

# Manufacture of thermoplastic molds by fused filament fabrication 3D printing for rapid prototyping of polyurethane foam molded products

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## Abstract

**Purpose** – Polyurethane (PUR) foam parts are traditionally manufactured using metallic molds, an unsuitable approach for prototyping purposes. Thus, rapid tooling of disposable molds using fused filament fabrication (FFF) with polylactic acid (PLA) and glycol-modified polyethylene terephthalate (PETG) is proposed as an economical, simpler and faster solution compared to traditional metallic molds or three-dimensional (3D) printing with other difficult-to-print thermoplastics, which are prone to shrinkage and delamination (acrylonitrile butadiene styrene, polypropylene-PP) or high-cost due to both material and printing equipment expenses (PEEK, polyamides or polycarbonate-PC). The purpose of this study has been to evaluate the ease of release of PUR foam on these materials in combination with release agents to facilitate the molding/demolding process.

**Design/methodology/approach** – PETG, PLA and hardenable polylactic acid (PLA 3D870) have been evaluated as mold materials in combination with aqueous and solvent-based release agents within a full design of experiments by three consecutive molding/demolding cycles.

**Findings** – PLA 3D870 has shown the best demoldability. A mold expressly designed to manufacture a foam cushion has been printed and the prototyping has been successfully achieved. The demolding of the part has been easier using a solvent-based release agent, meanwhile the quality has been better when using a water-based one.

**Originality/value** – The combination of PLA 3D870 and FFF, along with solvent-free water-based release agents, presents a compelling low-cost and eco-friendly alternative to traditional metallic molds and other 3D printing thermoplastics. This innovative approach serves as a viable option for rapid tooling in PUR foam molding.

**Keywords** 3D printing, Fused filament fabrication, Rapid tooling, Rapid prototyping, Polyurethane foam, Thermoplastic mold

**Paper type** Research paper

## 1. Introduction

The application and use of polyurethane (PUR) in its different formulations is widely extended in different products of common use in our daily life and for very diverse applications such as adhesives, coatings and sheets or elastomeric parts or even with a foam structure, among others (Olietti *et al.*, 2018; Romero *et al.*, 2021; De Souza *et al.*, 2021).

PUR is a polymeric material based on the exothermic reaction of poly-isocyanates with polyol molecules that is easily synthesized at low temperature by addition between the isocyanate and the alcohol. In addition, PUR foam can have quite different qualities depending on the proportions and structure of the polyol and isocyanate mixed, and the reaction temperature (Das and Mahanwar, 2020; De Souza *et al.*, 2021; Zhao *et al.*, 2014). Thus, when a polyol with a linear structure, high molecular weight and low cross-linking capacity is used, an elastic PUR can be obtained, while if we use an aromatic

polyol of low molecular weight and a high capacity to generate cross-links, greater rigidity is obtained in the product (Akindoyo *et al.*, 2016; De Souza *et al.*, 2021). Scheme 1 shows

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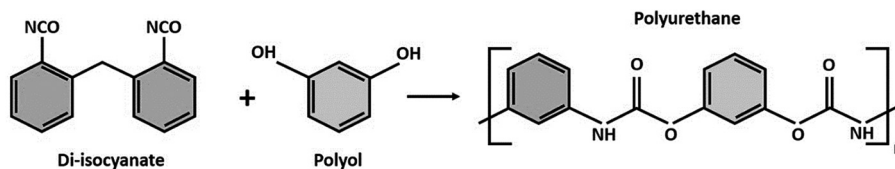
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**Scheme 1** Synthesis of PUR by reaction of bifunctional isocyanate with polyol

Source: Scheme by authors

the basic formulation to obtain PUR by the reaction between a diisocyanate and a bifunctional polyol (De Souza *et al.*, 2021).

For the formation of the PUR foam, the isocyanate and the polyol must be suitably mixed and stirred to pour them into the mold that has to be previously preheated at a low temperature of up to 70°C–80°C (Olietti *et al.*, 2018). The molds commonly used in the plastic manufacturing industry are made of aluminum alloy, which offers good durability for mass production and very good thermal behavior for molding of thermoplastics and polymers (Akinci and Cobanoglu, 2009; Benavides-Treviño *et al.*, 2022; Pereira *et al.*, 2013). However, it is known that the reaction of the bifunctional groups of the isocyanate-based methylene diphenyl isocyanate (MDI), transforming nitrogen-carbon-oxygen isocyanates (NCO) into nitrogen-hydrogen-carbon-oxygen amides (NHCOO) with hydroxyl groups existing on the surface of aluminum, is responsible for the appearance of urethane bonds closely linked to the surface, causing a strong chemical adhesion between the compound and the aluminum metal alloy (Kim *et al.*, 2005). Thus, in the PUR molding industry, it is common to apply mold release agents (RAs) to the mold surface to avoid this problem (Althoff *et al.*, 2010; Olietti *et al.*, 2018; Schröder, 1988). These mold RAs, based on waxes, soaps, fats, silicone oils, fluorinated silicones, among others, are applied integrated into a solvent-based solution, although hybrid or even 100% water-based solutions should preferably be used to avoid all the drawbacks derived from the use of solvents (volatility, odors, toxicity, flammability and cost) (Harakal *et al.*, 1990; Liang *et al.*, 2022). Even so, it must be considered that a water-based mold RA generally offers a worse release performance, is less easily removed from the surface of the piece and also has the capacity for chemical reaction with isocyanate, which can cause decomposition in the mass in formation producing bubbles, craters and other defects in the final PUR product (Olietti *et al.*, 2018).

On the other hand, additive manufacturing (AM) techniques are technologies that are currently booming and offer certain advantages for direct rapid prototyping of all types of parts and mechanical tools such as fixtures, inserts and molds (rapid tooling) (Altaf *et al.*, 2018; Bere *et al.*, 2020). In this sense, previous works mainly developed solutions for vacuum thermoforming purposes by the manufacturing of resin-based tooling and molds suitable to conform sheets of diverse materials such as polyethylene terephthalate (PET), high impact polystyrene (HIPS) (Gajdoš *et al.*, 2016) or even other that requires higher pressures and temperatures such as carbon fiber for aircraft wing sections (Stratasys Ltd., 2023) manufactured by Wehl & Partner company (Wehl & Partner Muster und Prototypen GmbH, Zimmern/Rottweil, Germany), by printing a preform in ULTEM 1010 in a Stratasys F900 FDM printer (Stratasys Ltd., Rejovot, Israel). Other authors (Dizon *et al.*, 2020; Ilyas *et al.*, 2019) and companies proposed

stereolithography three-dimensional (3D) printed molds for the injection molding process, but no previous works have been found that use this type of tooling for the molding of PUR foam.

Traditionally, the process used for the manufacture of durable metal molds for the injection of PUR foam parts involves complex design (CAD) and computer-aided manufacturing tasks, using subtractive techniques and equipment commanded by computerized numerical control (CNC) (ASM International, 1989; Krajnik and Kopač, 2004), a process that is expensive and difficult. Thus, the development of this type of molds is only justified for a large volume of production, when the unit cost is reasonable. Although AM makes it possible to manufacture molds that are not very durable, previous works demonstrated that they can be economically viable to manufacture one or a few units in an initial phase of prototyping and optimization of the process with thermoforming techniques (Boca *et al.*, 2021; Haeberle and Desai, 2019). Thus, the polymer fused filament fabrication modeling (FFF) technique could be an alternative for PUR foam molding because certain thermoplastic materials can withstand temperatures of up to 80°C without practically deforming, which are necessary for the curing of the foam. In this sense, previous works have been consulted in which the FFF technique has been already used for the manufacture of rapid tooling elements for various applications such as lost wax sacrificial models, for investment casting or for silicone molds or injection molding inserts, including biomedical models (Boparai *et al.*, 2016). In this sense, Ruiz-Huerta *et al.* developed a polymethylmethacrylate (PMMA) mold using FFF, considerably reducing the waiting time for a craniomaxillofacial implant (Ruiz-Huerta *et al.*, 2016). Ferretti *et al.* proposed a mold made of polyvinylbutyral by FFF to produce a carbon fiber protection cover by vacuum, demolding the piece without great difficulties. Many other works have focused on the development of injection molding solutions (Bagalkot *et al.*, 2019; Kampker *et al.*, 2019a; Vasco *et al.*, 2019). However, there are hardly any works that study the use of the FFF technique in the manufacture of molds for PUR foam parts, considering that the difficulty of demolding this material is going to be the main enemy of the process (Kampker *et al.*, 2019a, 2019b; Lozano *et al.*, 2022). Thus, in a proposal for the molding of PUR foam parts in molds manufactured by 3D FFF printing, it will be of vital importance to study the ease of demolding when working with materials commonly used for this technique, such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) or glycol-modified polyethylene terephthalate (PETG).

It should be noted that, apart from the many advantages of the FFF technique, the surface quality obtained is not very good and components manufactured layer by layer often require post-processing to improve their surface finish. Consequently, FFF-based rapid tooling applied to injection

molding presents limitations in terms of precision, durability and surface finishing quality (Golhin *et al.*, 2023). In this sense, Mahmood *et al.* analyzed the adhesion capacity of PUR foam with various thermoplastics (Mahmood *et al.*, 2007). In their experiments, they sought to increase the adhesion between the polymer and the foam after a climatic treatment, measuring the force necessary to remove the foam by means of a peel test and without applying any type of RA in the interface. All these investigations corroborated that a high roughness in the substrate translates into a greater surface where bonds between materials can be formed, increasing the adhesion capacity and, therefore, making it difficult to unstick.

A recent study has proposed, as a solution to the problem of foam adhesion in metal molds, the application of nonstick coatings (Sánchez-Urbano *et al.*, 2018). This complete work had as objective the proposal of various fluoropolymeric, sol-gel or elastomeric coatings, all of them materials that improve the release of PUR by having low surface energy and nonstick properties even under demanding chemical, mechanical and thermal conditions. Thus, they proposed techniques for measuring the surface roughness (Ra, Rz), sliding angle of fluids over it ( $\theta_s$ ) and detachment force ( $F$ ) of the PUR foam from this surface, also measuring the condition of the coatings against isocyanate, one of the main components of PUR which could even chemically attack the coating. Molds coated with perfluoro-alkoxide (PFA), polytetrafluoroethylene (PTFE) and FEP fluoropolymers were the most suitable, with the lowest values of peel force and sliding angle. Among them, the PFA allowed 1,500 PUR foam molding/demolding cycles run without incident. Despite the excellent results that these fluoropolymers have shown in their behavior with PUR foam, they cannot be used as a filament in FFF 3D printing due to their high extrusion temperature and the impossibility of adhesion between layers, in addition to the fact that it is very difficult to obtain pure PTFE filament, but there are advanced filaments that include it as filler additive for nonsticking purposes (Rajakaruna *et al.*, 2022; Vidakis *et al.*, 2023). Nevertheless, the formation of toxic fumes that would be generated from this material when melted using fused deposition technology should not be omitted either (Sajid and Ilyas, 2017).

An alternative for the manufacture of molds for rapid prototyping could then be the use of easily printable materials by FFF. In this line, Romero *et al.* (2021) evaluated the behavior of molds created by AM with PUR foam. This study focused on improving the surface finish obtained in FFF printed ABS and HIPS specimens, trying to reduce the roughness values by chemical polishing to improve mold release of PUR foam applied over them. Thus, they demonstrated that it is possible to improve the surface quality of both, ABS and HIPS samples by polishing. However, the results obtained in this research work showed that, for the release of the PUR on these two materials, the impact of the degree of surface roughness is minimal compared to the effect caused by the progressive loss of the RA on the mold surface and the degradation that the isocyanate causes as consecutive molding/demolding cycles are applied. Along with this, other recent works have been assessed solutions based on FFF technique for fast prototyping with so diverse part materials such as resins, ethylene vinyl acetate (EVA) or alumina-based ceramics (Bere *et al.*, 2020; Gohn *et al.*, 2022;

Li *et al.*, 2015; Wick-Joliat *et al.*, 2021). The results of all these works confirmed the great importance of the application of diverse treatments for the surface finish of the manufactured molds to avoid the appearance of the printing lines typical of the FFF technique on the surface of the molded product. However, some of them corroborated that mold surface roughness is not as important when it comes to molded products such as heating elements (ceramic), in which rough surfaces are not a problem or products made with soft foamed polymers such as EVA. In the case of PUR foam molding, the composition of the foamed material itself and the composition of the RA allows to obtain more or less porous, smooth or clear surfaces on the molded part in addition to facilitating the extraction, regardless of the surface finish of the mold (Schröder, 1988).

Besides, in addition to roughness, certain characteristics on the surface of the materials used to manufacture molds determine the release of PUR foam, mainly surface energy of the mold material. In this line, Majewski and Hopkinson (2007) showed that the higher the surface energy, the worse the foam extraction. By experimenting with substrates made of different polymers with lower or higher surface energy in contact with PUR, they were able to verify that, if a material cannot completely wet the surface of the mold, which occurs with materials with low surface energy, it will adhere less strongly. However, in the case of FFF printed molds for rapid prototyping of PUR foam parts, treatments to improve and reduce surface roughness could be avoided with the use of a low surface energy material combined with the action of a suitable RA. Additionally, a surface with a certain level of roughness will allow the RA to remain better on the mold surface, improving its effectiveness over more molding cycles.

Today, the use of RAs in the manufacture of PUR foam components is unavoidable to achieve the correct release of the formed part. These substances must be applied in the form of a viscous liquid or greasy paste, creating a separating layer between the surface of the mold and the PUR foam that lasting a limited number of cycles (Majewski and Hopkinson, 2007). On the other hand, some of these compounds are based on highly volatile organic formulations (solvents) that can be harmful to health. Thus, although they are practically essential, it is necessary to evaluate and improve their durability and efficiency to avoid the environmental and health impact that they can cause, in addition to the additional economic cost that their use entails. For this reason, PUR manufacturers are increasingly demanding mold release products with low environmental impact and high efficiency. There are some previous studies that have demonstrated the economic and environmental viability of water-based mold RAs, but the presence of water can cause an unwanted reaction with the isocyanate, worsening the quality of the foam, as well as affecting corrosion in metallic molds (Liang *et al.*, 2022; Masateru and Haruyuki, 2009; Rigby, 2000).

This work proposes a way to apply AM in the field of rapid tooling of molds for rapid prototyping of PUR molded parts. Thus, this new path has proposed the use of commonly used thermoplastic materials, whose performance can be improved through post-processing and using mold RAs. The present work, unlike others, proposes the use of PETG filament and two different types of PLA filament for the manufacture of a mold that will be used in combination with two types of RAs thus

avoiding the need for superficial post-processing treatments, to finally manufacture a PUR part. The experimental study has allowed us to conclude that the combination of PLA with different types of RA is viable, allowing a satisfactory quality to be obtained when one or two units of the designed part are intended to be manufactured.

**2. Materials and methods**

**2.1 Design of experiments**

A design of experiments (DoE) has been proposed to evaluate three different materials as PLA, hardenable polylactic acid (PLA 3D870) and PET, in combination with both a water-based and solvent-based RAs. Besides, and to reduce the effect of possible erroneous measurements, each of 6 possible material/RA combinations has been reiterated for 3 times in the experiment for a total of 18 runs. Then, once the RA has been applied on the virgin surface of the specimen, each run consisted of a sequence of 3 consecutive molding/demolding cycles with the corresponding pull-off test, constituting a total of 54 pull-off tests that are summarized in the Table 1.

In each case, the specimen has been impregnated with RA only once, at the beginning of the sequence. Then, it has been subjected to direct contact with the molded PUR to be detached by means of a tensile force, repeating the operation in a sequence of three consecutive molding/demolding cycles and measuring the pull-off force (*F*) evolution in each cycle. The methodology for this work has been summarized in Figure 1.

Once the specimen has been printed for each of the experiments, quality has been checked. The diameter and the flatness of the contact surface object of study has been manufactured with a maximum tolerance of ±0.1 mm, in both cases and the absence of defects in the specimen was also verified (delamination, shrinkage and lack of union between layers). Then, its surface roughness has been then measured. Next, wettability has been characterized by means of the sliding angle measurements ( $\theta_s$ ), determining the impregnability of the

substrates. Following with the specimen preparation, contact surface has been carefully cleaned with air and a thin, even layer of RA has been applied. Subsequently, the specimen must be mounted on site in the mold and then a dose of PUR foam can be prepared and mixed to fill the mold, which will then be closed and introduced into an oven at about 55°C–60°C for 7 mins. Then, the mold is allowed to cool at room temperature for 5 mins before proceeding to the measurement of the pull-off force. A sequence of three consecutive molding/demolding cycles has been applied on each experiment to appreciate the evolution of the takeoff force, tension and energy required for the demolding of the specimen applying RA only once and at the beginning of the experiment. In the flowchart, the “c” is a counter of molding/demolding cycles variable and *c* = 0 at the beginning of the experiment with a new specimen. Once the surface is impregnated at the beginning, before successive molding/demolding cycles, the “c” counter increases its value for each cycle up to *c* = 3. Finally, the % of adhered foam on the contact surface under study after the third cycle and, after cleaning the foam rests, the affectation of the surface and surface roughness has been determined. This procedure is repeated for each experiment.

**2.2 Fabrication, surface characterization of the specimens and release agents**

The geometry of the attachable specimen and the metal support have been modeled using the SolidWorks CAD software application (Dassault Systemes, Vélizy-Villacoublay, France). The design of the specimen allows its assembly/disassembly by means of a mechanical coupling in the traction support as indicated in Figure 2.

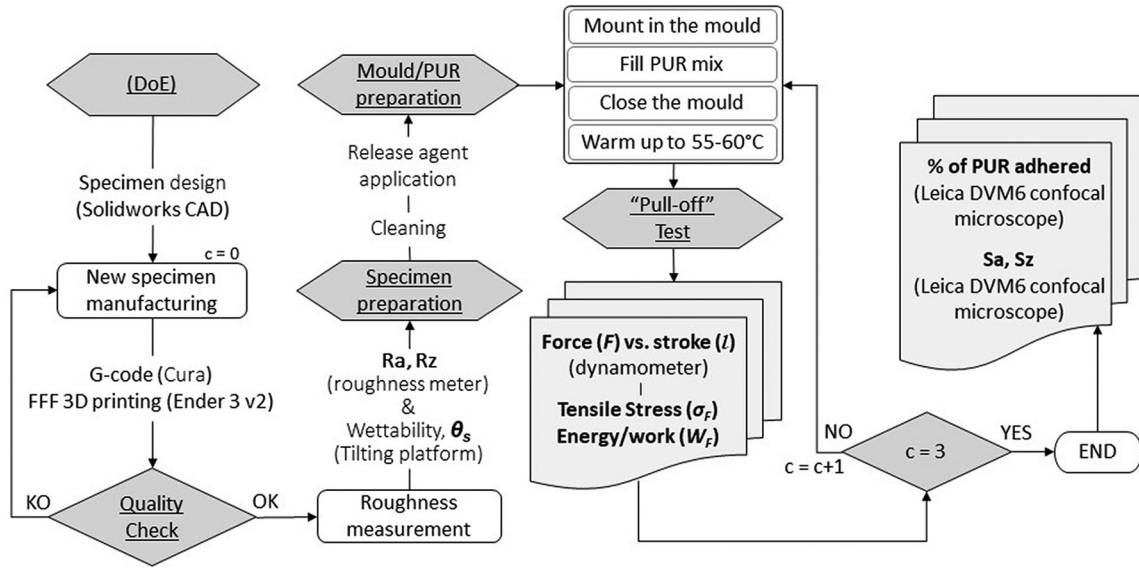
Once modeled, an STL file has been generated and later imported in the Cura v. 5.2.1 (Ultimaker B.V., Utrecht, The Netherlands) to obtain the ISO-G code for the Ender 3 v.2 3D printer (Creality 3D Technology, Shenzhen, China). The PETG, PLA and PLA 3D870 filaments used are 1.75 mm in diameter (Smartfil, SmartMaterials, Alcalá la Real, Jaén, Spain). The specimens have been printed in the horizontal position, with the flat

**Table 1** Design of experiments (DoE): materials, sequences and reiterations

Material	Release agent	“Pull-off” test Nr.	Reiterations
PETG	Ecolease (water-based)	1 (application of release agent)	3
		2	3
		3	3
	Gorapur (solvent-based)	1 (application of release agent)	3
		2	3
		3	3
PLA	Ecolease (water-based)	1 (application of release agent)	3
		2	3
		3	3
	Gorapur (solvent-based)	1 (application of release agent)	3
		2	3
		3	3
PLA 3D870	Ecolease (water-based)	1 (application of release agent)	3
		2	3
		3	3
	Gorapur (solvent-based)	1 (application of release agent)	3
		2	3
		3	3

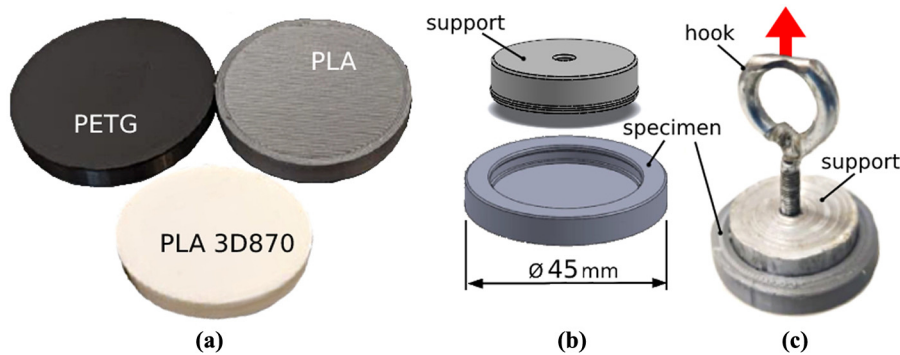
Source: Table by authors

Figure 1 Flowchart of the experimental methodology proposed for each run



Source: Figure by authors

Figure 2 Attachable specimen system



Notes: (a) Materials; (b) support system with mechanical coupling; (c) specimen/support/ traction hook assembly

Source: Figure by authors

surface resting on the printer table, and implementing a pattern with parallel lines by the printing conditions defined in Table 2.

To determine the sliding angle ( $\theta_s$ ) in the materials object of study, a device with a tilting platform driven by a stepper motor and controlled by CNC Mach3 software (Newfangled Solutions LLC., Livermore Falls, ME, USA) has been used, programmed at a constant speed of 20°/min. Thus, for sliding angle measurement, a drop of the liquid (demineralized water, water-based mold RA and solvent-based mold RA) has been deposited on the specimen surface with an adjustable micropipette. A Mitutoyo Pro360 digital goniometer (Mitutoyo Corporation, Kawasaki, Kanagawa, Japan), attached to the platform, indicates the angle with an accuracy of 0.01° just when the drop begins to slide over the surface. The drop volumes studied have been 50 and 100  $\mu$ l, for all the liquids tested. Thus, the impregnability of each material with each liquid was determined.

Prior to the different destructive tests, the surface roughness of the specimens printed has been measured in each of the three

Table 2 Printing parameters used in the manufacture of the specimens

Parameter	PETG	PLA	PLA 3D870
Nozzle diameter (mm)	0.4	0.4	0.4
Layer height (mm)	0.2	0.2	0.2
Extrusion temperature (°C)	235	220	220
Bed temperature (°C)	90	60	60
Fill density at the bottom (%)	100	100	100
Fill density on the wall (%)	100	100	100
Fill pattern	Lines	Lines	Lines
Fill density (%)	100	100	100
Number of bottom layers	12	12	12
Bottom thickness (mm)	2.4	2.4	2.4
Printing time	1 h 13 m	52 m	52 m
Filament weight (g)	8	7	7
Filament length (m)	2.53	2.26	2.26

Source: Table by authors

materials under study. Thus,  $R_a$  and  $R_z$  have been determined in the contact surface of the specimen by a Mitutoyo SJ-201 contact roughness meter (Mitutoyo Corporation, Sakada, Japan). Roughness parameters have been measured in the parallel and perpendicular directions with respect to the printing direction on the contact surface of the specimens according to UNE-EN ISO 21920-3:2023 standard (International Organization for Standardization, 2023a). According to the specifications of UNE-EN ISO 21920-2:2023 standard,  $R_a$  is defined as the arithmetic mean height of the absolute values of the profile deviations from the mean line of the roughness profile and  $R_z$  is the maximum value of the difference between the highest ordinate value and the lowest ordinate value calculated within a section of length  $l$  moving over the evaluation length ( $l_e$ ). It must be noted that the SJ-201 roughness meter has been configured at its maximum evaluation length  $l_e = 12.5$  mm corresponding to a cut-off  $\lambda_c = 2.5$  mm because all the expected values or  $R_a$  are higher than  $2 \mu\text{m}$ . Thus, the mean values of  $R_a$  and  $R_z$  were determined by performing a total of five reiterations of the measurement in different zones throughout the entire surface area of the specimen.

Besides, areal surface roughness  $S_a$ ,  $S_z$  have been measured as a reference in the virgin specimens (raw specimens) using Leica DVM6 confocal microscope and Leica Map Start software (Leica Microsystems S.L.U., Barcelona, Spain), according to the UNE-EN ISO 25178-2:2023 standard (International Organization for Standardization, 2023b). Subsequently, the changes in the final state of  $S_a$ ,  $S_z$  after three cycles of foaming/molding/demolding have been analyzed to evaluate the effect that the whole process produced on the surface of the specimen. It must be noted that this technique has been able to be used after carrying out a thorough cleaning of the remains of foam adhering to the surface.

At the beginning of each experiment and just before placing the specimen in its housing in the mold lid, the contact face that goes into the mold has been manually impregnated with a thin and homogeneous layer of RA. The mold RA has only been applied before the first foaming/release cycle because it is desired to observe the durability of its effect during three consecutive cycles over the same specimen.

The RAs used have been one aqueous-based (Ecolase 03 3580 J5W) and another solvent-based (Gorapur LK 8910-7B),

both supplied by Grupo Copo (Grupo Copo, Vigo, Spain). Gorapur (Evonik Industries AG, Essen, Germany) has been formulated as a dispersion in iso-paraffin-based solvents that may be flammable at a relatively low temperature and harmful by inhalation, with very good impregnability resulting in higher efficiency in the number of cycles per application; while Ecolase (Logco Manufacturing, Elland, UK) is based on a water emulsion with environmentally friendly components, fully biodegradable, free of volatile organic compounds (VOCs) and with an ignition temperature above  $100^\circ\text{C}$ , showing a good impregnability and efficiency in cycles per application. In all cases, a thin layer of RA was applied with a brush and removing the excess carefully.

### 2.3 Fabrication and molding of polyurethane foam

Figure 3 shows a schematic of the procedure corresponding to one experiment, from mixing and filling to closing, the growth of the foam inside the mold and the measurement of the “pull-off” force required to separate the specimen in contact with foamed PUR.

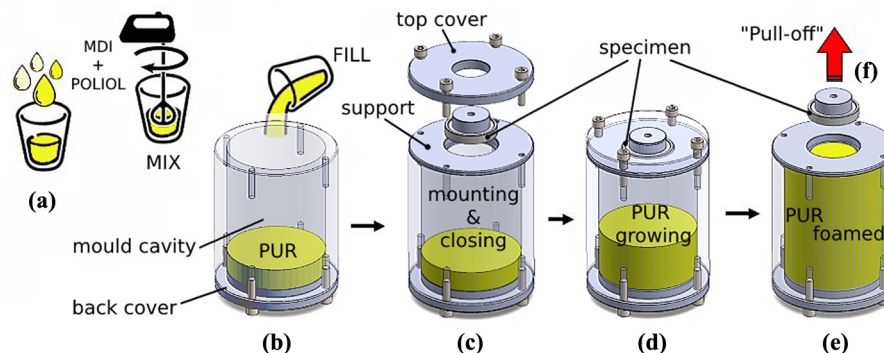
Diphenylmethane diisocyanate (MDI) and polyol (Grupo Copo, Vigo, Spain) were used to form the PUR foam, and it must be mixed in a 100/50 ratio (polyol/MDI) according to the supplier’s instructions. The mold used for the “pull-off” test, made of aluminum alloy, and coated with a PFA formula as an anti-adherent in its interior cavity, has a volumetric capacity of  $500 \text{ cm}^3$ . After several tests to determine the better mixture proportions, exactly a mass of 19 g of MDI isocyanate and 36.86 g of polyol has been used, adequate for the correct filling of the mold cavity.

### 2.4. “Pull-off” force, stress, work and quantity of adhered foam

The evolution of the required “pull-off” force ( $F$ ) to detach the specimen from the molded PUR foam has been recorded by the Imada MX2 500 N vertical motorized test bench, equipped with a digital load meter model DS-2 of up to 100 N (Figure 4).

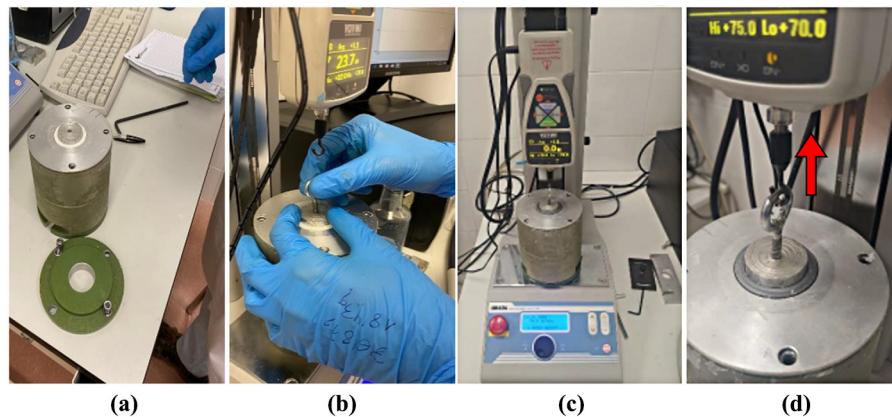
This equipment, that is connected to a computer with the Force Recorder Professional software (Imada Co. Ltd., Toyohashi, Aichi, Japan), has allowed recording the information corresponding to the evolution graphs of “pull-off” force ( $F$ ) vs displacement in all the experiments programmed in the DoE.

**Figure 3** Procedure for the “pull-off” test on the specimen



**Notes:** (a) Mixing; (b) filling; (c) mounting and closing; (d) growth of the foam; (e) “pull-off” test

**Source:** Figure by authors

**Figure 4** Adhered specimen preparation and “pull-off” test


**Notes:** (a) Specimen release; (b) hook placement; (c) bench mounting; (d) “pull-off” test

**Source:** Figure by authors

The contact diameter between the specimen and the foamed PUR inside the cylindrical mold has been defined by the dimension of the opening in the specimen mounting lid-bracket, which is 42.7 mm.

These experiments allowed to measure the takeoff force ( $F$ ) vs displacement ( $l$ ), and the evolution of the pull-off stress ( $\sigma_F$ ) necessary to detach each specimen in contact with the PUR foam has been determined as a function of the maximum force ( $F$ ) required and the contact area ( $a$ ), in the sequence of three consecutive molding/demolding cycles applied on each specimen. Thus, the evolution of the equivalent detachment work ( $W_F$ ) has been determined in N.mm and is equivalent to the energy consumption for demolding, expressed in milli-Joules (mJ).

To determine the percentage of PUR foam adhered to the specimens (% PUR), once three foaming and “pull-off” consecutive cycles had been carried out, high-quality two-dimensional images have been taken using the Leica DVM6 confocal microscope (Leica Microsistemas S.L.U., Barcelona, Spain), resting the specimen onto a green cardboard to facilitate later image editing. The images have been processed with Adobe Lightroom software (Adobe Systems, Inc., Mountain View, CA, USA) to improve the contrast of the foam adhered on the specimen surface. Once treated for maximum contrast, the images have been analyzed using Image Pro-Plus software (Media Cybernetics, Inc., Rockville, MD, USA), an application that has a plugin extension capable of differentiating colors within an image to determine what is the percentage of each tone with respect to the total of a certain area.

### 2.5 Case study: mold for the manufacture of a “cushion” foamed in polyurethane

Once the best material and RA have been determined, a mold has been designed for the manufacture of a PUR foam cushion or seat on a 1:6 scale. For this, the CAD Solidworks software has been used, through which the two parts of the mold (cavities) have been generated from the model of the part to be molded. Thus, this mold, manufactured by 3D printing on the Ender 3 V2 printer, has been tested manufacturing three units of the part checking its functionality and durability. To do this,

the total volume of mixture necessary to generate the foamed part has been determined. At first, the cavities and closing surfaces of the mold have been impregnated with the selected RA to immediately proceed to pour the mixture inside the cavity and close the mold, keeping it with closed by a clamping screw. The mold has remained in an oven for 7 mins at 60°C to ease the reaction, before letting it cool and proceeding with demolding of the final part.

## 3. Results and discussion

### 3.1 Initial characterization of the specimens

Initially, the manufactured specimens have been characterized, determining their surface roughness and surface wettability in contact with pure water, the water-based RA or the solvent-based RA that are the object of this study.

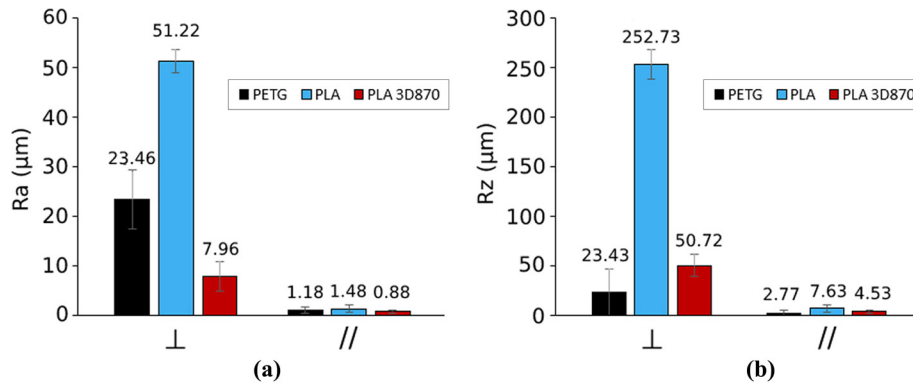
The bar charts of [Figure 5](#) show the roughness values  $R_a$  and  $R_z$ , measured in the parallel and perpendicular directions with respect to the printing direction on the contact surface of the virgin specimens. [Figure 6](#) shows the results obtained for the sliding angles ( $\theta_s$ ) measured on the different surfaces.

The measurement of the sliding angle ( $\theta_s$ ) of the distilled water and of the two different types of RA used in the study is of great interest to determine the possible correlation that this characteristic may have with the ease release of the PUR on the surfaces impregnated with these RAs. In addition, it is interesting to know the capacity of each of the RAs to impregnate in a homogeneous way and remain on the surface during several consecutive molding/demolding cycles. Thus, while PLA 3D870 has shown the worst ability to retain water, however, a better behavior has been observed in PLA and PLA 3D870 with RAs because higher values of the sliding angle ( $\theta_s$ ) have been recorded for this material than those obtained in PETG. In PLA 3D870, when the droplet size is larger (amount of RA), the retention/impregnation of the RA onto the surface is even better.

### 3.2 Determination of pull-off force, tensile stress and required energy

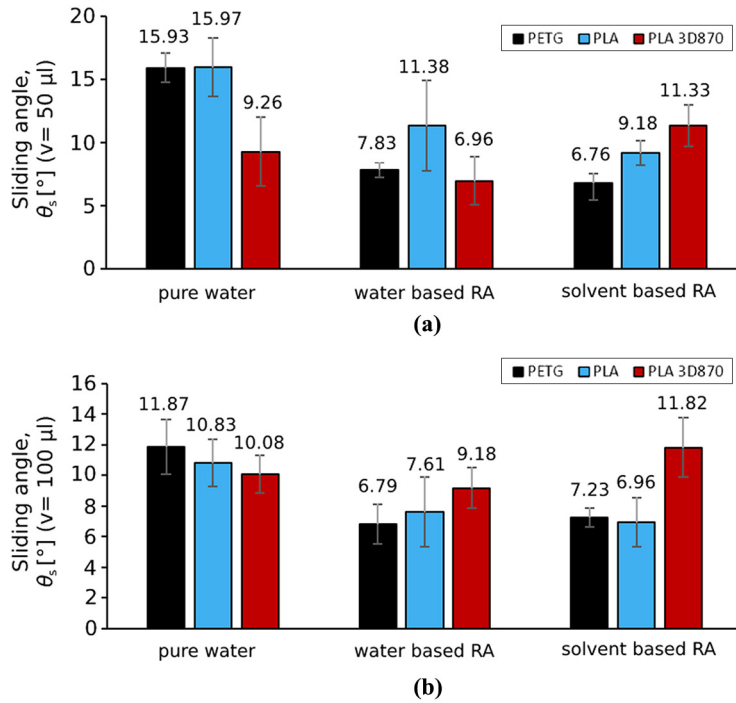
In a second phase, the proposed DoE has allowed the use of up to six different combinations from the three filament materials

**Figure 5** Roughness (Ra, Rz) measured on the virgin specimens



Source: Figure by authors

**Figure 6** Sliding angles ( $\theta_s$ ) measured for pure water, the water-based release agent and the solvent-based release agent



Notes: (a) For a 50 µl drop; (b) for a 100 µl drop

Source: Figure by authors

(PETG, PLA and PLA 3D870) and the two types of RAs (Ecolase 03 3580 J5W water-based and Gorapur LK 8910-7B with solvent base) used for the manufacture and testing of the specimens.

A summary of the results concerning detachment force ( $F$ ) stress ( $\sigma_F$ ) and the required energy/work ( $W_F$ ) measured in the experiments is shown in Table 3.

From these data, it can be anticipated that the pull-off force ( $F$ ) starts low and remains the lowest in the case of PLA 3D870 with solvent-based Gorapur, with low required stresses and the

lower total energy/work in the sequence of three molding/demolding cycles.

Thus, to determine these results that characterizes the performance of these materials in the molding of PUR foam, tensile tests have been performed recording “pull-off” force vs displacement. Thus, after reiterating the test three times for each of the material/RA combinations, force vs displacement graphs have been obtained showing the evolution of the average “pull-off” force ( $F$ ) in a sequence of three consecutive foaming/molding/demolding cycles made on the specimen initially



**Table 3** Summary of the results obtained for the mean values of pull-off force ( $F$ ), stress ( $\sigma_F$ ) and energy/work ( $W_F$ ) measured in the experiments

Cycle Nr.	Material	Release agent	Force (N)	Stress (kPa)	Energy/work (mJ)
1	PETG	Gorapur (solvent-based)	2.87	2.00	1.74
2			17.13	11.96	35.30
3			39.33	27.47	92.24
1	PETG	Ecolease (water-based)	2.93	2.05	1.02
2			54.50	38.06	116.54
3			61.47	42.92	184.31
1	PLA	Gorapur (solvent-based)	5.43	3.79	8.18
2			12.17	8.50	22.11
3			24.13	16.85	44.30
1	PLA	Ecolease (water-based)	3.80	2.65	2.66
2			12.67	8.85	24.89
3			17.13	11.96	27.51
1	PLA 3D870	Gorapur (solvent-based)	1.13	0.79	0.63
2			2.63	1.84	2.36
3			8.80	6.15	17.98
1	PLA 3D870	Ecolease (water-based)	1.67	1.16	0.93
2			8.27	5.77	8.94
3			16.67	11.64	17.98

Source: Table by authors

impregnated with RA. The results obtained are shown in Figure 7.

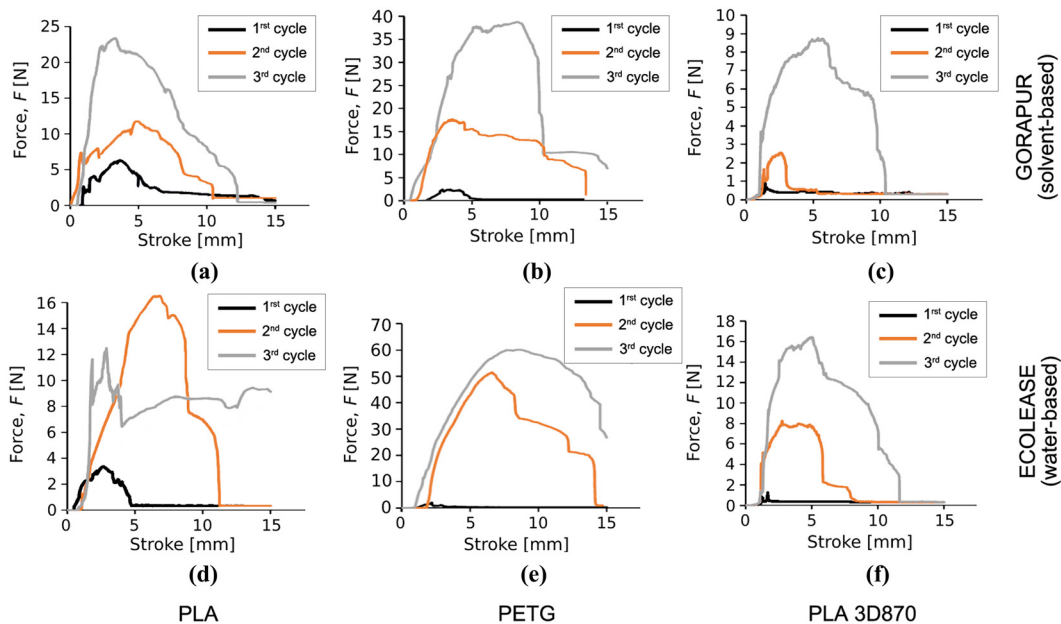
From the pull-off measurements, it has been observed that in the first “pull-off,” when the RA has just been applied to the specimen, the force in the different materials and RAs present lower values in PETG and PLA 3D870 (Figure 7, black color records). However, after the second and third foaming cycles,

the RA that remained on the surface is gradually lost and therefore the force increases considerably, but in a much more pronounced way in the case of PETG.

Figure 8 shows a comparative summary of the “pull-off” stress values ( $\sigma_F$ ) compared with those obtained without any RA.

The RA loses its effect quickly in the PETG + Ecolease (water-based RA) combination, which goes from a value of

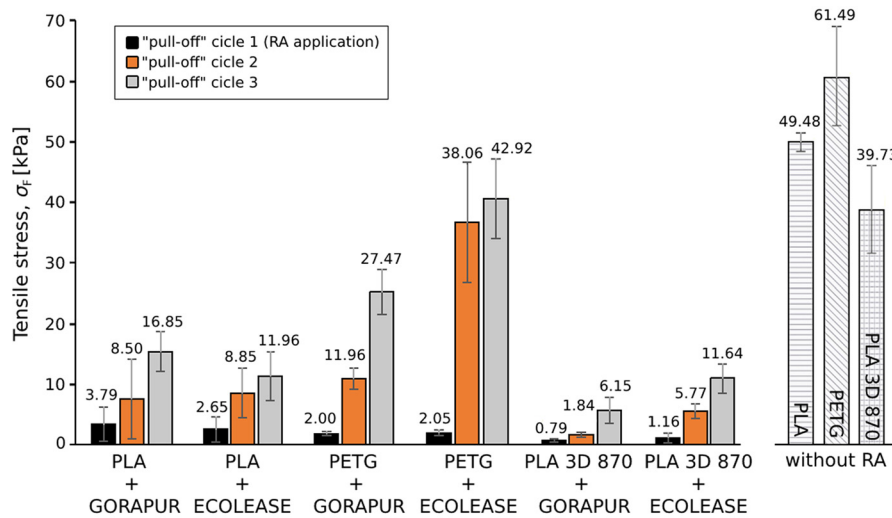
**Figure 7** Evolution of the mean value of the “pull-off” force ( $F$ ) recorded during the three “pull-off” tests, for the different material/release agent combinations



**Notes:** (a) PLA/solvent-based; (b) PETG/solvent-based; (c) PLA 3D870/solvent-based; (d) PLA/water-based; (e) PETG/water-based; (f) PLA 3D870/water-based

Source: Figure by authors

**Figure 8** Comparison of the maximum values of the mean “pull-off” stress ( $\sigma_f$ ) measured for all the material/release agent combinations and without release agent



Source: Figure by authors

stress of 2.05 kPa in the first pull-off to 42.92 kPa in the third when there is hardly any RA left on the contact surface with the foam. In addition, it is appreciable how the Gorapur RA, solvent-based, presents a better behavior in combination with PLA 3D870 and, however, not with PETG and not so good with PLA. Furthermore, the results have shown that the use of RAs drastically affects the required “pull-off” stress, going from values around 1 and 3 kPa to 62 kPa, 60 times more when these are not used in the process. In this line, Schäfer *et al.* have already demonstrated the high adhesion capacity of PUR in direct contact with different thermoplastic materials such as PA or PET, obtaining “pull-off” stress values between 25 kPa and 60 kPa for these materials (Schäfer *et al.*, 2018). Besides, the low detachment stress in the first “pull-off,” when the RA is present on the surface of the specimen, is agree with the results published by other authors (Ashida, 2006; Romero *et al.*, 2021), in which the ability of the RAs to drastically reduce the demolding force on the PUR foam has been proven.

Romero *et al.* obtained tensile stresses between 12.8 kPa and 28.8 kPa in the first demolding of ABS specimens impregnated with a solvent-based RA in contact with PUR and 14.4 kPa–15.3 kPa with HIPS specimens (Romero *et al.*, 2021), showing worst results in a first demolding than those obtained with any of the materials used in this work (PLA 3D870, PLA and PETG), with any of the materials used in this work, even with any of the two RAs applied.

Figure 9 shows the evolution of the mean value of the work/energy ( $W_F$ ) required to demold the specimen in each of the material/RA combinations.

Again, the material that required the lower energy to detach the specimen in contact with the molded PUR is PLA 3D870 in three consecutive cycles, specifically in its combination with the solvent-based RA Gorapur (17.98 mJ). These values are almost three times lower than PLA and five times lower than PETG with the same RA.

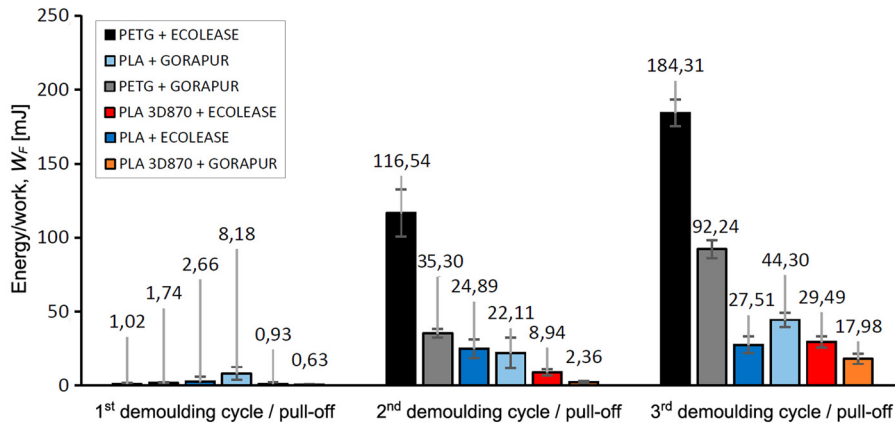
### 3.3 Evaluation of superficial affection

Subsequently, the surface roughness has been measured on each specimen after the sequence of three consecutive demolding cycles, for each of the different material + RA combinations. It must be noted that, before carrying out this measurement, the foam adhering to the surface has been completely removed and the surface has been carefully cleaned with air under pressure. This measurement allowed to observe roughness changes suffered on the contact surface after exposing the materials to the chemical reaction that causes the foaming of PUR. The results obtained for Sa and Sz are summarized in Figure 10.

It has been possible to observe a clear decrease in the values of Sa, Sz after the three foaming cycles carried out on the specimen, in comparison with the values measured on the virgin surface. This effect is produced in the three materials objects of study, although in a much more pronounced way in PETG and PLA 3D870. Thus, in terms of raw surfaces, it has been possible to verify that PLA 3D870 has a significantly less rough surface than the other two manufactured materials. In this sense, it should be noted that this “smoothing” effect could have been produced because of the initial effect of the RA and, mainly because of the chemical attack of the diisocyanate of the mixture of PUR on the surface of the specimen during the whole process sequence. However, this surface smoothing does not improve demoldability in consecutive cycles nor does it improve the quality of the demolded PUR foam surface. It must be noted that recent works concluded that PLA filaments allow obtaining flat surfaces with lower Ra values between 7  $\mu\text{m}$  and 35  $\mu\text{m}$  (Golhin *et al.*, 2023; Heshmat *et al.*, 2023), confirming that the values obtained in the present study, both for Ra and Sa, are of normal quality for this material when processed by FFF.

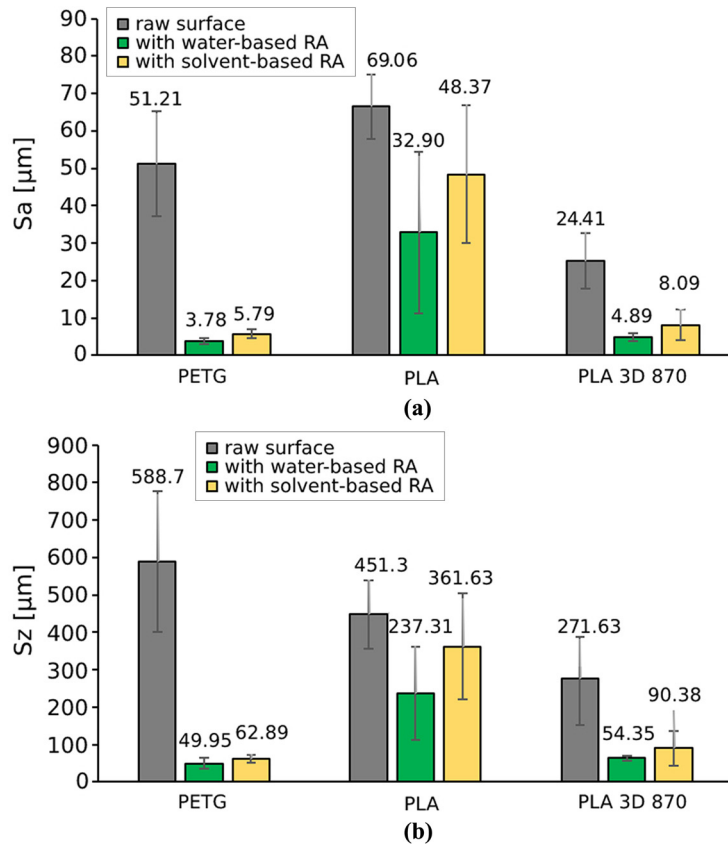
Regarding the possible correlation between the evolution of the surface roughness, defined by Sa, Sz and the values of the detachment force and stress ( $F$ ,  $\sigma_f$ ), it has been

**Figure 9** Evolution of the energy/work ( $W_f$ ) with all the different material/release agent combinations



Source: Figure by authors

**Figure 10** Surface roughness parameters measured on the specimens, after three consecutive cycles of foaming/molding/demoulding



Notes: (a) Sa; (b) Sz

Source: Figure by authors

corroborated that the PLA 3D870 shows a good behavior with low values while PETG, with a similar surface evolution due to the effect of isocyanate, on the contrary, has yielded the higher values of “pull-off” force ( $F$ ) from the second cycle. Normal PLA, which showed higher Sa and Sz values and the worst evolution after the process, however,

has also offered better performance than PETG in the “pull-off” test, although not as good as the PLA 3D870 composition. From these observations, it can be deduced that the chemical effect that the isocyanate of the PUR mixture produces on the PETG surface worsens its release conditions in contact with the PUR.

In the same line, a previous work developed by Majewski and Hopkinson demonstrated that a surface with a higher roughness like PMMA ( $R_a = 0.65 \mu\text{m}$ ) provides a greater surface area over which PUR adhesive bonds may form than PTFE ( $R_a = 0.19 \mu\text{m}$ ), resulting in an overall increase in adhesive force (Majewski and Hopkinson, 2007). This conclusion is agreed with the results of the present work, in which PLA 3D870 ( $R_a \approx 8 \mu\text{m}$ ) has shown the better easy to demold PUR compared to standard PLA ( $R_a \approx 51.22 \mu\text{m}$ ) or PETG ( $R_a \approx 23.46 \mu\text{m}$ ). In addition, Romero *et al.* (2021) also confirmed that the surface roughness of the contact surface is an important factor in the demolding operation of PUR, concluding that substrates printed in ABS and HIPS have less adhesion to the PUR foam when their surface roughness is lower, obtaining the best results for  $R_a \approx 6 \mu\text{m}$  in both cases and very similar to the roughness obtained in the PLA 3D870 specimens of the present work.

Images in Figure 11 shows the appearance of the surface of the specimens once each of the three molding/demolding cycles has been performed.

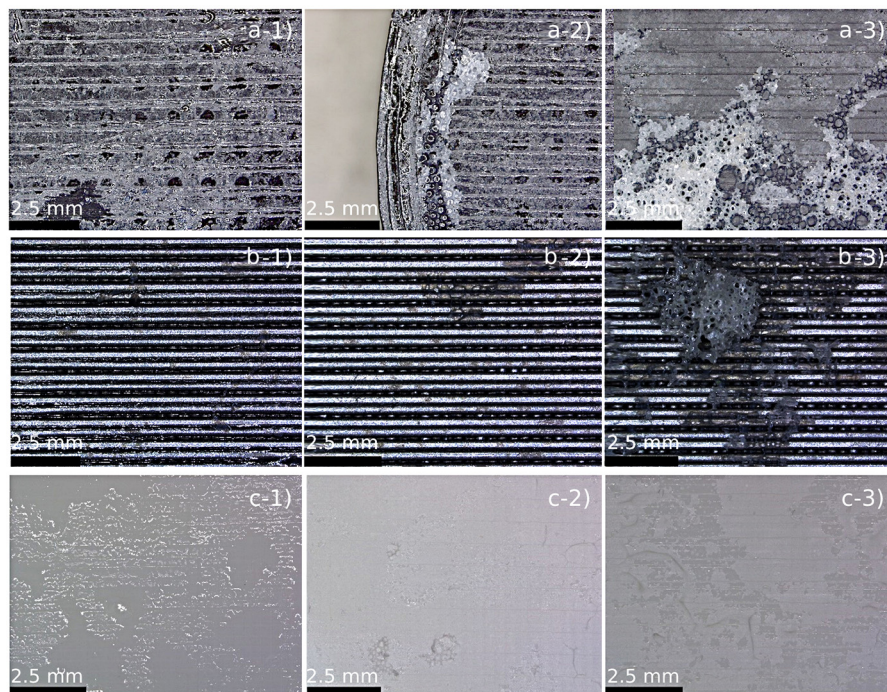
Analyzing the foam adhered to each of the specimens in the images, it has been proven that the material/RA combination that shows the least interaction in terms of anchoring the PUR foam after the three release cycles is PLA 3D870 + Gorapur solvent-based RA [Figure 11(c)]. The results obtained are consistent with the measured “pull-off” force ( $F$ ) and stress ( $\sigma_F$ ) values, also leaving a higher percentage of foam retained in those specimens that have offered greater resistance to demolding or detachment, as shown in Table 4.

In addition, it has been possible to appreciate how the RA, initially applied on the surface, gradually disappears as the successive foaming cycles have been carried out and is replaced by the foam adhered to the surface of the specimen. On the other hand, it has been observed that, after the first “pull-off,” there is still a large amount of RA on the surface, and after the second and third molding cycles, the amount of RA that remains on the surface is minimal. In addition, the Gorapur solvent-based mold produces a very porous finish on the contact surface with the PUR, just after the first foaming/molding/demolding cycle, when it has just been applied to the specimen. This effect caused always by Gorapur is due to the chemical action of the solvent in direct contact with the surface of molded PUR. On the contrary, the use of Ecolease water-based has produced a smoother surface in PUR in contact with the surface of the specimen, in all cases.

On the other hand, previous works have been consulted in which different treatments are proposed to improve the surface quality in parts manufactured using FFF with PLA. In a recent review work, the most common post-processing treatments are cited for improving the surface roughness of parts manufactured in PLA by FFF/FDM. Among these treatments, the use of vapors or immersion in dichloromethane, chloroform or ethyl acetate, although it has been shown that the use of ethyl acetate is more advisable through either of the two techniques with the advantage of its reduced toxicity, availability and economical price (Lavecchia *et al.*, 2022; Mathew *et al.*, 2023).

In the present work, relatively smooth surfaces were obtained for PETG and PLA 3D870, of the order of  $R_a$  between  $8 \mu\text{m}$

Figure 11 Evolution of the foam adhered to the specimens during the three consecutive foaming cycles



Notes: (a) PLA specimen + Gorapur (solvent-based); (b) PETG specimen + Ecolease water-based; (c) PLA 3D870 specimen + Gorapur solvent-based

Source: Figure by authors

**Table 4** Values of area occupied by the adhered PUR foam and percentage of adhered foam in the tested specimens after the sequence of three consecutive molding/demolding

Specimen Nr.	Material	Release agent	Contact area (mm <sup>2</sup> )	PUR area (mm <sup>2</sup> )	PUR (%)	Mean PUR (%)	SD
1	PETG	Gorapur (solvent-based)	1,432	196.69	13.74	8.83	5.74
2				146.71	10.24		
3				36.06	2.52		
1		Ecolease (water-based)		118.27	8.26	12.49	3.71
2				217.83	15.21		
3				200.49	14.00		
1	PLA	Gorapur (solvent-based)		120.35	8.40	10.31	1.67
2				157.43	10.99		
3				165.17	11.53		
1		Ecolease (water-based)		19.79	1.38	4.33	4.87
2				142.45	9.95		
3				23.67	1.65		
1	PLA 3D870	Gorapur (solvent-based)		11.60	0.81	1.23	1.00
2				7.30	0.51		
3				34.08	2.38		
1		Ecolease (water-based)		69.88	4.88	1.97	2.55
2				13.03	0.91		
3				1.58	0.11		

Source: Table by authors

and 24 μm, respectively, for which the possibility of post-processing the surfaces obtained by FFF was raised. Finally, this solution was discarded for several reasons:

- the molding of PUR foam requires the use of RAs for correct release and these agents remain for more work cycles on relatively rough surfaces;
- the PUR foam does not come into direct contact with the surface of the mold but with the interface between RA and polymer, which allows a smooth finish on the molded product;
- the RA produces a slight smoothing effect on the mold when deposited in the surface valleys of the mold; and
- PUR foam products are generally not exposed to direct weathering and are almost always finished with a textile or other covering.

Furthermore, if we analyze the results of this experiment, we can observe that, as a greater number of molding/demolding cycles are applied, the action of the RA and the degradation due to chemical interaction (Figueiredo *et al.*, 2012) causes a considerable decrease in the surface roughness Sa of the substrate, especially in PETG and PLA 3D870 specimens. However, this repeated use implies a progressive loss of the effect of the RA, which significantly affects the force necessary to release the PUR from the mold. In short, it can be concluded that, in this particular case of PUR foam molding, the degree of roughness obtained through the FFF/FDM technique does not negatively affect the quality of the molded part thanks to the predominant effect of the RA.

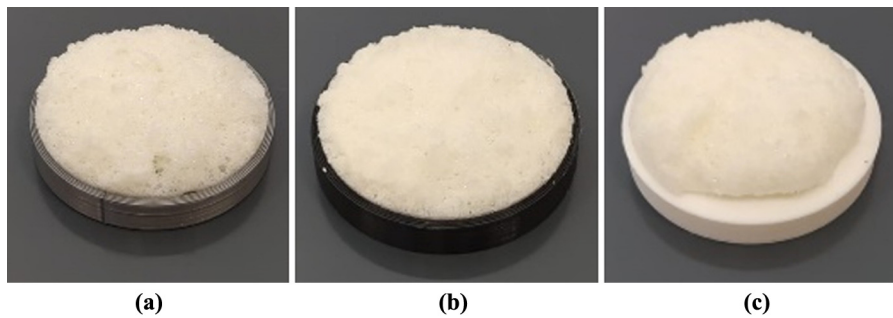
The image of Figure 12 demonstrates that if demolding is accomplished without using any RA, the foam is literally torn off and remains completely fixed on the contact surface of the specimen. Thus, demolding without the prior application of RAs is not feasible with any of these three thermoplastic materials.

Table 4 shows the results of the measurements of the percentage of PUR foam adhered to the contact surface of each of the specimens, per unit area, after the three consecutive cycles of foaming/molding/demolding applied in each case.

A certain correlation emerges between the measured initial roughness values and the amount of adhered foam because the lowest initial values of both Ra, Rz and Sa, Sz have been obtained with PLA 3D870, which is the material that presents the best behavior for its detachment from PUR foam. This observation is in line with the results obtained by Majewski and Hopkinson(2007), which included the roughness of the mold material as one of the key aspects that determined the necessary tensile force to carry out the demolding of the foam, concluding that it is also convenient to increase the level of finishing in the mold to lower the roughness and improve the ease of detachment of the PUR part. Thus, the optimum set of results in terms of less % adhered foam has been obtained for PLA 3D870 + solvent-based RA (1.23%), followed by PLA 3D870 + water-based (1.97%) and, with somewhat worse result PLA + water-based (4.33%). The water-based RA (Ecolease) has given higher values of percentage adhered foam than those achieved with the solvent-based mold RA, when applied to PETG and PLA 3D870, while in the case of PLA standard the opposite has occurred. This effect may be due to the fact that, although the force required in the case of PLA + Ecolease water-based have been slightly lower than those required with PLA + Gorapur solvent-based, PLA + Ecolease held for a longer stroke/time thus requiring more takeoff energy.

In any case, the effect of RAs has been reduced, especially after the second and third work cycles. This reduction it is mainly due to three causes:

- 1 evaporation: during the curing process of the PUR, the solvent evaporates, diminishing the effect of the RA;
- 2 absorption: during the molding process, some of the RAs may get absorbed by the PUR foam being this effect more pronounced in porous or open-cell PUR foam; and

**Figure 12** Specimens after detachment from foamed PUR, without using RA

**Notes:** (a) PLA; (b) PETG; (c) PLA 3D870

**Source:** Figure by authors

3 reaction: mainly in water-based RAs, water reacts with isocyanate producing polyureas, deteriorating/contaminating the mold as a buildup of residue strongly adhered on its surface (Figueiredo *et al.*, 2012).

These causes may worsen the quality of the molded product and the RA's effectiveness on the mold surface may decrease with each cycle (Wypych, 2005).

Definitively, PLA 3D870 + Gorapur solvent-based RA allowed a first release of PUR foam with forces/stresses up to 2.5 times lower than those required by PETG and almost 5 times lower than standard PLA, and up to near 2 times lower than those required by PETG or standard PLA with the Ecolease water-based mold RA. Furthermore, in terms of required energy, once again PLA 3D870 has given the best results both with solvent-based and water-based RA (0.63 mJ and 0.93 mJ, respectively), followed by PLA and finally PETG. The observations about the percentage of PUR foam adhered confirm the PLA 3D870 again as the better choice, with 1.23%–1.97%, in front of the 4.33%–10.31% and 8.83%–12.49% of foam adhered to PLA and PETG specimens, respectively. According to these results, PLA 3D870 could be suitable for demolding PUR foam in combination with a solvent-based mold RA (Gorapur).

### 3.4 Case study: hardenable polylactic acid mold testing

Considering the main conclusion of the study, the molding of a prototype in a mold printed with PLA 3D870 has been proposed, a first manufacturing cycle using solvent-based RA and a second unit molded with water-based RA, to approve the feasibility of the process. For this purpose, a scaled mold has been manufactured. The geometry of the mold cavity has been verified by means of a Metris 3D coordinate measuring machine, with a work volume of 700 × 700 × 500 mm and commanded by the Geopack CNC MCosmos software (Metris N.V., Leuven, Belgium). The check control yielded deviations of less than 1 mm with respect to the original designed model of the mold. Figure 13 shows the scalable mold designed by Solidworks CAD software and printed in PLA 3D870 with the same printing parameter settings used in the manufacture of the specimens tested in the DoE.

For the manufacture of the prototype, the mixture has been also made in the same polyol/MDI ratio used in the experiments. In addition, the volume of the mixture that is appropriate to the

volume of the mold cavity has been calculated to avoid excess of foam. The foaming process has been materialized into an oven at 60°C for 6 mins, and then the mold has been allowed to cool to room temperature before opening it to remove the part. Results showing the obtained prototypes are shown in Figure 14.

In a first test, a part has been molded using the PLA 3D870 + Gorapur (solvent-based) combination, the best option according to the experimental results obtained from the point of view of less effort in demolding. Thus, this RA allowed opening and removal of the part without difficulties, but the part obtained resulted in a porous surface finish. The result of this prototyping can be seen in Figure 14(a).

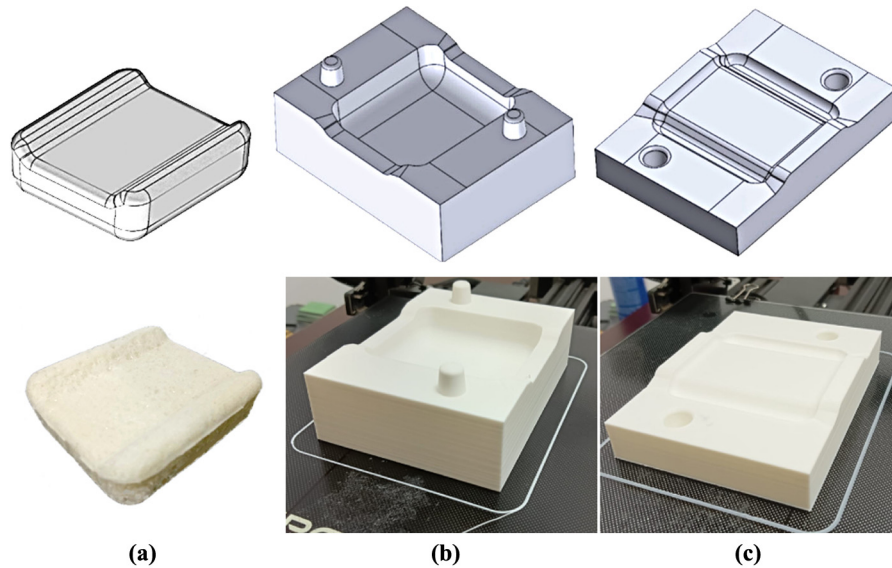
Then, re-using the same mold a second part has been molded, this time using the water-based RA (Ecolease). On this occasion, the foam remained strongly adhered to the edges of the cavity due to the inferior capacity of the aqueous RA to remain on the vertical walls, a fact that complicated the opening of the mold. The part has been able to be extracted from the mold with relative difficulty and the surface finish has been also somewhat porous. This prototype can be seen in Figure 14(b).

Once these results were analyzed, it was concluded that a RA with a higher density seems to offer better results because it is easier to apply than an aqueous one, facilitating the formation of a more homogeneous layer on all surfaces of the mold and maintaining a more homogeneous thickness on all surfaces, including vertical walls, without accumulating on the bottom of the cavities. Consequently, a third part has been manufactured re-using the same mold again, but this time a 50% mixture of a solvent-based mold RA (Gorapur) and a generic mold release grease has been tested. This mixture allowed a better and more homogeneous application and once again the part it has been possible to extract but with relative difficulty. The result in terms of part quality was very similar to that obtained only with the solvent-based RA (Gorapur), as can be seen in Figure 14(c).

It should be noted that, although it has been possible to carry out three manufacturing cycles of the proposed prototype using the same mold manufactured by FFF 3D printing, slight deformations have been accumulated in both parts of the mold that have become accentuated after the third manufacturing cycle. These deformations are minimal, but they have affected the precision of the closing of the parts of the mold.

As the surface finish and the final quality of the manufactured parts do not depend so much on the final finish of the surfaces of

**Figure 13** Mold printed in PLA 3D870, used for the manufacture of the prototype on a reduced scale



**Notes:** (a) Molded part; (b) lower mold; (c) upper mold  
**Source:** Figure by authors

the mold cavity as on the formulation of the polyol/MDI mixture and the type of RA used in the process, the use of inserts or parts of a mold manufactured by the FFF AM technique with this type of PLA formulation has been definitely postulated as an advantageous alternative for rapid prototyping of PUR foamed/molded parts. Thus, the present work demonstrated that, through the prototyping of tools for molding PUR foamed parts made of materials such as PLA 3D870 and thanks to AM by 3D FFF printing, engineers can refine and optimize the design of the mold parts, carrying out real tests at a very low cost.

#### 4. Conclusions

In this study, the feasibility of a rapid mold making approach using the filament fusion 3D printing (FFF) technique with commercial PETG, PLA and hardenable PLA filaments for rapid prototyping of PUR foam parts has been demonstrated.

Different material and RA combinations were tested, and a full DoE has been proposed to evaluate the ease and efficiency in the process of PUR foam molding/demolding. Raw surface characterization showed that PLA 3D870 specimens, allow to print mold surfaces with the lowest roughness ( $R_a = 7.96 \mu\text{m}$  in the direction perpendicular to the filament vs 51.22 for PLA and 23.46 for PETG), which has allowed the PUR foam to be detached and demolded more easily.

Although PLA 3D870 has shown the worst ability to retain water, it is the one that best retains the RAs used together with the standard PLA, showing a sliding angle ( $\theta_s$ ) in contact with RAs that is practically double that of PETG. In PLA 3D870, when the amount of RA is higher, the retention/impregnation is even better. In this sense, it has been demonstrated that is not possible to adequately release PUR from the materials under study without using one of the two RAs.

Regarding the ease of demolding the PUR foam, PLA 3D870 impregnated with the solvent-based RA Gorapur has

shown the best response in terms of the required pull-off force ( $F$ ) and stress ( $\sigma_F$ ), resulting  $\sigma_F = 6.15 \text{ kPa}$  in the third cycle, while for PLA and PETG the stress values were ranging from 16.85 kPa and 27.47 kPa with the same RA, respectively. Also, the same printing material worked well with Ecolease, a water-based mold RA, offering detachment stress values from  $\sigma_F = 1.16 \text{ kPa}$  in the first molding/demolding cycle to  $\sigma_F = 11.64 \text{ kPa}$  in the third cycle.

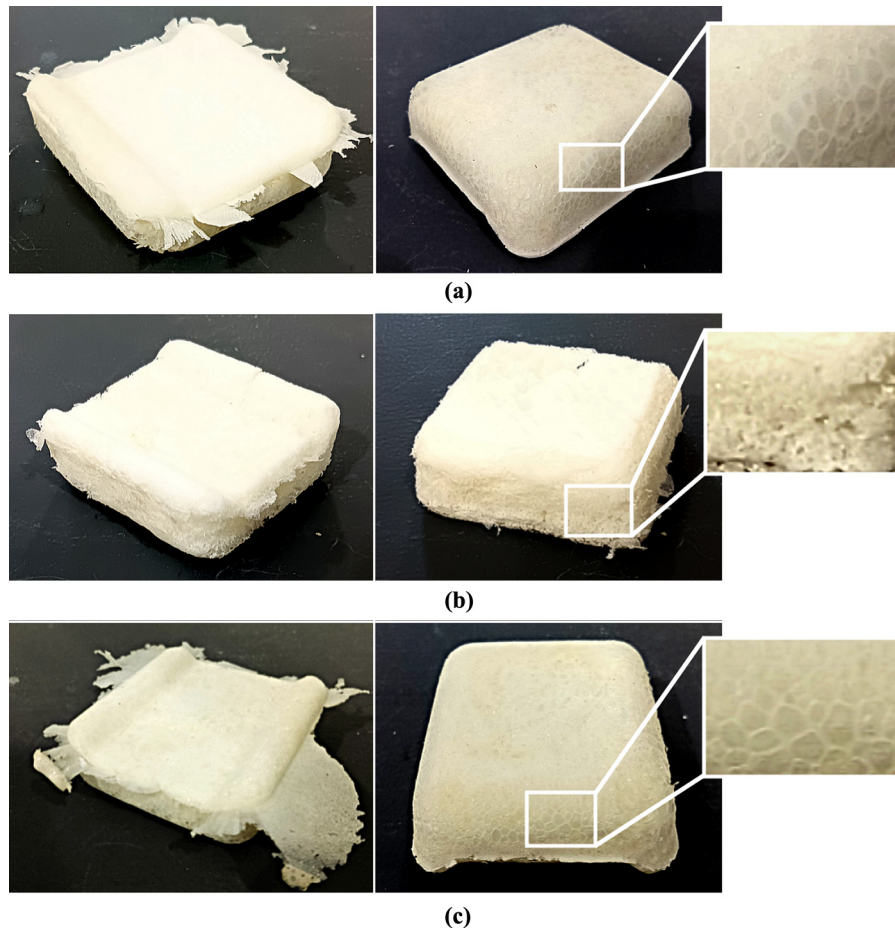
Again, PLA 3D870 required the lower energy to detach the specimen in contact with the molded PUR in three consecutive cycles, but specifically in its combination with the solvent-based RA Gorapur (17.98 mJ in the third cycle). These values are approximately three times lower than PLA (44.30 mJ in the third cycle) and five times lower than PETG (92.24 mJ in the third cycle) with the same RA.

Observations of the surface affectation and measurements of the percentage amount of adhered foam in the contact surface area of the specimens have confirmed the best performance of PLA 3D870 as a rapid tooling material for PUR foam molding.

The execution of a mold made by FFF with PLA 3D870 allowed to test prototyping of a molded product. In this test, the results obtained with PLA 3D870 combined with Ecolease water-based RA have been practically just as good as those obtained with Gorapur for a single foaming cycle. In the process, it has been observed that the use of the water-based RA (Ecolease) provided a softer and less porous surface finish compared to the solvent-based RA, with the advantage that this type of RA is more respectful of the environment and health as it does not contain VOCs. On the other hand, slight deformations have become accentuated after the third manufacturing cycle. These deformations are minimal, but they affect the precision of the closing of the mold after 2–3 cycles.

The present work has been demonstrated that the combination of PLA 3D870 with this type of RAs represents an

**Figure 14** Results obtained in the rapid prototyping of the scalable model in a PLA 3D870 mold impregnated with (a) solvent-based mold release agent, (b) water-based mold release agent and (c) a mix of solvent-based mold release agent and 50% release grease



Source: Figure by authors

effective solution for rapid prototyping and single-use mold making in the field of PUR foam products. These results have important implications for rapid prototyping and the manufacture of low-cost and environmentally friendly moulds.

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