DEVELOPMENT OF NON-STICK SURFACES FOR RIGID PACKAGING

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Abstract: The use of rigid packaging is present in several moments of life and, therefore, there is a need for packaging with specific characteristics for each use, such as the need for non-stick packaging to assist in the complete use of products. In this work, the surface modification of three substrates (metal, glass and polymer) was evaluated in order to reduce the adhesion of polar and non-polar liquid media. Five surface modifying agents based on organosilanes and fluoropolymer were used to obtain non-stick surfaces. Samples were analyzed for wettability and adherence, chemical and morphological properties. Significant increase in hydrophobicity was observed with the application of the modifiers Resysil 263, Resysil 902 and Resyfluor 2308 forming non-adherent surfaces in relation to water. It was observed that the use of coatings on substrates increased their oleophobicity, reaching higher values of contact angles.

Keywords: Non-stick, organosilanes, fluoropolymer, wettability, hydrophobic.

1. INTRODUCTION.

The packaging market grows daily, as these are present in products used in everyday life, whether ceramic, metallic or polymeric. Packaging has always been present in humanity and has helped in the development of commerce and cities, its main function is to protect and enable the transport and storage of the product [1,2]. Over time, packaging acquired new functions, such as exposing, selling and conquering the consumer by its look, as a measure to strengthen the brand's image, in order to attract and awaken the desire to buy [2].

It can be considered that the packaging has the power to sell itself. As an example, one can mention supermarket shelves, where there is an infinity of products that perform the same function, however, in some cases, the one that presents the best packaging, from the aesthetic or functional point of view, tends to be better appreciated by the consumer [2]. In addition, the packaging is the first contact with the product and will awaken the sense of sight, making the product in question come to mind when looking at similar packaging [3].

However, concerns with the aesthetic and functional characteristics of the product also influence the financial aspect, in high viscosity products, such as sunscreens, nail polishes and bases, mechanisms with lids or suction pumps are used to facilitate the removal of the product, which increases the cost of packaging. Thus, if the material used in the packaging assists in removing the entire product contained in the container, it becomes possible to discard some of these mechanisms and, thus, reduce the cost of the final product. In addition, the residues of products that remain inside the packaging make it difficult to completely clean and subsequently recycle [4].

Modification of packaging surfaces has been used to facilitate product removal. Surface modification is the process of altering the physical, chemical or biological characteristics of the surface, which may be roughness, wettability, surface energy and biocompatibility characteristics that, when altered, can help in the removal of the product [5].

A surface modification consolidated and present in everyday life are the frying pans/pans with non-stick coating of polytetrafluoroethylene (PTFE), known by its widely spread trade name Teflon®. This polymer has characteristics arising from its molecular structure formed by fluorine linked to a long carbon chain, which result in low adhesion of food to the material, facilitating the subsequent cleaning of the utensil [6].

In the case of packaging for cosmetics, it is necessary to use a non-stick mechanism with a modification that transforms the surface of the material into hydrophobic and oleophobic, since the main cosmetics are produced based on water and oil [7,8].

Surface modifications can be applied in different ways, with the sol-gel method presented by Carneiro, Ferreira and Houmard (2018) [9] and Sacilotto (2015) [10] being quite widespread. In this method, hydrolysis and condensation reactions form a colloidal suspension of solid particles in a fluid that is deposited on the surface of interest by methods such as dip-coating, where the substrate is immersed vertically in the solution and then dried to obtain the desired properties. Kehrwald (2009) [11] used a simpler method for deposition, where the organosilanes to be used were mixed with water and then poured over the desired surface, after the water present had evaporated, the samples were cured in an oven. Another method used by researchers is vaporization, where the organosilane is kept in liquid condition in a container that will be covered with the surface to be covered, in which case both are isolated from the environment and will go to the oven, generating steam from the organosilane that will adhere the surface of interest [12].

Adhesion is the permanent union of two bodies through the contact of their surfaces, this phenomenon can occur by different mechanisms such as: thermodynamic, electrostatic, diffusion and mechanical. The mechanical adhesion mechanism occurs due to surface roughness such as pores and grooves that make breaking difficult. Thermodynamic adhesion is related to surface molecular forces, thus being linked to surface free energy [11].

Several studies [11,10,13-15] point to the use of organosilanes for the production of superhydrophobic and non-stick surfaces. Kehrwald (2009) [11], studied the behavior of the polymeric coating based on fluorosilane and identified that the presence of CFx groups in the structure made the material hydrophobic and oleophobic. Sacilotto (2015) [10] obtained hydrophobic films based on vinyltriethoxysilane silane (VTES) on AISI 204 stainless steel sheets, which helped to protect the metal against corrosion. Cellulose/nanocellulose fibers have been the subject of studies to transform the material into a hydrophobic one, given that they are biodegradable and can be used to separate oil and water in oil spills at sea [13-15].

In more recent studies Jianliang, et al (2022) [16] used organosilanes to modify the seaweed Enteromorpha so that it became hydrophobic and maintained the oleophilic characteristic, being able to absorb oil spills in the ocean. Meanwhile, Usman et al (2020) [17] analyzed the use of organosilanes for the modification of ceramic membranes used in the recovery of oil in waters arising from the extraction of oil and natural gas.

Thus, the present work aims to evaluate the surface alteration of metallic, ceramic and polymeric substrates using different coatings based on organosilanes and fluoropolymers that were applied through the immersion method.

2. MATERIALS AND METHODS.

Materials: Surface modifiers based on organosilanes and fluoropolymers have been used to change adhesion on metallic, polymeric and ceramic substrates. The modifiers Resysil 263 (organosilane), Resysil 902 (organosilane), Resyfluor 2308 (fluoropolymer), Resysil 2003 (fluoropolymer + organosilane) were provided by the company PG Química and the organosilane GPTMS (3-0 n-789-Glycidoxypropyltrimethoxysilane) was purchased from company Sigma-Aldrich (Merk). As a substrate, sandblasted AISI 1020 steel plates, glass and poly(methyl methacrylate) – PMMA, commercial and popular name for acrylic, were used for the deposition of surface modifying agents. The plates used are 70 mm x 50 mm in size.

As substances for the adherence and contact angle tests, water and multipurpose non-polar lubricating oil from King were used. According to the manufacturer, the oil has the following characteristics: density from 0.850 to 0.860 g/cm^3, kinematic viscosity at 40 ºC from 9 to 11 cSt and main application as a multipurpose lubricant. Composition based on petroleum derivatives.

Methods: In this work, the application method of surface modifiers by immersion was used. However, before application, all plates were cleaned with acetone to avoid possible contaminants.

Dip coating application method: Initially, the GPTMS modifying agent was first hydrolyzed. 96 mL of 48° alcohol in 250 mL beaker was added, then 4 mL of the modifying agent were added. Under stirring, the pH of the solution was adjusted to 4.0 by adding acetic acid. The solution was kept at rest for 24 h [10].

To avoid oxidation of the AISI 1020 steel substrate, the plates were covered with Acrilex primer. Afterwards, the plates of all substrates were immersed in the GPTMS solution and other modifying agents for 2 min and then taken to an oven for 3 hours at 150°C for drying and curing of the modifying agents. The modifiers Resysil 902, Resysil 263, Resyfluor 2308, Resysil 2003 are commercialized ready for use, not being necessary to make any modification of composition for application.

Characterizations

Wettability: The wettability on a surface can be analyzed through the contact angle formed between the drop of fluid and the surface of the analyzed material, depending on the angle formed it is possible to determine whether the material is hydrophilic/oleophilic or hydrophobic/oleophobic [9,18,14,10]. This characteristic is verified with the contact angle technique, where the characteristics of the deposition of a drop on the surface of the material are observed at times 0 and after 5 min of the application of drops of water and lubricating oil on the plates. The drops were deposited using a dropper, for greater uniformity, and the images were obtained through photos taken at 20 cm from the analyzed sample. Using the Surftens software, the contact angle was analyzed to determine the wettability of the material.

Adherence: The verification of the adhesion of liquids (water and oil) on the plates was analyzed using the method developed by the authors, in which the plate to be tested is at an angle of 60° with a straight surface. At the top of the plate, a drop of the sample to be tested is placed with the aid of a dropper (the mass varies with the variation in the density of the liquid), and at the lower end of the plate in contact with the surface, the amount of sample is collected. It ran over the surface in 5 s and it is checked whether all the sample deposited at the top is contained at the end of the process, as described in Equation 1. For this test, water and lubricating oil were used as samples. Equation 2 was used to verify the occurrence of increase or reduction in adhesion compared to plates without coating. Figure 1 presents specifications of the method assembly and the equations used.

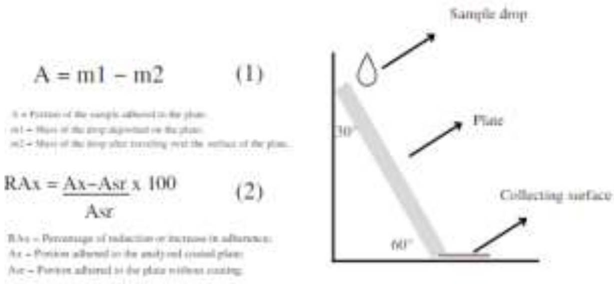

Figure 1 – Illustration of the scheme used for the adherence test. Source: From the Authors, 2022.

Fourier Transform Infrared Spectroscopy (FTIR): The FTIR test was carried out to verify the variation in the structural components of the modifying agents, using Shimadzu equipment, model IR-Prestige 21, with the test carried out in the spectrum range of 4000 to 500 cm-1 at room temperature. Surface modifying agents were evaluated before and after being applied to the plates.

3. RESULTS.

Figure 2 shows the photographic images and the contact angle using water as a liquid medium. It is observed that all surfaces after coating with the different modifying agents suffered an increase in the contact angle when compared to the uncoated surface. When the angle was greater than 90°, the liquid tends not to wet the surface of the solid, and the material is considered hydrophobic. If the angle is less than 90°, the liquid is considered to wet the solid and the material is considered hydrophilic. If the angle is 0°, there is complete wettability. However, only samples coated with Resysil 902 on glass and acrylic plates, Resysil 263 on acrylic plates and Resyfluor 2308 on metal plates, reached angles greater than 90° and remained above 5 min after drop deposition, configuring hydrophobic surfaces with greater stability. The magnitude of the contact angle is not independent of time, as it can change in seconds or minutes, depending on the liquid used and the nature of the solid.

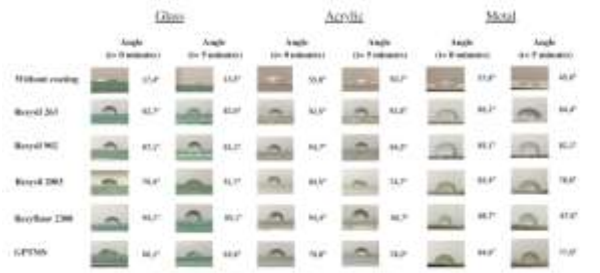

Figure 2 - Photographic images and measurements of the contact angle for the different substrates with and without modification, using water as the means of analysis. Source: From the Authors, 2022.

On the glass plates, only the surface coated with the agent Resysil 902 remained hydrophobic, with a contact angle of 97.1° at t=0 and 91.2° at t=5. On acrylic, two modifying agents deposited generated hydrophobic surfaces, namely Resysil 263, with 92.5° at t=0 and 91.6° at t=5, and also Resysil 902, with 94.7° at t=0 and 94.3° at t=5. For metallic plates, hydrophobicity was achieved with the Resyfluor 2308 coating, where the value of the angle at t=0 was 98.7° and at t=5 97.6°, these being the highest contact angle values found during rehearsals. Thus, the best modifying agent for water analysis was Resyfluor 2308 on the metal sample.

The contact angle of the samples tested with lubricating oil increased for the coated surfaces, however the values obtained remained below 90° as can be seen in Figure 3. According to Polak (2010) [19], the term oleophobicity is broader, and no strict definition can be found in the literature, as oils tend to spread over surfaces, therefore, they have a much smaller contact angle than those found with water. A surface with high oleophobicity needs a structure that contains micro and nano-roughness, making production difficult [20].

It is observed that after coating there was an increase in the contact angle for all samples, with the exception of the GPTMS coating which, after 5 min, on the acrylic and AISI 1020 steel plates, had a lower contact angle than the uncoated plate. This result indicates that these coatings present an increase in the oleophobic behavior of the materials.

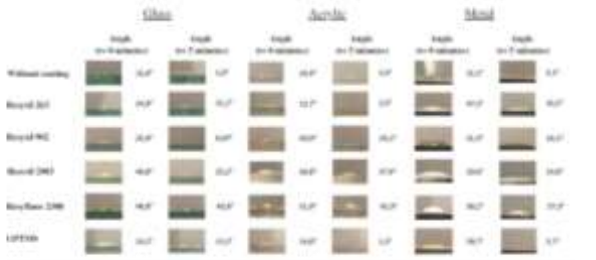

Figure 3 - Photographic images and measurements of the contact angle for the different substrates with and without modification, using oil as the means of analysis. Source: From the Authors, 2022.

Tables 1 and 2 present the results for the analysis of water and oil adherence on the surface of the substrates before and after application of the modifying agents. The weight of a drop of water is equivalent to 0.050 g, while that of a drop of lubricating oil weighs 0.016 g, this difference is a result of the difference in the density of liquids. The measurement of adherence used the variation of the initial and final weight of the drop, as previously mentioned.

In the test with water, all the boards tested showed a reduction in the adherence of the liquid to its surface when it was covered by some modifying agent (Table 1). On glass plates there were adhesion reductions of up to 76.9%, on acrylic 94.4% and on metal up to 100%. For glass and acrylic plates, the best coating was Resysil 902, while for metal, the best agent was Resyfluor 2308.

Table 1 – Adherence of water on the plates with and without coating.

Sample	Glass		Acrylic		Metal	
	Adhered portion (g)	Reduction (%)	Adhered portion (g)	Reduction (%)	Adhered portion (g)	Reduction (%)
Without coating	0,013 ± 0,001	-	0,018 ± 0,004	-	0,019 ± 0,002	-
Resysil 263	0,004 ± 0,003	-69,2	0,005 ± 0,003	-72,2	0,001 ± 0,001	-94,7
Resysil 902	0,003 ± 0,005	-76,9	0,001 ± 0,001	-94,4	0,002 ± 0,002	-89,5
Resysil 2003	0,004 ± 0,003	-69,2	0,002 ± 0,003	-88,9	0,006 ± 0,004	-68,4
Resyfluor 2308	0,004 ± 0,004	-69,2	0,002 ± 0,003	-88,9	0	-100
GPTMS	0,004 ± 0,003	-69,2	0,002 ± 0,002	-88,9	0,001 ± 0,001	-94,7

Source: From the Authors, 2022.

Observing the data in Table 2, on boards where the adhesion of lubricating oil was tested, it is noted that in some cases there was a reduction in adhesion, while in others there was an increase, with increases of up to 66.7% and reductions of up to 50 ,0%. The agents Resysil 2003 and Resyfluor 2308 generated a greater reduction in the adhesion of oil on the glass, in acrylic the improvement occurred with Resysil 2003 and GPTMS and in metal with the agent Resyfluor 2308.

For the metal plates, the modifying agent that resulted in the decrease in the adhesion of both oil and water was Resyfluor 2308, but in the other plates, the agents that caused the decrease in adhesion were different for each of the tested samples.

Figures 4a and 4b show the spectra obtained by FTIR of the modifying agents before and after application. It is observed that in the wavelength range from 3000 to

Table 2 – Adherence of oil on the plates with and without coating.

Sample	Glass		Acrylic		Metal	
	Adhered portion (g)	Reduction (%)	Adhered portion (g)	Reduction (%)	Adhered portion (g)	Reduction (%)
Without coating	0,003 ± 0,000	-	0,004 ± 0,000	-	0,004 ± 0,001	-
Resysil 263	0,004 ± 0,002	33,3	0,004 ± 0,002	0,0	0,005 ± 0,001	25,0
Resysil 902	0,003 ± 0,002	66,7	0,005 ± 0,001	25,0	0,004 ± 0,001	0,0
Resysil 2003	0,002 ± 0,001	-33,3	0,003 ± 0,001	-25,0	0,006 ± 0,001	50,0
Resyfluor 2308	0,002 ± 0,001	-33,3	0,004 ± 0,001	0,0	0,002 ± 0,001	-50,0
GPTMS	0,003 ± 0,001	0,0	0,003 ± 0,003	-25,0	0,004 ± 0,001	0,0

Source: From the Authors, 2022.

3500 cm^{-1}, the presence of O-H bonds from silanols is related to all reagents, except for Resysil 902, as this reagent does not use a polar solvent. After curing, all samples no longer showed this band. The bands shown between 2750 and 3000 cm^{-1} refer to deformations of the C-H groups present in the reagents before and after application. These groups appear in the Resysil 2003 agent and disappear in the Resyfluor 2308 agent after application. Between 1000 and 1250 cm^{-1} there are two more representative bands in the spectrum, which is related to siloxane bonds (Si-O-Si), and this band remains before and after application [9,11,10]. Through the spectra obtained, it is noted that the modifiers used have similarity between their compositions and behave similarly after application on the plates and oven drying.

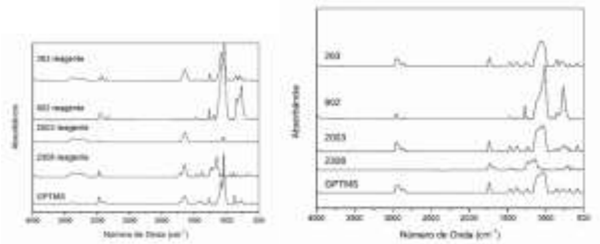

Figure 4 – FTIR spectrum of the modifying agents used (a) before and (b) after application. Source: From the Authors, 2022.

4.- CONCLUSIONS.

This study showed the possibility of modifying hydrophobic and oleophobic surfaces through treatment with modifying agents based on organosilanes and fluoropolymers, with results of a contact angle of 98.7° on metallic plates with the agent Resyfluor 2308 for water. When treated with oil, an increase in the oleophobicity of the plates coated with modifying agents was observed, reaching angles greater than those of the uncoated plates, with values of up to 58.8° in the acrylic plates with Resysil 2003. Furthermore, it was possible to demonstrate the relationship between the contact angle, adhesion and surface roughness of the material, proving that, with the increase in roughness, there is an increase in the contact angle and a decrease in adhesion, generating more hydrophobic and repellent surfaces (reduction in adhesion).

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