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Technical Report

Functional and perceptive aspects of non-stick coatings for cookware

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ABSTRACT

In this product design study the functional and perceptive properties characterizing non-stick coatings for cookware were investigated.

The recent introduction of so-defined "ceramic" coatings allowed to offer consumers new perceptive experiences thanks to their light shade opposite to those typical of polytetrafluoroethylene (PTFE) coatings in dark colour. These innovations made possible to counteract the general decline in consumers interest towards non-stick aluminium cookware, due to news – later proved unfounded – about the alleged toxicity of PTFE, having these products a good market success.

In this work a method was individuated for testing the non-stick properties of coatings in a more technical and repeatable way, compared to the standards usually adopted by the cookware manufacturers. The coatings were later mechanically damaged in order to simulate an intense use and the non-stick properties on these abraded surfaces were newly investigated. Ceramic coatings presented a reduced functionality compared to PTFE coatings with diminished non-stick properties both on new and damaged samples.

1. Introduction

Cookware present several characteristics that significantly differentiate one from another. This product differentiation has its origin from the necessity to satisfy the different customer requests, offering them a functional and aesthetically appealing product.

The supply of non-stick cookware on the market has recently grown, presenting coatings and finishes of various kind. In fact, surface engineering have a key role to improvement the performance of engineering components [1]. These coatings are continuously more advanced from the technical point of view and they all have the non-stick capability as main purpose. In order to satisfy this aim they use various materials like polymeric coatings made of PTFE (commonly called Teflon®) or, recently, ceramic coatings. Beside these systems, other types of cookware coatings have been tested in these years as – for example – Al–Cu–Fe–Cr quasicrystalline coating and PTFE impregnated aluminium [2–4].

The frenzied life of the modern age has certainly facilitated the diffusion of non-stick aluminium cookware in kitchens all over the world. Non-stick coatings indeed can guarantee optimal thermal conductivity, like uncoated aluminium, but can also offer some additional benefits which now cannot be waived. Food does not stick to cookware, these are easy to clean and light courses can be prepared, without oil and butter abuse. The habit of considering non-stick cookware a must-have item in the kitchen, however, had a setback in early 2006, when spread the news of the alleged toxicity of Teflon® (commercial name for polytetrafluoroethylene products patented by DuPont). Teflon® is an organic auto-lubricant material, it is resistant to high temperatures and it is used for coating metal surfaces in order to provide non-stick properties [5–7]. To restrain this loss of interest towards non-stick aluminium products, many cookware manufacturers, especially the bigger ones, introduced the non-stick "ceramic" coated cookware. With this new kind of cookware, manufacturers could offer consumers original features to the industrial design point of view. These features can arouse in consumers feelings and emotions totally new compared to those provided by the PTFE coated cookware. In addition, the environmental sustainability of these new type of coatings in comparison with old "plastic" ones is highlighted. New "ceramic" coatings could also give impulse to non-stick market, with excellent economic results for manufacturers. However on the technical design side the functionality and other features of these coatings are still to be verified.

Cookware manufacturers follow the standard AFNOR NF D 21-511 [8] to evaluate the non-stick properties of coatings. This standard provides two similar tests on brand-new coatings called "milk test" and "egg test". In the first one some milk is boiled on a gas cooker until the water component completely evaporates and then the remaining film is carbonized. The pan is then washed under running water and the non-stick property of the coating is classified in 4 different classes, depending on the ease whereby the film of milk is removed. In the "egg test" the method is similar but in this case an average-sized egg is cooked on an electric plate

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for 8 or 9 min between 150 and 170 °C. Both tests are surely very similar to the real use of cookware. However the "milk test" and the "egg test" appear to be useful mostly to distinguish between non-stick and stick products, rather than to create a detailed classification and a fine comparison between a wide range of many different products. So a method has been researched in order to evaluate in a detailed way the functional properties of the coatings. Nevertheless there are few papers about this topic. Ashokkumar et al. tried to scientifically approach to test the nonstick properties of different coatings [5]. In literature was found other article about non-stick properties of fluoroalkylsilane coatings against glucose [9]. This article presents a block-on-plate test to evaluate the adhesion of glucose on coated steel plates. A block, internally coated with PTFE, is filled with glucose and placed on a coated steel plate and then the whole system is heated in an oven in order to liquefy the glucose. The "adhesive" assembly is then tested using a tensile machine. However the geometry of this test cannot prevent from multi-axial forces, reducing therefore the repeatability of the test and increasing the difficulty with data analysis and comparison. For this reason we wanted to do non-stick evaluation with a mono-axial test and we decided to use the standard ASTM: D4541, one of the most widely used standard for coatings adhesion tests.

Until now, the non-stick aluminium market was dominated by PTFE-based products and it was deemed necessary and convenient to replace coated cookware when scratched or damaged. This has been done for perceptive reasons about safety and health but also for an alleged reduced functionality of these products when scratched. Starting from these assumptions some tests were researched in order to evaluate the evolution of non-stick capability after the mechanical damage of the coatings. Cookware manufacturers follow the CEN/TS 12983-2 standard [10] to test the coatings wear resistance. The standard indicates, after heating the pan, to damage the surface of the coating with rotating brass brushes. Then a crêpe batter is poured into the frying pan and it is cooked for some minutes. Non-stick capability is evaluated according to the fraction of mixture that sticks on the pan. This kind of test, like "milk test" and "egg test", try to reproduce the actual conditions of use for cookware. Nevertheless these tests cannot provide detailed and precise results in order to emphasize little differences between many different non-stick products. They have an intense qualitative character and they are strongly conditioned by the operator ability and by his personal evaluation. So it is difficult to use these tests to distinguish between different products and there is the necessity to develop a test to make a fine distinction between products, a test which is definitely independent from the operator ability. For this reason the abrasive damage was simulated using a Taber Abraser apparatus, according to ASTM: D4060 standard, and the further non-stick tests were carried out.

In the selection of a cookware by the buyer the perceptive aspects are very important, in some cases, probably most remarkable than the technical properties.

The most important innovation introduced with ceramic coatings is the new colours they can offer. A radical change has been made compared with the dark tone of polymeric coatings, offering new and multiple possibilities on the industrial design side. There are many different ceramic coatings on the market today, produced by different manufacturers, and, despite having various shines and surface effects, they all are of a white or light shade. Precisely the white colour revealed as a cornerstone for designers, who could start associating with cookware the ideas of purity, cleanliness, essentiality and freshness, until now completely distant from dark cookware [11]. These concepts have direct reference in the names of products lines: *Blanche*, *Cloud* and *Total White* make an immediate recall to the colour, while *Corvara* and *Cortina* make people think about famous alpine resorts, with cool climate and snowy landscapes. Thanks to these new tones of inner coatings, there are now new possibilities for the colour combination with external finishes of cookware. With PTFE-based coatings designers have always gambled on the dark-light contrast between the inner and the outer side. Thanks to ceramic coatings manufacturers can create new product lines with a linear and essential aspect and with new aesthetic and perceptive features. After the introduction of ceramic, the colour of the outer side of pans moved to lighter tone. These shades have led to new products with an almost monochromatic aspect or otherwise with more subtle and sober colour combinations. In most cases gaudy finishes and decorations previously used have been set apart to make way for easy painting and in order to emphasize even more the ideas of naturalness, essentiality and cleanliness attributed to this new kind of cookware.

Though the introduction of ceramic coatings, with their light shades, has led to new problems. In particular these new coatings could undergo some colour change by use and by the passing of the time. In fact polymeric matrix showed in several cases an interaction with the solar light with a colour change to yellowish hue. In addition, in other cases, a modification of colour is observed caused by the contact with colored food matter like tomato and tomato products. So users could easily think that these variations are caused by low quality materials production involving reduction of functionality and performances. Cookware manufacturers noticed some stain susceptibility for ceramic coatings so some design solutions could be proposed in order to limit the visual impact of the phenomenon. A new shade ceramic coating could be created with a colour that should be different from the usual light shades varying from pure white to cream. Tomato, with its deep red colour, could be one of the most staining foodstuffs and for this reason a warm shade coating can be introduced, in order to hide possible changes better than light or white coatings can do. An important Italian cookware manufacturer moved exactly in this way, bringing into cookware market a new non-stick product line with deep orange coloured coating [12]. With this new kind of coating the stain problem is limited. In addition, considering the perceptive aspects, the deep and intense orange colour reminds people to earthenware, so creating a direct recall to those atmospheres and household traditions typical of past times. This new colour can so strengthen the ideas of tradition, genuineness and naturalness proper of ceramic coatings.

Considering materials perception it is important here to underline that there is a big difference between the actual nature and features of the materials and their perception for users. As said before, one of the most important innovations offered by ceramic coatings is the white or light colour. Many cookware manufacturers indeed tried to imitate the chromatic features of ceramics introducing light-coloured PTFE-based coatings. Some samples, considered in this paper (T4, T5 and T6, see experimental part) exhibit new shade, different from usual black colour. The first one is a Teflon® coating and it is named *Pearl* because of its brilliant gray colour. This name makes not only a recall to the light shade, but it wants also to give to a PTFE coating the naturalness and durability perception. The other two products exhibit a cream PTFE coating and so this colour is very similar to the one of some ceramic coatings.

Other methods to produce an idea of appealing and innovative products is the cookware decoration with printed sketches, drawings or colours. In one case some indelible decorations representing icons, short messages or sketches are printed in the interior side of cookware [13]. A strong touch of colour to cookware was until now dull and featureless. New colours studied for different customer segments [14]. Red is a bright colour, it draws the purchasers attention and it is suitable for young customers. Red colour is related to chilli pepper, so evoking ideas like energy and vitality. Blue colour is related to lavender, it makes people think about summer and rest and gives a serenity and naturalness perception. Blue colour is unusual enough to stand out in the crowd, while its familiarity stimulates the decision to buy. Gold brown reminds to the ideas of luxury and preciousness and it is easily related to the concepts of high quality and elegance. It also arouses in customers a sense of vintage, which gave a great success to non-stick ceramic coatings.

Another important product detail is the cookware bottom and top-side thickness, which can arouse in customers various feelings. A high thickness for both these parts gives users the idea of a strong, durable and well-made product, with high technological content. A high thickness bottomed cookware makes people be persuaded they can prepare every course in the best way. As a matter of fact today it is widely diffused the consciousness that as the higher the bottom thickness, as better the heat distribution and control. Designers tend to create cookware with high thickness aluminium substrate while manufacturers have the necessity to reduce material use and thus industrial costs. A widely adopted solution is to produce cookware with variable substrate thickness, having the bottom and the upper border more metal on them. Thanks to modern manufacturing processes it is now possible to produce cookware with increased thickness bottom and sides. Fig. 1 shows the cross-section of three different pans. Observing these pans it is possible to notice that sometimes the high thickness perception is only deceitful, actually having the bottom and the side of the pan the same thickness. On some samples the bottom and the side present really a higher thickness obtained reducing the metal quantity in the lower part of the side. In most cases customers cannot notice the variation in aluminium thickness and its drastic reduction in some zones. These aspects can be perceived only through cross-section observations. Customer can though perceive the attention paid in product manufacturing and the product technical character, so making a precise choice within the wide market offering.

2. Materials and experimental methods

In this work a product design study has been made on fourteen different aluminium pans of six different producers available on the market. Eight of these have non-stick "ceramic" coating and the other six have fluorinated polymer based coating (Table 1).

Table 1
Studied samples.

Sample	Coating type	Coating colour	Manufacturer
C1	Ceramic	Off white	Prod-1
C2	Ceramic	Light-cream	Prod-1
C3	Ceramic	Pure white	Prod-1
C4	Ceramic	Black metallic	Prod-1
C5	Ceramic	White metallic	Prod-6
C6	Ceramic	Pure white	Prod-2
C7	Ceramic	Pure white	Prod-3
C8	Ceramic	Pure white	Prod-4
T1	Triple layer PTFE	Black	Prod-1
T2	DuPont Teflon Classic®	Black	Prod-1
T3	DuPont Teflon Platinum®	Black	Prod-1
T4	DuPont Teflon Pearl®	Pearl grey	Prod-4
T5	Ceramic reinforced PTFE	Cream	Prod-5
T6	Ceramic reinforced PTFE	Cream	Prod-5

Two of these (T5 and T6 samples) present ceramic particles in the organic coating, as affirmed by the producer itself.

The products were selected in order to have a wide overview on the market and considering an average consumer target. Hence was chosen cookware with a price lower than 50 € and, at the same time, trying not to have overlapping between similar products. For industrial privacy reasons the names of the samples and the manufacturers are kept confidential. This aspect, however, does not affect the validity of the research. The same kind of product, 26 cm frying pan (Fig. 2), was considered for all fourteen samples.

Before testing functional properties, some analysis were made to study the physical and morphological features of the different coatings, so optical and electron microscope observations were carried out using a Philips XL30 system. Fourier Transform Infrared Spectroscopy (FT-IR) analysis were carried out using a Varian 4100 FT-IR spectrometer to investigate the nature of the coatings. Thickness coatings measurements were carried out according to EN ISO 4287 using a Phynix Surfix FN thickness gauge. The surface roughness, R_a parameter, was measured with a MAHR Marsuf PS1 roughness tester according to ISO 468 standard. As highlighted in the introduction part, to evaluate the adhesion properties between layer and its substrate uniaxial tensile test is indicated reducing the influence of the testing procedures and operator action in the obtained data. Adhesion pull off test is the most used method in particular for organic layers [15–17]. In our case, the study of non-stick properties of the surface represents a specular condition of adhesion evaluation, then this test could be considered a good

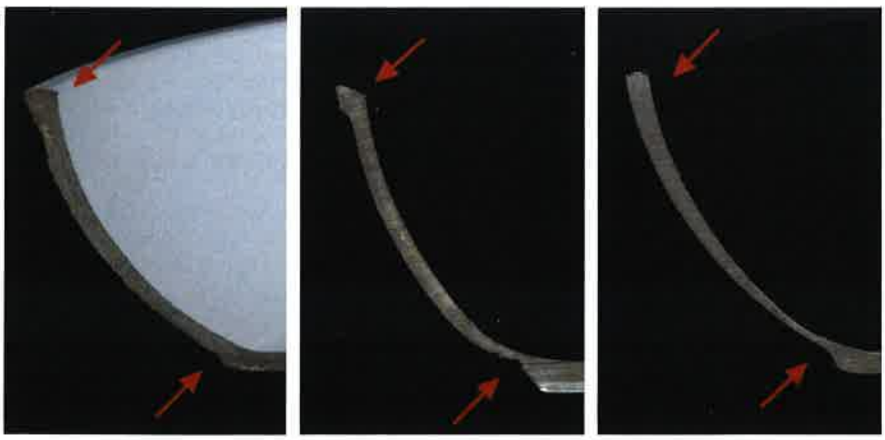

Fig. 1. Aluminium thickness variation in most relevant functional and perceptive zones ((a) C7 sample, (b) T1 sample, and (c) T2 sample).

Fig. 2. 26 cm diameter frying pan used in this research.

methods to have useful information about these aspects. Pull-off tests were carried out measuring the stress detachment values with a DeFelsko Positest Adhesion Tester according to ASTM: D4541 standard. The aluminium studs were glued on the frying pan surface using an epoxy adhesive. To obtain significant data, 10 tests on new surface and 4 on damaged surface for each sample are carried out.

During the use of a cookware the most frequent mechanical damage is produced by the interaction of the non-stick surface with kitchen tools producing an abrasion action. Taber apparatus is the most used test to study the abrasion damage of a surface particularly for a protective coatings [18–20]. This test produces a very reproducible data, then it is preferable to other tests. Considering these aspects, to study the maintaining of non-stick properties after abrasion, mechanical damage was produced by Taber Abraser test, according to ASTM: D4060 standard, using 1 kg loaded CS-10 abrading wheels. This kind of wheels is one of the most widely used for industrial tests on coatings and polymeric materials. These wheels provide a mild, medium abrading action, like that of normal handling, cleaning or polishing. Then the non-stick capability on the abraded area after 500 cycles was evaluated by pull-off tests.

3. Results and discussion

3.1. Technical aspects

The first purpose of this work is to highlight the differences between ceramic coatings and PTFE-based coatings.

Fig. 3 shows the FT-IR spectra of ceramic coatings. It can be seen how ceramic coatings are all comparable one to another. These coatings show an absorption peak at 995 cm^{-1}, corresponding to Si–O–Si bond. The peaks at 1268, 766 and 857 cm^{-1} reveal the presence of organic compound in these kind of coatings. These absorptions are supposed to be associated with methylene ($-CH_2$) and methyl ($-CH_3$) groups, localized at the extremity of silicon atoms chains as fitted using program with database KnowItAll by Bio Rad. It seems therefore appropriate to define this kind of ceramic coatings as silicon–organic compound, using the "ceramic" adjective to indicate the presence of Si–O–Si bond. It can be noticed that C5 sample appears lightly different from other samples, this having a wider part of organic fraction. FT-IR spectra of PTFE-based coatings (Fig. 4) can be distinguished in two different groups and it is easy to associate this distinction to the colour of the films. In the highest part of the graph we can find the spectra of T1, T2, and T3 samples, that is the dark coatings. On the bottom there are the spectra of light tone samples, T4, T5 and T6. These samples show a higher absorption at wavelength from 800 to 600 cm^{-1}, probably due to the presence of light colour pigments. These FT-IR spectra result very similar to that of PTFE in his pure state.

The microscope observation underlines that all ceramic coatings show a similar structure. A single layer coat is present, with a thin superficial layer, fragmented and not homogeneous (Fig. 5). This layer could be made by a silane compound, with silicon–hydrogen bonding, as highlighted by the previous FT-IR analysis. The presence of this thin superficial layer is supposed to give to ceramic coatings their non-stick properties: silanes are in fact widely used as sealant agents, water repellents and to protect surfaces from external agents [21].

While non-stick ceramic coatings are all similar one to another, PTFE based coatings exhibit various and different features. The six samples with fluorinated coatings (T1–T6) place themselves in different market sectors depending on the quality, therefore on the durability, of their coating. A clear distinction can be made between Teflon® products and the producer itself explains this differentiation on its official website [22]. Fig. 6 shows the section of T2 sample, where a double-layer system is present, with a mean thickness of about 20 μm. This value is smaller than other PTFE-based coatings, this guaranteeing lower performances, as affirmed by the producer itself. Fig. 7 shows T3 sample, triple-layers system, made of primer, midcoat and topcoat, with a total thickness of about 35 μm.

Figs. 8 and 9 show the electronic pictures of ceramic and PTFE-based coatings surfaces. Defects are present both on ceramic and PTFE-based layers. On the first ones these defects are localized only in some areas of the coating. On the contrary on PTFE films the defects are homogeneously diffused on the surface. The porosity has variable and irregular shapes and its dimensions vary from about 10 to 50 μm. Considering the porosity form, it is possible to think about fracture phenomena occurred during coating curing. Energy-dispersive X-ray spectroscopy (EDXS) analysis on defected areas does not highlight any change in composition compared to the coating surface. Considering the non-stick capabilities of PTFE [5,22], the porosity does not have detrimental effects on functional properties.

Fig. 10 reports the coatings thickness of the samples. Analyzing the thickness values of the fourteen samples no relevant differences between ceramic and PTFE systems are present. Most of the coatings has a thickness between 30 and 40 μm and only few samples do not go in this interval. Among the PTFE-based coatings group the thickness differences are greater than that among ceramic coatings group and it is supposed to be related to the fact that every coating has peculiar formulations and features, which are optimized from different companies in order to insert in a precise market sector.

Fig. 11 shows the R_a roughness values on brand-new samples, confirming the results of the microscope observations. PTFE coatings present a considerable greater roughness. The non-stick capability of PTFE-based coatings is due to the inertia of C–F bonding [5,23], this guaranteeing low stress detachment values – as later showed – despite the higher surface area compared to ceramic coatings.

After the characterization of new coatings, functional properties and their variations resulting from abrasion damage were investigated. It is important indeed that the coatings maintain their functional – and perceptive – properties during the whole service life. The most important functional property required to these cookware coatings is the non-stick capability. Fig. 12 shows the stress detachment values measured before and after abrasion damage action. It should be noticed that the results of this test have to be interpreted in an opposite manner to the traditional one. Indeed, as higher the pressure value results, as poorer is the non-stick capability of the sample. T1–T6 samples, despite having different morphological features to each other, show similar and moderate

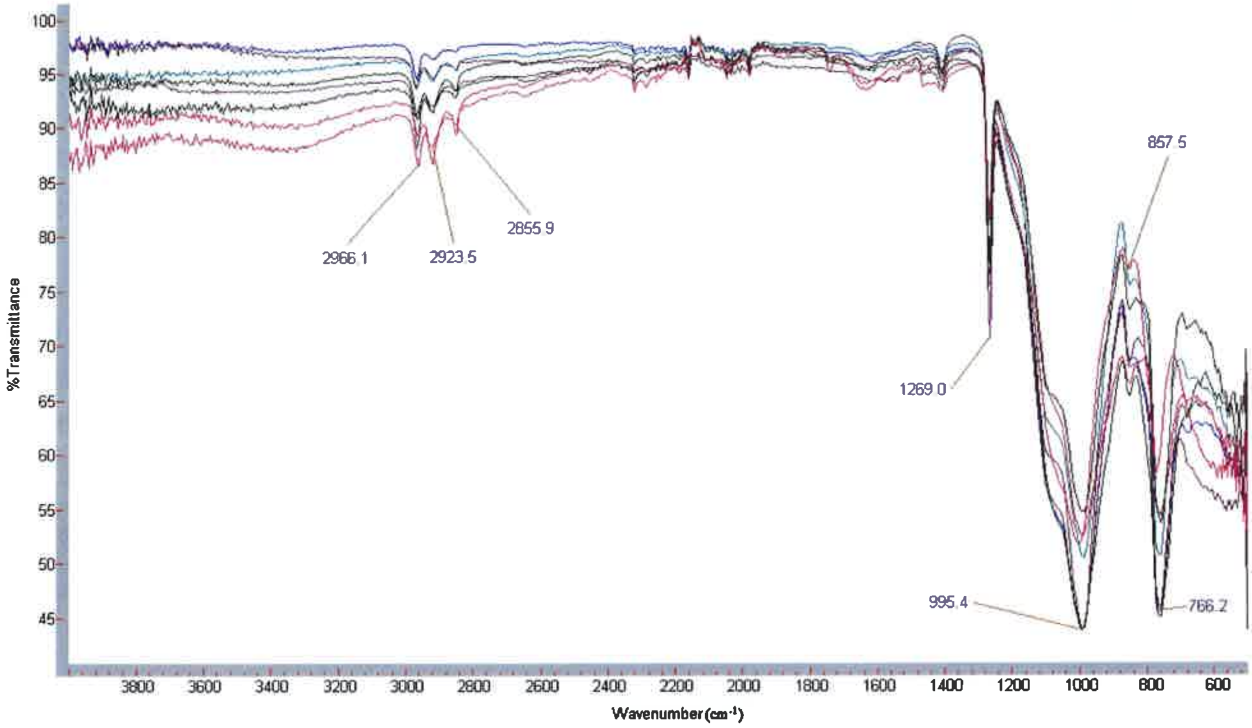

Fig. 3. FT-IR spectra of ceramic coatings.

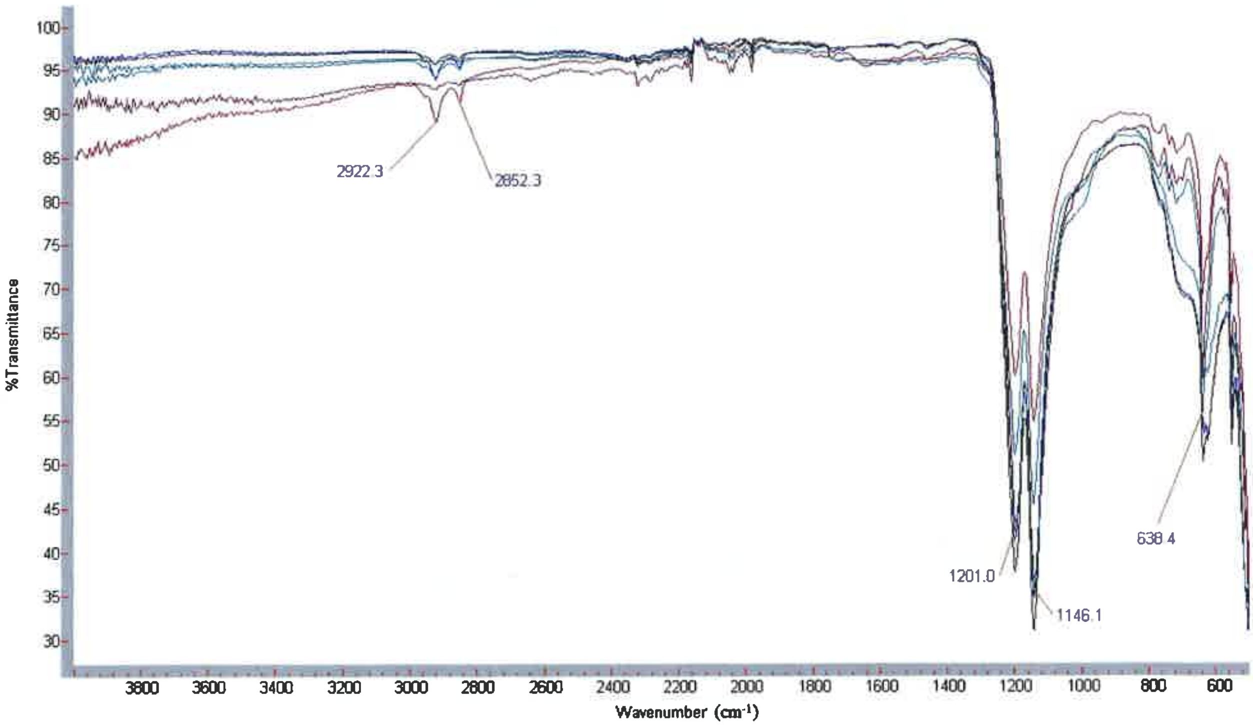

Fig. 4. FT-IR spectra of PTFE-based coatings (samples, top-down: T1, T2, T3, T4, T5, T6).

stress detachment values, nearly always lower than 1 MPa. The higher surface roughness of PTFE coatings, this leading to a greater contact area, does not decrease the non-stick capability of these products, differently from the usual idea. Ceramic coatings seem to be non-completely non-sticky and show a high variability for the separation values. Only C5 and C6 samples show stress

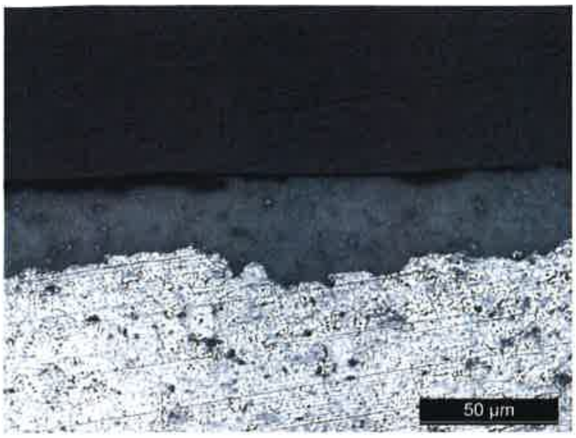

Fig. 5. Optical micrography showing the typical structure of ceramic coatings (C2 sample).

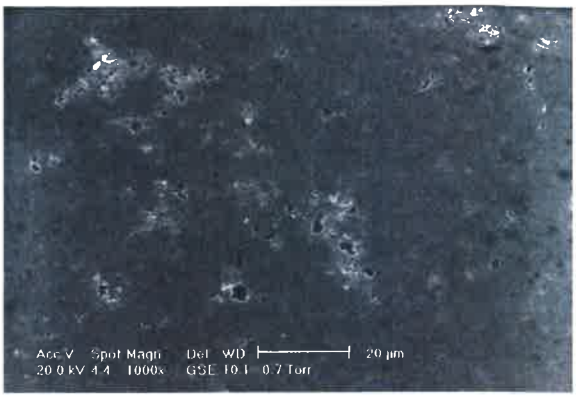

Fig. 8. ESEM micrography of defectiveness on ceramic coating (C7 sample).

detachment values lower than 1 MPa, thus comparable with PTFE coatings ones. The reduced adhesion values of C5 sample may be related to the greater organic fraction present in this coating, as emerged from previous FT-IR analysis. This fact may prove how ceramic films are not themselves non-stick, like conversely PTFE molecules are. Moreover, the reduced non-stick capability of ceramic coatings may be really associated to the non-uniform presence of silanic compound on the surface of this kind of coatings, as previously observed.

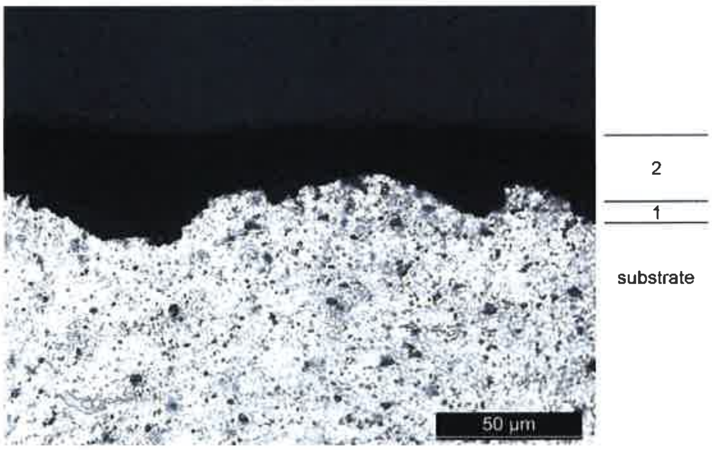

Fig. 6. Optical micrography showing a double-layer PTFE-based coating (T2 sample).

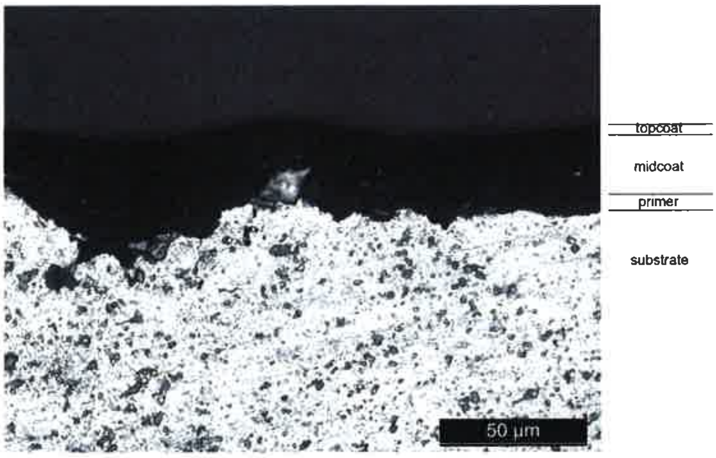

Fig. 7. Optical micrography showing a triple-layer PTFE-based coating (T3 sample).

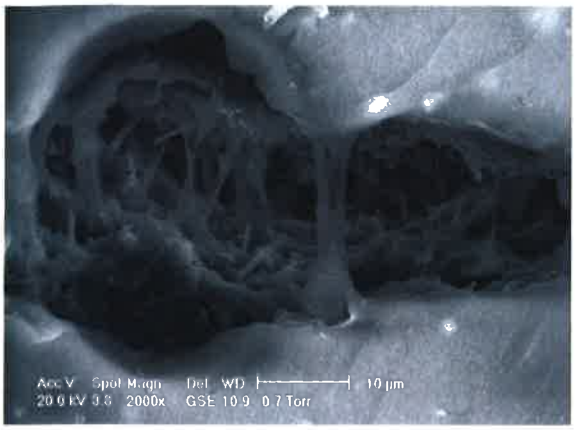

Fig. 9. ESEM micrography of defectiveness on fluoropolymeric coating (T3 sample).

Then pull-off tests were carried out on the toroidal mechanically damaged area produced by the abrading wheels during Taber Abraser cycles [24] are now considered. The adhesion values for PTFE coatings remain low and this fact proves that the non-stick properties of these systems are substantially preserved also after mechanical damage. This may be due to the high chemical inertia of C–F bond and to the fact that PTFE tends to be spread on the sample surface during abrasion cycles. Considering the variation of roughness values between new and damaged surfaces it is possible to observe that high variations, with high dispersions too, are measured on ceramic coatings. It is therefore clear that the mechanical damage significantly decreases the functional non-stick properties of this kind of coatings (Fig. 12). It can be well noticed that the coating becomes very sticky towards epoxy adhesive exactly in the worn areas, so as to cause the detachment and delamination of the coating. The decrease of non-stick properties of ceramic coatings could be attributed to the heavy damage of the silanic compounds layers. In addition the increase of the roughness produced by mechanical action improves the interaction active surface with most easy possibility to formation of chemical bonds. Differently than the PTFE, where the C–F bond produces an inert surface, in this case with roughness increasing chemical bonds are favoured.

As shown in introduction, the pull off test is more independent and precise method to evaluate the adhesion properties in comparison to the industrial one like "milk test" and "egg test". Then we could affirm, without doubts, that the pull-off produces a real data.

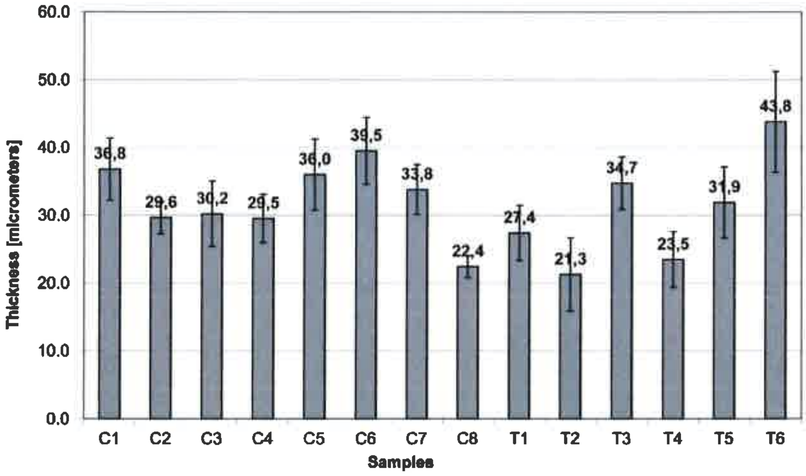

Fig. 10. Cookware coatings thickness.

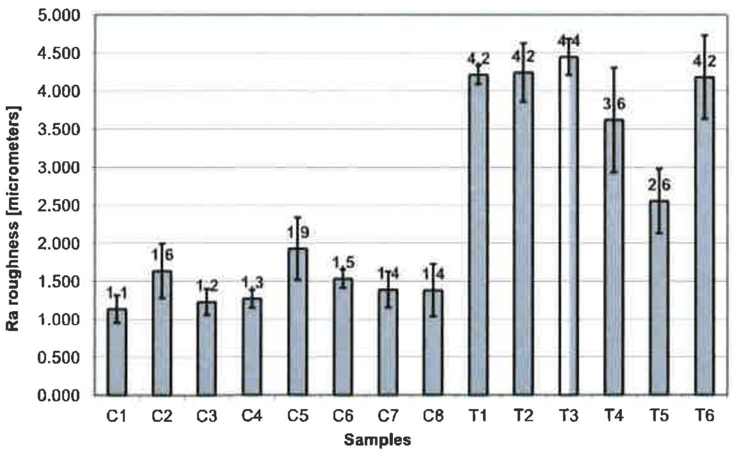

Fig. 11. R_a roughness measurements on new samples.

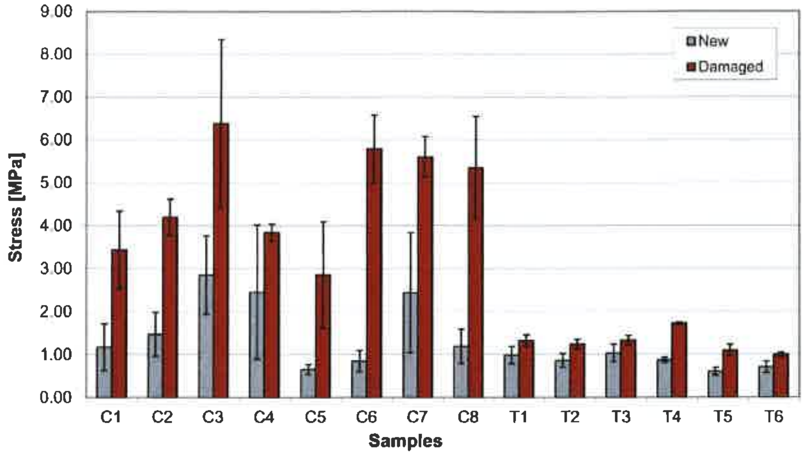

Fig. 12. Pull-off data of new and mechanically damaged samples.

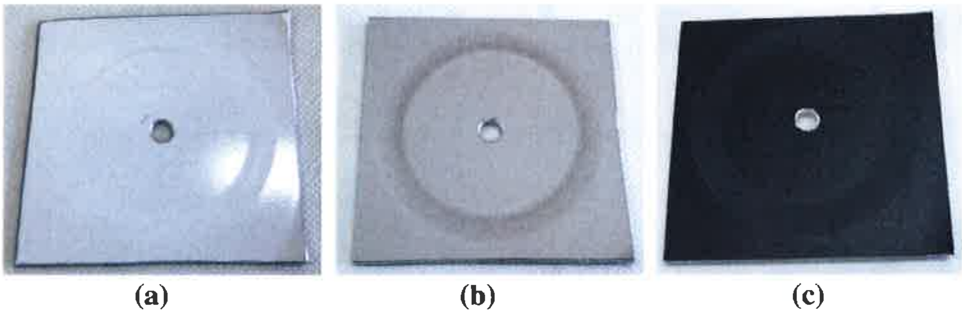

Fig. 13. Aspect of coatings surface after abrasion cycles ((a) ceramic, (b) light colour PTFE, and (c) black PTFE).

3.2. Aesthetical aspects

As well as functional properties, cookware coatings are required to maintain their original aspect and perceptive properties too, without changing their appearance during their service life. Fig. 13 shows the aspect of ceramic and PTFE coated surfaces after 500 cycles of abrasion. For ceramic coatings, abrasive wear has negative effects on the perceptive side too. Considering the sensorial aspect, ceramic coatings loose their typical gloss (Fig. 13a), which manufacturers have always count on to offer a product with original and brand-new look. Light colour PTFE coatings show wear signs too (Fig. 13b) and this can arouse in users the idea of a decayed, poor quality and no more functional product, even if the functionality is actually not compromised. Moreover an accentuate colour change, tending the coating to dark shades, completely eliminates the sense of cleanliness and food suitability that should always be typical for cookware. For black colour PTFE samples the aesthetic variation due to mechanical damage is less relevant. On this kind of coatings no colour change occur, but only a light gloss modification can be observed (Fig. 13c) and so the black colour, even if it is not at all innovative on the industrial design side, can be said to well conceal use and wear signs.

4. Conclusions

The tests to evaluate the non-stick capabilities could emphasize the differences in functionality between the two non-stick systems – PTFE-based or ceramic – both as unused and after mechanical damage. Pull off test results a very precise method to evaluate the non-stick properties of the surface at beginning and to highlight the difference among the samples. This methods is very sensitive and considering the technical design aspects, ceramic coatings exhibit some reduced functionality compared to PTFE films, both as unused and especially after mechanical damage. On the contrary, PTFE-based coatings, both dark- and light-coloured, offer complete functionality with very good non-stick capabilities and excellent durability against wear cycles. Nevertheless these ceramic cookware had a great market success thanks to the possibilities they can offer on the industrial design side, with new aesthetic and perceptive features, appreciated by customers. For this kind of products, cookware manufacturers promoted mainly the perception of visual features, counting on light colour and bright and glossy look, rather than the perception of functional properties. Dark-coloured PTFE-based coatings have aesthetic and perceptive features unchanged over time, these reminding customers to safety and environmental problems, actually nonconfirmed. Many cookware manufacturers tried then to imitate the ceramic coatings visual features introducing light-coloured PTFE-based coatings. These systems vouch for complete functionality and good abrasion resistance but undergo some aesthetic durability problems.

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