



# Validation of adhesion characterization methods for antistick coatings applied in cooking systems

Stefano Rossi, Federico Valdrè, Massimo Calovi 

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**Abstract** This study aims to validate an effective methodological analysis for the characterization of the adhesion values of antistick coatings employed in cooking systems. The morphology and chemistry of four different industrial products were investigated by roughness measurements, electron microscopy observations and infrared spectroscopy analysis. The adhesion of the coatings was evaluated comparing various techniques, such as the surface contact angle measurements, the pull-off test and the single lap-joint tensile shear method, in synergy with degradation phenomena simulated by P.E.I. abrasion and dishwashing tests. The single lap-joint tensile shear test was able to evaluate evident differences between all the proposed coatings, regardless of their state of deterioration, featuring the best selectivity among the used methods. However, the pull-off test proved to be a viable and more economical alternative for fast evaluation techniques, considering the overall instrument costs. While all the polytetrafluoroethylene-based systems turned out to be totally uninfluenced by the chemical attacks performed during the dishwasher cycles, the sol-gel coating exhibited lower performances of the applied releasing agent, before and after the mechanical degradation tests. Therefore, sol-gel coatings, despite being proposed as valid alternatives to PTFE ones, do not achieve the same quality standards in terms of releasing properties, being in addition much more sensible to degradation and loss in performances.

**Keywords** Cookware, Antistick layer, Adhesion test, Abrasion, PTFE, Sol-gel

## Introduction

The history of cookware and pottery is as old as the discovery of fire and the development of cooking techniques. In fact, the first historical remains have been developed in Mesopotamia, the cradle of human civilization. Initially, when metals were lowly diffused, the main production material was terracotta. However, its heavy weight and brittleness led to the creation of metal-based pottery relying on copper and bronze already available in the Egyptian period, iron in the medieval age, and aluminum since the twentieth century.<sup>1</sup>

Since humankind developed cooking techniques, several concerns were moved toward pottery cleaning and hygiene, as ease of cleaning and a certain degree of antistick was a desirable property even in the past millennia. As an example, the Roman historian Apicio refers to the “cumanae testae”<sup>2</sup> as a reddish terracotta pan, coated inside in vitreous enamel, exhibiting higher antistick properties with respect to standard cookware and advising its use for long low temperature recipes.

These writings underlined how a way to modify surface properties was already found in the past ages, through the deposition of thin coatings upon common pottery enhancing their antistickiness. This concept has been subsequently improved through the centuries and nowadays enormous technological steps have been taken in the field of antistick coatings, mostly related to the discovery of polytetrafluoroethylene (PTFE), developed accidentally by DuPont researcher, Roy Plunkett, in 1938, while experimenting with fluorocarbon refrigerating gasses. PTFE is obtained by the polymerization of tetrafluoroethylene (TFE), the simplest fluorocarbon compound. Thanks to the C–F bond, presenting the highest bond energy in organic compounds, it exhibits superior self-lubrication and antistick properties, and chemical and thermal resistance. In a pure state, PTFE is a white, smooth and ductile

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S. Rossi, F. Valdrè, M. Calovi (✉)  
Department of Industrial Engineering, University of Trento,  
Via Sommarive 9, 38123 Trento, Italy  
e-mail: massimo.calovi@unitn.it

thermoplastic polymer, exhibiting a melting temperature of 327 °C with a relatively high melt viscosity and crystallinity. Despite being thermoplastic, PTFE is not melt processable and, as expected, does not exhibit high adhesion properties when directly applied on metal substrates. In order to solve these concerns, several PTFE copolymers have been developed, such as FEP (tetrafluoroethylene + hexafluoropropylene) and PFA (tetrafluoroethylene + perfluoroethers), improving coating deposition, wear resistance and substrate adhesion.

Despite being very effective, several studies of the past decade revealed how PTFE precursors such as perfluorooctanoic acid (PFOA)<sup>3, 4</sup> or perfluorooctane sulfonate (PFOS)<sup>5</sup> may have had toxic effects on human health. Concerns were related to the possibility of depolymerization of PTFE in the cited precursors when subjected to high temperature cooking.<sup>6, 7</sup> Indeed, the impossibility to be metabolized by the body causes an accumulation of these chemicals in cells, possibly increasing the occurrence of gene modification and cancer development.<sup>8–10</sup> As a consequence of these studies, PTFE-based coatings market experienced a heavy setback and even after the development of alternative synthesis methods for PTFE, customers trust was way less than before.<sup>11</sup>

In order to recover part of the lost market, companies started to research alternative PTFE-free paints. A different approach to antistick coatings came from the use of a sol-gel ceramic based one, which aimed to develop a harder, more wear resistant and safer film. Sol-gel coatings rely on the ability of specific silane solutions to produce Si–O–Si polymeric structure when mixed at low temperature. A silane is an organic-inorganic compound featuring the possibility to generate Si–OH silanol groups when dispersed in a solvent. The main concern related to sol-gel antistick capability is its reliability in long usage periods and when subjected to wear. In fact, contrary to PTFE coatings, a ceramic one is not intrinsically antistick, relying only on the action of the functionalized groups of the topcoat, which can be easily removed by every day usage.<sup>12</sup> However, sol-gel ceramic coatings garnered great success thanks to their glossy and colorful surface.

Nowadays, even if the technologies have evolved and a variety of coatings have been developed by cookware companies, pretty much every kitchen utensil has some sort of non-stick film on it, whether PTFE or sol-gel ceramic based.<sup>13</sup> The food industry has prompted many researchers to evaluate the adhesion processes of foods and liquids on the packaging surfaces in different ways. Some studies evaluated the liquid food adhesion by means of a tilting surface method,<sup>14</sup> the contact angle and surface tension methods, and the atomic force microscopy technique.<sup>15, 16</sup> Other works estimated the contribution of surface tension,<sup>17</sup> hydrophilicity and hydrophobicity,<sup>18</sup> and surface roughness<sup>19</sup> on food adhesion. Regarding the coating systems, the adhesion between a PTFE-coated metallic plates and food products has been assessed by

means of a block-plate test<sup>20</sup> and a particular frying test.<sup>21</sup> However, these works represent isolated studies of a problem that still puts the food and cookware manufacturing field in difficulty.

As a matter of fact, despite the cookware market being highly competitive and of economic interest, the antistick property evaluation represents a critical factor, as it has always been difficult to quantify due to the variable working condition at which cookware is exposed. This condition evidenced the need to develop effective and reliable testing methods, trying to overcome the intrinsic difficulties in the evaluation of antistick performance and making possible a quantitative comparison between different coatings. In fact, companies still rely on very old standards, not providing quantitative results, such as the egg release test (BS 7069:1988)<sup>22</sup> and the milk test (AFNOR N.F. D 21.511:1989),<sup>23</sup> simply evidencing the easiness or not of food removal, without providing any valuable data.

In particular, BS 7069:1988 standard indicates the cooking of a medium size egg in the middle of the pan at a temperature between 150 and 170 °C for 8–9 min. The test is passed if the egg is easily detached from the surface only by using a polymeric spatula and without the addition of oil during the cooking. On the other hand, for the AFNOR N.F. D 21.511:1989 standard, milk is poured on the pan until all the surface is covered, and then a 2 kW electric cooker is used to heat the liquid until evaporation and degradation of the milk film. Degradation occurs when the residua reach a dark carbonized color with smoke emission. Once this condition has been achieved, the pan is rapidly cooled down under a water jet and depending on the easiness of residua removal, antistick capacity is classified in three different classes. No further specifications are given, and the test does not provide quantitative data nor an analysis on wear effects upon antistick properties. These tests were created in order to easily distinguish between antistick and non antistick systems, in a period where this was a revolutionary discovery.

However, nowadays these standards undoubtedly present a series of technical limitations, being not able to distinguish between the performances of various antistick coatings. In fact, the adhesive strength of milk and cooked eggs, even if simulated for everyday usage, is not sufficiently high to allow a clear distinction between coatings performance flattening all the results.

Thus, the aim of this work is to produce an effective methodological analysis, evaluating several alternative methods for antistick and wear resistance properties definition, able to provide quantitative results and being more effective in the comparison between different coatings. Four different industrial coatings have been subjected to the investigation, taking as a methodological reference the typical adhesion and wear tests. Furthermore, this study aims to verify whether sol-gel methods can represent a valid alternative to PTFE coatings in terms of antistick performance.

## Experimental

### Materials

In order to define quantitative antistick evaluation methods, trying to improve their efficiency and propose new alternative procedures, four commercial products were characterized in this study. The fluoropolymeric and ceramic coatings have been delivered already applied on 17 cm diameter disks of aluminum 1050 (Al 99.5 wt.%), and on 17 cm pans of aluminum 3003 (Si 0.6 wt.%, Fe 0.7 wt.%, Cu 0.05–0.20 wt.%, Mn 1–1.5 wt.%, Zn 0.1 wt.%, Al bal.).

The sol-gel silane product, labeled as “S,” is composed by a basecoat flashed at 120 °C for 5 min, plus a topcoat cured at 330 °C for 10 min, with a total thickness approximately between 30 and 40 μm.

The three different PTFE-based coatings represent the middle, high and top-level industrial products. The first proposed coating, named “P1,” is a dual-layer film advertised as the system providing the best antistick properties and reliability through time. The application is performed through a drying and an initial curing step for the basecoat, respectively, at 120 °C for 5 min and 250 °C for 10 min. Subsequently, the topcoat is deposited and cured at 440 °C for 5 min, reaching an average thickness of 25–35 μm.

The second proposed coating, named “P2,” is a triple-layer, titanium oxide-reinforced film, advertised as a hard, scratch resistant and price valuable system. The application is performed through two drying steps, one for basecoat and one for midcoat, respectively, at 120 °C for 5 min and 250 °C for 7 min. Finally, the topcoat is deposited and curing is performed at 430 °C for 5 min. Thickness is approximately between 25 and 35 μm.

The third and last PTFE coating, named “P3,” is a triple-layer PTFE-based film, reinforced in PEEK. It maximizes abrasion and antistick endurance, providing high coating thickness and an easy application process. Layers deposition is effectuated with two drying steps for basecoat and midcoat, respectively, at 120 °C for 5 min and 300 °C for 8 min, with a final curing step performed at 440 °C for 7 min. P3 exhibits the highest thickness among all the provided coatings, stated over 70 μm together with a higher surface roughness. The characteristic rugged surface of this coating has been intentionally developed in order to provide a stone-like perspective effect, being more satisfactory and interesting for customers.

Table 1 summarizes the features of the four coatings employed for the antistick methods validation.

### Characterization

#### Coatings morphology and chemical characterization

The roughness of the samples was measured using a Mahr MarSurf PS1 roughness tester. An evaluation

**Table 1: Coatings used for antistick methods validation**

Sample name	Chemical family	Layers
S	Silane	2
P1	PTFE	2
P2	PTFE	3
P3	PTFE	3

length ( $l_n$ ) of 2.5 mm was used in accordance with the UNI EN ISO 4287<sup>24</sup> and UNI ISO 568<sup>25</sup> standards to measure the  $R_a$  parameter, defined as the arithmetic average of the roughness profile, and  $R_z$  value, as the average maximum peak to valley of five consecutive sampling lengths within the measuring length. For every coating product, 3 samples were taken under consideration and 5 measures were made each, thus obtaining 15 measurements from which the mean  $R_a$  and  $R_z$  roughness values were extrapolated.

Each coating has been analyzed through FTIR spectroscopy, making a comparison between the difference compositions, additionally evidencing chemical variations inside the coating thickness, removing each layer through subsequent sandpapering. The FTIR spectra were recorded in the transmission mode on KBr pellets using a Varian Excalibur 4100 instrument at 4000–550  $\text{cm}^{-1}$ . In total, 64 scans with a resolution of 4  $\text{cm}^{-1}$  were recorded.

The morphology of the coatings in cross section was observed by low-vacuum scanning electron microscope SEM JEOL IT 300, in order to underline differences in deposition layers, reinforcement, occurring defects, and composition.

#### Adhesion tests

In this study, the efficacy of different characterization techniques was evaluated as valid alternatives to the typical egg release test and the milk test.

The surface contact angle parameter is used in a variety of fields to evaluate surface energy, surface tension and work of adhesion, parameters directly related to antistick performances. The test is performed evaluating the contact angle of labeled liquids when deposited on coating surface. This work proposes two different methods: The first one analyzes contact angle between the surface and three commonly used liquids, water, oil and milk at room temperature, while the second one involves the evaluation of contact angle between molten sucrose and coating, providing an external source of heat. The contact angle evaluation has been set up using two height-adjustable supports: one for the sample and one for the optical camera (Nikon DS-Fi2) acquiring the images. Then, two 5 μL drops of the chosen liquids have been deposited on each sample, placing a white contrast paper as a

background and appropriately tuning light and focus to evidence drops edges before taking the images. On other hand, for sucrose test, samples were additionally placed upon an electric heater set at 220 °C, while 500 mg of substance was deposited on the surface. Both the methods were carried out following the UNI EN 828:2013 standard.<sup>26</sup>

The pull-off test, according to ASTM D4541 standard,<sup>27</sup> is widely used in paint industry to evaluate coating–substrate adhesion through the gluing of aluminum studs on coating surface and subsequent tensile test, assessing eventual defects causing coating failure and detachment. However, in this work the standard has been applied in a reverse mode, where the desirable effect was the evaluation of the separating load between testing machine and coating surface, instead of a high adhesive strength at coating–substrate interface.<sup>12</sup> Indeed, the lower the separating load, the better the antistick performances of the coating will be. The aluminum studs were sanded with a 600 emery paper and surfaces degreased with acetone. In order to have a real idea of the behavior of common foods, some preliminary studies have been carried out using melted sugar. However, its fragile behavior, combined with the difficulties encountered in confining it, has resulted in poor and non-reproducible results. Consequently, Araldite 2011 was used as epoxy glue for the test. This product, widely used as a high performance glue, is mainly composed of bisphenol A, epoxy resin and *N*(3-dimethylaminopropyl)-1,3-propylenediamine. Initially, the 2K compound is mixed to activate the glue; subsequently, a small film of adhesive is deposited on the 20 mm dolly and joined to the coating surface, having the attention to gently press and rotate the part in order to remove the excess of glue. Finally, the assembly is held in position with a piece of tape and placed in a pre-heated oven at 150 °C for 30 min. The testing machine (PosiTest Pull-Off Adhesion Tester, DeFelsko) consisted of a hydraulic piston connected to a load cell, the assembly is clamped on the dolly, and the fluid is gradually pumped in the circuit to apply tension. In this way, the instrument is able to measure the maximum detaching force, a key parameter to evaluate adhesion. Once the detachment has occurred, the two separating surfaces are observed under an optical microscope Nikon SMZ25 in order to detect coating failure and cracking, if present.

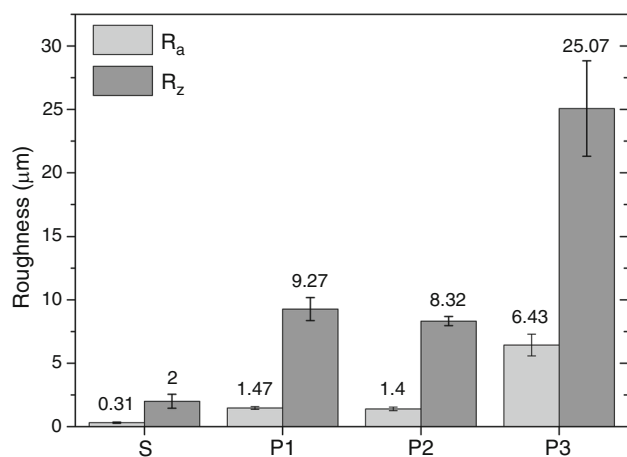
Detachment of sticky food residua on cookware surfaces usually involves some sort of rubbing with a soft kitchen utensil; this condition is well portrayed by a tensile shear test, providing further information on coatings antistick behavior in addition to the one provided by the uniaxial pull-off test. The single lap-joint tensile shear test (UNI EN 1465:2009 standard<sup>28</sup>) is used in the adhesive industry to evaluate adhesive strength, where two rectangular plates are glued together and subjected to a tensile test until adhesive failure. The possibility to evaluate adhesion through tensile shear tests had been already pointed out in the literature<sup>20,1</sup> and in this study the concept has been

expanded considering the application of already in-use EN/ASTM regulated standards, capable of providing more robust data. Also in this case, the test has been proposed in a reversed and modified way, where the aim was the evaluation of the detaching shear stress between an antistick coated plate and adhesive, similar to the pull-off test. In order to perform the single lap-joint test, 3 rectangular plates of 25 mm × 100 mm × 2 mm have been cut from each pre-applied coating disk and glued on reference aluminum 1050 plates of the same dimensions superimposing both edges for 12.5 mm. Araldite 2011 has been used as adhesive, and the assembly has been cured at 150 °C for 30 min. A gradual cooling has been performed in a foam polystyrene box. Once the samples were ready, they have been installed on the Tinius Olsen H10KT tensile testing machine through the use of self-tightening clamps and each side of the specimen has been shimmed with 2 mm spacers in order to center the welded section with respect to the vertical axis of the clamps. The test has been effectuated at a constant crosshead speed of 1.3 mm/min until adhesive failure, measuring the load displacement curve and the maximum detaching force. Each test has been repeated three times per coating type, in order to provide a statistical analysis, making in addition a comparison between the results of the others testing methods.

#### *Wear resistance tests*

The mechanical abrasion resistance of the coatings was studied by means of the P.E.I abrasion tester, according to the ISO 10545-7 standard.<sup>29</sup> Each sample has been incrementally subjected to steps of 100 abrasion cycles until an overall number of 400 has been reached. Sample preparation involved disk reshaping, in order to obtain rectangular panels of 10 cm width washed and degreased before the test. After each block, mass loss,  $R_a$  and  $R_z$  roughness, and optical surface analysis has been performed, evaluating the overall behavior of each coating.

Finally, the samples were subjected to the dishwashing test, following the standard UNI EN 12875-1:2005,<sup>30</sup> which prescribes a series of 250 cycles at an operating temperature of 60 °C. In order to increase the test efficiency, the standard has been improved, increasing its aggressiveness, by means of a sanitizing dishwasher, capable of reaching an operating temperature of 93 °C. Each coating has been subjected to an overall of 100-h cycles at the maximum temperature, employing a commercial cleaning powder product. These powders are usually composed of several oxidative compounds, such as sodium carbonate peroxide or sodium persulfate,<sup>31</sup> which once in contact with water will release hydrogen peroxide, capable of interacting with the organic chains characterizing the antistick layers. This chemically active environment in conjunction with the high temperature reached during dish-



**Fig. 1: Average coatings  $R_a$  and  $R_z$  roughness**

washing cycles may cause an evident loss in coatings performances.

## Results and discussion

### Coatings characterization

The average  $R_a$  and  $R_z$  roughness values of the four coating systems are exhibited in the graph of Fig. 1.

The graph outlines how the sol-gel production process allows for better surface finishing and homogeneity with respect to PTFE-based coatings, which exhibit a quite inhomogeneous coating distribution, underlined by the discrepancy between  $R_a$  and  $R_z$ . The reason for this different behavior must be researched inside the production and application of the process itself. In fact, the sol-gel application needs a curing process, during which Si-O-Si bonds are formed and the coating transforms initially in a gel and then in a solid compound. On the contrary, the PTFE-based systems are composed of a suspension of several thermoplastic polymers in water, which is then removed by heating, promoting the formation of vapor and shrinkage porosities.

Subsequently, each coating has been analyzed in an interval of  $4000\text{--}550\text{ cm}^{-1}$ , making a comparison between the different compositions, additionally evidencing chemical variations inside the coating thickness: The analyses were carried out at different depths by removing the material mechanically, through emery paper steps. Figure 2a compares the P1, P2 and P3 behavior with the typical PTFE spectrum. The three coatings spectra were superimposable to PTFE, with two C-F bond stretching peaks at  $1200\text{ cm}^{-1}$  and at  $1145\text{ cm}^{-1}$  and a peak at around  $630\text{--}620\text{ cm}^{-1}$  representative of C-F skeletal vibration.<sup>32</sup> This analysis evidenced that, despite claiming to be different coatings, P1, P2, and P3 rely on the same releasing agent, therefore providing similar antiadhesion properties.

Once the surface composition has been stated, further investigations have been performed in order to evaluate compositional variations inside coating thickness. Therefore, each sample has been exposed to 3 abrasion steps with an 800 SiC emery paper for 1 min each, underlining any chemical variation. The analysis pointed out how P1 and P2 were fully PTFE based, providing just a linear shift in intensity but not in peaks position, phenomena related to an overall decrease in coating thickness. On the contrary, P3 presented remarkable variations, which are reported in Fig. 2b. The spectra demonstrate how P3 relies on a PTFE-based topcoat and on a reinforced midcoat to provide antistick properties, while a PEEK primer supplies increased abrasion resistance due to its higher hardness and toughness.

Thus, the three PTFE-based coatings were observed by SEM, in order to detect further information on coatings morphology, defining how chemical composition change within the layers and how reinforcement particles are distributed inside the matrix.

Figure 3a shows the cross section of sample P1. The analysis confirmed how reinforcement involved in the coating is divided in coarse (approx.  $13\text{ }\mu\text{m}$ ) and fine (approx.  $1\text{ }\mu\text{m}$ ) particles. The first one being distributed also in the topcoat, while the second one just inside the primer, as the brighter zone suggests. The EDXS chemical map analysis evidenced that the topcoat is mainly composed of PTFE, presenting small traces of Ba related to some fillers dispersed in the matrix. Instead, in the basecoat the amount of fluoropolymer is sensibly reduced in favor of an increase in Si-based reinforcement particles. In addition, small traces of S are present, underlining other inorganic fillers added in the primer.

Differently, sample P2 exhibited a higher amount of coarse reinforcement particles (Fig. 3b), with several porosities primarily located in the basecoat and caused by coating volume contraction. No clear distinction can be observed between topcoat and midcoat matrix, evidencing the absence of finer reinforcement particles in these layers. Wear resistance is therefore delivered just by coarse particle interaction. In this case, the EDXS analysis identified a primer and midcoat sharing approximately the same PTFE matrix: the differences stand in the reinforcement, which is concentrated in the sub-surface layer being constituted of coarse  $\text{SiO}_2$ -based particles. Small traces of O can be found in the primer possibly suggesting the presence of fine oxide particles acting as fillers or the use of specific primers such as PAI (polyamide-imide) presenting several carbonyl bonds.

Finally, Fig. 3c shows the cross section of coating P3. Three different layers can be easily distinguished. In particular, a high thickness basecoat, a heavily reinforced midcoat and a lightly reinforced topcoat. Referring to company specifications, the thick basecoat provides higher wear resistance involving a PEEK matrix reinforced with fine inorganic particles, while the antistick properties are provided by the PTFE-

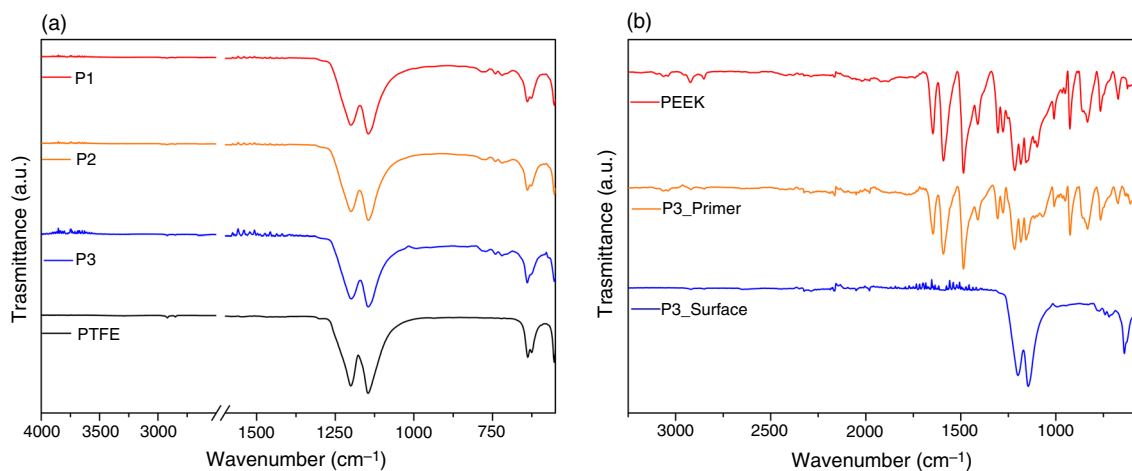


Fig. 2: FTIR-ATR spectra of (a) PTFE-based systems and (b) P3 primer analysis

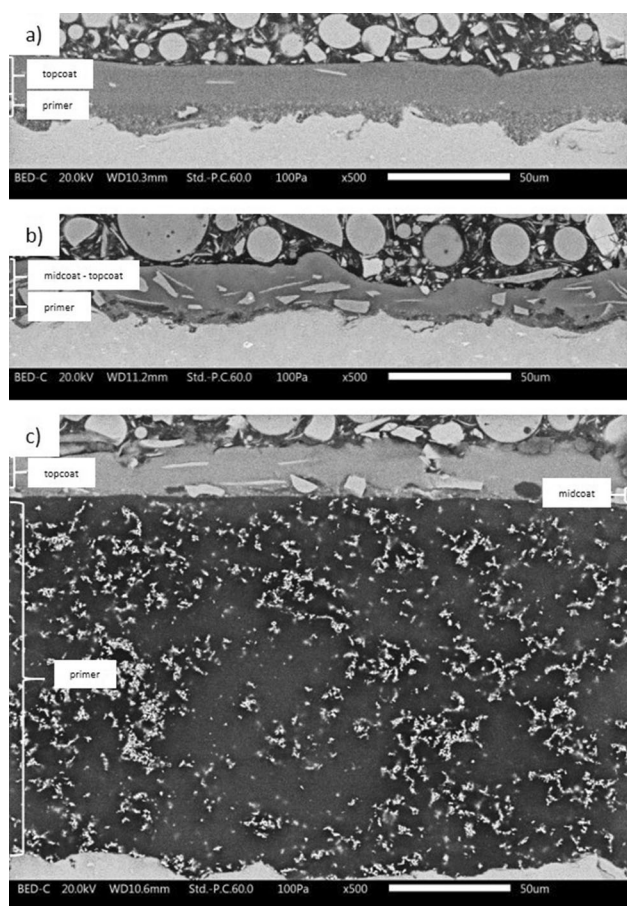


Fig. 3: SEM cross section of (a) sample P1, (b) sample P2 and (c) sample P3

based midcoat and topcoat. Further EDX analysis pointed out the presence of Si, related to coarse  $\text{SiO}_2$ -based particles used as reinforcement in the midcoat. Whereas the presence of Ba in the basecoat may suggest the use of Ba-based compounds, widely used in paint industry as reinforcement and economic fillers.

This study confirmed the hypothesis made toward the absence of fluorinated polymers in the primer; therefore, the antistick properties are delivered exclusively by top and midcoat. Additionally, the higher C concentration, detectable in the primer with respect to the other layers, expresses a consistent difference in chemical composition between topcoat and basecoat, confirming the FTIR analysis. Moreover, reinforcement in the outer layers is obtained through the addition of Si-based coarse particles, while it is interesting to notice how the primer has been filled in with fine Ba-based conglomerates.

In conclusion, all three PTFE-based samples presented a gradual reduction in inorganic particles the more the layers were close to the surface. This occurrence suggests that an increase in reinforcement, despite being effective in enhancing wear resistance, turns out to be detrimental in terms of releasing properties and therefore, a compromise between coating performance and cookware lifetime must be accepted.

Differently, the FTIR-ATR spectra of the sol-gel based coating, shown in Fig. 4a, exhibited several peaks evidencing a consistent more complex chemical composition. As the coating is based on silane/siloxane, which is able to crosslink through oxygen bridging, the main Si-O-Si structure together with  $\text{SiO}_2$  can be easily detected, presenting Si-O stretching at 1100 and 1000  $\text{cm}^{-1}$  and  $\text{SiO}_2$  vibration at 760  $\text{cm}^{-1}$ . The organic nature of the coating can be evidenced by the presence of residual Si-( $\text{CH}_3$ )<sub>3</sub>, Si- $\text{CH}_3$ , Si- $\text{CH}_2$ -R and  $\text{CH}_3$  at 850, 1250, 1400 and 2975  $\text{cm}^{-1}$ , respectively, as a consequence of the lower curing temperature used for coating application.<sup>33</sup> The releasing properties of sol-gel coatings are indeed related to the presence of this organic layer, which can be also functionalized by the addition of sol-gel bonded compounds.

The investigation inside the coating thickness (Fig. 4 b) evidenced a sudden decrease in the organic components Si-( $\text{CH}_3$ )<sub>3</sub>, Si- $\text{CH}_3$ , Si- $\text{CH}_2$ -R and  $\text{CH}_3$  peaks, which can be observed after the first abrading step.

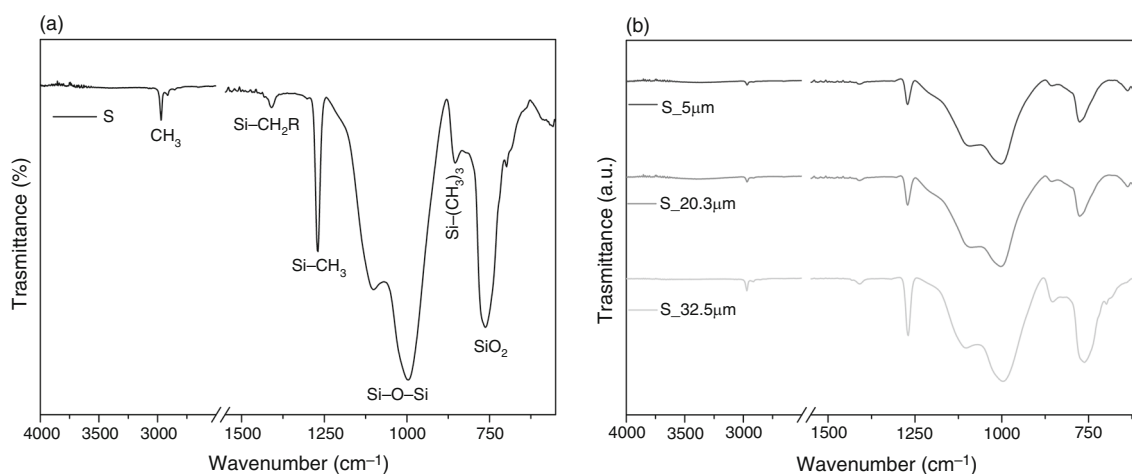


Fig. 4: FTIR-ATR spectra of (a) sol-gel coating and (b) layers analysis

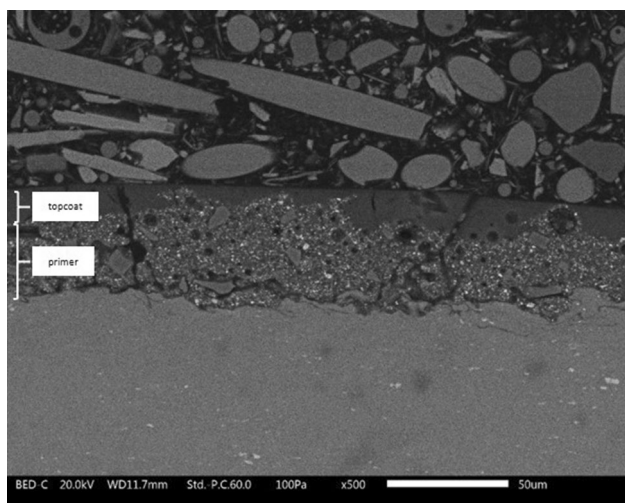


Fig. 5: SEM cross section of sample S

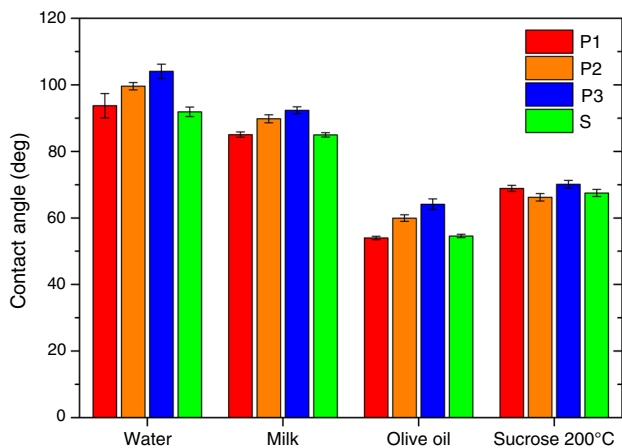
This result underlines how these functional groups could be responsible for the releasing properties of the coating, being located only on the sample's surface, while the bulk exhibits mainly a  $\text{SiO}_2$  network.

Despite not being a fully inorganic coating, sol-gel layers are far more brittle with respect to their PTFE counterpart. Therefore, the occurrence of fracture defects inside the coating, such as the ones in Fig. 5, requires more care during handling and every day usage. Companies tend to refer to this type of material as “ceramic” in order to catch the customer's attention, providing at the same time further limitation on the maximum dishwasher operating condition to preserve coating performance. The SEM micrograph exhibits a clear distinction between topcoat and primer, being the first one a homogeneous compact layer without any reinforcement particle. On the contrary, the primer presents a heterogeneous composition embedding coarse reinforcement particles, high density fine conglomerates and porosities underlined

by the black spots in the matrix. Finally, coating cracks have been analyzed, evidencing crack propagation within the coating and at metal substrate interface. This phenomenon is related to the increased brittleness of sol-gel ceramic coatings with respect to the PTFE one, making them more sensitive to delamination when in the case of impacts with other kitchenware. The residual organic component, even if identified by the ATR analysis, is not detectable by EDX technique, due to its lower detection limit. However, the analysis pointed out the absence of F in sol-gel coatings evidencing the producer's efforts to develop PTFE-free antistick systems. As expected, intense Si and O signals in the matrix are detected, underlining that the main constituent of the coating could be  $\text{SiO}_2$ , present at higher concentration in the topcoat with respect to the primer, which is enriched with different kinds of inorganic particles. These particles, embedded in the  $\text{SiO}_2$  matrix, can be divided in two groups, Si-based reinforcement, in the areas where O signal is lower, and stable Cr and Cu oxides, used as pigments in paint industry.  $\text{Cr}_2\text{O}_3$  and  $\text{CuO}$ , respectively, are used to deliver a green and reddish glittering effect to the coating emerging below the clear topcoat. This condition is possible thanks to the transparency of sol-gel systems developed during curing, when amorphous Si-O-Si structure forms. The aim of these effects is to diversify sol-gel coatings from the common, opaque, black, or white colors of PTFE-based ones, making them clearly distinguishable and more attractive.

#### Antistick properties evaluation

The surface contact angle was the first performed test, due to the non-invasive characteristics of the method, allowing for further analysis on the same samples. Indeed, by simply wiping the liquids off the surface and degreasing with acetone it was possible to reuse the samples for further tests.

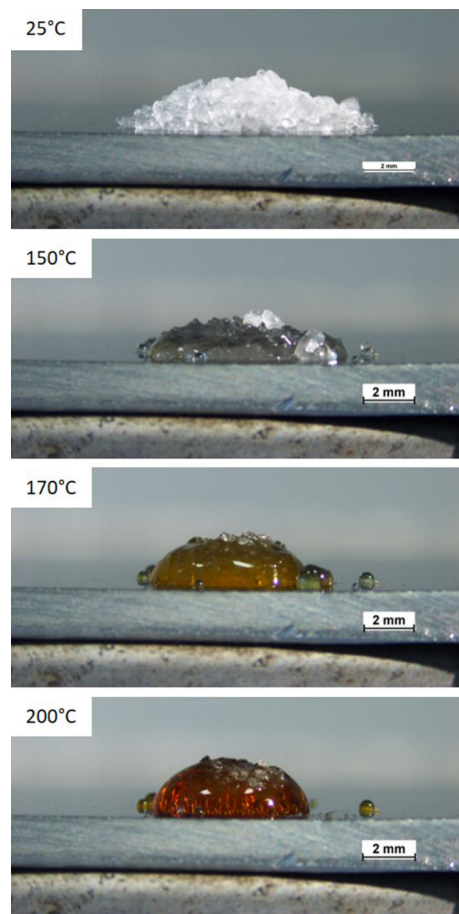


**Fig. 6: Coatings surface contact angle test results, as a function of different matters**

Figure 6 exhibits the results of the behavior of the four coatings, as a function of the liquid employed in the test. The graph evidenced that PTFE-based coatings generally behave better in terms of antistick performances, scoring the highest contact angles with all the room temperature used liquids. In fact, sample P2 and sample P3 showed the best results, while P1 was comparable with S sol-gel coating. These data underline how effective the development in sol-gel coatings has become, which, despite still exhibiting lower performances with respect their PTFE counterpart, are on the way to being comparable with them, at least as an un-worn product. Differences within the PTFE samples should be related to surface characteristics and reinforcement type, influencing the contact area and the amount of C-F bonds present at surface.

Separate considerations should be made for the high-temperature sucrose test: in this case coatings exhibited more flattened results, contrary to the room temperature evaluation. The reasons behind these data have to be found in coatings thermal conductivity differences. In fact, variability in thickness and chemical composition of the coatings determined differences in heat conduction and uncertainties in sucrose melting time, oscillating between 15 and 45 min. This heating time variability determined temperature increase and gas bubble formation, even in the early stages of the fusion process. As a consequence of molten sucrose viscosity, bubbles tend to remain trapped inside the liquid drops, expanding as the melting process proceeds, as exhibited in Fig. 7. The gas expansion determined a contraction in sucrose drop and an apparent modification in the surface contact angle, leading to values misunderstandings.

By making a comparison between testing liquids composition and samples reaction, a progressive decrease in contact angle can be noticed while detecting coatings behavior under water (0% fat), milk (3.5% fat), and olive oil (100% fat). The reason behind this occurrence is related to the increasing amount of fatty



**Fig. 7: Progressive sucrose polymerization**

acids contained in fluids. In fact, surface tension is related to molecules polarity and electrostatic interactions. Therefore, since fats are apolar molecules, they determine an increase in spreading of these liquids over the antistick surfaces. In conclusion, this method proved to be quite accurate and robust, producing similar results when room temperature liquid substances were used.

Subsequently, pull-off tests on new samples have been performed evaluating coatings behavior toward epoxy Araldite 2011. The graph in Fig. 8 highlights a significant distinction between PTFE-based coatings and sol-gel one. The three samples P1, P2, and P3 exhibited a sensibly low detachment stress, while the coating S presented a value 3 times higher, as a confirmation of the reduced antiadhesive power of ceramic coatings, even as an un-worn product. In all cases, the detachment surface analysis did not present any coating failure, evidencing how, even with differences in performances, all the coatings were able to deliver efficient antistick properties.

Finally, the single lap-joint tensile shear test was performed on new coatings, evaluating performances as data reference for the subsequent wear analysis. As can be seen in Fig. 9, this test was able to make an



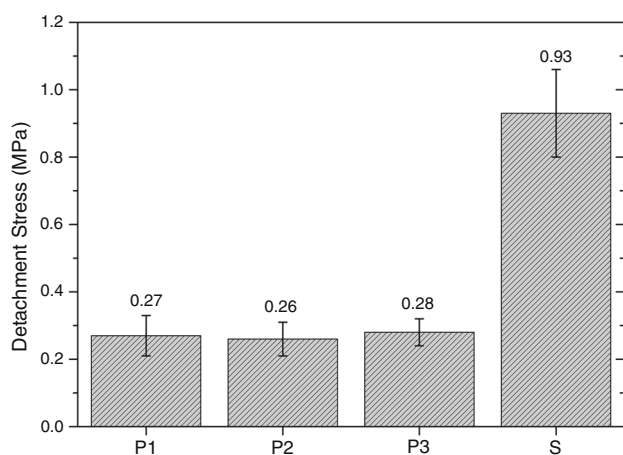


Fig. 8: Pull-off test results

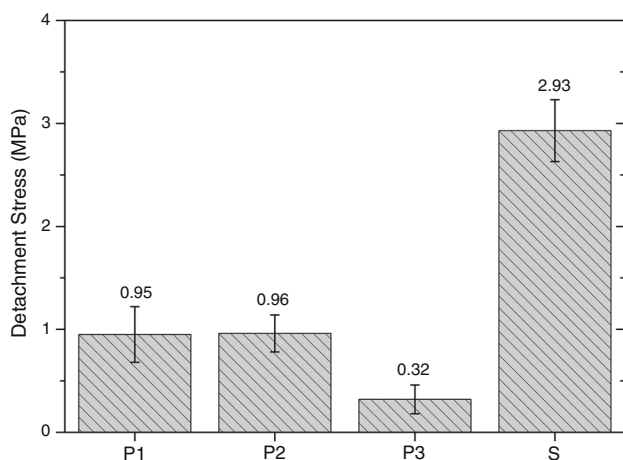


Fig. 9: Single lap-joint tensile shear test results

effective distinction between PTFE-based coatings and sol-gel one. As previously shown in the other tests, the sol-gel coating S exhibited the lowest antistick properties among the four systems, a condition related to the different releasing agent being more sensible to adhesive bonding. In addition, the tensile test evidenced a distinction between coating P3 and the other two PTFE-based samples, P1 and P2, which have behaved similarly in approximately all the tests.

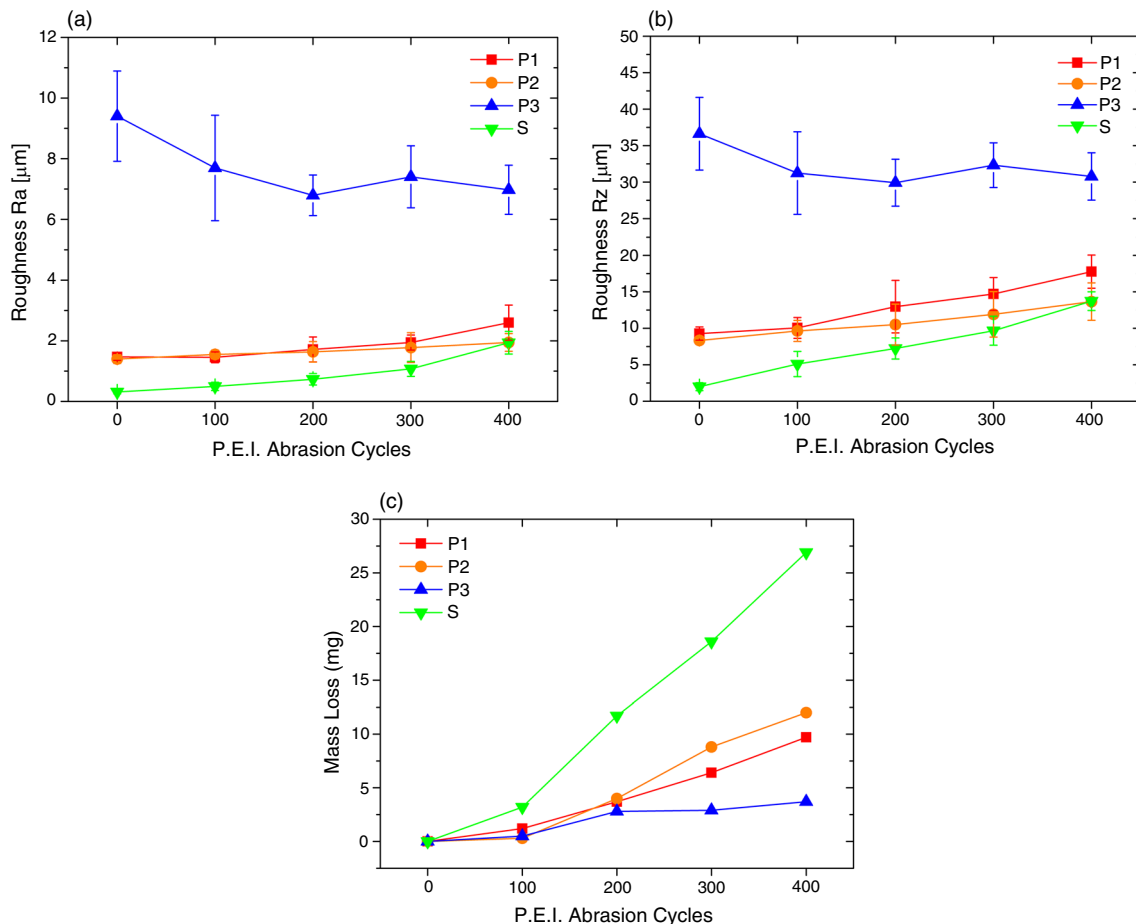
The reason behind the increased antistick properties of sample P3 coating should be related to its specific surface characteristics and reduced liquids spreading as demonstrated in the contact angle tests (Fig. 6). In fact, the higher roughness exhibited by the sample and the reduced capability of fluids to spread upon the coating, induced a non-uniform distribution of the glue and defects formation, decreasing adhesive strength of the epoxy resin and favoring the detachment. On the other hand, sample P1 and sample P2 featuring the same chemical composition at surface, but lower roughness and higher liquid spreading with respect to P3, showed higher, separating stresses.

A comparison among all the proposed methods highlights that the tests were able to evidence distinctions between antistick coatings based on different chemical constituents (PTFE/sol-gel) and, in some cases, even a classification within the same coating family was possible. In particular, the surface contact angle tests presented high accuracy, resolution, and reproducibility, with a very limited standard deviation. This method was able to detect slight performance differences in each coating, remaining unchanged independent of the testing liquid. Instead, the pull-off test featured good selectivity between PTFE and sol-gel systems, but it was not able to detect differences within samples sharing the same chemical composition. Finally, the single lap-joint tensile shear test demonstrated a good capability to distinguish between several types of coatings, exhibiting accuracy and acceptable reproducibility of the results. Indeed, a certain amount of variability is present in all the methods using adhesives as testing media, related to curing temperature and polymerization degree fluctuations occurring during sample preparation. For these methods, a consistent amount of performed tests is advisable to produce an accurate statistical analysis.

However, there is a fundamental aspect to consider regarding the antistick properties evaluation carried out. Epoxy Araldite 2011 was used as the adhesive for the pull-off and single lap-joint tensile shear tests, as it possesses the necessary adhesive features. Nevertheless, epoxy resin is not fully representative of food chemistry: the adhesion levels of Araldite 2011 are not achievable by food products. Recent work<sup>34</sup> has associated Maillard chemistry reactions with adhesion phenomena between food and cookware during cooking. As a matter of fact, when cooking and baking, sugar carbonyls can react with protein amines, generating crosslink reactions, thus increasing solution viscosities and adhesion.<sup>35–38</sup> The development of the so-called Amadori compounds involves the reaction of OH groups and amines, which can favor the adhesion of food with the surface of the cookware.<sup>39, 40</sup> Definitely, kitchen chemistry can make high strength adhesives out of proteins. These chemical reactions are similar to the behavior of the diamines contained in Araldite 2011, even if the outcome, in terms of adhesion, is not comparable. Thus, the results obtained with Araldite 2011 ensure lower adhesion levels observed when cooking food. Finally, although it is not possible to make a real comparison between the performance of epoxy resin and common foods, this work presents a reference point for the realization of antistick tests on cookware.

### Wear and abrasion resistance

The evaluation of coating behavior when subjected to mechanical damage and abrasion has been effectuated by collecting  $R_a$ ,  $R_z$  and mass loss data after each P.E.I. step and keeping track of the variation trends. In



**Fig. 10: (a)  $R_a$ , (b)  $R_z$  roughness change and (c) coatings mass loss during P.E.I. test**

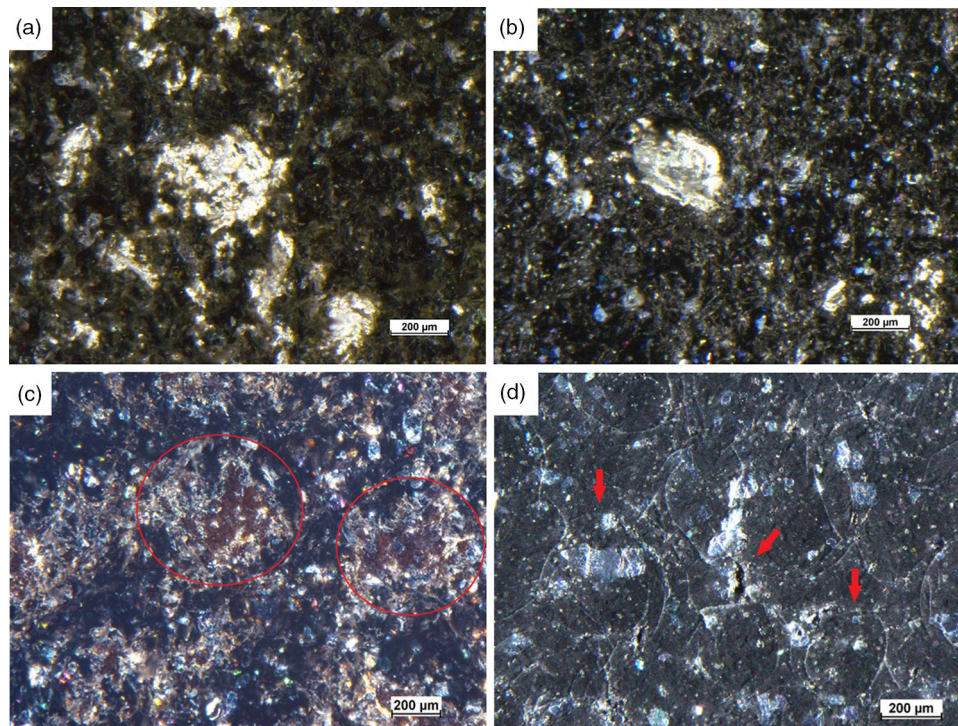
addition, samples degradation has been progressively evidenced by acquiring images at magnification under an optical microscope. This test was carried out with a double valence: in order to evaluate the effectiveness of the reinforcement used by the producers to counteract abrasion and its detrimental effects on appearance, but also to prepare the samples for the subsequent residual antistickiness characterization.

The graphs reported in Fig. 10 highlight a decreasing roughness trend for the sample P3 and an increasing one for systems P1, P2 and S. The reason behind this behavior is related to samples initial roughness; indeed P3 featured high values for both  $R_a$  and  $R_z$ , characteristic of the stone-like rugged surface. Therefore, the abrasive action of the slurry used in P.E.I. tests performed a smoothing effect on coating peaks determining the overall roughness reduction. On the other hand, initially smoother samples experienced an  $R_a$  and  $R_z$  increase, related to the progressive damaging of the surface determined by the abrading slurry.

Moreover, P1 and P2 presented a limited increase in both roughness parameters,  $R_a$  and  $R_z$ : higher for the first one than for the second sample due to the increased amount of reinforcement particles embedded in the P2 matrix. On the other hand, sample S

exhibited a progressive and sudden increase in both. This result can be linked to the different chemical composition of the coatings. In fact, while the PTFE (P1, P2) layers are able to absorb steel ball impacts through deformation and spreading, the sol-gel S, due to its fragile structure, gets cracked generating fragments and deep valleys.

Parallel to the  $R_a$  and  $R_z$  evaluations, mass loss analysis has been performed to evaluate coatings response to abrasion effects. As a confirmation of what was stated in the  $R_a$  and  $R_z$  analysis, the mass loss evaluation (Fig. 10c) pointed out as sample P3 was more resistant to fragmentation and particle detaching thanks to its PEEK reinforced matrix,<sup>41</sup> while the sol-gel coating S presented the highest mass loss upon all samples, a behavior again related to the absence of ductility in the coating, easily subjected to cracking and fragment release. Finally, systems P1 and P2 exhibited a similar intermediate behavior between the other two coatings. In the first 200 cycles, abrasion behavior of P3 was the same as P1 and P2, whereas it sensibly diverged afterward. Again, by relating the results to coatings chemical composition, it is possible to assess that, at the beginning of the test, all three samples presented a PTFE antistick layer determining the



**Fig. 11: Optical microscope damage magnification on (a) sample P1, (b) sample P2, (c) sample P3 and (d) sample S, after the P.E.I. test**

similar wear behavior. However, while P1 and P2 did not present any substantial chemical variation within the layers, the coating P3 exhibited a tough PEEK matrix laying underneath the PTFE antistick topcoat, determining a decrease in mass loss once the first layer had been damaged/removed.

The optical microscope image in Fig. 11a shows the abrasive damage on sample P1 due to the P.E.I. test. The low thickness of the coating determined the progressive rise of the aluminum substrate laying beyond. In this case, the coating did not present any visible cracking, confirming that the soft PTFE layers are susceptible to plastic deformation and abrasion rather than fragmentation and particle detachment.

Even coating P2, when subjected to P.E.I tests, presented a progressive rise of the aluminum substrate as a consequence of the abrasive action (Fig. 11b). However, thanks to the increased amount of reinforcement particles, it managed to better sustain mechanical degradation. This reinforcement enrichment can be easily detected, underlined by the presence of several crystalline particles in the coating. In addition, degradation extent in P2 is sensibly lower presenting just some areas in which the coating has been removed as a consequence of the abrading action.

Differently, the progressive wear acting on sample P3 partially removed the dark PTFE topcoat, exposing the yellowish PEEK primer laying underneath, as highlighted in Fig. 11c. In particular, dark yellow PEEK areas can be distinguished by the surrounding black PTFE zones: This selective wear was related to

the relatively high initial roughness of the sample determining a major amount of abrasion in proximity of the coating deposition peaks. In comparison with sample P1, P3 surface turned out to be much more reinforced by hard particles confirming the increased abrasion resistance stated by the P.E.I. tests previously performed.

Finally, the sol-gel coating S showed a progressive reduction in gloss and smoothness, while the topcoat was removed as a consequence of wear action. Localized detachment spots have been evidenced in contrast to a more uniform degradation exhibited by PTFE-based coatings and related to the more brittle behavior of sol-gel antistick systems. By observing crack shapes in Fig. 11d, the circular mark characteristics of the abrasive steel balls can be identified, underlining how impacts, coating cracking and fragment detachment are responsible for degradation in ceramic systems. In this case, reinforcement particles were not able to counteract impacts and cracking, due to the higher brittleness of the matrix, causing severe damage on the coating.

Definitely, P.E.I abrasion test is highly efficient in defining coatings mechanical resistance to wear, making possible a clear distinction between all the samples. However, in order to define its influence on antistick properties, these data must be considered in conjunction with antistick tests, because not necessarily the system presenting the lower mass loss performs better in preserving its antiadhesive features.

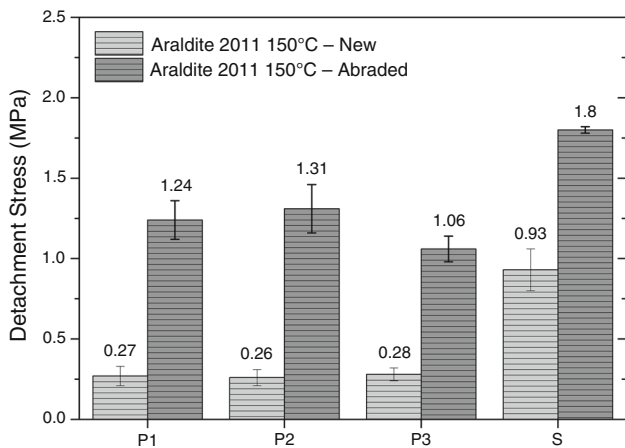


Fig. 12: Araldite 2011 pull-off tests comparison, new vs abraded samples

**Antistick and degradation correlations**

Once the effectiveness of the proposed antistick evaluation methods has been assessed on new coatings, the same tests were performed on samples which were previously subjected to mechanical abrasion.

Pull-off tests on abraded samples have been performed evaluating coatings behavior toward epoxy Araldite 2011. As shown in Fig. 12, Araldite 2011 confirmed a good selectivity upon all the tested coatings, being able to distinguish antistick performance differences based on coatings chemical composition and even within PTFE samples. In this case, sample P3 scored the best results, followed by P1 and P2, confirming the outcome of the previous tests. Finally, the ceramic coating S exhibited the worst result in the testing batch, presenting diffused failure and detachment of the coating from the substrate. All PTFE coatings revealed an increase in adhesion between 500 and 600%, underlining how intensively antistick performances are influenced by mechanical degradation. However, an aluminum plate representing an un-coated pan exhibited a detachment stress around 4.6 MPa. Thus, the damaged coatings still provide adhesion values 4 times lower than the pure substrate, without presenting any coating failure. The difference in performances exhibited by the three PTFE samples should be related to the overall thickness of the coatings. Indeed, P1 and P2 being approximately three times less thick with respect to P3, they suffered a more consistent mechanical damage upon these coatings. Therefore, the aluminum substrate spots on the abraded surface of these coatings once in contact with the Araldite 2011 determined an increase in the pull-off detaching stress values.

The single lap-joint tensile shear test was used to evaluate coatings behavior when subjected to mechanical degradation, whose results are presented in Fig. 13, in comparison with the reference new samples. As confirmed by the previous tests, the coatings exhibited

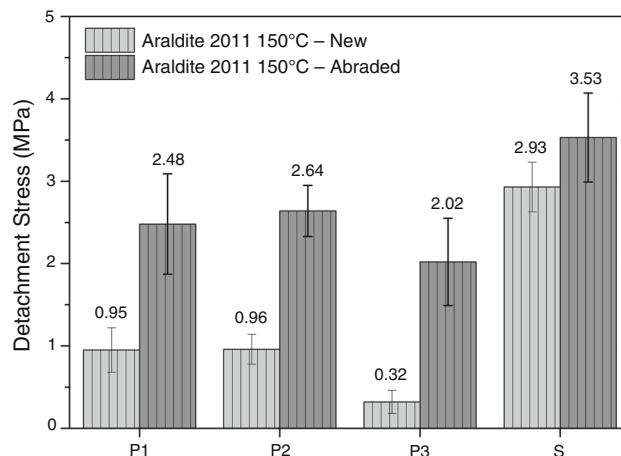


Fig. 13: Araldite 2011 tensile shear tests comparison, new vs abraded samples

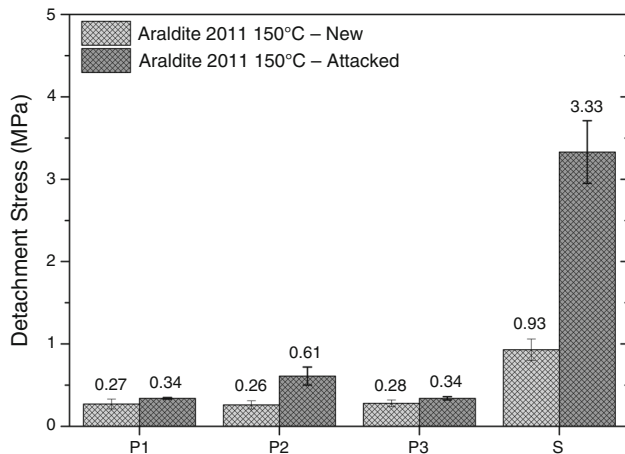
the same trends in terms of antistick performances, where the PTFE-based systems revealed the best behavior, while the sol-gel displayed the most consistent loss in antistick capacity. In particular, P3 was the best in preserving its properties, while P1 and P2 again exhibited a similar behavior either as new or abraded samples. Finally, the sol-gel coating S totally failed the test, evidencing coating decohesion along the degraded areas, while all the other PTFE systems were totally undamaged.

Once the mechanical damage effects upon the antistick systems were evaluated, the samples exposed to the thermochemical attacks during the dishwasher cycles were analyzed by means of the pull-off method. As described in Fig. 14, the performances of all the PTFE-based coatings were mainly unchanged before and after the dishwasher cycles, evidencing how these systems are not experiencing degradation under high temperature and chemically aggressive environments. On the contrary, the sol-gel coating S approximately tripled the adhesion force, totally losing its antistick feature.

By comparing the effects of wear and chemical degradation on coatings performances, it can be assessed that mechanical abrasion was detrimental for all the evaluated antistick systems. While all the PTFE-based coatings seemed to be unaffected by thermochemical attacks, ceramic ones experienced more sensitivity to this type of degradation.

**Conclusions**

The aim of this work was to define alternative methods for antistick property evaluation, together with the need to investigate degradation effects upon antiadhesive coatings performances. Evident limits in the standard evaluation methods in use were present, as the impossibility to produce quantitative and reliable data from the analysis and the complexity in distin-



**Fig. 14: Araldite 2011 pull-off test comparison, new vs chemically attached samples**

guishing between performance levels of several antistick systems. Indeed, due to the technological advance developed in this field, the egg test (BS 7069:1988) and the milk test (AFNOR N.F. D 21.511:1989), were no able to provide a classification based on coatings performances, except from a general distinction between antistick and sticky surfaces, without considering degradation effects.

In this study, three different methods have been proposed for antistick evaluation: the surface contact angle (UNI EN 828:2013) test, the pull-off (UNI EN 4624:2016) test and the single lap-joint tensile shear test (UNI EN 1465:2009), taking as a reference the standard procedures due to their industrial worldwide diffusion, while modifying the tests media in order to better tune the methods on the detection of small adhesion variations. In particular, the surface contact angle test has been performed using four different substances, water, milk, olive oil and sucrose, while the pull-off and the tensile shear test involved epoxy Araldite 2011 as bonding adhesives. In parallel, the main culprits in antistick cookware degradation were identified as mechanical wear/abrasion and chemical damage during the washing cycles. Therefore, simulant tests were selected, using the P.E.I abrasion tester ISO 10545-7 and a harshened dishwasher test based on the UNI EN 12875-1:2005 standard.

Four different commercial samples have been characterized in terms of coatings thickness, roughness, layers deposition, and chemical structure, in order to collect robust reference data to be used in conjunction with the antistick tests results and the behavior when subjected to degradation.

Concerning the proposed method efficiency, a classification based on the results has been made. Respectively, the single lap-joint tensile shear test featured the best selectivity independently on the degradation state of the analyzed coatings, being able to evaluate evident differences between all the proposed samples, whether new or damaged. However, in case of fast evaluation

tests, the pull-off method presented a viable and more economical alternative, considering the overall instrument costs. Indeed, this method presented high selectivity in tracing the degradation of the antistick layer, while losing some accuracy in the analysis of new samples, especially in case of very similar PTFE-based systems. All methods were influenced by the degradation state of the surfaces and especially for the mechanical abrasion, homogeneity of the wear degree on the sample turned out to be a key point in the reproducibility and accuracy in the tests. Therefore, the choice of the abrading tester will influence the outputs considering that the more uniform the produced wear on the surface is, the more accurate the evaluations of degradation effect on antistick properties will be.

Finally, several considerations can be made toward coatings performances during the tests. In particular, all the PTFE-based samples presented good antistick properties, being able to withstand both mechanical and chemical degradation without exhibiting failure. A higher sensibility to mechanical abrasion has been expressed leading to an increase in the adhesive forces, related to the progressive consumption of the topcoat and the exposure of the underlying lesser PTFE-filled layers; however, this in any case determined coating failure. All PTFE-based systems turned out to be totally uninfluenced by the chemical attacks performed during the dishwasher cycles.

On contrary, the analyzed sol-gel ceramic coating exhibited a totally different behavior. At the beginning of the tests performed on new samples the sol-gel presented a detaching force approximately three times higher with respect to their PTFE-based counterpart, already underlying the lower performances of the applied releasing agent. This condition has emerged even more after exposing the samples to degradation. In the case of mechanical damaging, the increased fragility of the coating caused its cracking and fragmentation, which once under testing determined a consistent detaching force and the failure of the antistick system, being entirely removed from the substrate. Analogously, after the exposure to a series of dishwasher cycles together with a commercial detergent, surface modification and porosities increase was detected, underlining a detrimental interaction between the chemicals contained in the detergent and the thin organic layer responsible for the antistick properties in sol-gel coatings. The subsequent adhesion tests evidenced a generalized failure of the system and a detaching force even higher than the one characterizing the mechanically abraded samples. Therefore, these kinds of coatings despite being proposed as valid alternatives to PTFE ones do not successfully match comparable releasing properties because they are much more sensible to degradation and loss in performances.

In conclusion, this study successfully produced a series of alternative methods for antistick properties evaluation, being able to provide quantitative results

and to determine degradation effects upon coatings performances. Moreover, a detailed overview of recent antistick systems behavior has been produced, considering the performances of the different releasing agents and the degradation effects in terms of wear/abrasion and chemical interaction occurring during the cleaning procedures.

**Authors contributions** Stefano Rossi was involved in conceptualization, methodology, resources, writing—review and editing, supervision, and project administration. Federico Valdrè was involved in methodology, validation, investigation, data curation, and writing—original draft. Massimo Calovi was involved in methodology, validation, data curation, writing—original draft, writing—review and editing, and visualization.

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