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Advances in lubricated polydimethylsiloxane surfaces for polyurethane foam molding

Guillermo Guerrero-Vaca[1] | Óscar Rodríguez-Alabanda[1] |
Pablo Francisco Ibáñez-Ibáñez[2] | Miguel Ángel Rodríguez-Valverde[2]

[1]Department of Mechanical Engineering, University of Cordoba, Cordoba, Spain

[2]Laboratory of Surface and Interface Physics (LSIP), Applied Physics Department, Faculty of Sciences, University of Granada, Granada, Spain

Correspondence
Óscar Rodríguez-Alabanda, Department of Mechanical Engineering, University of Cordoba, Medina Azahara Avenue, ES 14071 Cordoba, Spain.
Email: orodriguez@uco.es

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Abstract

Adhesion problems are currently a challenge in the manufacture of molded polyurethane (PUR) foam products. Here, a novel solution has been proposed by infusing a polydimethylsiloxane (PDMS) matrix with a liquid lubricant to obtain slippery liquid-infused porous surfaces (SLIPS). These surfaces have been evaluated when PUR foam is molded on them. The level of adhesion, determined by tensile peel tests, helped to understand the relationship between adhesion phenomena, coating deformability and hysteresis contact angle. A wide variability of hydrophobicity and hardness was obtained among the tested samples. The percentage of oil infused and the way it is integrated into the coating matrix determine the coating performance. The adhesion strength has been significantly reduced thanks, on the one hand, to the lubricating layer generated from the infiltrated oil and, on the other hand, to a porous system capable of self-healing the altered SLIPS surface after demolding. An optimal balance between the elasticity and hydrophobicity of the surface has been obtained; the best surfaces with the least adherence and the greatest durability have been identified for obtaining the foam.

KEYWORDS

PDMS, polydimethylsiloxane, polyurethane, release agent, slippery liquid, SLIPS

1 | INTRODUCTION

Polyurethanes (PUR) are a family of polymers obtained from hydroxyl bases combined with poly-isocyanates in a wide variety of compositions conditioning its properties for diverse applications as adhesives, fibers, foams, coatings, supports, and insulation, among others.[1-5] In this sense, a wide range of industrial products such as carpets, mattresses, pillows, household appliances, footwear soles, joints, packaging containers or seats, and other components of automobiles, trains and airplanes are commonly manufactured by molding of PUR into foam.

The PUR foam is created by polycondensation of poly-isocyanates with polyols.[6] The mix of these liquid agents at room temperature produce a strong chemical reaction that releases CO_2, forming bubbles that cause a rapid expansion of the volume of the mixture once injected into the mold cavity.[7] This exothermic reaction produces heat that evaporates the blowing agents during the expansion process while the PUR foam part is formed into the mold.

In the industrial process, the liquid mix is poured or injected into a pre-heated aluminum mold that is cooled just before the extraction of the part, when the adhesion occurs. This is a recurring problem that is due to the high adhesion that particularly this foam produces in contact with practically any type of surface. Thus, the industry commonly uses release agents in the form of ointments that are applied directly on the contact surfaces into the mold to ease extraction.[8] Aqueous dispersions with amine accelerators, foam stabilizers with siloxanes, polyethylene waxes or polybutadienes represent a high consumption in the PUR industry and its reduction or elimination is of great interest not only for a question of direct costs and associated with the tasks of cleaning molds, but also toward the common goal in the development of industrial processes that are more respectful with the people and environment. In this way, the challenge of minimizing the high adhesion of the PUR foam to the mold has been faced in several previous investigations.

Although high efficiency release agents have been developed in the last decades, the scientific community is lately making progress in the development of new surfaces that minimize or even eliminate their use.[8,9] In this sense, Figueiredo et al. demonstrated that perfluoroalkoxy (PFA) polymer coating retains up to 10 times less isocyanates than polytetrafluoroethylene coating (PTFE) when used as coating applied on aluminum and in contact with PUR.[10] This effect is translated into a foam-to-coating adhesion increased steadily after each molding cycle for PTFE due to the porous morphology of the PTFE surface while a durable low adhesion behavior is obtained with PFA. Previous works have been demonstrated that the use of sol–gel compounds gives an improvement of the scratch resistance of the coatings improving durability in contact with polystyrene or PUR foams, but the problem of adherence is not improved in comparison with organic coatings.[11,12] The results have been promising but not definitive, especially since the progressive deterioration in the performance of these coatings after several foam molding-demolding cycles significantly limits their use. On the contrary, nonrigid materials must be considered as a possible alternative and there are previous works that have been shown the high demolding efficiency of silicone resins used as mold coatings for bakeware/cookware applications and for anti-icing purposes thanks to their deformability.[13,14] Thus, elastomeric SLIPS represent an interesting option as a non-stick coating when it is necessary to facilitate the detachment of the polyurethane part out of the mold.

In different lines of research, the most known applications of SLIPS surfaces are found related with biological repellency objectives, anti-icing, anti-fogging, self-cleaning and corrosion resistance purposes, among others but no previous contributions have been found that address the problem of extracting polyurethane (PUR) foam in contact with SLIPS surfaces.[15–21]

In the present work, a wide selection of elastomeric surfaces made of PDMS impregnated with silicone oil have been analyzed looking for the best SLIPS surfaces able to self-regenerate to maintain their PUR anti-adhesion capacity.

The tensile adhesion of PUR has been measured and its relationship with deformability and hydrophobicity has been analyzed. The results obtained points towards a solution to reduce the typical adhesion problems in the manufacture of molded PUR foam products since an adequate PDMS/curing agent/infused oil proportion has allowed obtaining consistent surfaces with exceptionally low sliding angles (SAs) and tensile force values, properties that have been maintained even after process-induced wear.

2 | MATERIALS AND METHODS

2.1 | PUR foam and aluminum mold

The necessary products for the formulation of PUR foam, diphenylmethane diisocyanate (MDI) and polyol, have been supplied by Grupo Copo (Grupo Empresarial Copo S.A, Pontevedra, Spain). Both components have been formulated with the same composition as those used in the industrial manufacturing processes of foamed automotive parts and have been mixed in a 100/57.7 weight ratio (polyol/MDI). Thus, the polyol has been stirred at 1000–1500 rpm for 10 s in a disposable plastic container and then the MDI has been added to continue stirring at the same speed for another 10 s. Then, the mixture must be poured into the pre-heated mold at 60°C to close it quickly, since the reaction that generates the foam occurs at high speed. After pouring, the filled mold is placed into an oven at 60°C for 5 min.

Figure 1 shows a diagram of the production of a specimen of the PDMS surface and the PUR foam for the pull-off test.

Due to their low cost and high thermal conductivity, aluminum alloys are the preferred ones to manufacture the molds used in the polyurethane industry.[22] Thus, the experimental mold has been made of EN AW2030 aluminum-copper alloy (Broncesval, Valencia, Spain). The mold consists of a cylinder of Ø110 mm × 150 mm height designed with two covers, one at each end. One of the covers is blind and the other one houses an intermediate support that allows the insertion of the specimen:
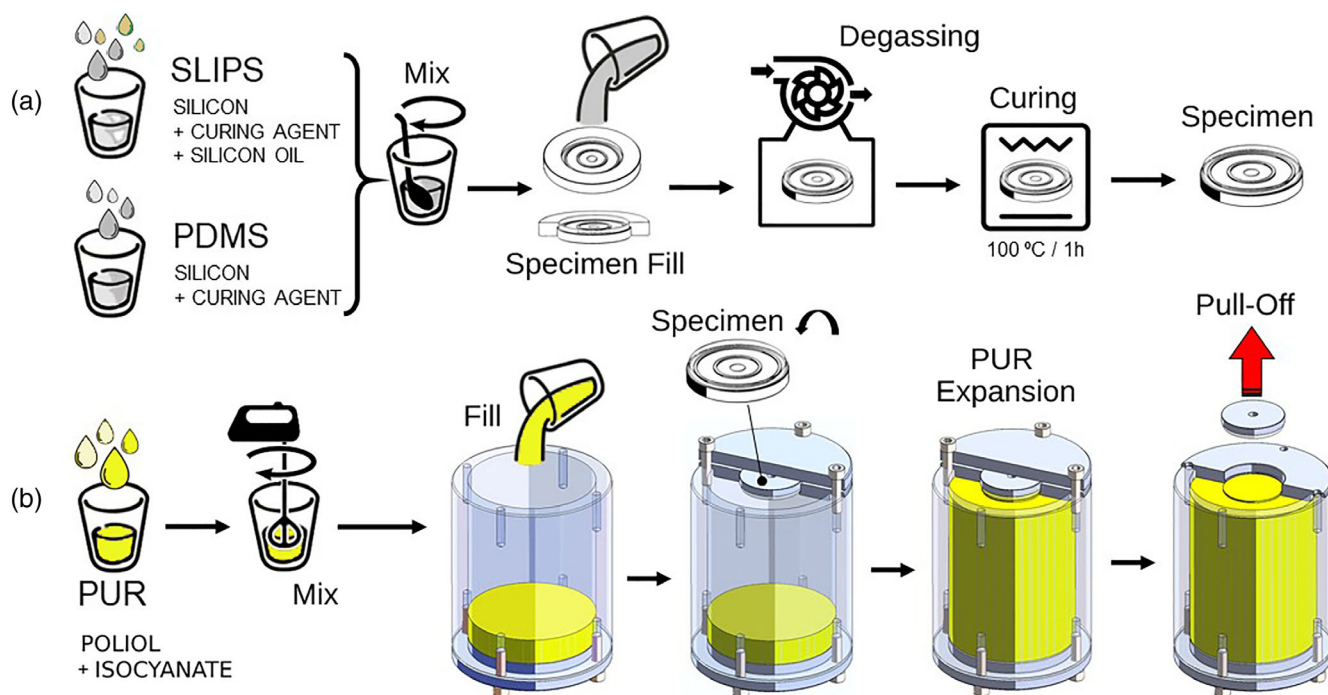
FIGURE 1 The scheme of working procedure: (a) sequence of elastic surface and SLIPS fabrication, (b) sequence of PUR foam fabrication and assembly for pull-off test [Color figure can be viewed at wileyonlinelibrary.com]
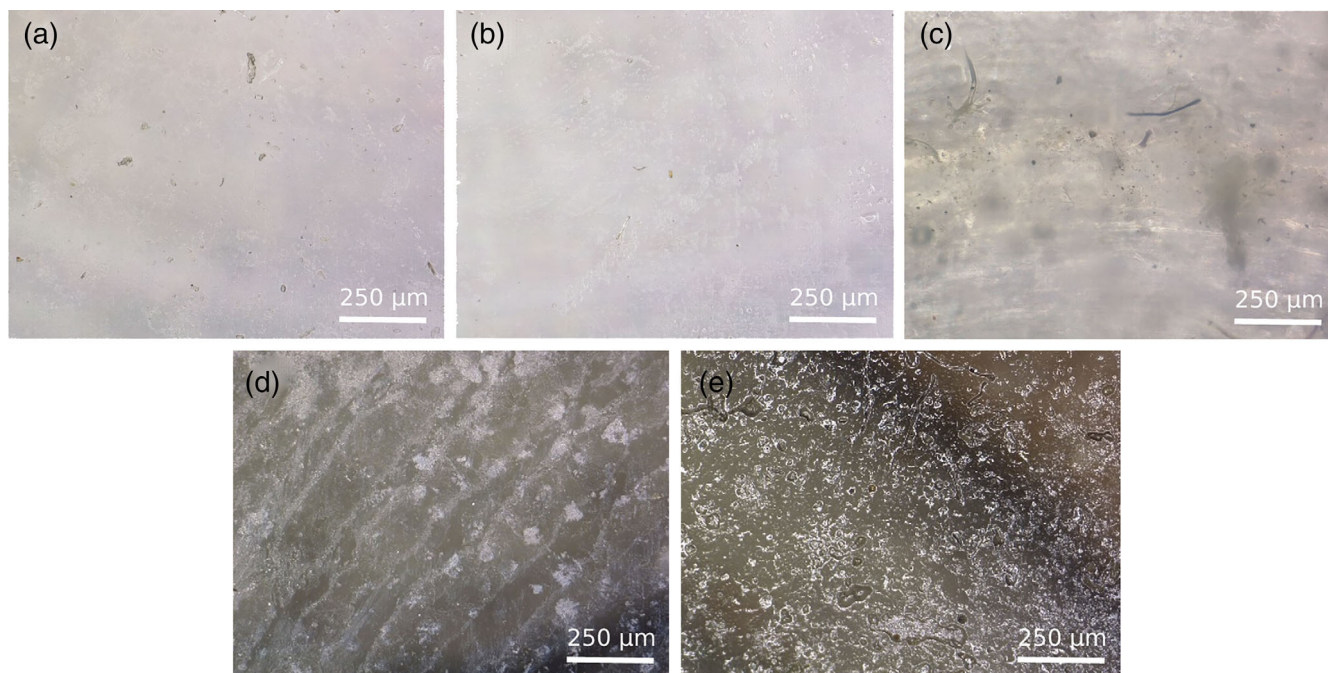

FIGURE 2 Photographs obtained with a Leica DVM6 digital confocal optical microscope with the FOV.43.75 objective at 140 X with different ratios between curing agent and PDMS (a) ratio 1:1, (b) ratio 1:2, (c) ratio 1:10, (d) ratio 1:30, and (e) ratio 1:50 [Color figure can be viewed at wileyonlinelibrary.com]

an aluminum disc on which PDMS coating layer has been fixed. This intermediate support disk allows the exposure of the PDMS sample in a Ø40 millimeters with the foam formed into the cavity of the mold.

2.2 | Surface preparation

To understand the adherence behavior of PUR foam against a deformable nonrigid surface, a representative

sample of PDMS-based elastomeric surfaces covering a wide range of stiffness have been prepared. For this, a bi-component Sylgard® 184 commercial kit (Dow Chemical Company, Midland-Michigan, USA) has been purchased that includes the curing agent and the silicone. In this first phase, specimens have been fabricated finding a representative scale of deformability as a function of curing agent versus silicone ratio, setting it at 1:1, 1:2, 1:10, 1:20, 1:30, and 1:50 for the experiments. The compound must be vigorously mixed and subsequently degassed in a vacuum chamber before being deposited as a coating on the aluminum disc. Thus, the aluminum disk is mounted on a flat ring/mold that allows the application of a uniform layer of PDMS of Ø 40 mm and 4 mm thickness. The samples were then allowed to cure for 48 h at room temperature (23°C) and then placed in a 100°C oven for 1 h. Visual evidence of the surfaces obtained with the different ratios between curing agent and PDMS are shown in Figure 2.

Transparent structures with different levels of opacity and firmness are observed for the 1:1, 1:2 and 1:10 ratios that venture cross-linked and hardened surfaces. Specimens 1:30 and 1:50 show heterogeneous dark gray surfaces mixed with white areas (probably the really cured ones) and that seem to predict curing deficiency. Particularly, the 1:50 ratio is difficult to handle and work with because it is flexible, soft, and sticky. In some way, graph 3 is an indication of the curing level reached by the samples and shows very low values for specimens with a 1:50 ratio. On the other hand, surfaces of this type have already been prepared previously[14] in which the elastic modulus is measured and it is verified that, although they are soft viscoelastic surfaces, they recover their original shape, and it can be considered that they are cured and consistent surfaces.

In the second phase, oil-infused elastomeric surfaces (SLIPS) have also been prepared. To do this, PDMS has subsequently been mixed in different proportions (1:2, 1:10, 1:50) and combined with different percentages by weight of Sigma-Aldrich 100 cSt silicone oil (Merkt KGaA, St. Louis, USA) at 5%, 20%, and 50%. The specimens have been prepared following the same procedure detailed in the first phase but, finally, these oil-impregnated surfaces have been rinsed with Milli-Q water prior to use.

Also, three control surfaces have been prepared. On the one hand, an untreated and hydrophilic aluminum EN AW2030 surface and, on the other hand, aluminum coated with PFA-type fluoropolymer and aluminum coated with RTV-1 elastomer.

The PFA and RTV1 coatings have been applied by Tecnimacor S.L. (Tecnimacor S.L, Villafranca de Córdoba, Spain), a specialist in this field. The fluoropolymer coating is known as TF-76521, type PFA (perfluoroalkoxy alkane), green color with a thickness of 55 ± 5 μm and H-F pencil hardness. The RTV-1 coating is a room temperature curing silicone rubber used as an anti-adhesive in the industrial field. It is coded as TS-RTV1 orange color with a thickness of 65 ± 8 μm and pencil hardness B-2B.

The untreated aluminum disks have been cleaned with acetone and ethanol, rinsed with distilled water and dried with a jet of compressed air before their use in the experiments.

2.3 | Surface characterization

2.3.1 | Roughness

The surface roughness has been characterized with a white light confocal microscope (PLμ 2300, Sensofar, Barcelona, Spain). The magnification has been fixed at 50x for a scan area of 285.38×209.62 mm^2. The mean roughness (Ra), the mean root square roughness (Rq) and the mean roughness of the peak-to-valley distances (Rz) have been measured.

2.3.2 | Surface topography

The surface characteristics of the SLIPS selected for the aging tests have been visually evaluated. On the one hand, a Leica DCM 8 confocal microscope with a 5x objective through which the surface texture of the samples has been determined and, on the other hand, a Leica DVM6 multifocus digital microscope (Leica Microsistemas SLU, Barcelona, Spain) with a PlanAPO FOV 3.60 objective with a maximum magnification of 2350x that has allowed to obtain high-quality images of the surfaces.

2.3.3 | Hardness

For the measurement of the hardness of the different mixtures used for the elastomeric surfaces, the normalized procedure established by the UNE-ISO 7619-1:2011 standard has been followed. This method is based on the measurement of the indentation hardness using the durometer method (Shore A hardness) and measures the depth of penetration of a specified indenter forced into the material under specific conditions. In this work, the chosen durometer has been the type A, which is suitable for general rubber, synthetic rubber, soft rubber, polyethylene grease, leather, and wax. It consists of a pressure foot, a hardened steel indenter, an indicating device, and

a calibrated spring. Five measurements have been made to determine the mean value, separated by at least 6 mm and at points on the entire surface of the specimen.

2.3.4 | Wettability

On the one hand, the static contact angle (CA) with water has been determined by the static sessile drop method. A theta lite optical tensiometer (Biolin Scientific, Manchester, UK) acquires images of the profile of a drop of 2.00 μl volume of demineralized water deposited onto the target surface by a micropipette. Then, the acquisition software establishes the theoretical profile and determines the CA that is close to the angle of advance (ACA). The mean value has been determined from three measure iterations. On the other hand, slip angle (SA) has been determined using a tilting platform device. A 50 μl drop of demineralized water has been deposited on the target surface of the specimen mounted on the platform that rotates at 10°/min. A digital goniometer (0.05° appreciation) shows the angle value. The mean value of SA has been determined from three measure iterations over the surface object of study.

2.3.5 | Adhesion with PUR (pull-off test)

The level of adhesion of PUR foam on the surface object of study has been determined by a tensile release test (pull-off). For this purpose, the specimen is in contact with the foam and mounted in the mold according to the assembly described in Figure 1. The mold, in turn, is fixed to the main table of a displacement control equipment that allows vertical displacement of a dynamometer; model MX2 500 N (IMADA, Northbrook, UK). Then, the specimen disc is detached from the PUR foam at a constant speed of 100 mm/min and the maximum force value is measured. The measurement has been reiterated three times with each specimen disc in a consecutive sequence allowing obtaining an average value for each test.

It must be noted that the pull-off test has been done initially to determine the PDMS surface with the lower PUR adhesion exclusively because of its stiffness/deformability. After this first filter, the best PDMS surfaces have been infiltrated with oil becoming SLIPS and the same procedure has been applied to determine the oil proportion for the lower

PUR adhesion. Finally, the best stiffness/deformability/oil proportion in terms of minimum PUR adhesion has been selected to evaluate the durability.

2.3.6 | Durability (aging test)

To simulate the effect of wear on PDMS SLIPS surfaces, they have been subjected to aging by contact with isocyanate reagent (MDI). Specimens with the best stiffness/low PUR adhesion balance have been exposed to isocyanate for 24, 72, and 168 h. For this, they have been used as plugs of a glass container placed downward to ensure maximum contact of the reagent with the surface to be aged. At the end of each wearing period, the pull-off test has been performed with the specimen in contact with PUR.

3 | RESULTS

3.1 | Pull-off strength and wettability of elastic PDMS surfaces

The results of the pull-off strength for the elastic, rigid and reference surfaces are shown in Table 1 and
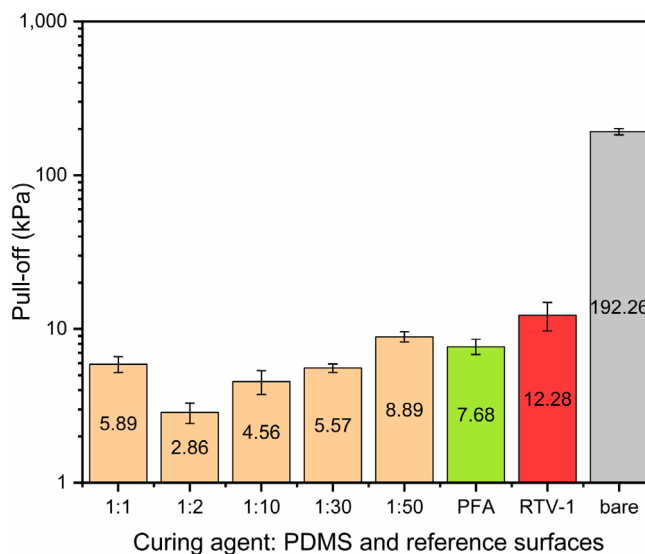

FIGURE 3 Tensile pull-off test between PUR foam and different surfaces with PDMS, with PFA, with RTV1 and with bare surface (the vertical scale is logarithmic) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Tensile pull-off (kPa) test between PUR foam and different surfaces with PDMS, with PFA, with RTV1 and with bare surface

	1:1	1:2	1:10	1:30	1:50	PFA	RTV-1	Bare
Pull-off (kPa)	5.9 ± 0.7	2.9 ± 0.4	4.60 ± 0.8	5.6 ± 0.4	8.9 ± 0,7	7.7 ± 0.9	12.3 ± 3.6	192.3 ± 8.3

TABLE 2 Sliding angle (SA) and static contact angle (CA) of PDMS and reference surfaces

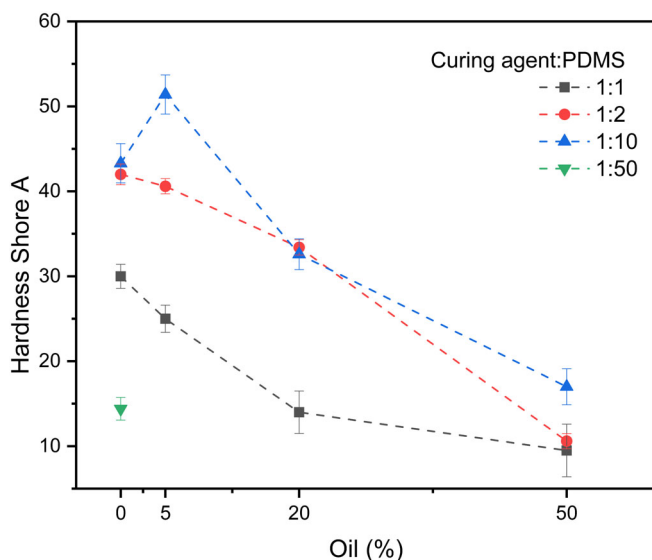|	1:1	1:2	1:10	1:30	1:50	PFA	RTV-1
SA (°)	19.25 ± 0.95	17.89 ± 1.15	18.56 ± 1.88	26.58 ± 2.14	$16.71 \pm 0,29$	13.52 ± 1.26	23.24 ± 0.83
CA (°)	63.31 ± 1.15	65.04 ± 2.24	69.06 ± 1.48	74.57 ± 1.79	69.99 ± 2.56	–	–

FIGURE 4 Shore A hardness of PDMS and SLIPS surfaces with different % of silicone oil [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 5 Pull-off strength of PUR foam versus SLIPS surfaces with different oil percentages [Color figure can be viewed at wileyonlinelibrary.com]

Figure 3. High tensile values have been measured, as expected, for the hydrophilic and rigid bare aluminum surface and substantially lower tensile values in the case of the hydrophobic elastic PDMS surfaces.

As can be seen in Figure 3, the lowest pull-off strength values are for 1:2 and 1:10 ratios, referring to the ratios between curing agent and PDMS. The pull-off strength values of the elastic PDMS surfaces are in the same order of magnitude or even lower than the reference surfaces, PFA (fluoropolymer), and RTV1 (silicone rubber). Adhesion values obtained on bare aluminum are 20–30 times higher than those measured on the elastic surfaces (PDMS).

The sliding SA and static CA for these surfaces have been determined and are shown in Table 2.

3.2 | Shore hardness, pull-off force, and wettability of PDMS SLIPS surfaces

On the other hand, the Shore A hardness of different PDMS elastomeric SLIPS surfaces has been determined. Figure 4 shows the results obtained for specimens prepared with different ratios of silicon/curing agent (1:1, 1:2, 1:10, and 1:50) in which silicone oil has been infused
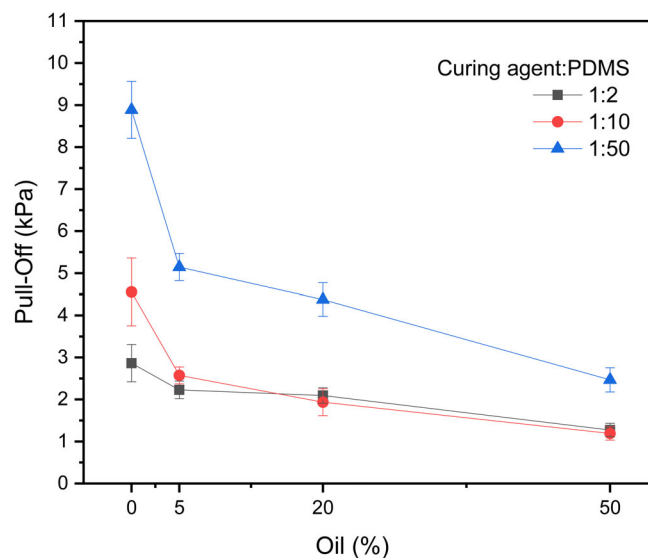
to convert them into SLIPS (5%, 20%, and 50% of oil). A change in trend can be seen (Figure 4) in the 1:10 sample with 5% oil, since the hardness increases with respect to the 1:10 sample without oil. We postulate that this increase could be due to the increased crosslinking of the silicone due to some type of interaction between this low percentage of infused oil and the curing agent. A similar but smaller anomaly has been reported in the previous work made by Ibañez-Ibañez et al.[14]

The 1:1 and 1:50 mixtures with high silicone oil content have thrown a Shore A hardness below 30. In particular, on the 1:50 surfaces with 5%, 20%, and 50% oil, the hardness could not be measured. The problem has been a consequence of the insufficient rigidity of these samples, since a low proportion of curing agent makes PDMS curing as an adhesive and very soft material. Since its structure deforms easily, it makes it impossible to determine the hardness by durometer method because of their lack of firmness.

The elastic response of PDMS surfaces analyzed through Shore A hardness have shown results compatible with those previously studied for ice adhesion with respect to the elastic modulus.[14] In parallel, the surfaces with maximum Shore A hardness and elastic modulus are those with 1:10 ratio (recommended by the supplier)

TABLE 3 Sliding angle and roughness of SLIPS surfaces

	PDMS 1:2 (0% oil)	SLIPS 1:2 (5% oil)	SLIPS 1:2 (20% oil)	PDMS 1:10 (0% oil)	SLIPS 1:10 (5% oil)	SLIPS 1:10 (20% oil)
SA (°)	17.89 ± 1.15	9.80 ± 1.02	5.39 ± 0.89	18.56 ± 1.88	8.72 ± 0.89	7.28 ± 1.11
CA (°)	65.04 ± 2.24	81.55 ± 1.56	90.75 ± 1.25	69.06 ± 1.48	87.50 ± 1.71	95.89 ± 1.71
Ra (μm)	0.21 ± 0.03	0.18 ± 0.04	0.25 ± 0.17	0.18 ± 0.06	0.14 ± 0.09	0.40 ± 0.23
Rz (μm)	6.25 ± 1.98	5.25 ± 2.25	7.89 ± 3.45	5.47 ± 2.18	5.16 ± 1.84	11.23 ± 4.65
Rq (μm)	0.45 ± 0.08	0.34 ± 0.19	0.56 ± 0.34	0.32 ± 0.14	0.25 ± 0.15	0.78 ± 0.48

and those with 1:50 ratio have shown minimum values, results consistent with a recent work consulted.[23] Values between 35 and 50 Shore A have allowed obtaining a better consistency and robustness of the SLIPS surface as in the case of 1:2 and 1:10 silicon/curing agent ratios with silicone oil contents between 5% and 20%.

On PDMS surfaces obtained with ratios of 1:2, 1:10, and 1:50 with silicone oil (5, 20 and 50%), the results of the PUR foam pull-off test are shown in Figure 5. It can be seen that, in all mixtures, the pull-off force decreased with the addition of silicone oil. The 1:2 surface, which obtained one of the lowest pull-off force values, proved to be relatively insensitive to the addition of silicone oil, so that, with the maximum proportion of silicone oil, the pull-off values decrease from 2.86 to 1.27 kPa.

All SLIPS surfaces with 50% oil are very soft, difficult to handle and also do not have the consistency for their hypothetical application as a permanent coating. In addition, the 1:50 ratio shows substantially higher pull-off strength values than the other silicone mix proportions. In the conclusion and considering the Shore A hardness analysis and the pull-off test, the ratios 1:10 and 1:2 with 5% and 20% oil are the SLIPS surfaces with more interest, with better balance between stiffness/consistence and lower PUR adhesion.

Sliding angle, apparent CA and roughness measured on these SLIPS surfaces are shown in Table 3. The 1:2 surfaces yield slightly lower SAs and CAs values than the 1:10 surfaces, although the tensile values are of the same order for 5% and 20% oil infused SLIPS. This relationship is more evident in the previously published study of the performance of these type of surfaces in contact with ice, where the hysteresis value of the 1:2 surface has been slightly lower than the 1:10.[14] Thus, water droplets will be retained to a lesser extent on these lower SA surfaces.

In this sense, SA values are strongly related to the transition from Wenzel to Cassie-Baxter state. In the case of these elastomeric PDMS surfaces without and with infused silicone oil, these values are relatively close. It must be noted that all the surfaces are very smooth, with very low Ra values and, therefore, far from that transition. Thus, it can be thought that the droplets rest in the Wenzel state and the surface morphology has little relevant role in the variation of the wettability properties of these surfaces.

3.3 | Durability, aging test and surface analysis of PDMS SLIPS surfaces

To determine the durability of the proposed solution, the 1:10 PDMS SLIPS surfaces have been visually analyzed. Figure 6 shows the 1:10 PDMS SLIPS, and Figure 7 show their topography, the different sizes and morphology of the oil drops, and their distribution on the surface of the PDMS matrix just after five consecutive PUR molding-demoulding cycles.

A structure with microcraters is shown for the case of the oil-free PDMS elastic surface (Figure 6a). This phenomenon is due to the loss of material by the mechanical pull-off effect of the PUR foam as already evidenced in other previous consulted works.[24]

Analyzing the aspect of PDMS SLIPS, smooth surfaces with traces of oil are visible in Figure 6b and c, showing the upwelling of the lubricant after demoulding. Thus, the regeneration of a new lubricant layer and the greater elasticity of the surface have prevented the early formation of microcraters that degrade the surface. The surface with 50% oil shows a different behavior (see Figure 6d) since the high oil content has generated an oil film throughout the structure and deposited on the surface.

The size of the droplets observed on the surface of the samples (Figure 6), with ratios of 1:10 with 5% and 20% silicone oil infused, indicate that the diameter of the droplet is less than 10 μm for the proportion of oil of 5% and less than 35 μm for those of 20%. In other works[25–27] with PDMS SLIPS it was determined that the pore size in
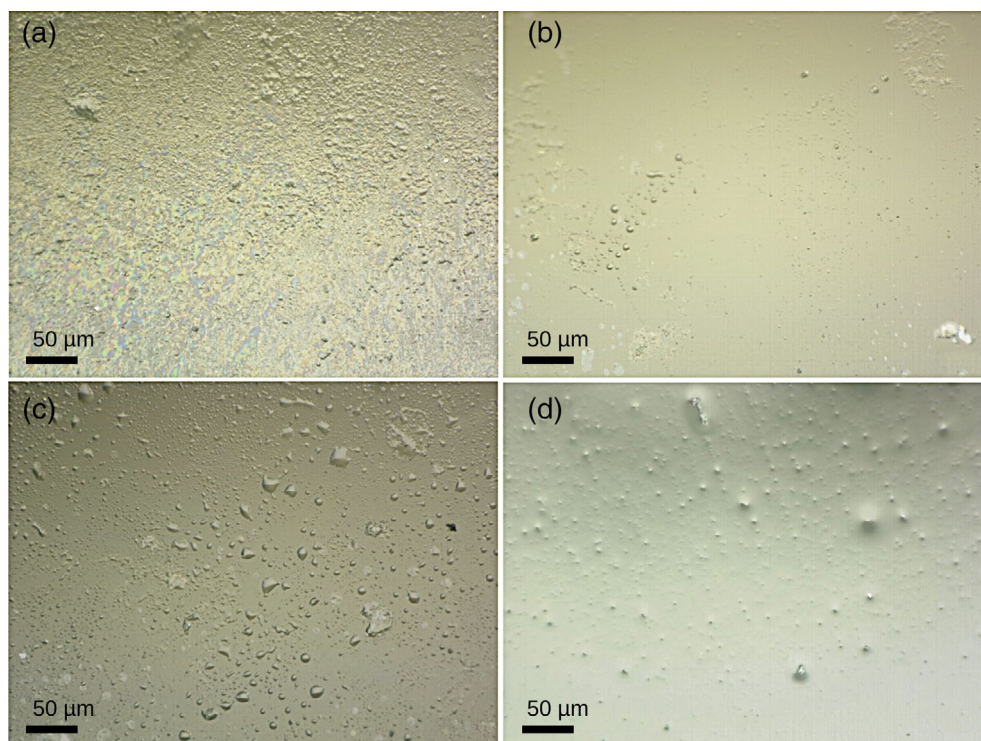
FIGURE 6 PDMS SLIPS 1:10 surfaces after five molding-demoulding cycles: (a) 0% oil, (b) 5% oil, (c) 20% oil, and (d) 50% oil [Color figure can be viewed at wileyonlinelibrary.com]

the PDMS matrix is increased when the concentration of the infused fluid in the matrix increased. It is reasonable to infer that the pore size in our case will also increase with the concentration of the silicone oil as the size of the microdroplets analyzed on the surface seems to show us. In short, high proportions of oil produce larger pores, which are associated with a better oil integration, lower breakout forces, and low slip angles.

The images of the confocal microscope evidence a bigger size of the oil drops deposited on the SLIPS surfaces with 5% and 20% oil and the distribution is more homogeneous in the case of 20% oil infused specimen.

Thus, of the two optimum surfaces (1:10 and 1:2), the 1:10 surface has been chosen for the aging test and specimens with 0%, 5%, and 20% of oil infused have been tested.

Figure 8 shows an increase in the tensile value after exposure to isocyanate that is clearly higher in the surfaces without oil and, among the SLIPS, in those with lower oil content. In any case, the behavior of these SLIPS-type PDMS surfaces against exposure to isocyanate is better when the oil content is higher and also if is compared with the behavior shown by the reference surfaces PFA and RTV-1.[12] On the other hand, the images in Figure 9 clearly shows the increasing in the proportion of PUR foam attached on the 1:10 SLIPS surfaces after an aging treatment by an exposure to isocyanate for 168 hours and after being subsequently subjected to a to a single cycle of PUR foam molding-demoulding.

4 | DISCUSSION

4.1 | Adhesion mechanism

The adhesion mechanisms of PUR foam with aluminum are related to a chemical interaction and the formation of covalent bonds between MDI (isocyanate) and aluminum.[28] In some polymers, other studies have shown, again, influences of chemical interactions between PUR foams and thermoplastics such as ABS and blends of PC with ABS.[24] Further, it has been determined that high surface energy, high roughness values and increased proportion of isocyanate in the PUR composition have very significant influence on the adhesion of PUR foam.[29] Thus, it has been determined that the most influential factor is the surface energy and the least influential is the isocyanate content. Hydroxyl groups produce an increase in surface energy and, therefore, among the polymers previously studied the best is PTFE, followed by polypropylene and finally PMMA. Thus, the recent work proposed an innovative solution by the use of thermoformed polypropylene thin sheets superimposed on the aluminum mold to minimize the use of release agents.[30]

In another way, consulted works propose fluoropolymers as coating materials in molds for the manufacture of PUR foam due to their low surface energy and inert structure without hydroxyl groups. These qualities have been evaluated in the case of PTFE and FEP, PTFE, and

FIGURE 7 Leica DCM8 confocal microscope images of 1:10 PDMS SLIPS surfaces prepared with, (a) 0% oil, (b) 5% oil, (c) 20% oil, and (d) 50% oil. The surface topography, drop size and distribution on the surface of PDMS [Color figure can be viewed at wileyonlinelibrary.com]
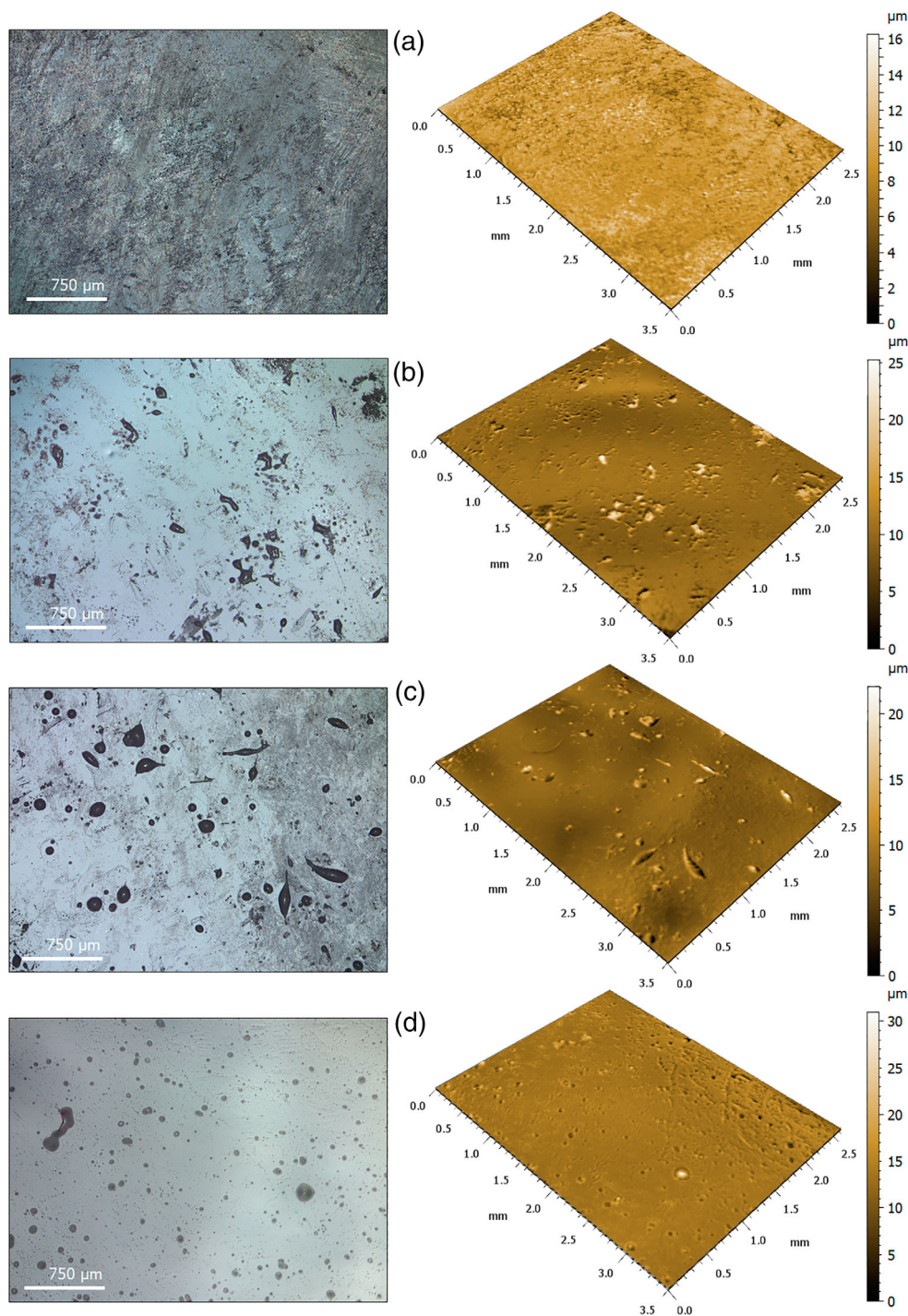
PFA and about PTFE, FEP, PFA, and other polymers and materials.[10,12,22] In the present work, the adhesion mechanism related to the porous structure of an elastomeric coating has been postulated. This structure allows the penetration of MDI isocyanate, responsible for the deterioration of the non-stick properties after the application of consecutive cycles of PUR foam molding. Of all these fluoropolymeric materials, the best performance has been obtained with low-porosity fluoropolymers such as FEP (fluorinated ethylene propylene) and PFA, while high-porosity polymers such as PTFE (polytetrafluoroethylene) offer the worst results.

Unlike the phenomena described above in various rigid fluoropolymeric coatings, it is known that the adhesion mechanisms of the PUR foam on PDMS surface is affected by the cracks and hollows generated mechanically in the PUR demolding process. These cracks allow the polymerization of the isocyanate and the generation of polyureas due to the inherent humidity of the process, which contaminate and deteriorate the silicone.[31,32]

In this work, it has been postulated that since the main mechanism of deterioration and failure of PUR-affected PDMS surfaces is due to the generation of micro-cracks by demolding, SLIPS surfaces have the ability of self-healing and self-regeneration by a protective surface layer that significantly reduces the speed of the degenerative effect.[33]
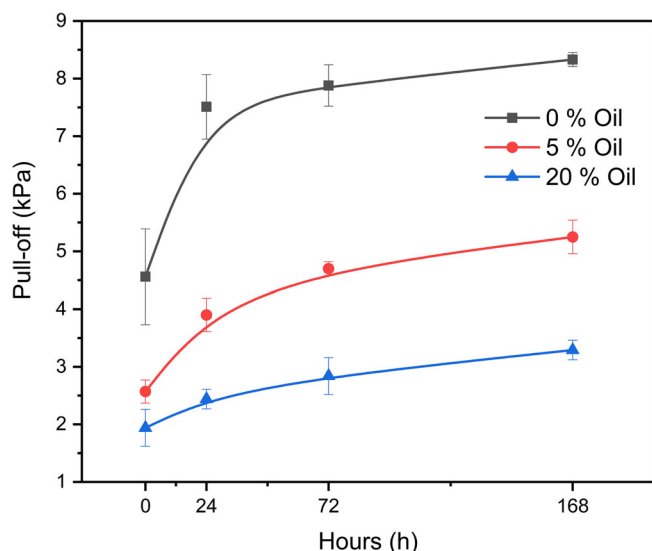

FIGURE 8 Pull-off test of SLIPS 1:10 surfaces after 24, 72, and 168 h contact with isocyanate (MDI) for the manufacture of PUR foam [Color figure can be viewed at wileyonlinelibrary.com]

It is observed that the surfaces with the 1:10 ratios with 5% and 20% of infused oil subjected to 5 cycles of molding and demolding of PUR foam, and in the same way the surfaces subjected to exposure for 168 h of isocyanate, after these states they show micro-drops of oil on the surface (see Figures 6 and 9) confirming self-regenerative capacity of SLIPS surfaces.

In addition, the homogeneous distribution of semi-free polymer chains (mobile polymer chains) from the oil can facilitate detachment from surfaces.[34] Both, these semi-free polymeric chains and the presence of microdroplets are referred to as "interfacial slippage." Although the presence of mobile polymeric chains (unlike micro-droplets) cannot be considered as a regenerative property but as a property that is found throughout the thickness of the coating, and therefore is not affected when the surface is damaged.

4.2 | Anti-adherent behavior (pull-off force)

The elastic surfaces object of the present study has shown low tensile force values in all cases. In the 1:10 and 1:2 ratios the lowest values have been obtained, 2.86 and 4.56 kPa, respectively. When these surfaces are infused with silicone oil with 5% and 20%, the tensile force required to detach the specimen is further reduced: for
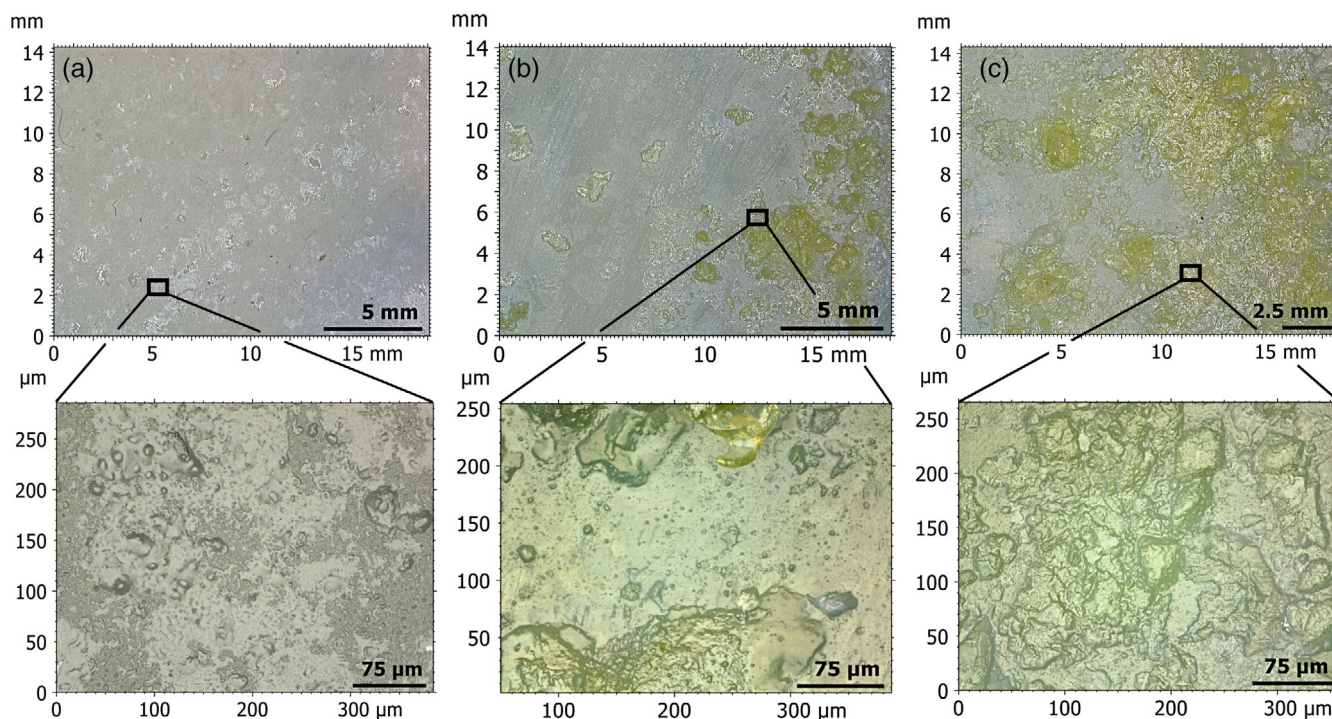

FIGURE 9 Aging effect caused by the exposure of the 1:10 SLIPS surface to isocyanate for 168 hours and subsequently subjected to a PUR foam molding-demoulding cycle: (a) 20% oil, (b) 5% oil, and (c) 0% oil [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Pull-off force of different materials in contact with PUR foam

Contribution	Materials	Release agent	Number of cycles	Pull-off (kPa)
Figueiredo et al.[10]	PTFE	Non	1–20	7.92–21.81
	PFA	Non	1–20	7.56–11.93
Sánchez-Urbano et al.[12]	Silicone rubber	Non	1–20	12.28–17.77
	PTFE	Non	1–20	7.44–17.76
	PFA	Non	1–20	5.92–7.68
	FEP	Non	1–20	7.23–10.23
	Sol–gel ceramic	Non	1–20	12.83–21.18
Romero et al.[35]	HIPS	Yes	1–7	6.91–54.32
	ABS	Yes	1–7	4.93–39.50
Guerrero et al. (current research)	SLIPS 1:10 PDMS (5%–20% oil)	Non	1–5	2.23–5.15
			168 h with isocyanate	3.29–5.25

Abbreviations: ABS, acrylonitrile butadiene styrene; FEP, fluorinated ethylene propylene; HIPS, high impact polystyrene; PDMS, polydimethylsiloxane; PFA, perfluoroalkoxy alkane; PTFE, polytetrafluoroethylene.

the 1:2 PDMS, from 2.86 to 2.23 kPa (5% oil) and 2.10 kPa (20% oil). For the 1:10 surfaces the values range from 4.56 to 2.57 kPa (5% oil) and 1.94 kPa (20% oil) decreasing more markedly.

The tensile values for 1:10 and 1:2 lubricated SLIPS are lower than the materials used as reference, 7.68 kPa of PFA and 12.28 kPa with RTV-1. Even after prolonged exposure to isocyanate (168 h), the values are 5.25 kPa (1:10 PDMS, 5% oil) and 3.29 kPa (1:10 PDMS, 20% oil), still lower than the obtained in the case of reference surfaces.

The present contribution has shown a low hysteresis of the elastic and oil infused surfaces (SLIPS), in the ratios 1:10 and 1:2, showing SA values between 5 and 7° that are very close to superhydrophobic regimes. These surfaces also have low roughness, showing Ra values of less than 0.4 μm and Rz of 5 μm. The pull-off force values shown in these SLIPS are significantly lower than in most of those materials tested in any of the previous works found and consulted and furthermore, the non-stick performance is maintained reasonably.

For the samples obtained with a 1:10 ratio with proportions of infused oil of 5 and 20%, the study was extended up to 12 consecutive cycles of PUR foam molding and demoulding, and the release pressure values obtained were 3.9 ± 0.3 kPa with the 1:10 ratio with 20% oil and 5.3 ± 0.5 kPa for 1:10 at 5%, values lower than 6 kPa and relatively low. The increase from 5 to 12 cycles, a jump of 7 cycles, for 1:10 at 5% has been about 3.0 kPa and for 1:10 at 20% 1.5 kPa. Considering that the values obtained without infused oil reach around 5 kPa for the 1:10 ratio of PDMS versus oil-free curing agent (see Table 1), it follows that in 12 cycles the 1:10 surface with 5% has reached the similar values of peel force than the surface without oil, in short, it is the threshold of SLIPS behavior for this concentration of oil (5%). However, for the ratio with 20% oil, the values are lower and according to the estimated jump of 1.5 kPa/7 cycles, a SLIPS behavior could be expected up to 18–20 PUR foam molding and demoulding cycles.

The summary of Table 4 shows the results obtained in the previous works consulted that are in the line of the present contribution. The pull-off tensile force values for different types of materials in contact with PUR foam are exposed and compared.

In short, the PDMS SLIPS surfaces generated with 1:10 and 1:2 proportion between curing agent and polydimethylsiloxane (PDMS) and a percentage between 5% and 20% of infused oil built the characteristics that favor interfacial sliding allowing very low tensile force values when the PUR is taken off. This property is in the order of up to 1.5–2.5 times lower than on the same surfaces without oil and with respect to the other reference surfaces, even after a prolonged contact with isocyanate.

5 | CONCLUSIONS

Polydimethylsiloxane elastic surfaces have been studied and the most suitable for PUR foam demolding have been experimentally selected. They have been characterized through hardness, hysteresis and tensile adhesion test against PUR foam. Silicone oil has been infused on the selected elastic surfaces in different percentages and SLIPS surfaces have been fabricated.

The SLIPS surfaces with the best anti-adhesion behavior against PUR foam and with adequate hardness/consistency properties have been characterized.

The 1:2 and 1:10 surfaces (curing agent: PDMS) and percentage of oil infused between 5% and 20% (SLIPS) with slip angle (SA) values between 5° and 10° and tensile values between 2–5 kPa have been identified as the optimal surfaces for better PUR foam detachment. This condition has been adequately maintained on the 1:10 PDMS and 20% oil infused SLIPS, even after prolonged exposure to isocyanate.

Finally, this research work proposes a promising route to establish elastomeric oil-infused surfaces (SLIPS) for coating aluminum molds used in the manufacturing of PUR foam products. The low surface energy of these surfaces, adequate elasticity and the formation of a thin and protective auto-regenerative layer of lubricant on the surface minimize the adhesion of the PUR foam and markedly improve the demolding efficiency.

AUTHOR CONTRIBUTIONS

Guillermo Guerrero-Vaca: Data curation (lead); investigation (equal); writing – original draft (equal); writing – review and editing (equal). **Óscar Rodríguez-Alabanda:** Data curation (equal); investigation (equal); visualization (equal); writing – original draft (equal); writing – review and editing (equal). **Pablo Francisco Ibáñez-Ibáñez:** Data curation (supporting); investigation (supporting); writing – review and editing (equal). **Miguel Ángel Rodríguez-Valverde:** Conceptualization (equal); data curation (equal); project administration (lead); writing – review and editing (equal).

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

ORCID

Guillermo Guerrero-Vaca https://orcid.org/0000-0002-7627-3385

Óscar Rodríguez-Alabanda https://orcid.org/0000-0002-9728-258X

Pablo Francisco Ibáñez-Ibáñez https://orcid.org/0000-0001-6479-7029

Miguel Ángel Rodríguez-Valverde https://orcid.org/0000-0003-4361-6721

REFERENCES

[1] J. O. Akindoyo, M. D. H. Beg, S. Ghazali, M. R. Islam, N. Jeyaratnam, A. R. Yuvaraj, *RSC Adv.* **2016**, *6*, 114453.

[2] S. H. Kim, H. C. Park, H. M. Jeong, B. K. Kim, *J. Mater. Sci.* **2010**, *45*, 2675.

[3] L. Marsavina, D. M. Constantinescu, E. Linul, F. A. Stuparu, D. A. Apostol, *Eng. Fract. Mech.* **2016**, *167*, 68.

[4] G. Li, L. Dong, Z. Bai, M. Lei, J. Du, *Constr. Build. Mater.* **2017**, *142*, 59.

[5] E. Kabakci, G. Sayer, E. Suvaci, O. Uysal, İ. Güler, M. Kaya, *J. Appl. Polym. Sci.* **2017**, *134*, 134.

[6] A. S. Dutta, *Polyurethane Foam Chemistry*, Elsevier Inc., Amsterdam, Netherlands **2018**.

[7] R. R. Rao, L. A. Mondy, K. N. Long, M. C. Celina, N. Wyatt, C. C. Roberts, M. M. Soehnel, V. E. Brunini, *AIChE J.* **2017**, *63*, 2945.

[8] A. Olietti, E. Pargoletti, A. Diona, G. Cappelletti, *J. Mol. Liq.* **2018**, *261*, 199.

[9] W. J. Schröder, *Elastomers Plast.* **1988**, *20*, 200.

[10] L. Figueiredo, P. Bandeira, A. Mendes, M. M. S. M. Bastos, F. D. Magalhães, *J. Coatings Technol. Res.* **2012**, *9*, 757.

[11] L. Y. L. Wu, S. Nemeth, *Mater. Res. Soc. Symp. - Proc.* **2003**, *778*, 271.

[12] F. Sánchez-Urbano, G. Paz-Gómez, O. Rodríguez-Alabanda, P. E. Romero, M. Cabrerizo-Vílchez, M. A. Rodríguez-Valverde, G. Guerrero-Vaca, *Coatings* **2018**, *8*, 1.

[13] J. D. Greene, S. L. Snyder, Silicone Non-Stick Coatings. *Patent US 2006/0079620 A1* **2006**.

[14] P. F. Ibáñez-Ibáñez, F. J. Montes Ruiz-Cabello, M. A. Cabrerizo-Vílchez, M. Rodríguez-Valverde, *J. Colloid Interface Sci.* **2022**, *608*, 792.

[15] X. Yao, Y. Song, L. Jiang, *Adv. Mater.* **2011**, *23*, 719.

[16] G. Wang, Z. Guo, *Nanoscale* **2019**, *11*, 22615.

[17] M. J. Kreder, J. Alvarenga, P. Kim, J. Aizenberg, *Nat. Rev. Mater.* **2016**, *1*, 1.

[18] F. L. Heale, Special wettability coatings, films and slippery liquid infused porous surfaces with self-cleaning, anti-icing and anti-fogging applications, **2020**.

[19] F. Xu, T. Wang, J. Bohling, A. M. Maurice, H. Y. Chen, L. Wu, S. J. Zhou, *Coatings Technol. Res.* **2018**, *15*, 1025.

[20] R. Deng, T. Shen, H. Chen, J. Lu, H.-C. Yang, W. J. Li, *Mater. Chem. A* **2020**, *8*, 7536.

[21] Y. Zhu, Y. He, D. Yang, E. Sacher, *Colloids Surfaces A* **2018**, *556*, 99.

[22] A. Akinci, E. Cobanoglu, *E-Polymers* **2009**, *033*, 1.

[23] J. Vaicekauskaite, P. Mazurek, S. Vudayagiri, A. L. J. Skov, *Mater. Chem. C* **2020**, *8*, 1273.

[24] N. Mahmood, K. Busse, J. Kressler, *J. Appl. Polym. Sci.* **2007**, *104*, 479.

[25] T. Li, Y. Zhuo, V. Håkonsen, J. He, Z. Zhang, *Ind. Eng. Chem. Res.* **2019**, *58*, 17776.

[26] T. Li, Y. Zhuo, V. Håkonsen, S. Rønneberg, J. He, Z. Zhang, *Coatings* **2019**, *9*, 9.

[27] Y. Zhuo, F. Wang, S. Xiao, J. He, Z. Zhang, *ACS Omega* **2018**, *3*, 10139.

[28] K. Shimizu, M. L. Abel, C. Phanopoulos, S. Holvoet, J. F. Watts, *J. Mater. Sci.* **2012**, *47*, 902.

[29] C. E. Majewski, N. Hopkinson, *Plast. Rubber Compos.* **2007**, *36*, 438.

[30] P. Heisler, S. D. Gick, J. Franke, *Procedia Manuf.* **2018**, *17*, 579.

[31] M. Wortmann, P. Krieger, N. Frese, E. Moritzer, B. Hüsgen, *ACS Omega* **2021**, *6*, 4687.

[32] M. Wortmann, N. Frese, W. Keil, J. Brikmann, J. Biedinger, B. Brockhagen, G. Reiss, C. Schmidt, A. Gölzhäuser, E. Moritzer, B. Hüsgen, *ACS Appl. Polym. Mater.* **2020**, *2*, 4719.

[33] C. Wang, Z. Guo, *Nanoscale* **2020**, *12*, 22398.

[34] K. Golovin, S. P. R. Kobaku, D. H. Lee, E. T. DiLoreto, J. M. Mabry, A. Tuteja, *Sci. Adv.* **2016**, *2*, 2.

[35] P. E. Romero, J. Arribas-Barrios, O. Rodriguez-Alabanda, R. González-Merino, G. Guerrero-Vaca, *CIRP J. Manuf. Sci. Technol.* **2021**, *32*, 32.