reservoir, which is then conveyed onto the surface of the drum during its rotation. In this way, the water solidifies, crystallizing into snowflakes, which, upon encountering a metal comb positioned at the bottom of the drum, detach and begin to fall to the ground.

Snow is created by controlling parameters such as temperature, humidity and fan speed that can be set from the machine's controls. By optimizing these parameters, it is possible to control the liquid water content (LWC) and snow density, crucial factors for the adhesion of snow to sample surfaces.

The chamber is also equipped with four fans that allow the adjustment of the airflow entering the chamber, simulating wind effects and helping maintain a uniform temperature in the environment. This machine is mounted on a track fixed to the ceiling of the refrigerated chamber, enabling forward and backward movement to uniformly snow the area below.

For conducting snowing tests on the components of electrical lines, segments of conductor cables and ground wires, approximately 80 cm in length, are mounted on special supports. These supports are equipped with motors that allow the rotation of the segments, simulating the movements responsible for snow sleeves formation. In the experimental area, up to three samples can be housed simultaneously, one of which serves as a reference, made of uncoated aluminium alloy. The anti-snow performance of the samples is evaluated by comparing the results obtained with those of the reference sample. To monitor the stages of formation, growth, and detachment of the snow sleeve, the supports are equipped with load cells, which measure the mass of snow

deposited in real time. The process is further monitored through a high-definition camera, which allows for the collection of precise visual data.

The specifications related to snow production and LWC measurements are presented in detail in the Experimental section.

The implementation of this experimental equipment has enabled a controlled snow testing on coatings, replicating scenarios typically occurring in outdoor environments and only during specific periods of the year¹⁸. This allows for a more realistic evaluation of material performance, useful for simulating exposure conditions to which they might be subjected in real-world applications. To evaluate the anti-snow properties of the elastomeric coatings, the Sylgard184 formulation was selected, and the 10:1 tt2 and 30:1 tt3 samples were chosen for testing. The polymer was applied to a 750 mm-long aluminium alloy conductor cable segment, which had been previously sandblasted and cleaned, as described in the Experimental section.

For the test, three types of snow with different LWC were produced: G0 (LWC <5%), G15 (LWC between 10% and 20%), and G35 (LWC between 30% and 40%), to simulate three different snowing scenarios with a dry, a semi-wet and a wet snow, respectively.

Under the three different snowfall conditions, the formation of snow sleeves around the segments is obtained, as depicted in Fig. 72.

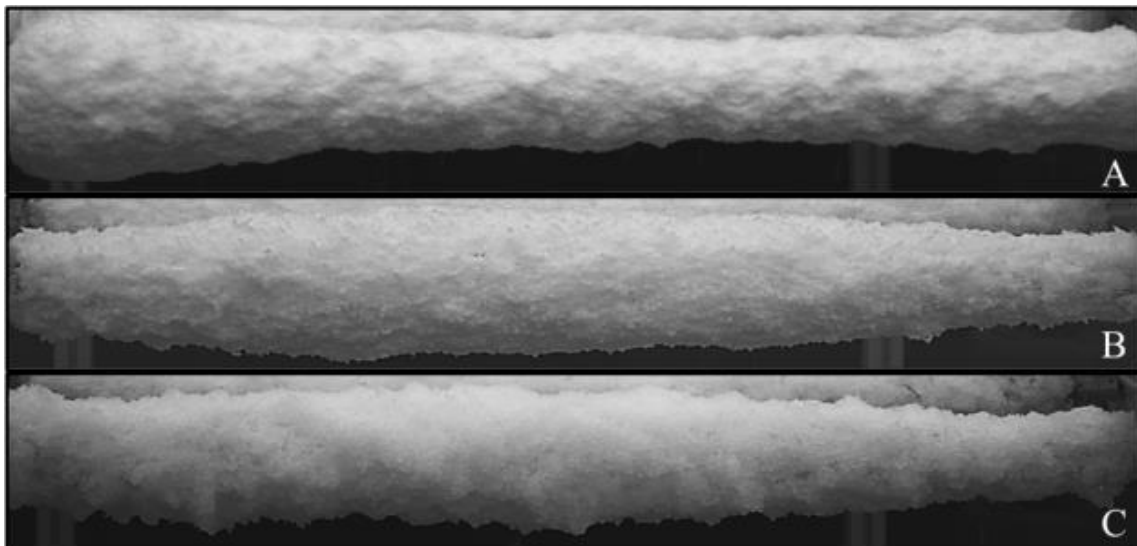


Fig. 72 Camera images of snow sleeves on segments under G0 (A), G15 (B), G35 (C) snowfall scenarios.

The tests were conducted over 6h, monitoring the snow mass accumulated on the tested samples. To numerically quantify the anti-snow properties, several parameters can be used to describe the experimental results, such as:

- Average mass of snow accumulated on the cable segment during testing period (Avg. mass).
- Maximum mass of snow accumulated on the cable segment (Max mass).
- Number of detachments during the test. A detachment is classified as either total, when the snow sleeve completely falls (i.e., its mass is reduced to zero), or partial, when its mass decreases by at least 50% of its initial value but does not reach complete detachment. The total number of detachments reported includes both total and partial detachments without distinction.

Moreover, similarly to what was done for ice adhesion measurements through the calculation of shear stress, important information can be obtained by calculating the Snow Reduction Factor (SRF) as the ratio between the mass of snow accumulated on the reference (m_{ref}) and that present on the coated sample (m_{sam}). Two different SRF can be defined:

$$SRF_{avg} = \text{Avg. mass}_{sam} / \text{Avg. mass}_{ref}$$

$$SRF_{max} = \text{Max. mass}_{sam} / \text{Max. mass}_{ref}$$

The first type, referred to as the average SRF (SRF_{avg}), is calculated at specific time intervals. In this test, measurements are taken every hour starting from time zero. The second type, referred to as the maximum SRF (SRF_{max}), is determined by considering the highest snow load recorded on both the reference and coated sample during the test.

5.1 Test with dry snow

The first test was carried out under "dry snow" (G0, LWC <5%) and the results are shown in Fig. 73.

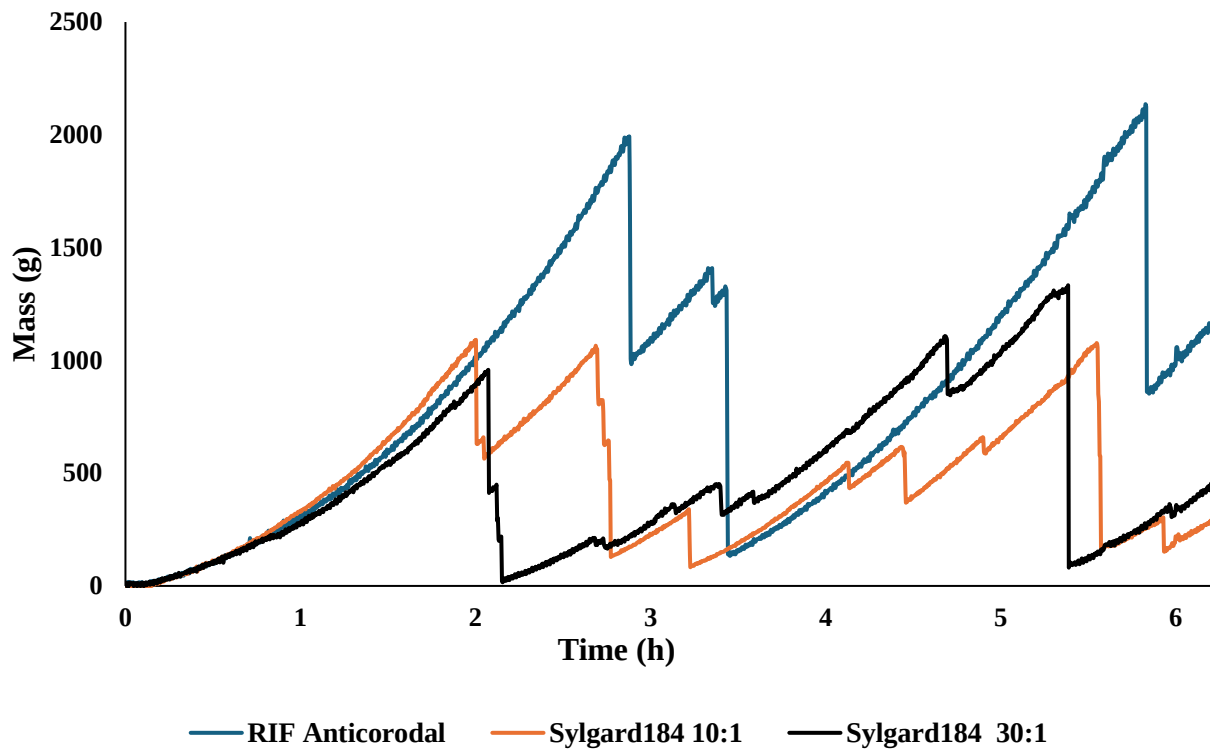


Fig. 73 Graph of dry snow sleeve mass increasing as a function of time. The test takes 21600 s (6h). In blue the uncoated reference in orange Sylgard184 10:1 tt3 and in black Sylgard184 30:1 tt3.

The graph shows that for both Sylgard184 10:1 and 30:1 tt3 samples, as well as the uncoated reference (RIF Anticorodal), the growth of the snow sleeve follows the same trend from time zero (0 h) until $t \sim 2$ h, where the first detachment of the sleeve can be observed for both elastomeric samples. The accumulated snow mass for Sylgard184 10:1 tt3 is 1074 g (~ 1 kg), while for Sylgard184 30:1 tt3 it is 946 g (~ 0.9 kg). Specifically, observing the behaviour of Sylgard184 10:1 tt3 (Orange line in Fig.73), it can be noted that the sleeve does not detach completely; instead, the mass decreases to 400 g and then grows again to approximately 1000 g ($t \sim 2$ h and 40min) before completely detaching from the cable.

For the uncoated cable segment (RIF Anticorodal), the sleeve continues to grow until $t \sim 3$ h, reaching a mass of 1962 g (~ 2 kg). Following a partial detachment, the mass drops to approximately 1 kg, then increases again to 1388 g (~ 1.4 kg) before completely detaching around $t \sim 3$ h and 20min. During the remaining 3h of the test, the formation of a new snow sleeve can be observed for both elastomeric samples and the reference. This time, the growth patterns diverge,

and a "sawtooth" trend is evident for the elastomeric samples, caused by small detachments of snow from the surface during the sleeve formation. For Sylgard184 30:1 tt3, the second sleeve detaches around $t \sim 5\text{h}$ and 20min with a load of 1319 g (~ 1.3 kg), while for Sylgard184 10:1 tt3, the second sleeve detaches slightly later around $t \sim 5\text{h}$ and 30min with a lower load of 1067 g (~ 1 kg).

On the Al6082 substrate, the growth of the second sleeve continues until $\sim 5\text{h}$ and 50min, reaching a mass of 2124 g (~ 2 kg) before detaching.

Through the snow laboratory and this test, it is possible to investigate the mechanism by which snow accumulation is mitigated. Observing the slope of the plotted lines, it becomes evident that the growth trend is initially like the reference during the early stages of the test. However, subsequent detachments are observed, confirming, that the mechanism relies on early detachments of the accumulated layers rather than delaying the formation of the initial layer.

As described in Chapter 3, these coatings are designed to reduce the adhesion of ice and snow to surfaces. In the specific case of power lines, their purpose is to facilitate the detachment of the snow sleeve, preventing its further growth or prolonged adhesion to the surface.

Since the first snow sleeve initially grows with the same trend on all three cable segments until the moment of detachment, measuring its mass at predefined time intervals does not allow a full understanding of the anti-snow performance of the coatings. These materials mainly act by anticipating the detachment of the sleeve under the effect of its own weight, rather than delaying its formation.

A useful parameter to represent the anti-snow behaviour of the tested elastomeric coatings is the temporal difference (Δt_{det}) between the moment of total sleeve detachment from the surface of the treated material and that of the reference (RIF Anticorodal). For both elastomeric coatings, the first sleeve completely detaches approximately 50 minutes earlier than on the untreated cable, while for the second sleeve, the total detachment occurs about 30 minutes earlier for Sylgard184 30:1 tt3 and about 15 minutes earlier for Sylgard184 10:1 tt3.

For Sylgard184 10:1 and 30:1 tt3 elastomeric coatings, SRF average values are respectively 1.7 and 1.5, indicating that the average mass of snow deposited on the coated samples during tests is almost half of that deposited on the reference.

In summary, the two tested coatings do not show significant differences in anti-snow properties (dry snow). Both can anticipate the detachment of the snow sleeve by up to 50 minutes compared to the reference sample, while simultaneously reducing the sleeve mass by approximately 50%.

The parameters necessary to describe the anti-snow performance of the coatings are reported in Tab. 13.

Samples	Avg. mass (g)	SRF _{avg}	Max mass (g)	SRF _{max}	Detachments	Δt_{det} first sleeve (s)	Δt_{det} second sleeve (s)
Sylgard184 10:1 tt3	479 ± 332	1.7	1074	1.9	3	3098 (51 min)	1000 (16 min)
Sylgard184 30:1 tt3	549 ± 392	1.5	1319	1.6	2	2858 (47 min)	1620 (27 min)
RIF Anticorodal	820 ± 374	-	2124	-	3	-	-

Tab. 13 Numerical parameters for describing the behaviour of selected samples toward dry snow. “Detachments” refers to both total and partial snow sleeve drops. “ Δt_{det} ” is calculated considering only total snow sleeve detachments.

5.2 Test with semi-wet snow

The second test was carried out under "semi-wet snow" (G15, LWC between 10% and 20%) and the results are shown in Fig. 74.

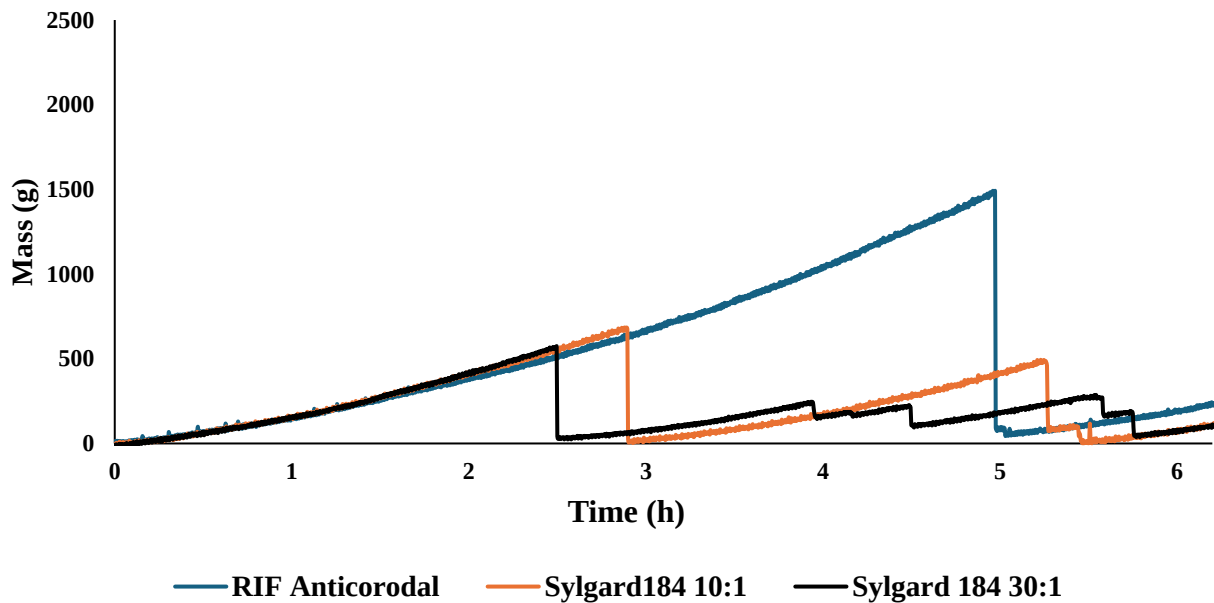


Fig. 74 Graph of semi-wet snow sleeve mass increasing as a function of time. The test takes 21600 s (6h). In blue the reference (RIF Anticorodal) in orange Sylgard184 10:1 tt3 and in black Sylgard184 30:1 tt3.

The growth rate of the semi-wet snow sleeves is almost identical for the Sylgard184 10:1 tt3, 30:1 tt3 samples, and for the reference, until the detachment. For Sylgard184 30:1 tt3, the detachment of the snow sleeve occurs at $t \sim 2\text{h } 30\text{min}$ with a mass of 567 g ($\sim 0.6\text{ kg}$). For Sylgard184 10:1, the detachment occurs at $t \sim 3\text{h}$ with a mass of 675 g ($\sim 0.7\text{ kg}$). For the reference detachment occurs at $t \sim 5\text{h}$ with a mass of 1472 g ($\sim 1.5\text{ kg}$). Following the detachment of the first sleeve, only Sylgard184 10:1 tt3 shows the formation of a second sleeve, which detaches at $t \sim 5\text{h } 20\text{min}$ with a mass of 460 g ($\sim 0.5\text{ kg}$). For Sylgard184 30:1, after the detachment of the first sleeve, a "sawtooth" pattern is observed, but it does not lead to the formation of a fully developed sleeve. However, we can consider a detachment occurring almost at the end of the test by observing the 'step' pattern between 5h and 6h. The Sylgard184 10:1 and 30:1 tt3 elastomeric coatings again exhibit similar anti-snow behaviour against hybrid snow with an earlier total sleeve detachment around 2h and 2h 30min respect to the reference. The SRF value is around 2.0 for both elastomeric coatings tested. The parameters describing the anti-snow performance of the coatings are reported in Tab. 14

Samples	Avg. mass (g)	SRF _{avg}	Max mass (g)	SRF _{max}	Detachments	Δt_{det} first sleeve (s)	Δt_{det} second sleeve (s)
Sylgard184 10:1 tt3	202 ± 165	2.0	675	2.2	2	7450 (2h)	-
Sylgard184 30:1 tt3	177 ± 123	2.3	567	2.6	2	8915 (2h 30 min)	-
RIF Anticorodal	413 ± 364	-	1472	-	1	-	-

Tab. 14 Numerical parameters describing the behaviour of selected samples in relation to hybrid snow. 'Detachments' refers to both total and partial snow sleeve drops. ' Δt_{det} ' is calculated considering only total snow sleeve detachments. In this case, Δt_{det} for the second sleeve cannot be calculated because no second detachment occurs for RIF Anticorodal during the test.

5.3 Test with wet snow

The third test was conducted by creating "wet snow" (G35, LWC between 30% and 40%) and the results are shown in Fig. 75. The growth-rate of the wet snow sleeve follows the same trend for the Sylgard184 10:1 tt3, 30:1 tt3 samples and the uncoated reference. In this case during 6h of monitoring it is possible to see the release of the snow sleeve only for Sylgard184 30:1 tt3 after 21009 s (~ 5h 50min) with a mass of 2703 g (~ 2.7 kg). The sleeve does not come off completely while maintaining a load on the conductor cable section with a mass of 1023 g (~1kg). For Sylgard184 10:1 tt3 and the reference (REF Anticorodal) the sleeve continues to grow without ever detaching throughout the test, reaching a mass of more than 3kg. It is not possible in this case to analyze the parameters that describe the anti-snow behaviour and make a comparison, since the detachment of the snow sleeve from the reference does not take place.

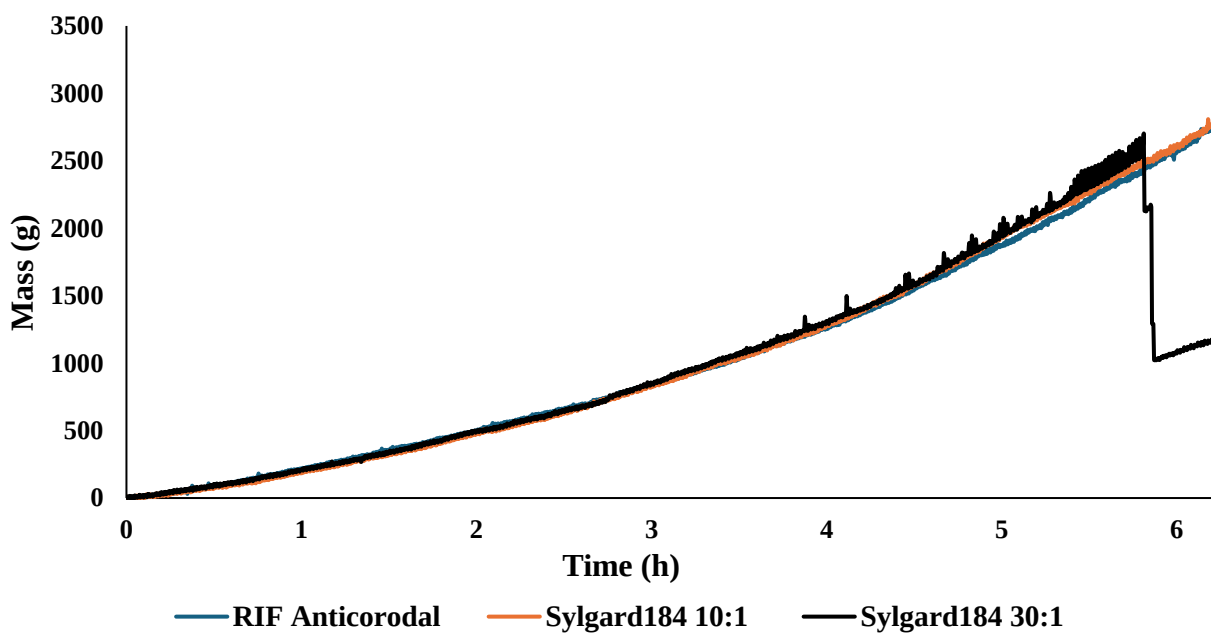


Fig. 75 Graph of wet snow sleeve mass increasing as a function of time. The test takes 21600 s (6h). In blue the reference (RIF Anticorodal), in orange Sylgard184 10:1 tt3 and in black Sylgard184 30:1 tt3.

In general, the selected Sylgard184 30:1 sample and 10:1 sample perform well against dry snow and hybrid snow, without showing big differences in terms of SRF. However, they do not show excellent properties versus wet snow protection since only the 30:1 tt3 sample shows wet snow sleeve release, although it cannot completely remove the load from its surface.

6. Composite materials for anti-icing applications

During the study on PDMS presented in Chapter 4, it was observed that surface friction plays a critical role in influencing the shear stress value, potentially limiting the anti-icing performance of the coatings. Reducing or eliminating surface adhesiveness may therefore enhance the detachment mechanism and improve overall performance.

For the Sylgard184 formulation, the 30:1 tt3 sample demonstrated the highest performance. Despite its low hardness value, which ensures high structural reversibility, the shear stress remains high and comparable to coatings with significantly greater hardness. This suggests that surface friction may counteract the expected benefits of high elasticity in facilitating ice detachment.

The following chapters will investigate potential strategies to mitigate surface friction and determine its true impact on the anti-icing performance of these materials.

6.1 Polydimethylsiloxane slippery

The aim of this study was to create a slippery and self-healing surface based on PDMS, inspired by the concept of SLIPS surfaces. The idea was to exploit the elastic properties of siloxane rubber, enhancing them by developing a coating capable of further reducing surface friction and facilitating ice detachment. The use of liquid fillers, such as silicone oils, to improve the mechanical properties of PDMS and mitigate surface friction is well known¹⁸⁵. However, traditional slippery surfaces suffer from limited lubricant stability, as the lubricant can be easily removed due to mechanical stress or surface contamination caused by external agents. To overcome these limitations, a Phase-Transition SLIPS (PTSLIPS)¹⁶² was developed. This slippery coating uses a solid lubricant at the typical temperatures of icing phenomena. This approach ensures better lubricant anchoring and greater durability over time. An additional advantage of this strategy is the combination of PDMS biocompatibility with the possibility of using natural oils that are cost-effective and environmentally friendly. In this context, peanut oil was chosen as the lubricant due to its melting temperature of +3°C, which makes it ideal for anti-icing applications requiring low operating temperatures. Peanut oil was incorporated into the Sylgard184 30:1 tt3 matrix, the coating that demonstrated the best performance during the study of curing conditions. The objective was to improve the coating's properties by creating a slippery layer that significantly reduces surface friction and optimizes its anti-icing capabilities.

The study began by creating samples using Sylgard184 with A:B:oil ratios: 30:1:6 (Fig. 76) on Al6082 50x50mm plates using tape casting method and curing them in oven at 100°C for 1h. Further characterizations were conducted to analyse the effect of the lubricant on the surface and how it influences anti-icing properties. Specifically, periodic measurements of shear stress, wettability, Hardness Shore A, and infrared (IR) spectroscopy were performed. The measurements were collected at regular intervals, every 24 hours, starting from preparation (0h) up to one week (168h, 7 days), to track the evolution of the coating's surface and mechanical properties. The static contact angle (SCA), hysteresis (CAH), and roll-off (RO) measurements are presented in Fig. 77.

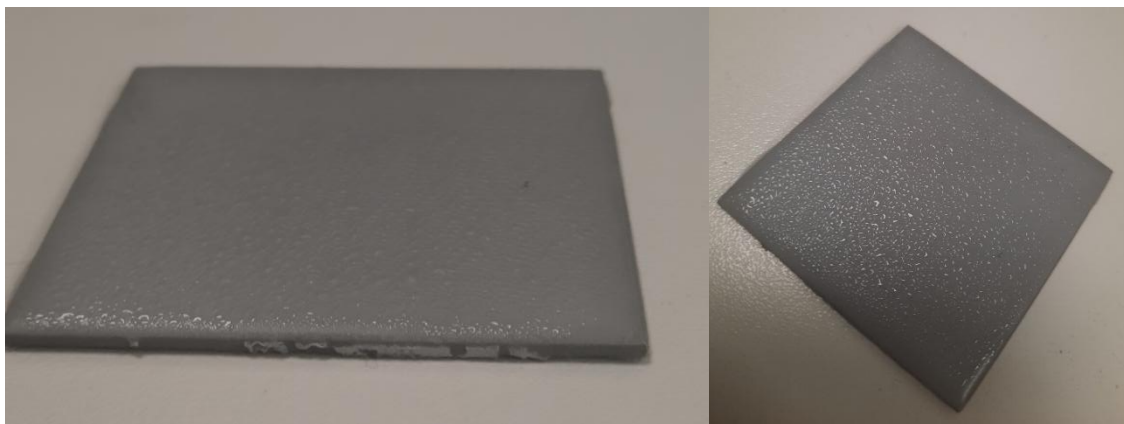


Fig. 76 Sample prepared with Sylgard184 and peanut oil in a ratio of 30:1:6 cross-linked at 100°C for 1h (tt3) and left to mature for 7 days. You can observe the presence of oil on the surface

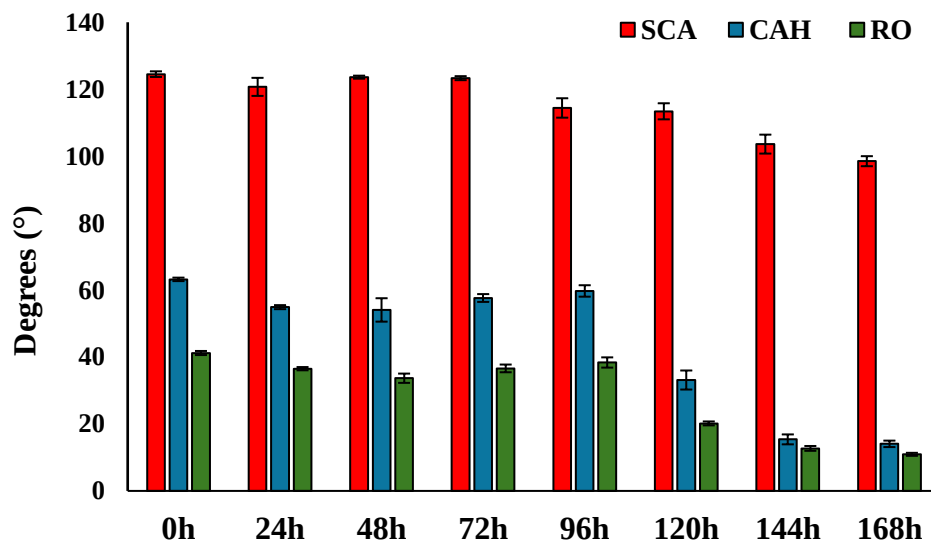


Fig. 77 Monitoring of sample surface wettability 30:1:6 in the time from moment zero (0h) to 7 days (168h). Advancing in days, the dynamic properties improve significantly demonstrating the presence of the oil layer.

At the end of the curing process (0h), the coating already exhibits improved dynamic wettability properties, with a RO around 40° and a CAH slightly above 60°. The SCA remains high, around 120°. In general, these values remain stable over time up to 72h, suggesting that a lubricant layer with a pronounced surface effect has not yet formed, although the properties are significantly better than those of Sylgard184 30:1 tt3.

After 96h (4 days), the CAH and RO values show a marked drop, with RO decreasing to around 20° and CAH reducing by another 20°. At 168h (7 days), further reductions in SCA, RO, and CAH values can be observed. This demonstrates that the oil requires time to migrate and stabilize on the surface, but its effect as a lubricant layer becomes evident after 96h.

The Shore A hardness measurements are shown in Fig. 78. The addition of oil acts as a liquid filler, softening the polymer and reducing its hardness below the value observed for 30:1 tt3. From the initial time point (0 days), the hardness remains stable over the 168h (7 days) period, suggesting that, despite the migration of oil to the surface, the high amount present remains stable within the matrix and is released gradually over time.

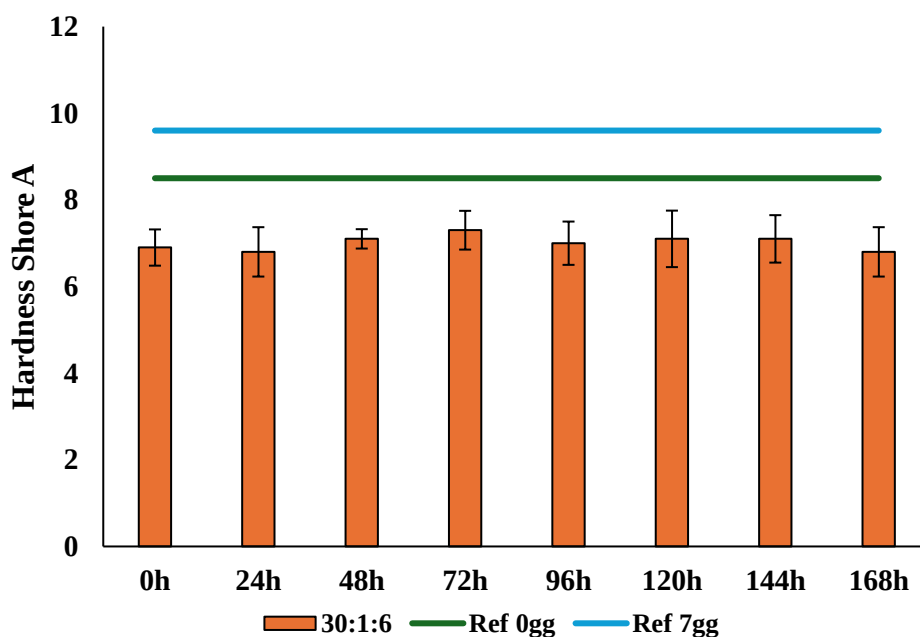


Fig. 78 Hardness Shore A measurements of 30:1:6 sample, compared to 30:1 tt3 0gg (green line, no aged) and 30:1 tt3 7gg (blue line, 7 days aged).

Fig. 79 shows the comparison between the IR spectra of Sylgard184 30:1 tt3 and the sample prepared by adding the oil in a ratio of 30:1:6 at time zero (0h) and after one week (168h). It is possible to recognize the diagnostic peaks of the PDMS for all the compared spectra. Observing the sample at time zero (0h) it is possible to note the presence of a low intensity peak at 1750 cm⁻¹.

¹ related to the stretching of the C=O bond characteristic of fatty acids. It increases in intensity over time up to 168h, where the peak is clearly visible. C-H stretching signals of asymmetric aliphatic bonds at 2921 cm⁻¹ and symmetrical at 2855 cm⁻¹ can be observed.

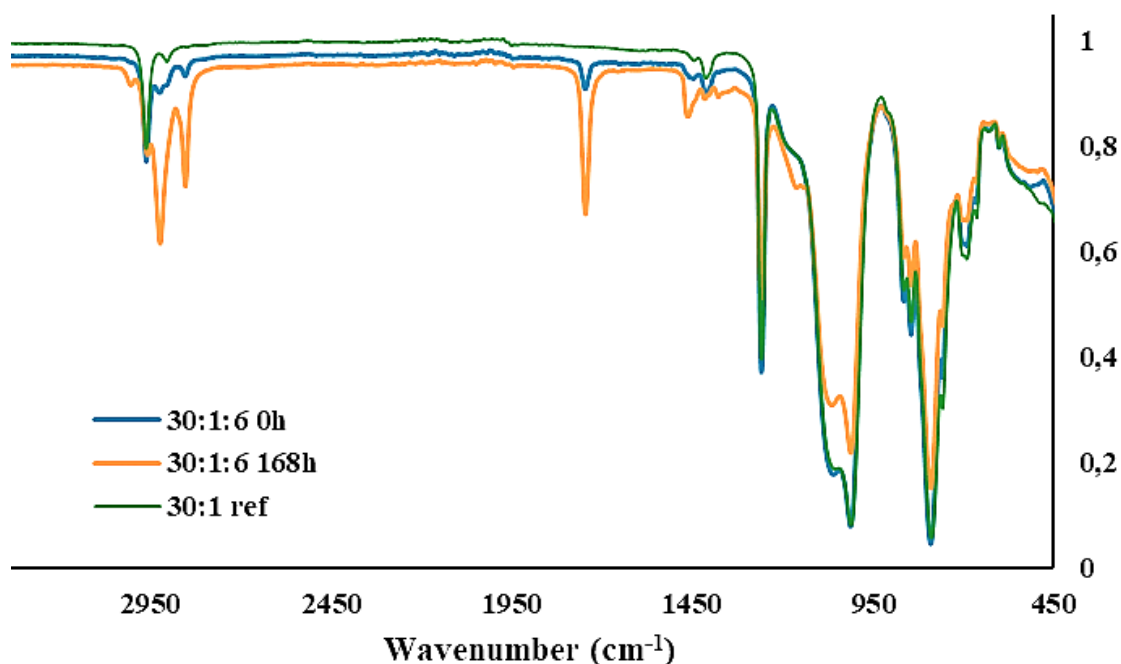


Fig. 79 Comparison of the IR spectra of Sylgard184 formulation in 30:1 tt3 ratio aged 7 days (green line) and the samples with peanut oil 30:1:6 at 0 time zero (0h) and after 7 days (168h).

The monitoring of anti-icing properties over time through shear stress measurements is shown in Fig. 80. The anti-icing properties remain stable for up to 72 hours, after which a decrease in the shear stress value can be observed up to 120h (5 days), after which a new decrease is observed going towards 168h (7 days). This suggests that the effect of the oil is already present at zero instant, but that after a week, thanks to its gradual migration to the surface of the PDMS, it gives the material excellent anti-icing properties.

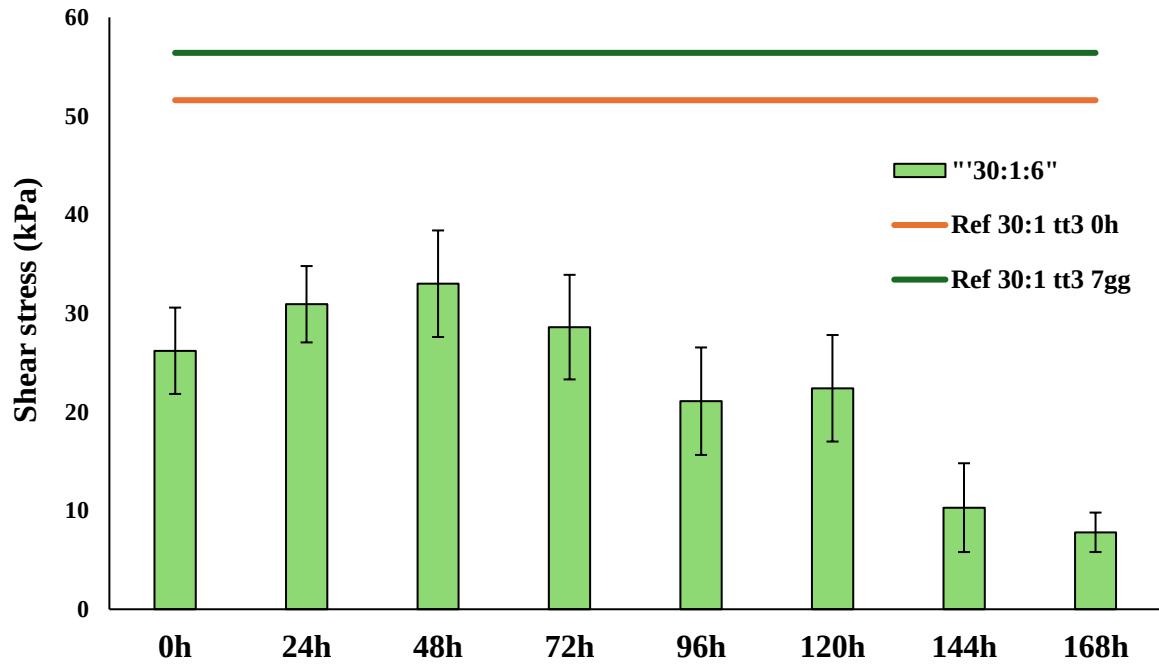


Fig. 80 Monitoring of anti-icing properties of the 30:1:6 sample over time, starting from time zero (0h) up to 7 days (168h).

To better understand the effect of different oil concentrations within the matrix on the overall performance of the coating, 30:1:6 slippery coating was compared with a coating prepared using a lower amount of oil, corresponding to a ratio 30:1:1. Shear stress cycle measurements were conducted to provide a comprehensive comparison in terms of durability and layer effectiveness. The test was performed ten days after the coating preparation allowing the oil to migrate to the surface and form a stable layer. After these cycles, wettability measurements were repeated and compared with the initial values. The shear stress results are reported in Fig. 81, while the values for static contact angle (SCA), contact angle hysteresis (CAH), and roll-off angle (RO) are listed in Tab. 15.

Samples	Cycle	SCA (°)	CAH (°)	RO (°)
30:1:1	1	102.3 ± 0.9	16.1 ± 1.3	11.7 ± 0.4
30:1:1	10	90.9 ± 4.8	20.7 ± 5.2	14.1 ± 2.5
30:1:6	1	98.5 ± 1.5	14.1 ± 1.0	10.9 ± 0.5
30:1:6	10	88 ± 4.6	8.1 ± 4.5	7.5 ± 0.8

Tab. 15 Valori di angolo di contatto statico (SCA), isteresi dell'angolo di contatto (CAH) e angolo di roll-off (RO) per 30:1:1 e 30:1:6 dopo 10 cicli di misure di shear stress.

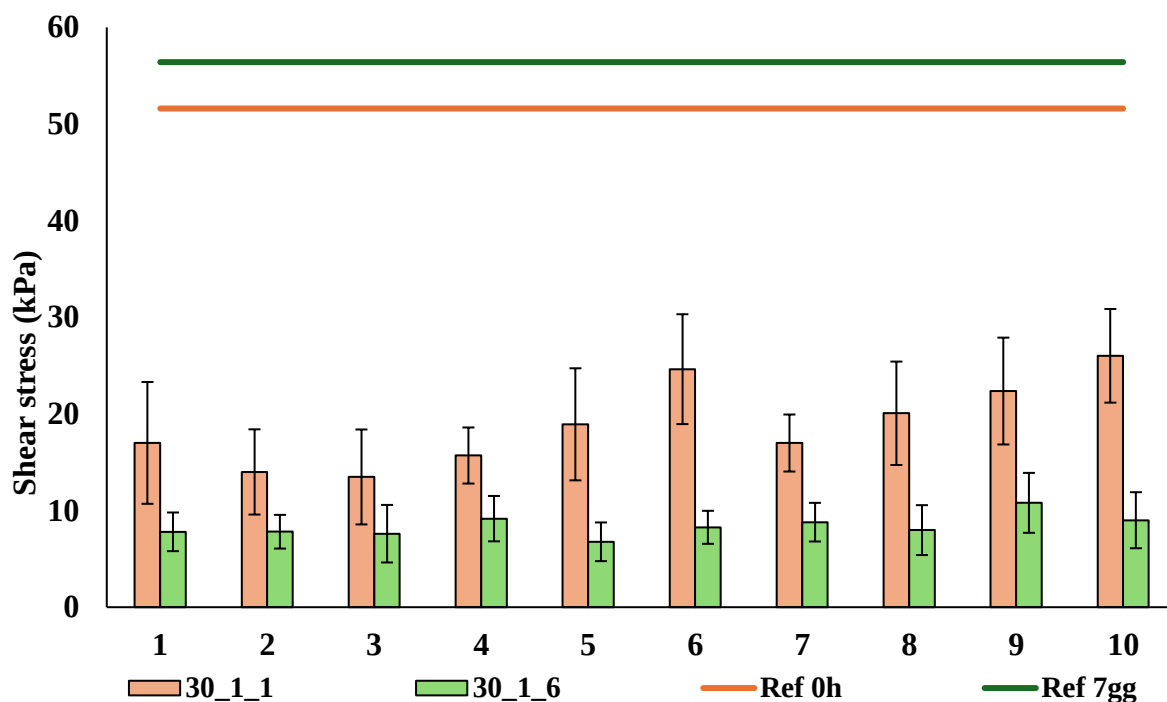


Fig. 81 Cycles of shear stress measurements on 30:1:1 and 30:1:6 samples. Reference values were also reported: 30:1 tt3 aged 0 days (orange line) and 30:1 tt3 aged 7 days (green line). The latter is reported because samples with oil were characterized 7 days after their preparation.

In both cases, the shear stress value is significantly reduced compared to the reference values of the unmodified 30:1 sample not containing oil. This could suggest that the 30:1:1 sample, which contains the lowest amount of oil, might be the best option when considering the compromise between low shear stress and minimal oil content. However, observing the shear stress values during the cycles, it is evident that the 30:1:1 sample exhibits a high standard deviation and unstable shear stress values, with oscillations exceeding 20 kPa. The 30:1:6 sample, in addition to showing the lowest initial shear stress value, maintains excellent anti-icing properties throughout all ten cycles. The results indicate that the 30:1:6 formulation offers superior performance in terms of shear stress and durability, suggesting better structural and functional stability.

Although 30:1:6 coating shows interesting properties, it is necessary to evaluate its durability in the long term, to apply it as an anti-icing solution. The sample was studied through the accelerated aging (AC) chamber test. After carrying out the test, the samples were characterized through shear stress measurements (Fig. 82), Hardness Shore A measurements (Fig. 83), wettability measurements with static contact angle (SCA) calculation, hysteresis (CAH) and roll-off angle (RO) (Fig. 84), and IR spectroscopy (Fig. 85).

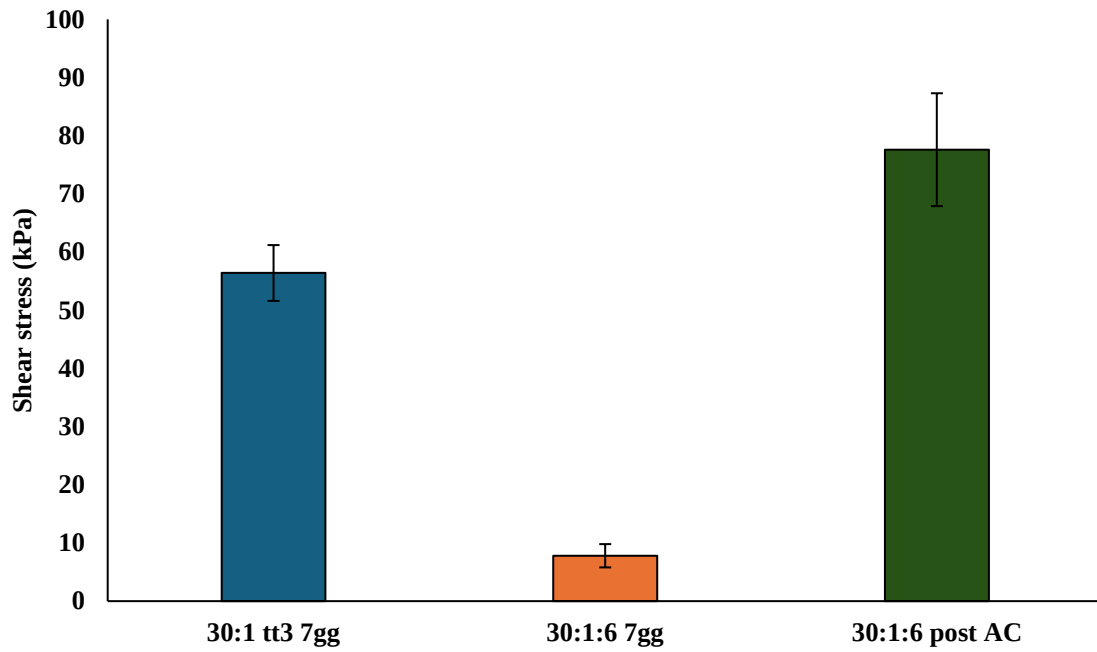


Fig. 82 Comparison of shear stress values of the sample without oil infusion (30:1 tt3 7gg), the 30:1:6 sample at 7 days of maturation (30:1:6 168h), and the 30:1:6 sample following accelerated aging (30:1:6 post AC). A deterioration of properties can be seen following the AC test.

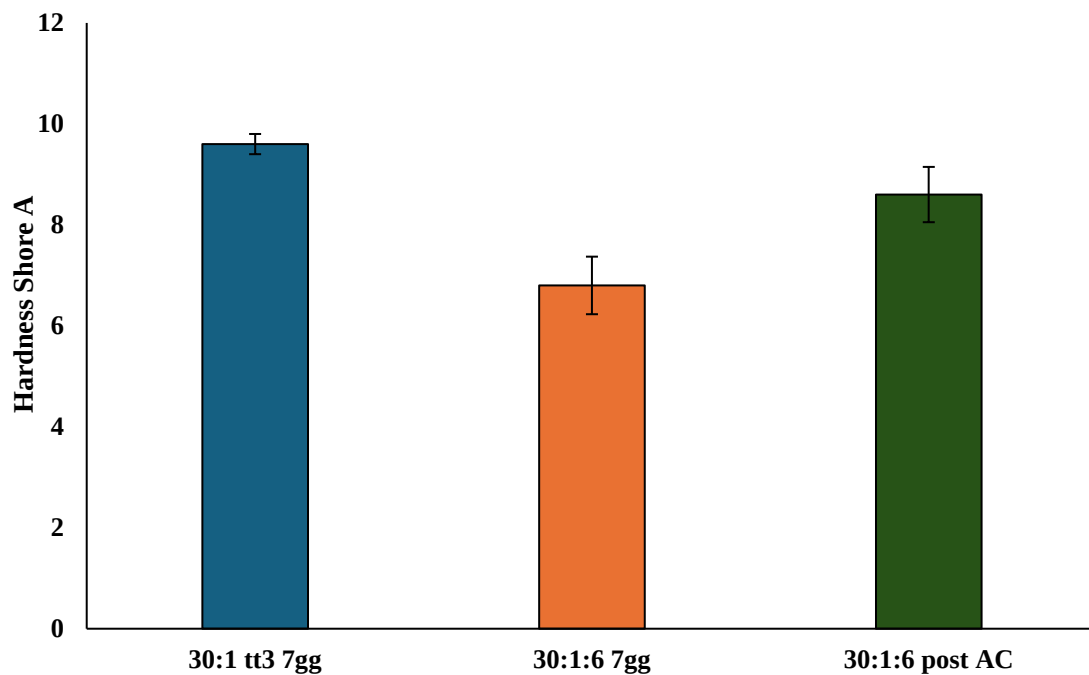


Fig. 83 Comparison of Hardness Shore A values of the sample without oil infusion (30:1 tt3 7gg), the 30:1:6 sample at 7 days of curing (30:1:6 168h), and the 30:1:6 sample after accelerated aging (30:1:6 post AC). A slight increase in hardness can be observed after AC.

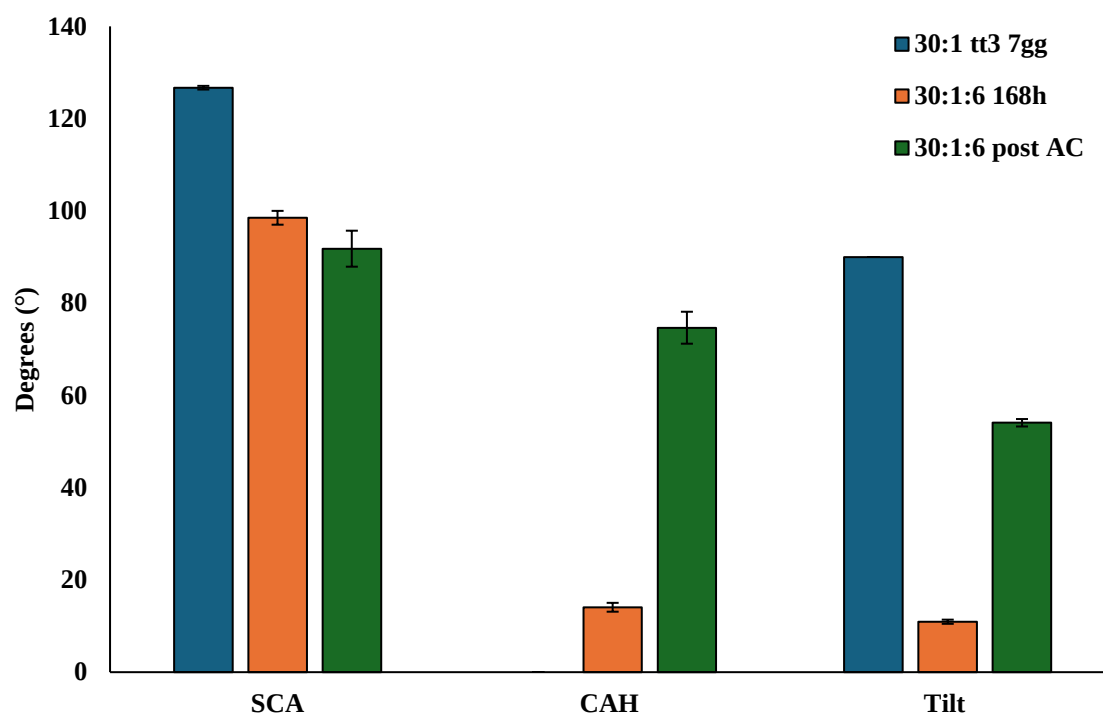


Fig. 84 Measurements of static contact angle (SCA), hysteresis (CAH) and roll-off angle (RO) for samples 30:1 tt3 aged seven days (30:1 tt3 7gg), 30:1:6 after 7 days aging and 30:1:6 after AC test.

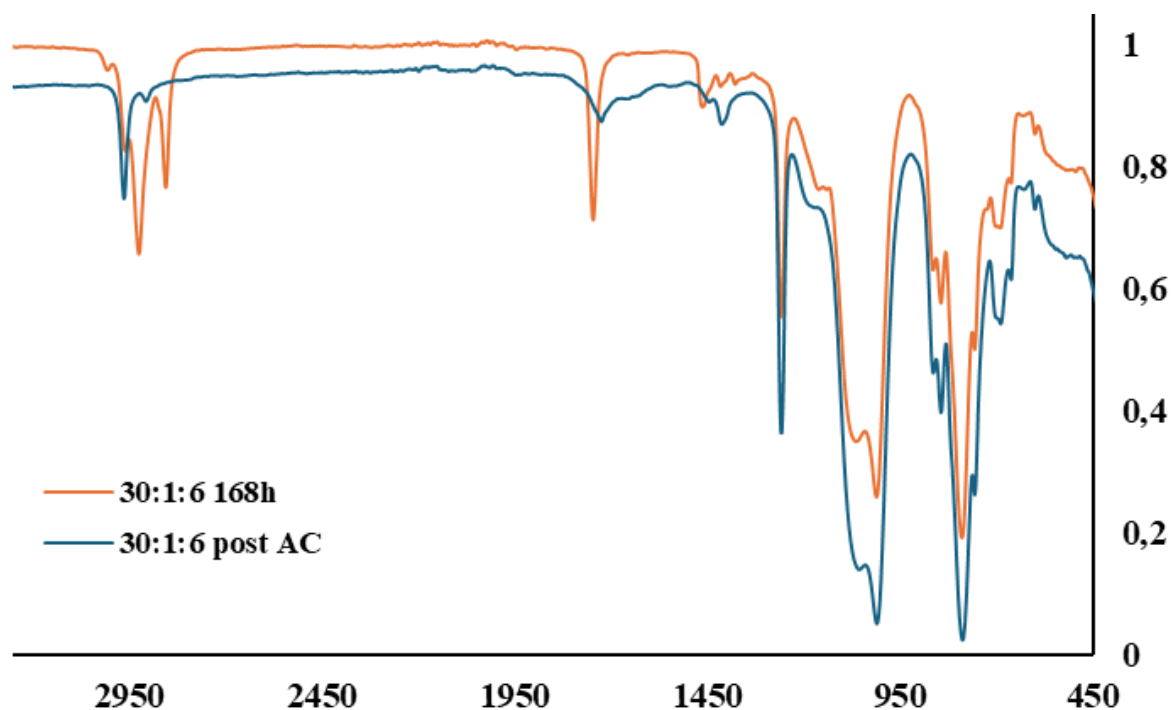


Fig. 85 Comparison of IR spectrum of 30:1:6 aged seven days (30:1:6 168h) and 30:1:6 post-test in accelerated aging chamber (30:1:6 AC).

The coating containing peanut oil prepared with Sylgard184 at a 30:1:6 ratio exhibits a general deterioration of its properties following the accelerated aging (AC) treatment. The shear stress value increases, exceeding the shear stress value of the 30:1 tt3 reference sample (Fig. 82). The

hardness value also increases, although it does not surpass the reference value of 30:1 tt3 (Fig. 83). Wettability worsens, with an increase in CAH and RO values, although it still shows better properties than 30:1 tt3 (Fig. 84). A comparison of the IR spectra of the 30:1:6 sample post-AC and the 30:1:6 sample at 168h reveals the disappearance of signals associated with C-H stretching of aliphatic bonds at 2921 cm^{-1} (asymmetric) and 2855 cm^{-1} (symmetric). Additionally, a weak signal corresponding to C=O stretching at 1740 cm^{-1} is observed. The samples underwent visible degradation, noticeable to the naked eye, with a visible colour change around the coating subjected to the accelerated aging test (Fig. 86).



Fig. 86 On the left is the 30:1:6 sample after seven days of maturation at room temperature in the laboratory. On the right is the 30:1:6 sample after the accelerated aging test in a chamber. The latter shows visible signs of degradation caused by the test.

PDMS-based coatings infused with peanut oil have demonstrated high effectiveness in anti-icing applications, achieving an adhesion reduction factor (ARF) of approximately 44 for the 30:1:6 formulation, with a seven-fold improvement with respect to the not infused 30:1 tt3 (6.2). The lack in durability of the slippery PDMS coating when subjected to prolonged stress over time is however evident, but still maintaining an ARF of 4.5. The idea of infusing oil into a (polydimethyl)siloxane matrix to create a slippery surface layer is intriguing, but it requires further investigation into the type of lubricant to be used to ensure excellent anti-icing properties while simultaneously maintaining the material's durability.

6.2 Polydimethylsiloxane Polyethylene composite coating

My doctoral project continued at the laboratories of Tampere University with the target of developing composite materials that combine the anti-icing properties of elastomers with those of other polymeric materials, using *Thermal Spraying*^{186,187}. Thermal spraying techniques are coating processes in which molten or heated materials are sprayed onto a surface using a manually controlled gun or a robotic arm. The feedstock powder, which serves as the precursor for the coating, is chemically heated using a combustion flame (Fig. 87)

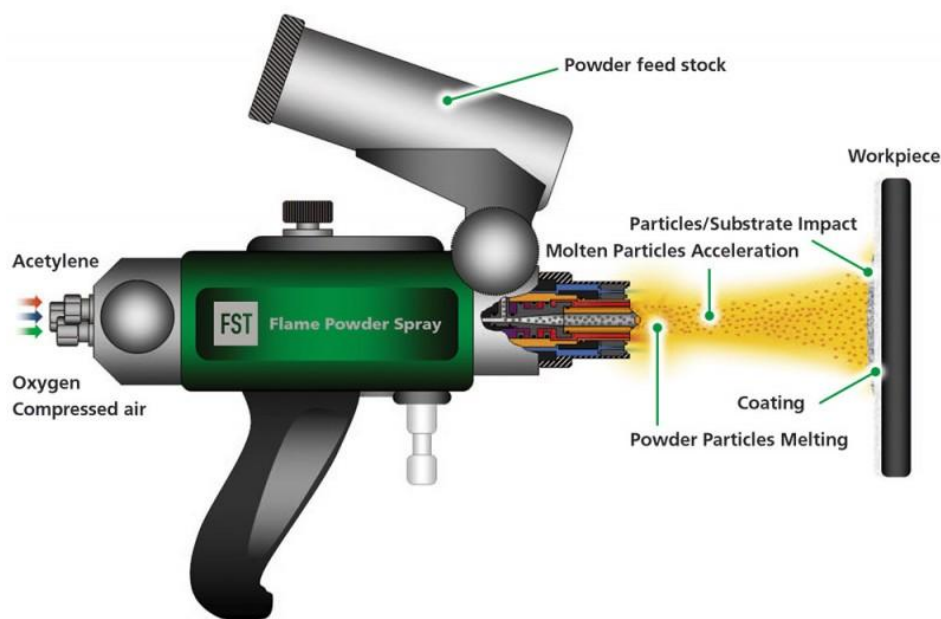


Fig. 87 Illustrative diagram of the different components of a thermal spray gun and how coating spraying works (Image from Airo Shot Blast Equipment (https://www.airoshotblast.net/blog.php?blog_id=What%20is%20Flame%20Spray%20Gun?))

Polyethylene (PE) is one of the most widely used synthetic thermoplastic polymers among all plastics. Its chemical structure is simple, consisting of long chains of carbon and hydrogen atoms that interact through dispersive forces, resulting in a solid, lightweight, and chemically resistant material. A distinctive feature of PE is the ability to tailor its mechanical properties by adjusting the degree of chain branching and the molecular weight distribution. These factors determine the material's density, which can be classified as low-density (LDPE), high-density (HDPE), or medium density (MDPE). Materials with higher density exhibit a more compact structure, which enhances stiffness and mechanical strength, while lower density provides greater flexibility and elasticity.

Additionally, its chemical nature imparts a low surface energy (30–35 mN/m), making PE an intrinsically hydrophobic material. Its moderate melting temperature ($T_{\text{melt}} = 128^{\circ}\text{C}$) makes it particularly suitable as a feedstock powder for the deposition of coatings via thermal spraying.

The combination of these characteristics makes PE an excellent candidate for creating anti-icing coatings through thermal spraying. Experimental studies have demonstrated that PE-based coatings exhibit significantly lower shear stress values compared to other polymeric or metallic surfaces^{188,189}.

The aim of this study is to deposit a layer of polyethylene (PE) onto the PDMS surface to reduce surface adhesion and overall improve the material's anti-icing properties. Several operational parameters can be adjusted to control the characteristics of the polyethylene layer, including nozzle-to-surface distance, gun movement speed, preheating temperature, post-heating temperature, and the number of layers. The thermal spraying process does not involve depositing the polyethylene layer in a single pass. The feedstock powder is conveyed to the flame through a pressurized gas (acetylene or O₂), and upon reaching the flame, the polymer is melted into small droplets that impact the surface with a diffuse flow. Depositing a single layer results in a non-uniform coating with irregular distribution on the surface. For this reason, a minimum of three layers is generally required to ensure uniform and homogeneous surface coverage. Increasing the number of layers improves coating uniformity and reduces surface roughness¹⁹⁰. However, increasing the number of layers also increases the overall thickness of the coating. The number of layers thus becomes a critical parameter in designing a composite material that combines the structural reversibility of elastomers with a thermoplastic polymer layer that reduces surface friction. If the PE layer is too thick, it may inhibit the elastic properties of the coating, compromising the intended synergy. Several tests were conducted, and the parameters selected to ensure homogeneous deposition of the PE coating are reported in

Tab. 16.

Feedstock powder: Polyethylene (PE)	Setting
Distance (mm) ¹	300
Speed (mm/s) ²	500
Preheating temperature (°C) ³	100
Number of layers ⁴	4
Post heating temperature (°C) ⁵	200

Tab. 16 1. Distance of the spray gun nozzle from the surface; 2. Gun movement speed during spraying; 3. Temperature used to activate the surface before coating deposition; 4. Number of polyethylene layers deposited on the surface; 5. Flame temperature used to heat the surface and promote coating uniformity.

The elastomeric coatings were previously prepared on Al6082 plates measuring 30x60x5mm with the Sylgard184 formulation in a 30:1 ratio with tt3 heat treatment (100°C – 1h). The thickness was in the range of 3 (750 – 900 μm). Composite coatings were created by spraying polyethylene onto the surface of elastomeric coatings using the setting reported in Tab. 16 (sample 30a), as detailed in the Experimental section (Fig. 88).



Fig. 88 Example of an elastomeric material coated with PE.

The samples were subjected to wettability measurements, and the results obtained were compared with the "PEa reference" and the uncovered elastomer (30:1 tt3). The results are presented in Fig. 89.

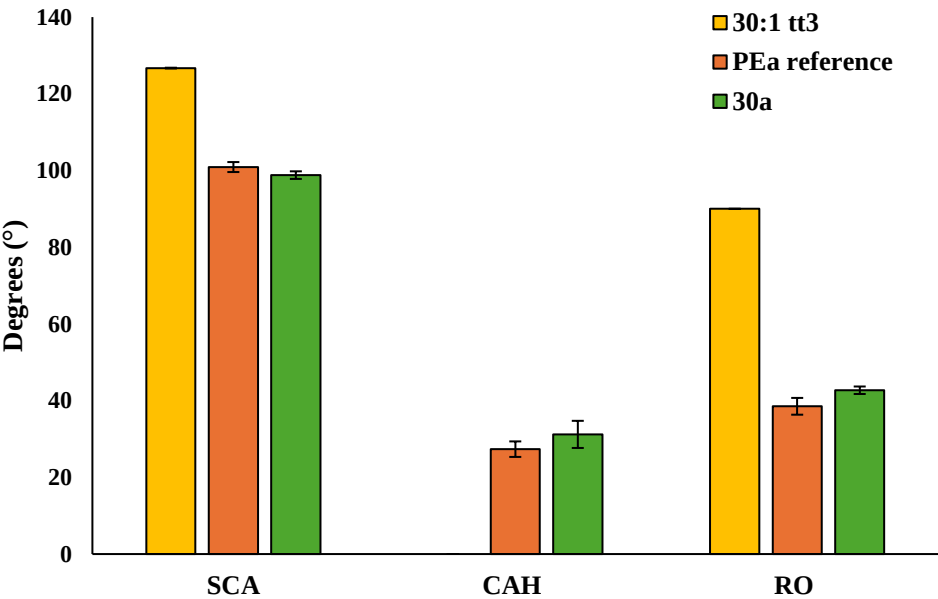


Fig. 89 Comparison of wettability measurements between composite coating (30a), uncoated reference (30:1 tt3) and polyethylene only (PEa reference).

The composite sample 30a exhibits an improvement in wettability compared to the uncovered sample (30:1 tt3). It behaves identically to the "PEa reference," displaying similar values of static contact angle (SCA), contact angle hysteresis (CAH), and roll-off angle (RO). This suggests that the thermal deposition of PE results in a surface-level effect.

Shear stress measurements were performed using the Centrifuge Adhesion Test (CAT), which determines the shear stress required for ice detachment by applying centrifugal force¹⁹¹ (see Experimental section for the details). With this technique, the ice is a “mixed glaze” ice. The results are presented in Fig. 90.

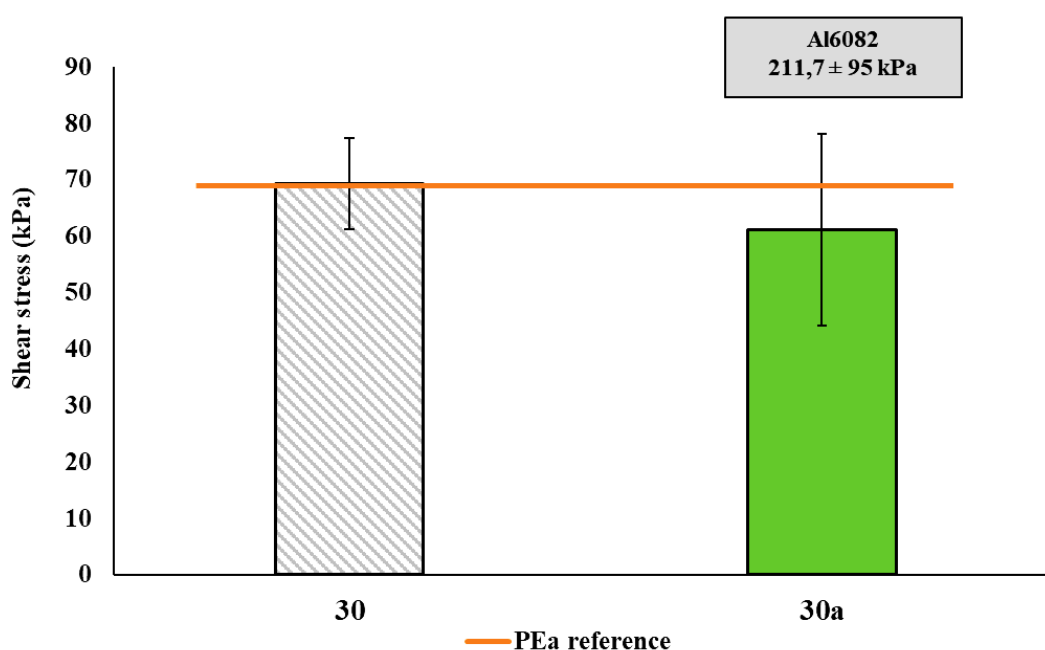


Fig. 90 Comparison between the *CAT* shear stress measurements of the PE-coated composite sample (30a) and the uncovered reference sample (30:1 tt3). The orange line is the polyethylene-only reference (PEa reference). The uncoated Al6082 shear stress reference value is also reported.

The test was also conducted on the uncovered sample (30:1 tt3) to evaluate the effect of the PE layer deposited on the elastomeric surface. The shear stress values of the "PEa reference" and the uncovered elastomer (30:1 tt3) showed no substantial differences, oscillating around 70 kPa.

The composite coating 30a exhibits a slightly lower shear stress value compared to the uncovered elastomeric sample (30:1 tt3) and the PEa reference. However, considering the standard deviation range, the 30a sample does not display significant differences in anti-icing properties when compared to the 30:1 tt3 and PEa samples. Although the deposition of the PE layer improves wettability by reducing surface adhesion, no improvements in anti-icing properties are observed. These results suggest that the deposition of the polyethylene layer may have masked the presence

of the underlying elastomeric layer. In fact, the PE coating can be detached from the surface, indicating that polyethylene did not penetrate the elastomeric matrix but simply rested on its surface (Fig. 91).

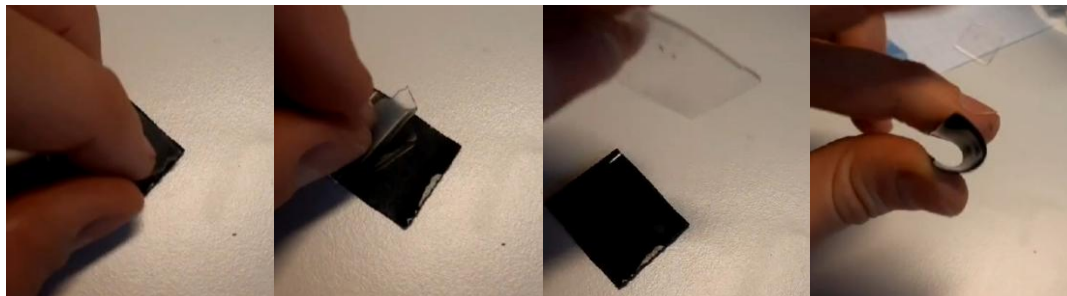


Fig. 91 Photograms depicting the process of mechanical peeling of the PE coating from the surface of PDMS.

The PDMS, due to the excessive thickness of the thermoplastic polymer, is unable to act at the ice-surface interface by reversibly modifying its structure. Measurements performed with electronic callipers indicate a PE coating thickness of approximately 1 mm, which is of the same order of magnitude as the elastomeric coating thickness. This suggests that it is necessary to reduce the thickness of the PE layer to achieve a synergistic effect. As previously discussed, reducing the thickness of the PE coating by depositing fewer layers is not still feasible, as this would prevent the formation of a uniform and well-distributed coating. To determine whether the ratio between the thickness of the thermoplastic coating and the elastomeric coating is the key parameter for achieving the target composite material, it was decided to strongly increase the thickness of the PDMS coating to 5mm using a mold, while maintaining the same PE deposition setting A which ensures a coating thickness of approximately 1 mm (see Experimental section for details). The composite coating prepared on Sylgard184 30:1 tt3 with a thickness of 5mm (30TPEa, Fig. 92) was compared with the 5mm thick elastomeric coating not coated with PE (30T) through shear stress measurements with CAT, the results are reported in Fig. 93.

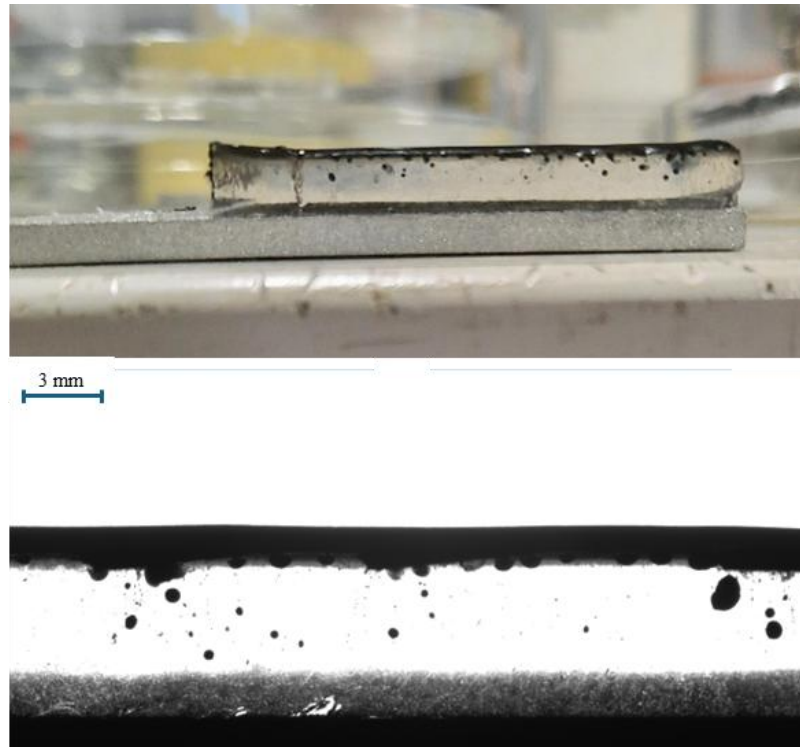


Fig. 92 Top: visual comparison between the coating thickness of PDMS and the PE layer. Bottom: image of the sample obtained from the contact angle camera.

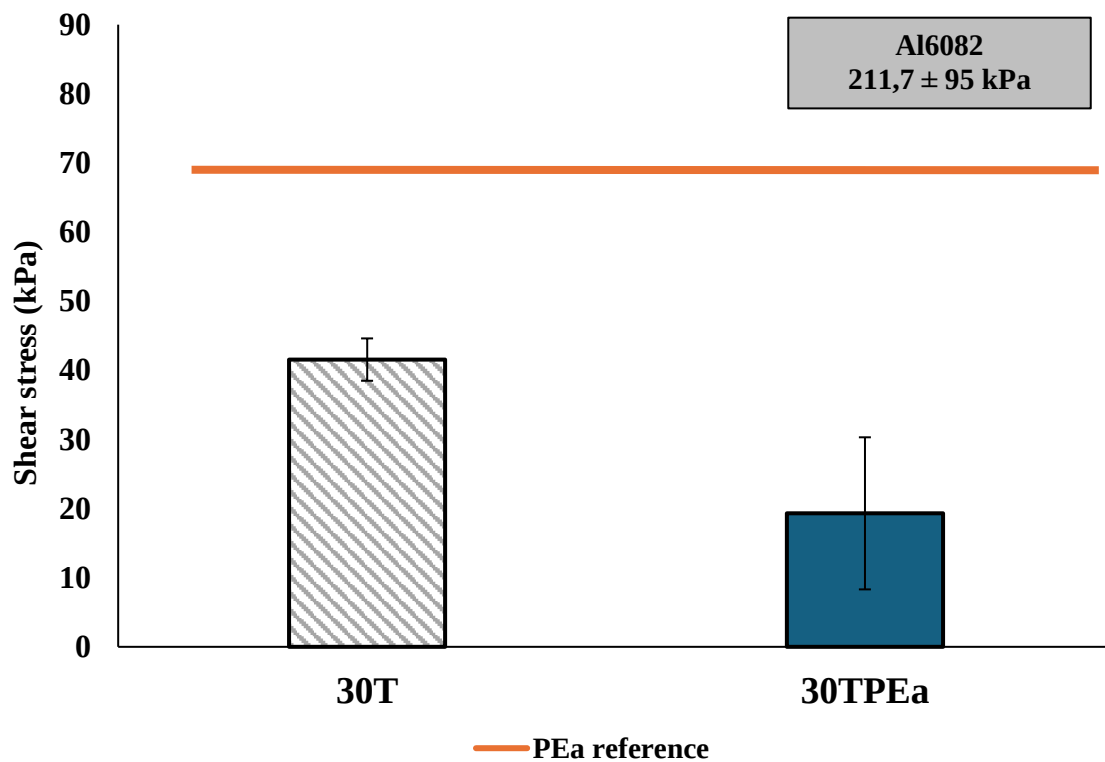


Fig. 93 Comparison of *CAT* anti-ice measurements of the thick composite coating (30TPEa) and the untreated reference 30:1 tt3 (30T). In orange is the polyethylene reference (PEa reference). The uncoated Al6082 shear stress reference value is also reported.

Now, the composite coating exhibits a lower shear value compared to both references (30T and PEa), supporting the hypothesis that the ratio between the thermoplastic layer thickness and the polymeric coating thickness is a crucial parameter in designing a composite coating that reduces surface adhesion while preserving elastomeric properties. Envisioning the creation of a composite coating by depositing a PE layer onto Sylgard184 30:1 tt3 with a thickness in the range of 750–900 μm (approximated to $\sim 1\text{ mm}$), it would be essential to apply a PE layer at least five times thinner ($\sim 200\text{ }\mu\text{m}$) than the elastomeric coating thickness to achieve the desired effect. However, this is not achievable using this technique with setting A.

The composite samples prepared by spraying PE on a PDMS substrate with a thickness of $\sim 1\text{ mm}$ (30PEa) and 5 mm (30TPEa) were characterized in Italy through push test with “mold ice,” and the results are presented in Fig. 94.

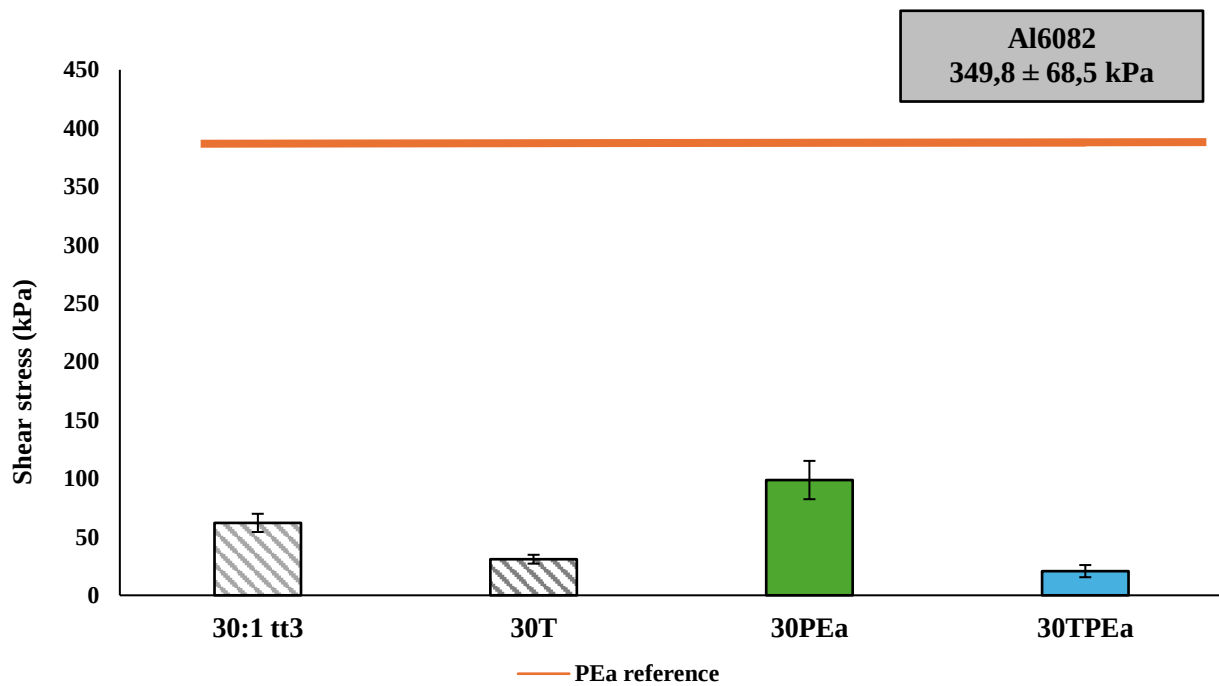


Fig. 94 Comparison of anti-icing measurements through **push test** conducted in Italy on PE-based composite coatings prepared on 1mm-thick (30PEa) and 5mm-thick (30TPEa) PDMS and untreated references of 1mm-thick (30:1 tt3) and 5mm-thick (30T) PDMS. The orange line is the polyethylene-only reference (PEa reference). The uncoated Al6082 shear stress reference value is also reported.

It is not possible to make a direct comparison between the results obtained with CAT and through the evaluation of shear stress with push-test, as the parameters used during the tests differ, as do the size and, most importantly, the type of ice (see Experimental part). PE does not perform well when subjected to the horizontal shear stress with “mold ice,” showing a value even higher than the untreated Al6082 substrate (~ 350 kPa). The composite coating prepared by spraying PE on Sylgard184 30:1 tt3 PDMS with a thickness of ~ 1 mm (30PEa) shows a much lower value compared to the PE reference (PEa reference) but still higher than the elastomeric reference without PE (30:1 tt3).

This observation confirms what was previously seen in the CAT test, where the deterioration of the 30PEa composite coating properties compared to the 30:1 tt3 reference is due to the loss of the elasticity effect of the elastomeric coating, which is completely covered by the PE layer.

On the other hand, when increasing the thickness of the initial elastomeric coating (30T) and depositing a much thinner PE layer (30TPEa), an improvement in anti-icing properties can be observed compared to the 30T reference.

To develop a composite coating that preserves both the elastic properties and the reduced surface adhesion, typical of low-crosslinked elastomers such as Sylgard184 30:1, it is essential to control the ratio between the thickness of the elastomeric coating and that of the surface layer. Indeed, for the elastomer to deform reversibly under the shear stress required to remove ice, the surface layer must be sufficiently thin. If it is too thick, the elastomer becomes completely covered, preventing it from acting according to the elastomeric ice detachment mechanism.

7. Superhydrophobic and Slippery on Aluminium surfaces

Anticorodal is a family of aluminium alloys widely used in industrial applications due to their combination of lightweight properties, mechanical strength, and good workability. These alloys belong to the 6000 series and are primarily composed of aluminium with the addition of silicon (Si), magnesium (Mg), and manganese (Mn), elements that enhance their mechanical properties and corrosion resistance^{24,25}. Among the various types of Anticorodal, Anticorodal6061 and Anticorodal6082 stand out, with the latter being extensively employed in the production of high-voltage components, thanks to its high electrical conductivity, which enables the efficient transport of current over long distances without significant losses. Anticorodal exhibits high surface energy, a characteristic common to metallic surfaces, which promotes interaction with water and facilitates the formation of ice and snow on its surface. A promising approach to directly modify aluminium surfaces and mitigate atmospheric icing consists of surface morphology modification aimed at creating superhydrophobic surfaces (SHP) or slippery liquid-infused porous surfaces (SLIPS). A common aspect in designing such surfaces is the creation of micro-nano roughness: in SHP surfaces, this ensures the establishment of a Cassie-Baxter state, enhancing their properties, while in SLIPS surfaces, it allows the lubricant to anchor effectively and act at the surface level (as discussed in detail in Chapter 3.1.2). An effective and green method that enables the creation of macro-roughness on metallic surfaces without the use of solution-based reactions is the cold spraying technique^{192–194} (Fig. 95): cold spraying is a coating deposition method in which solid powders are accelerated using gas expansion, and the kinetic energy of the particles is converted into plastic deformation energy upon impact with the substrate, ensuring adhesion to the surface. Metals, polymers, ceramics, composite materials, and nanocrystalline powders can be deposited, and unlike thermal spraying techniques, the powders are not melted during the spraying process but adhere to the surface by impacting with high kinetic energy.

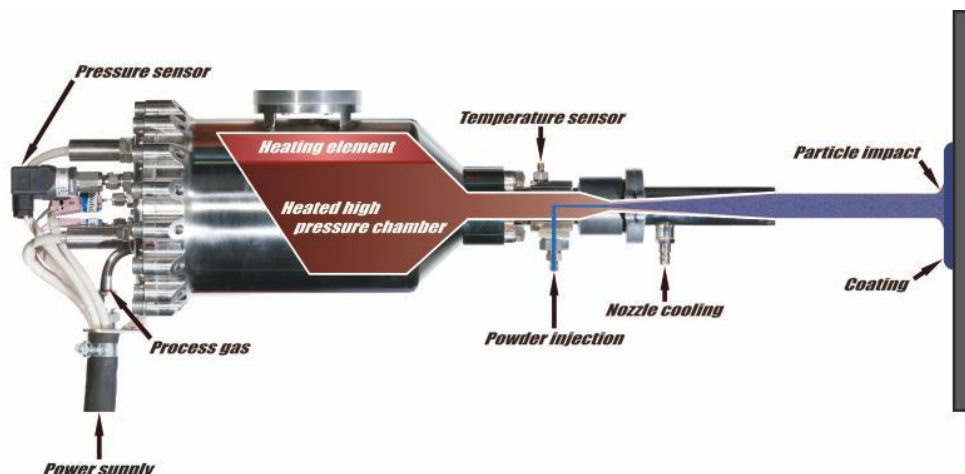


Fig. 95 Illustrative diagram of the different components of a cold spray gun (Image from Airo Shot Blast Equipment (https://www.airoshotblast.net/blog.php?blog_id=What%20is%20Flame%20Spray%20Gun?)).

The creation of nano-roughness often involves complex approaches from an operational standpoint, including techniques such as lithography, laser etching, and plasma treatments (as already discussed in Chapter 3.1.2). The development of simple and fast methodologies is challenging and primarily depends on the type of substrate of interest. Aluminium is a metal with a strong tendency to oxidize due to its negative standard reduction potential ($\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al(s)}$, $E^0 = -1.66 \text{ eV}$). This property allows it to react spontaneously with water, which has a more positive standard reduction potential ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$, $E^0 = -0.83 \text{ eV}$). This reaction is referred to as the Aluminium-Water reaction^{195–197}, and under specific ranges of pressure and temperature, it is possible to obtain basic oxides, which represent intermediate stages in the transition towards the most stable and anhydrous form of aluminium oxide, known as corundum (Al_2O_3)¹⁹⁸ (Fig. 96).

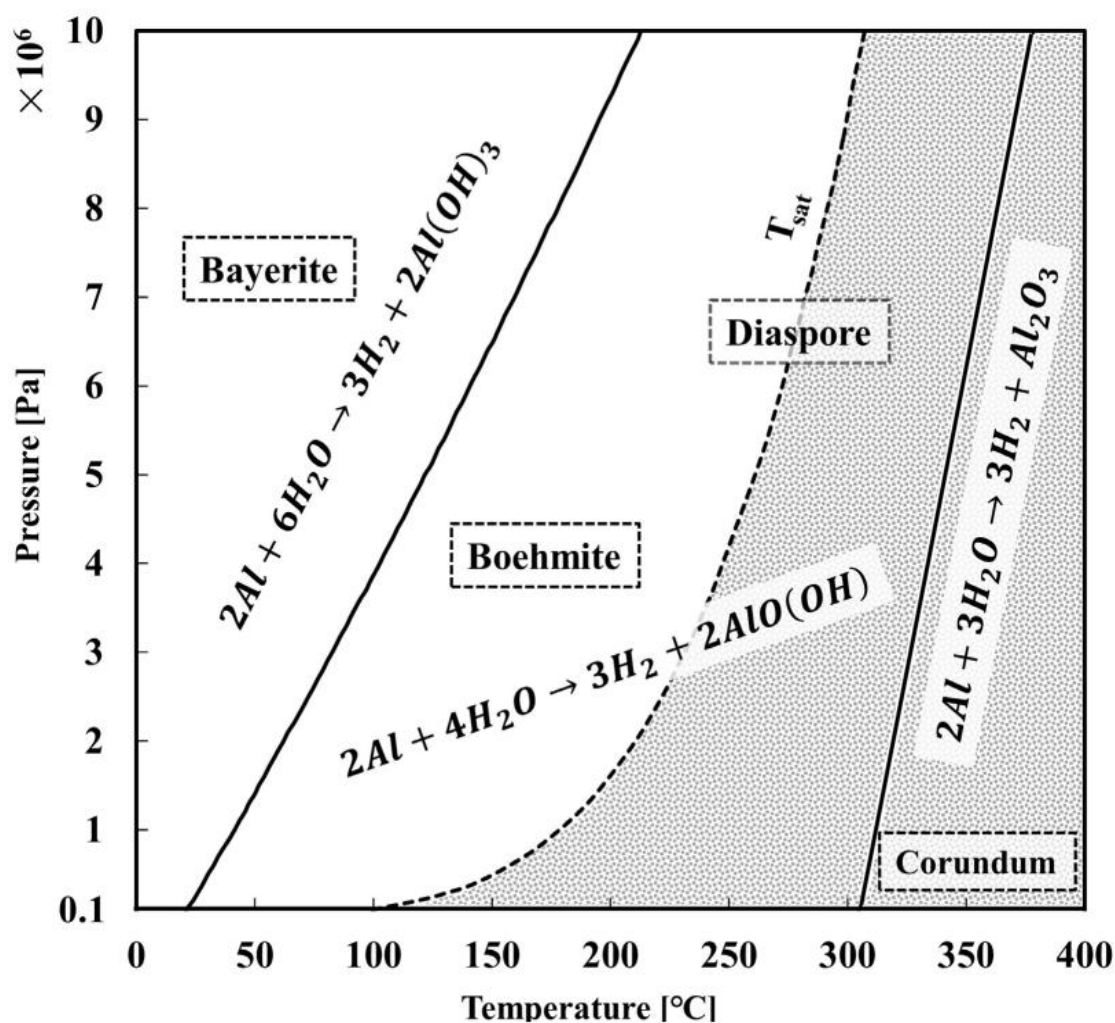


Fig. 96 Phase diagram distribution of the different corundum phases during the Aluminium-Water reaction. Under atmospheric pressure (0.1×10^6 Pa) the temperature range for the boehmite formation is $21^\circ\text{C} - 100^\circ\text{C}$ ¹⁹⁷.

Boehmite¹⁹⁹ is an extremely interesting aluminium basic oxide. First, compared to the other phases, it forms in a much lower temperature range (from 21°C to 100°C). Furthermore, the most important aspect of this species is that it has a whisker-like nanostructure characterized by the presence of functionalizable hydroxyl groups (Fig. 97).

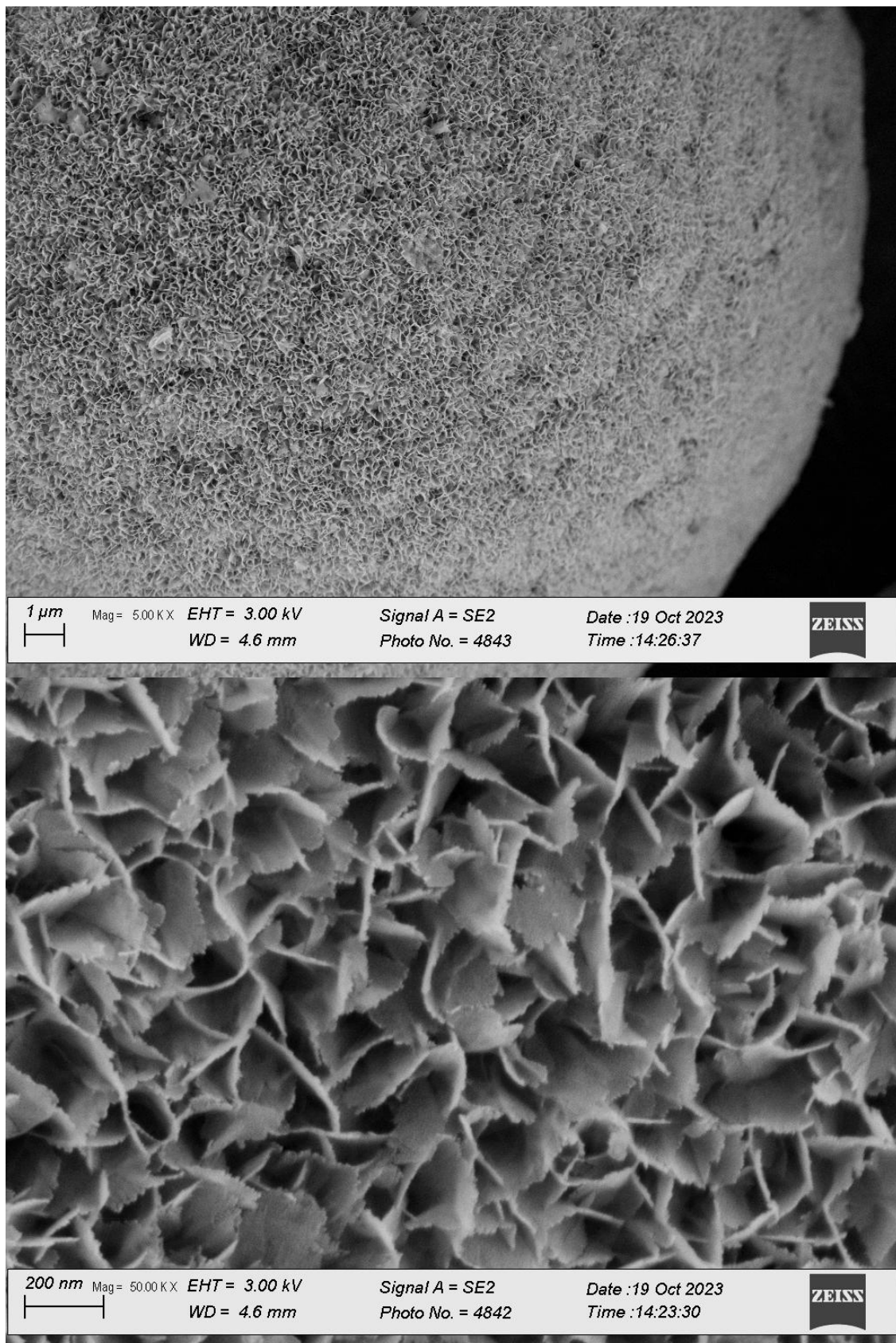


Fig. 97 Images of boehmite grown on an Al6061 substrate obtained by scanning electron microscope (SEM). Top magnification 5kx. Bottom magnification 50kx. At higher magnification the whisker-like structure becomes visible. Thanks to Reza Jafari for the amazing pics.

Boehmite has already been studied as a precursor of superhydrophobic anti-icing surfaces thanks to his easy formation at relatively moderate temperatures^{200,142} and functionalizable nanostructure. The approach normally followed deals with three steps: surface etching with acids or bases, water treatment to create the micro-nano roughness, and functionalization with hydrophobic agents.

At the Tampere University laboratories, the activity was focused on the creation and characterization of superhydrophobic (SHP) and slippery (SLIPS) surfaces on Anticorodal6061, with the aim of optimizing the Aluminium–Water reaction to obtain the formation of the micro-nanostructure in a single step. Subsequently, the effect of the initial roughness of the substrate on anti-icing properties was studied by creating different roughness through sandblasting and using the cold spray technique.

The optimization of the Aluminium-Water reaction was performed using smooth Anticorodal6061 surfaces (30x60 mm), evaluating the degree of hydrophobicity as a function of treatment time and concentration of the basic aqueous solution. The temperature was set at 30°C to maintain the mildest possible conditions. Sodium hydroxide solutions were used to create micro-nanostructure. PDMS oil (65 cP) was employed as a functionalizing agent throughout the process optimization. Detailed information regarding sample preparation is provided in the Experimental section. The parameters varied during the process optimization are summarized in Tab. 17.

NaOH solution concentration (wt%)	Time (min)
0.5	4
2.5	3
5.0	2

Tab. 17 NaOH solution concentrations and contact times used during optimization; in all cases the temperature was kept at 30°C.

The first parameter optimized was the concentration of the basic solution, from 0.5wt% to 5wt%. For all samples, the temperature (30 °C) and contact time (4 minutes) were kept constant. Roughness measurements at the nanoscale using Atomic Force Microscopy (AFM) have been conducted and the results are reported in Tab. 18.

NaOH solution concentration (wt%)	RMS roughness (Sq) (nm)	Mean roughness (Sa) (nm)
0.5	8.4	6.8
2.5	15.5	12.0
5.0	69.9	53.4

Tab. 18 Surface roughness measurements performed by atomic force microscope (AFM) on samples prepared by varying the concentration of the base.

An increase in the concentration of the basic solution at the same time (4min) and temperature (30°C) leads to an increase in surface roughness. Let's go to see how this affects surface wettability, and which conditions lead to the highest degree of hydrophobicity. The results are presented in Fig. 98.

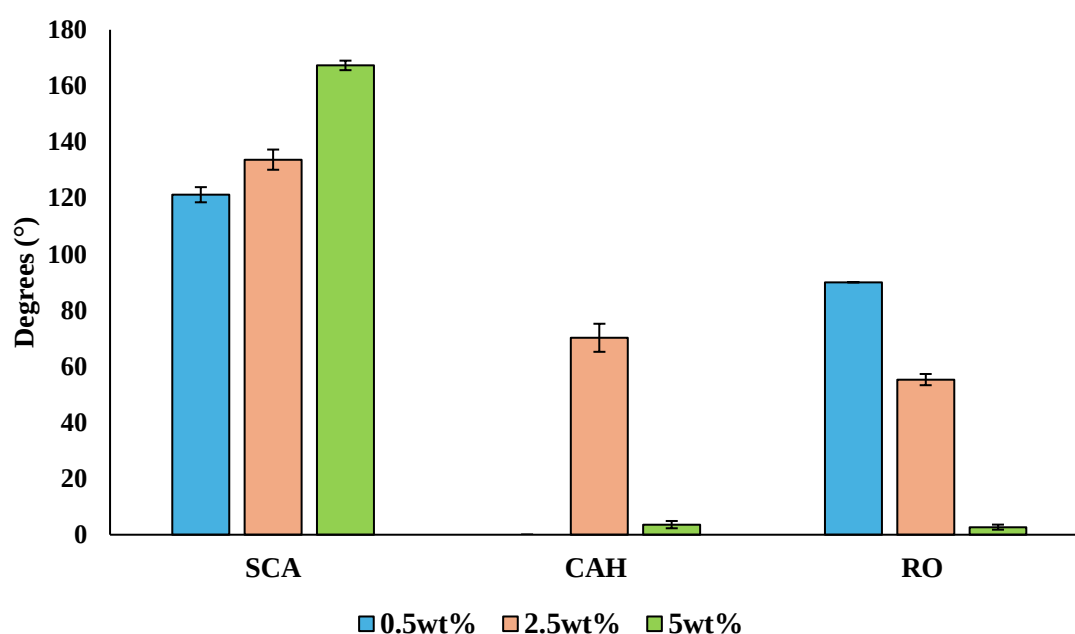


Fig. 98 Wettability measurements in function of the NaOH solution concentration. Temperature (30 °C) and contact time (4min) where the same for all samples. For the sample treated with 0.5wt% base solution the CAH is absent, and RO is 90°.

Increasing the concentration of the basic solution improves the effectiveness of the process: with the most diluted solution (0.5wt%), the static contact angle (SCA) oscillates around 120°, but hysteresis (CAH) is absent, and the roll-off angle (RO) is 90°. With a five-fold increased concentration (2.5wt%), an improvement in surface wettability is observed (SCA and a CAH of 70° and a RO of 55°). The condition of superhydrophobicity is achieved by increasing the concentration of the base tenfold up to 5wt%, with an SCA around 170° and a CAH and RO less than 5°. The next step was aimed at decreasing the contact time to make the process faster. This was varied from 4 to 2 minutes, and the roughness values obtained through AFM were reported in Tab. 19.

Time treatment (min)	RMS roughness (Sq) (nm)	Mean roughness (Sa) (nm)
2	19.2	14.9
3	29,4	24.1
4	69.9	53.4

Tab. 19 Surface roughness measurements performed by atomic force microscope (AFM) on samples prepared by varying the contact time.

As the treatment time decreases, the surface roughness decreases, and this affects the surface wettability (Fig. 99).

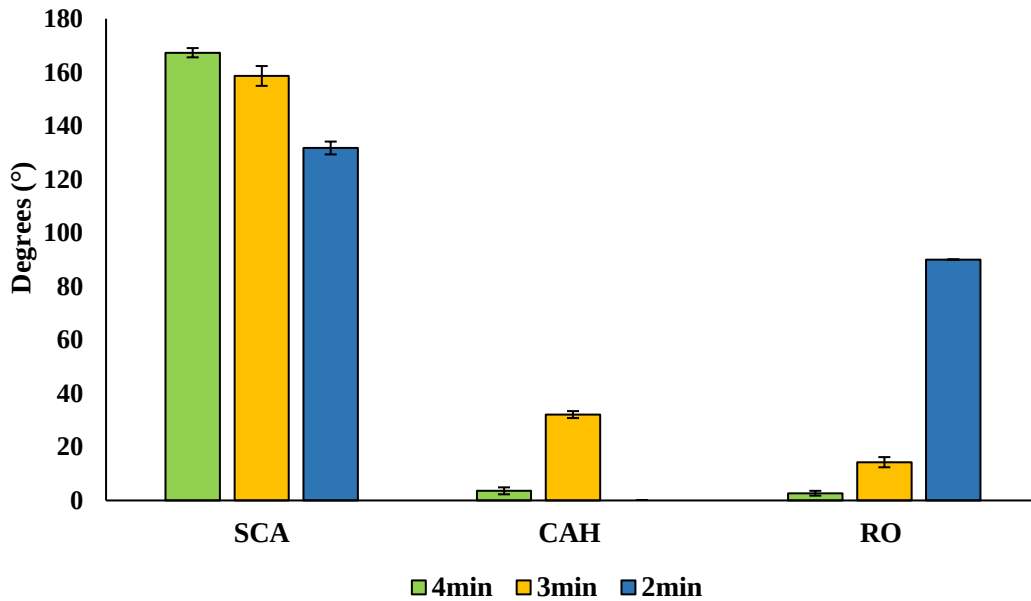


Fig. 99 Wettability measurements of surfaces prepared with different contact time ($T = 30^{\circ}\text{C}$, $\text{NaOH (aq.)} = 5\text{wt\%}$).

A contact time of three minutes shows a worsening of surface wettability, with a decrease in SCA and an increase in CAH and RO. Even worse is the situation found for the sample treated for two minutes, which shows an SCA of 130° with no hysteresis, with the drop remaining adhered to the surface with a RO of 90° . Treatments in low-concentration basic solutions or excessively short treatment times do not allow achieving a high degree of superhydrophobicity.

Hence, the parameters that lead to superhydrophobicity condition are:

- Concentration of the basic solution: 5wt%
- Contact time: four minutes
- Temperature: 30°C

Following the optimization of the "Aluminium-water reaction", the effect of the roughness of the initial substrate was evaluated. Three substrates were selected: smooth Anticorodal6061 surface (s, the one used for parameter optimization), a sandblasted Anticorodal6061 surface (sb) and a surface obtained by spraying Al6061 powder (15-50 microns) by cold spraying (cs) using the

setting reported in Experimental section (Fig. 100). Through measurements with an optical profilometer, the roughness of the three surfaces was calculated at the microscale and the values are reported in Tab. 20.



Fig. 100 Left: smooth sample (s); Middle: sandblasted sample (sb); Right: sample prepared by cold spraying (cs).

Substrate	RMS roughness (Sq) (μm)	Mean roughness (Sa) (μm)
Smooth (s)	0.6	0.5
Sandblasted (sb)	10.9	8.6
Cold sprayed (cs)	34.2	26.9

Tab. 20 Surface roughness measurements performed by optical profilometer with the samples collected in Fig. 116.

Each sample was treated following the conditions optimized in the previous phase (base solution concentration = 5wt%, temperature = 30°C and contact time = 4 minutes); for each sample images were collected through Scanning Electron Microscopy (SEM) (Fig. 101).

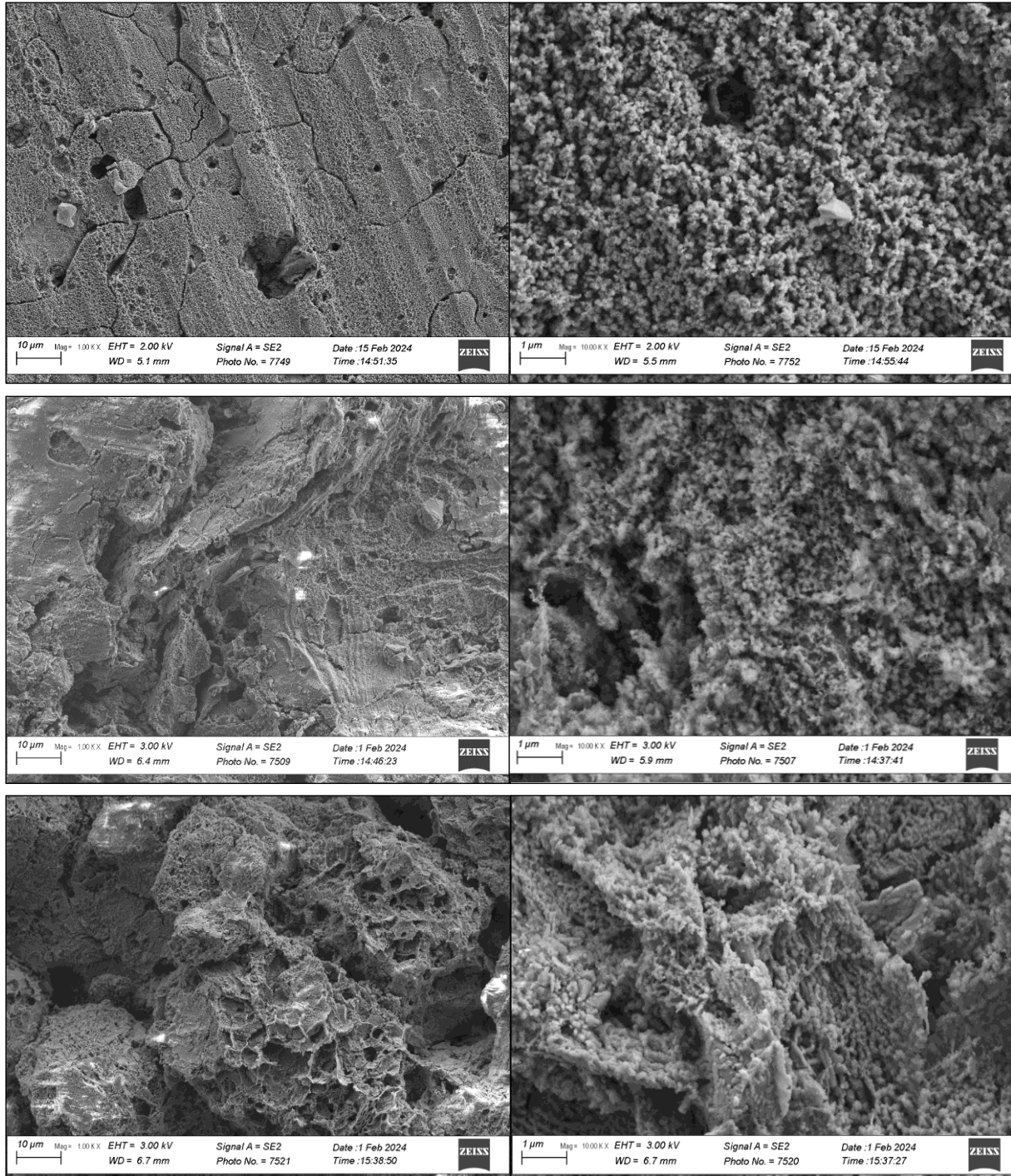


Fig. 101 Images obtained by scanning electron microscopy (SEM). Top: smooth sample (s) with magnification 1kx (left) and 10kx (right). Middle: sandblasted sample (sb) with magnification 1kx (left) and 10kx (right). Bottom: cold sprayed sample (cs) with magnification 1kx (left) and 10kx (right).

The three starting substrates already differ from each other at the lowest magnifications, where the difference between the smooth sample (s) and the two samples on which roughness has been created (sb and cs) is clearly visible (Fig. 101 left column, magnification 1kx). Looking deeper, it is possible to see the characteristic structure of boehmite (Fig. 101 right column, magnification 10kx). Subsequently, for each type of sample, superhydrophobic and slippery surfaces were created by grafting or infusing PDMS oil 65 cP, as reported in detail in the Experimental section. Tab. 21 collects the type of samples created with the different treatments.

Starting substrate	Type of surface	Sample
Smooth (S)	SHP	sSHP
	SLIPS	sSLIPS
Sand blasted (SB)	SHP	sbSHP
	SLIPS	sbSLIPS
Cold sprayed (CS)	SHP	csSHP
	SLIPS	csSLIPS

Tab. 21 Samples created using the three different treatments.

Surfaces were characterized by static contact angle (SCA) (Fig. 102) and hysteresis and roll-off angle (RO) measurements (Fig. 103).

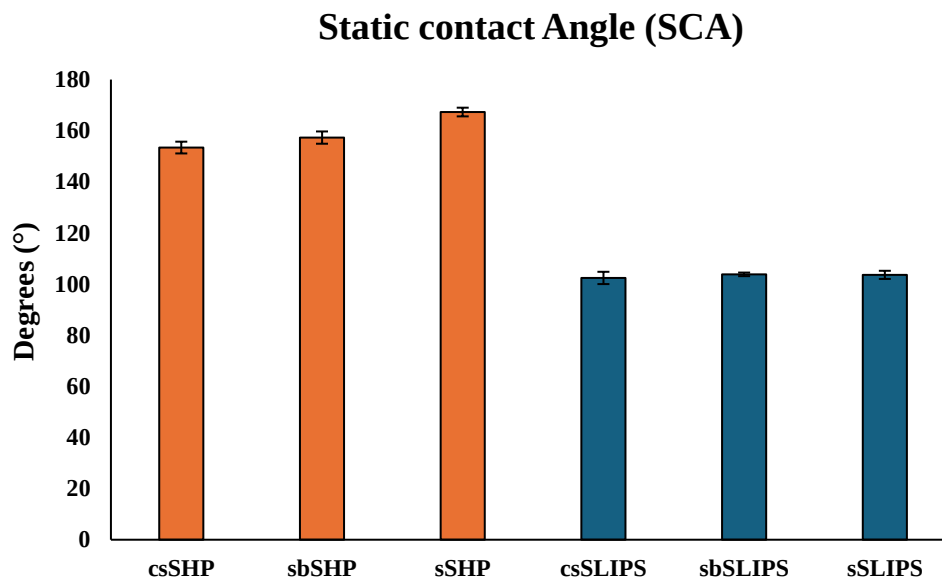


Fig. 102 Static contact angle (SCA) measurements of the superhydrophobic samples (sSHP, sbSHP, csSHP) and SLIPS (sSLIPS, sbSLIPS, csSLIPS) created from the three substrates with different roughness.

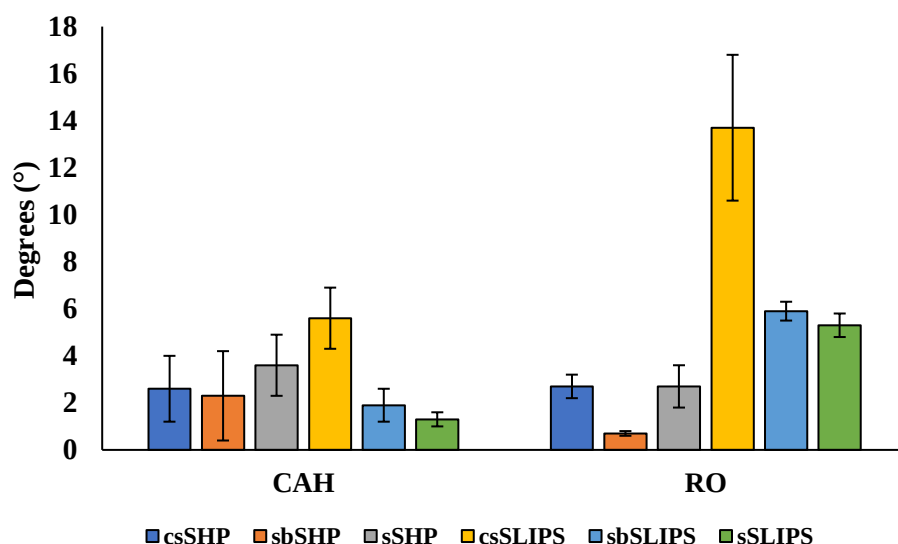


Fig. 103 Contact angle hysteresis (CAH) and roll-off angle (RO) measurements of the superhydrophobic samples (sSHP, sbSHP, csSHP) and SLIPS (sSLIPS, sbSLIPS, csSLIPS) created from the three substrates with different roughness.

csSHP, sbSHP and sSHP samples exhibit excellent wettability properties with SCA above 150° and CAH and RO lower than 5° . The slippery surfaces csSLIPS, sbSLIPS and sSLIPS have lower SCA values and higher CAH and RO values, as expected. Decreasing the roughness (from csSLIPS to sSLIPS) leads to a decrease in CAH and RO values. Anti-icing cycling measurements by CAT were conducted on all prepared samples and the results are shown in Fig. 104.

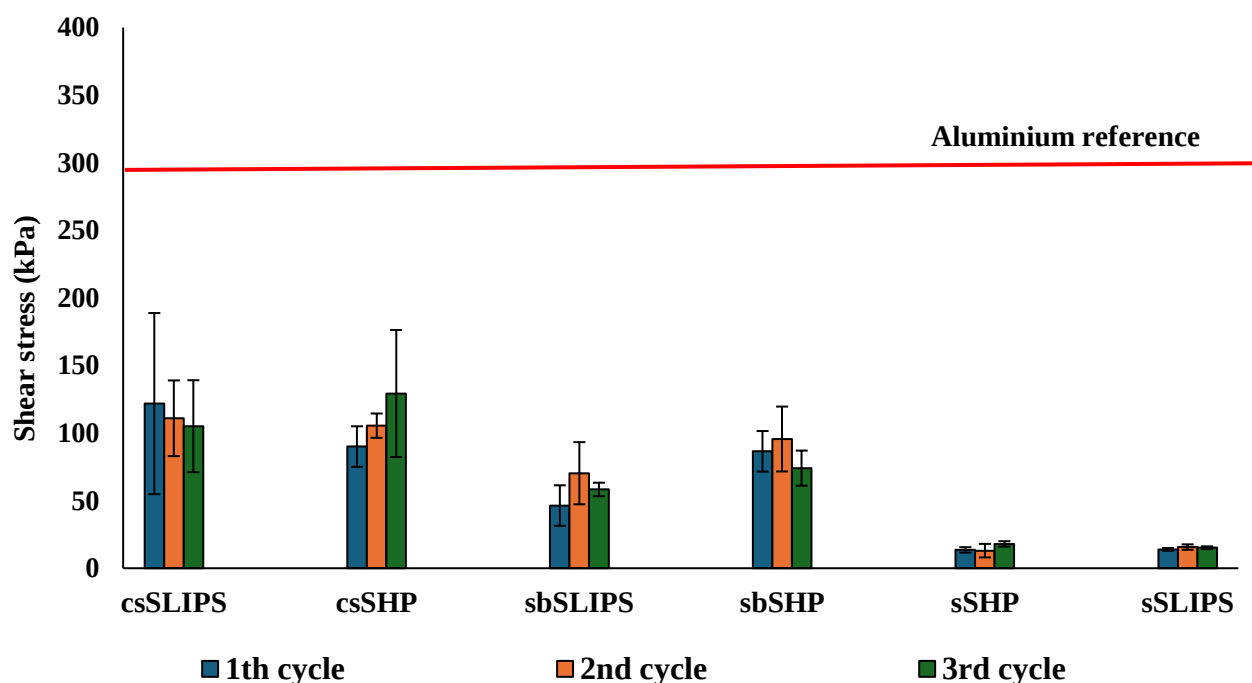


Fig. 104 Cyclic anti-icing measurements by CAT performed on superhydrophobic samples (sSHP, sbSHP, csSHP) and SLIPS (sSLIPS, sbSLIPS, csSLIPS). Red line is the aluminium reference.

In general, the SHP and SLIPS samples prepared from smooth substrates (sSHP and sSLIPS) exhibit excellent anti-icing properties and outperform the SHP and SLIPS samples prepared from rougher substrates (csSHP, csSLIPS, sbSHP, sbSLIPS) across all three cycles. Due to the high standard deviations, it is not possible to make precise comparisons between the different samples or to accurately determine whether the samples prepared from sandblasted substrates (sb) or through cold spraying (cs) perform better. Observing csSHP and sbSHP, it is evident that the sample prepared on the less rough sandblasted substrate retains its properties better than the superhydrophobic substrate, which shows an increase in shear stress value after three cycles. In the case of slippery samples, after three cycles, a decrease in shear stress value is observed for csSLIPS, while sbSLIPS retains its properties better during repeated ice detachment cycles. In conclusion, the samples prepared on smoother substrates appear to ensure better anti-icing properties in both superhydrophobic and slippery surfaces, offering greater durability when subjected to repeated ice detachment cycles. Thanks to my friend and colleague, Amit Goswami, for his invaluable support during the development of the synthetic method for creating the superhydrophobic and slippery substrates.

8. Conclusions

This thesis investigates innovative solutions to mitigate the impact of atmospheric icing on the reliability of electrical infrastructures. With the increasing frequency of extreme weather events linked to climate change, there is an urgent need to implement effective, sustainable, and long-lasting anti-icing solutions. Through a multidisciplinary approach, this research highlighted the potential of passive anti-icing strategies that exploit the chemical and physical properties of materials to mitigate ice and snow accumulation on surfaces.

Elastomeric coatings represent a promising solution to address this issue. Polydimethylsiloxane (PDMS), with its mechanical properties and chemical features, was selected as the ideal candidate. PDMS-based samples were prepared using the commercial formulations Sylgard184 and Sylgard186, with the initial objective of identifying which formulation offered the best performance. During the study, PDMS elastomeric coatings were prepared with the two formulations in the prepolymer-to-curing-agent ratio (A:B) of 10:1, varying the thickness from 200 μm to 950 μm . Coatings prepared with Sylgard186 demonstrated superior anti-icing properties compared to Sylgard184 across all tested thicknesses. The samples were then subjected to ice detachment cycles and 90 days of outdoor aging to evaluate their durability. Both formulations retained their anti-icing properties, with only minor performance degradation due to particulate accumulation on the surface.

The comparison between the two formulations continued by varying the A:B ratio from 1:1 to 30:1. Once again, Sylgard186 demonstrated better anti-icing performances than Sylgard184 across all tested ratios. However, due to the challenging processability of Sylgard186, mostly due to its high viscosity, the study focused on Sylgard184, analysing how anti-icing properties were influenced by variations in curing temperature (25–200°C) and curing time (35 minutes – 24 hours). For the selected ratios (5:1, 10:1, 20:1, and 30:1), the optimal temperature was found to be 100°C, with a curing time between 35 and 60 minutes. Subsequently, the durability of the coatings was tested by analysing the evolution of their properties over 60 days of maturation and subjecting the samples to stress in an accelerated aging chamber. Among the tested samples, the coating prepared with Sylgard184 at a 30:1 ratio and cured at 100°C for 1 hour (Sylgard184 30:1 tt3), exhibited the best anti-icing properties and durability, with an ARF of 6.

The anti-snow properties of the Sylgard184 30:1 tt3 and 10:1 tt2 samples were tested in the artificial snow laboratory (LNA) by applying the coatings to conductor cable segments and simulating dry, hybrid, and wet snowfall conditions. Both coatings performed well against dry

and hybrid snow, with similar behaviour and SRF values around 2. However, the elastomeric coatings showed limited detachment capabilities against wet snow, with only the 30:1 tt3 sample demonstrating partial detachment of the snow sleeve.

Then, Sylgard184 30:1 tt3 sample exhibited the best anti-icing and anti-snow performance, although the surface's high friction coefficient could counteract the expected benefits of the coating's elasticity in facilitating ice detachment.

The 30:1 tt3 sample was used as a substrate for creating a slippery elastomeric coating by infusing a natural lubricant into the PDMS matrix to promote the formation of a stable slippery layer on the surface, further facilitating ice detachment. Different oil concentrations were tested within the matrix, and the effect of oil migration onto the surface was studied over time. The coating prepared with an A:B:lubricant ratio of 30:1:6 exhibited excellent anti-icing properties, achieving an ARF of 44. However, its durability was limited when subjected to stress in an accelerated aging chamber, with the surface lubricant effect degrading and the ARF dropping to 4.5.

Another approach employed to address the issue of high surface friction involved the use of Thermal Spraying to deposit a polyethylene layer onto the coating surface, aiming to create a composite material with enhanced anti-icing properties. The properties were evaluated using two different techniques: a push-test and a centrifuge adhesion test (CAT). The results demonstrated that the desired effect could be achieved, improving anti-icing performance. However, the success of the coating was critically dependent on the thickness of the polyethylene layer. If too thick, the polyethylene layer masked the underlying elastomeric layer, compromising the overall performance of the coating. These findings suggest that while the 30:1 tt3 coating exhibits excellent properties, further optimization is possible by reducing surface friction. Nevertheless, it is essential to preserve the elastomeric properties and ensure the material's durability.

Finally, additional solutions were explored through the creation of superhydrophobic (SHP) and slippery (SLIPS) surfaces on aluminium substrates. The study began with the optimization of the Aluminium-Water reaction, a process that, depending on the experimental parameters, promotes the growth of basic oxides such as boehmite. This oxide, with its distinctive functionalizable nanostructure, significantly enhances the surface's superhydrophobic properties. Subsequently, samples with varying roughness were prepared through sandblasting (sb) and Cold Spraying (cs). Smooth (s) sandblasted (sb), and cold-sprayed (cs) substrates were subjected to the optimized Aluminium-Water reaction and then transformed into superhydrophobic (sSHP, sbSHP, and csSHP) and slippery (sSLIPS, sbSLIPS, and csSLIPS) samples. The properties of these coatings were evaluated through wettability measurements and CAT testing. While superhydrophobic and

slippery surfaces deriving from smooth, sandblasted, and rough substrates exhibited excellent wettability, only the smooth samples (sSHP and sSLIPS) showed outstanding anti-icing properties. These results provide valuable insights for designing superhydrophobic and slippery surfaces for anti-icing applications, highlighting the importance of finding optimal conditions to balance high wettability with effective and durable anti-icing performance.

These findings underscore the potential of elastomeric coatings and surface functionalization in mitigating the effects of atmospheric icing, offering innovative and sustainable solutions. To enable an effective transition to industrial applications, it is crucial to study the durability of coatings under conditions as close as possible to real operational environments, ensuring their ability to maintain anti-icing properties over time despite exposure to environmental and mechanical stress.

This research paved a solid foundation for the development of advanced anti-icing solutions, addressing a global challenge by enhancing the reliability and safety of infrastructures exposed to atmospheric icing phenomena. The next step involves validating these systems in real operational environments, a milestone that will further confirm the effectiveness of the proposed strategies and open new opportunities for industrial-scale implementation.

9. Experimental section

In this chapter, we provide a detailed description of the experimental procedures used for the preparation of the samples, outlining the methodologies employed for their characterization. Additionally, the specifications of the instruments used in the analysis are also presented, highlighting the tools and techniques that enabled the thorough examination of the material properties.

9.1 Materials and Reagents

Aluminium alloy (6082) flat samples ($50 \times 50 \times 2$ mm) and aluminium alloy (6061) flat sample ($30 \times 60 \times 2$ mm) were used as substrates. Sylgard184[®] (Syl184) was purchased from DowSil[™]. The elastomeric kit is constituted by a prepolymer (A) and a cross-linker (B). Data technical sheet for the two formulations are reported at the following links:

<https://www.dow.com/en-us/pdp.sylgard-184-silicone-elastomer-kit.01064291z.html#overview>

<https://www.dow.com/en-us/pdp.sylgard-186-silicone-elastomer-kit.01040286z.html#overview>

Commercially available and thermally sprayable polyethylene (PE, particle size 230 μ m and melting point 128 °C) were used as feedstock powder for preparation of composite materials. Al6061 powder (15 – 50 μ m) was used as feedstock powder for cold spraying deposition. Sodium hydroxide pellets (NaOH) were purchased from Carlo Erba[®]. PDMS silicon oil (65 cP) was purchased from Sigma Aldrich[®].

9.2 Sample preparation

E.3.1 Elastomeric coatings

Part A and Part B of the Sylgard18x elastomer kit were mixed in different A:B weight ratios (1:1, 2:1, 5:1, 10:1, 20:1, 30:1) manually and using a mechanical stirrer. The mixture was degassed under high vacuum for 30 minutes to 1 hour to remove air bubbles trapped during the mixing process.

Al6082 substrates (50 x 50 x 2 mm), which had been previously sandblasted, were cleaned by sonication in acetone for ten minutes and allowed to dry at room temperature. The mixture was deposited using the tape casting method, ensuring control over the coating thickness. Three thickness ranges were used during this doctoral project:

- Range 1 → 0 – 200 μm
- Range 2 → 300 – 600 μm
- Range 3 → 750 – 950 μm

The samples were cured at 25°C (room temperature) for 48 hours or in an oven, with the temperature varied between 100°C and 200°C and the curing time adjusted from 18 minutes to 24 hours. After removal from the oven, the samples were allowed to cool to room temperature and stored in a desiccator. Samples were not washed prior to measurements.

E.3.2 Elastomeric coatings on conductor cable segment

Part A and Part B of the Sylgard184 elastomer kit were mixed in two different A:B weight ratios 10:1 and 30:1 manually and using a mechanical stirrer. The mixtures were degassed under high vacuum for 30 minutes to 1 hour to remove air bubbles trapped during the mixing process.

Segments of aluminium-conductor steel-reinforced (ACSR) cable($\varnothing$ 31.5mm x 750mm) were cleaned by using acetone and allowed to dry at room temperature. The coating was manually applied to the conductor surface using a brush while the system was kept rotating to ensure the formation of a uniform layer around the cylindrical segment. The coated segment was subsequently cross-linked in an oven at 100°C, following the designated heat treatment protocol (ttx).

E.3.3 Elastomeric slippery coatings

Part A and Part B of the Sylgard184 kit were mixed with peanut oil in different A:B:oil weight ratios (30:1:1, 30:1:6) manually and using a mechanical stirrer. The mixture was degassed under high vacuum for 30 minutes to 1 hour to remove air bubbles trapped during the mixing process. Al6082 substrates (50 x 50 x 2 mm), previously sandblasted, were cleaned by sonication in acetone for ten minutes and allowed to dry at room temperature. The mixture was deposited onto the aluminium plates using the "tape casting method," controlling the coating thickness within range 3 (750–950 μm). The samples were cured in an oven at 100°C for 1 hour. After removal from the oven, the samples were allowed to cool to room (25°C) temperature and stored in a desiccator.

E.3.4 Elastomeric composite coatings

PDMS substrates with a thickness within range 3 were prepared following the procedure described in E.3.1, using Sylgard184 30:1 and curing in an oven at 100°C for 1 hour.

PDMS substrates with a thickness of approximately 5 mm were prepared as described in E.3.1, using Sylgard184 30:1 through molds and curing in an oven at 100°C for 1 hour. Molds made of PMMA, with dimensions of either 30 x 60 x 2 mm or 50 x 50 x 2 mm (Fig. E1), were used based on the size of the aluminium substrate. Once cured, the samples were coated with polyethylene (PE) via thermal spraying, using the parameters detailed in Tab. E1. The coated samples were then allowed to cool to room temperature and stored in a desiccator



Fig. E1 PMMA moulds in size 30 x 60 x 5mm and 50 x 50 x 5mm. Thanks to Betul Aktas for the molds.

Feedstock powder: Polyethylene (PE)	Setting a
Distance (mm)	300
Speed (mm/s)	500
Preheating temperature (°C)	100
Number of layers	4
Post heating temperature (°C)	200

Tab. E1

E.3.5 Superhydrophobic and slippery surfaces

Al6082 substrates with dimensions of 30 x 60 x 2 mm and a smooth surface (s) were treated to modify their surface roughness. The samples were either sandblasted (sb) or coated using Al6061 feedstock powder via cold spraying (cs), following the parameters detailed in Tab. E 2

Feedstock powder: Al6061 (15 – 50 μm)	Setting 3
Gas	N ₂
p (barr)	20
Gas pre-heating (°C)	400
Distance (mm)	40
Post heating temperature (°C)	200
Feed (rpm)	2
Speed (m/min)	20
Step (mm)	1.5
Number of layers	4

Tab. E 2

The three different substrates smooth(s) sandblasted (sb) and cold sprayed (cs) were washed by sonicating in ethanol for five minutes and left to dry at room temperature. The 5wt% sodium hydroxide (NaOH) solution was placed inside a glass crystallizer and brought to temperature at 30°C – 35°C using a plate and controlling the temperature with a thermocouple. The substrates are treated in a basic solution for 4 minutes, after which they are extracted and washed with distilled water and left to dry at room temperature. Superhydrophobic samples (SHPs) were created by thermally activating the substrates at a temperature of approximately 100°C and depositing PDMS silicon oil on the surface using a pipette to create a uniform layer. The plates are treated at 250°C to promote the grafting of the PDMS on the surface. After allowing the samples to cool gradually to room temperature, they were washed in hexane to remove excess PDMS and allowed to dry at room temperature. Slippery (SLIPS) samples (sSLIPS, sbSLIPS and csSLIPS) are created by infusion of PDMS silicon oil (65 cP) on the surface through a pipette and stored before measurements at room temperature in a dryer. Thanks to Amit Goswami for his cooperation in developing the method.

9.3 Instruments and Methods

FT-IR spectroscopy

The FT-IR characterizations were conducted with a FT-IR Alpha 1 (Bruker, Billerica, MA, USA) spectrometer with ATR apparatus (diamond crystal was used as the internal reflection element).

Hardness Shore A

Hardness was measured with a Shore A type durometer, according to the ASTM D2240 standard test method⁸⁸ specific for softer elastomer, defining a value within 0–100 H_A (Shore A hardness units). Five measures were recorded on each sample at a distance of at least 6 mm from the edge and 6 mm apart from each other. The spring is indented onto the sample surface for a minimum of 15 seconds and a maximum of 30 seconds to allow the value to stabilize.

Wettability measurements

Static contact angle (SCA) measurements were conducted with a DSA 30 Drop Shape Analyzer (Kruss, Hamburg, Germany) with the sessile drop method using 5 µL volume of water at 20 °C on at least 5 points for each sample. Contact angle hysteresis (CAH), and roll-off angle (RO) measurements were performed at 20 °C with the tilting plate method using a 20 µL volume of water. Five replicates were performed on each sample.

Surface energies measurements

The calculation of the surface energy (SFE) was performed according to the UNI EN 828 standard²⁰¹, using water (SFE = 72.80 mN/m), glycerol (SFE = 63.40 mN/m), and diiodomethane (SFE = 50.80 mN/m) as solvents. The dosing needle was positioned 1 mm above the sample surface. Drops were dispensed with a volume ranging from 2 µL to 6 µL, at a dosing rate not exceeding 100 µL/min. For each coating tested, ten static contact angle measurements were performed for each of the three solvents.

According with literature^{202,203}, the interfacial energy between a solid body and a liquid is the sum of surface tension of two phases ($\sigma_S + \sigma_L$), reduced by the disperse and the polar interactions at the phase border. These interactions are described as the doubled sum of the geometric mean values of the disperse ($\sqrt{\sigma_S^D + \sigma_L^D}$) and the polar ($\sqrt{\sigma_S^P + \sigma_L^P}$) tension components of the individual phases:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2(\sqrt{\sigma_S^D + \sigma_L^D} + \sqrt{\sigma_S^P + \sigma_L^P}) \quad (3)$$

Substitution γ_{SL} from young formula (6) and rearrangement of (3) to the general form of the straight-line $y = mx + q$ leads to the following formula

$$\frac{(1 + \cos \theta)\sigma_L}{\sqrt{\sigma_L^D}} = \sqrt{\sigma_S^P} \frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}} + \sqrt{\sigma_S^D}$$

The square of the slope m is the polar proportion of the solid body surface energy σ_S^P , the square of the ordinate intercept q is the disperse proportion σ_S^D . The sum of the two proportions is the total surface free energy of the solid body. For the evaluation of the surface free energy, the term

$\frac{(1+\cos \theta)\sigma_L}{\sqrt{\sigma_L^D}}$ is plotted against the term $\frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}}$, where θ is the measured contact angle for the individual

liquids, σ_L is the total surface tension of the liquids, σ_L^P and σ_L^D are the polar and the disperse proportions of the total surface tensions of liquids that are tabulated and known. Subsequently, the slope m and the ordinate intercept q of the straight line are determined by linear regression.

Atomic force microscopy

The Atomic force microscopy (AFM) images were collected with Nanosurf Pure Drive both in tapping and wave mode. Young Modulus AFM measurements were collected at CIMAINA, UniMi, using spherical tip with 5 μm of diameter and a maximum indentation around e 2 μm and the data was elaborated using Hertz model on 200 measurements.

Scanning electron microscopy

The surface morphologies were examined using a field emission scanning electron microscope (FE-SEM) (Tescan) and the compositional analysis was conducted with the Energy Dispersive X-ray Spectroscopy (EDX) (Bruker), collecting at least 10 measurements for each sample.

Profilometer

A Bruker Dektak mechanical profilometer was used to measure elastomeric coatings thickness, data are averaged over at least 5 runs for each sample.

Optical profilometer

Surface properties and imaging (Sq and Sa values) were performed using an Alicona Infinite Focus G5 profilometer (Alicona Imaging GmbH, Germany), equipped with the IF-SensorC100 G1 optical system operating with focus variation technique. A grid of 5 rows $\times$ 5 columns was used for imaging, with no vignetting correction applied.

The measurements were performed using an Alicona Infinite Focus G5 profilometer (Alicona Imaging GmbH, Germany) equipped with the IF-SensorC100 G1 optical system, designed for high-resolution surface measurements.

Push-test

Ice adhesion was evaluated using a push-test method performed with a homemade apparatus described elsewhere^{142,204}. Shortly, ice was formed on the surface of the samples in a 10 $\times$ 10 $\times$ 10 mm mold filled with deionized water cooled at -15°C for 2 h. The type of ice reproduced with this method is glaze ice. The sample surface was kept at a constant temperature by means of a Peltier cell, and the experiment was carried out in less than 30 s. A mechanical probe, moved with a constant speed of 0.3 mm/s, detached the ice from the surface by applying a tangent force. Thanks to a load cell connected to the probe, the peak force F needed to detach the ice from the sample was registered. The ice adhesion strength (τ) in shear values can be calculated as follows: $\tau = F/A$, where A is the surface of the specimen in contact with the ice. The shear stresses were measured by performing 4 tests on different specimens for each sample. An untreated aluminium alloy surface was also measured for comparison purposes. Results are also reported in terms of Adhesion Reduction Factor (ARF), the ratio between the shear stress of bare and coated samples: the higher the ARF, the more ice phobic the sample.

*Centrifuge adhesion test*¹⁹¹

Ice adhesion was evaluated using the Centrifuge Adhesion Test (CAT, Fig. E2). The test is divided into two phases: sample preparation and centrifuge testing. During the first phase, the samples are fixed onto a metal bar (340x30mm) and placed inside a chamber with controlled temperature (-10°C) and humidity (77%) for approximately 3 hours. Subsequently, the samples are positioned under the "Icing Wind Tunnel," a system capable of producing various types of ice with different LWC (Liquid Water Content) by adjusting parameters such as flow velocity, water supply rate, pressure, and temperature. Once the ice growth phase is completed, the samples are left overnight in the chamber. The following day, the second phase begins, which involves balancing the metal

bar, securing it to the central rotating pin, closing the protective dome, and initiating the test. The bar is rotated with constant acceleration until ice detachment occurs, which is detected using an acceleration sensor. The bar is weighed before and after the test to measure the mass of ice removed. By measuring the adhesion area and knowing the rotation speed at the time of detachment, it is possible to calculate the shear stress (kPa) required to remove the ice from the surface.



Fig. E2 Left Icing wind tunnel used to create ice on the surface of the samples. At right is the centrifuge used to calculate anti-icing properties through shear stress evaluation¹⁹¹. Thanks to Niklas Kandelin and Ruqaya Khammas for help during measurements.

Outdoor aging

The outdoor aging of Sylgard184 and Sylgard186 was conducted by placing the samples on a 45-degree inclined support, where they were left exposed to the outdoor environment for 3 months (90 days). The coatings were exposed from 5/10/22 to 4/1/23. To assess the effect of UV radiation, the samples were washed with ethanol prior to analysis to remove any particulate matter and dirt. In addition, some samples were analysed without the washing step to evaluate the direct impact of weathering, along with the accumulation of particulate matter and dirt on the surface.

Accelerated aging

Accelerated aging involves stress test cycles: stress phases named A, B, C, D, with a total duration of about one week. The transition interval from one step to the next lasts 1 hour. The weekly test cycle is repeated 4 times for a total of 564 hours of tests. The duration and the description of the applied parameters is reported in Tab. E3. The accelerated aging was performed using two different chambers: an Atlas® Xenotest 440 climate weathering test chamber (Fig. E3, left) was

used for phases A to C, and a Weiss Technik® ClimeEco C7.1000 climate chamber (Fig. E3, right) was used for the tests required in phase D. For the generation of the required test parameters, the accelerated climate aging chambers is equipped with an ultrasonic nebulizer for humidity control, and nozzles used for sprinkling the samples, which use demineralized water. To generate and maintain the temperature required by the technical prescription, the machine uses the heat produced by Xenon arc lamps placed in the centre of the test space. The effect of solar radiation is provided by two Xenon lamps with a total power of 4.4 kW.

Phase	Duration	Environmental stress	Description
A	24h	Thermal cycle	In a climatic chamber, specimens are subjected to follow cycle: ● Stay at $+80^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for $1\text{h} \pm 10\text{min}$. ● Transition from $+80^{\circ}\text{C}$ to -30°C in $1\text{h} \pm 10\text{min}$. ● Stay at -30°C to $+80^{\circ}\text{C}$ in $1\text{h} \pm 10\text{min}$. ● Transition from -30°C to $+80^{\circ}\text{C}$ in $1\text{h} \pm 10\text{min}$. The relative humidity (RH) of the air at 80°C must be $\geq 95\%$, achieved through steam or by misting demineralized water. Cycle is repeated for 6 times
B	71h	Irradiation by UV lamps	In an aging chamber, specimens are homogeneously irradiated with UV lamps from 300 to 400 nm at the following conditions: ● Power (P) = $1 \pm 0.1 \text{ kW/m}^2$ ● Relative humidity (RH) $\leq 30\%$ ● T = $80 \pm 2^{\circ}\text{C}$
C	23h	Irradiation by broad-spectrum lamps and spraying with demineralized water	Specimens are homogeneously irradiated with UV lamps from 300 to 400 nm and sprayed with demineralized water at the following conditions: ● Power (P) = $1 \pm 0.1 \text{ kW/m}^2$ ● Relative humidity (RH) $\geq 60\%$ ● T = $60 \pm 2^{\circ}\text{C}$ ● Water flux = $0.2 \pm 0.4 \text{ ml/min}$ ● Water temperature = $15 - 30^{\circ}\text{C}$ ● Spraying duration = 5 minutes ● Spraying frequency = 25 minutes
D	23h		Specimens are homogeneously irradiated with UV lamps from 300 to 400 nm and sprayed with demineralized water at the following conditions: ● Power (P) = $1 \pm 0.1 \text{ kW/m}^2$ ● Relative humidity (RH) $\leq 60\%$ ● T = $80 \pm 2^{\circ}\text{C}$ ● Water flux = $0.2 \pm 0.4 \text{ ml/min}$ ● Water temperature = $15 - 30^{\circ}\text{C}$ ● Spraying duration = 5 minutes ● Spraying frequency = 25 minutes

Tab. E3



Fig. E3 On the left Atlas® Xenotest 440 climate weathering test chamber. On the right Weiss Technik® ClimeEco C7.1000 climate chamber. Thanks to Paolo Gadia for the tests.

Test in Artificial Snow Laboratory

The different types of snow were obtained by varying the following parameters (Tab. E4):

Parameters	Dry snow	Hybrid snow	Wet snow
Air setpoint (°C)	-1.0	-0.5	-0.5
Brine setpoint (°C)	-8.0	-8.0	-8.0
Air compressor (ON/OFF)	OFF	ON	ON
Brine to SM setpoint (°C)	-2.0	-1.0	-1.0
SM basin temp setpoint (°C)	5.0	5.0	5.0
Sm housing temp setpoint (°C)	5.0	5.0	5.0
Water level setpoint (%)	100	100	100
Drum speed setpoint (%)	150	150	175

Tab. E4

Snowphobicity tests were carried out in an artificial snow laboratory, maintained at temperatures near 0 °C. The ACSR conductors, both coated and bare, were slowly rotated (1 rpm) under a flux of artificial snow for 6 hours, to induce the growth of the snow sleeve. The weight of the snow sleeve grown on the samples and on the reference was recorded throughout the duration of the snowfalls.

This method is based on measuring the heat exchanged during the melting of snow in hot water: when hot water, at temperature T_1 , is added to wet snow, the heat lost by the mass of hot water is equal to the heat absorbed by the ice fraction melting added to heat needed to bring the whole mass of water from 0°C to the final temperature T_2 .

The general relationship that describes the energy balance during the melting process of the snow is:

$$m_w C_{p,w} = (T_1 - T_2) = m_{sn} [(1 - LWC) L_f + C_{p,w} (T_2 - T_0)]$$

where m_w is the mass of hot water, $C_{p,w}$ its specific heat capacity, m_{sn} is the mass of snow, L_f is the latent heat, and T_0 is the freezing temperature of ice. The procedure to perform the calorimetric test is relatively quick: initially, the mass of the empty container (M_T) is measured, and it is filled with a defined amount of warm water between 33 and 35°C, measuring the total mass (M_1) and the initial temperature (T_1). After adding the snow sample, the final mass (M_2) and the final temperature (T_2) of the water-snow mixture are measured. The mass of hot water (m_w) and the mass of the snow (m_{sn}) can be expressed as:

$$m_w = M_1 - M_T \text{ and } m_{sn} = M_2 - M_1$$

The formula can now be expressed as follows:

$$LWC = 1 - k[R(T_1 - T_2) - T_2]$$

$$R = \frac{M_1 - M_T}{M_2 - M_1}, k = \frac{C_{p,w}}{L_f} = 1.25 * 10^{-2} K^{-1}$$

The materials and practical steps required for measuring the Liquid Water Content (LWC) are outlined below.

Required instruments:

- Calorimeter or thermally insulated container.
- Balance (sensitivity: 0.01 g);
- Temperature probe (sensitivity: 0.01 °C).

Procedure:

- Weigh the empty, completely dry container (MT).
- Open the container and pour water at approximately 35 °C into the calorimeter (between 250 and 500 g of water).
- Close the container and weigh it again (M1).
- Close the calorimeter and shake it.
- Insert the temperature probe into the container and record the temperature once it stabilizes (T1).
- Take a sample of snow (preferably with a mass between approximately 1/6 and 1/9 of the mass of water previously added).

10. Appendix

10.1 Focus on polydimethylsiloxane (PDMS)

Silicones play a fundamental role in materials science due to their properties and versatility, which allow for their use in various forms, from lubricating fluids to solid elastomers^{205,206}. They are characterized by a backbone of silicon-oxygen bonds (Si-O-Si) with substituents of varying chemical nature attached along the chain (Fig. A1).

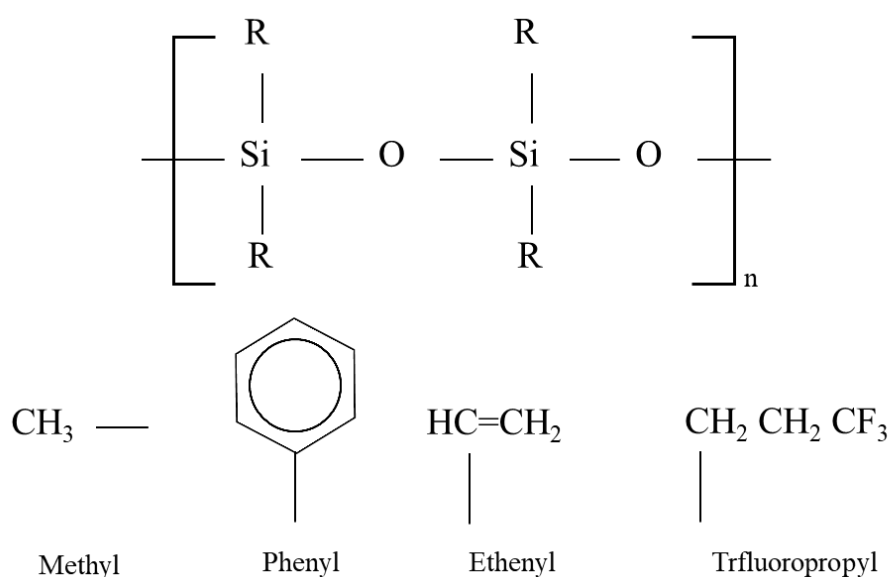
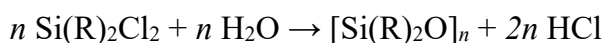


Fig. A1 Structure formula of silicones with some examples of possible substituents on the side chain.

Silicones are synthesized through the hydrolysis of chlorosilanes, producing oligomeric and/or cyclic species that subsequently react to extend the polymer chain²⁰⁷:



One of the most compelling aspects that makes this class of polymers unique is the ability to control and modulate the chemical-physical properties of materials by selecting various chlorosilane monomers and introducing specific functional groups along the polymer chain^{208–210}. Polydimethylsiloxane (PDMS)^{211–213} is one of the most prominent and widely used polymers within the silicone family, characterized by the presence of methyl groups (CH₃) (Fig. A2). In this case, dimethyldichlorosilane is used as the monomer, which undergoes hydrolysis to form intermediate species that condense to create the main polymer backbone. As previously noted, the synthesis yields not only oligomeric species but also cyclic compounds such as octamethylcyclotetrasiloxane (D4) and hexamethylcyclotrisiloxane (D3), which can be separated

by distillation and used as monomers in a ring-opening polymerization (ROP) process²¹⁴ (Fig. A3).

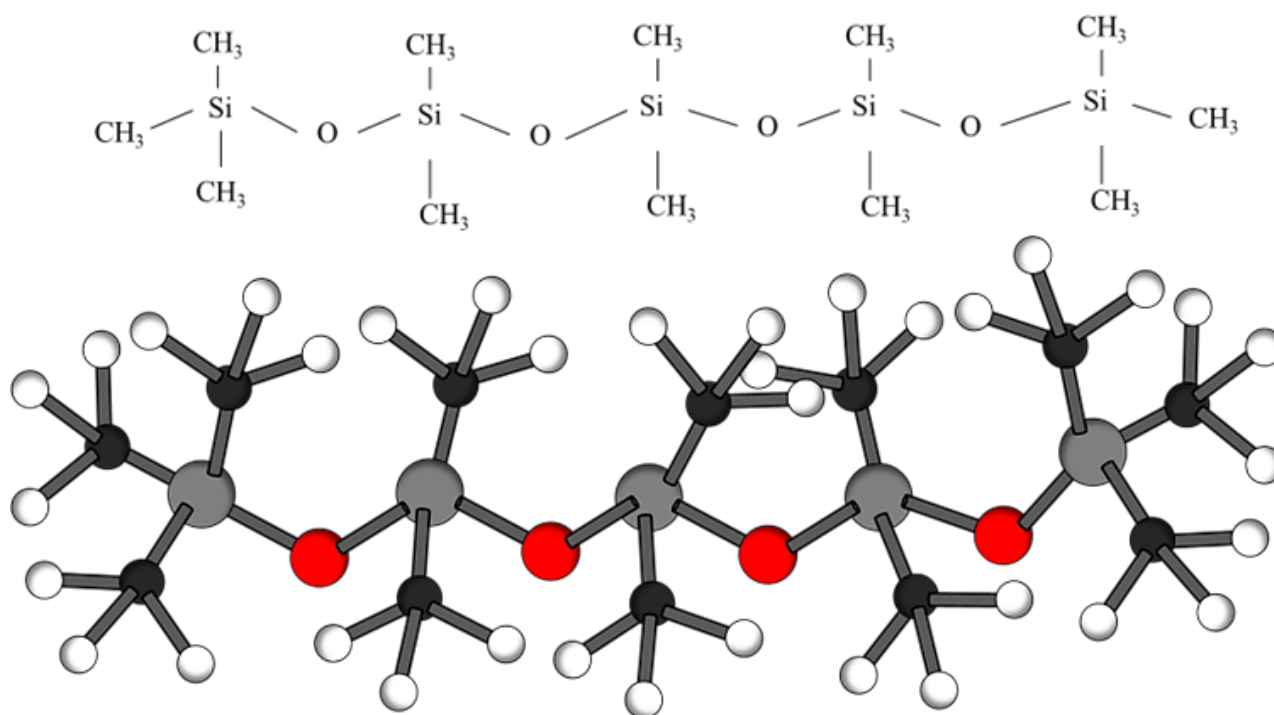


Fig. A2 Polydimethylsiloxane (PDMS). White ball = Hydrogen; Black ball = Carbon; Grey ball = Silicon; Red ball = Oxygen.

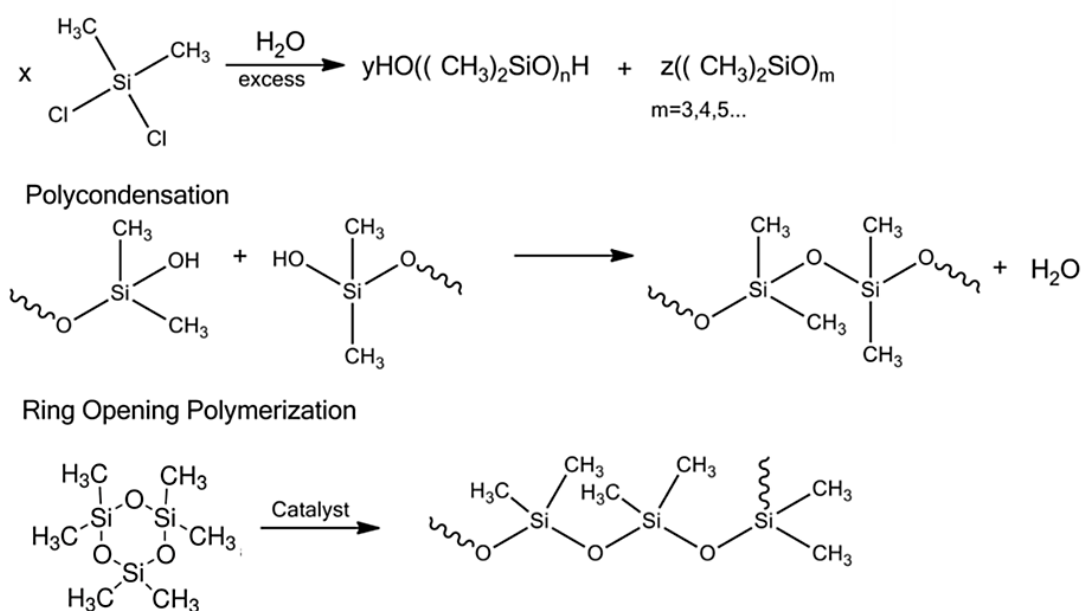


Fig. A3 Preparation mechanism of polydimethylsiloxane.

The Si-O bond has a length of approximately 1.63 Å, longer than the typical C-O bond length (1.42 Å). This length, combined with a low rotational energy barrier (3.3 kJ/mol), grants the polymer chains high conformational freedom and flexibility. Due to the lower electronegativity

of silicon (1.8) compared to carbon (2.5), the Si-O bond is polarized and exhibits a highly ionic character, with a bond energy of 451 kJ/mol as opposed to 355 kJ/mol for the C-O bond. In contrast, the Si-C bond has a strength comparable to the single C-C bond (318 and 348 kJ/mol, respectively). These values partly account for the thermal and chemical stability of PDMS: the Si-O bond, characterized by high energy, is particularly strong and endows the structures with durability by resisting homolytic cleavage typically involved in oxidative degradation. The O-Si-O bridge involves partial overlap between the empty d orbitals of silicon and the filled p orbitals of oxygen. This delocalization reduces the basicity and nucleophilicity of the oxygen atoms, rendering the system chemically inert²⁰⁷. The presence of methyl groups enhances the hydrophobicity of the polymer, limiting potential interactions with water and bringing the surface energy of PDMS down to around 20.4 mN/m—substantially lower than that of many other polymer classes. The siloxane chain adopts a configuration that ideally exposes as many side groups as possible outward, creating a hydrophobic layer. This synergy contributes to the material's inertness and durability²¹¹. Weak intermolecular interactions between chains significantly lower the glass transition temperature, while conformational freedom provides a higher free volume, resulting in high gas permeability and hydrocarbon solubility and swelling^{205,212}. This structure gives PDMS a unique combination of properties: flexibility, chemical resistance, thermal stability. In the context of anti-icing applications, PDMS is particularly attractive due to its ability to reduce ice nucleation and adhesion, thanks to its hydrophobic and elastic properties. To fully exploit the elastic properties of this polymer, a cross-linking step is required. PDMS can be vulcanized using three main approaches^{205,210}:

- Condensation cross-linking^{67,215}
- Peroxide cross-linking^{216,217}
- Hydrosilylation cross-linking^{71,218,219}

Condensation cross-linking, which employs curing agents such as alkoxysilanes (e.g., TEOS, TMOS, MTEOS, methyltriacetoxysilane), which may also be directly anchored to the main polymer chain (Fig. A4)

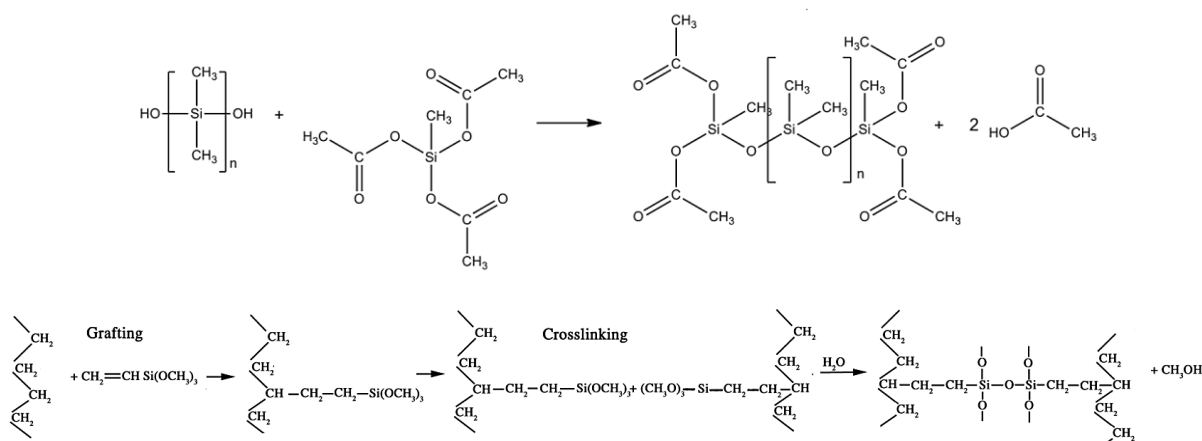


Fig. A4 Example of cross-linking mechanism through condensation for PDMS. The process can be catalyzed by acids and bases.

Alternatively, monomers such as trichloromethylsilane can be used during polymerization to restrict linear growth, thereby favouring the formation of a three-dimensional network due to an increased number of hydroxyl groups along the chain.

Cross-linking with peroxides is less commonly employed, as it requires the presence of vinyl functionalities along the polymer chain, which can be introduced by adding monomers such as 1,3-divinyltetramethyldisiloxane during polymerization²²⁰. Subsequently, cross-linking can proceed through the thermal activation of a peroxide initiator, as shown in Fig. A5²²¹.

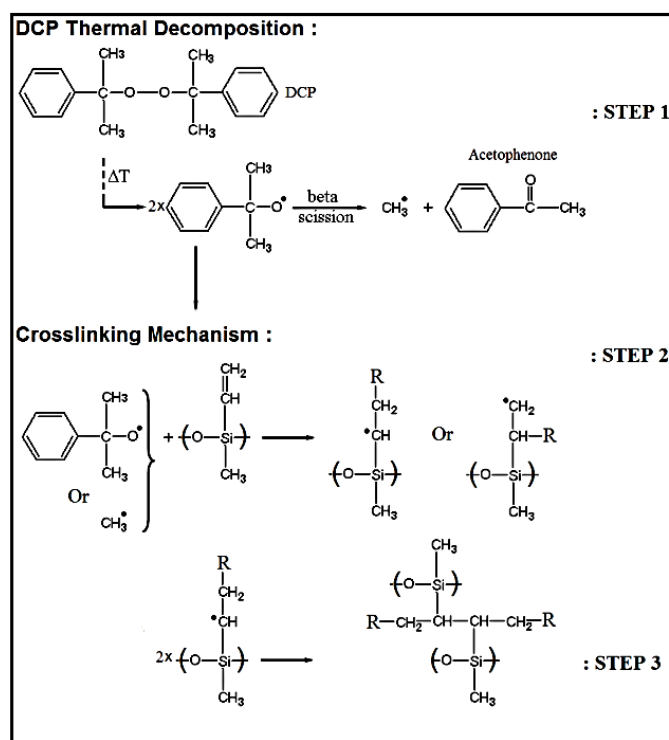


Fig. A5 The initiation step is the thermal decomposition of the initiator to give two cumyloxy free radicals (step 1). Therefore, next step is the addition of cumyloxy radicals to a double bond of the polymer molecule (step 2). Two of these polymeric radicals then combine to form a cross-link that is a more stable bond (higher bonding energy, 347 kJ/mol) with superior heat aging and oxidation resistance (step 3).

A third crosslinking method involves the hydrosilylation reaction (2) between a vinyl group ($\text{H}_2\text{C}=\text{CHR}$) and an Si-H bond in the presence of a metal-based catalyst, such as Karstedt's catalyst (Fig. A6).

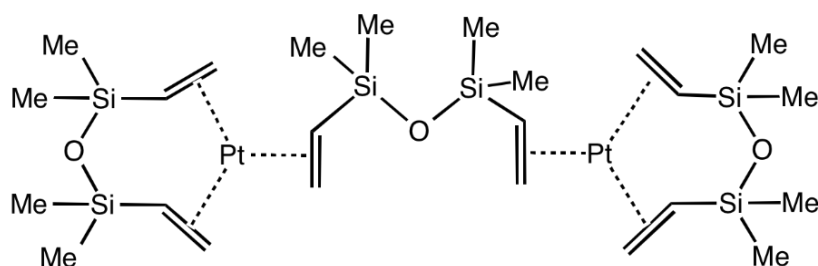
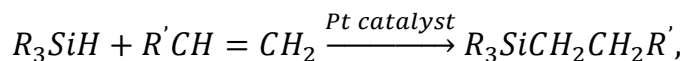


Fig. A6 Karstedt's catalyst.

The commonly invoked mechanism is the Chalk-Harrod cycle²²² (Fig. A7), which involves the following steps:

- I. *Oxidative addition* with the cleavage of the Si-H bond and σ -coordination of a hydride (M-H) and a trialkylsilyl group (M-SiR₃)
- II. *π -coordination* of the alkene to the metal
- III. *Migratory insertion* of the alkene into the Si-H bond (rate-determining step)
- IV. *Reductive elimination* with formation of the Si-C bond and restoration of the starting catalyst

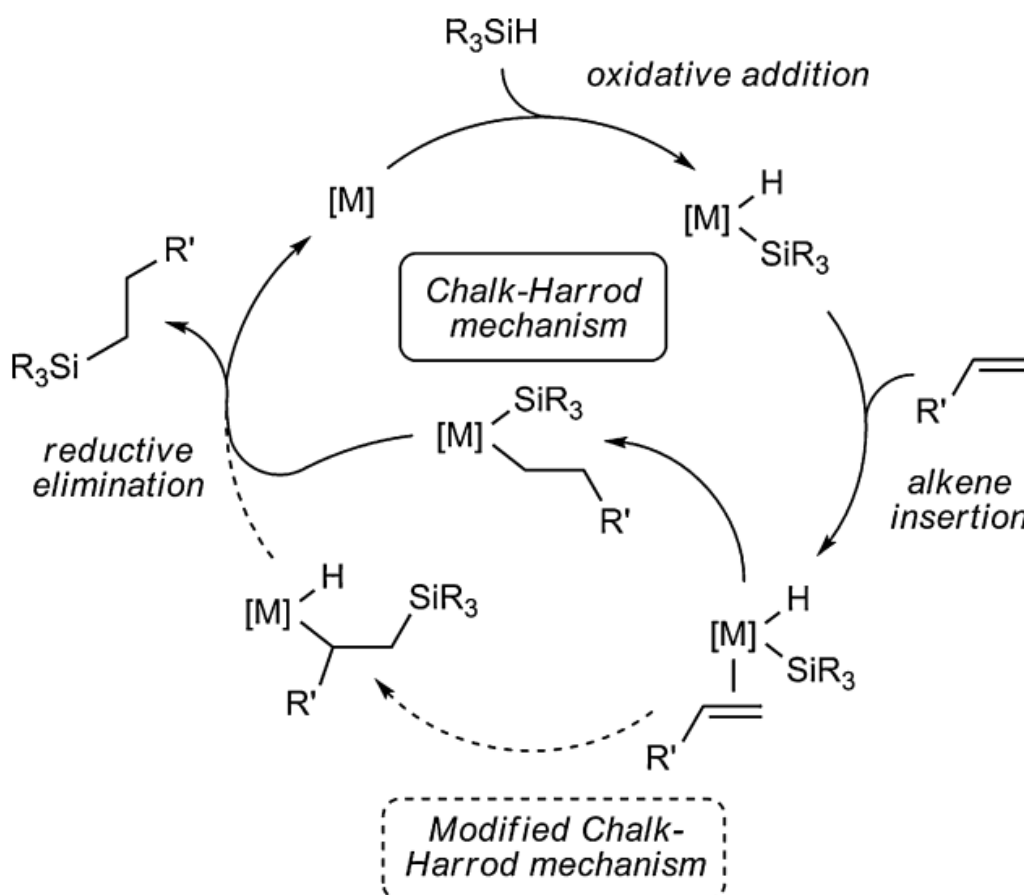


Fig. A7 Chalk-Harrod mechanism²²²

The hydrosilylation reaction typically proceeds through an *anti-Markovnikov mechanism*, where silicon tends to bond with the terminal carbon during the reductive elimination step, promoting the linear growth of the chains²²³.

Unfortunately, crosslinking methods do not always proceed as expected, and often side reactions can occur, leading to reduced yields of the desired product due to the reactivity of the functional groups involved^{224,225}. In some cases, during the crosslinking step, by-products may be released that affect PDMS properties and interact with the target substrate to be coated²⁰⁷. Peroxide-based crosslinking is less commonly used for PDMS due to its lower stability and the high temperatures required, which can alter the hydrophobic properties of the material²²¹. In the field of advanced materials, it is crucial to develop formulations that ensure the production of polymers with well-defined and reproducible properties, essential for ensuring effectiveness in specific applications.

10.2 Supporting Materials

FT-IR spectroscopy

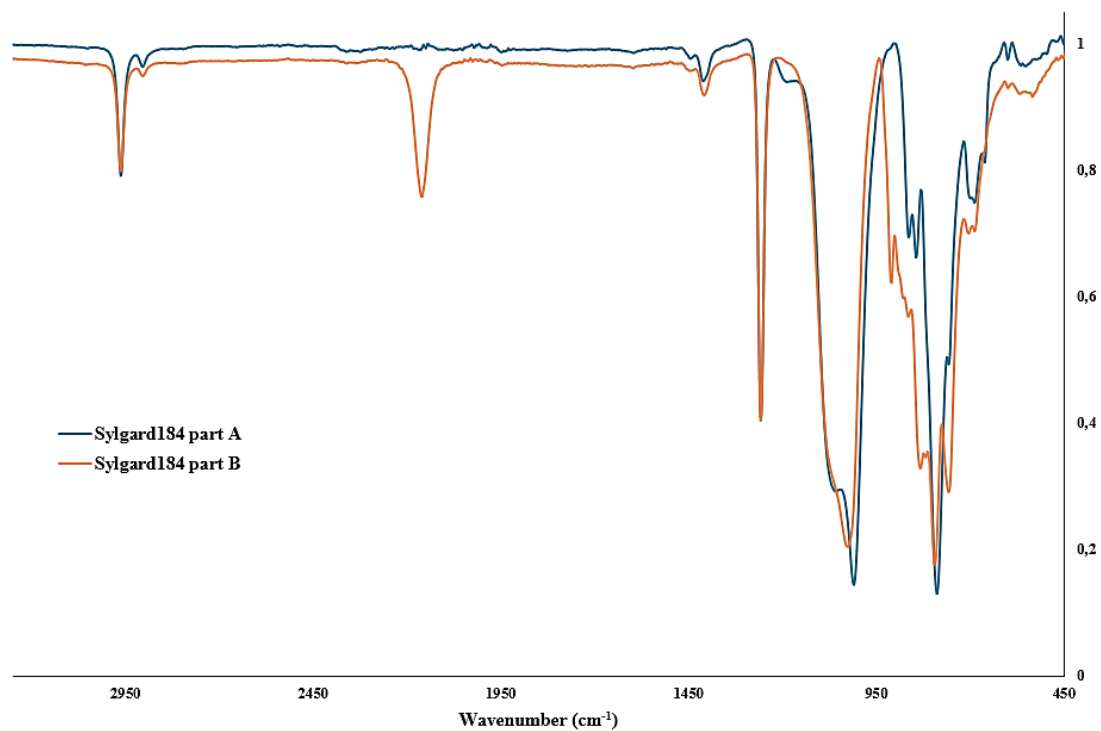


Fig. A8 Comparison of the IR spectra of part A and part B of Sylgard184.

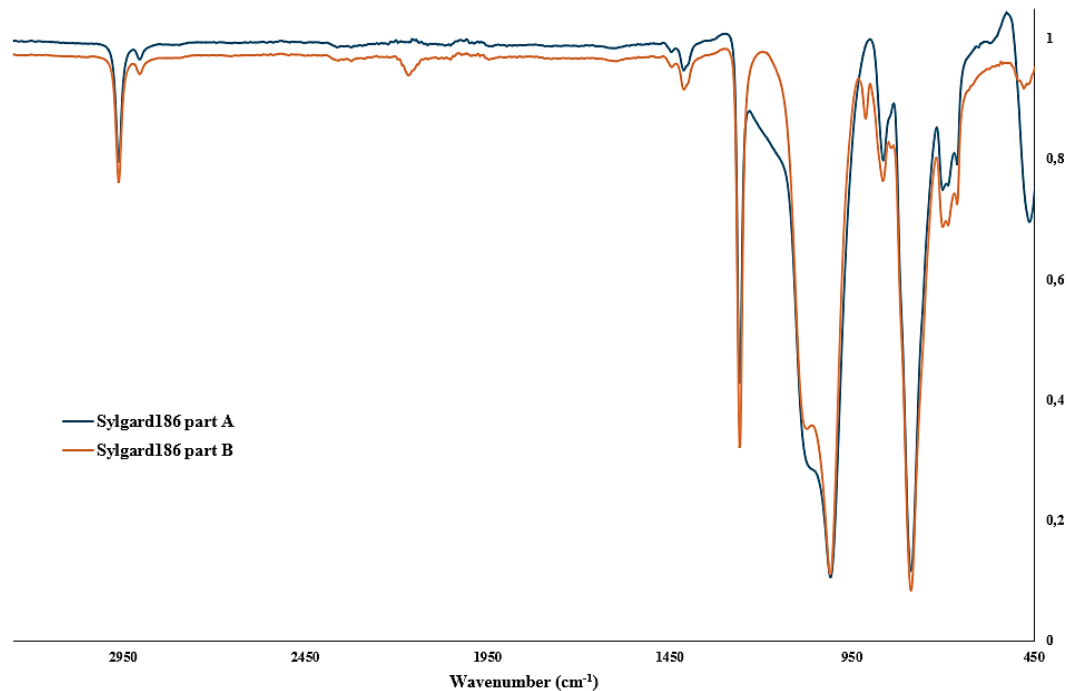


Fig. A9 Comparison of the IR spectra of part A and part B of Sylgard186.

For both formulations (Fig. A8 and Fig. A9), both Part A and Part B exhibit signals corresponding to the asymmetric stretching of the methyl groups (2962 cm^{-1}), the stretching of the Si-CH₃ bond (788 cm^{-1}), the bending of the C-H bonds (1258 cm^{-1}), and Si-O-Si stretching ($1010\text{-}1061\text{ cm}^{-1}$). For Sylgard184 Part B, the Si-H stretching peak at 2160 cm^{-1} is observable, which is absent in Part A (Fig. 41a). For Sylgard186 Part B, the intensity of the Si-H peak at 2163 cm^{-1} is lower compared to Sylgard184 (Fig. 41b). Again, the Si-H signal is absent in Part A, while the vinyl C-H deformation signal (1460 cm^{-1}) is present in both Part A and Part B.

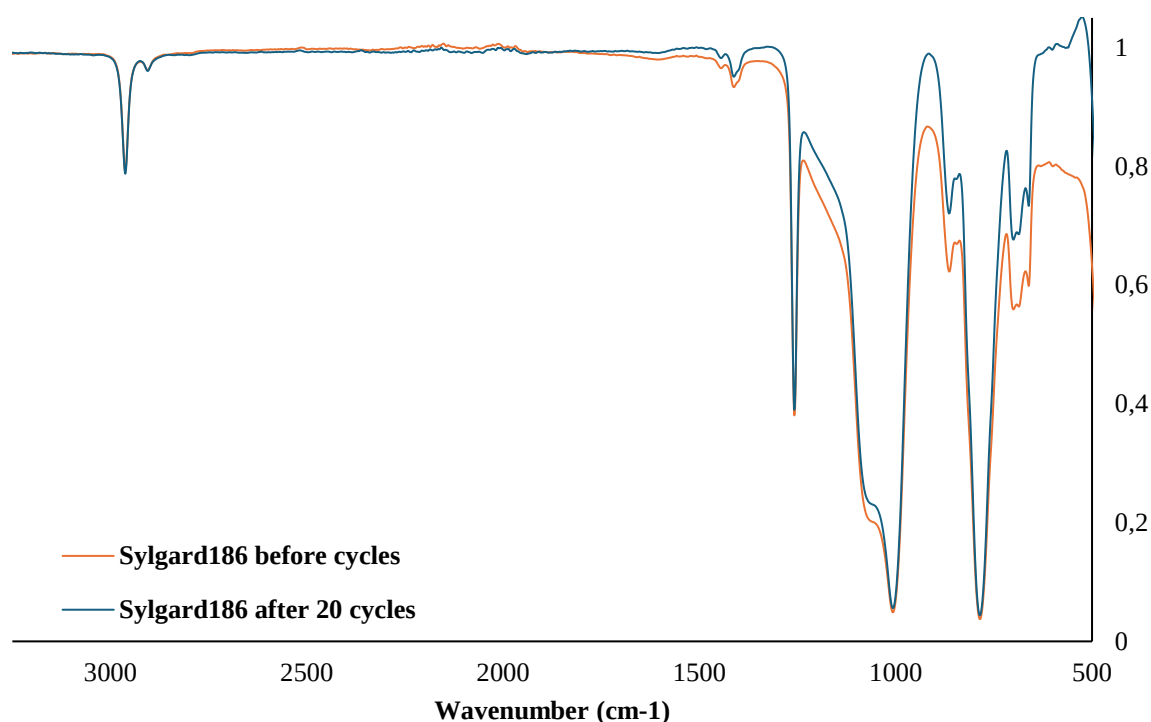


Fig. A10 IR spectra of Sylgard186 prior (orange) and after (blues) stress cycles.

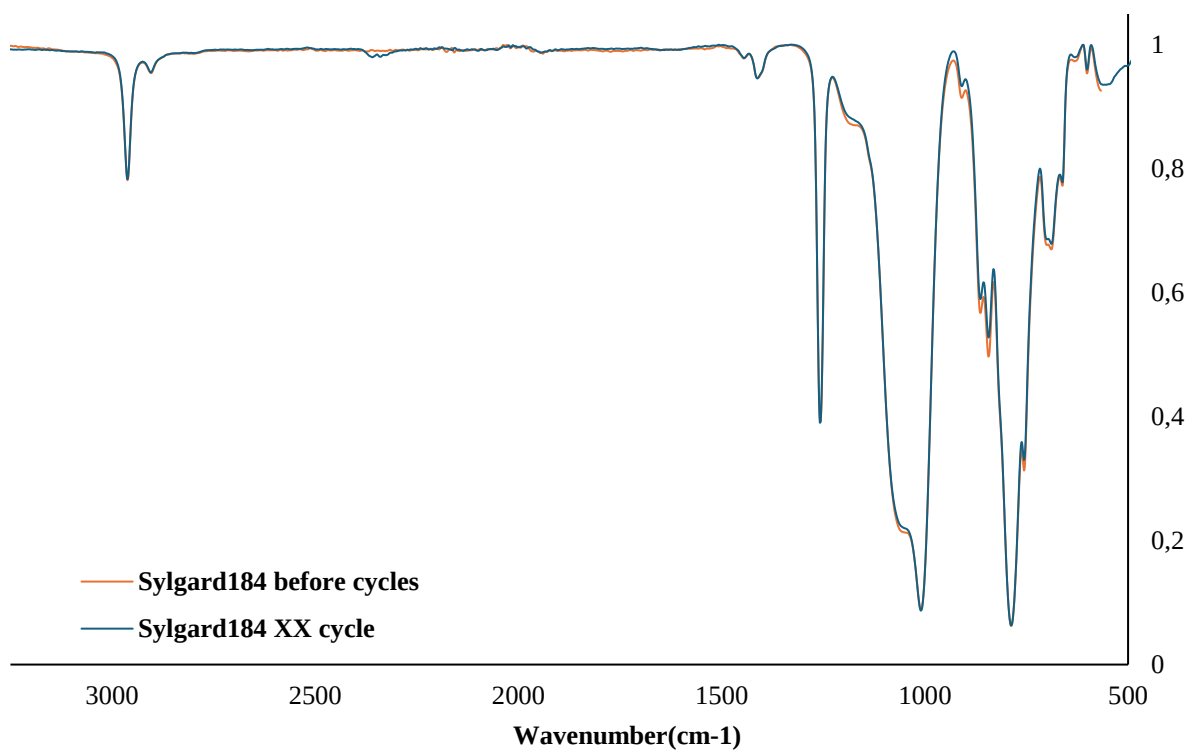


Fig. A11 IR spectra of Sylgard184 prior (orange) and after (blues) stress cycles.

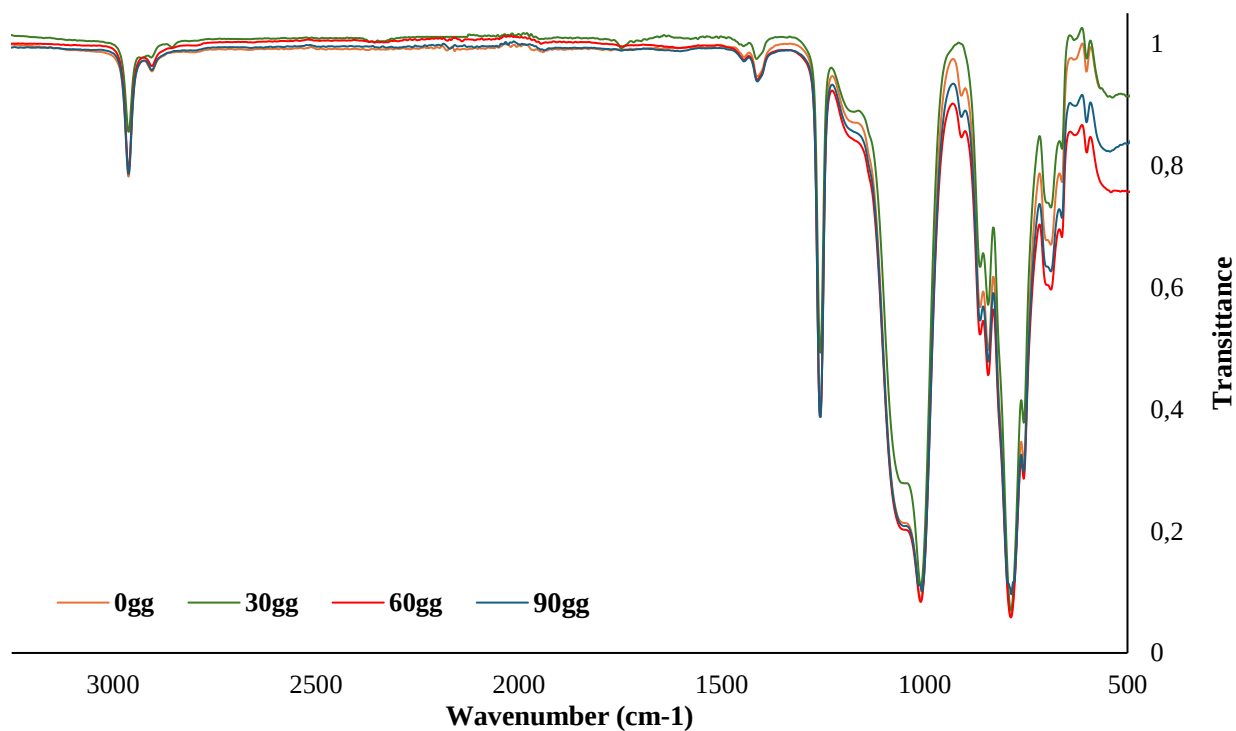


Fig. A12 FTIR spectra of Sylgard184 10:1 aged outdoor for different time periods (the surfaces are washed before FTIR analysis to isolate the possible effect of solar radiation of the PDMS).

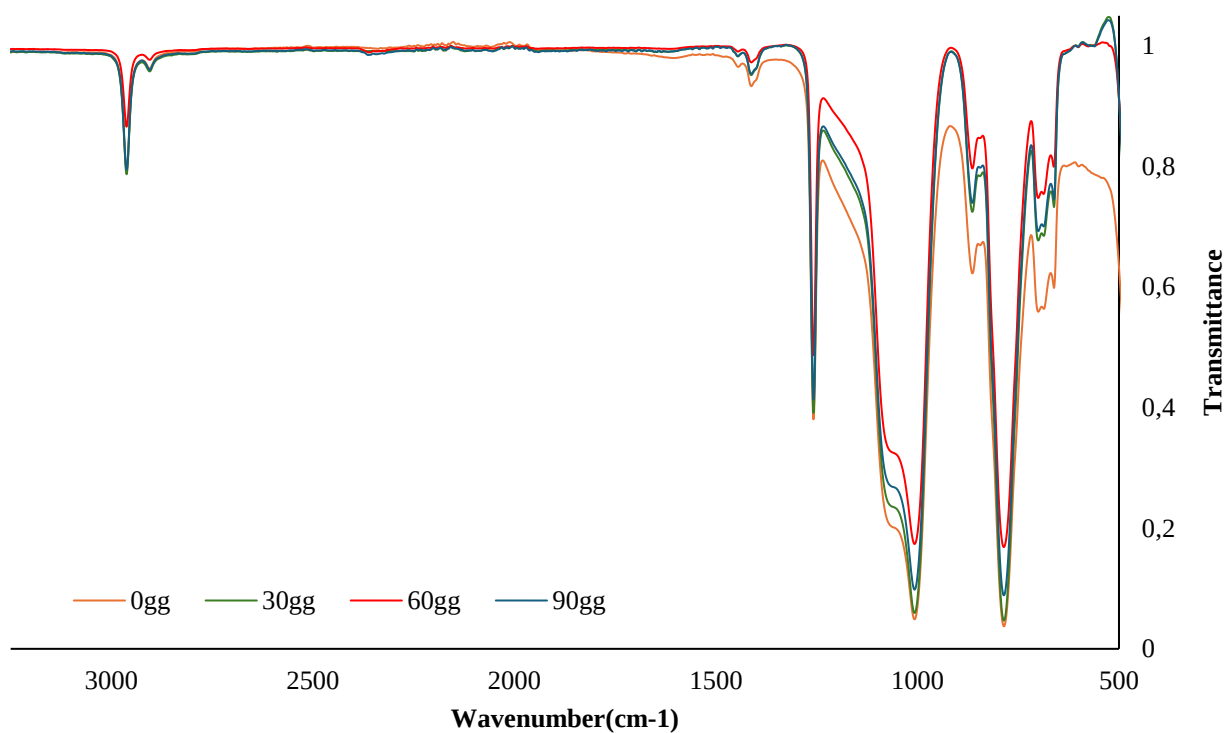


Fig. A13 FTIR spectra of Sylgard186 10:1 aged outdoor for different time periods (the surfaces are washed before FTIR analysis to isolate the possible effect of solar radiation of the PDMS).

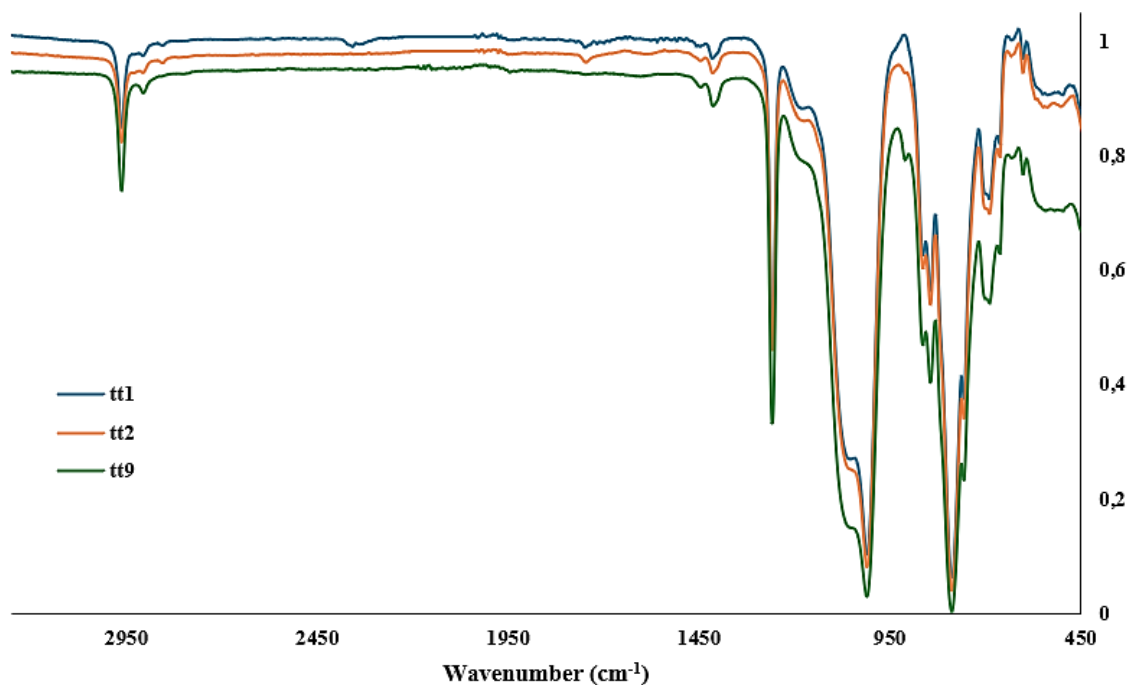


Fig. A14 Sylgard184 tt1, tt2 and tt9 IR spectrum comparison.

In Fig. A14 we can observe the asymmetric stretching of the methyl groups (2962 cm^{-1}), the stretching of the Si-CH₃ bond (788 cm^{-1}), the bending of the C-H bonds (1258 cm^{-1}), and the Si-O-Si stretching ($1010\text{-}1061\text{ cm}^{-1}$).

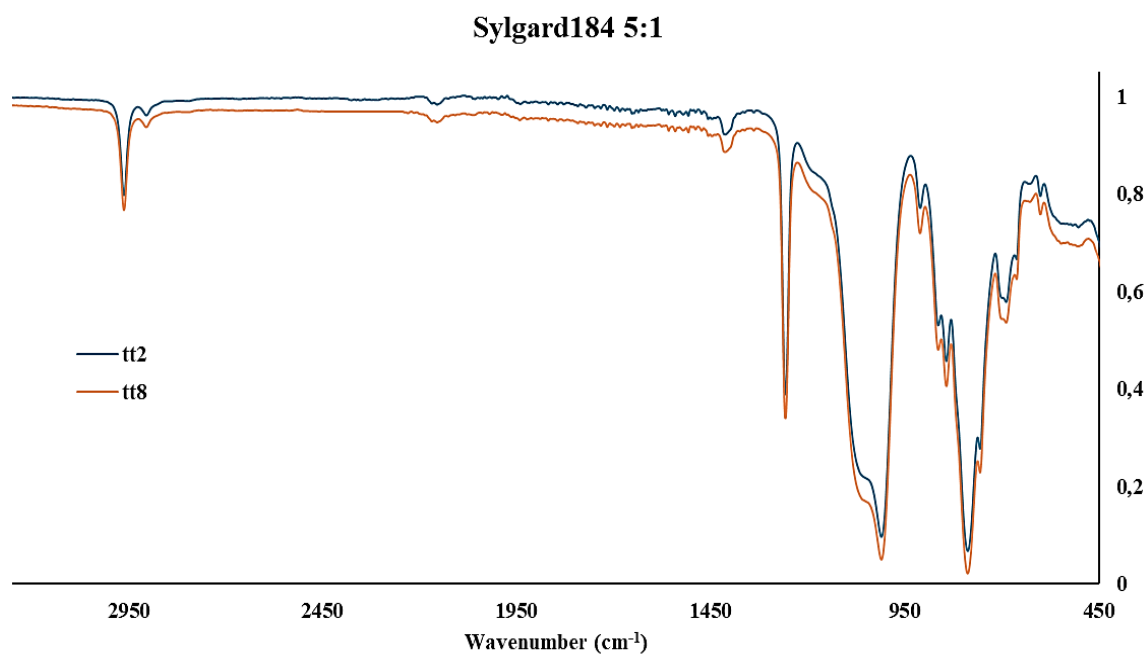


Fig. A15 Comparison of the spectrum of Sylgard184 5:1 tt2 and tt8 sample. No differences are observed between the two thermal treatment, with the Si-H stretching peak at 2150 cm^{-1} visible up to 24h (tt8) of treatment.

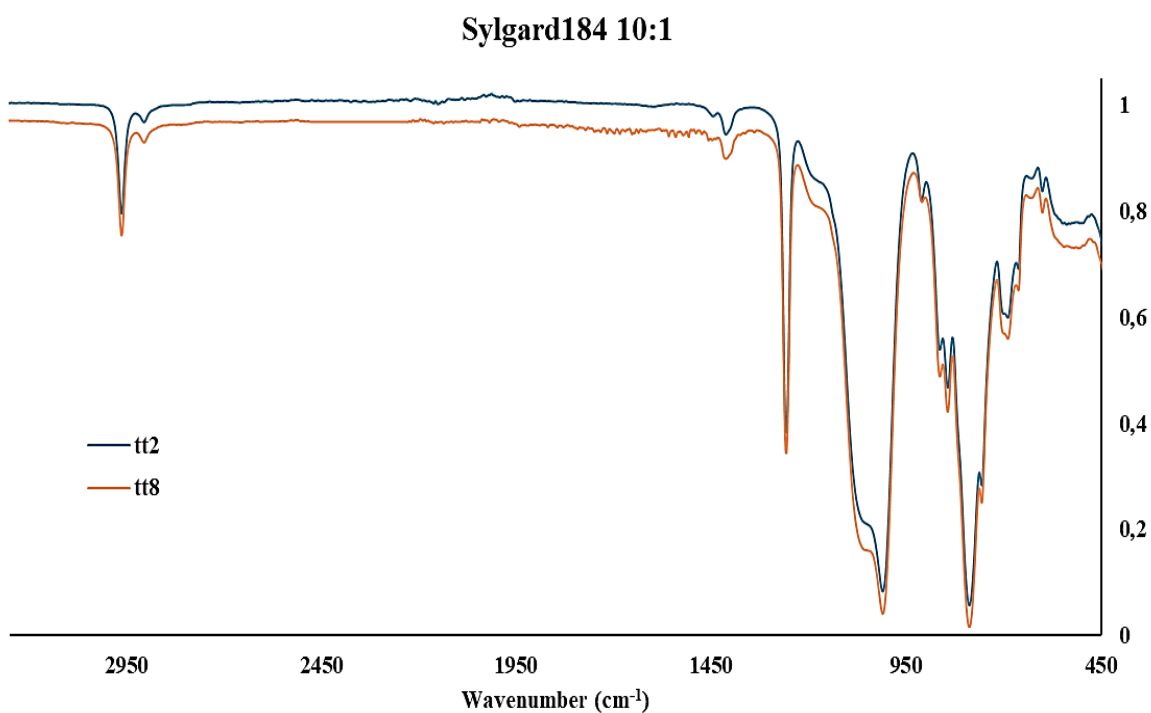


Fig. A16 Comparison of the spectrum of Sylgard184 10:1 prepared with tt2 and tt8. No differences are observed between the two thermal treatment.

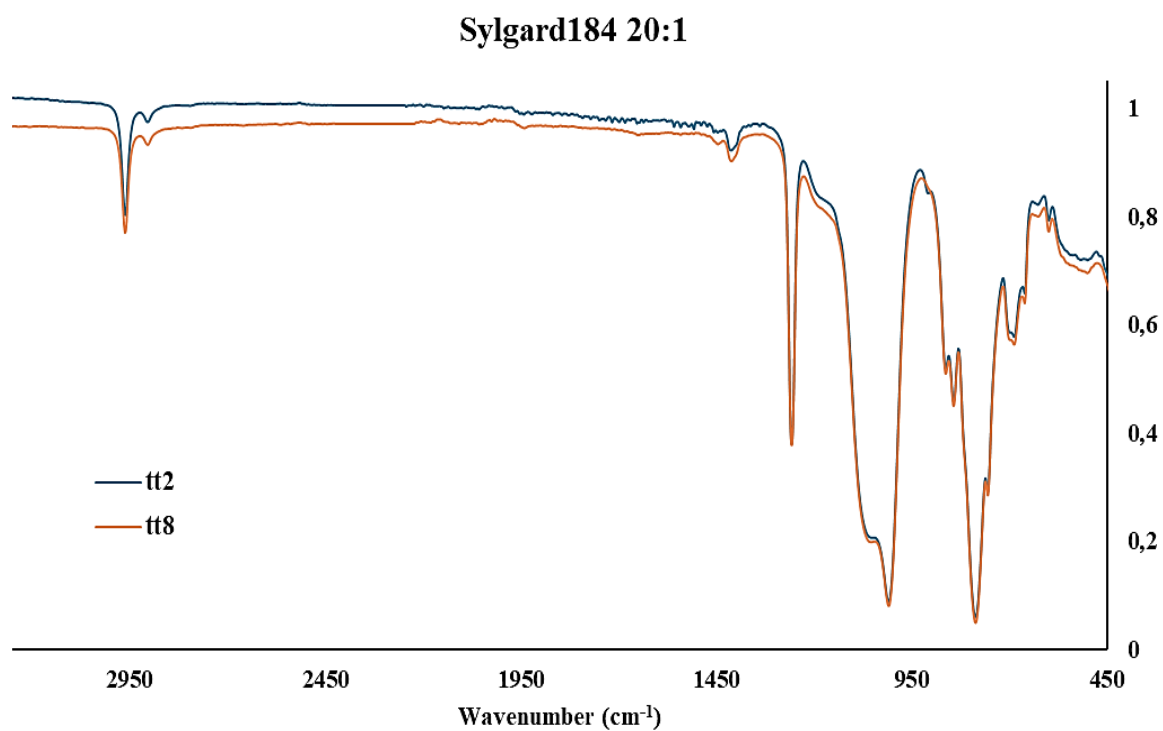


Fig. A17 Comparison of the spectrum of Sylgard184 20:1 tt2 and tt8. No differences are observed between the two thermal treatment.

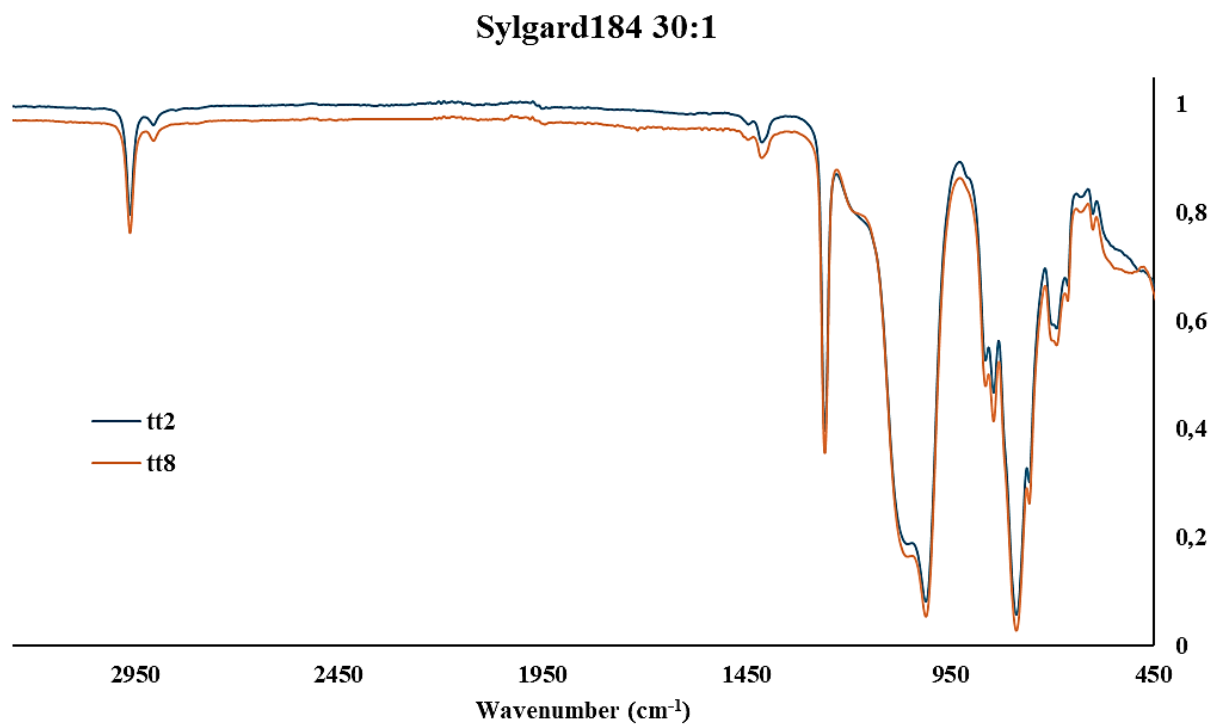


Fig. A18 Comparison of the spectrum of Sylgard184 30:1 tt2 and tt8. No differences are observed between the two thermal treatment.

For each A:B mixing ratio, only the spectra corresponding to the least intensive heat treatment (tt2) and the most prolonged heat treatment (tt7) are presented for comparison, to streamline the analysis and avoid displaying an excessive number of spectra.

Sylgard184 5:1 tt2

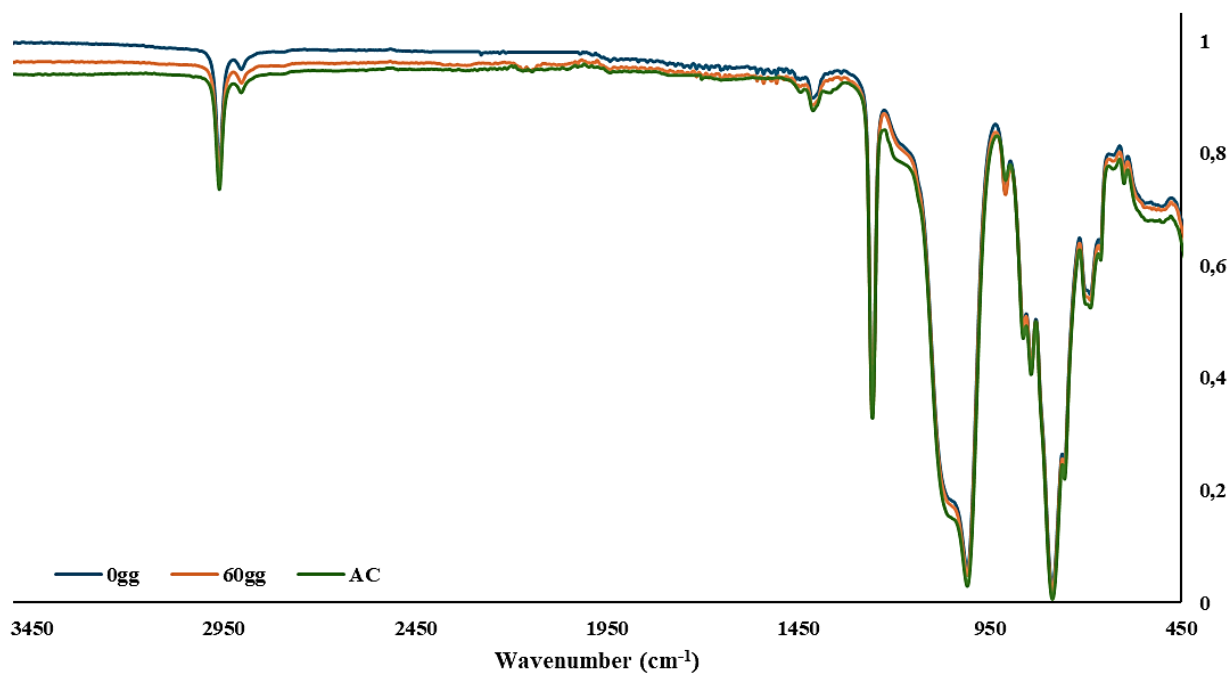


Fig. A19

Sylgard184 5:1 tt7

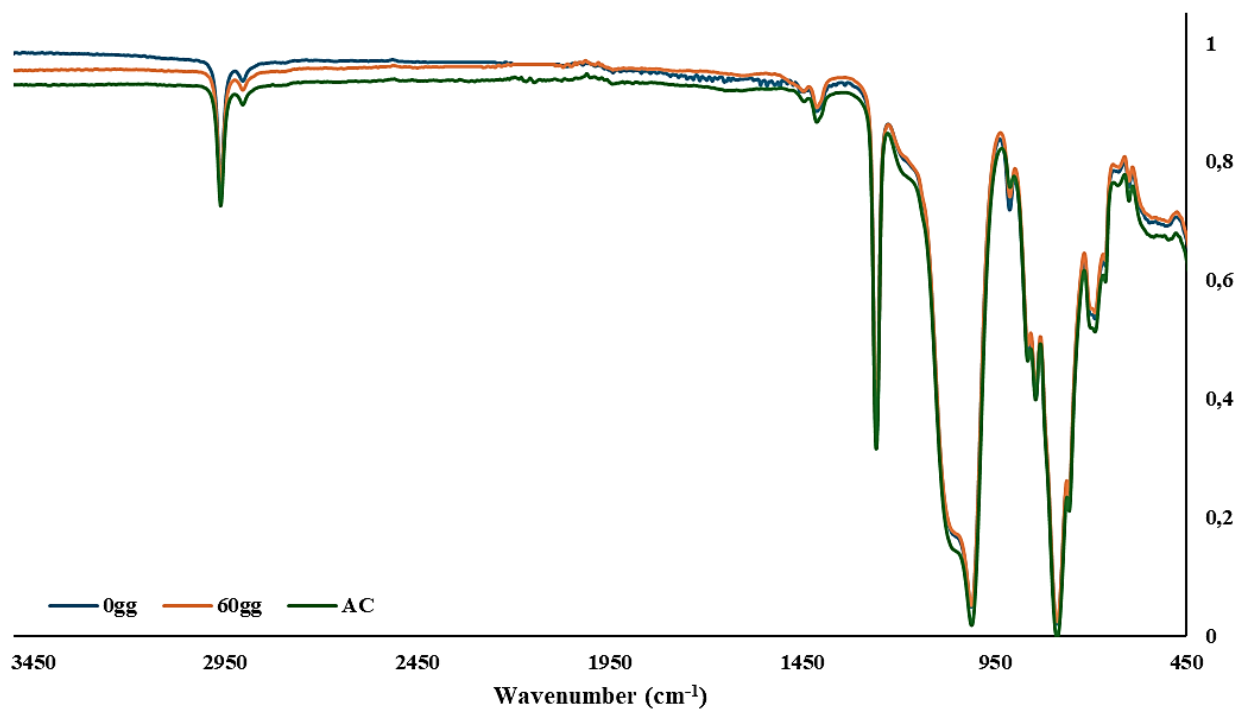


Fig. A 20

Sylgard184 10:1 tt2

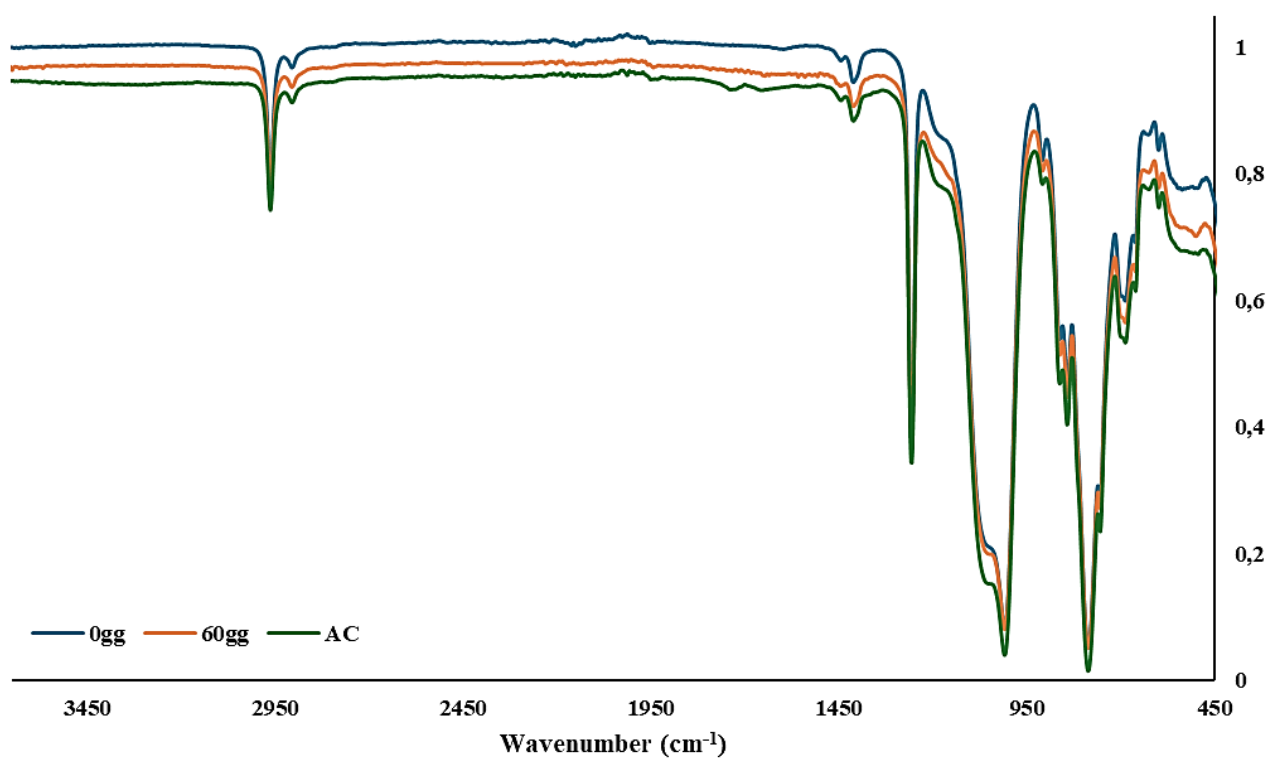


Fig. A21

Sylgard184 10:1 tt7

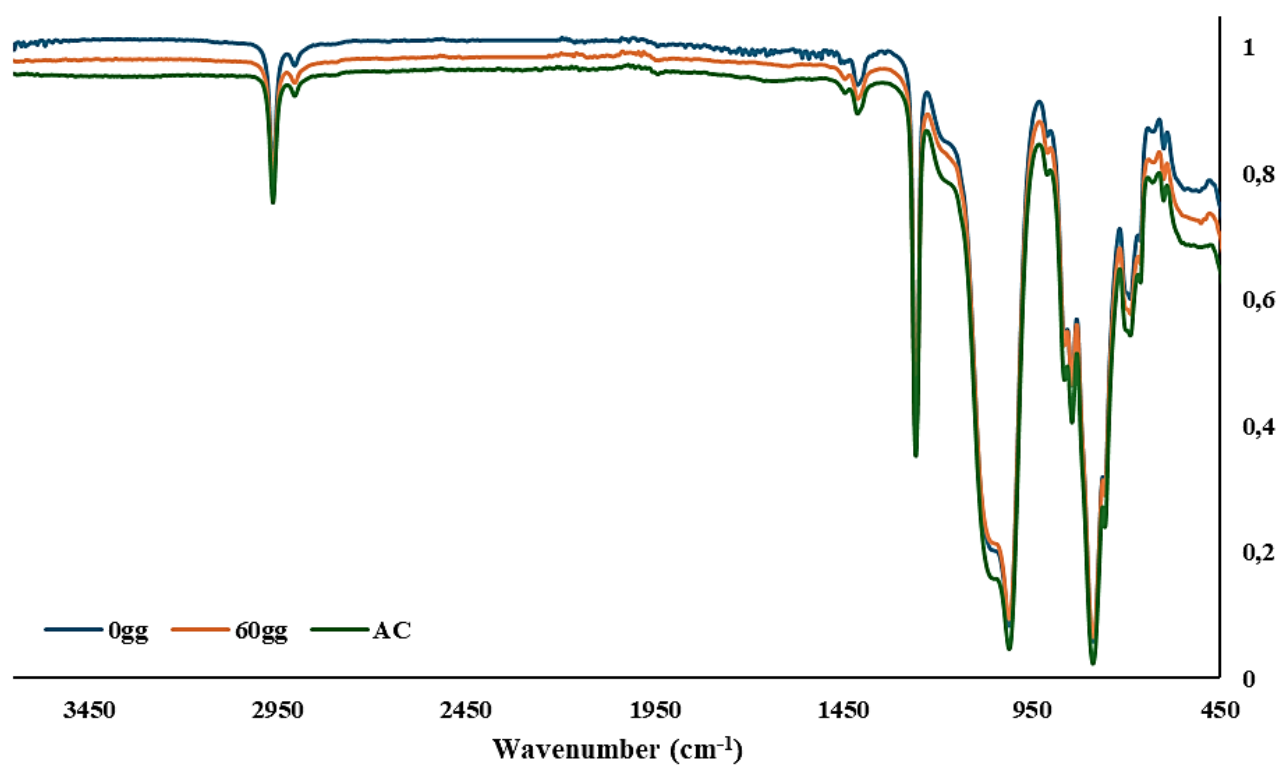


Fig. A22

Sylgard184 20:1 tt2

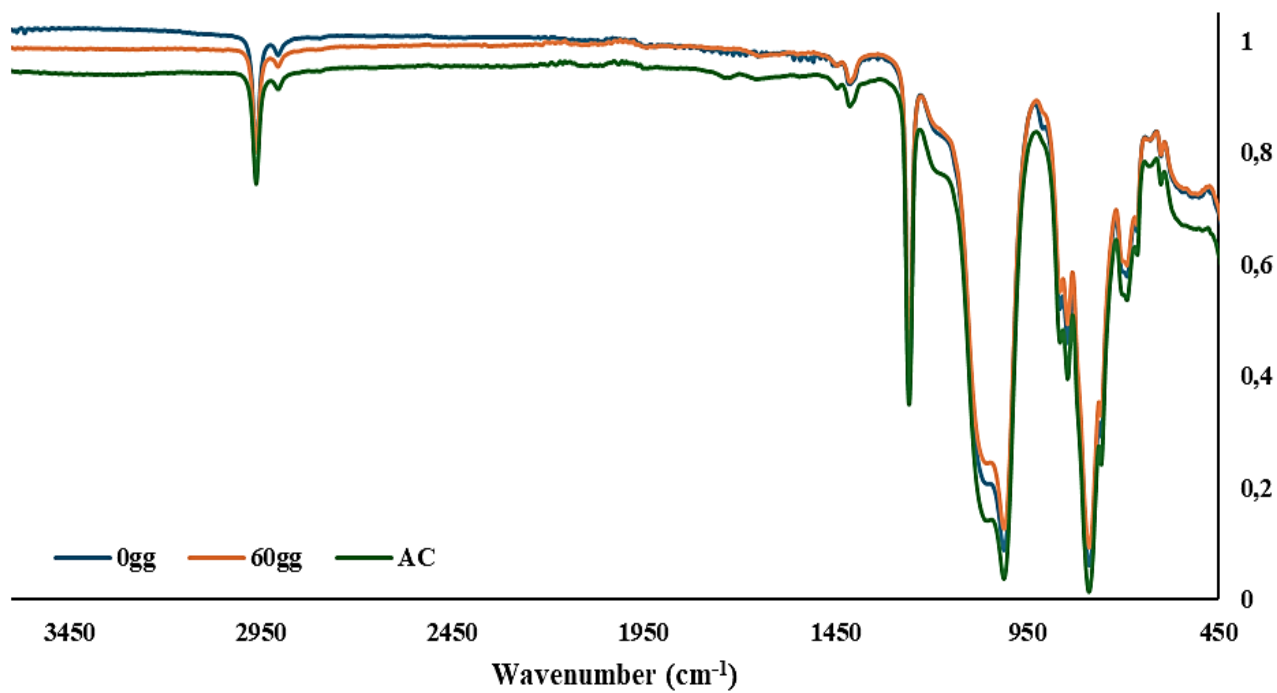


Fig. A 23

Sylgard184 20:1 tt7

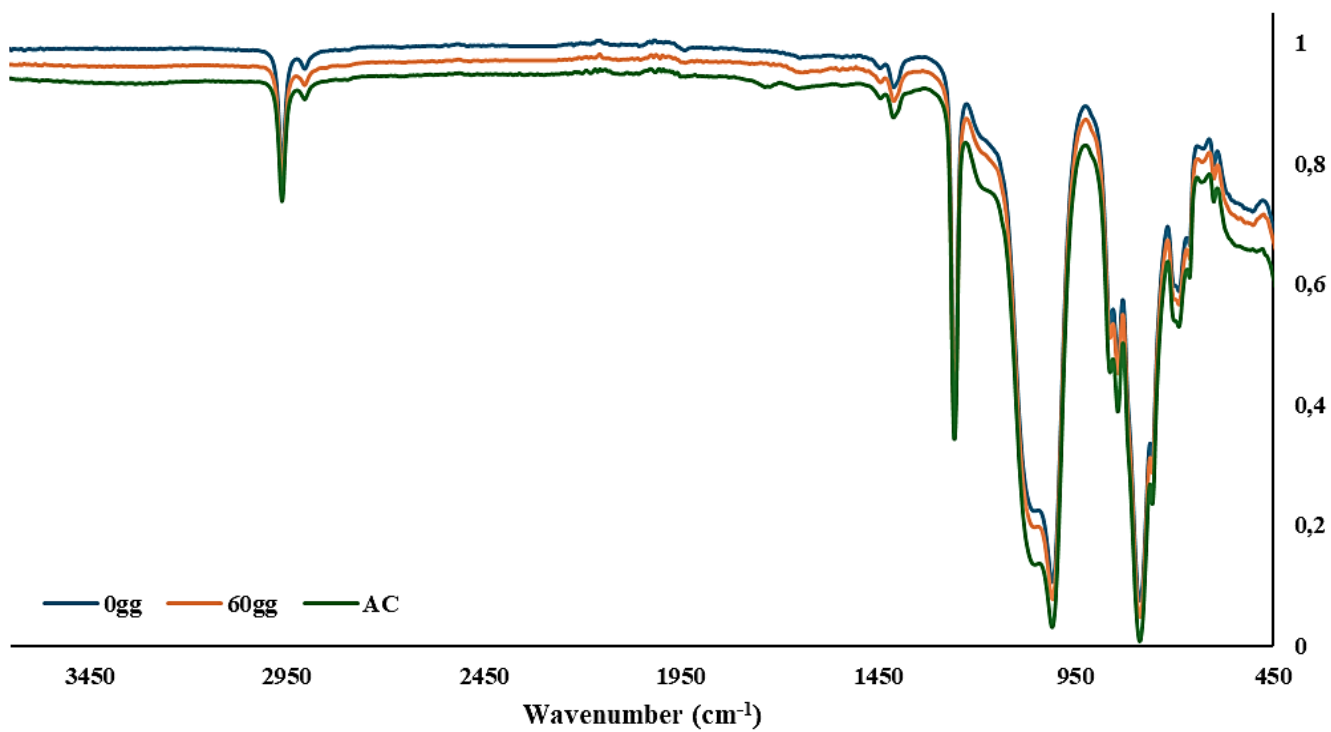


Fig. A 24

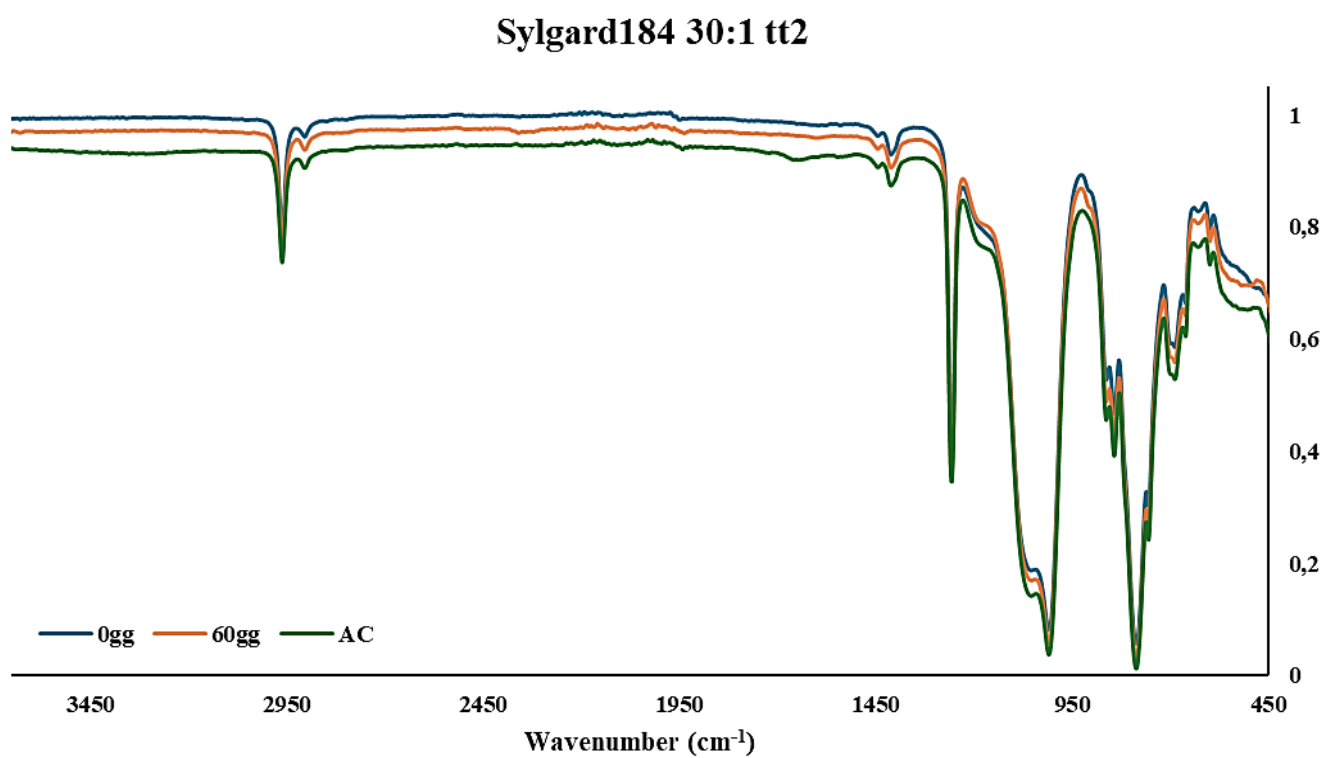


Fig. A 25

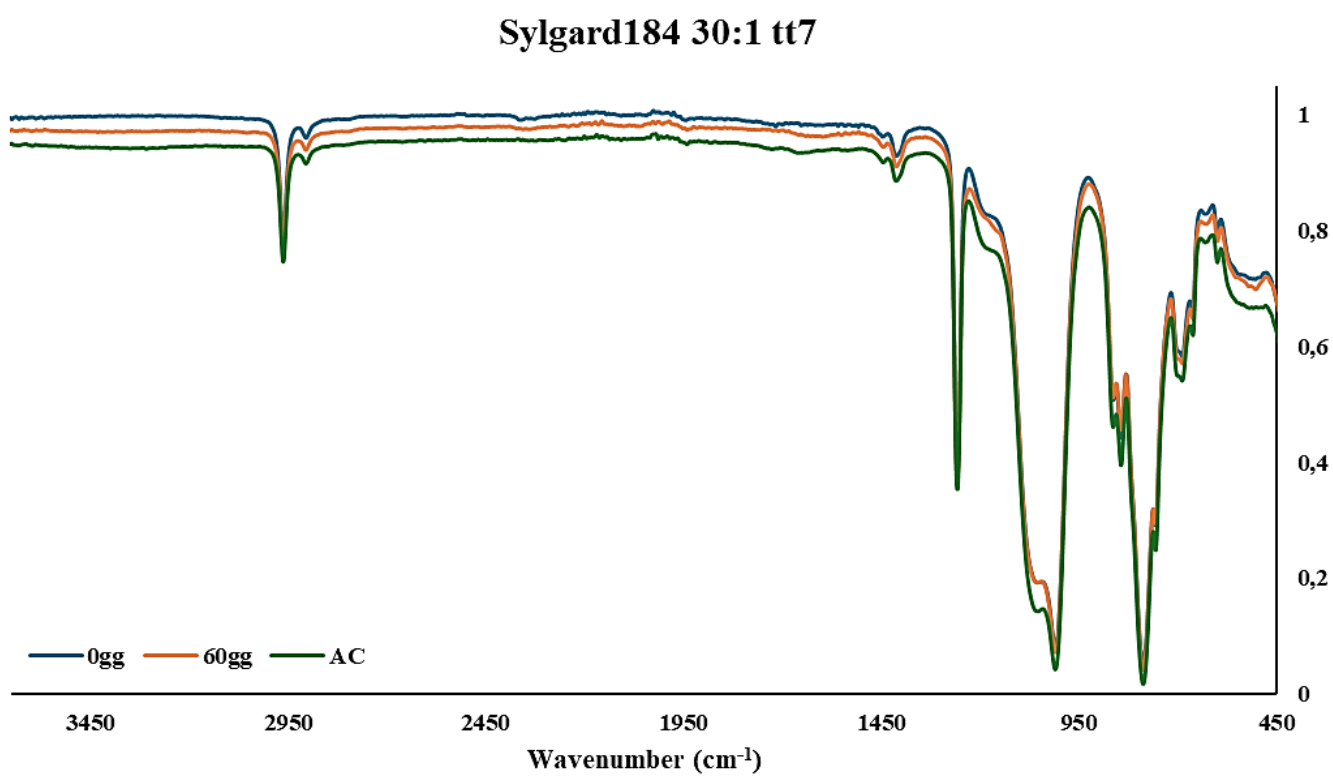


Fig. A 26

AFM

The following pre-processing steps were applied to correct the surface irregularities and noise of the analysed samples for the optimization of Aluminium-Water reaction parameters: first, the 'Plane Level' function was used to correct surface tilt and ensure planar alignment. Subsequently, the 'Horizontal Scars' tool was applied to address any horizontal artifacts present on the surface. Finally, the 'Remove Polynomial Background' function was utilized to eliminate higher-order surface irregularities.

Sample: NaOH 0.5wt%, 4min, 30°C (Fig. A27); NaOH 2.5wt%, 4min, 30°C (Fig. A28); NaOH 5wt%, 2min, 30°C (Fig. A 29); NaOH 5wt%, 3min, 30°C (Fig. A30); NaOH 5wt%, 4min, 30°C (Fig. A31).

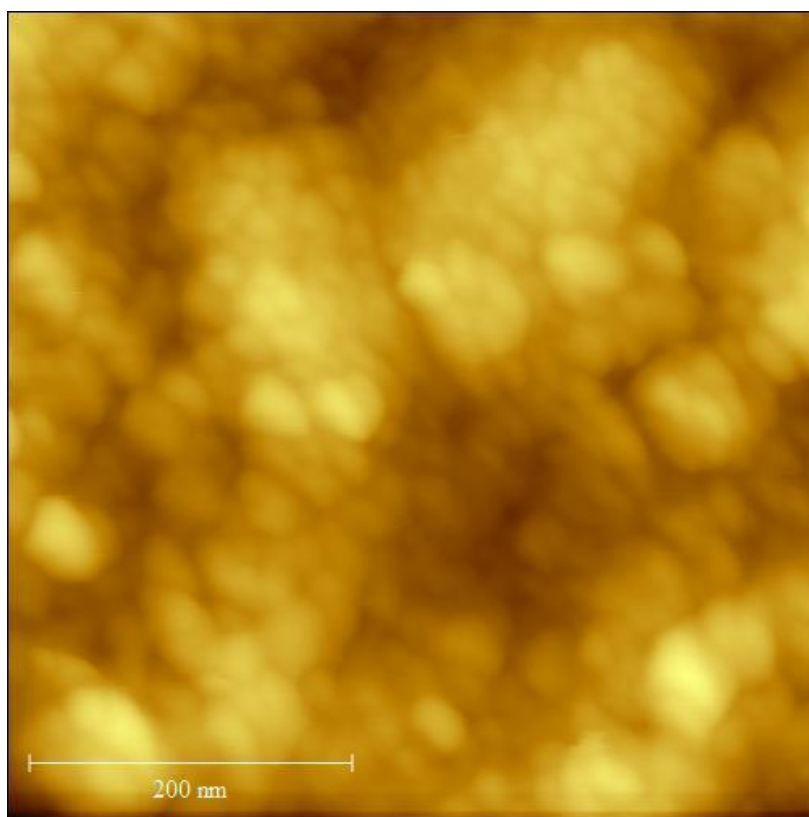


Fig. A27 NaOH 0.5wt%, 4min, 30°C

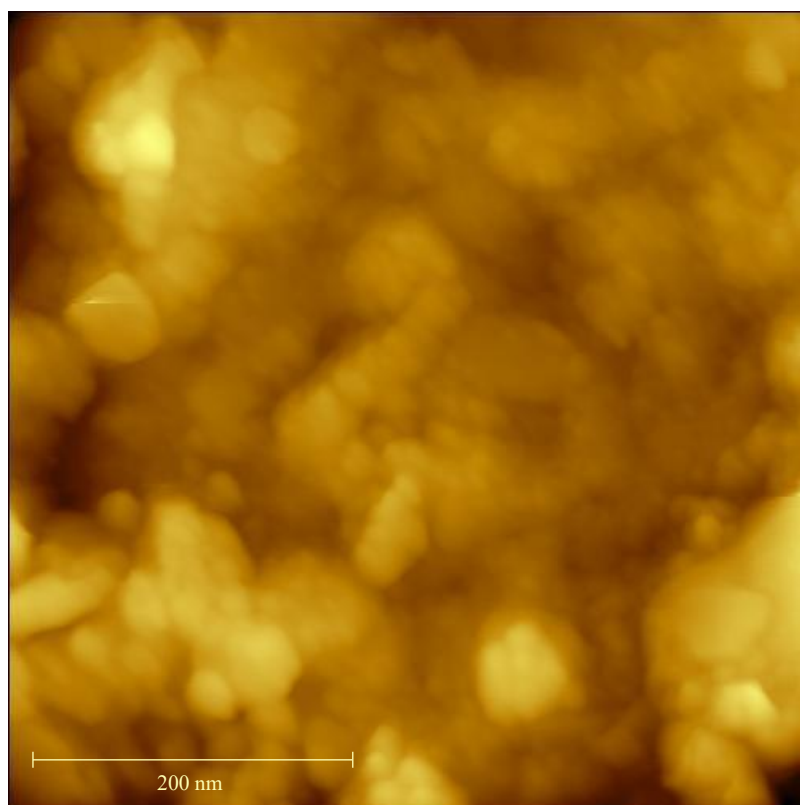


Fig. A28 NaOH 2.5wt%, 4min, 30°C.

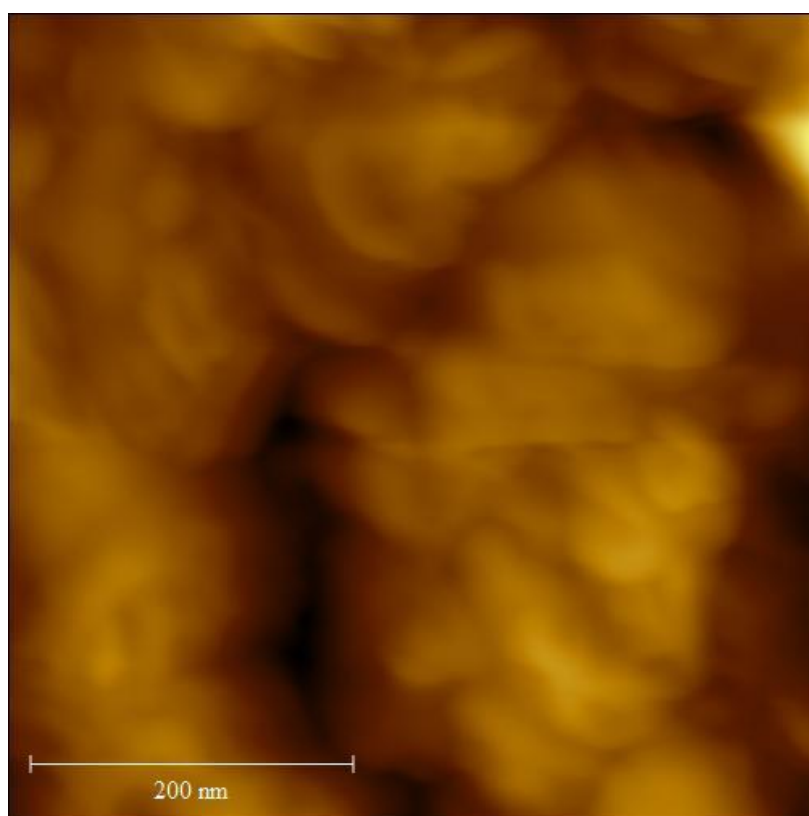


Fig. A29 NaOH 5wt%, 2min, 30°C.

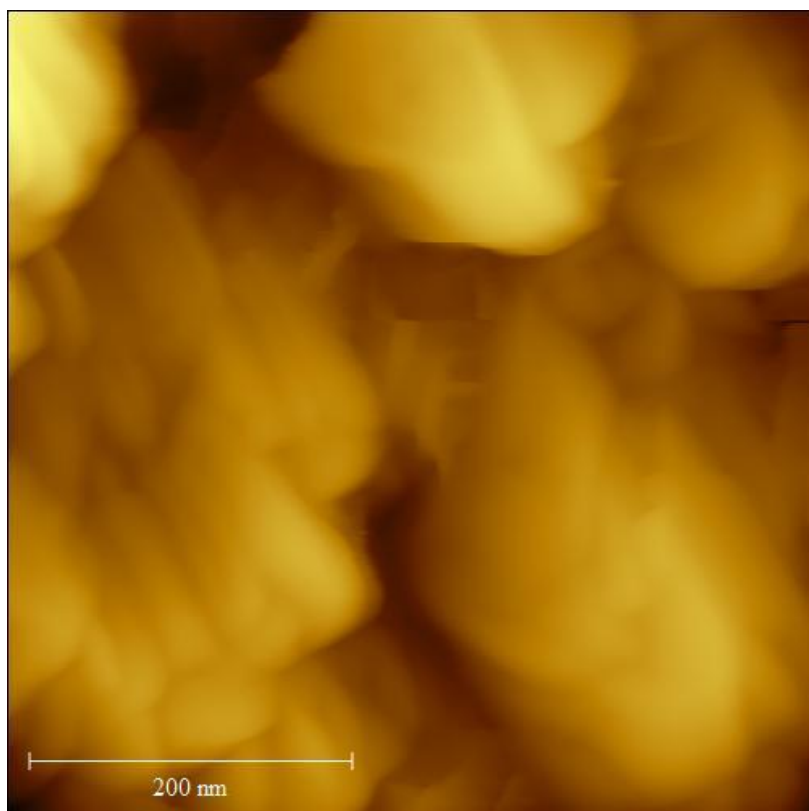


Fig. A30 NaOH 5wt%, 3min, 30°C.

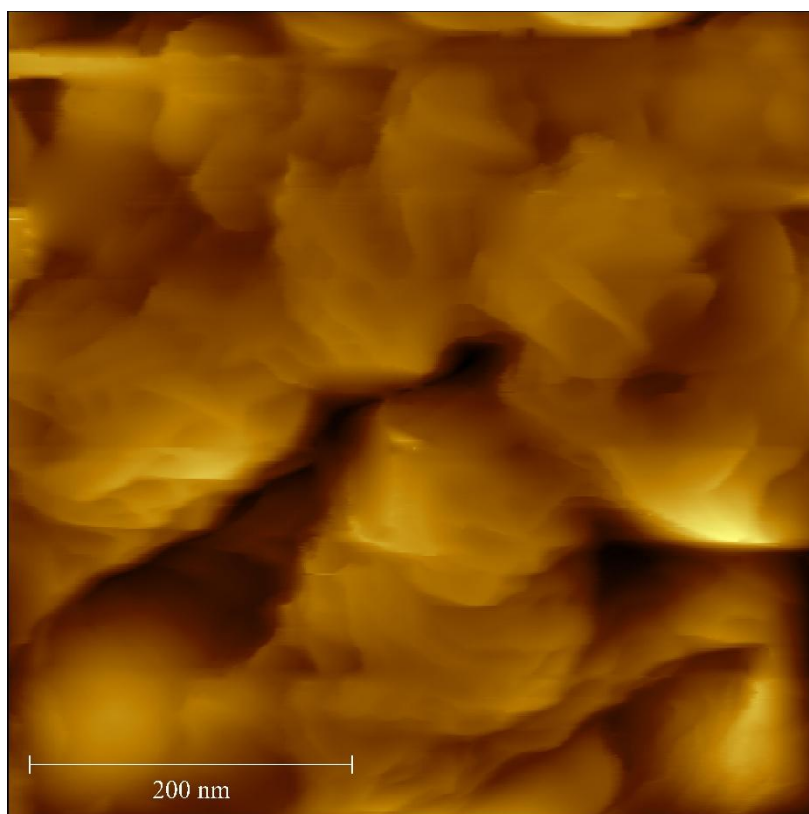


Fig. A31 NaOH 5wt%, 4min, 30°C.

OPTICAL PROFILOMETER

Images obtained using the optical profilometer on smooth (s) substrates (Fig. A32), sandblasted (sb) substrates (Fig. A33), and cold-sprayed (cs) substrates (Fig. A34). after the Aluminium-Water reaction. Thanks to Eero Helmi for the measurements.

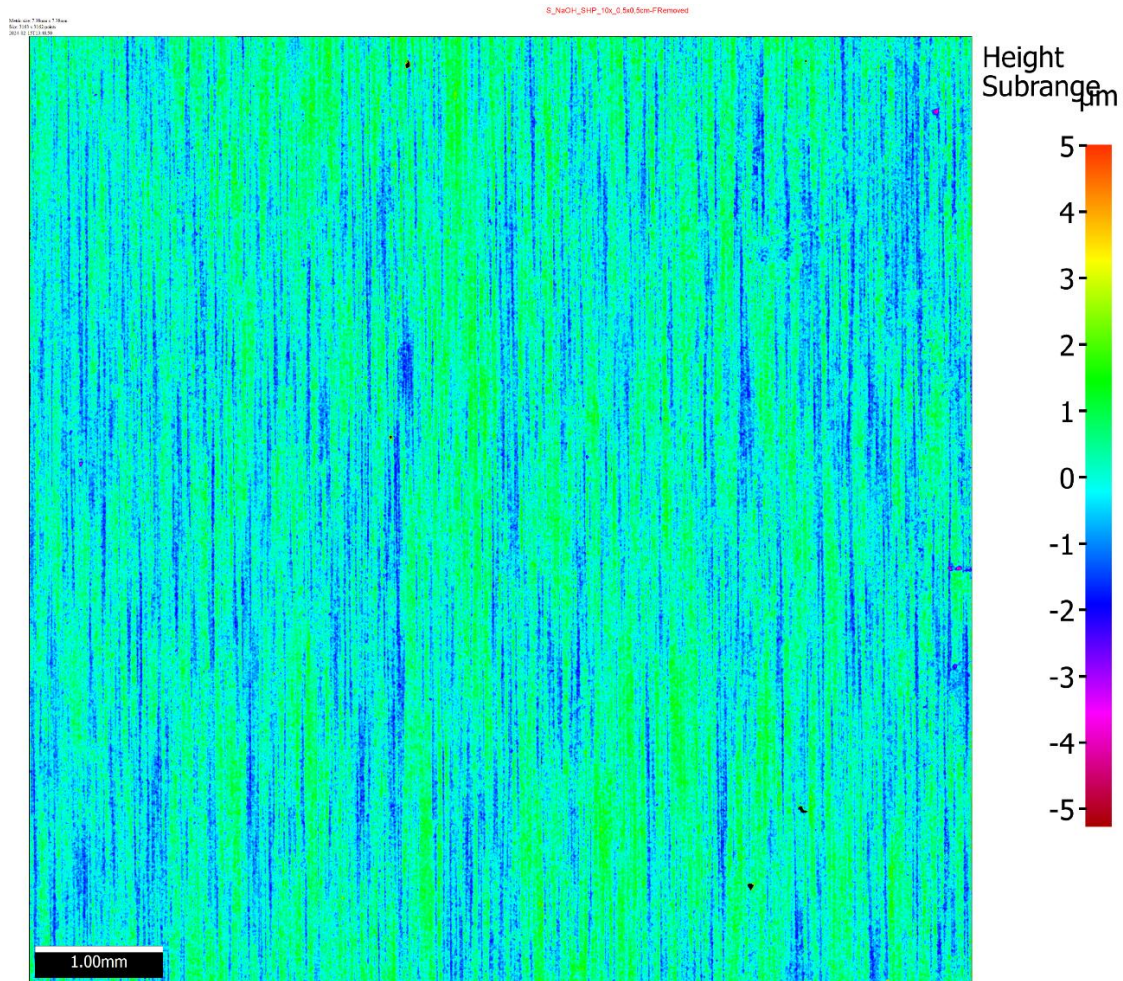


Fig. A32 Smooth sample (s). Measurements settings: Exposure Time: 31.99 μs ; Contrast: 0.93; Magnification: 10.0029x; z-Position before Measurement: 121.73 μm ; Saturation: 1; Gain: 1; Histogram Lower Bound: 0 / 255; Histogram Upper Bound: 255 / 255; XSmartFlash: No; Use Autofocus: No; Adapt Sampling Distance to Lateral Resolution: No; Polarizer: Deactivated; Estimated Vertical Resolution: 0.09 μm ; Estimated Lateral Resolution: 3.91 μm .

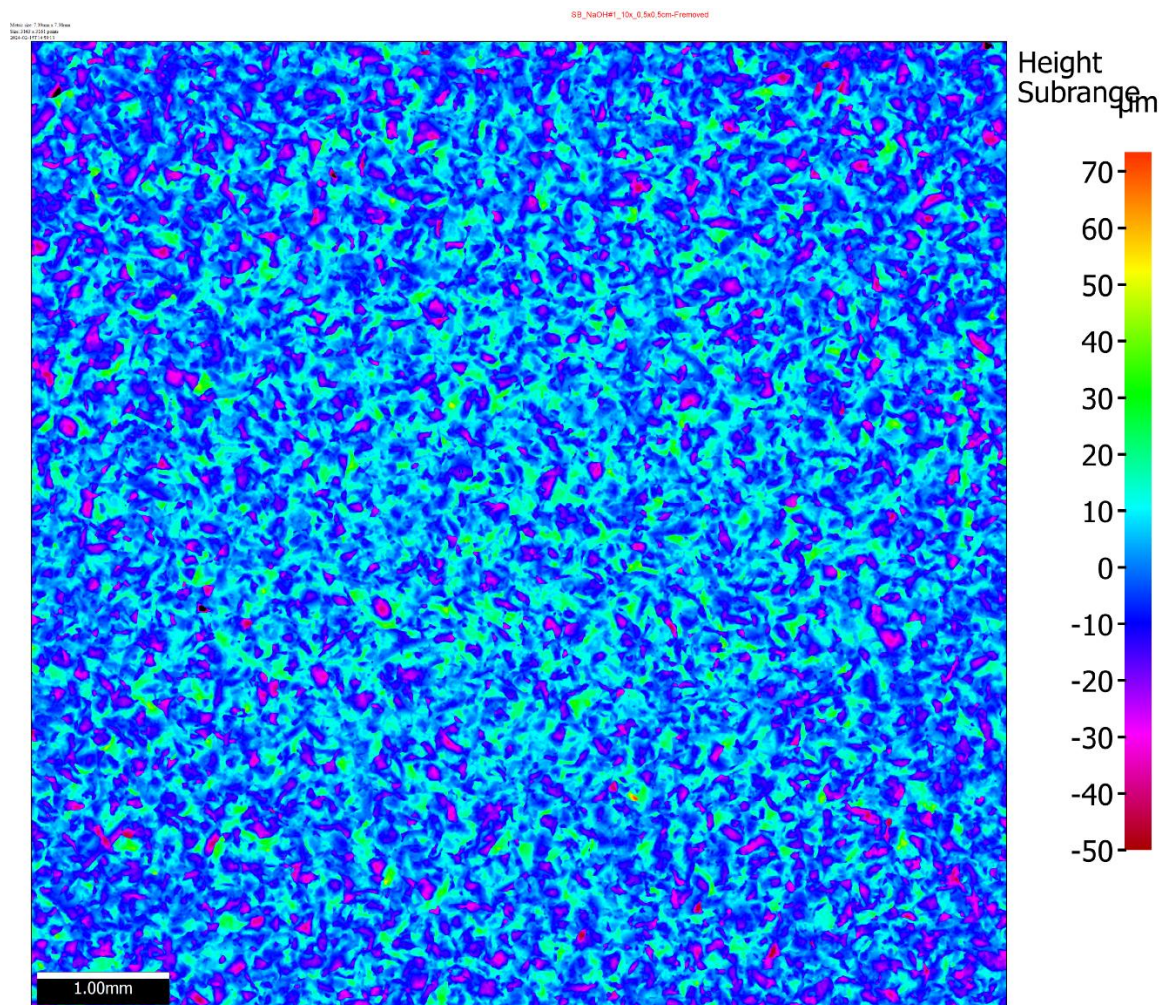


Fig. A33 Sand blasted sample (sb). Measurements settings: Exposure Time: 134.6 μs ; Contrast: 0.82; Magnification: 10.0029x; z-Position before Measurement: 97.42 μm ; Saturation: 1; Gain: 1; Histogram Lower Bound: 0 / 255; Histogram Upper Bound: 255 / 255; XSmartFlash: No; Use Autofocus: No; Adapt Sampling Distance to Lateral Resolution: No; Polarizer: Deactivated; Estimated Vertical Resolution: 0.05 μm ; Estimated Lateral Resolution: 3.91 μm .

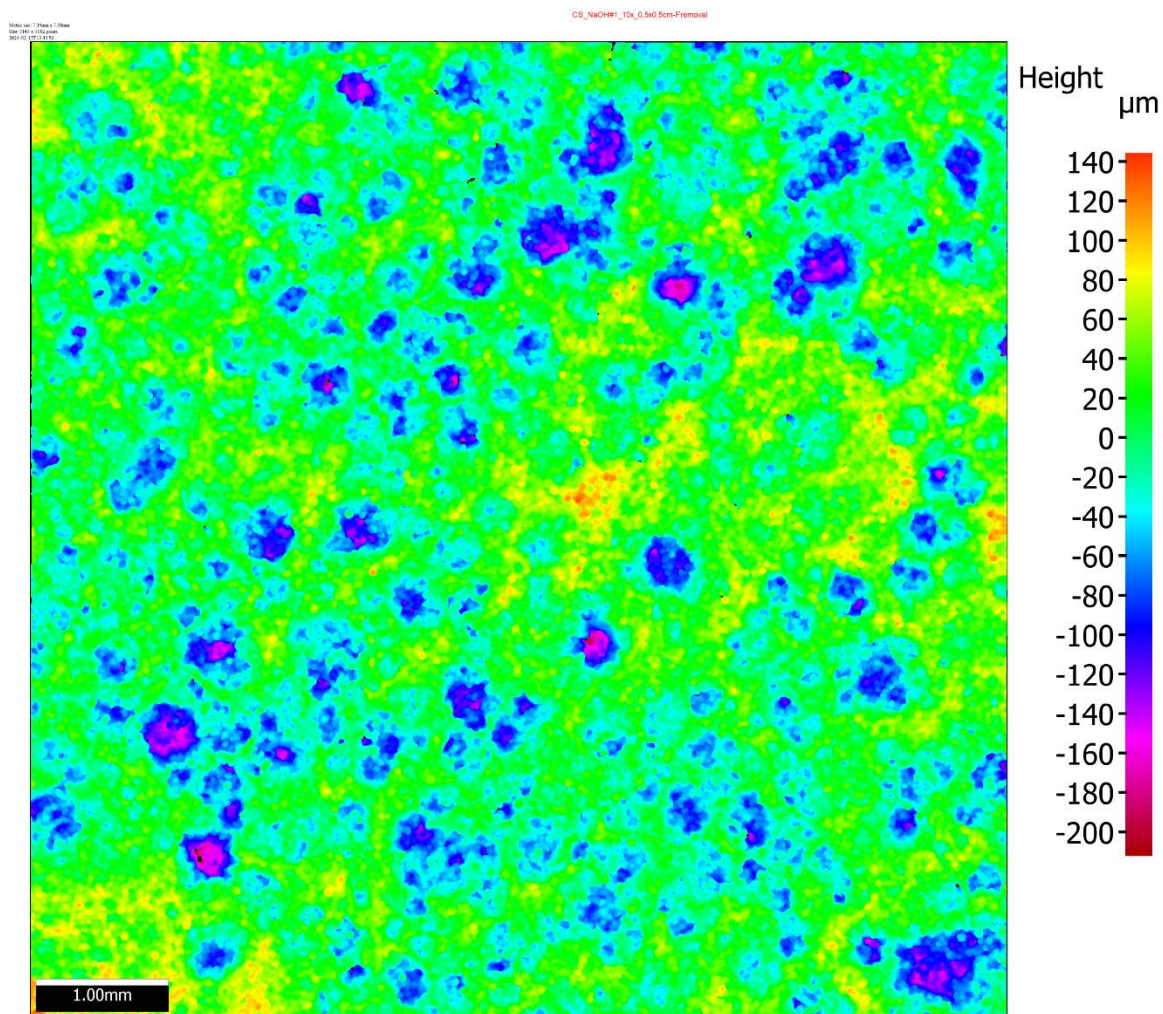


Fig. A34 Sand blasted sample (sb). Measurements settings: Exposure Time: 343.0 μs ; Contrast: 0.82; Magnification: 10.0029x; Light intensity: 0.621195; z-Position before Measurement: 340.70 μm ; Saturation: 1; Gain: 1; Histogram Lower Bound: 0 / 255; Histogram Upper Bound: 255 / 255; XSmartFlash: No; Use Autofocus: No; Adapt Sampling Distance to Lateral Resolution: No; Polarizer: Deactivated; Estimated Vertical Resolution: 0.10 μm ; Estimated Lateral Resolution: 3.59 μm .

11. List of Publications and Conference Contributions

During my PhD research, I actively contributed to the writing and publication of the following peer-reviewed articles and conference papers, which reflect the key findings and advancements made throughout this study:

Peer-Reviewed Publications

Balordi, M.; Santucci de Magistris, G.; Casali, A.; Pini, F.; Cammi, A.; Lacavalla, M.; Rotella, V. The Anti-Snow Behaviour of Icephobic Coatings: Laboratory and In-Field Testing. *Coatings* 2023, 13, 616. <https://doi.org/10.3390/coatings13030616>

Santucci De Magistris, G.; Balordi, M.; Casali, A.; Pini, F. Artificial Snow Laboratory for Indoor Snowphobicity Testing. *IWAIS* 2024, 5.

Casali, A.; Pelagatti, P.; Balordi, M.; Santucci De Magistris, G.; Pini, F. Anti-Icing Elastomeric Coatings: Striking the Hydrophobicity-Elasticity Balance; Narvik (Norway), 2024; p. 4.

Balordi, M.; Casali, A.; Santucci De Magistris, G.; Gadia, P.; Pelagatti, P.; Pini, F. Effects of Precursors Ratio and Curing Treatment on the Icephobicity of Polydimethylsiloxane. *Coatings* 2024, 14(7), 901. <https://doi.org/10.3390/coatings14070901>

Conference Contributions

As part of my research dissemination activities, I participated in the following conferences and scientific events, where I had the opportunity to present my work and engage with the scientific community:

European Material Research Society – Spring Meeting 2024, Convention & Exhibition Centre of Strasbourg (France), May 27–31, 2024.

Oral presentation: Effect of surface roughness on the anti-icing performance of aluminium-based surfaces.

20th International Workshop on Atmospheric Icing of Structures (IWAIS), UiT – The Arctic University of Norway, Narvik (Norway), June 18–21, 2024.

Oral presentation: Anti-Icing Elastomeric Coatings: Striking the Hydrophobicity-Elasticity Balance.

Metallurgy Summer School – Surface Engineering of Metals, Centro Residenziale Università di Bertinoro (FC), Italy, July 24–27, 2022

European Researchers' Night 2024, Chiesa del Carmine, Piacenza (Italy) 27/09/2024

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Finally, my deepest gratitude goes to all the people who have stood by my side and believed in me, encouraging and motivating me to never give up

13. Bibliography

- (1) Heimo, A.; Wichura, B.; Makkonen, L.; Fikke, S. M.; Ronsten, G.; Persson, P.-E.; Laakso, T.; Sääntti, K. COST-727: Atmospheric Icing on Structures Measurements and Data Collection on Icing: State of the Art. **2006**.
- (2) CIGRE, S. W. 03. *Guidelines for Meteorological Icing Models, Statistical Methods and Topographical Effects*; 291; CIGRE, 2006.
- (3) Lamraoui, F.; Fortin, G.; Benoit, R.; Perron, J.; Masson, C. Atmospheric Icing Severity: Quantification and Mapping. *Atmospheric Res.* **2013**, *128*, 57–75. <https://doi.org/10.1016/j.atmosres.2013.03.005>.
- (4) Gent, R. W.; Dart, N. P.; Cansdale, J. T. Aircraft Icing. *Philos. Trans. R. Soc. Lond. Ser. Math. Phys. Eng. Sci.* **2000**. <https://doi.org/10.1098/rsta.2000.0689>.
- (5) Parent, O.; Ilinca, A. Anti-Icing and de-Icing Techniques for Wind Turbines: Critical Review. *Cold Reg. Sci. Technol.* **2011**, *65* (1), 88–96. <https://doi.org/10.1016/j.coldregions.2010.01.005>.
- (6) Rashid, T.; Khawaja, H. A.; Edvardsen, K. Review of Marine Icing and Anti-/de-Icing Systems. *J. Mar. Eng. Technol.* **2016**, *15* (2), 79–87. <https://doi.org/10.1080/20464177.2016.1216734>.
- (7) Innes, H. M.; Haugen, J. E.; Kristjánsson, J. E.; Nygaard, B. E. K.; Rasmussen, R.; Blennow, K.; Tveito, O. E. Wind Ice and Snow Load Impacts on Infrastructure and the Natural Environment (WISLINE).
- (8) B. Wareing; B. Nygaard. WRF Simulation of Wet Snow and Rime Icing Incidents in the UK. *WRF Simul. Wet Snow Rime Icing Incid. UK* **2009**, *13th International Workshop on Atmospheric Icing of Structures*, 5.
- (9) Bonelli, P.; Lacavalla, M.; Marcacci, P.; Mariani, G.; Stella, G. Wet Snow Hazard for Power Lines: A Forecast and Alert System Applied in Italy. *Nat. Hazards Earth Syst. Sci.* **2011**, *11* (9), 2419–2431. <https://doi.org/10.5194/nhess-11-2419-2011>.
- (10) Bonanno, R.; Lacavalla, M.; Sperati, S. A New High-resolution Meteorological Reanalysis Italian Dataset: MERIDA. *Q. J. R. Meteorol. Soc.* **2019**, *145* (721), 1756–1779. <https://doi.org/10.1002/qj.3530>.
- (11) Balordi, M.; Santucci De Magistris, G.; Casali, A.; Pini, F.; Cammi, A.; Lacavalla, M.; Rotella, V. The Anti-Snow Behaviour of Icephobic Coatings: Laboratory and In-Field Testing. *Coatings* **2023**, *13* (3), 616. <https://doi.org/10.3390/coatings13030616>.
- (12) Fikke, S. M.; Kristjánsson, J. E.; Kringlebotn Nygaard, B. E. Modern Meteorology and Atmospheric Icing. In *Atmospheric Icing of Power Networks*; Farzaneh, M., Ed.; Springer Netherlands: Dordrecht, 2008; pp 1–29. https://doi.org/10.1007/978-1-4020-8531-4_1.
- (13) CIGRE, S. W. 44. *Coatings for Protecting Overhead Power Network Equipment in Winter Conditions*; 631; CIGRE, 2015.
- (14) Makkonen, L. Modeling of Ice Accretion on Wires. *Model. Ice Accretion Wires* **1983**, *Journal of climate and applied meteorology*, 11.
- (15) Kringlebotn Nygaard, B. E.; Ágústsson, H.; Somfalvi-Tóth, K. Modeling Wet Snow Accretion on Power Lines: Improvements to Previous Methods Using 50 Years of Observations. *J. Appl. Meteorol. Climatol.* **2013**, *52* (10), 2189–2203. <https://doi.org/10.1175/JAMC-D-12-0332.1>.
- (16) Farzaneh, M. *Atmospheric Icing of Power Networks*; Springer: Dordrecht, 2008.
- (17) INTERNATIONAL STANDARD ISO 12494:2001(E).
- (18) Santucci De Magistris, G.; Balordi, M.; Casali, A.; Pini, F. Artificial Snow Laboratory for Indoor Snowphobicity Testing. *Artif. Snow Lab. Indoor Snowphobicity Test. IWAIS* **2024**, 5.

- (19) Koch, F.; Prash, M.; Schmid, L.; Schweizer, J.; Mauser, W. Measuring Snow Liquid Water Content with Low-Cost GPS Receivers. *Sensors* **2014**, *14* (11), 20975–20999. <https://doi.org/10.3390/s141120975>.
- (20) Donahue, C.; Skiles, S. M.; Hammonds, K. Mapping Liquid Water Content in Snow at the Millimeter Scale: An Intercomparison of Mixed-Phase Optical Property Models Using Hyperspectral Imaging and in Situ Measurements. *The Cryosphere* **2022**, *16* (1), 43–59. <https://doi.org/10.5194/tc-16-43-2022>.
- (21) Abdelaal, A.; Sarayloo, M.; Nims, D. K.; Mohammadian, B.; Heil, J.; Sojoudi, H. A Flexible Surface-Mountable Sensor for Ice Detection and Non-Destructive Measurement of Liquid Water Content in Snow. *Cold Reg. Sci. Technol.* **2022**, *195*, 103469. <https://doi.org/10.1016/j.coldregions.2021.103469>.
- (22) Fasani, D.; Cernuschi, F.; Colombo, L. P. M. Calorimetric Determination of Wet Snow Liquid Water Content: The Effect of Test Conditions on the Calorimeter Constant and Its Impact on the Measurement Uncertainty. *Cold Reg. Sci. Technol.* **2023**, *214*, 103959. <https://doi.org/10.1016/j.coldregions.2023.103959>.
- (23) Goel, A. Design of Transmission Lines for Atmospheric Icing. In *Atmospheric Icing of Power Networks*; Springer; Masoud Farzaneh, 2008; pp 327–371.
- (24) Tabella Composizione Leghe Di Alluminio.
- (25) Trevigiana Metalli. Scheda Tecnica Anticorodal6082 - Normativa Di Riferimento UNI 9006/4.
- (26) Makkonen, L.; Lozowski, E. P. Numerical Modelling of Icing on Power Network Equipmen. In *Atmospheric Icing of Power Networks*; Springer; Masoud Farzaneh, 2008; p 35.
- (27) Van Dyke, P.; Havard, D.; Laneville, A. Effect of Ice and Snow on the Dynamics of Transmission Line Conductors. In *Atmospheric Icing of Power Networks*; Springer; Masoud Farzaneh, 2008; p 53.
- (28) Zhou, C.; Yin, J. Numerical Analysis of Glaze Ice Accretion on Cables by Considering the Effects of Typical In-Plane Vibrations. *J. Fluids Struct.* **2024**, *131*, 104229. <https://doi.org/10.1016/j.jfluidstructs.2024.104229>.
- (29) Zanelli, F.; Mauri, M.; Castelli-Dezza, F.; Tarsitano, D.; Manenti, A.; Diana, G. Analysis of Wind-Induced Vibrations on HVTL Conductors Using Wireless Sensors. *Anal. Wind-Induc. Vib. HVTL Conduct. Using Wirel. Sens.* **2022**, *Sensors* (8165), 22.
- (30) Admirat, P. Wet Snow Accretion on Overhead Lines. In *Atmospheric Icing of Power Networks*; Springer; Masoud Farzaneh, 2008; p 45.
- (31) Sakamoto, Y. Snow Accretion on Overhead Wires. *Philos. Trans. R. Soc. Lond. Ser. Math. Phys. Eng. Sci.* **2000**, *358* (1776), 2941–2970. <https://doi.org/10.1098/rsta.2000.0691>.
- (32) Veerakumar, R.; Gao, L.; Liu, Y.; Hu, H. Dynamic Ice Accretion Process and Its Effects on the Aerodynamic Drag Characteristics of a Power Transmission Cable Model. *Cold Reg. Sci. Technol.* **2020**, *169*, 102908. <https://doi.org/10.1016/j.coldregions.2019.102908>.
- (33) Wang, T.; Zheng, Y.; Raji, A.-R. O.; Li, Y.; Sikkema, W. K. A.; Tour, J. M. Passive Anti-Icing and Active Deicing Films. *ACS Appl. Mater. Interfaces* **2016**, *8* (22), 14169–14173. <https://doi.org/10.1021/acsami.6b03060>.
- (34) Solangi, A. R. Icing Effects on Power Lines and Anti-Icing and De-Icing Methods. Master Thesis, The Arctic University of Norway (UiT) - Faculty of Science and Technology Department of Safety and Engineering, 2018.
- (35) CIGRE, W. B. 69. *Coatings for protecting overhead power networks against icing, corona noise, corrosion and reducing their visual impact*; 838; CIGRE, 2021.
- (36) Rekuviene, R.; Saeidiharzand, S.; Mažeika, L.; Samaitis, V.; Jankauskas, A.; Sadaghiani, A. K.; Gharib, G.; Muganlı, Z.; Koşar, A. A Review on Passive and Active Anti-Icing and

de-Icing Technologies. *Appl. Therm. Eng.* **2024**, *250*, 123474.

<https://doi.org/10.1016/j.applthermaleng.2024.123474>.

- (37) Farzaneh, M.; Volat, C.; Leblond, A. Anti-Icing and De-Icing Techniques for Overhead Lines. In *Atmospheric Icing of Power Networks*; Springer; Masoud Farzaneh, 2008.
- (38) Petrenko, V. F.; Sullivan, C. R.; Kozlyuk, V.; Petrenko, F. V.; Veerasamy, V. Pulse Electro-Thermal de-Icer (PETD). *Cold Reg. Sci. Technol.* **2011**, *65*, 70–78.
<https://doi.org/10.1016/j.coldregions.2010.06.002>.
- (39) Redondo, O.; Prolongo, S. G.; Campo, M.; Sbarufatti, C.; Giglio, M. Anti-Icing and de-Icing Coatings Based Joule's Heating of Graphene Nanoplatelets. *Compos. Sci. Technol.* **2018**, *164*, 65–73. <https://doi.org/10.1016/j.compscitech.2018.05.031>.
- (40) Huneault, M.; Langheit, C.; St-Arnaud, R.; Benny, J.; Audet, J.; Richard, J.-C. A Dynamic Programming Methodology to Develop De-Icing Strategies during Ice Storms by Channeling Load Currents in Transmission Networks. *IEEE Trans. Power Deliv.* **2005**, *20* (2), 1604–1610. <https://doi.org/10.1109/TPWRD.2004.838463>.
- (41) Cloutier, R.; Bergeron, A.; Brochu, J. On-Load Network De-Icer Specification for a Large Transmission Network. *IEEE Trans. Power Deliv.* **2007**, *22* (3), 1947–1955.
<https://doi.org/10.1109/TPWRD.2007.899772>.
- (42) Brochu, J.; Beauregard, F.; Coultier, R.; Bergeron, A.; Garant, L. Innovative Applications of Phase-Shifting Transformers Supplemented with Series Reactive Elements. In *CIGRE TB291*; 838; CIGRE, 2006; p 10.
- (43) Zhang, Z.; Zhang, H.; Yue, S.; Zeng, W. A Review of Icing and Anti-Icing Technology for Transmission Lines. *Energies* **2023**, *16* (2), 601. <https://doi.org/10.3390/en16020601>.
- (44) Liqing, L.; Yazı, Z.; JiWu, Z.; En, X.; Shihua, Z. Comparison between AC and DC Short-Circuit-Current Ice-Melting Methods.
- (45) Laforte, J. L.; Allaire, M. A.; Laflamme, J. State-of-the-Art on Power Line de-Icing. *Atmospheric Res.* **1998**, *46* (1), 143–158. [https://doi.org/10.1016/S0169-8095\(97\)00057-4](https://doi.org/10.1016/S0169-8095(97)00057-4).
- (46) Laforte, J.-L.; Allaire, M.-A.; Laforte, C. Demonstration of the Feasibility of a New Mechanical Method of Cable De-Icing. **2005**.
- (47) Montambault, S.; Pouliot, N. The HQ LineROver: Contributing to Innovation in Transmission Line Maintenance. *2003 IEEE 10th Int. Conf. Transm. Distrib. Constr. Oper. Live-Line Maint. 2003 IEEE ESMO 2003*, 33–40.
<https://doi.org/10.1109/TDCLLM.2003.1196466>.
- (48) Zhao, J.; Guo, R.; Cao, L.; Zhang, F. Improvement of LineROver: A Mobile Robot for de-Icing of Transmission Lines. *2010 1st Int. Conf. Appl. Robot. Power Ind.* **2010**, 1–4.
<https://doi.org/10.1109/CARPI.2010.5624458>.
- (49) Francesco, P. Development and Characterization of Anti-Icing and Anti Fouling Coatings for Overhead Lines, Università degli Studi di Pavia, 2020.
- (50) Liu, B.; Zhang, K.; Tao, C.; Zhao, Y.; Li, X.; Zhu, K.; Yuan, X. Strategies for Anti-Icing: Low Surface Energy or Liquid-Infused? *RSC Adv.* **2016**, *6* (74), 70251–70260.
<https://doi.org/10.1039/C6RA11383D>.
- (51) Koltzenburg, S.; Maskos, M.; Nuyken, O. *Polymer Chemistry*; Springer: Berlin, Heidelberg, 2017. <https://doi.org/10.1007/978-3-662-49279-6>.
- (52) Yuebin Lin; Haifeng Chen; Guanyu Wang; Aihui Liu. Recent Progress in Preparation and Anti-Icing Applications of Superhydrophobic Coatings. *Coatings* **2018**, *8*, 208.
- (53) Li, W.; Zhan, Y.; Yu, S. Applications of Superhydrophobic Coatings in Anti-Icing: Theory, Mechanisms, Impact Factors, Challenges and Perspectives. *Prog. Org. Coat.* **2021**, *152*, 106117. <https://doi.org/10.1016/j.porgcoat.2020.106117>.

- (54) Kreder, M. J.; Alvarenga, J.; Kim, P.; Aizenberg, J. Design of Anti-Icing Surfaces: Smooth, Textured or Slippery? *Nat. Rev. Mater.* **2016**, *1* (1), 1–15. <https://doi.org/10.1038/natrevmats.2015.3>.
- (55) Heydarian, S.; Jafari, R.; Momen, G. Recent Progress in the Anti-Icing Performance of Slippery Liquid-Infused Surfaces. *Prog. Org. Coat.* **2021**, *151*, 106096. <https://doi.org/10.1016/j.porgcoat.2020.106096>.
- (56) Shanks, R. A.; Kong, I. General Purpose Elastomers: Structure, Chemistry, Physics and Performance. In *Advances in Elastomers I: Blends and Interpenetrating Networks*; Visakh, P. M., Thomas, S., Chandra, A. K., Mathew, Aji. P., Eds.; Springer: Berlin, Heidelberg, 2013; pp 11–45. https://doi.org/10.1007/978-3-642-20925-3_2.
- (57) Aprem, A. S.; Joseph, K.; Thomas, S. Recent Developments in Crosslinking of Elastomers. *Rubber Chem. Technol.* **2005**, *78* (3), 458–488. <https://doi.org/10.5254/1.3547892>.
- (58) Koltzenburg, S.; Maskos, M.; Nuyken, O. Elastomers. In *Polymer Chemistry*; Koltzenburg, S., Maskos, M., Nuyken, O., Eds.; Springer: Berlin, Heidelberg, 2017; pp 477–491. https://doi.org/10.1007/978-3-662-49279-6_18.
- (59) Koltzenburg, S.; Maskos, M.; Nuyken, O. Important Polymers Produced by Chain-Growth Polymerization. In *Polymer Chemistry*; Koltzenburg, S., Maskos, M., Nuyken, O., Eds.; Springer: Berlin, Heidelberg, 2017; pp 381–406. https://doi.org/10.1007/978-3-662-49279-6_14.
- (60) Koltzenburg, S.; Maskos, M.; Nuyken, O. Polymers as Materials. In *Polymer Chemistry*; Koltzenburg, S., Maskos, M., Nuyken, O., Eds.; Springer: Berlin, Heidelberg, 2017; pp 141–162. https://doi.org/10.1007/978-3-662-49279-6_7.
- (61) Jiang, B.; Shi, X.; Zhang, T.; Huang, Y. Recent Advances in UV/Thermal Curing Silicone Polymers. *Chem. Eng. J.* **2022**, *435*, 134843. <https://doi.org/10.1016/j.cej.2022.134843>.
- (62) Chemistry (IUPAC), T. I. U. of P. and A. IUPAC - Vulcanization (VT07153). <https://doi.org/10.1351/goldbook.VT07153>.
- (63) Akiba, M.; Hashim, A. S. Vulcanization and Crosslinking in Elastomers. *Prog. Polym. Sci.* **1997**, *22* (3), 475–521. [https://doi.org/10.1016/S0079-6700\(96\)00015-9](https://doi.org/10.1016/S0079-6700(96)00015-9).
- (64) Guise-Richardson, C. Redefining Vulcanization: Charles Goodyear, Patents, and Industrial Control, 1834-1865. *Technol. Cult.* **2010**, *51* (2), 357–387.
- (65) The Goodyear Rubber Cases. *Dent. Regist.* **1868**, *22* (11), 476–484.
- (66) Heiner, J.; Stenberg, B.; Persson, M. Crosslinking of Siloxane Elastomers. *Polym. Test.* **2003**, *22* (3), 253–257. [https://doi.org/10.1016/S0142-9418\(02\)00081-8](https://doi.org/10.1016/S0142-9418(02)00081-8).
- (67) Jurásková, A.; Møller Olsen, S.; Dam-Johansen, K.; Brook, M. A.; Skov, A. L. Reliable Condensation Curing Silicone Elastomers with Tailorable Properties. *Molecules* **2021**, *26* (1), 82. <https://doi.org/10.3390/molecules26010082>.
- (68) Jurásková, A.; Dam-Johansen, K.; Olsen, S. M.; Skov, A. L. Factors Influencing Mechanical Long-Term Stability of Condensation Curing Silicone Elastomers. *J. Polym. Res.* **2020**, *27* (11), 341. <https://doi.org/10.1007/s10965-020-02272-5>.
- (69) Loan, L. D. Mechanism of Peroxide Vulcanization of Elastomers. *Rubber Chem. Technol.* **1967**, *40* (1), 149–176. <https://doi.org/10.5254/1.3539040>.
- (70) Kruželák, J.; Sýkora, R.; Hudec, I. Vulcanization of Rubber Compounds with Peroxide Curing Systems. *Rubber Chem. Technol.* **2017**, *90* (1), 60–88. <https://doi.org/10.5254/rct.16.83758>.
- (71) Lukin, R. Y.; Kuchkaev, A. M.; Sukhov, A. V.; Bekmukhamedov, G. E.; Yakhvarov, D. G. Platinum-Catalyzed Hydrosilylation in Polymer Chemistry. *Polymers* **2020**, *12* (10), 2174. <https://doi.org/10.3390/polym12102174>.

- (72) Miranian, Z.; Ostad Movahed, S.; Ostad Movahed, N. The Phenolic Cured Butyl Rubber Reclamation Using Different De-Crosslinking Agents. *Prog. Rubber Plast. Recycl. Technol.* **2024**, *40* (1), 33–47. <https://doi.org/10.1177/14777606231186631>.
- (73) Spontak, R. J.; Patel, N. P. Thermoplastic Elastomers: Fundamentals and Applications. *Curr. Opin. Colloid Interface Sci.* **2000**, *5* (5), 333–340. [https://doi.org/10.1016/S1359-0294\(00\)00070-4](https://doi.org/10.1016/S1359-0294(00)00070-4).
- (74) Abdou-Sabet, S.; Puydak, R. C.; Rader, C. P. Dynamically Vulcanized Thermoplastic Elastomers. *Rubber Chem. Technol.* **1996**, *69* (3), 476–494. <https://doi.org/10.5254/1.3538382>.
- (75) Fazli, A.; Rodrigue, D. Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers. *Materials* **2020**, *13* (3), 782. <https://doi.org/10.3390/ma13030782>.
- (76) Kong, S. M.; Mariatti, M.; Busfield, J. J. C. Effects of Types of Fillers and Filler Loading on the Properties of Silicone Rubber Composites. *J. Reinf. Plast. Compos.* **2011**, *30* (13), 1087–1096. <https://doi.org/10.1177/0731684411416267>.
- (77) Ke, Q.; Fu, W.; Jin, H.; Zhang, L.; Tang, T.; Zhang, J. Fabrication of Mechanically Robust Superhydrophobic Surfaces Based on Silica Micro-Nanoparticles and Polydimethylsiloxane. *Surf. Coat. Technol.* **2011**, *205* (21), 4910–4914. <https://doi.org/10.1016/j.surfcoat.2011.04.073>.
- (78) Koltzenburg, S.; Maskos, M.; Nuyken, O. Polymers in Solution. In *Polymer Chemistry*; Koltzenburg, S., Maskos, M., Nuyken, O., Eds.; Springer: Berlin, Heidelberg, 2017; pp 17–37. https://doi.org/10.1007/978-3-662-49279-6_2.
- (79) Shanks, R. A.; Kong, I. General Purpose Elastomers: Structure, Chemistry, Physics and Performance. *Mater. Sci. Phys. Chem.* **2013**.
- (80) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley & Sons, 2015.
- (81) Alemán, J. V.; Chadwick, A. V.; He, J.; Hess, M.; Horie, K.; Jones, R. G.; Kratochvíl, P.; Meisel, I.; Mita, I.; Moad, G.; Penczek, S.; Stepto, R. F. T. Definitions of Terms Relating to the Structure and Processing of Sols, Gels, Networks, and Inorganic-Organic Hybrid Materials (IUPAC Recommendations 2007). *Pure Appl. Chem.* **2007**, *79* (10), 1801–1829. <https://doi.org/10.1351/pac200779101801>.
- (82) *Quantities, Units, and Symbols in Physical Chemistry*, 2nd ed.; Mills, I., International Union of Pure and Applied Chemistry, International Union of Pure and Applied Chemistry, Eds.; Blackwell Scientific Publications ; CRC Press [distributor]: Oxford ; Boston : Boca Raton, Fla, 1993.
- (83) Hopcroft, M. A.; Nix, W. D.; Kenny, T. W. What Is the Young’s Modulus of Silicon? *J. Microelectromechanical Syst.* **2010**, *19* (2), 229–238. <https://doi.org/10.1109/JMEMS.2009.2039697>.
- (84) Hirschberg, V.; Lyu, S.; Wilhelm, M.; Rodrigue, D. Nonlinear Mechanical Behavior of Elastomers under Tension/Tension Fatigue Deformation as Determined by Fourier Transform. *Rheol. Acta* **2021**, *60* (12), 787–801. <https://doi.org/10.1007/s00397-021-01310-3>.
- (85) Mott, P. H.; Dorgan, J. R.; Roland, C. M. The Bulk Modulus and Poisson’s Ratio of “Incompressible” Materials. *J. Sound Vib.* **2008**, *312* (4), 572–575. <https://doi.org/10.1016/j.jsv.2008.01.026>.
- (86) Koltzenburg, S.; Maskos, M.; Nuyken, O. Polymers in Solid State. In *Polymer Chemistry*; Koltzenburg, S., Maskos, M., Nuyken, O., Eds.; Springer: Berlin, Heidelberg, 2017; pp 93–103. https://doi.org/10.1007/978-3-662-49279-6_4.

- (87) Jastrzebski, Z. D.; Komanduri, R. The Nature and Properties of Engineering Materials. In *Journal of Engineering Materials and Technology*; 1988; Vol. 110, pp 294–294. <https://doi.org/10.1115/1.3226051>.
- (88) *Standard Test Method for Rubber Property—Durometer Hardness*. <https://www.astm.org/d2240-15r21.html> (accessed 2024-12-28).
- (89) Gent, A. N. On the Relation between Indentation Hardness and Young's Modulus. *Rubber Chem. Technol.* **1958**, *31* (4), 896–906. <https://doi.org/10.5254/1.3542351>.
- (90) Meththananda, I. M.; Parker, S.; Patel, M. P.; Braden, M. The Relationship between Shore Hardness of Elastomeric Dental Materials and Young's Modulus. *Dent. Mater.* **2009**, *25* (8), 956–959. <https://doi.org/10.1016/j.dental.2009.02.001>.
- (91) Chaudhury, M. K.; Kim, K. H. Shear-Induced Adhesive Failure of a Rigid Slabin Contact with a Thin Confined Film. *Eur. Phys. J. E* **2007**, *23* (2), 175–183. <https://doi.org/10.1140/epje/i2007-10171-x>.
- (92) Jiang, X.; Lin, Y.; Xuan, X.; Zhuo, Y.; Wu, J.; He, J.; Du, X.; Zhang, Z.; Li, T. Stiffening Surface Lowers Ice Adhesion Strength by Stress Concentration Sites. *Colloids Surf. Physicochem. Eng. Asp.* **2023**, *666*, 131334. <https://doi.org/10.1016/j.colsurfa.2023.131334>.
- (93) Zhang, W.; Lv, S.-L.; Gao, X.; Srivatsan, T. S. The Elastic-Plastic Properties of an Anti-Icing Coating on an Aluminum Alloy: Experimental and Numerical Approach. *J. Mech. Behav. Mater.* **2021**, *30* (1), 1–8. <https://doi.org/10.1515/jmbm-2021-0001>.
- (94) Ibáñez-Ibáñez, P. F.; Montes Ruiz-Cabello, F. J.; Cabrerizo-Vílchez, M. A.; Rodríguez-Valverde, M. A. Ice Adhesion of PDMS Surfaces with Balanced Elastic and Water-Repellent Properties. *J. Colloid Interface Sci.* **2022**, *608* (Pt 1), 792–799. <https://doi.org/10.1016/j.jcis.2021.10.005>.
- (95) Beemer, D. L.; Wang, W.; Kota, A. K. Durable Gels with Ultra-Low Adhesion to Ice. *J. Mater. Chem. A* **2016**, *4* (47), 18253–18258. <https://doi.org/10.1039/C6TA07262C>.
- (96) Mozetič, M. Surface Modification to Improve Properties of Materials. *Materials* **2019**, *12* (3), 441. <https://doi.org/10.3390/ma12030441>.
- (97) Wieszczycka, K.; Staszak, K.; Woźniak-Budych, M. J.; Litowczenko, J.; Maciejewska, B. M.; Jurga, S. Surface Functionalization – The Way for Advanced Applications of Smart Materials. *Coord. Chem. Rev.* **2021**, *436*, 213846. <https://doi.org/10.1016/j.ccr.2021.213846>.
- (98) Darmanin, T.; Guittard, F. Superhydrophobic and Superoleophobic Properties in Nature. *Mater. Today* **2015**, *18* (5), 273–285. <https://doi.org/10.1016/j.mattod.2015.01.001>.
- (99) Lee, H. J.; Michielsen, S. Lotus Effect: Superhydrophobicity. *J. Text. Inst.* **2006**, *97* (5), 455–462. <https://doi.org/10.1533/joti.2006.0271>.
- (100) Haas, L. Wettability Contrast Surfaces: Fabrication and Applications. *Rev. Educ. Pedagogy Cult. Stud.* **1995**, *17* (1), 1–6. <https://doi.org/10.1080/1071441950170102>.
- (101) Young, T. III. An Essay on the Cohesion of Fluids. *R. Soc.* **1805**, 65–87. <https://doi.org/10.1098/rstl.1805.0005>.
- (102) Quéré, D. Non-Sticking Drops. *Rep. Prog. Phys.* **2005**, *68* (11), 2495. <https://doi.org/10.1088/0034-4885/68/11/R01>.
- (103) Gao, L.; McCarthy, T. J. Wetting 101°. *Langmuir* **2009**, *25* (24), 14105–14115. <https://doi.org/10.1021/la902206c>.
- (104) van Oss, C. J. Chapter Two - The Apolar and Polar Properties of Liquid Water and Other Condensed-Phase Materials. In *Interface Science and Technology*; van Oss, C. J., Ed.; The Properties of Water and their Role in Colloidal and Biological Systems; Elsevier, 2008; Vol. 16, pp 13–30. [https://doi.org/10.1016/S1573-4285\(08\)00202-0](https://doi.org/10.1016/S1573-4285(08)00202-0).
- (105) Sadullah, M. S.; Xu, Y.; Arunachalam, S.; Mishra, H. Predicting Droplet Detachment Force: Young-Dupré Model Fails, Young-Laplace Model Prevails. *Commun. Phys.* **2024**, *7* (1), 1–9. <https://doi.org/10.1038/s42005-024-01582-0>.

- (106) Eral, H. B.; 't Mannetje, D. J. C. M.; Oh, J. M. Contact Angle Hysteresis: A Review of Fundamentals and Applications. *Colloid Polym. Sci.* **2013**, *291* (2), 247–260. <https://doi.org/10.1007/s00396-012-2796-6>.
- (107) Butt, H.-J.; Liu, J.; Koynov, K.; Straub, B.; Hinduja, C.; Roismann, I.; Berger, R.; Li, X.; Vollmer, D.; Steffen, W.; Kappl, M. Contact Angle Hysteresis. *Curr. Opin. Colloid Interface Sci.* **2022**, *59*, 101574. <https://doi.org/10.1016/j.cocis.2022.101574>.
- (108) Miwa, M.; Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. Effects of the Surface Roughness on Sliding Angles of Water Droplets on Superhydrophobic Surfaces. *Langmuir* **2000**, *16* (13), 5754–5760. <https://doi.org/10.1021/la991660o>.
- (109) Bormashenko, E. Progress in Understanding Wetting Transitions on Rough Surfaces. *Adv. Colloid Interface Sci.* **2015**, *222*, 92–103. <https://doi.org/10.1016/j.cis.2014.02.009>.
- (110) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.* **1936**, *28* (8), 988–994. <https://doi.org/10.1021/ie50320a024>.
- (111) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40* (0), 546–551. <https://doi.org/10.1039/TF9444000546>.
- (112) Reyssat, M.; Yeomans, J. M.; Quéré, D. Impalement of Fakir Drops. *Europhys. Lett.* **2007**, *81* (2), 26006. <https://doi.org/10.1209/0295-5075/81/26006>.
- (113) Bhushan, B.; Nosonovsky, M. The Rose Petal Effect and the Modes of Superhydrophobicity. *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* **2010**. <https://doi.org/10.1098/rsta.2010.0203>.
- (114) Milne, A. J. B.; Amirfazli, A. The Cassie Equation: How It Is Meant to Be Used. *Adv. Colloid Interface Sci.* **2012**, *170* (1), 48–55. <https://doi.org/10.1016/j.cis.2011.12.001>.
- (115) Gao, L.; McCarthy, T. J. The “Lotus Effect” Explained: Two Reasons Why Two Length Scales of Topography Are Important. *Langmuir* **2006**, *22* (7), 2966–2967. <https://doi.org/10.1021/la0532149>.
- (116) Simpson, J. T.; Hunter, S. R.; Aytug, T. Superhydrophobic Materials and Coatings: A Review. *Rep. Prog. Phys.* **2015**, *78* (8), 086501. <https://doi.org/10.1088/0034-4885/78/8/086501>.
- (117) Carrascosa, L. A. M.; Zarzuela, R.; Botana-Galvín, M.; Botana, F. J.; Mosquera, M. J. Achieving Superhydrophobic Surfaces with Tunable Roughness on Building Materials via Nanosecond Laser Texturing of Silane/Siloxane Coatings. *J. Build. Eng.* **2022**, *58*, 104979. <https://doi.org/10.1016/j.jobbe.2022.104979>.
- (118) He, H.; Guo, Z. Superhydrophobic Materials Used for Anti-Icing Theory, Application, and Development. *iScience* **2021**, *24* (11), 103357. <https://doi.org/10.1016/j.isci.2021.103357>.
- (119) Zeng, Q.; Zhou, H.; Huang, J.; Guo, Z. Review on the Recent Development of Durable Superhydrophobic Materials for Practical Applications. *Nanoscale* **2021**, *13* (27), 11734–11764. <https://doi.org/10.1039/D1NR01936H>.
- (120) Pozzato, A.; Zilio, S. D.; Fois, G.; Vendramin, D.; Mistura, G.; Belotti, M.; Chen, Y.; Natali, M. Superhydrophobic Surfaces Fabricated by Nanoimprint Lithography. *Microelectron. Eng.* **2006**, *83* (4), 884–888. <https://doi.org/10.1016/j.mee.2006.01.012>.
- (121) Atthi, N.; Nimittrakoolchai, O.-U.; Supothina, S.; Supadech, J.; Jeamsaksiri, W.; Pankiew, A.; Hruanun, C.; Poyai, A. An Effect of Silicon Micro-/Nano-Patterning Arrays on Superhydrophobic Surface. *J. Nanosci. Nanotechnol.* **2011**, *11* (10), 8967–8973. <https://doi.org/10.1166/jnn.2011.3505>.
- (122) Pal, C. A.; Angaru, G. K. R.; Lingamdinne, L. P.; Choi, Y.-L.; Momin, Z. H.; Kulkarni, R.; Koduru, J. R.; Chang, Y.-Y. Fabrication of Plasma-Treated Superhydrophobic Polydimethylsiloxane (PDMS) – Coated Melamine Sponge for Enhanced Adhesion

- Capability and Sustainable Oil/Water Separation. *Sep. Purif. Technol.* **2024**, *330*, 125483. <https://doi.org/10.1016/j.seppur.2023.125483>.
- (123) Li, D.; Xu, K.; Zhang, Y. A Review on Research Progress in Plasma-Controlled Superwetting Surface Structure and Properties. *Polymers* **2022**, *14* (18), 3759. <https://doi.org/10.3390/polym14183759>.
- (124) Abu Jarad, N.; Imran, H.; Imani, S. M.; Didar, T. F.; Soleymani, L. Fabrication of Superamphiphobic Surfaces via Spray Coating; a Review. *Adv. Mater. Technol.* **2022**, *7* (10), 2101702. <https://doi.org/10.1002/admt.202101702>.
- (125) Jafari, R.; Kiilakoski, J.; Honkanen, M.; Vippola, M.; Koivuluoto, H. Wetting Behavior and Functionality Restoration of Cold-Sprayed Aluminum-Quasicrystalline Composite Coatings. *J. Therm. Spray Technol.* **2023**, *32* (2), 609–626. <https://doi.org/10.1007/s11666-022-01522-w>.
- (126) Qian, B.; Shen, Z. Fabrication of Superhydrophobic Surfaces by Dislocation-Selective Chemical Etching on Aluminum, Copper, and Zinc Substrates. *Langmuir* **2005**, *21* (20), 9007–9009. <https://doi.org/10.1021/la051308c>.
- (127) Han, S. W.; Jeong, J.; Lee, D. H. Ice-Phobic Behavior of Superhydrophobic Al Surface Undervarious Etching Conditions. *J. Electroceramics* **2014**, *33* (1), 82–88. <https://doi.org/10.1007/s10832-014-9924-2>.
- (128) Wang, Z.; Li, Q.; She, Z.; Chen, F.; Li, L.; Zhang, X.; Zhang, P. Facile and Fast Fabrication of Superhydrophobic Surface on Magnesium Alloy. *Appl. Surf. Sci.* **2013**, *271*, 182–192. <https://doi.org/10.1016/j.apsusc.2013.01.158>.
- (129) Min Ruan; Wen Li; Baoshan Wang; Binwei Deng; Fumin Ma; Zhanlong Yu. Preparation and Anti-Icing Behavior of Superhydrophobic Surfaces on Aluminum Alloy Substrates. *Langmuir* **2013**, *29* (27), 8482–8491.
- (130) Manoharan, K.; Bhattacharya, S. Superhydrophobic Surfaces Review: Functional Application, Fabrication Techniques and Limitations. *J. Micromanufacturing* **2019**, *2* (1), 59–78. <https://doi.org/10.1177/2516598419836345>.
- (131) Wang, N.; Xiong, D.; Li, M.; Deng, Y.; Shi, Y.; Wang, K. Superhydrophobic Surface on Steel Substrate and Its Anti-Icing Property in Condensing Conditions. *Appl. Surf. Sci.* **2015**, *355*, 226–232. <https://doi.org/10.1016/j.apsusc.2015.06.203>.
- (132) Rivero, P. J.; Rodriguez, R. J.; Larumbe, S.; Monteserín, M.; Martín, F.; García, A.; Acosta, C.; Clemente, M. J.; García, P.; Mora, J.; Agüero, A. Evaluation of Functionalized Coatings for the Prevention of Ice Accretion by Using Icing Wind Tunnel Tests. *Coatings* **2020**, *10* (7), 636. <https://doi.org/10.3390/coatings10070636>.
- (133) Li, B.; Bai, J.; He, J.; Ding, C.; Dai, X.; Ci, W.; Zhu, T.; Liao, R.; Yuan, Y. A Review on Superhydrophobic Surface with Anti-Icing Properties in Overhead Transmission Lines. *Coatings* **2023**, *13* (2), 301. <https://doi.org/10.3390/coatings13020301>.
- (134) Liu, H.; Li, X.; Lv, L.; Liu, Z.; Chen, J. Fast Fabrication of Silicone-Modified Polyurethane/SiO₂ Composite Superhydrophobic Coating with Excellent Anti-Icing and Self-Cleaning Behaviour. *Mater. Res. Express* **2020**, *7* (11), 116403. <https://doi.org/10.1088/2053-1591/abadee>.
- (135) Ke, Q.; Fu, W.; Jin, H.; Zhang, L.; Tang, T.; Zhang, J. Fabrication of Mechanically Robust Superhydrophobic Surfaces Based on Silica Micro-Nanoparticles and Polydimethylsiloxane. *Surf. Coat. Technol.* **2011**, *205* (21), 4910–4914. <https://doi.org/10.1016/j.surfcoat.2011.04.073>.
- (136) Yang, C.; Wang, F.; Li, W.; Ou, J.; Li, C.; Amirfazli, A. Anti-Icing Properties of Superhydrophobic ZnO/PDMS Composite Coating. *Appl. Phys. A* **2015**, *122* (1), 1. <https://doi.org/10.1007/s00339-015-9525-1>.

- (137) Casali, A.; Pelagatti, P.; Balordi, M.; Santucci De Magistris, G.; Pini, F. Anti-Icing Elastomeric Coatings: Striking the Hydrophobicity-Elasticity Balance; Narvik (Norway), 2024; p 4.
- (138) Petrenko, V. F.; Peng, S. Reduction of Ice Adhesion to Metal by Using Self-Assembling Monolayers (SAMs). *Can. J. Phys.* **2003**, *81* (1–2), 387–393. <https://doi.org/10.1139/p03-014>.
- (139) Arianpour, F.; Farzaneh, M.; Jafari, R. Hydrophobic and Ice-Phobic Properties of Self-Assembled Monolayers (SAMs) Coatings on AA6061. *Prog. Org. Coat.* **2016**, *93*, 41–45. <https://doi.org/10.1016/j.porgcoat.2015.12.008>.
- (140) Brown, P. S.; Bhushan, B. Bioinspired, Roughness-Induced, Water and Oil Super-Philic and Super-Phobic Coatings Prepared by Adaptable Layer-by-Layer Technique. *Sci. Rep.* **2015**, *5* (1), 14030. <https://doi.org/10.1038/srep14030>.
- (141) Balordi, M.; Cammi, A.; Santucci de Magistris, G.; Chemelli, C. Role of Micrometric Roughness on Anti-Ice Properties and Durability of Hierarchical Super-Hydrophobic Aluminum Surfaces. *Surf. Coat. Technol.* **2019**, *374*, 549–556. <https://doi.org/10.1016/j.surfcoat.2019.06.001>.
- (142) Balordi, M.; Santucci de Magistris, G.; Chemelli, C. A Novel Simple Anti-Ice Aluminum Coating: Synthesis and In-Lab Comparison with a Superhydrophobic Hierarchical Surface. *Coatings* **2020**, *10* (2), 111. <https://doi.org/10.3390/coatings10020111>.
- (143) Jamil, M. I.; Ali, A.; Haq, F.; Zhang, Q.; Zhan, X.; Chen, F. Icephobic Strategies and Materials with Superwettability: Design Principles and Mechanism. *Langmuir* **2018**, *34* (50), 15425–15444. <https://doi.org/10.1021/acs.langmuir.8b03276>.
- (144) Huang, W.; Huang, J.; Guo, Z.; Liu, W. Icephobic/Anti-Icing Properties of Superhydrophobic Surfaces. *Adv. Colloid Interface Sci.* **2022**, *304*, 102658. <https://doi.org/10.1016/j.cis.2022.102658>.
- (145) Li, W.; Zhan, Y.; Yu, S. Applications of Superhydrophobic Coatings in Anti-Icing: Theory, Mechanisms, Impact Factors, Challenges and Perspectives. *Prog. Org. Coat.* **2021**, *152*, 106117. <https://doi.org/10.1016/j.porgcoat.2020.106117>.
- (146) Latthe, S. S.; Sutar, R. S.; Bhosale, A. K.; Nagappan, S.; Ha, C.-S.; Sadasivuni, K. K.; Liu, S.; Xing, R. Recent Developments in Air-Trapped Superhydrophobic and Liquid-Infused Slippery Surfaces for Anti-Icing Application. *Prog. Org. Coat.* **2019**, *137*, 105373. <https://doi.org/10.1016/j.porgcoat.2019.105373>.
- (147) Makkonen, L. Ice Adhesion —Theory, Measurements and Countermeasures. *J. Adhes. Sci. Technol.* **2012**.
- (148) Golovin, K.; Kobaku, S. P. R.; Lee, D. H.; DiLoreto, E. T.; Mabry, J. M.; Tuteja, A. Designing Durable Icephobic Surfaces. *Sci. Adv.* **2016**, *2* (3), e1501496. <https://doi.org/10.1126/sciadv.1501496>.
- (149) Meuler, A. J.; Smith, J. D.; Varanasi, K. K.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. Relationships between Water Wettability and Ice Adhesion. *ACS Appl. Mater. Interfaces* **2010**, *2* (11), 3100–3110. <https://doi.org/10.1021/am1006035>.
- (150) He, Z.; Vågenes, E. T.; Delabahan, C.; He, J.; Zhang, Z. Room Temperature Characteristics of Polymer-Based Low Ice Adhesion Surfaces. *Sci. Rep.* **2017**, *7* (1), 42181. <https://doi.org/10.1038/srep42181>.
- (151) Rønneberg, S.; Xiao, S.; He, J.; Zhang, Z. Nanoscale Correlations of Ice Adhesion Strength and Water Contact Angle. *Coatings* **2020**, *10* (4), 379. <https://doi.org/10.3390/coatings10040379>.
- (152) Mostofi Sarkari, N.; Mesonero Peralta, A.; Aktan, M. K.; Lök, S.; Smets, J.; Ameloot, R.; Killian, M. S.; Braem, A.; Nisol, B.; Molina-Lopez, F.; Seveno, D. Experimental Debate on the Overlooked Fundamental Concepts in Surface Wetting and Topography vs. Ice

- Adhesion Strength Relationships. *J. Colloid Interface Sci.* **2025**, *682*, 825–848. <https://doi.org/10.1016/j.jcis.2024.11.140>.
- (153) Ding, M.; Hussong, J.; Roisman, I. V. Freezing of a Supercooled Water Drop after an Impact onto a Solid Wall. *Cold Reg. Sci. Technol.* **2025**, *229*, 104359. <https://doi.org/10.1016/j.coldregions.2024.104359>.
- (154) Wong, T.-S.; Kang, S. H.; Tang, S. K. Y.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. *Nature* **2011**, *477* (7365), 443–447. <https://doi.org/10.1038/nature10447>.
- (155) Zhang, S.; Huang, J.; Cheng, Y.; Yang, H.; Chen, Z.; Lai, Y. Bioinspired Surfaces with Superwettability for Anti-Icing and Ice-Phobic Application: Concept, Mechanism, and Design. *Small* **2017**, *13* (48), 1701867. <https://doi.org/10.1002/smll.201701867>.
- (156) Samaha, M. A.; Gad-el-Hak, M. Slippery Surfaces: A Decade of Progress. *Phys. Fluids* **2021**, *33* (7), 071301. <https://doi.org/10.1063/5.0056967>.
- (157) Bohn, H. F.; Federle, W. Insect Aquaplaning: Nepenthes Pitcher Plants Capture Prey with the Peristome, a Fully Wettable Water-Lubricated Anisotropic Surface. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101* (39), 14138–14143. <https://doi.org/10.1073/pnas.0405885101>.
- (158) Long, Y.; Yin, X.; Mu, P.; Wang, Q.; Hu, J.; Li, J. Slippery Liquid-Infused Porous Surface (SLIPS) with Superior Liquid Repellency, Anti-Corrosion, Anti-Icing and Intensified Durability for Protecting Substrates. *Chem. Eng. J.* **2020**, *401*, 126137. <https://doi.org/10.1016/j.cej.2020.126137>.
- (159) He, Z.; Mu, L.; Wang, N.; Su, J.; Wang, Z.; Luo, M.; Zhang, C.; Li, G.; Lan, X. Design, Fabrication, and Applications of Bioinspired Slippery Surfaces. *Adv. Colloid Interface Sci.* **2023**, *318*, 102948. <https://doi.org/10.1016/j.cis.2023.102948>.
- (160) Li, B.; Bai, J.; Pu, Z.; Liu, B.; Hua, X.; Zhu, T.; Dai, X.; Xiang, H.; Yuan, Y. Anti-Icing Performance of SLIPSs Injected with Different Lubricants. *J. Phys. Conf. Ser.* **2024**, *2879* (1), 012042. <https://doi.org/10.1088/1742-6596/2879/1/012042>.
- (161) Deng, J.; Guo, Y.; Yu, H.; Huang, Y.; He, B. Effect of Lubricant Loading in Slippery Liquid-Infused Surface for Persistent Anti-Icing Performance. *Prog. Org. Coat.* **2024**, *197*, 108797. <https://doi.org/10.1016/j.porgcoat.2024.108797>.
- (162) Wang, F.; Ding, W.; He, J.; Zhang, Z. Phase Transition Enabled Durable Anti-Icing Surfaces and Its DIY Design. *Chem. Eng. J.* **2019**, *360*, 243–249. <https://doi.org/10.1016/j.cej.2018.11.224>.
- (163) Subramanyam, S. B.; Rykaczewski, K.; Varanasi, K. K. Ice Adhesion on Lubricant-Impregnated Textured Surfaces. *Langmuir* **2013**, *29* (44), 13414–13418. <https://doi.org/10.1021/la402456c>.
- (164) SYLGARD™ 184 Silicone Elastomer Kit. <https://www.dow.com/en-us/pdp/sylgard-184-silicone-elastomer-kit.01064291z.html> (accessed 2024-12-29).
- (165) SYLGARD™ 186 Silicone Elastomer Kit. <https://www.dow.com/en-us/pdp/sylgard-186-silicone-elastomer-kit.01040286z.html> (accessed 2024-12-29).
- (166) Brassard, J.-D.; Laforte, C.; Guerin, F.; Blackburn, C. Icephobicity: Definition and Measurement Regarding Atmospheric Icing. In *Contamination Mitigating Polymeric Coatings for Extreme Environments*; Wohl, C. J., Berry, D. H., Eds.; Springer International Publishing: Cham, 2019; pp 123–143. https://doi.org/10.1007/12_2017_36.
- (167) Balordi, M.; Cammi, A.; Santucci De Magistris, G.; Pini, F. Effect of Experimental Parameters on Icephobic Measurements; Montréal, 2023.
- (168) Ghauch, A.; Deveau, P.-A.; Jacob, V.; Baussand, P. Use of FTIR Spectroscopy Coupled with ATR for the Determination of Atmospheric Compounds. *Talanta* **2006**, *68* (4), 1294–1302. <https://doi.org/10.1016/j.talanta.2005.07.046>.

- (169) Kent Larson. Can You Estimate Modulus From Durometer Hardness for Silicones?, 2017.
- (170) Pericet-Cámara, R.; Best, A.; Butt, H.-J.; Bonaccorso, E. Effect of Capillary Pressure and Surface Tension on the Deformation of Elastic Surfaces by Sessile Liquid Microdrops: An Experimental Investigation. *Langmuir* **2008**, *24* (19), 10565–10568. <https://doi.org/10.1021/la801862m>.
- (171) Zhu, L.; Xue, J.; Wang, Y.; Chen, Q.; Ding, J.; Wang, Q. Ice-Phobic Coatings Based on Silicon-Oil-Infused Polydimethylsiloxane. *ACS Appl. Mater. Interfaces* **2013**, *5* (10), 4053–4062. <https://doi.org/10.1021/am400704z>.
- (172) Ospina, C.; Ibáñez-Ibáñez, P. F.; Tagliaro, I.; Stendardo, L.; Tosatti, S.; Antonini, C. Low Ice Adhesion on Soft Surfaces: Elasticity or Lubrication Effects? *J. Colloid Interface Sci.* **2025**, *677*, 494–503. <https://doi.org/10.1016/j.jcis.2024.08.042>.
- (173) Chen, D.; Gelenter, M. D.; Hong, M.; Cohen, R. E.; McKinley, G. H. Icephobic Surfaces Induced by Interfacial Nonfrozen Water. *ACS Appl. Mater. Interfaces* **2017**, *9* (4), 4202–4214. <https://doi.org/10.1021/acsami.6b13773>.
- (174) Ibáñez-Ibáñez, P. F.; Montes Ruiz-Cabello, F. J.; Cabrerizo-Vílchez, M. A.; Rodríguez-Valverde, M. A. Ice Adhesion of PDMS Surfaces with Balanced Elastic and Water-Repellent Properties. *J. Colloid Interface Sci.* **2022**, *608* (Pt 1), 792–799. <https://doi.org/10.1016/j.jcis.2021.10.005>.
- (175) Lopes, M. C.; Bonaccorso, E. Evaporation Control of Sessile Water Drops by Soft Viscoelastic Surfaces. *Soft Matter* **2012**, *8* (30), 7875. <https://doi.org/10.1039/c2sm25958c>.
- (176) Mukhopadhyay, R. When PDMS Isn't the Best.
- (177) Maeda, N.; Chen, N.; Tirrell, M.; Israelachvili, J. N. Adhesion and Friction Mechanisms of Polymer-on-Polymer Surfaces. *Science* **2002**, *297* (5580), 379–382. <https://doi.org/10.1126/science.1072378>.
- (178) Yu, Y.; Sanchez, D.; Lu, N. Work of Adhesion/Separation between Soft Elastomers of Different Mixing Ratios. *J. Mater. Res.* **2015**, *30* (18), 2702–2712. <https://doi.org/10.1557/jmr.2015.242>.
- (179) Placet, V.; Delobelle, P. Mechanical Properties of Bulk Polydimethylsiloxane for Microfluidics over a Large Range of Frequencies and Aging Times. *J. Micromechanics Microengineering* **2015**, *25* (3), 035009. <https://doi.org/10.1088/0960-1317/25/3/035009>.
- (180) Liu, M.; Sun, J.; Chen, Q. Influences of Heating Temperature on Mechanical Properties of Polydimethylsiloxane. *Sens. Actuators Phys.* **2009**, *151* (1), 42–45. <https://doi.org/10.1016/j.sna.2009.02.016>.
- (181) Sales, F. C. P.; Ariati, R. M.; Noronha, V. T.; Ribeiro, J. E. Mechanical Characterization of PDMS with Different Mixing Ratios. *Procedia Struct. Integr.* **2022**, *37*, 383–388. <https://doi.org/10.1016/j.prostr.2022.01.099>.
- (182) Seghir, R.; Arscott, S. Extended PDMS Stiffness Range for Flexible Systems. *Sens. Actuators Phys.* **2015**, *230*, 33–39. <https://doi.org/10.1016/j.sna.2015.04.011>.
- (183) Casali, A.; Balordi, M.; Santucci De Magistris, G.; Gadia, P.; Pelagatti, P.; Pini, F. Effects of Precursors Ratio and Curing Treatment on the Icephobicity of Polydimethylsiloxane. *Coatings* **2024**, *14* (7), 901. <https://doi.org/10.3390/coatings14070901>.
- (184) Balordi, M.; de Magistris, G. S.; Pini, F. Investigation on Snowphobic and Icephobic Behavior of Superhydrophobic Surfaces.
- (185) Kolle, S.; Ahanotu, O.; Meeks, A.; Stafslie, S.; Kreder, M.; Vanderwal, L.; Cohen, L.; Waltz, G.; Lim, C. S.; Slocum, D.; Greene, E. M.; Hunsucker, K.; Swain, G.; Wendt, D.; Teo, S. L.-M.; Aizenberg, J. On the Mechanism of Marine Fouling-Prevention Performance

- of Oil-Containing Silicone Elastomers. *Sci. Rep.* **2022**, *12* (1), 11799. <https://doi.org/10.1038/s41598-022-15553-4>.
- (186) Koivuluoto, H.; Hartikainen, E.; Niemelä-Anttonen, H. Thermally Sprayed Coatings: Novel Surface Engineering Strategy Towards Icephobic Solutions. *Materials* **2020**, *13* (6), 1434. <https://doi.org/10.3390/ma13061434>.
- (187) Koivuluoto, H. A Review of Thermally Sprayed Polymer Coatings. *J. Therm. Spray Technol.* **2022**, *31* (6), 1750–1764. <https://doi.org/10.1007/s11666-022-01404-1>.
- (188) Koivuluoto, H.; Stenroos, C.; Kylmälahti, M.; Apostol, M.; Kiilakoski, J.; Vuoristo, P. Anti-Icing Behavior of Thermally Sprayed Polymer Coatings. *J. Therm. Spray Technol.* **2017**, *26* (1), 150–160. <https://doi.org/10.1007/s11666-016-0501-x>.
- (189) Donadei, V.; Koivuluoto, H.; Sarlin, E.; Vuoristo, P. Icephobic Behaviour and Thermal Stability of Flame-Sprayed Polyethylene Coating: The Effect of Process Parameters. *J. Therm. Spray Technol.* **2020**, *29* (1), 241–254. <https://doi.org/10.1007/s11666-019-00947-0>.
- (190) Donadei, V. Icephobicity of Flame-Sprayed Polymer Coatings. PhD thesis, Tampere University, 2022. <https://trepo.tuni.fi/handle/10024/143284>.
- (191) Koivuluoto, H.; Stenroos, C.; Ruohomaa, R.; Bolelli, G.; Lusvarghi, L.; Vuoristo, P. Research on Icing Behavior and Ice Adhesion Testing of Icephobic Surfaces.
- (192) Koivuluoto, H.; Larjo, J.; Marini, D.; Pulci, G.; Marra, F. Cold-Sprayed Al6061 Coatings: Online Spray Monitoring and Influence of Process Parameters on Coating Properties. *Coatings* **2020**, *10* (4), 348. <https://doi.org/10.3390/coatings10040348>.
- (193) Kumar, S.; Kumar, M.; Jindal, N. Overview of Cold Spray Coatings Applications and Comparisons: A Critical Review. *World J. Eng.* **2020**, *17* (1), 27–51. <https://doi.org/10.1108/WJE-01-2019-0021>.
- (194) Khammas, R.; Koivuluoto, H. Durable Icephobic Slippery Liquid-Infused Porous Surfaces (SLIPS) Using Flame- and Cold-Spraying. *Sustainability* **2022**, *14* (14), 8422. <https://doi.org/10.3390/su14148422>.
- (195) Vedder, W.; Vermilyea, D. A. Aluminum + Water Reaction. *Trans. Faraday Soc.* **1969**, *65* (0), 561–584. <https://doi.org/10.1039/TF9696500561>.
- (196) Godart, P.; Fischman, J. Z.; Seto, K. C.; Hart, D. Hydrogen Production from Aluminum-Water Reactions Subject to Varied Pressures and Temperatures. *Author Website* **2019**.
- (197) Cheng, X.; Yang, G.; Wu, J. Spontaneously Grown Boehmite Structures Improve Pool Boiling Heat Transfer on Aluminium Surfaces. *Int. J. Heat Mass Transf.* **2022**, *192*, 122937. <https://doi.org/10.1016/j.ijheatmasstransfer.2022.122937>.
- (198) Wefers, K. Oxides and Hydroxides of Aluminum.
- (199) Mineral Data Publishing. Boehmite AlO(OH). *Mineral Data Publishing*; 2001; Vol. 1, p 1.
- (200) Balordi, M.; Cammi, A.; Chemelli, C.; Santucci De Magistris, G. Effect of Micro-Roughness of Aluminum Alloy Surface on Anti-Ice and Durability Properties of Hierarchical Structured Coatings; Reykjavík, 2019; p 5.
- (201) UNI - Ente Nazionale Italiano di Unificazione. UNI EN 828 Determination by Measurement of Contact Angle and Surface Free Energy of Solid Surface, 2013.
- (202) Dispersion-Polar Surface Tension Properties of Organic Solids. *ResearchGate* **2024**. <https://doi.org/10.1080/0021846708544582>.
- (203) Kaelble, D. H. Dispersion-Polar Surface Tension Properties of Organic Solids. *J. Adhes.* **1970**, *2* (2), 66–81. <https://doi.org/10.1080/0021846708544582>.
- (204) Rehfeld, N.; Brassard, J.-D.; Yamazaki, M.; Sakaue, H.; Balordi, M.; Koivuluoto, H.; Mora, J.; He, J.; Pervier, M.-L.; Dolatabadi, A.; Asenath-Smith, E.; Järn, M.; Hou, X.; Stenzel, V. Round-Robin Study for Ice Adhesion Tests. *Aerospace* **2024**, *11* (2), 106. <https://doi.org/10.3390/aerospace11020106>.

- (205) *Advances in Elastomers I*; Springer; Andreas ÖchsnerLucas F. M. da SilvaHolm Altenbach, 2013; Vol. 11.
- (206) Shit, S. C.; Shah, P. A Review on Silicone Rubber. *Natl. Acad. Sci. Lett.* **2013**, *36* (4), 355–365. <https://doi.org/10.1007/s40009-013-0150-2>.
- (207) Silicones: Preparation, Properties and Performance - Dow Corning. *Mater. Sci.* **2015**.
- (208) Gubanski, S. M. Properties of Silicone Rubber Housings and Coatings. *IEEE Trans. Electr. Insul.* **1992**, *27* (2), 374–382. <https://doi.org/10.1109/14.135608>.
- (209) Shit, S. C.; Shah, P. A Review on Silicone Rubber. *Natl. Acad. Sci. Lett.* **2013**, *4* (36), 355–365. <https://doi.org/10.1007/s40009-013-0150-2>.
- (210) Zhuo, Y.; Xiao, S.; Amirfazli, A.; He, J.; Zhang, Z. Polysiloxane as Icephobic Materials – The Past, Present and the Future. *Chem. Eng. J.* **2021**, *405*, 127088. <https://doi.org/10.1016/j.cej.2020.127088>.
- (211) Eduok, U.; Faye, O.; Szpunar, J. Recent Developments and Applications of Protective Silicone Coatings: A Review of PDMS Functional Materials. *Prog. Org. Coat.* **2017**, *111*, 124–163. <https://doi.org/10.1016/j.porgcoat.2017.05.012>.
- (212) Miranda, I.; Souza, A.; Sousa, P.; Ribeiro, J.; Castanheira, E. M. S.; Lima, R.; Minas, G. Properties and Applications of PDMS for Biomedical Engineering: A Review. *J. Funct. Biomater.* **2021**, *13* (1), 2. <https://doi.org/10.3390/jfb13010002>.
- (213) Li, S.; Zhang, J.; He, J.; Liu, W.; Wang, Y.; Huang, Z.; Pang, H.; Chen, Y. Functional PDMS Elastomers: Bulk Composites, Surface Engineering, and Precision Fabrication. *Adv. Sci.* **2023**, *10* (34), 2304506. <https://doi.org/10.1002/advs.202304506>.
- (214) Fauziah, U.; Sandi, D.; Arini, V. F.; Aulia, D. G.; Setiadji, S.; Fitrilawati; Risdiana. Synthesis of Polydimethylsiloxane with Hydrolysis and Condensation Methods Using Monomer of Dichlorodimethylsilane as Vitreous Humour Substitute. *J. Phys. Conf. Ser.* **2022**, *2165* (1), 012026. <https://doi.org/10.1088/1742-6596/2165/1/012026>.
- (215) David Contreras López; Javier Vallejo Montesinos; José Amir González Calderón. Polysiloxanes as Polymer Matrices in Biomedical Engineering: Their Interesting Properties as the Reason for the Use in Medical Sciences. *Polym. Bull.* **2019**, *77* (5), 2749–2817.
- (216) Mani, S.; Cassagnau, P.; Bousmina, M.; Chaumont, P. Cross-Linking Control of PDMS Rubber at High Temperatures Using TEMPO Nitroxide. *Macromolecules* **2009**, *42* (21), 8460–8467. <https://doi.org/10.1021/ma901521v>.
- (217) Azevedo, M.; Monks, A.-M.; Kerschbaumer, R. C.; Schlögl, S.; Holzer, C. Peroxide-Based Crosslinking of Solid Silicone Rubber, Part I: Insights into the Influence of Dicumylperoxide Concentration on the Curing Kinetics and Thermodynamics Determined by a Rheological Approach. *Polymers* **2022**, *14* (20), 4404. <https://doi.org/10.3390/polym14204404>.
- (218) Lewis, B. L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchins, G. Platinum Catalysts Used in the Silicones Industry: Their Synthesis and Activity in Hydrosilylation. *Platin. Met. Rev.* **1997**, *41* (2), 66–75. <https://doi.org/10.1595/003214097X4126675>.
- (219) *In Situ Determination of the Active Catalyst in Hydrosilylation Reactions Using Highly Reactive Pt(0) Catalyst Precursors* | *Journal of the American Chemical Society*. <https://pubs.acs.org/doi/10.1021/ja9825377> (accessed 2024-12-28).
- (220) Wang, S.; Peng, Z.; Huang, Y.; Zhu, M.; Liu, Y.; Zhang, Y. Synthesis, Characterization and Properties of Vinyl-Terminated Poly[Dimethylsiloxane-Co-Methyl(Phenyl)Siloxane]. *Polymer* **2024**, *311*, 127554. <https://doi.org/10.1016/j.polymer.2024.127554>.
- (221) Mani, S.; Cassagnau, P.; Bousmina, M.; Chaumont, P. Cross-Linking Control of PDMS Rubber at High Temperatures Using TEMPO Nitroxide. *Macromolecules* **2009**, *42* (21), 8460–8467. <https://doi.org/10.1021/ma901521v>.

- (222) Troegel, D.; Stohrer, J. Recent Advances and Actual Challenges in Late Transition Metal Catalyzed Hydrosilylation of Olefins from an Industrial Point of View. *Coord. Chem. Rev.* **2011**, *13–14* (255), 1440–1459. <https://doi.org/10.1016/j.ccr.2010.12.025>.
- (223) Zaranek, M.; Pawluc, P. Markovnikov Hydrosilylation of Alkenes: How an Oddity Becomes the Goal. *ACS Catal.* **2018**, *8* (10), 9865–9876. <https://doi.org/10.1021/acscatal.8b03104>.
- (224) *Hydrosilylation: A Comprehensive Review on Recent Advances (Advances in Silicon Science, 1) [2009 ed.]* 9781402081712, 9781402081729, 1402081715 - DOKUMEN.PUB. <https://dokumen.pub/hydrosilylation-a-comprehensive-review-on-recent-advances-advances-in-silicon-science-1-2009 ed-9781402081712-9781402081729-1402081715.html> (accessed 2024-12-29).
- (225) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press, 1992.