Adhesive joint use and aging in food machinery: A case-study on beverage filling systems

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A. Pirondi[*,1], F. Dazzi[2], L. Zomparelli[3]

[1]Dipartimento di Ingegneria e Architettura, Università di Parma, Parco Area delle Scienze 181/A, 43124 Parma, Italy
[2]Sidel SpA, Via La Spezia 241/A, 43126 Parma, Italy
[3]Centro Interdipartimentale SITEIA.PARMA, Università di Parma, Parco Area delle Scienze 181/A, 43124 Parma, Italy

Abstract

The objective of this work is to evaluate the introduction of bonding technology in the assembly of beverage filling machines. In this specific field, bonding has two potential great advantages with respect to welding, that are the speed of application and the absence of thermal distortions. Furthermore, since it presents fewer risks for safety at work, it allows the simultaneous execution of other assembly operations. On the other hand, the use of bonding requires a design process integrated by tests related to the specific application and operating conditions, that in the case of food machinery are: i) bonding of low surface roughness, austenitic stainless steel without surface preparation but degreasing; ii) contact of the joint with the chemically aggressive substances used for cleaning and sanitization. In the present study, first a technical-economical comparison with welding (business case) was done on a component of the structure of a filling machine. Then the adhesive appropriate for the application was identified experimentally with tests on single-lap joints (SLJ) with different surface finishes and subjected to chemical aging under the cleaning and sanitization agents. Finally, the scale-up to a larger and more complex structure was performed by joining two modules of the outer casing of a filling machine.

Keywords

Beverage filling machines, bonding, stainless steel, chemical aging, demonstrator

1. Introduction

The need to reduce lead time and production costs is increasingly marked in the manufacturing industry, especially in the case of made-to-order food machinery where the minimization of the lead time becomes essential for competitiveness.

*Corresponding author: alessandro.pirondi@unipr.it

The assembly technique currently used in the majority of the food machinery joints is welding, a process with a high lead time due to the advancement times that it entails and the need for subsequent pickling of the welded area in order to restore the passive surface layer that protects the weld seam from corrosion. In addition, welding requires highly specialized labor and, in the case of food machinery metallic carpentry, the operation is carried out on thin sheets (1.5-3 mm) resulting in distortions that negatively affect the subsequent assembly phases.
Structural bonding is gaining more and more application in the industrial field due to the variety and flexibility of solutions it allows [1], but it should be borne in mind that its use requires a design process integrated by tests related to the specific application and operating conditions [2], [3].
The objective of this work is to evaluate the introduction of bonding in place of welding in the assembly of beverage filling machines. In this specific field, bonding has two potential great advantages compared to welding, which are the speed of application and the absence of thermal distortions [1]. Furthermore, since it presents fewer risks for safety at work, bonding allows the simultaneous execution of other assembly operations, which would otherwise have had to be suspended while welding. The application of bonding in the construction of food machinery is foreseen in some technical documents [4], [5], but from the point of view of the scientific literature it is still apparently limited to a previous work by some of the authors [6]. It should also be borne in mind that the geometry and materials of the joint must comply with, or be brought back through appropriate measures, to the standards and guidelines of "hygienic" design [4], [5]. Concerning this point, the case-study will concentrate on the application in parts that are not in contact with the beverage, therefore the only concern is to provide a good cleanability of the joint, but there is no potential risk of migration of substances from the adhesive to the bottled product.
In the case of food machinery, it is also necessary to evaluate two peculiar aspects: i) the material of the substrates is in majority austenitic stainless steel with low-roughness surface finish for cleanibility reasons; ii) the machines are subjected to a periodic sanitization cycle with chemically aggressive substances. Regarding the first point, austenitic stainless steel is considered a material with a high surface energy, therefore abrasion and subsequent cleaning and degreasing already ensure a good resistance of the joint as shown in [7], even though a chemical treatment with mixtures of inorganic acids (sulfuric, nitric, nitrofluoridric) may be more effective [8]. On the other hand, performing such treatment in the manufacturing line of food machines is troublesome for cleanliness and safety reasons, therefore only degreasing and possibly primerization can be easily accepted by manufacturers. The durability of stainless steel

joints has been evaluated instead in several studies [9]-[14], in which aging is accelerated by exposure to cycles of high temperature and humidity, or salt spray, but no elements are found regarding the effect of prolonged exposure to the substances used in the sanitization of food machinery, i.e. strong acid and alkaline inorganic compounds. In the study it is therefore necessary to evaluate the effect of different surface finishes after a simple degreasing and, possibly, primerization, and of the aforementioned chemical agents, that are specific of the beverage filling machine cleaning cycle, on the resistance of the joint over time, in order to select the adhesive appropriate for the application in this field. The feasibility study of using structural adhesives in the assembly of the stainless sheet metal has been done with reference to the inner casing of the protection structure of a filling machine. The specific component was chosen as a case-study, but it is representative of numerous other parts of a filling machine, beside in general joints in stainless steel food machinery carpentry.

2. Methods

2.1 Case-study description

In high production rate beverage filling machines, empty bottles are continuously transferred by a series of handling modules to a rotating structure (also named “carousel”) with nozzles (filling valves) on its periphery to fill the bottle with product (water, Carbonated Soft Drink - CSD, beer, milk, etc..). The bottling area must be protected both from human access for safety reason, and from external bodies and contamination for food safety and hygiene reasons: wide perimetral protections prevent access to the filling zone from operators, while smaller protections close to the nozzles can prevent the access of foreign bodies and other sources of contamination. Inside the protected volume are performed, periodically, cleaning cycles called Surface Cleaning (called in the common practice Cleaning-Out-of- Place or COP), that apply acid and alkaline cleaning products, plus a certain amount of water for preparation and rinsing. A protection type that realize a volume where bottle transfer and filling are performed, is shown in Figure 1.

(a) (b)

Figure 1 – example of protection: a) outer side; b) inner side (machine under construction).

The protection is composed of an inner casing , visible on the left in Figure 1b, which function is to separate the internal of the carousel from the region where the bottles are filled and that is subjected to the COP. The inner casing is made up of calendered, sheet metal sectors, in a number depending on the diameter of the carousel welded along the nip and reinforced by welded strap on the outer face. An outline of the inner casing and of the connection to the carousel the is given in Figure 2; the inner casing is moving at the same rotational speed of the carousel. Mechanical and environmental actions are summarized in Table 1.

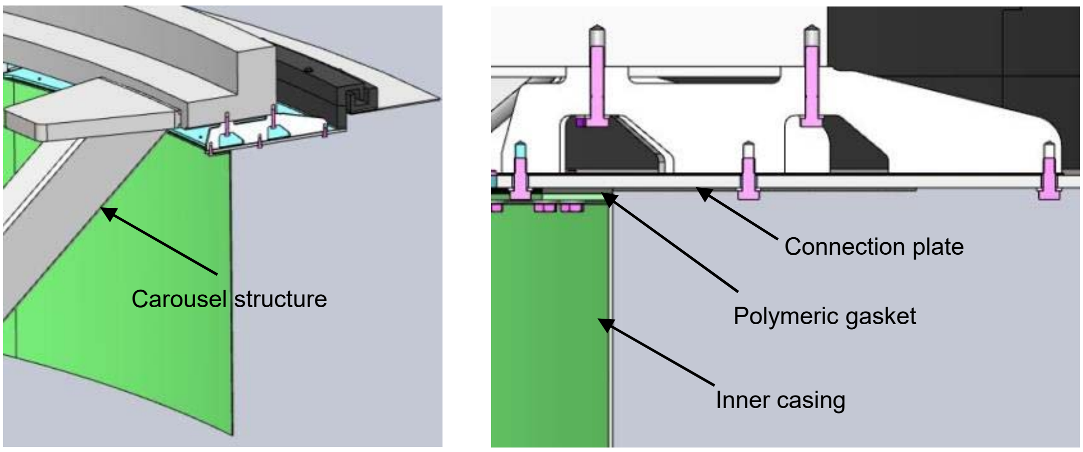


Figure 2 – Outline of the inner casing and detail of its joint with the connection plate.

Table 1 – Mechanical and environmental actions on the inner casing of RE machines.

Action	Type

Mechanical	Centrifugal body force in service
	Inertial body force in case of emergency stop
	Thermal eigenstress during sanitization
	Gravity body force
Environmental	Sanitization agents
	Sanitization temperature (max 40 °C)

The inner casing has three joint, shown in Figure 3. Joint 1 is a bolting to the carousel connection plate shown in Figure 2, with the interposition of a polymeric gasket. Joint 2 is instead a butt-strap welding carried out by TIG (Tungsten Inert Gas) technique. Joint 3 is a butt-strap TIG welding done in order to seal the seam between the connection plate sectors. The use of bonded joints would also eliminate the need of the polymeric gasket in Joint 1.

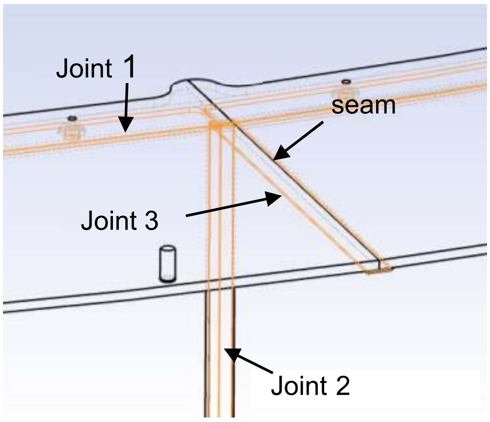
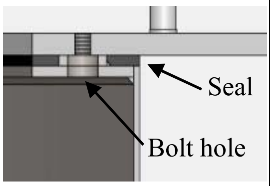
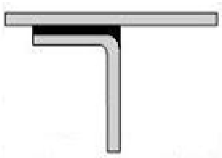


Figure 3 – Joints in the inner casing to be substituted by bonding.

The three joints can be easily converted into butt or butt-strap bonded joints as outlined in Table 2, minimizing the changes to drawings and to the manufacturing process and making the bonded solution applicable also in case of maintenance of existing machines.

Table 2 – Outline of joints in the inner casing and corresponding bonded solution.

Joint	Present solution	Bonded solution	Bonded area (cm^2)
1			3600
2			90

3			40

The joint 1 has also the structural function to support the weight of the casing and the actions originating from the rotation of the carousel to which the casing is connected. Although these actions do not achieve large values, they generate traction on the bond and it is therefore good to evaluate in advance the level of stress induced on the joint. The average stresses on the joint are:

$$\sigma_z = \frac{P}{A} \quad (1)$$

$$\tau_{r\theta} = \frac{J \cdot \alpha \cdot R}{I_p} \quad (2)$$

where P and J are respectively the weight and the moment of inertia of the inner casing around the rotation axis, A and I_p the area and the polar moment of inertia of the joint and α the angular deceleration of the carousel during the emergency stop. Given the large bonding area (see Table 2), the resulting average stresses assume extremely low values $\sigma_z = 3.3*10^{-3}$ MPa, $\tau_{r\theta} = 0.4*10^{-3}$ MPa, so even considering that the real distribution may show stress concentration at the ends of the joint, that would hardly lead to critical values for the strength. To estimate more in detail the stress distribution, a finite element analysis of Joint 1 is done using the Abaqus software (Figure 4). In order to keep the modeling and computational effort at an acceptable level, only the connection plate (thickness 4 mm), the inner casing (thickness 2 mm) and the interposed adhesive layer (thickness 0.2 mm) are considered and modeled with axisymmetric two-dimensional (2D) finite elements. The model is loaded with body forces corresponding to the gravity and to the centrifugal acceleration produced by the rotation at 12 rotations per minute (rpm), while the emergency stop deceleration direction is out-of-plane and therefore could not be accounted for in the 2D model. The adhesive layer is modelled with two rows of four-node elements and the stresses are evaluated at its midplane. The analysis is linear elastic with the Young's modulus taken from Table 3 for Adhesive 1 and Adhesive 2, respectively, and a Poisson's ratio taken as a typical values found in epoxies $\nu = 0.4$. The low stiffness of Adhesive 3 would give for sure a smoother stress distribution than with Adhesive 1 or 2 and Adhesive 4 Young's modulus is intermediate between Adhesive 1 and 2, therefore the results would also take intermediate values. The analysis revealed that the gravity alone produces a peak of peel at the outside corner with a value σ_z = 0.02-0.03 MPa depending on the adhesive, while in service a stress distribution, characterized by both peel and shear, is shown in Figure 5. Taking the maximum principal stress as uniaxial equivalent stress measure that account for the sign of peel stress, the most stressed point is located at the peak of peel stress, with a value $\sigma_{PRIN,MAX}$ = 0.57 MPa for Adhesive 1 and $\sigma_{PRIN,MAX}$ = 0.88 MPa for Adhesive 2.

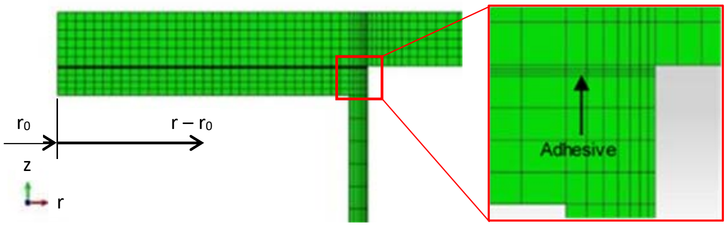


Figure 4 – axisymmetric finite element model of Joint 1.

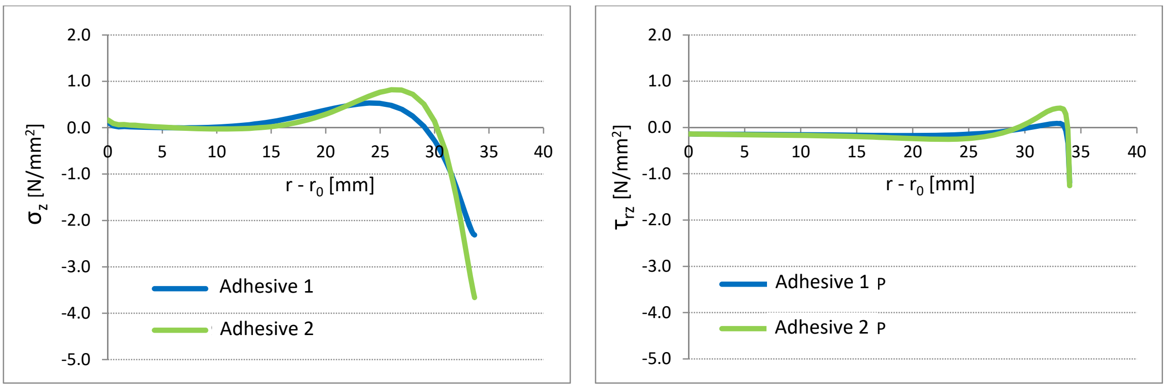


Figure 5 – Peel (left) and shear (right) stresses in Joint 1.

2.2 Adhesives

Technical datasheets of structural adhesives report generally the value of strength under standard test conditions and on specific materials and surface finishes, which are difficult to transfer to a generic case where joint shape, environmental conditions, materials and finishes strongly differ from those of a standard test. It is therefore necessary to carry out a design integrated by tests, i.e. the experimental evaluation of the behavior of the adhesive in the specific conditions envisaged for the joint to be made. To verify the performance of the selected adhesives, an experimental test campaign was therefore set up, verifying both the characteristics in terms of strength on the specific surface finish and the effect of chemical aging by the COP agents.

For a first experimental campaign, three adhesives were selected, which will later be referred to for simplicity as Adhesive 1, 2, and 3, respectively. The main features are:

Adhesive 1: LOCTITE® Hysol® 9466™ (currently rebranded as LOCTITE® EA® 9466™), a two-component thixotropic epoxy with high mechanical strength, reaches full strength after 24 h and has an open time (work-life) of about 60 minutes, which allows precise assembly and possible adjustment of the position of the adherends;

Adhesive 2: LOCTITE® Hysol® 9492™ (currently rebranded as LOCTITE® EA® 9492™), a two-component thixotropic epoxy for high temperatures, reaches full strength after 24 h. It is declared to be resistant to some chemical agents of interest, such as NaOH and acetic acid, as well as to water and humidity.

Adhesive 3: TEROSON MS 9399, a two-component, flexible MS (Modified Silane) adhesive, cures completely in 24 h. It allows excellent adhesion on metals without pre-treatment, but cleaning and degreasing. A good chemical resistance is declared with acids and bases at the concentrations of interest in this study.

A second experimental campaign involved other two adhesives, which will be therefore called Adhesive 4 and 5, respectively, in the following. In these cases, the tests were conducted only for the 2B tumbled surface finish (see description of surface finishes in the following).

Adhesive 4: 3M Scotch-Weld™ 7240 FR B/A, a high performance, two-component, toughened epoxy adhesive that exhibits a good strength in contact with oil derivates and salt fog.

Adhesive 5: Elantas Elan-tech® AS 50/AW 50, a two-component epoxy system loaded with non-abrasive fillers with chemical resistance to engine oil, petrol, acids and bases.

A third experimental campaign involved Adhesive 4 for which, unlike Adhesives 1-3 and 5, a specific primer was available (3M™ Surface Pre-Treatment AC-130) and it was applied after cleaning. In this way, the good resistance to chemical aging of the adhesive itself was combined with the improvement of the adhesion and chemical resistance of the interface provided by the primer. The basic mechanical properties of Adhesives 1-5 are listed in Table 3.

Table 3 – Adhesives basic mechanical properties from suppliers datasheets (in MPa).

Property	Adhesive 1	Adhesive 2	Adhesive 3	Adhesive 4	Adhesive 5
Lap shear strength*	23	12	2	24	17
Tensile strength**	32	31	3	N/A	50***
Young's modulus	1718	6700	3	3750	4000

*on stainless steel; **bulk adhesive; ***flexural strength

2.3 Specimen and test procedure

Since the geometry of the joints hypothesized in Sect. 2.1 for bonding of the inner casing is a butt-strap type, a single-lap joint specimen defined by the standard [15] and represented in Figure 6, is a reasonable choice to test the strength. Samples with an adherend thickness of 1.5

mm were used and tabs of the same thickness and material were applied to the ends of the adherends to keep the alignment. The material is AISI 304 L (X2 CrNi 18-9). The thickness of the adhesive layer 0.25 ± 0.01mm, controlled by adding stainless steel spheres with a diameter of 0.24-0.26mm. In the case of Adhesive 3, a thickness of 1.5 mm was set, as typical for highly elastic adhesives. At the same time, thicker tabs were also used to ensure the alignment of the specimen.

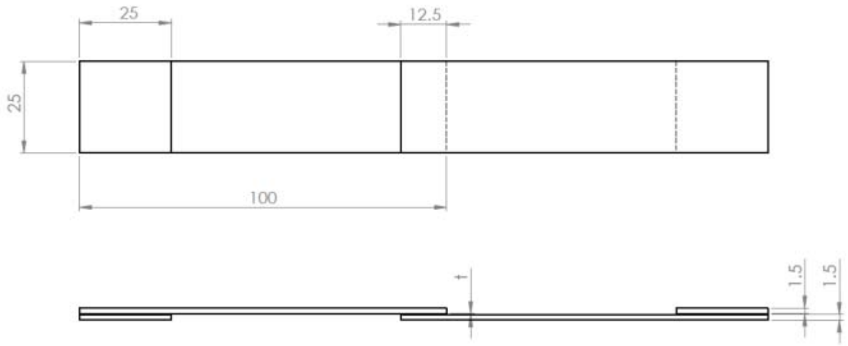


Figure 6 - single-lap joint specimen used in the experiments.

Five specimens were tested for each condition examined as indicated in [15]. The specimens were bonded in a PolyEthilene (PE) template to ensure the alignment of the adherends and the length of the overlap. The tests were performed using an Instron 4467 electromechanical machine with an acquisition rate of 10 Hz. As prescribed in [15], they were performed under displacement control until the sample was broken. The displacement speeds used are 1.3 mm/min for joints with stiff epoxies and 10 mm/min for joints with flexible MS adhesive so that, according to [15], the test lasts no longer than 65 ± 20 s in any case. The Chauvenet criterion was applied to the results to identify any outliers with respect to a normal distribution assumed for each batch of specimens.

2.4 Surface finish

The surface finish of the stainless steel sheets commonly used in food machinery are indicated in Table 4 with the nomenclature according to the European standard EN 10088-2 and the related value of roughness R_a; the sandblasting treatment is also indicated for comparison. A surface with a low roughness clearly limits adhesion, however mechanical, physical or chemical surface treatments are hardly applicable in this case because of hygienic and safety risks management at the manufacturing line, so that one can only resort to cleaning and degreasing and, possibly, apply a specific primer or coupling agent.

Table 4 – Average values of roughness R_a of the adherends.

Surface finish type	R_a [µm]
2B bright (2R)	0.13
2B Scotch-Brite (2J)	0.29
2B (tumbled)	1.07
Micro shot-peened	1.54
Sandblasted	3.56

Comparative tests were then performed to evaluate the effect of these types of surface finish on the strength of the joint and compared to a conventional sandblasting treatment. The MS adhesive was not tested with the 2B bright finish or with the sandblasted one since for the other three surfaces, tested initially, the failure was always cohesive meaning a substantial insensitivity to roughness.

2.5 COP-SOP aging simulation

The cleaning cycle of the machine surfaces (Cleaning-Out-of-Place, COP) involves a first washing with an alkaline, sodium hydroxide (NaOH) foaming solution and a subsequent sanitization (Sanitization-Out-of-Place, SOP) with a PerAcetic Acid (PAA) solution. Rinsing with process water is performed before and after each phase. The cycle is commonly between daily and weekly and it is supplemented monthly and after each maintenance operation by washing with an acid-based solution (HNO_3 or H_3PO_4) with a descaling function. This process takes place at temperatures ranging from ambient up to 40 °C. Table 5 shows an indicative recipe of the daily external washing cycle (COP and SOP).

Table 5 – Typical cleaning cycle for external surfaces (COP-SOP).

Step	Agent	Temperature (°C)	Duration (min)
Rinsing	Water	Ambient	10
Cleaning	Foaming with 2% NaOH	Max 40	10
Rinsing	Water	Ambient	10
Sanification	Foaming with 2% PAA	Max 40	10
Rinsing	Water	Ambient	10

Considering an average machine life of 20 years as a reference target and summing the minutes of contact with the solutions, a total contact time of approx. 50 days (1200 h) is found.

The aging caused by contact with COP-SOP agents was simulated by immersing the joints in solutions indicated in Table 6. To maintain the temperature at 40 °C, two thermostatic baths were used in which containers with the solutions were immersed in hot water. The solutions were renewed every 7 days, in order to keep them active, in particular this is important for the product VT70-Diverfoam which contains PAA which is known to degradate rapidly.

Table 6 – COP-SOP chemicals (supplier: Diversey).

SOL.	Agent	Conc. [% vol.]	Active principle	Conc. of active principle in the agent (% vol.)	T [°C]
1	VE3 EnduroSuper	2	KOH EDTA Propanol	3-10 % 3-10 % 3-10 %	23-40
2	VE9 EnduroEco	2	H_3PO_4 Propanol	30-50 % 3-10 %	23-40
3	VT70 Diverfoam Active	2	CH_3COOOH CH_3COOH H_2O_2	1-3 % 3-10 % 10-20 %	23-40

For the conditioning temperature, a weekly cycle of 5 days at 40 °C, the maximum temperature recommended for external washing, was applied followed by 2 days at room temperature (corresponding to the thermostatic bath being switched off during the weekend for safety reasons). The total immersion time was set at 50 days (1200 h), corresponding to 7 cycles plus one day, that corresponds to the sum of the minutes of contact with the PAA sanitizing solution, that being an oxidant should be the most aggressive for adhesives. These conditions do not exactly repeat those present in the COP-SOP, as there is no continuous immersion but periodic daily contact followed by rinsing and drying. Keeping the specimens immersed for a period of several consecutive weeks will however favor the diffusion in the polymer up to the interface with the metal, affecting but cohesion and adhesion strength.

At least two groups of 5 specimens, made out of tumbled 2B surface finish sheet metal plates, were immersed and at least one group was picked up for testing before the end of the period in order to evaluate a possible damage trend. The values of strength obtained for the unaged joints were used as a reference of strength. The solution with VE3 (alkaline solution) was not used with the Adhesive 2, since the technical datasheet already indicated a strength of 115% with respect to the unaged one after 3000 h of immersion in a 4% NaOH solution.

3. Results and Discussion

3.1 Adhesives 1-3: unaged strength and effect of the surface finish

Regarding adhesive 1, the force (P) vs. displacement (Δ) plots are shown in Figure 7 for the various roughnesses tested and the average shear strength is summarized in Table 7 along with standard deviation.

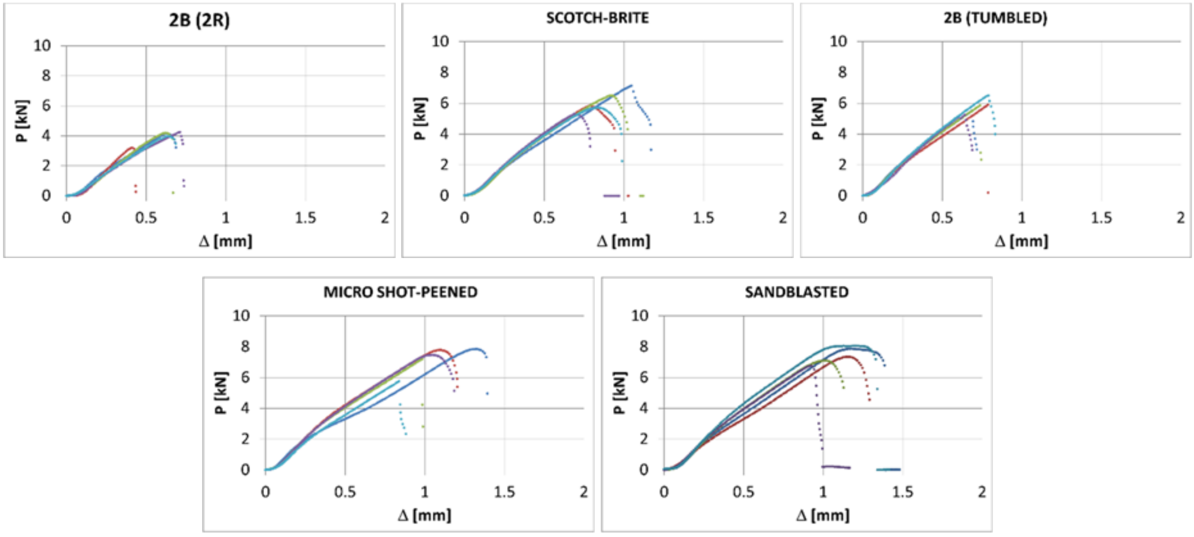


Figure 7 - Force vs. displacement plots of unaged Adhesive 1 at different surface finishes.

The strength of micro-shot-peened substrate is comparable to that obtained with sandblasting, so this surface is very favorable for bonding with Adhesive 1, probably due to its light but very uniform roughness. It can be noticed in both these cases that failure occurs in most of the specimens after reaching a force plateau, meaning that plastic yielding of the adherends is attained and the force cannot increase any longer.

Table 7 – Average shear strength τ and standard deviation s(τ) of Adhesive 1 as a function of surface finish.

Surface finish type	Ra [μm]	τ [MPa]	s(τ) [MPa]
2B - (2R)	0.13	13.3	0.38
SCOTCH-BRITE	0.29	19.6	2.30
2B (tumbled)	1.07	18.6	1.51
Micro shot-peened	1.54	24.3	0.97
Sandblasted	3.56	23.8	1.71

Overall, even for fairly smooth surfaces (2B and above all Scotch-Brite) good strength values are obtained, while a consistently lower value is recorded on the less rough surface, as expected. Figure 8 shows the failure surfaces which are always totally or mainly adhesive even in the case of sandblasting. In this case, however, as in that of the micro-blasted surface, the value reached (24-24.5 MPa) seems to be the upper limit due to yielding of the AISI 304 sheet metal (Figure 8f) that increases the shear deformation of the adhesive at the ends of the joint and causes in turn the failure to start from the most deformed interface.

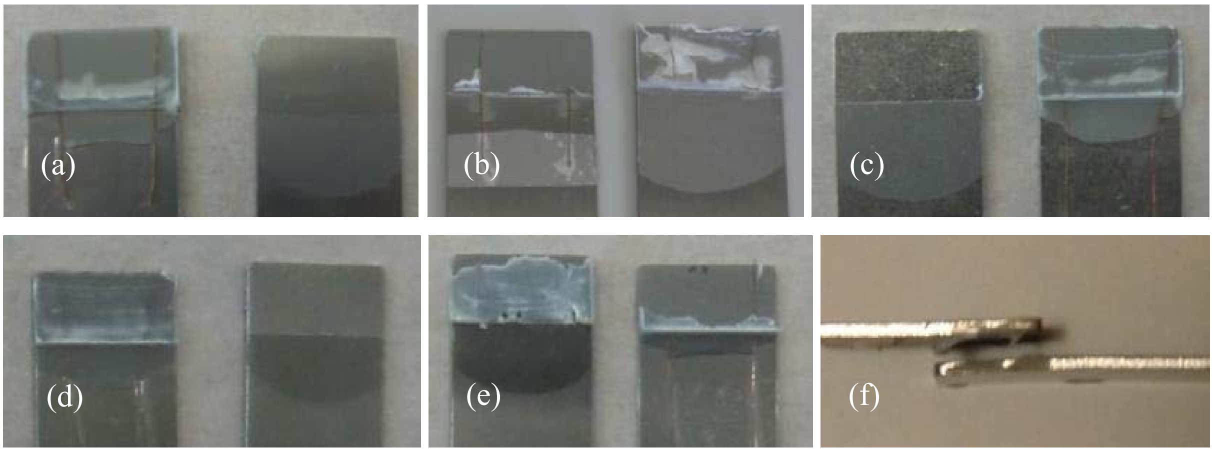


Figure 8 – Failure surfaces of the specimens made with Adhesive 1 and 2B-2R (a), Scotch-Brite (b), 2B tumbled (c), Shot-peened (d) and Sandblasted (e) surface finish. The sandblasted and micro-shot-peened specimens are plastically deformed near the ends of the overlap (f).

In the case of Adhesive 2, the force vs. displacement data are shown in Figure 9. The force peaks, hence the shear strength values (Table 8) are lower than those of Adhesive 1 as could be expected from the data declared by the supplier in the respective technical data sheets, albeit referring to metal alloys different from AISI 304. It is interesting to notice that, different from Adhesive 1, the increase in performance is not uniquely related to the surface roughness, but quite overlapping values are found for all the surface treatments but sandblasting, that yields the higher joint strength.

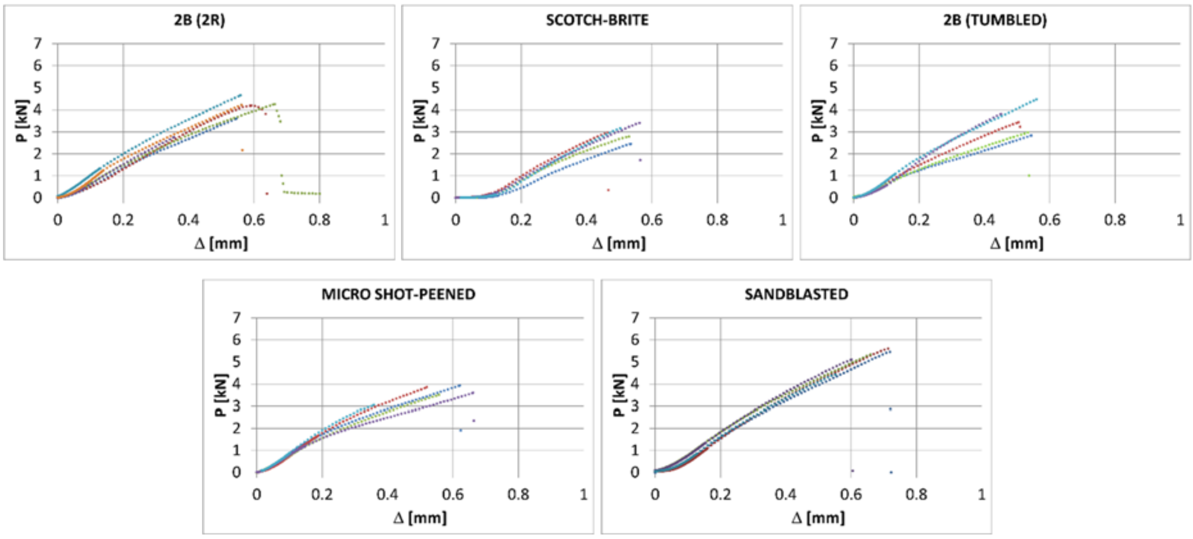


Figure 9 - Force vs. displacement plots of unaged Adhesive 2 at different surface finishes.

Table 8 – Average shear strength τ and standard deviation s(τ) of Adhesive 2 as a function of surface finish.

Surface finish type	Ra [μm]	τ [MPa]	s(τ) [MPa]

2B - (2R)	0.13	13.4	1.20
SCOTCH-BRITE	0.29	9.5	1.17
2B (tumbled)	1.07	11.4	2.04
Micro shot-peened	1.54	11.9	0.64
Sandblasted	3.56	16.6	1.47

The failures are adhesive also in this case (Figure 10) with the only exception of sandblasting, in which the visual inspection detects a thin layer of adhesive on the surface in one of the two adhesions, so that the breakage occurs near the interface, but still cohesive.

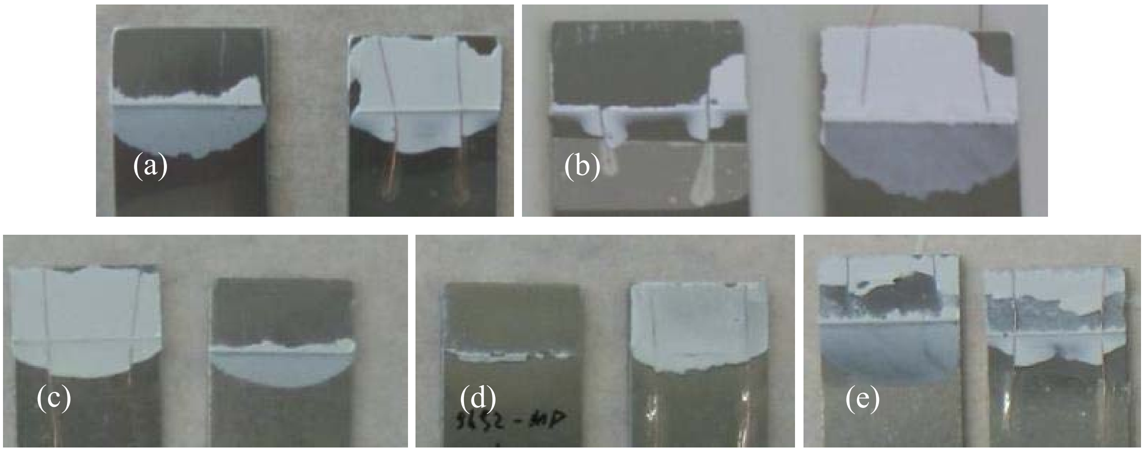


Figure 10 – Failure surfaces of the specimens made with Adhesive 2 and 2B-2R (a), Scotch-Brite (b), 2B tumbled (c), Shot-peened (d) and Sandblasted (e) surface finish.

Adhesive 3, being elastic, also has a much lower resistance in absolute terms than the others, but it has the advantage of being almost insensitive to roughness (see Figure 11 and Table 9) and always presents cohesive cracks (Figure 12), that is, it has a good adhesion to the surface relative to the performance provided.

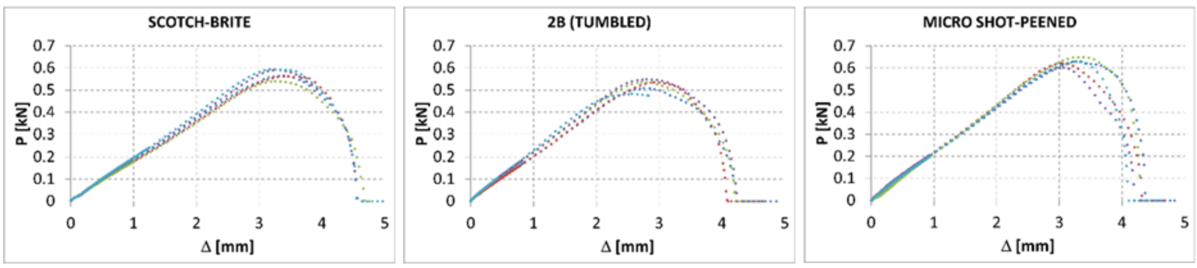


Figure 11 - Force vs. displacement plots of unaged Adhesive 3 at different surface finishes.

The cohesive failure is reflected also by the ratio s(τ)/τ lower than the other two adhesives that exhibited the interfacial failure, as this latter yields generally a higher scatter of the strength.

Table 9 – Average shear strength τ and standard deviation s(τ) of Adhesive 3 as a function of surface finish.

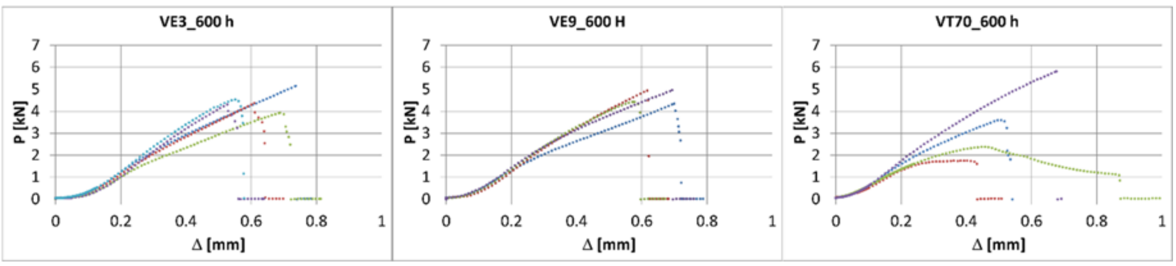
Surface finish type	Ra [µm]	τ [MPa]	s(τ) [MPa]
SCOTCH-BRITE	0.29	1.83	0.07
2B (tumbled)	1.07	1.67	0.08
Micro shot-peened	1.54	2.01	0.05

Figure 12 – Failure surfaces of the specimens made with Adhesive 3 and Scotch-Brite (b), 2B tumbled (c) and Shot-peened (d) surface finish.

From the whole of the tests on the three adhesives it can also be said that the 2B (tumbled) surface finish selected for the subsequent immersion tests in the COP-SOP solutions, which represents also the most commonly used one, provide a value of strength intermediate among those examined.

<u>3.2 Adhesives 1-3: resistance to COP-SOP agents</u>

With Adhesive 1, spontaneous debondings of some joints occurred in the first part of the immersion period (at 14 and 25 days) in VE9, therefore the processes leading to debonding are rather rapid during during the immersion period. The results obtained from the tests carried out on the residual samples are reported in Figure 13, bearing in mind that ten samples were immersed for each type of joint.



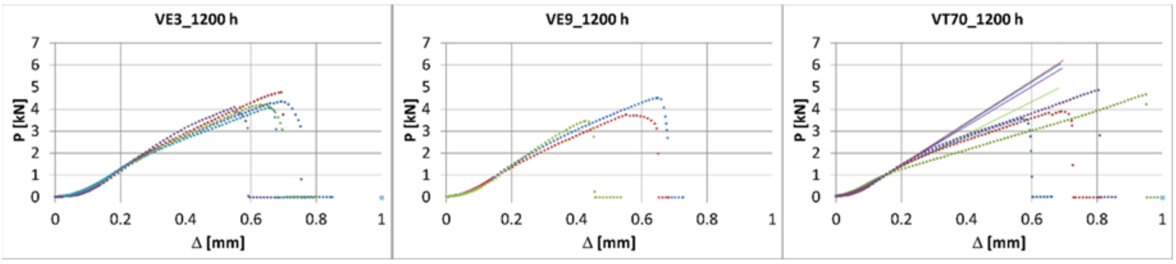


Figure 13 - Force vs. displacement plots of Adhesive 1 aged in different chemicals and at increasing times.

Table 10 summarizes the residual shear strength values and the related standard deviation, along with the percent residual strength with respect to the unaged samples. It can be observed that the decrease in resistance in VE9 solution is approximately linear and that that due to VE3 varies little in the second half of the conditioning time. Although the residual strength is quite high both in absolute and relatively to the unaged condition and it would sufficient for the application under examination, the development of spontaneous failures in VE9 can make this adhesive critical in service.

Table 10 – Average shear strength of Adhesive 1 with respect to aging time. The % indicates the residual strength with respect to the unaged joint.

Aging time	600 h		1200 h	
Solution	**τ [MPa]**	**s(τ) [MPa]**	**τ [MPa]**	**s(τ) [MPa]**
VE3	14.7 (76.7 %)	1.426	13.4 (71.9 %)	0.390
VE9	15.0 (80.3 %)	1.045*	12.5 (67.3 %)	1.726*
VT70	12.0 (64.3 %)	2.41	10.6 (56.8 %)	2.690

*As three joints failed spontaneously before 600 h, of the remaining seven, three were tested after 600 h and four after 1200 h.

By evaluating the stiffness of the joint as the slope of the load-displacement values close to the origin of data it can be seen that this too undergoes a reduction due to aging, that is a symptom of a partial plasticization effect (Table 11). The reduction is relatively small, and it is due not only to modifications of the polymer, but probably also to effects on the edges of the bondline, where in many cases an adhesive debonding has begun during immersion.

Table 11 – Reduction of joint stiffness with Adhesive 1 after immersion in the various solutions.

Aging time	Unaged	600 h	1200 h
Solution	**Stiffness [kN/mm]**	**Residual stiffness (%)**	**Residual stiffness (%)**
VE3	10.507	86. 6	87.8
VE9	10.507	93.5	90.3

VT70	10.507	77.7	88.3

In the specimens tested after conditioning in VE3 there were no visible effects (with the exception of air bubbles under the excess adhesive film), and the adhesive failures are similar to those of the unaged one, Figure 14a-b. In the specimens conditioned in VE9 there was a slight "wrinkling" of the adhesive in excess at the end of the joint, Figure 14c-d.

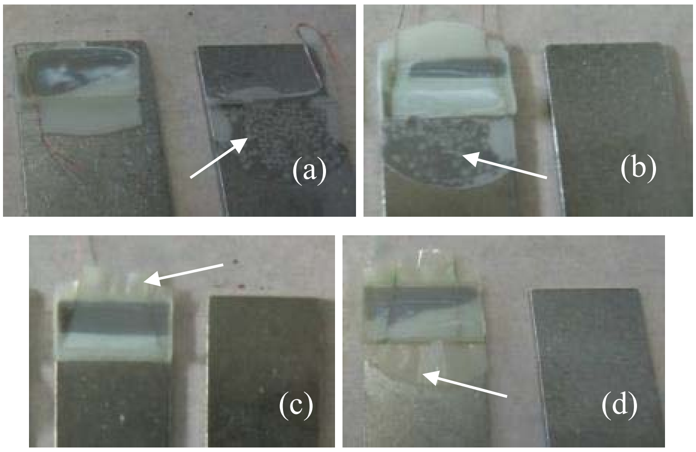


Figure 14 – Failure surface of Adhesive 1 aged in VE3 tested after 25 and 50 days (a and b, respectively) and in VE9 after 25 and 50 days (c and d, respectively). The arrows indicate the wrinkled excess adhesive.

In the samples conditioned in VT70, reddish-brown deposits were also found, that leads to suppose the presence of contaminating particles of dirt bound to the stainless steel microspheres used to keep the adhesive layer thickness, which have not in fact been cleaned before bonding. In the other samples with microspheres, however, there are no signs of corrosion and the failure is anyway adhesive, without spontaneous debondings during immersion.

Together with the described phenomenon, there is also a light brown patina on the adherend near the joint, with a consistency similar to powder, typical of a liquid solution with PAA that stagnates and then dries on a metal surface. It is not a sign of corrosion, but it is a phenomenon that is found also in machines, and which in this case is due to the liquid that remained under the excess adhesive at the ends of the joint. It is also noted that in almost all the samples the excess adhesive in the vicinity of the fillets has lifted away from the surface, which may have favored the aggression of the bondline.

With Adhesive 2, tested only with VE9 and VT70, a high rate of spontaneous debondings was detected, which occurred in even shorter times than those occurred in the samples with Adhesive 1, so much that at the end of the conditioning period just one sample for each solution was still integer, as it can be seen from Figure 15.

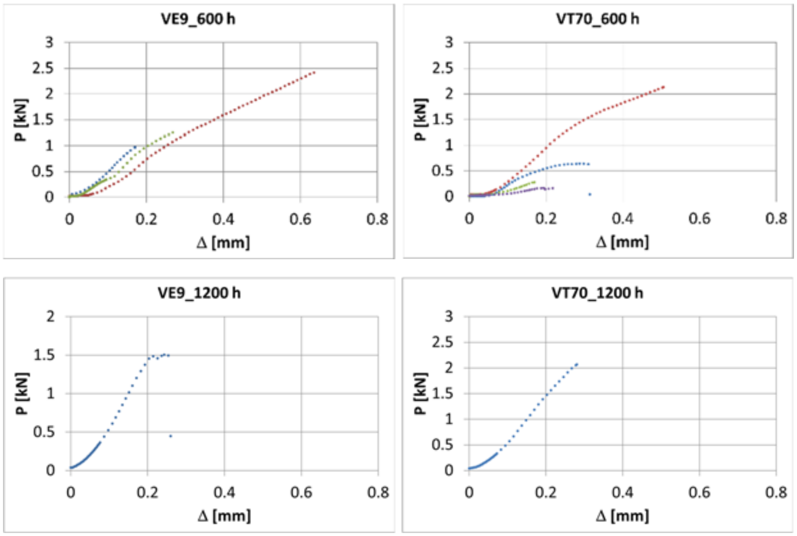


Figure 15 - Force vs. displacement plots of Adhesive 2 aged in different chemicals and at increasing times.

The results are summarized in Table 12. The residual strength is lower than Adhesive 1 and the number of spontaneous debondings before the end of immersion is even higher, making the data of Table 12 purely indicative: if the strongest specimen at 600 h was treated as an outlier, the residual strength would have been much lower and, treating as an outlier for coherence the only specimen that lasted 1200 h, it could be said that there was no residual strength after the maximum aging time.

Table 12 – Average shear strength of Adhesive 2 with respect to aging time. The% indicates the residual strength with respect to the unaged joint.

Aging time	600 h		1200 h	
Solution	**τ [MPa]**	**s(τ) [MPa]**	**τ [MPa]**	**s(τ) [MPa]**
VE9	5.34 (47.0 %)*	*	4.82 (42.4 %)	**
VT70	6.83 (60.0 %)*	*	6.62 (58.3 %)	**

*Only the strongest specimen was reported for comparison with the one survived at 1200 h.

**it can not be calculated since only one specimen was left after spontaneous failures during immersion.

The only difference found with respect to the unaged joint, were the yellowed bands in correspondence with where the excess adhesive on the outside of the joint was raised and probably provided a preferential attack path for the solutions (Figure 16).

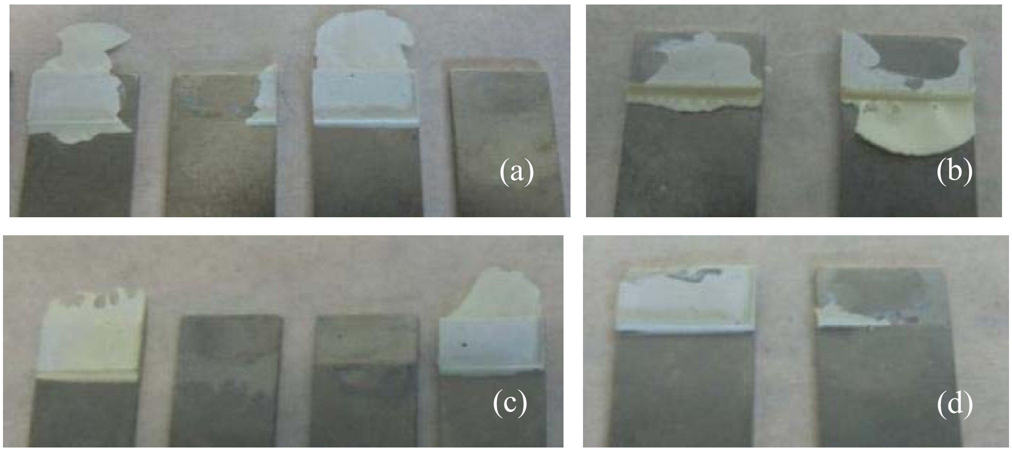


Figure 16 – Joints made with Adhesive 2 immersed in VE9 and tested at the intermediate interval (a) and at the end of aging (b); immersed in VT70 and tested at the intermediate interval (c) and at the end of conditioning (d).

Concerning this adhesive, the main outcome is the poor adhesion after aging. The spontaneous failures indicate that the combination of stainless steel surface without specific preparation treatment does not allow a durable joint in aggressive environmental conditions with this adhesive.

The force-displacement results of Adhesive 3 are presented in Figure 17. Spontaneous failures under immersion occurred also for Adhesive 3, particularly in acid solutions. However, they turned out to be much more gradual, i.e. the degradation and the beginning of debonding was detectable, as also indicated by the samples immersed in VT70 which at the end of conditioning appeared only partially debonded.

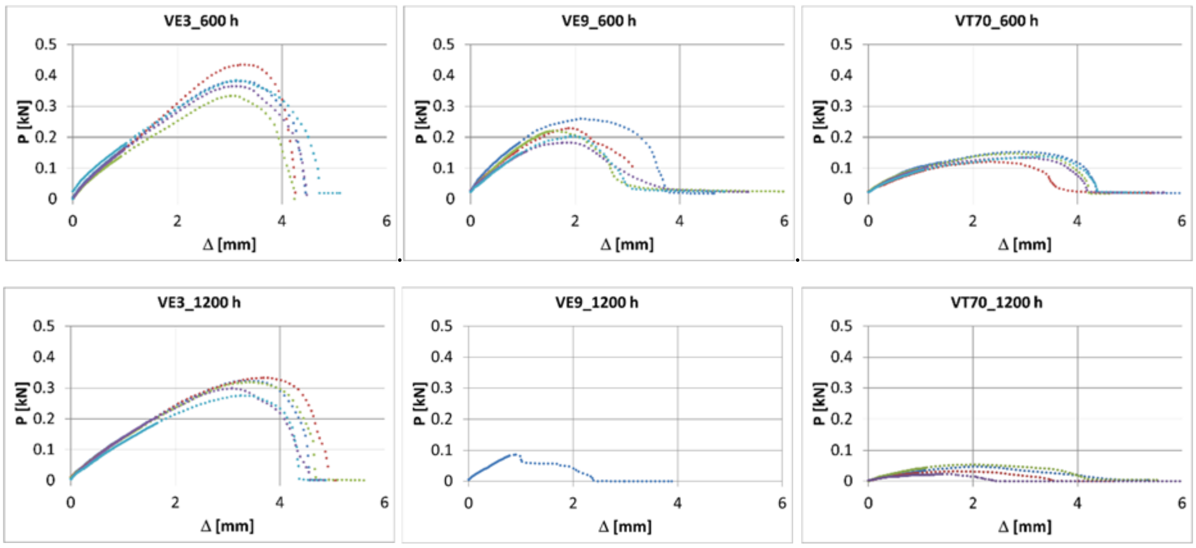


Figure 17 - Force vs. displacement plots of Adhesive 3 aged in different chemicals and at increasing times.

However, it should be noted that in general the samples showed also a visible swelling and deformation of the adhesive. As can be seen from Table 13 and Table 14, this seriously compromised both the strength and stiffness of the joint. Furthermore, the failures have turned from cohesive in the unaged joint to adhesive after aging, therefore Adhesive 3 seems to be particularly sensitive to the chemical agents used in COP-SOP and therefore not very suitable for the application.

Table 13 – Average shear strength of Adhesive 3 with respect to aging time. The% indicates the residual strength with respect to the unaged joint.

Aging time	600 h		1200 h	
Solution	**τ [MPa]**	**s(τ) [MPa]**	**τ [MPa]**	**s(τ) [MPa]**
VE3	1.28 (76.6 %)	0.074	0.99 (59.3 %)	0.074
VE9	0.70 (42.0 %)	0.091	0.28 (16.5 %)	*
VT70	0.45 (26.8 %)	0.045	0.13 (7.60 %)	0.045

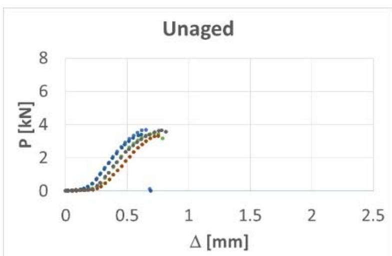
*it can not be calculated since only one specimen was left after spontaneous failures during immersion.

Table 14 – Reduction of joint stiffness with Adhesive 3 after immersion in the various solutions.

Aging time	Unaged	600 h	1200 h
Solution	**Stiffness [kN/mm]**	**Residual stiffness (%)**	**Residual stiffness (%)**
VE3	0.216	82.12	58.93
VE9	0.216	71.33	35.58
VT70	0.216	30.66	-

3.3 Adhesive 4-5: unaged strength and resistance to COP-SOP agents

Since none of the first three adhesives tested provided both a sufficient residual strength and full integrity after immersion in chemical agents, a second campaign was carried out on Adhesive 4-5 under unaged condition and after immersion in VE3 (alkaline) and VE9 (acid) solutions. The force-displacement plots of Adhesive 4 are reported in Figure 18 at different aging times. It is immediate to notice that some tests are missing at 1200 h because there were spontaneous debondings also in this case.



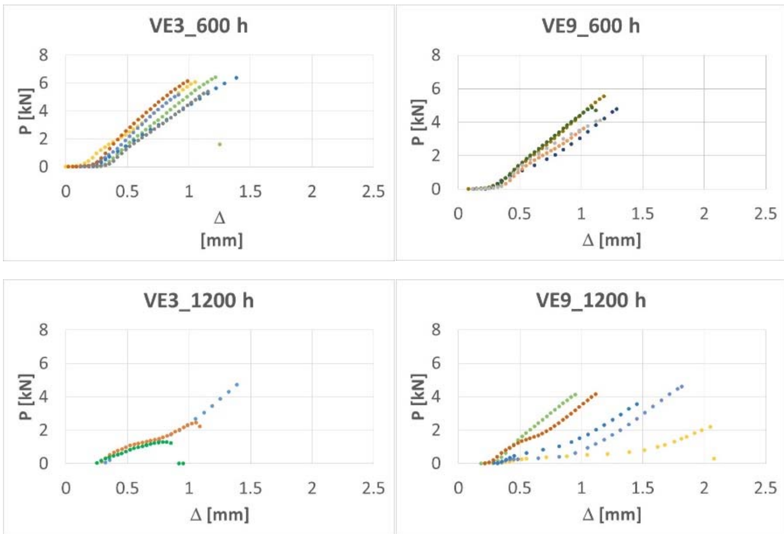


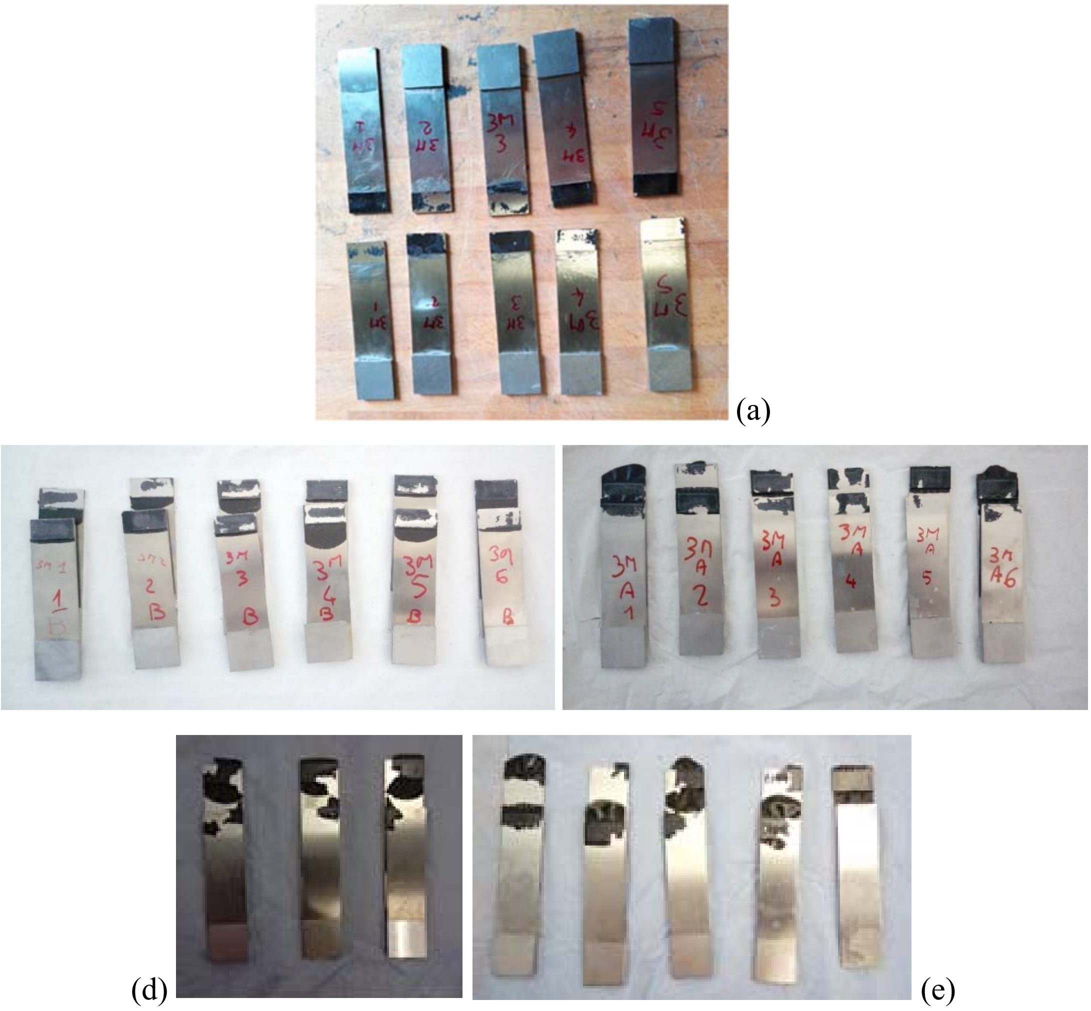
Figure 18 - Force vs. displacement plots of Adhesive 4 unaged and aged in different chemicals and at increasing times

Looking at the values of average shear strength in Table 15, a net increase is visible after the first 600 h of immersion, that may be the beneficial result of a post-curing of the adhesive that overrides aging. After 1200 h instead, the strength gets lower or similar to the unaged one, as a result of chemical aggression. Most important 3 over 6 specimen failed spontaneously in VE3 and 1/6 in VE9, and those that resisted show a quite large scatter of the results, therefore there is a long-term reliability problem also for Adhesive 4 under these aging conditions.

Table 15 - Average shear strength of Adhesive 4 with respect to aging time. The% indicates the residual strength with respect to the unaged joint.

Aging time	**600 h**		**1200 h**	
Solution	**τ [MPa]**	**s(τ) [MPa]**	**τ [MPa]**	**s(τ) [MPa]**
VE3	18.7 (169%)	1.67	8.98 (81.4%)	5.67
VE9	14.2 (129%)	2.15	11.7 (106%)	2.97

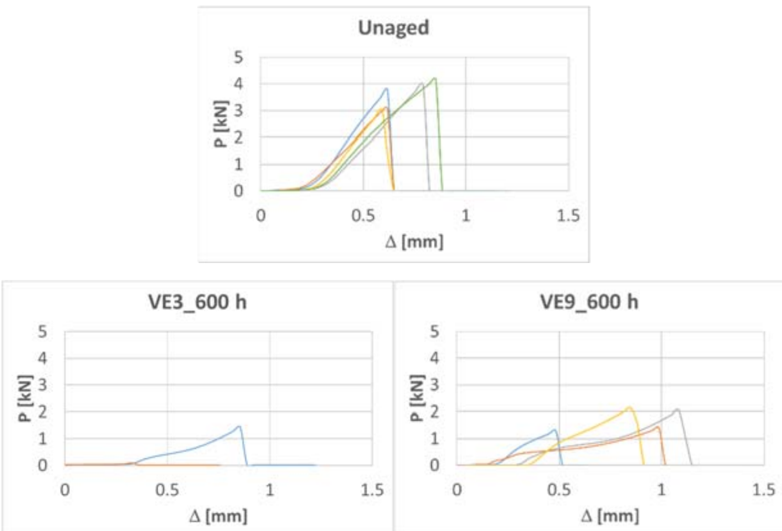
Figure 19 reports the failure surfaces of Adhesive 4 at different aging stages in VE3 and VE9. The rupture is mixed cohesive-adhesive, especially after 600 h in VE3, or adhesive alike Adhesive 1-3. However, mixed or adhesive failure was already present in the unaged joints due to the low surface roughness and the absence of surface pretreatment but degreasing, therefore aging does not change fundamentally the failure mechanism.



(a) (b) (c) (d) (e)

Figure 19 - Failure surface of Adhesive 4 unaged (a), aged in VE3 tested after 25 and 50 days (b and c, respectively) and in VE9 after 25 and 50 days (d and e, respectively). In b-e the adherends are overlapped each other so that the failure surfaces are shown one over the other.

From the force-displacement plots of Adhesive 5 reported in Figure 20, it is immediately visible that several tests are missing after aging, because of spontaneous failures during immersion.



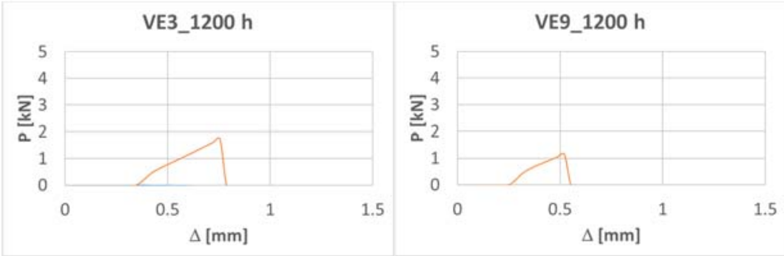


Figure 20 - Force vs. displacement plots of Adhesive 5 unaged and aged in different chemicals and at increasing times

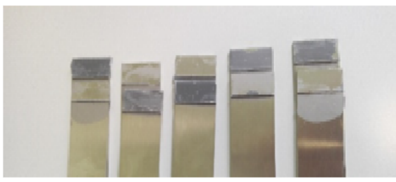
As also testified by the values of average shear strength and the related standard deviation in Table 16, Adhesive 5 seems to be particularly affected by the chemicals used in COP-SOP, thereby little suitable for the application.

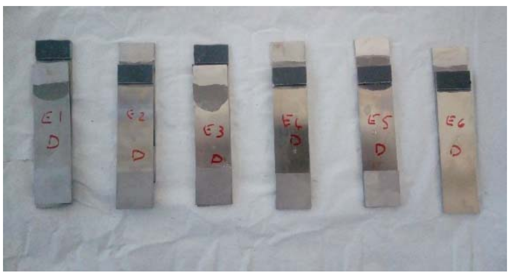
Table 16 - Average shear strength of Adhesive 5 with respect to aging time. The% indicates the residual strength with respect to the unaged joint

Aging time	600 h		1200 h	
Solution	**τ [MPa]**	**s(τ) [MPa]**	**τ [MPa]**	**s(τ) [MPa]**
VE3	4.494	-*	5.528	-*
VE9	5.416	1.381	3.694	-*

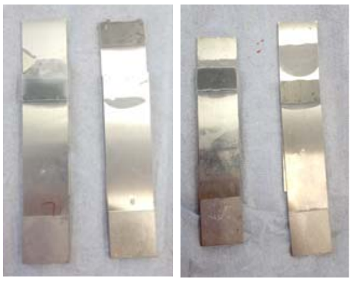
*it can not be calculated since only one specimen was left after spontaneous failures during immersion

The failure surfaces (Figure 21) exhibit always interfacial debonding while the unaged failure was mixed, therefore in this case there is an evident deterioration with respect to the initial conditions.


(a)

(b)


(c)

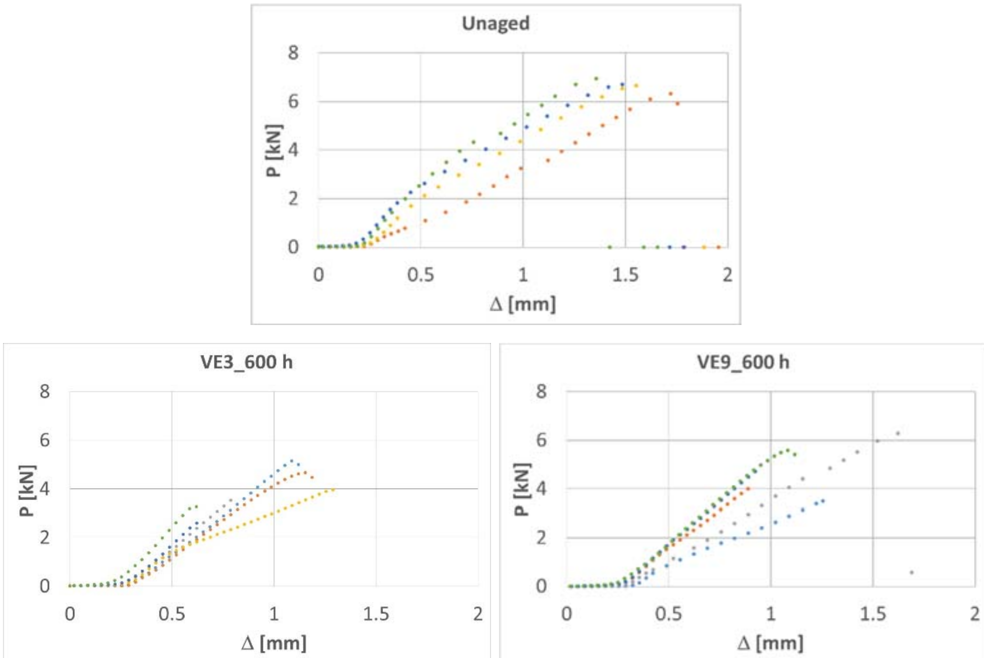


(d) (e)

Figure 21 - Failure surface of Adhesive 5 unaged (a), aged in VE3 tested after 25 and 50 days (b and c, respectively) and in VE9 after 25 and 50 days (d and e, respectively). The adherends are overlapped each other so that the failure surfaces are shown one over the other.

<u>3.4 Adhesive 4 with chemical surface pretreatment: unaged strength and resistance to COP-SOP agents</u>

Since also Adhesive 4-5 alone failed to provide a complete reliability in terms of both residual strength and integrity after aging a third campaign was done on Adhesive 4 plus primer under unaged condition and after immersion in VE3 (alkaline) and VE9 (acid) solutions; alike the second experimental campaign, tests were done after 600-800-1000-1200 h of immersion. The force vs. displacement diagrams are collected in Figure 22 while Figure 23 and Figure 24 show the average values of the shear stress at failure and the relative standard deviation for the solutions VE3 and VE9 respectively.



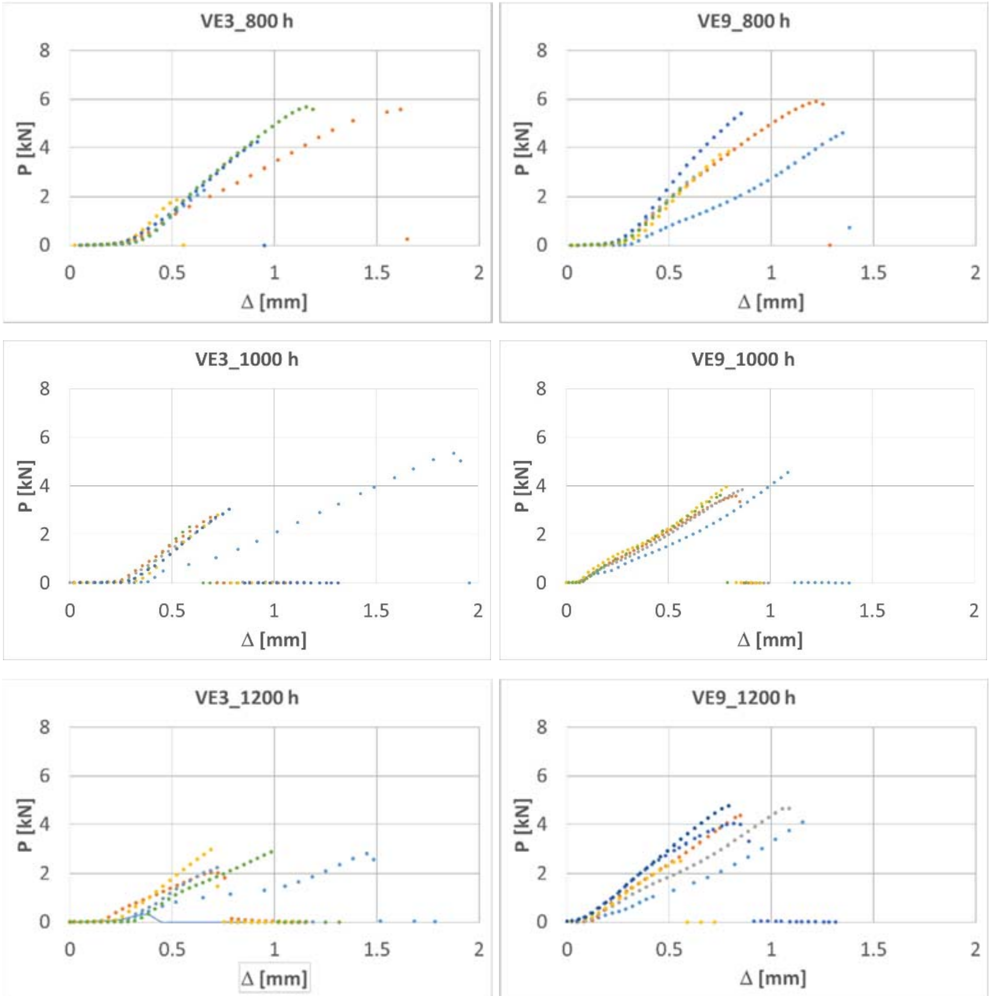


Figure 22 - Force vs. displacement plots of Adhesive 4 unaged and aged in different chemicals and at increasing times

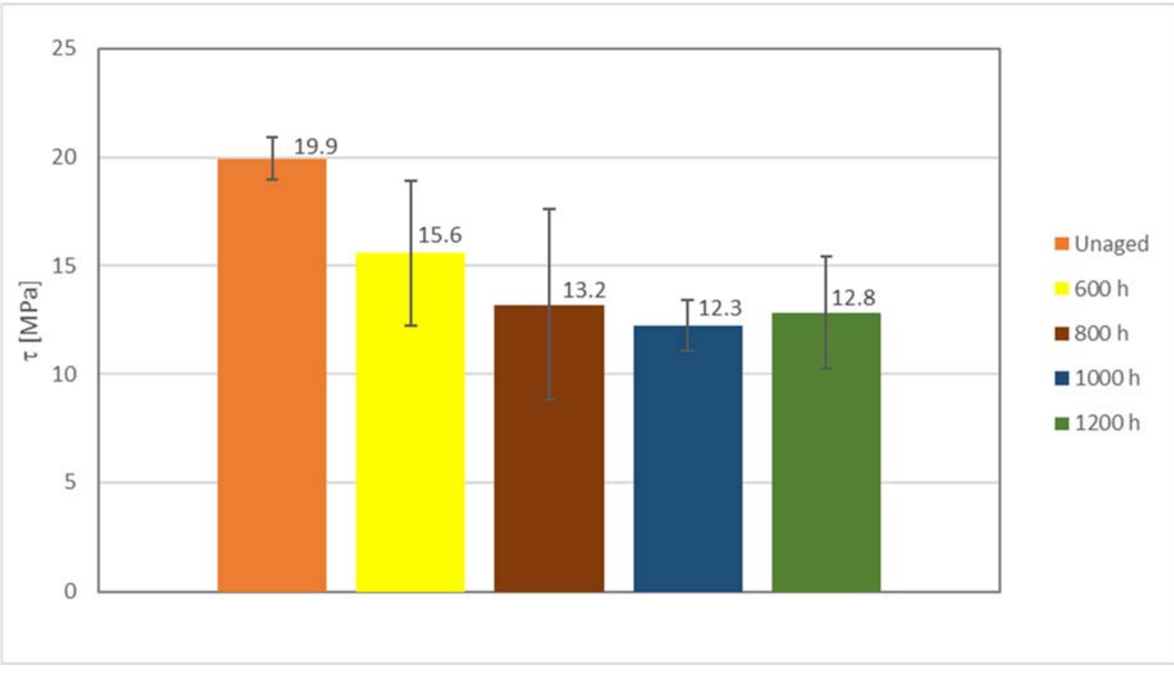


Figure 23 – Average shear strength of Adhesive 4 + primer with respect to aging time in VE3.

It can be noticed that in the alkaline solution (VE3) the strength undergoes a degradation, stabilizing around 65% of the unaged value starting from 800 hours of immersion. In the acid solution (VE9), on the other hand, it tends to progress, reaching a residual strength equal to 35% of the non-aged at the end of the test. Even though these values are comparable or even lower than Adhesive 1, the presence of a primer protected the stainless steel adhesive interface improving long-term adhesion such that a sufficient strength is preserved over time and no spontaneous failures were recorded. For this reason, Adhesive 4 can be preferred for the application in beverage filling machines. A feature of Adhesive 4 common also to the other adhesives tested is a relatively high coefficient of variation (std. dev./average); this is related to the low surface roughness, as found also in unaged joints, and also to the aging process that promotes further the interfacial failure especially in the case of Adhesive 3. However, as the stress on the parts to be joined are very low, a good reliability can be achieved anyway.

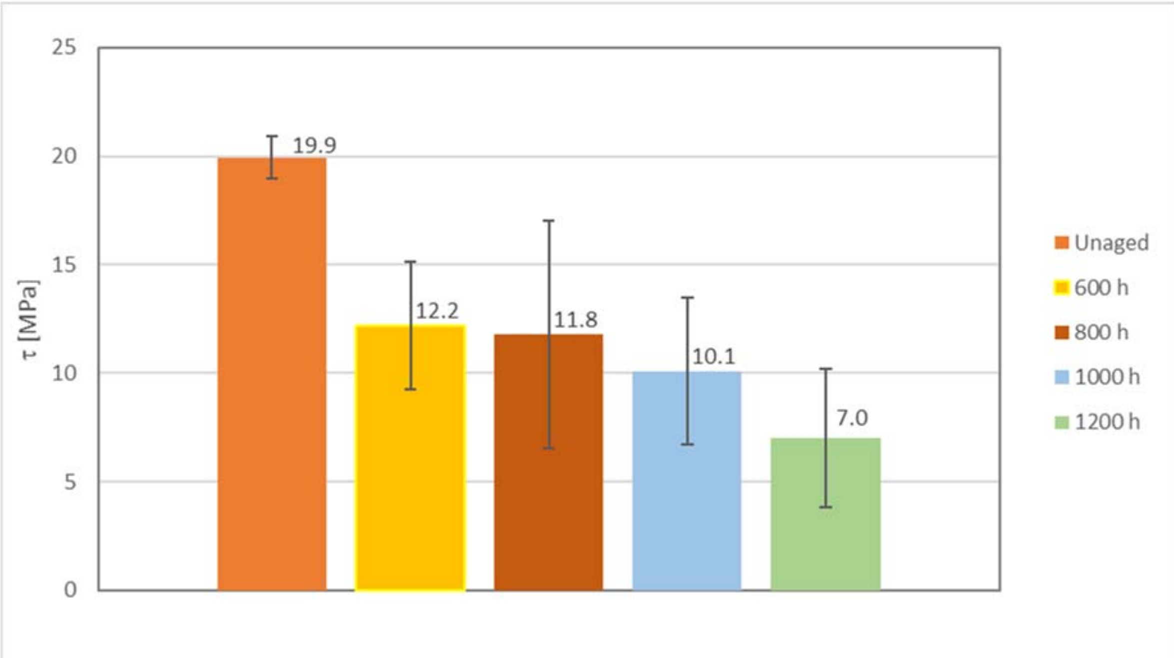
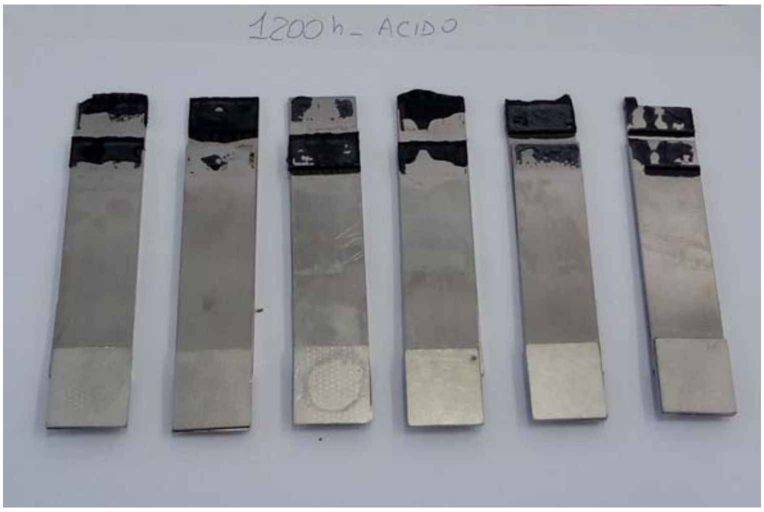


Figure 24 – Average shear strength of Adhesive 4 + primer with respect to aging time in VE9.

In Figure 25 the failure surfaces of the specimens used in the non-aged and end-of-aging tests in the two solutions are shown. The failure appears cohesive before aging, testifying the beneficial effect of the primer, while at the end of aging partially cohesive failures occur which are reflected in the degradation of strength recorded in the tests.


(a)


(b)



(c)

Figure 25 – Failure surfaces of Adhesive 4 plus primer specimens unaged (a), aged 1200 h in VE3 (b) and aged 1200 h in VE9 (c).

4. **Conclusions**

The introduction of bonding technology in place of welding in the assembly of beverage filling machines was approached by the experimental identification of an adhesive appropriate for bonding low surface roughness stainless steel joints subject to chemical aging due to cleaning and sanitization. Three epoxy adhesives, two without and one with a primer, and one modified silane were pre-selected as potentially suitable for application on the AISI 304 stainless steel sheet with different surface finishes and in contact with the acid and alkaline solutions used in COP-SOP.

The effect of surface finish evidenced that bonding to just degreased surfaces yields an average shear strength equal or lower than that obtained by sandblasting, as expected, even though in general the value can be sufficient for practical applications without aging.

The identification of aging effects required a specifically designed experiment. Joints with 2B tumbled surface finish were immersed in thermostatic baths for aging up to 1200 h corresponding to 20 years of overall contact with the chemicals. A too high rate of spontaneous debondings during immersion characterized Adhesives 2 and 3, making them unreliable for the application. Adhesive 1 showed a good residual strength but also some spontaneous debondings, therefore a second campaign was done on other two epoxy adhesives (Adhesive 4 and 5). The latter again showed a substantial number of debondings, while Adhesive 4 yielded results qualitatively similar to Adhesive 1. Adhesive 4 was finally tested also in conjuction with a chemical surface pre-treatment that was made available by the supplier. The results showed no spontaneous debondings after the end of aging so that, even though the residual strength was lower than Adhesive 1 (but still high enough for the application), Adhesive 4 plus primer was the combination that satisfied the demanding aging conditions along with low surface roughness of the material adopted, giving the necessary reliability for the application on this long-lasting type of machinery.

Acknowledgments

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