DEVELOPMENT OF POLYURETHANES WITH NON-STICK PROPERTIES

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Abstract
This study is focused on obtaining elastomeric polyurethanes with non-stick properties to optimize the processability of low-performance elastomeric polyurethane specimens. Fluorinated non-stick additives and fluorine-functionalized silica nanoparticles in different mass proportions and coating in low-performance elastomeric polyurethanes are incorporated. The surface contact angle of the tested low-performance polyurethane samples is measured to evaluate their hydrophobic behavior. Subsequently, the high-performance elastomeric polyurethane is prepared, and the additives with higher hydrophobicity obtained are applied.
Keyboards: Development of Polyurethanes, non-stick properties, fluorine-functionalized

Improved non-stick properties
Rubbers (elastomeric polyurethanes) are widely used for their lightweight, design flexibility and processability. However, these composite materials exhibit less attractive mechanical properties, such as low strength and modulus, than metals and ceramics. Adding micrometer- or nanometer-

sized inorganic filler particles to reinforce polymeric materials has been standard practice in the composites industry for decades. Today, functional fillers are used that, in addition to modifying the mechanical and rheological properties of rubbers, affect other properties such as chemical reactivity, biodegradability, color, thermal, magnetic or electrical properties. The mechanical and physical properties of the composite material are mainly dominated by the nature of the filler, while the polymeric matrix determines the environmental characteristics of the composite material. Therefore, filler and matrix resin can tailor the composite properties to suit the desired application.1

Non-stick properties

Some examples of modifying materials' surface energy by adding fillers and additives have been found in scientific literature. There are mainly two factors that help to create a "superhydrophobicity" on the surface: components with low surface energy, such as fluorine- or silica-containing substances, and micro- and nano-scale roughness structures.2 Wu et al. have prepared a hydrophobic waterborne polyurethane from nano-SiO2 (silica nanoparticles, hereafter SiNPs) and depending on the percentage of SiNPs added, different degrees of hydrophobicity is achieved up to superhydrophobicity with a contact angle greater than 150°. Figure 1 shows the polyurethane surface modified with different percentages of SiNPs. In this article, SiNPs are fabricated by the Stöber method using TEOS (tetraethoxysilane) as a precursor and modified with TMES (trimethylethoxysilane).3

SiNPs are good candidates for this project due to their large specific area, small particle size, thermal stability and commercial availability. In addition, incorporating SiNPs into polymer films is also known to enhance the film's mechanical properties, reduce its thermal degradation at high temperatures, improve its insulating properties, and increase the barrier properties of solvents and volatiles. It is also common for nanoparticles to be coated with fluorinated long-chain molecules, thus providing them with a hydrophobic surface. For some applications, a surfactant effect has been developed by adsorbing amphiphilic molecules with hydrophobic and hydrophilic segments.4

Figure 1. Images of the polyurethane surface modified with SiNPs at different percentages.
Source: Wu, G. et al. Prog. Org. Coatings 2019, 127 (May 2018), 80-87.

In addition, superhydrophobic polyurethane (PU) coatings of SiO2 NPs designed under the sol-gel process based on the reaction between GPTS (3-Glicidoxypropyltrimethoxysilane) groups

activated on the surface of FAS-SiO2 NPs, polyol monomers, octalamine and isocyanate have been created. This new superhydrophobic coating exhibits good toughness and repels water with contact angles (CA) of 159°. The easy fabrication of the PU-SiO coating2 with improved hydrophobicity and durability provides a new avenue for developing high-performance superhydrophobic surfaces, as shown in Figure 2. The outstanding properties of the synthesized PU-SiO2 coating are mainly due to the surface energy reduction by fluoroalkylsilanes, the formation of micro- and nano-scale hierarchical roughness structures on the coating surface, and the stable adhesion of SiO2 NPs on polyurethane resin after crosslinking with isocyanate.[5]
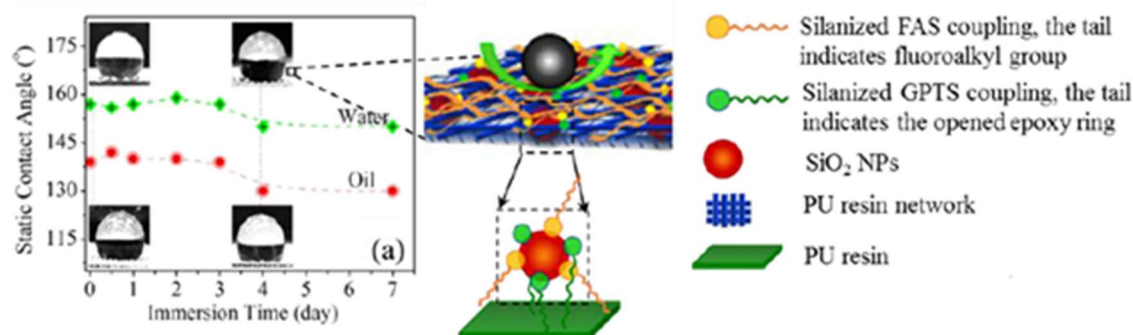

Figure 2. Coating of polyurethane resin with SiO2 NPs
Source: Yousefi, E. et al. Appl. Surf. Sci. 2018, 454, 201-209.

There are novel techniques that, through a simple process combined with sandpaper templates and nanosilica embellishments to thermoset polyurethane (TSU) surfaces, generate highly hydrophobic micro- and nanostructures. Using sandpapers with grit sizes ranging from 240 to 700 grits to obtain microscale roughness on an intrinsically hydrophilic TSU surface. It was found that the highest contact angle of the TSU surface without nanoparticles at 102 ± 3 ° was obtained when the template was 240-grit sandpaper and the molding progress started after 45 min of TSU curing. Polydimethylsiloxane-modified silica nanoparticles were dispersed on the surfaces of both the polymer and the template to build the desirable nanostructures.[6]

Commercial fluoropolymer-coated formulations based on polytetrafluoroethylene (PTFE) and perfluoroalkoxyalkanes (PFA) provide low-energy surfaces on metal substrates. The porosities present in the PTFE surfaces allow resin penetration and, after curing, adhere by mechanical interlocking.[7]

High strength properties

The literature review cites that applying fillers to the elastomer formulation improves its mechanical properties. Cellulose nanocrystals (CNC) produced from renewable cellulosic raw materials have been used in polymer reinforcement, significantly improving mechanical properties. Adding 0.5% CNC by weight to polyurethane (PU) resin increases tensile strength,

Young's modulus, elongation at break and abrasion resistance of approximately 30%, 55%, 70% and 40%, respectively.[8] On the other hand, the use of calcite ($CaCO_3$) and dolomite $CaMg(CO_3)_2$ of 6nm at 35 % improves tensile strength and elongation at break more than fillers of the same molecules at micro and macroscale in flexible polyurethane foam materials.[9]

The waterborne polyurethane (WPU) adhesive modified with nano-SiO_2 in the range of 2.0% to 2.5% showed that the concentration of nano-SiO_2 significantly impacted these properties, such as mechanical performance and water resistance.[10] Furthermore, the elastomeric polyurethane elastomer with 10% carbon black loading ISAF shows a tensile strength of 2.010 MPA and the addition of a further 8% by weight of carbon black gives a tensile strength of 2.746 MPa. [11]

Polyurethanes

Polyurethane is a polymer that today finds multiple applications. Its name is due to the repetitive presence of urethane groups in its main chain, whose structure is shown in Figure 3.
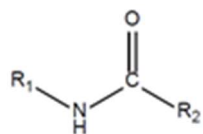

Figure 3. Urethane group structure.

Polyurethanes are a special group of polymeric materials that have a wide range of applications to create all kinds of industrial and consumer products, making our life more practical and comfortable. They are generally obtained from two main components: polyols and diisocyanates.[12]

Its discovery is due to Professor Otto Bayer synthesizing polymer fibers to compete with nylon when he developed the first fiber-formed polyurethane in 1937. His invention was among the major breakthroughs in polymer chemistry, but his superiors discarded the polymer at I.G. Farbenindustrie. For more than 20 years, Germany has been at the forefront of synthetic fiber technology, beginning with the introduction of polyvinyl chloride (PVC) fibers in 1913. Germany remained preeminent in the fiber field until 1935 when Carothers in the United States discovered nylons; DuPont in America introduced and began marketing nylon fibers, protected by a series of patents that proved impossible to beat. There was nothing as versatile and practical as polyamides, leading Bayer to investigate similar polymers not covered by the impenetrable DuPont patents. In 1938, Rinke and co-workers succeeded in reacting 1,8-octane diisocyanate with 1,4-butanediol to form a low-viscosity melt from which they could extract fibers. These early efforts resulted in what is now known as polyurethanes: carbamic acid esters. These polyurethanes could be spun from the melt. The yarns and monofilaments that could be made from their new polymer were of high quality. Rinke and Associates obtained the first U.S. patent on polyurethanes in 1938. I.G. Farbenindustrie's first polyurethane had a melting point of 185°C and was available for producing artificial silk and synthetic fabrics. Foams were also produced by adding water to isocyanates in

the presence of hydroxyl-terminated polyesters to form carbonamides and release carbon dioxide as a blowing agent. DuPont recognized the elastomeric properties of polyurethanes that led to industrial-scale production in the 1940s. Water was used as the chain extender, and the diisocyanate was naphthalene-1,5-diisocyanate (NDI). DuPont was at the forefront of polyurethane technology in the United States and received patents in 1942 covering the far-reaching reactions of diisocyanates with glycol, diamines, polyesters and some other hydrogen-containing active chemicals.13

Currently, polyurethanes are widely used in different fields such as the automotive industry, wiring in the electrical and electronics industry, footwear components, fibers in the textile industry, paints, coatings and sealants, elastomers, foams, in the marine industry, sports equipment, engineering applications or biocompatible materials in medical engineering.14

Polyurethanes can be classified into three groups according to their mechanical behavior under temperature:

- Thermoplastic polyurethanes are so called because they are sensitive to the action of heat and solvents; therefore, they can be melted and dissolved without changing their original chemical composition. This behavior is because they are made up of chains with a linear or branched structure, which are held together by intermolecular forces (Figure 4, a).
- Thermosetting polymers do not melt at higher temperatures but degrade. In this case, the polymer chains are arranged in a three-dimensional network and are held together by covalent bonds at very high temperatures (Figure 4, b).
- Elastomers are materials that exhibit permanent elastic behavior; that is, they deform when subjected to stress, but once the stress ceases to act, they recover their original shape and dimensions. This behavior is related to their structure since they are constituted by linear chains that present some covalent bonding points (Figure 4, c). This characteristic allows a certain relative sliding between the chains, but at the same time, the covalent bonds prevent this from being complete and permanent.
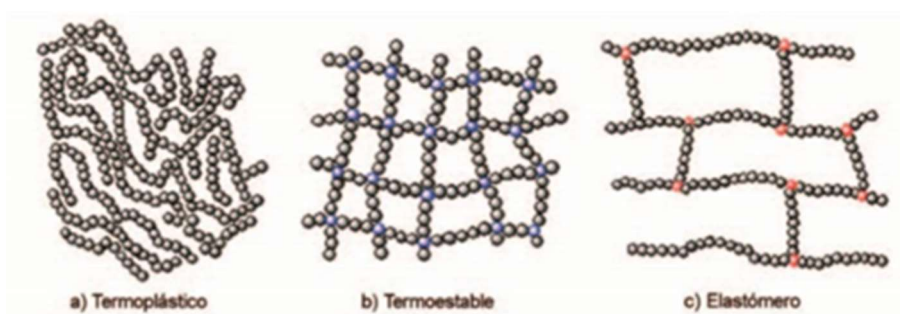

Figure 4. Schematic structures of different types of polyurethanes
Source: Szycher, M. Handbook of Polyurethanes; 2013; Vol. 37.

Chemistry of polyurethanes

The chemistry of polyurethanes is based mainly on the high reactivity of the isocyanate group (-NCO). This group contains a highly electrophilic carbon atom that can be attacked by different nucleophilic groups provided with labile hydrogens. The hard segment blocks are the result of isocyanate chain extension reactions. The chain extender can be low molecular weight polyols, polyamines or water,15 as shown in Figure 5.
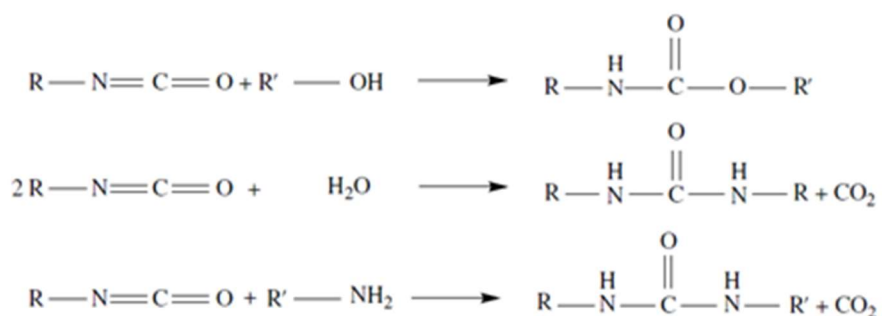

Figure 5. Chemistry of polyurethanes

Liquid prepolymers, i.e., moldable urethane elastomers, are synthesized to have a slight excess of NCO groups present so that the back-chain extension reaction can be performed. The higher the molar ratio of diisocyanate present, i.e., the higher the OH/NCO blocking ratio, the higher the free or available NCO content. Higher NCO contents always produce faster chain extension reaction rates; therefore, this characteristic can sometimes help control the pot life or gel time (the time a liquid polyurethane system remains processable by casting or pouring) in prepolymer systems. Liquid fusible urethane elastomers cover the hardness range <10 to > 95 IRHD (International Rubber Hardness Grading).16

Procedure for mixing liquid prepolymer and obtaining polyurethane

The liquid polyurethane prepolymer is melted and preheated generally between 80 -100 °C and degassed under vacuum for at least 30 minutes until foaming and bubbling cease. Due to surface tension effects, the prepolymer rises in large quantities in the container during the degassing operation; therefore, a container of 2 to 3 times the prepolymer load should be used for this operation. The chain extender, which should be in the form of a low-viscosity liquid (if it is normally a solid that melts before use), is mixed into the heated prepolymer by stirring. This chain extender also acts as a crosslinking agent for cast urethane elastomer systems. The catalyzed prepolymer is cast in preheated molds at approximately 100°C, and the surface is gas-flamed by rapidly passing a naked flame over the molten elastomer; this removes air bubbles causing localized expansion (alternatively, an electrically heated hot air gun can be used). Complete curing takes between 1 and 24 hours at 100°C, depending on the chemical system. Generally, however, the molding achieves dimensional stability only part way through the full cure time and, therefore, can be de-molded by removing it from its mold and completing the full cure by a different cure,

thus releasing the mold for further service. After heat curing, a conditioning time of 7 days should be allowed to elapse before any product testing to allow secondary chemical reactions and the physical structure to form.

Theoretically, the added chain extender should be equivalent to the isocyanate content of the prepolymer, but to promote the degree of branching and crosslinking is minimal, and likewise, the resistance of the polymer to physical stress is maximized. However, a curing agent concentration of 90-95% of theoretical is commonly used to obtain an acceptable level of overall properties, including compression set.17

Objectives

The project's main objective is to obtain elastomeric polyurethanes with improved non-stick properties.
The specific objectives of the work have been:
- ☐ To carry out a bibliographic review on the anti-adherent properties of elastomeric polyurethanes.
- ☐ To optimize the process of obtaining low-performance elastomeric polyurethane specimens.
- ☐ Measure the contact angles of the elastomeric polyurethane surfaces obtained.

Experimental Part
Materials
Low-performance elastomeric polyurethane

The low-performance elastomeric polyurethane (PU) used in this project corresponds to a two-component system, component A: polyol consisting of a blend of polyols containing catalysts, crosslinkers and surfactants, and component B: isocyanate consisting of modified diphenylmethanedioisocyanate. The A / B mixture ratio is 100/65 by weight. The characteristics of this polyurethane are shown in Table 1. This low-performance elastomeric polyurethane is used for processing optimization tests and incorporating non-stick additives because it requires low temperatures and no vacuum conditions to degas the polyol.

Table 1. Low-performance elastomeric polyurethane

Features	Units	PU low performance
Gel time	min	4 ± 1
Density	kg / m^3	1100
Shore hardness	ShA	95
Tensile strength	kg /cm^2	150 ± 20
Resistance Elongation	%	150 ± 50
R. Tear	kg /cm	50 ± 10

High-performance elastomeric polyurethane

The high-performance elastomeric polyurethane used corresponds to a system consisting of component A: a prepolymer made up of polyether and toluene diisocyanate, and component B: a curing agent made up of aromatic diamines. The characteristics of this polyurethane are shown in Table 2.

Table 2. High-performance elastomeric polyurethane

Features	Units	PU high performance
Specific gravity	kg / m^3	1120
Shore hardness	ShA	93 ± 3
Tensile strength	kg /cm^2	357
100 % Module	kg /cm^2	113,2
Resistance Elongation	%	530
Abrasion resistance 10N	mm^3	51

Polyurethane painting

A polyurethane paint consisting of component A: polyol and component B: isocyanate is used for coating the surface of elastomeric polyurethanes. Butyl acetate (density: 0.88 g/mL) is used as a solvent.

3.1.4 Non-stick additives

The additives used consist of fluorinated particles and fluorine-functionalized silica nanoparticles, as shown in Table 3.

Table 3. Anti-stick additives

Code	Additive
F1	Fluorinated liquid 1 PFPE Perfluoropolyether (PFPE-ethoxylated dialcohol)
F2	Fluorinated with liquid silica 2 PFPE Perfluoropolyether (PFPE-trialkoxysilane)
F3	Fluorinated powder 3 PFA Perfluoroalkoxyalkoxyalkane
F4	Fluorinated powder 4 PTFE Polytetrafluoroethylene
NS1	Fluorinated silica nanoparticles 1 NPs Si 12 nm with fluorocarbons
NS2	Fluorinated silica nanoparticles 2 Si 200 nm NPs with fluorocarbons

Testing Techniques
Drop drop contact angle measurement method

Liquids spread on the material in different ways. Wettability is the degree to which a liquid spreads on a solid and can be determined by measuring the contact angle (CA). This measurement allows, where the liquid is water, to distinguish surfaces of materials that are hydrophilic or hydrophobic. In addition, CA could be used to calculate the surface free energy using an appropriate mathematical model.[18]

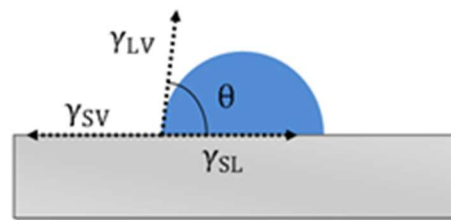

Figure 6. Schematic of a liquid drop contact angle placed on a solid surface.
Source: from Schuster, J. M. et al. Procedia Mater. Sci. 2015, 8 (2009), 742-751.

The most common method for measuring CA is the sessile drop method. In this method, a liquid droplet is placed on the surface of the material, forming, in this case, a three-phase system: solid (solid surface), liquid (droplet) and gas (surrounding atmosphere). The three phases create three interfaces: liquid-vapor (droplet atmosphere), solid-liquid (droplet of solid material) and solid-vapor (solid atmosphere material) interfaces. The intersection of the three interfaces forms a line called the three-phase line or contact line, according to Figure 6.[19] The contact angle is defined as the angle formed by the tangent of the vapor-liquid interface and the solid-liquid interface at the contact line. The physicist Thomas Young proposed a simple equation relating the AC to the interfacial tension of the system (eq 2).

$$Cos\theta = \frac{\gamma^{SV}+\gamma^{SL}}{\gamma^{LV}} \qquad (2)$$

where γ^{SV}, γ^{SL}, γ^{LV} are the solid-vapor, solid-liquid and liquid-vapor surface tensions, respectively.

The contact angle test is used to study the hydrophilic/hydrophobic behavior of the surfaces of elastomeric polyurethane modified in mass or with the application of non-stick additive coating against water, comparing some samples with others under the same starting conditions, without taking into account the hysteresis of the contact angle, which depends on several factors: (a) the contact angle hysteresis, which depends on several factors; (b) the contact angle hysteresis, which depends on several factors; (c) the contact angle hysteresis, which depends on several factors; and (d) the contact angle hysteresis, which depends on the contact angle,[20] and depends on the following factors:

☐ Drop size
☐ Surface moisture
☐ Type of substrate
☐ Substrate roughness
☐ Parameter verticality

☐   Existing particles in the droplet

The data obtained from the contact angle measurement give reference to whether the surface tested is hydrophilic or hydrophobic (Figure 7), as follows:

- Hydrophilic surface: high surface energy and low contact angle: $\theta < 90°$.
- Hydrophobic surface: low surface energy and high contact angle: $\theta > 90°$.
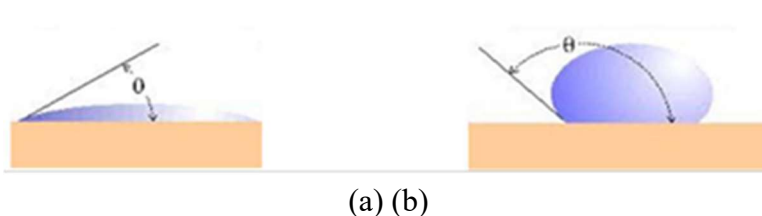

(a) (b)
Figure 7. (a) Hydrophilic surface and (b) Hydrophobic surface
Source: Wu, G. et al. Prog. Org. Coatings 2019, 127 (May 2018), 80-87.

To measure the contact angle, an OCA droplet drop method surface tension measuring device is used, consisting of a high-resolution optical system, an accurate liquid dosing system, a stabilizer and software to measure the contact angle according to Figure 8.
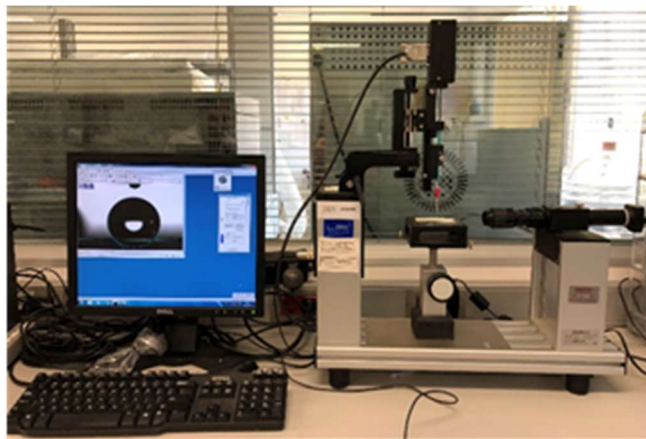

Figure 8. Equipment for measuring surface tension/contact angle by the droplet drop method.

Low-performance polyurethane processing
Experimental designs were carried out to obtain optimum preparation conditions according to the A/B mixture ratio, 100/65 by weight for the system of component A: polyol and component B diphenylmethanedioisocyanate. The agitation is done manually, and the curing is done in a metallic mold of 15 cm x 15 cm x 1 cm for 100 g of mixture.

☐   Low-performance polyurethane is usually processed manually.
☐   Component A should be homogenized by mechanical agitation before use.
☐   The components are kept at a temperature of 20 to 25 ° C.

◻ The molds are coated with a release agent.

◻ Mixing the components manually for 1 min 30 s avoids the incorporation of air.

◻ Preheating between 20 to 25 ° C of the metal mold 15 cm x 15 cm x 1 cm.

◻ The mixture is cured in the heating press at 30, 40 and 50°C for 10, 15, 20 and 30 min at 60 kN as shown in Table 4.

Table 4. Low performance polyurethane processing tests at different temperatures and times.

T (° C) /Time (min)				
30	x	x	x	
40	x	x	x	
50	x	x	x	x

◻ The specimen is demolded and curing continues at room temperature.

(a) (b)

Figure 9. (a) Fortune Presses heating plate and (b) Tecni paint spray booth

Application of additives in mass and in the coating in low-performance polyurethane.
An experimental scheme of mass addition in component A (polyol) and component B (isocyanate) and coating is carried out. For the mass tests, the fluorinated additives F1, and F2 are added in a ratio of 1%, 5% and 10% each, F3 at 5% and F4 at 15%, both in component A (polyol) in some tests and others in component B (isocyanate). The incorporation of the additive is done manually for 30 s in the formulation and followed according to the processing method described above for low-performance polyurethane.

The coating is prepared based on polyurethane paint consisting of components A (polyol) and B (isocyanate) in a ¼ A/B mixture ratio. 5 g of Component A + 1.25 g Component B + 5 mL of butyl acetate is prepared. The dispersion of the additive is carried out in Component A and homogenized in an ultrasonic bath for 20 min at 25° C. The paint with the additive is applied with an airbrush at 1 bar air pressure on the side in contact with the mold in the paint chamber.

The coating is applied on the surface of the prepared elastomer. Additives F1 and F2 are added at a ratio of 0.5 %, 1 %, 3 % and 5 % each, F3 at 4 %, F4 at 15 %, and F5 and F6 at 2.5 %.

High-Performance Polyurethane Processing

The aim is to obtain 100 g of high-performance polyurethane; the proportion is calculated based on equation (1) which relates theoretical percentage. Then, the agitation is done manually, and the curing is done in a metal mold of 15 cm x 15 cm x 1 cm, according to the following.

- ☐ Heating of the prepolymer to 80 ±5 C.
- ☐ Prepolymer degassing -95 kPa vacuum until no foam is present and heating to 80 ±5 °C.
- ☐ The curing agent or component B is kept at room temperature.
- ☐ Preheat the molds to 100 °C and maintain them at that temperature during curing.
- ☐ Coat the molds with a release agent.
- ☐ Manual mixing of the prepolymer with the curing agent for 1 minute, avoiding incorporating air.
- ☐ Pouring of casting in a metal mold of 15 cm x 15 cm x 1 cm.
- ☐ Curing of the product in a heating press at 100 C for 20 min at 60 kN. Demolding time will vary with prepolymer and part size. Small parts (2 kg) can generally be demolded after 20 min.
- ☐ Post-curing for 16 h at 100 °C in an oven.

Calculation of high-performance polyurethane prepolymer and polyurethane curing parts

To determine the amount of cure required for 100 parts of prepolymer A, it is calculated from the following equation:

Curing or component (B) = %NCO x 2.55 x % Theory (1)

where the theoretical percentage to obtain better resistance to tearing and elongation is 95% (0.95) and the %NCO is between 6.00 ± 0.20.

Application of additives in mass and coating in high-performance polyurethane.

The proportion of anti-adhesion additives applied in mass and coating to the low-performance polyurethane resulting in high contact angle values are tested on the high-performance polyurethane obtained.

Results and discussion
Low-performance elastomeric polyurethane
Processing test results

The processing of low-performance polyurethane, as it requires low temperatures and does not need a vacuum to degas the polyol, makes it manageable, allowing testing with different temperatures and curing times, as shown in Table 5. The conditions that determine the best curing of the specimen are replicated to process the high-performance polyurethane. The gelling or manipulation time tested for the preparation of the low-performance polyurethane is 2min 56 s.

Table 5. Low performance elastomeric polyurethane process tests

| Test	Working time (min)	Temperature (°C)	Curing time (min)	Remarks
1	2'38	30	10	Soft and sticky consistency
2	2'33	30	15	Soft and sticky consistency
3	2'33	30	20	Soft consistency
4	2'54	40	10	Sticky and bubbly surface
5	2'48	40	15	Surface bubbles
6	2'51	40	20	Surface bubbles
7	2'40	50	10	Sticky surface
8	2'32	50	15	Sticky edges and bubbles on the surface
9	2'41	50	20	Complete curing
10	2'52	50	30	Polyurethane degradation. Sticking and cracking

(a)

(b)
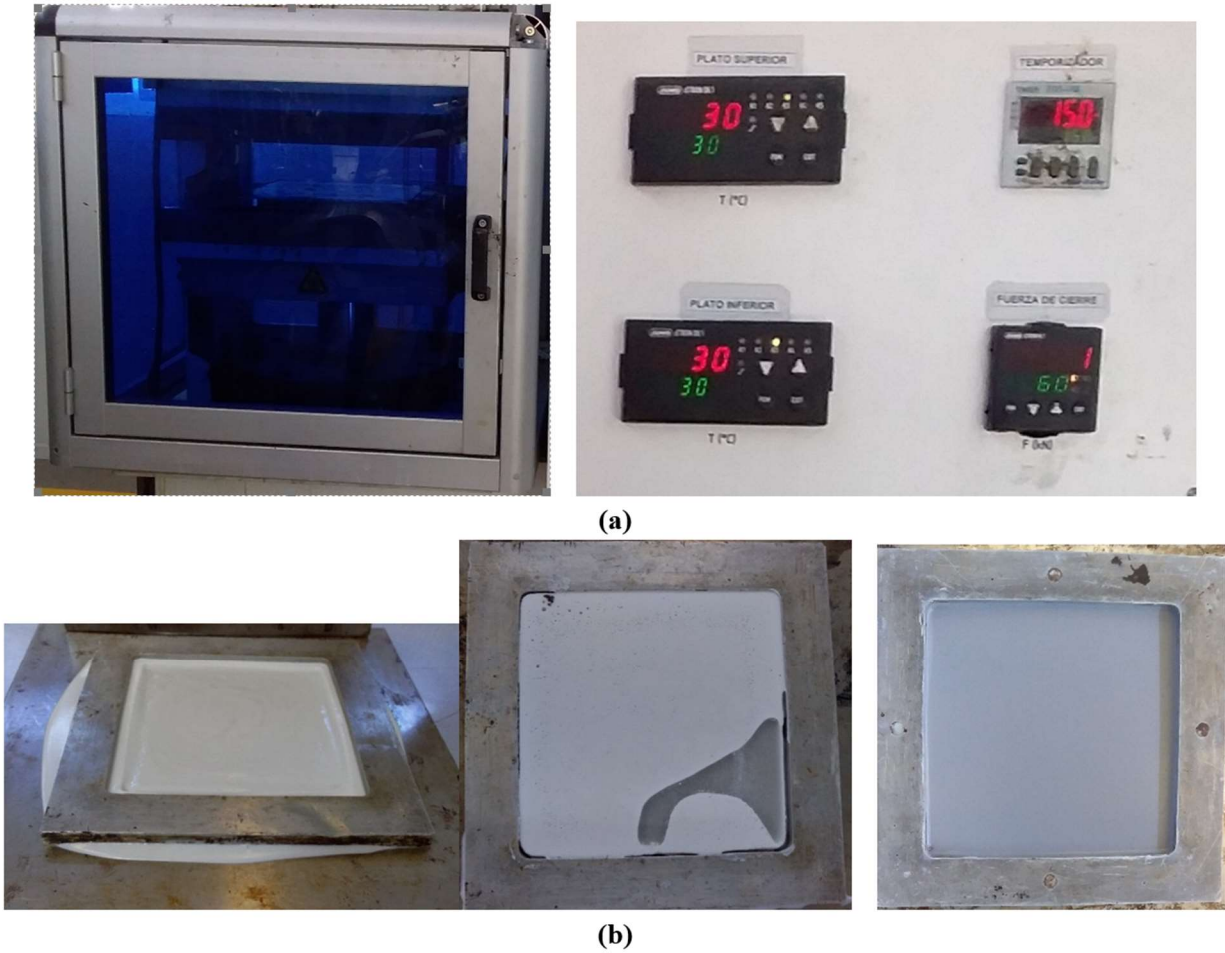
Figure 10. Heating press (a) and low-performance elastomeric polyurethane processing test (b)
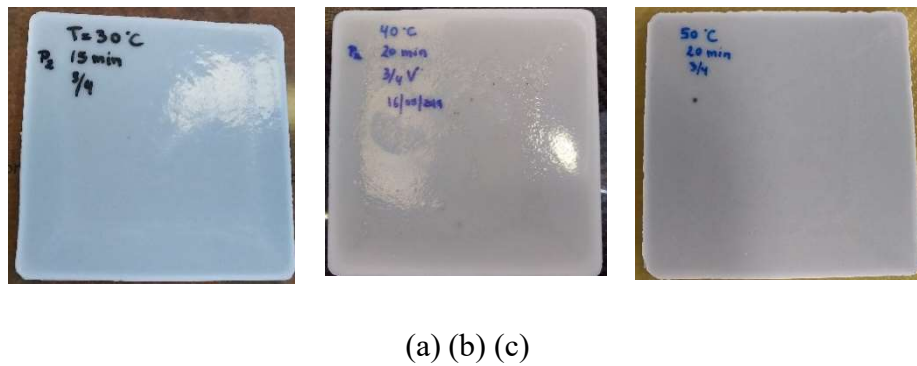

(a) (b) (c)

Figure 11. Specimens obtained at 30°C (a), 40°C (b) and 50 °C (c).

Table 5 shows that the best curing conditions for the low-performance elastomer mixture are 50 °C for 20 min with manual mixing. Therefore, the bulk filler addition and coating application tests are carried out under these preparation conditions.

Test results for incorporation of additives by mass

In this phase of the project, the evaluation of the different anti-adhesion additives has been carried out by incorporating them in the mass formulation of the polyol and isocyanate in a comparative way so that the results are contrasted with a white polyurethane sample.

Table 6. Incorporation of anti-adhesion additives in low-performance polyurethane polyol and evaluation of the contact angle.

Additive	Test (%)	Contact angle (°)	
-	Sample blank		105,3
F1	1	102,9	103,5
	5	95,6	97
	10	96	95
F2	1	112	110
	5	97	97
	10	112	110
F3	5	103,5	103,9
F4	15	-	-

The addition of 10% of the liquid fluorinated additives F1, F2 and 5% of the additive F3 to the polyol affected the mechanical properties of the polyurethane obtained, showing brittle and sticking in the mold; however, the additions of 1% and 5% preserve its properties. When incorporated to the polyol, the fluorinated additive with solid microparticles F4 develops a foamed polymer with memory because the additive acts as a foaming agent, so its contact angle cannot be evaluated.
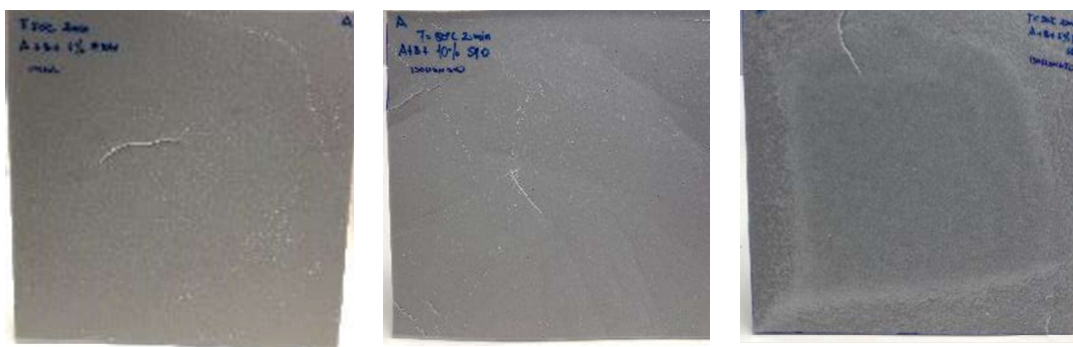
Table 7. Incorporation of anti-adhesion additives in low-performance polyurethane isocyanate and evaluation of the contact angle.

Additive	Test (%)	Contact angle (°)	
	Sample blank		105,3
F1	1	105,4	104,5
	5	100,1	98,5
	10	96	97,1
F2	1	112,3	113,5
	5	101,4	102
	10	103,8	104,3
F3	5	103,1	102,8

The addition of additives in isocyanates is not usually due to the high reactivity derived from the decrease of urethane bonds that can modify mechanical properties and viscosity. However,

mechanical properties were only affected when 10% of the liquid fluorinated additives F1, F2 and 5% of F3 were added to the polyurethane obtained, showing brittle and sticking in the mold, see Figure 12.

The incorporation of 1% of the liquid fluorinated F2 additive in both polyol and isocyanate increases the contact angle from 105° to 112°, with the F2 additive obtaining the best results.

(a) (b) (c)

Figure 12. Degradation of polyurethane structure incorporating 10% of additives F1(a) and F2(b) by mass; 5% of F3 (c).

Test results for incorporation of additives in coating

In this phase of the project, the evaluation of the different anti-adherent additives has been carried out by incorporating them in the polyurethane base paint that will serve as coating of the low-performance polyurethane surfaces, in such a way that the results are contrasted with a sample coated with the polyurethane paint without additives.

Table 8. Incorporating anti-adhesion additives in low performance elastomeric overpolyurethane coatings and evaluating the contact angle.

Additive	Test (%)	Contact angle (°)	
	Sample blank	101,8	100,6
F1	0,5	117,3	117,9
	1	120,7	119,1
	3	76,8	78,7
	5	69,4	73,4
F2	0,5	114,8	120,9
	1	118,8	120,4
	3	109,1	107,6
	5	101,8	103,3
F3	4	103,9	103,2
F4	15	145,9	148,6

NS1	2,5	126,5	129,3
NS2	2,5	139,9	137,7

The additive that results in a surface of greater hydrophobicity is F4 at 15 %, however, its coating is rough, generates difficulty for its application, and a priori would not be valid to obtain surfaces with the quality required in the processing of ceramic pieces. The F1 and F2, 1% additives, show higher contact angle results for the white ones. NS1 and NS2 additives show better adhesion and homogeneity of the surface, as shown in Figure 13.
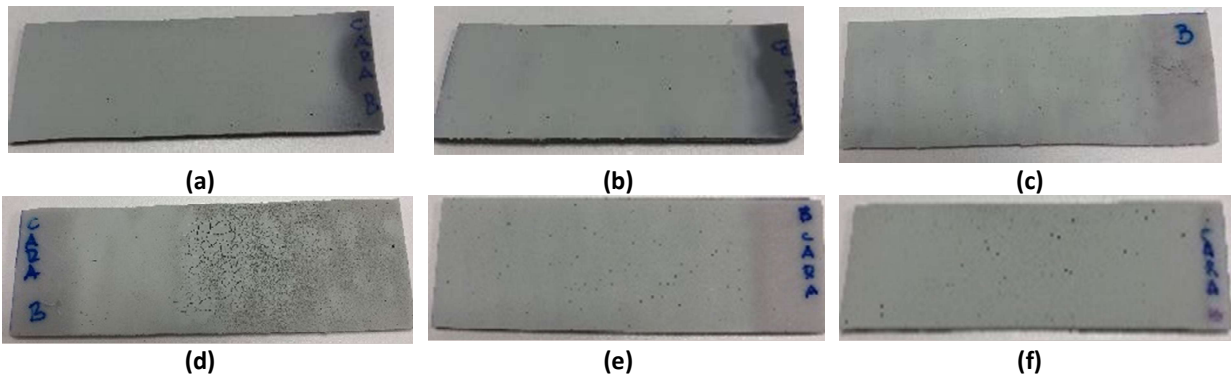

Figure 13. Coating with non-stick additives applied to low-performance elastomeric polyurethane F1 at 1 % (a), F2 at 1 % (b), F3 at 4 % (c), F4 at 15 % (d), NS1 at 2.5 % (e) and NS2 at 2.5 % (f)
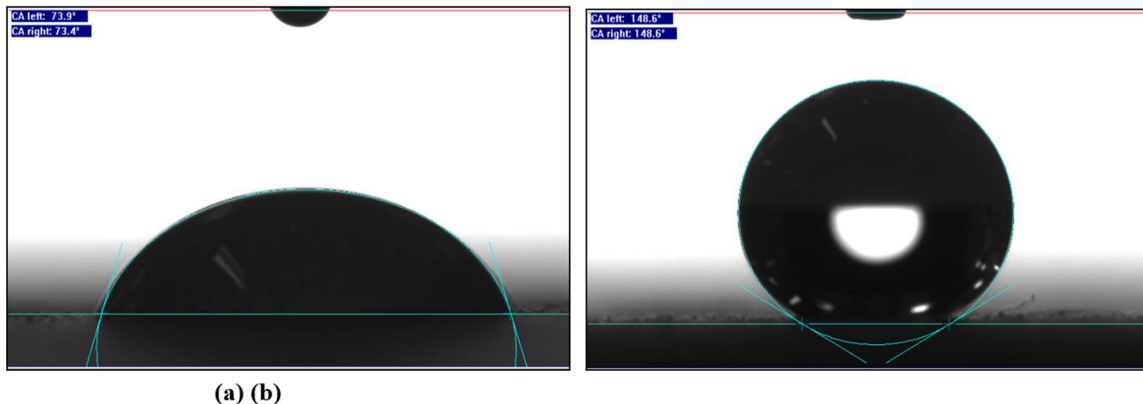

(a) (b)

Figure 14. Comparison of measured contact angles: (a) hydrophilic surface: 73.4° per coating application with 5% F1 additive and (b) hydrophobic surface: 148.6° per coating application with 15% F4 additive.

Retesting

With the combination of processing parameters and additives that have shown the best results, repeat samples have been carried out to ensure repeatability.

Table 9. Retesting of fluorinated F2 additive incorporation in mass and coating in low-performance polyurethane and evaluation of contact angles.

Additive	Type of test	Addition (%)	Contact angle (°)	
F2	Coating	0,5	108	109,5
		1	123,5	128,5

	3	108,3	107,2
By mass of component A	1	111	110
	5	111	113

The addition of 5% by mass of F2 is not similar to that shown in the initial tests according to Table 8; probably in the first test, the test was not performed correctly since the other results have similar orders of magnitude (around 110°) according to Table 9. However, it is justified that adding 1% of F2 is better since similar results are obtained than with 5%, in such a way that less material is used and the mechanical properties of the elastomeric polyurethane would be less compromised.

The additives NS1 and NS2 of silica nanoparticles functionalized with fluorine hydrocarbon chains present higher contact angles. However, the application cannot be continued because the company is still investigating, not have enough quantity for its application in new tests. The results of the evaluations of high contact angles obtained in coating at 1 % of F1, 1 % of F2, and 5 % of F4 and in a mass of 1 % of F2 will be tested in the high-performance elastomeric polyurethane that is the object of the project.

High-performance elastomeric polyurethane
Processing Test Results

Based on the experience and processing of low-performance elastomeric polyurethane, the processing tests for high-performance elastomeric polyurethane have been developed and optimized. Curing in the heating press is carried out for 20 min at 100 °C. The mixing of the prepolymer and curing agent is carried out mechanically; however, the incorporation of air bubbles (whitish appearance) is observed, so manual mixing is chosen, considerably reducing the incorporation of bubbles in the material.
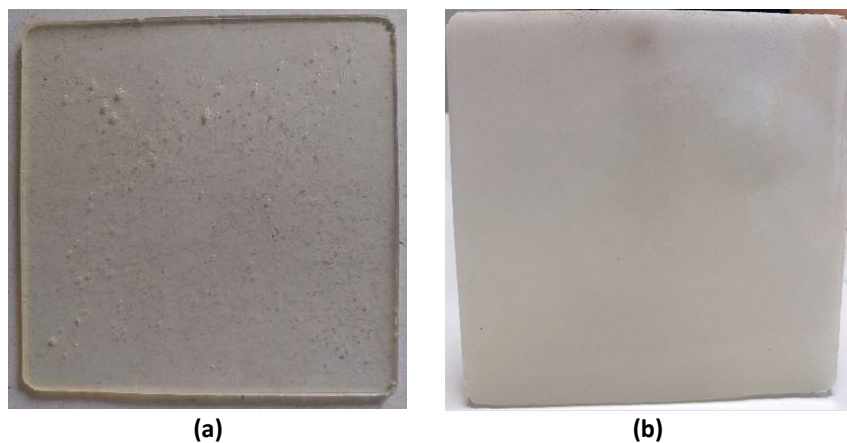

(a)   **(b)**

Figure 15. High-performance elastomeric polyurethane (a) with manual agitation and (b) mechanical agitation.

Test results of incorporation of better additives in coating and mass

The application of additives that better evaluate the contact angle is carried out. For example, adding 15 % of F4 to the low-performance elastomeric polyurethane shows high contact angle results but presents cracks and a lack of homogeneity in the application, so it is decided to lower the proportion to 5 % to improve the workability of the coating. However, these inconveniences are still maintained, so testing with 3 % and 1 % is recommended.

Table 10. Incorporation of better additives in coating and mass to high-performance elastomeric polyurethane and evaluation of contact angle.

Type of test	Additive	Test (%)	Contact angle (°)	
Coating	-	Sample blank	108,1	107,1
	F1	1	113,3	112,9
	F2	1	135,9	138,2
	F4	5	137,7	138,6
Mass		Sample blank	105,3	103,2
	F1	1	110,3	111,8

Tests on applying anti-adherent additives in a coating on elastomeric polyurethanes show more hydrophobic surfaces than tests with anti-adherent additives incorporated in mass. The additive with the best results in F4 at 5% with a contact angle of 138.6 °, however, it presents roughness and lack of adherence on the applied surface, so it is suggested to lower its dosage to 3% and 1%. According to Table 10, the 1% F2 additive reaches a contact angle of 138.2° compared to the white sample of 107.1°, achieving a surface close to superhydrophobicity; this coating presents uniformity and high adherence to the surface of the high-performance elastomeric polyurethane.
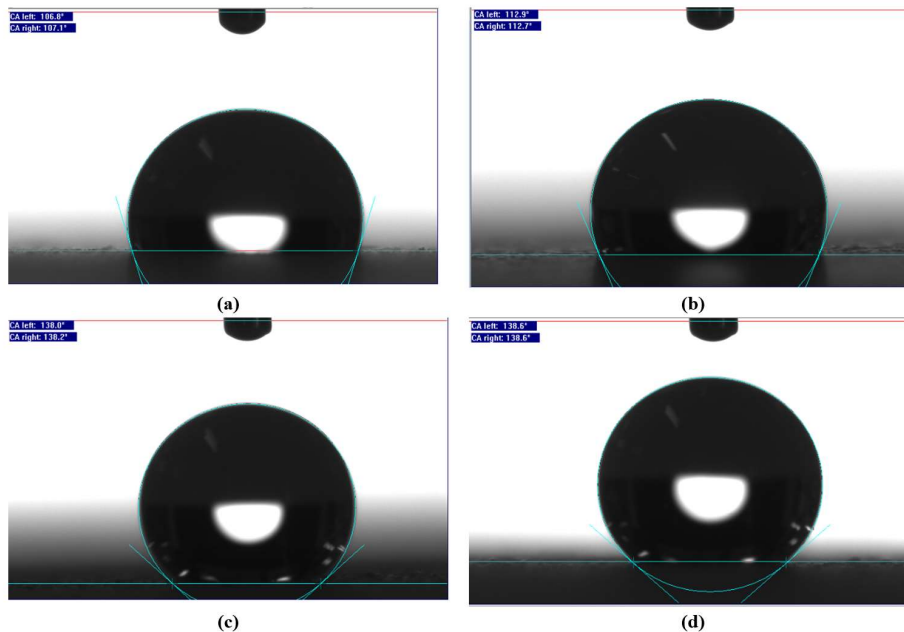

(a) (b) (c) (d)

Figure 16. Contact angles obtained from the application of improved anti-adhesion additives in the coating on high-performance elastomeric polyurethane; white sample 107.1 ° (a), 1 % F1 additive - 112.9 ° (b), 1 % F2 additive - 138.2 ° (c), 5 % F4 additive - 138.6 ° (d).
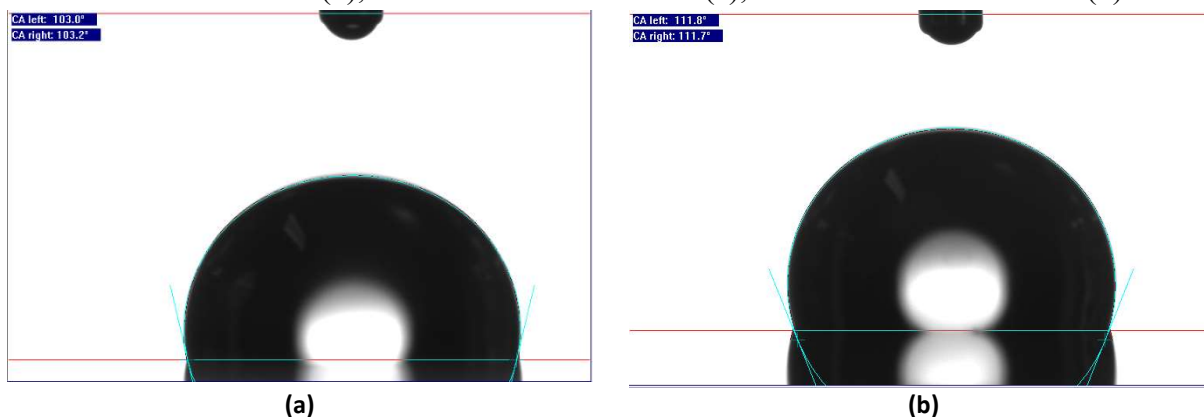

(a)　　　　　　　　　　　　　　　　(b)

Figure 18. Contact angles obtained by incorporating F2 anti-adhesion additive in high-performance elastomeric polyurethane mass; white sample 103.2 ° (a), F2 at 1 % 111.8 ° (b).

Conclusions and future prospects
Conclusions

Based on the scientific publications reviewed and the experience through this project, the addition of fluorine-functionalized silica particles and nanoparticles and fluoropolymer particles as coatings, called coatings, on the surface layer of the polyurethane is recommended to minimize dust adhesion.

This work has optimized the processing to obtain low-performance elastomeric polyurethane specimens at 50 ° C for 20 min. Liquid fluorinated additives, fluoropolymer particles and fluorine functionalized silica nanoparticles have been incorporated in mass and coating in low-performance elastomeric polyurethane. The liquid fluorinated additives F1 and F2 applied as coatings in proportions of 0.5% and 1% increase the contact angle significantly. The additives of silica nanoparticles functionalized with fluorinated hydrocarbon chains SN1 and SN2 show a considerable increase in the surface contact angle, remaining an open line of research for this type of material. The addition of 15% F4 additive shows high contact angles but presents a lack of adhesion and cracks on the polyurethane surface. The F2 additive incorporated in mass in low proportions improves the contact angle of the polyurethane surface.

The best anti-adhesion additives are identified and applied to high-performance polyurethane, achieving an increase in the contact angle from 107.1° to 138.2° when the 1% liquid fluorinated additive F2 corresponding to a fluoroalkylsilane is applied as a coating and to 138.6° when the 5% solid particulate fluorinated additive F4 is applied.

Prospects

Silica nanoparticles of different sizes functionalized with fluorinated hydrocarbon chains present a broad line of research for the fabrication of non-stick materials to be studied. Furthermore, the proposed results can be scalable in applying high-performance non-stick polyurethanes used for molding molds at the industrial level.

References

(1)   Vikas Mittal, P.; Kuk Kim, J. Recent Advances in Elastomeric Nanocomposites; Mittal, V., Ed.; 2001.

(2)   Ganesh, V. A.; Raut, H. K.; Nair, A. S.; Ramakrishna, S. A review on self-cleaning coatings. J. Mater. Chem. 2011, 21 (41), 16304-16322. https://doi.org/10.1039/c1jm12523k.

(3)   Wu, G.; Liu, D.; Chen, J.; Liu, G.; Kong, Z. Preparation and properties of super hydrophobic films from siloxane-modified two-component waterborne polyurethane and hydrophobic nano SiO2. Prog. Org. Coatings 2019, 127 (May 2018), 80-87.

(4)   Liberman, A.; Mendez, N.; Trogler, W. C.; Kummel, A. C. Synthesis and surface functionalization of silica nanoparticles for nanomedicine. Surf. Sci. Rep. 2014, 69 (2-3), 132-158. https://doi.org/10.1016/j.surfrep.2014.07.001.

(5)   Yousefi, E.; Ghadimi, M. R.; Amirpoor, S.; Dolati, A. Preparation of new superhydrophobic and highly oleophobic polyurethane coating with enhanced mechanical durability. Appl. Surf. Sci. 2018, 454, 201-209.

(6)   Yang, G.; Song, J.; Hou, X. Fabrication of highly hydrophobic two-component thermosetting polyurethane surfaces with silica nanoparticles. Appl. Surf. Sci. 2018, 439, 772-779.

(7)   Sánchez-Urbano, F.; Paz-Gómez, G.; Rodríguez-Alabanda, Ó.; Romero, P.; Cabrerizo-Vílchez, M.; Rodríguez-Valverde, M.; Guerrero-Vaca, G. Non-Stick Coatings in Aluminium Molds for the Production of Polyurethane Foam. Coatings 2018, 8 (9), 301.

(8)   Kong, X.; Wolodko, J.; Zhao, L.; Curtis, J. M. The preparation and characterization of polyurethane reinforced with a low fraction of cellulose nanocrystals. Prog. Org. Coatings 2018, 125 (August), 207-214. https://doi.org/10.1016/j.porgcoat.2018.08.034.

(9)   Latinwo, G. K.; Aribike, D. S.; Susu, A. A.; Kareem, S. A. Effects of different filler treatments on the morphology and mechanical properties of flexible polyurethane foam composites. Nat. Sci. 2010, 8 (6), 23-31.

(10)   Jia-Hu, G.; Yu-Cun, L.; Tao, C.; Su-Ming, J.; Hui, M.; Ning, Q.; Hua, Z.; Tao, Y.; Wei-Ming, H. Synthesis and properties of a nano-silica modified environmentally friendly polyurethane adhesive. RSC Adv. 2015, 5 (56), 44990-44997.

(11)   Benli, S.; Yilmazer, Ü.; Pekel, F.; Özkar, S. Effect of fillers on thermal and mechanical properties of polyurethane elastomer. J. Appl. Polym. Sci. 1998, 68 (7), 1057-1065.

(12)   Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. Polyurethane types, synthesis and applications-a review. RSC Adv. 2016, 6 (115), 114453-114482.

(13)   Szycher, M. Handbook of Polyurethanes; 2013; Vol. 37. https://doi.org/10.5860/choice.37-1904.

(14)   Smela E. Conjugated Polymer Actuators for Biomedical Applications. Adv. Mater. 2003, 15 (6), 481-494.

(15)   Hofmann, A. W. Action of bromine in alkaline solution on amides. Chem. Ges.

(16)   Van Der Schuur, M.; Noordover, B.; Gaymans, R. J. Polyurethane elastomers with amide chain extenders of uniform length. Polymer (Guildf). 2006, 47 (4), 1091-1100.

(17)   Hepburn, C.; Hepburn, C. Polyurethane Elastomer Chemistry. Polyurethane Elastomers 2011, 29-50.

(18)   Schuster, J. M.; Schvezov, C. E.; Rosenberger, M. R. Influence of Experimental Variables on the Measure of Contact Angle in Metals Using the Sessile Drop Method. Procedia Mater. Sci. 2015, 8 (2009), 742-751.

(19)   Kwok, D. Y.; Neumann, A. W. U. Contact angle measurement & contact angle interpretation; 1999.

(20)   De la Peña, P. R.; Alfonso, G.; Castellote Armero, M. Generación de un nuevo revestimiento arquitectónico, a partir del grafeno, aplicado a pinturas exteriores de los edificios, Universidad Politécnica de Madrid, 2017.