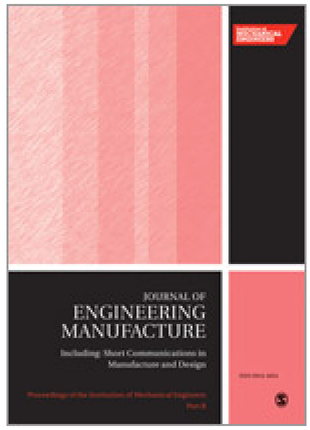

Soft 3D Printing of Thermoplastic Polyurethane: Preliminary Study

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Keywords:	Rapid Prototyping < Optimisation, Additive Layer Man < Optimisation, Assembly, Process Modelling & Planning < Optimisation, Manufacturing Management < Optimisation
Abstract:	Thermoplastic polyurethane (TPU) is a highly elastic linear polymer composed of soft segments, usually flexible polyester, or polyether. It is widely used in 3D printing technologies, being FFF the most common technique. However, stiffness and hardness values of 3D printed TPU in filament form are higher that it would be desirable for some applications, which require softer parts. Therefore, it was seen necessary to find a new methodology for 3D printing soft TPU. In this way, the present study seeks to be the first research study which focuses on the possibility of 3D printing TPU using DIW (Direct Ink Writing) technology with UV light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. Then, both bulk and 3D printed TPU samples were characterized in terms of shear strength using the Warner-Bratzler shear test and hardness using the Shore hardness test. It was seen that the 3D printed samples showed higher softness than bulk samples as well as in comparison with TPU filament. Finally, it was concluded that the 3D printing of TPU is challenging due to several points: (1) the viscosity of the TPU; (2) their

	main issue is their sticky behavior; and (3) the shrinkage which takes place after the thermal treatment and for some applications, it might be a problem. Despite that, TPU appears to be a promising material to be used in different industrial applications.

Soft 3D Printing of Thermoplastic Polyurethane: Preliminary Study

F. Fenollosa-Artes [1,2], L. Jorand [1], A. Tejo-Otero [1], P. Lustig-Gainza [1], G. Romero-Sabat [3], S. Medel [3], R. Uceda [1,2]

[1]*Centre CIM, Universitat Politècnica de Catalunya (CIM UPC), Carrer de Llorens i Artigas, 12, 08028, Barcelona, Spain*
[2]*Universitat Politècnica de Catalunya. Departament of Mechanical Engineering. School of Engineering of Barcelona (ETSEIB). Av. Diagonal, 647. 08028, Barcelona, Spain*
[3] *Polymer Synthesis Unit, Leitat Technological Center, Carrer Innovació, 2, 08225 Terrassa, Barcelona*

Abstract

Thermoplastic polyurethane (TPU) is a highly elastic linear polymer composed of soft segments, usually flexible polyester or polyethers. It is widely used in 3D printing technologies using FFF (Fused Filament Fabrication), SLS (Selective Laser Sintering) or inkjet printing. Among these options, FFF is the most common. However, stiffness and hardness values of 3D printed TPU in filament form are higher that it would be desirable for some applications, which require softer materials. Therefore, it was seen necessary to find a new methodology for 3D printing soft TPU. In this way, the present study seeks to be first research study which focuses on the possibility of 3D printing TPU using DIW (Direct Ink Writing) technology with UV light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. It was concluded that the 3D printing of this TPU is challenging due to several points: (1) the viscosity of the TPU; (2) their main issue is their sticky behavior; and (3) shrinkage which takes place after the thermal treatment and for some applications, it might be problem. Despite that ,TPU appears to be a promising material to be used in different industrial applications.

Keywords

3D Printing; additive manufacturing; thermoplastic polyurethane;

Corresponding author

*ffenollosa@cimupc.org

Article Type

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1. Introduction

Since its discovery in 1937 by Otto Bayer, Polyurethane polymers (PU) have advanced until becoming part of our everyday life as both commodities and High-Tech materials. Within Polyurethanes, Thermoplastic polyurethanes (TPUs) are usually randomly composed of linear polymer with flexible soft-chain (soft-domain) segments chemically bonded with low-mobile segments (hard-domain) that act as crosslinking points within the structure. The selection and hard/soft segment ratio can affect significantly the overall polymer behavior as well as producing its well-known versatility. Generally, it offers high elongation, low hardness (45-85 Shore A), moderate tensile strength (5-15 MPa) and elastic modulus (2400 N/mm^2) as well as excellent abrasion and tear resistance [1,2]. Additionally, it appears to have an excellent biocompatibility [3,4].

The use of additive manufacturing (AM) technologies has bloomed up during the last years. There are seven categories, according to ISO/ASTM 52900:2015 [5]: binder jetting (BJ), direct energy deposition (DED), material extrusion (includes FFF-Fused Filament Fabrication- and DIW-Direct Ink Writing-), material jetting, powder bed fusion (includes SLS-Selective Laser Sintering- or SLM -Selective Laser Melting-), sheet lamination and vat photopolymerisation (includes SLA-stereolithography- and DLP-Digital Light Processing).

TPU has mainly been additive manufactured using material extrusion, powder bed fusion and material jetting. Among these technologies the most widely used is material extrusion, specifically FFF, since it is a cost-effective technology. For instance, [6] 3D printed TPU samples with the honeycomb structure using FFF technology. The material is selected due to its impact strength and abrasion resistance and therefore is used to create energy absorbing structures. Also, FFF technology is used to study the adhesion strength between soft TPU and ABS (Acrylonitrile Butadiene Styrene)/ASA (Acrylonitrile Styrene Acrylate) [7] aiming to further investigate the multi-material possibilities of 3D printing. It was found that TPU can adhere to both ASA and ABS, which allows them to be printed together in a multi material 3D printer. According to this study, the adhesion strength was comparable to commercial adhesives. Additionally, [8] 3D printed for the first-time elastomeric PU using vat photopolymerisation technology, in which the material is built and polymerized by UV light.

In recent years, TPU has also been 3D printed using the DIW technology. For instance, Valentine et al. [9] 3D printed TPU with added silver flakes using DIW for the development of soft electronics. Then, Ahmed et al. [10] developed a 3D printed TPU/CNPs strain sensor using

In the medical sector, the use of TPU in filament form for FFF is common. For example, [3] 3D printed TPU filaments containing levofloxacin (LFX) in various concentrations for the production of vaginal meshes. Then, Li et al. [11] additive manufactured medical grade TPU using FFF technology was found to have potential to produce medical devices and surgical tools. Then, [12] manufactured TPU composed of nanocrystalline hydroxiapatite (HA) nanopowder to construct artificial blood vessels.

The mechanical parameters of the 3D printed TPU parts are very rigid and hard, limiting the use of these TPUs for certain applications that require softer materials like the manufacture of surgical planning prototypes requires a material able to be 3D printed as well as soft. Additionally, the FFF 3D printing of TPU is a challenge for several reasons: (1) sometimes the filament is not inserted into the hotend correctly, causing a jam in the knurled pulley of the extruder and the bearing; (2) an excessive filament friction producing a more pressure on the drive gear consequently more filament feed problems can happen as a result; (3) the need to be 3D printed at low temperatures; however, higher is the temperature, the lower is the pressure need to be applied, but the possibility of breaking the filament also increases; (4) difficult to post-process; and (5) hotend intern pressure.

Therefore, it is necessary to look for another TPU AM technology which can reach a higher softness. The solution explored is 3D printing TPU using DIW technology: working with liquids should make it possible to avoid the feeding problems related with soft filaments. An important point is the novelty of this research: it has not been found any previous mention about it the literature, may be due to the intrinsic difficulty about working with too soft materials in 3D printing.

Hence, by taking everything into account, the aim of the present study is to present a soft TPU (softer than standard FFF TPU) to be processed by DIW technology using UV curing light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed.

2. Materials and Methods

2.1. TPU Synthesis

Hybrid UV photocurable thermoplastic Polyurethane (TPU) - acrylate were manufactured following a pre-polymer solution method as follows: Polypropylene Glycol (PPG) with a molecular weight of 1000 g/mol and Tetrahydrofuran (THF) were introduced in a 100 mL 5-neck mini-reactor (Scharlab). The mixture was stirred at 260 rpm and heated to 60ºC in an Argon inert atmosphere to remove possible presence of moisture. Once the set temperature was reached, Isophorone Diisocyanate (IPDI) was incorporated dropwise followed by three drops of Dibutyltin Dilaurate (DBTDL) as reaction catalyst. The Polyol to isocyanate ratio was kept around 0.5:1 to ensure plenty of isocyanate free groups in the prepolymer for further functionalization. The reaction was monitored by FTIR-ATR (Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflection mode) observing the NCO peak at 2272 cm-1(Figure 1, B). Once the NCO peak was not further reduced due to complete reaction between PPG and IPDI (approximately 2 hours), a half of the theoretically required quantity of 1,4-Butanediol (BDO) was introduced with a previously dispersed photoinitiator (Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide). When no more NCO peak reduction was observed from the FTIR spectra again, an acrylic molecule containing both a hydroxyl and a vinyl terminal was added and left to react. Finally, the rest of the BDO was introduced and the completion of the reaction was determined when no free isocyanate was observed. The final ideal chemical structure of the molecule and follow-up of the reaction by FTIR-ATR can be observed in Figure 1A & 1B respectively. To procure a minimal shrinking effect on the UV post-curing process, the samples were left in a vacuum oven at 60ºC for at least 48h to eliminate the solvent from the product.

Two hybrid TPU-acrylates with different hard/soft segment ratio were synthesized by varying the polyol and isocyanate concentrations in the formulation: (1) sample A, 20:80 rigid and flexible (soft) segments, respectively; and (2) sample B, 35:65 rigid and flexible (soft) segments, respectively.

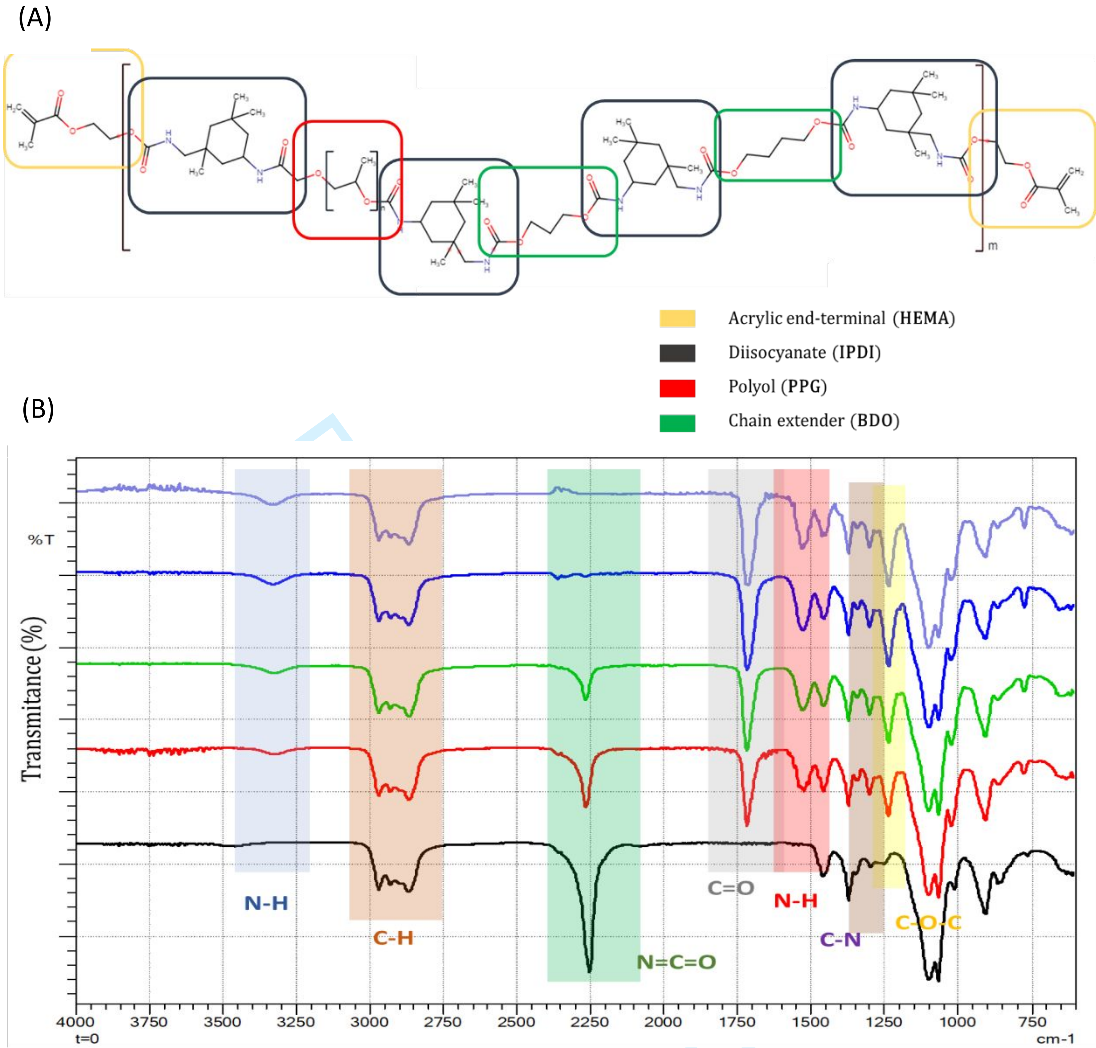

Figure 1. *(A) Ideal chemical structure of the synthesized hybrid TPU-acrylates. (B) FTIR-ATR spectra of the hybrid TPU-acrylates at different reaction times. Evolution of the polymerization reaction was monitored by following the decrease of the NCO peak at 2272 cm*$^{-1}$ *(bottom-up observation, being the black spectra the beginning of the synthesis and the clear blue, the final*

2.2. 3D Printing

A personalized DIW technology 3D printer was developed at CIM UPC facilities in Barcelona to face the challenge of 3D printing slurry-based TPU. Design and manufacture of unique and research-oriented bespoken 3D printers are part of the technology-transfer activities at CIM UPC. The TPU is injected through a pressurized syringe (Optimum Syringe Barrel Opaque Black 55cc) provided by Nordson Corporation, USA, and cured using a source of UV-light, which is a Lightningcure LC-L1, from Hamamatsu, Japan. This is a standard type of irradiation beam shape and an irradiation area of 3 mm ray. The led head unit is a L14310 model with a mounted condenser lens E11923-110, producing radiation with a wavelength of 365 nm. For printing the UV light, different tool parts were designed, and 3D printed as can be seen in Figure 2. Additionally, a UV mask was also designed and placed in the tool for avoiding the tip for being cured due to the UV light. Once a sample is 3D printed, it is left in an isopropanol bath in order to remove the TPU that is not cured. Then, the sample is placed for 2-3 hours at 70 ^{0}C in an oven from Memmert GmbH, Germany, so that the sticky part is removed.

a) b)

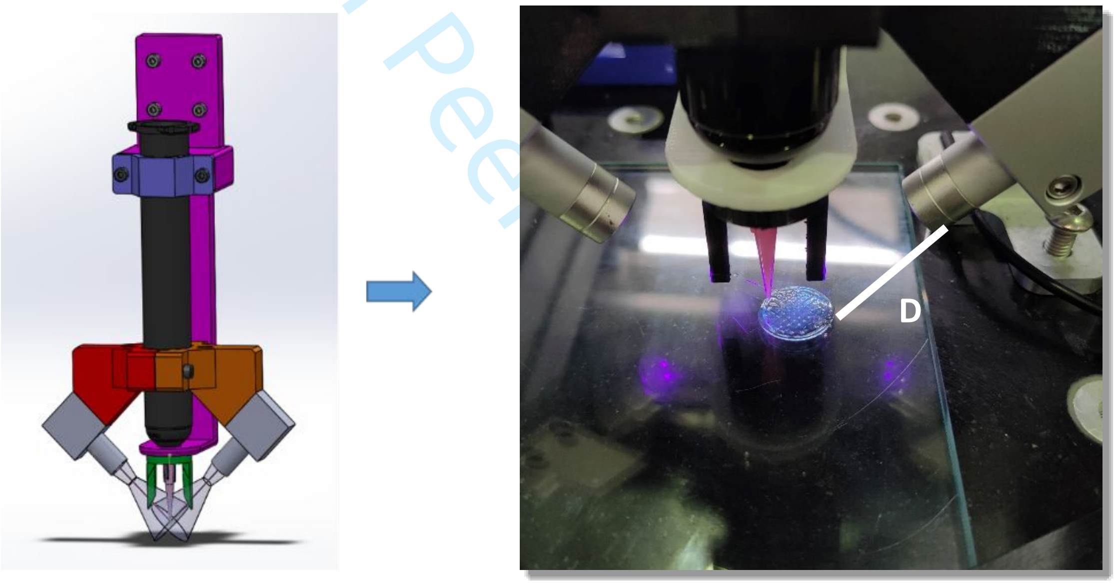

Figure 2. *a) CAD simulation of the tool-head assembly, made from specially designed and FFF 3D-printed components. Design of the shadow-generator pins has been optimized to protect the tip from clogging. b) Photopolymeric TPU being 3D-printed: parameter D is the distant between the UV light source and the sample.*

2.2.1. Curing Tests on TPU – Parameters

As not many research studies like this has been found (except from [8], where a elastomeric polyurethane (EPU) material is built and polymerized using an ultraviolet light, and [9,10] that 3D printed TPU but without using any UV light), it was necessary to do a preliminary curing study for the 3D printed TPU samples, so that the best parameter values for the TPU samples were achieved. Once these parameter values were obtained, the final TPU 3D printed parts were manufactured.

At first, two parameters were considered: (1) Power Rate, that is percentage of UV light power applied, which varies from 1 to 100 %; and (2) the distance D between the source and the 3D printed samples (see Figure 2). Both parameters are necessary to obtain the irradiance of the UV, that is the amount of energy that falls on a given surface, expressed in W/m^2 in the ISU, but most commonly expressed in mW/cm^2. The maximum irradiance this source can provide is 14000 mW/cm^2 at a distance of 10 mm from the lamp and at the center of the irradiation area.

Distance D varies the irradiance with an inverse square law: irradiance is inversely proportional to the square of D. This means that the higher is the distance to the sample, not only the irradiance is significantly lower, but also much more uniform regarding the distance to the center of the exposure's area. D is defined at approximate ranges, between 0 and 10 mm, between 10 and 15, then 15 to 20, 20 to 25, 25 to 30 mm and finally 50mm.

2.2.2. 3D Printing Parameters

After all this previous research about these two basic parameters (D and Power Rate), two solid cylinders of different composition of TPU (n=4) were 3D printed. The dimensions for sample A: 12.36±0.96 mm of diameter and 8.11±2.11 mm height. The dimensions for the sample B: 12.82±0.49 mm of diameter and 8.16±1.13 mm height

The printing parameters used in the 3D printing process can be divided into two categories: (1) fixed parameters, and (2) variable parameters.

The considered fixed parameters are 6: (1) D; (2) SR or speed rate of the 3Dprinting tool-head; (3) TDN or tip diameter of the nozzle; (4) LT or layer thickness of the 3Dprinting part (z height movement of the tool-head to change the layer); (5) time in isopropoyl alcohol; and (6) PCT or post-curing temperature. Some considerations about the reasons for fixing them are also detailed

(1) D: distance (D) between the UV source and the samples is fixed within a range between 40 and 50 mm, according to the preliminary curing test results.

(2) SR is fixed at 160 mm/min, a medium and common value for DIW. Future research could explore the influence of its variation, but is not considered a key parameter in this first exploring research.

(3) TP is fixed at a diameter of 0.58 mm, also a very common value for Nordson standard syringe tips for DIW.

(4) LT is fixed at a height value of 0.35 mm, corresponding to a value considered optimal taking in account previous parameters as SR, TP and LT.

(5) time in isopropoyl alcohol for removing any residual monomers (10 minutes)

(6) PCT is fixed at 70 ^{0}C, a standard value for polyurethanes.

The considered variable parameters are 3: PR, p or pressure applied in the syringe and t or time in the oven.

(1) PR: power rate of the UV light (considering the movement of the print-head is slow enough to keep the part enlightened during the process) was comprised between 10 % to 35 % of the maximum capacity of the device.

(2) p is allowed to vary between 0.5 and 2 Bar, in order to adjust the printing process to different viscosities of the sample. The more viscous the sample is; the more pressure is needed in order to guarantee an optimal flux from the nozzle.

(3) t is not considered a key factor, and its value can vary within a large range without any special consequence on the properties of the samples. Time in the oven has been added in some samples trying to eliminate their remaining stickiness after the 3D printing process. Its value for every sample has been recorded, and probably further research should explore this factor.

3. Results and Discussion

3.1. Curing Tests on TPU

The 3D printed samples manufactured for the preliminary study of the curing tests were different samples of A and B. There were four different outcomes from the curing tests (see Figure 3): (1) totally cured in which the sample is completely solidified at any point; (2) partially cured in which the sample contains an uncured area, commonly on a side; and (3) only cured at the center which is commonly when the area covered by the light is too small (implying the UV light is too close) and does not cure 100 % of the area of the cylinder; and (4) too cured. Table 1 summarizes the results. Then, the height H of the sample was also measured. Additionally, after the thermal treatment of the samples to eliminate the stickiness, a shrinkage between 15 % and 30 % was observed.

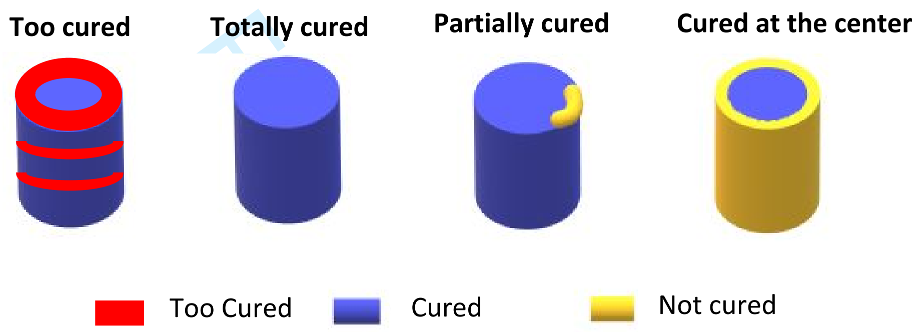

Figure 3. *Different outcomes of the curing tests.*

Table 1. *Qualitative results of the curing tests.*

Power Rate [%]	Sample Number	D [mm]	H [mm]	Curing
10	#1	0-10	4.85	Cured at the center
	#2	10-15	6.8	Cured at the center
	#3	15-20	5	Cured at the center
	#4	20-25	6.6	Cured at the center
	#5	25-30	6.1	Cured at the center
	#6	50	5.65	Partially cured
25	#7	0-10	4	Cured at the center
	#8	10-15	8	Cured at the center
	#9	15-20	6.5	Cured at the center
	#10	20-25	5.5	Partially cured
	#11	25-30	5	Partially cured
	#12	50	7	Totally cured
50	#13	0-10	4.5	Cured at the center
	#14	10-15	6.8	Partially cured
	#15	15-20	6.2	Cured at the center
	#16	20-25	5.6	Cured at the center
	#17	25-30	4.4	Partially cured
	#18	50	8	Totally cured

75	#19	0-10	2.2	Partially cured
	#20	10-15	3	Totally cured
	#21	15-20	4.6	Totally cured
	#22	20-25	4.25	Totally cured
	#23	25-30	5.5	Too cured
	#24	50	11	Too cured
100	#25	0-10	2.5	Totally cured
	#26	10-15	4.75	Totally cured
	#27	15-20	6.1	Totally cured
	#28	20-25	2.5	Too cured
	#29	25-30	3.4	Too cured
	#30	50	5.1	Too cured

As it can be seen, at approximately 50 mm distance to the source, the polymer is almost cured even for power rates where it is partially cured at other distances, which indicates that to be totally cured, it does not require a very high irradiance but rather a full exposure of the piece to the UV radiation. Additionally, a high irradiance might cure the tip (although the "shadowers" tips have been optimized, see Figure 2), which is something to consider, because if the tip is cured, the 3D printing process stops. Also, too much Power Rate can result in a too much cured part, corresponding to an accelerated ageing of the 3D printed sample.

Therefore, it had been considered that the best option to follow on with more tests was to place the source at D= 40-50 mm distance and apply low-medium power rates (between 10% and 35%). However, low power rates can cause a partial curing of the sample, which it may be addressed afterwards with UV exposure out of the 3D printer. Anyway, this low Power Rate is going to prevent two major issues: clogging of the 3D printing tip and excessive curing.

3.2. 3D Printed TPU Samples

After all the curing tests are finished and these two basic parameters (D and Power Rate), two solid cylinders of different composition of TPU (n=4) were 3D printed. Table 2 summarizes every value used for this three parameters.

Table 2*. 3D printing variable parameters of the TPU samples.*

Sample Name	Sample Number	Power Rate [%]	Pressure [Bar]	Time in the Oven [Hours]
A	#1	15	0.3	17
	#2	10	0.9	4
	#3	10	0.9	4
	#4	10	1.1	4
B	#5	10	0.9	68
	#6	15	0.9	66
	#7	25	1	3
	#8	35	1	3

Figure 4 shows the 3D printed samples. It can be seen that 3D printed samples with the A composition showed much more consistency, while B composition 3D printed TPU samples showed to be more liquid, due to its more proportion of soft parts.

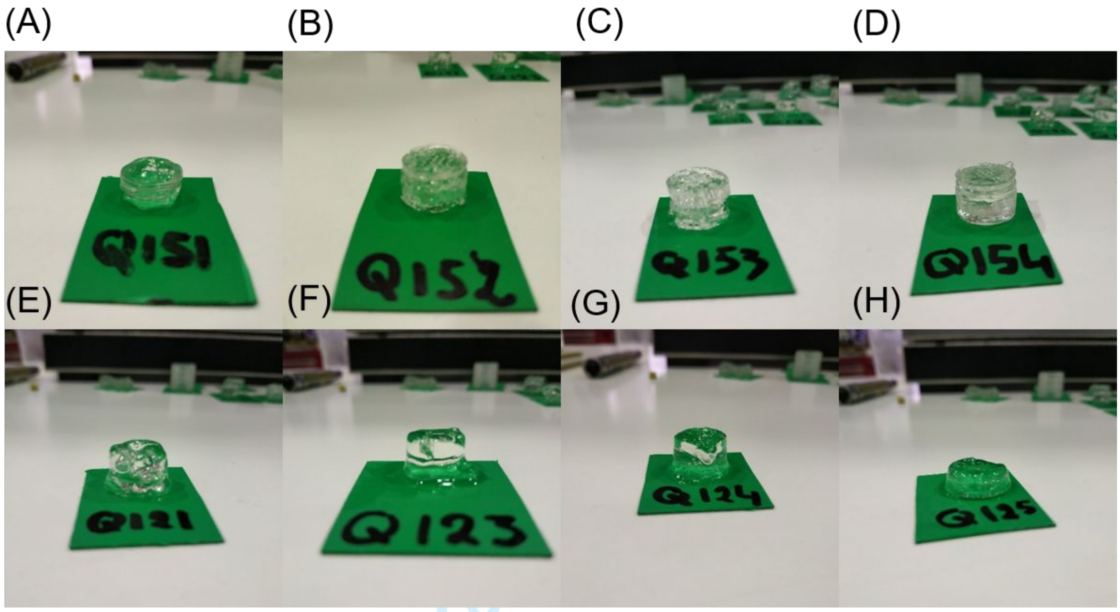

Figure 4. *3D printed TPU samples. Sample A: (A) Sample #1. (B) Sample #2. (C) Sample #3. (D) Sample #4. Sample B: (E) Sample #5. (F) Sample #6. (G) Sample #7. (H) Sample #8.*

As can be seen, the 3D printing of this TPU is challenging due to several points. Firstly, the viscosity of the TPU makes very difficult to 3D print TPU samples, while it also gives the material a sufficient shear strength not to collapse during the 3D printing process. Secondly, once the TPU samples are additive manufactured, their main issue is their sticky behavior. It seems the softer the TPU samples is, the stickier is its behavior. Another major point to mention is the shrinkage which takes place after the thermal treatment and for some applications, it might be problem. This normally takes place with 3D printed ceramic parts after the sintering process.

4. Conclusion

The present paper achieved to 3D print for the first time slurry-based TPU using DIW with UV light. This is a step forward in the state-of-the-art, not only in the AM field, but also in the finding of TPU and soft materials that opens the door for future research studies. By this way, these materials could be used for the manufacturing of soft 3D printed parts, for example, in health/bioprinting applications, as for example the manufacture of phantoms for preoperative surgical planning. Also, in the future, slurry-based TPU could be used in hybrid multi-material 3D printers along with filaments or other materials, opening the possibilities of new technologies and applications in the AM field.

Acknowledgments

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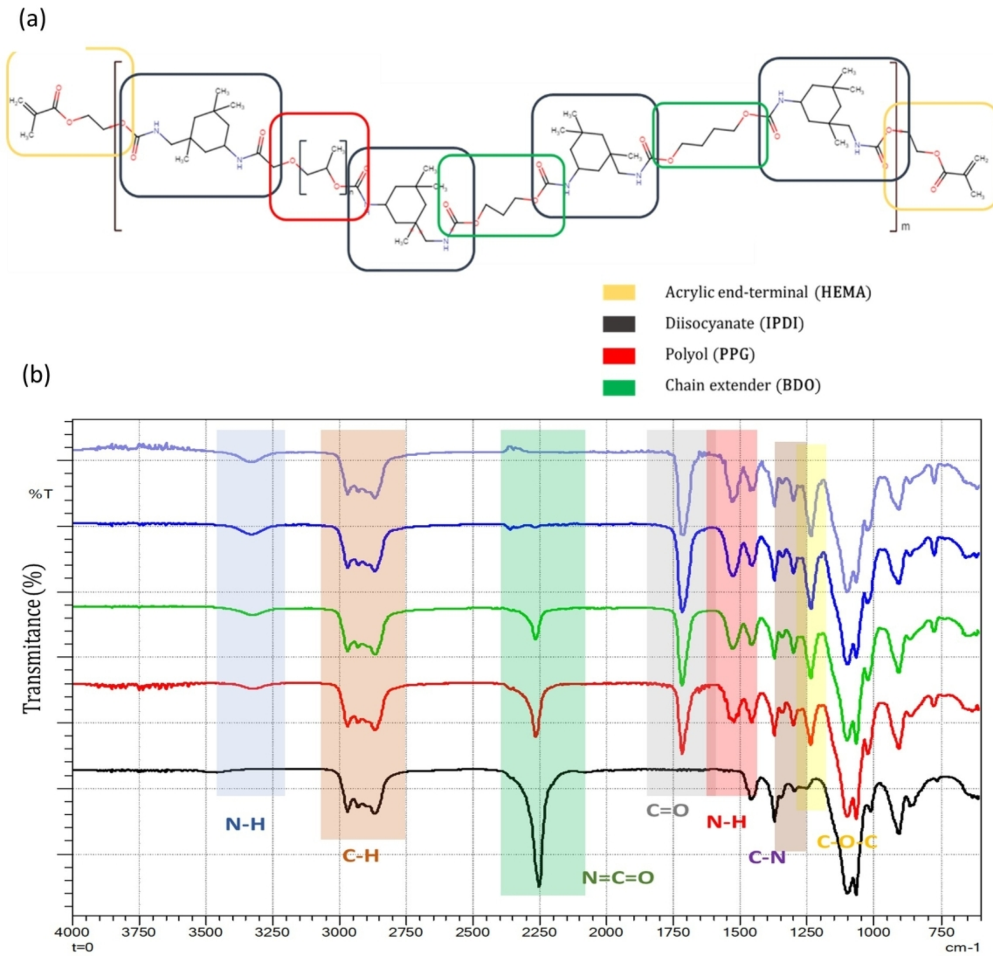

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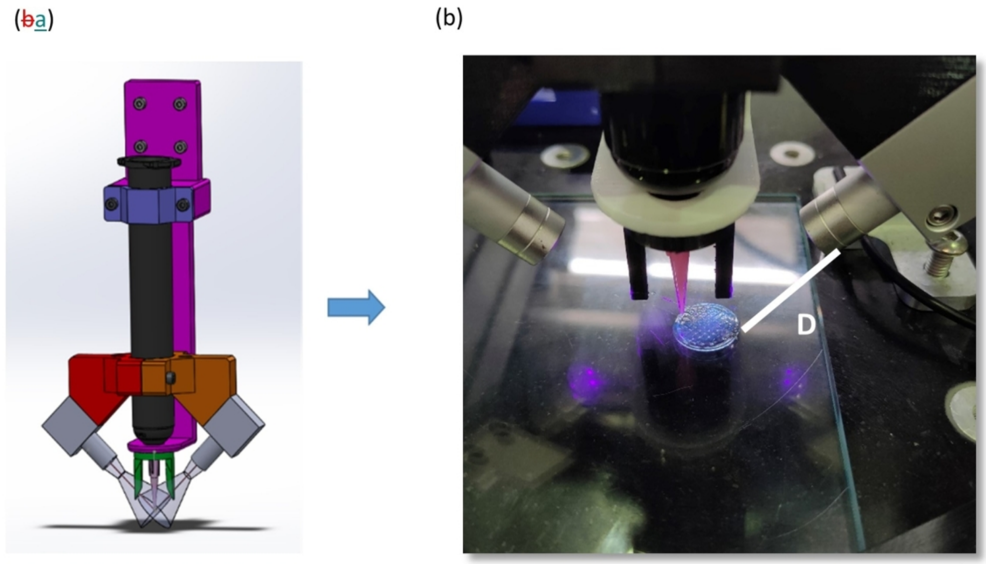

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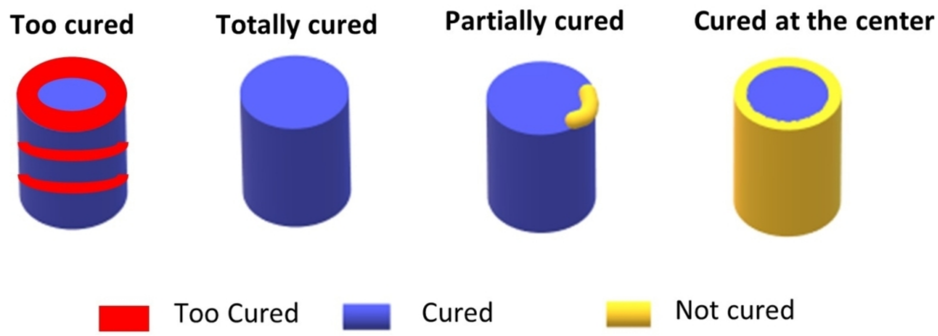

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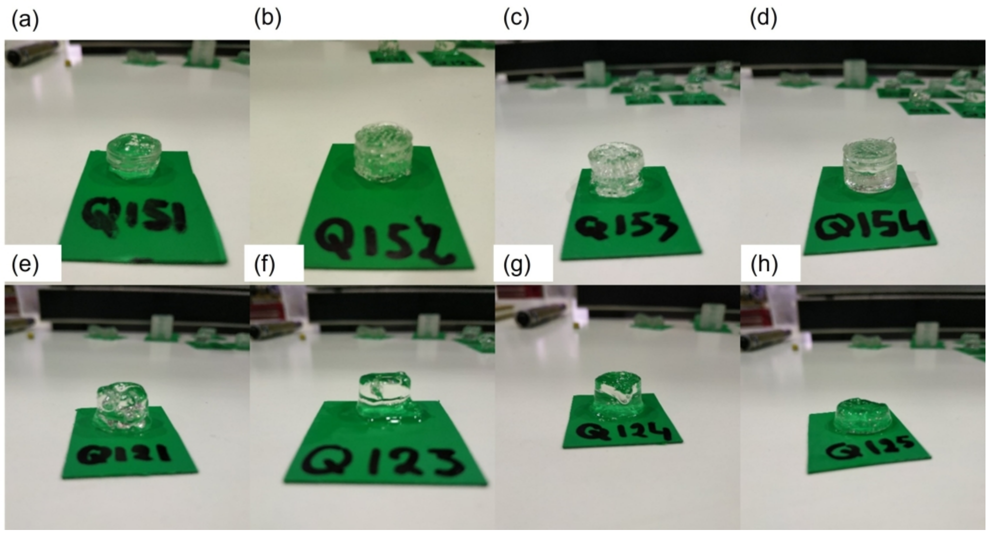

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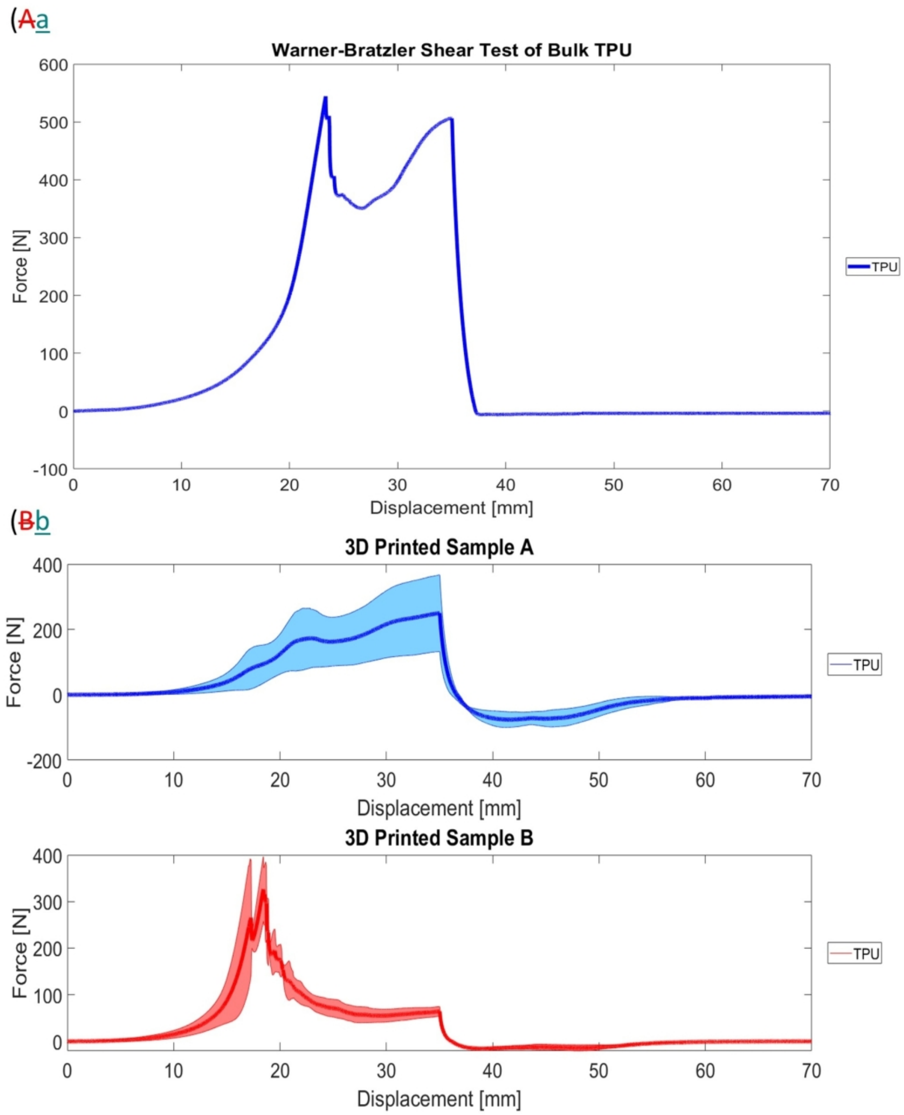

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152x198mm (300 x 300 DPI)

Soft 3D Printing of Thermoplastic Polyurethane: Preliminary Study

F. Fenollosa-Artes [1,2], L. Jorand [1], A. Tejo-Otero [1], P. Lustig-Gainza [1], G. Romero-Sabat [3], S. Medel [3], R. Uceda [1,2]

[1]*Centre CIM, Universitat Politècnica de Catalunya (CIM UPC), Carrer de Llorens i Artigas, 12, 08028, Barcelona, Spain*
[2]*Universitat Politècnica de Catalunya. Departament of Mechanical Engineering. School of Engineering of Barcelona (ETSEIB). Av. Diagonal, 647. 08028, Barcelona, Spain*
[3] *Polymer Synthesis Unit, Leitat Technological Center, Carrer Innovació, 2, 08225 Terrassa, Barcelona*

Abstract

Thermoplastic polyurethane (TPU) is a highly elastic linear polymer composed of soft segments, usually flexible polyester, or polyether. It is widely used in 3D printing technologies, being FFF the most common technique. However, stiffness and hardness values of 3D printed TPU in filament form are higher that it would be desirable for some applications, which require softer parts. Therefore, it was seen necessary to find a new methodology for 3D printing soft TPU. In this way, the present study seeks to be the first research study which focuses on the possibility of 3D printing TPU using DIW (Direct Ink Writing) technology with UV light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. Then, both bulk and 3D printed TPU samples were characterized in terms of shear strength using the Warner-Bratzler shear test and hardness using the Shore hardness test. It was seen that the 3D printed samples showed higher softness than bulk samples as well as in comparison with TPU filament. Finally, it was concluded that the 3D printing of TPU is challenging due to several points: (1) the viscosity of the TPU; (2) their main issue is their sticky behavior; and (3) the shrinkage which takes place after the thermal treatment and for some applications, it might be a problem. Despite that, TPU appears to be a promising material to be used in different industrial applications.

Keywords

3D Printing; additive manufacturing; thermoplastic polyurethane

Corresponding author

*ffenollosa@cimupc.org

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1. Introduction

Since its discovery in 1937 by Otto Bayer, Polyurethane polymers (PU) have advanced until becoming part of our everyday life. Within Polyurethanes, Thermoplastic polyurethanes (TPUs) are usually randomly composed of linear polymer with flexible soft-chain (soft-domain) segments chemically bonded with low-mobile segments (hard-domain) that act as crosslinking points within the structure. The selection and hard/soft segment ratio can significantly affect the overall polymer behavior as well as producing its well-known versatility. Generally, it offers high elongation, low hardness (45-85 Shore A), moderate tensile strength (5-15 MPa) and elastic modulus (2400 N/mm^2) as well as excellent abrasion and tear resistance [1,2]. Additionally, it appears to have an excellent biocompatibility [3,4].

TPU has mainly been additive manufactured [5] using material extrusion, powder bed fusion and material jetting. Among these technologies the most widely used is material extrusion, specifically FFF, since it is a cost-effective technology. For instance, Bates et al. [6] 3D printed TPU samples with the honeycomb structure using FFF technology. The material is selected due to its impact strength and abrasion resistance and therefore is used to create energy absorbing structures. Also, FFF technology is used to study the adhesion strength between soft TPU and ABS (Acrylonitrile Butadiene Styrene)/ASA (Acrylonitrile Styrene Acrylate) [7] aiming to further investigate the multi-material possibilities of 3D printing. It was found that TPU can adhere to both ASA and ABS, which allows them to be printed together in a multi material 3D printer. According to this study, the adhesion strength was comparable to commercial adhesives. Additionally, Hossain et al. [8] 3D printed for the first-time elastomeric PU using vat photopolymerisation technology, in which the material is built and polymerized under UV light. In recent years, TPU was tried to be 3D printed using the Direct Ink Writing (DIW) technology. For instance, Valentine et al. [9] 3D printed TPU with added silver flakes using DIW for soft electronics development. Then, Ahmed et al. [10] developed a 3D printed TPU/CNPs strain sensor using the mentioned technology. Nevertheless, none of them used UV light, as it is sought in the present manuscript. Then, Dadbakhsh et al. [11] used SLS for the manufacture of TPU with an average hardness of 87 Shore A, with the aim of finding the importance of the powder morphology.

In the medical sector, the use of TPU in filament form for FFF is common. For example, Domínguez-Robles et al. [3] 3D printed TPU filaments containing levofloxacin (LFX) in various concentrations for the production of vaginal meshes. Then, Li et al. [12] additively manufactured medical grade TPU using FFF technology was found to have potential to produce medical devices and surgical tools. Then, Esmaeili et al. [13] manufactured TPU composed of nanocrystalline hydroxiapatite (HA) nanopowder to construct artificial blood vessels. In case porous scaffolds were needed for a certain medical application, SLS could be used according to Yang et al. [14] as well as laser powder bed fusion (LPBF) [15].

But TPU filaments are not soft enough for certain applications, as trying to mimic living tissue hardness in surgical planning prototypes. Additionally, the FFF 3D printing of TPU is a challenge for several reasons: (1) sometimes the filament is not inserted into the hotend correctly, causing a jam in the knurled pulley of the extruder and the bearing; (2) an excessive filament friction producing a more pressure on the drive gear consequently more filament feed problems can happen as a result; (3) the need to be 3D printed at low temperatures; however, higher is the temperature, the lower is the pressure need to be applied, but the possibility of breaking the filament also increases; (4) difficult to post-process; and (5) hotend intern pressure.

The solution explored to reach a higher softness is 3D printing special formulations for soft TPU using another material extrusion technology: DIW technology, as working with liquids should make it possible to avoid the feeding problems related with soft filaments. An important point is the novelty of this research: it has not been found any previous mention about it the literature, may be due to the intrinsic difficulty about working with too soft materials in 3D printing. Hence, by taking everything into account, the aim of the present study is to present a soft TPU (softer than standard FFF TPU) to be processed by DIW technology using UV curing light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. And then, both bulk and 3D printed TPU samples are characterized in terms of shear strength using the Warner-Bratzler shear test and hardness using the Shore hardness test.

2. Materials and Methods

2.1. TPU Synthesis

Hybrid UV photocurable thermoplastic Polyurethane (TPU) - acrylate were manufactured following a pre-polymer solution method as follows: Polypropylene Glycol (PPG) with a molecular weight of 1000 g/mol and Tetrahydrofuran (THF) were introduced in a 100 mL 5-neck mini-reactor (Scharlab). The mixture was stirred at 260 rpm and heated to 60ºC in an Argon inert atmosphere to remove possible presence of moisture. Once the set temperature was reached, Isophorone Diisocyanate (IPDI) was incorporated dropwise followed by three drops of Dibutyltin Dilaurate (DBTDL) as reaction catalyst. The Polyol to isocyanate ratio was kept around 0.5:1 to ensure plenty of isocyanate free groups in the prepolymer for further functionalization. The reaction was monitored by FTIR-ATR (Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflection mode) observing the NCO peak at 2272 cm-1(Figure 1B). Once the NCO peak was not further reduced due to complete reaction between PPG and IPDI (approximately 2 hours), a half of the theoretically required quantity of 1,4-Butanediol (BDO) was introduced with a previously dispersed photoinitiator (Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide). When no more NCO peak reduction was observed from the FTIR spectra again, an acrylic molecule containing both a hydroxyl and a vinyl terminal was added and left to react. Finally, the rest of the BDO was introduced and the completion of the reaction was determined when no free isocyanate was observed. The final ideal chemical structure of the molecule and follow-up of the reaction by FTIR-ATR can be observed in Figure 1A & 1B respectively. For example, regarding Figure 1A, each color corresponds to a chemical compound: (1) yellow to acrylic end-terminal (HEMA); (2) black to diisocyanate (IPDI); (3) red to polyol (PPG); and (4) green to chain extender (BDO). On the other hand, Figure 1B shows one color for each covalent bond, which is placed to the corresponding color in vertical. To procure a minimal shrinking effect on the UV post-curing process, the samples were left in a vacuum oven at 60ºC for at least 48h to eliminate the solvent from the product.

Two hybrid TPU-acrylates with different hard/soft segment ratio were synthesized by varying the polyol and isocyanate concentrations in the formulation: (1) sample A, 20:80 rigid and flexible (soft) segments, respectively; and (2) sample B, 35:65 rigid and flexible (soft) segments, respectively.

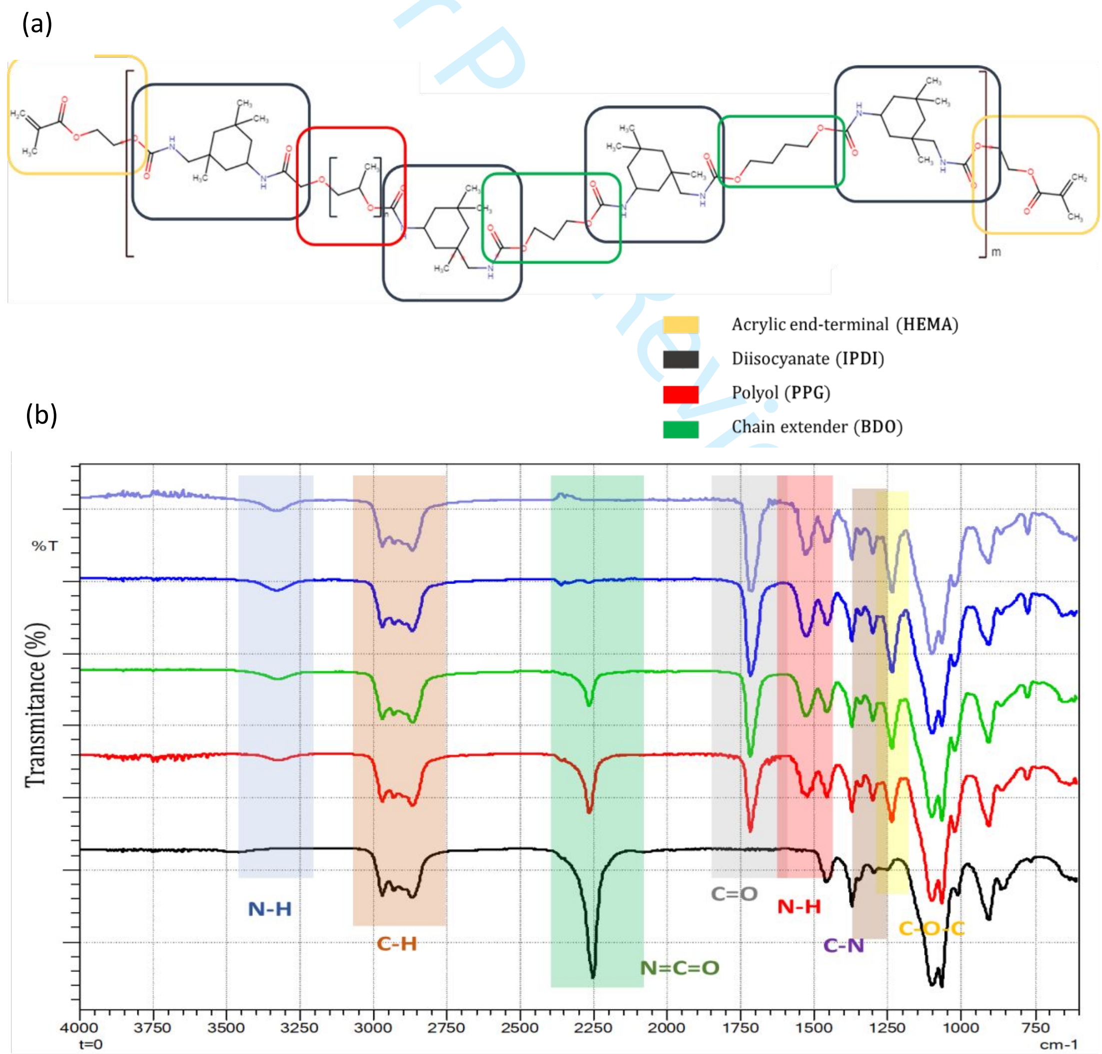


Figure 1. *(a) Ideal chemical structure of the synthesized hybrid TPU-acrylates. (b) FTIR-ATR spectra of the hybrid TPU-acrylates at different reaction times. Evolution of the polymerization reaction was monitored by following the decrease of the NCO peak at 2272 cm*$^{-1}$ *(bottom-up observation, being the black spectra the beginning of the synthesis and the clear blue, the final).*

2.2. 3D Printing

A personalized DIW technology 3D printer was developed at CIM UPC facilities in Barcelona to face the challenge of 3D printing slurry-based TPU. Design and manufacture of unique and research-oriented bespoken 3D printers are part of the technology-transfer activities at CIM UPC. The TPU is injected through a pressurized syringe (Optimum Syringe Barrel Opaque Black 55cc) provided by Nordson Corporation, USA, and cured using a source of UV-light, which is a Lightningcure LC-L1, from Hamamatsu, Japan. This is a standard type of irradiation beam shape and an irradiation area of 3 mm ray. The led head unit is a L14310 model with a mounted condenser lens E11923-110, producing radiation with a wavelength of 365 nm. To hold and fix this UV-light next to the printing tip, different tool parts were designed, and 3D printed in PLA filament material in a SIGMA BCN3D printer as can be seen in Figure 2. Additionally, a UV mask was also designed and placed in the tool for avoiding the tip for being cured due to the UV light. Once a sample is 3D printed, it is left in an isopropanol bath in order to remove the TPU that is not cured. Then, the sample is placed for 2-3 hours at 70 ^{0}C in an oven from Memmert GmbH, Germany, so that the sticky part is removed.

(ba) (b)

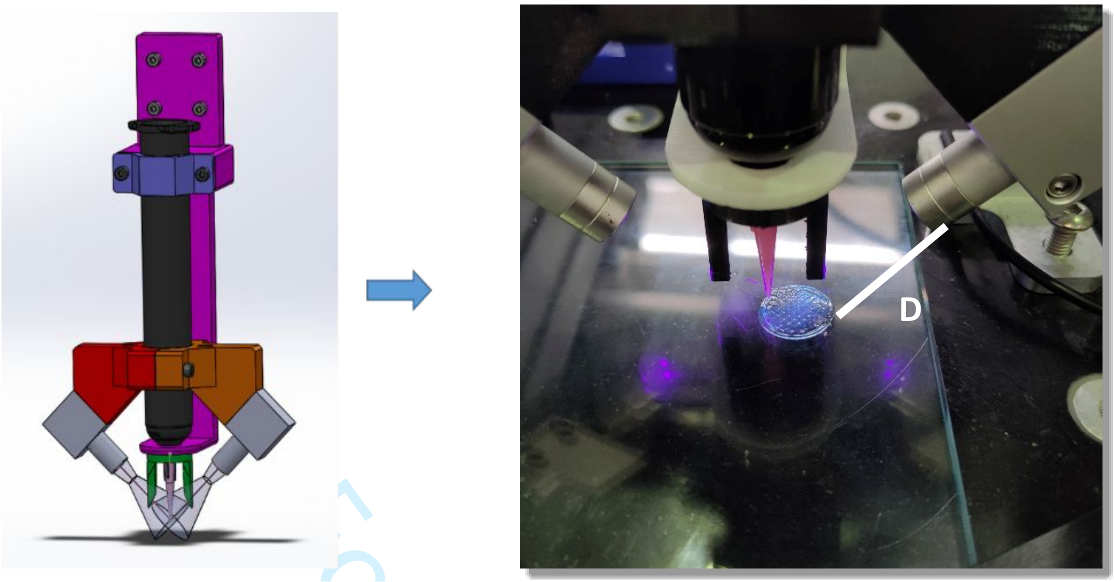


Figure 2. *a) CAD simulation of the tool-head assembly, made from specially designed and FFF 3D-printed components. Design of the shadow-generator pins has been optimized to protect the tip from clogging. b) Photopolymeric TPU being 3D-printed: parameter D is the distance between the UV light source and the sample.*

a) b)

2.2.1. Curing Tests on TPU – Parameters

As not many research studies like this has been found (except from [8], where a elastomeric polyurethane (EPU) material is built and polymerized using an ultraviolet light, and [9,10] that 3D printed TPU but without using any UV light), it was necessary to do a preliminary curing study for the 3D printed TPU samples, so that the best parameter values for the TPU samples were achieved. Once these parameter values were obtained, the final TPU 3D printed parts were manufactured.

At first, two parameters were considered: (1) Power Rate, that is percentage of UV light power applied, which varies from 1 to 100 %; and (2) the distance D between the source and the 3D printed samples (see Figure 2). Both parameters are necessary to obtain the irradiance of the UV, that is the amount of energy that falls on a given surface, expressed in W/m^2 in the ISU, but mostly expressed in mW/cm^2. The maximum irradiance this source can provide is 14000 mW/cm^2 at 10 mm from the lamp and at the center of the irradiation area.

Distance D varies the irradiance with an inverse square law: irradiance is inversely proportional to the square of D. This means that the greater the distance to the sample, not only is the irradiance significantly less, but also much more uniform with respect to the distance to the center of the exposure's area. D is defined at approximate ranges, between 0 and 10 mm, between 10 and 15, then 15 to 20, 20 to 25, 25 to 30 mm and finally 50mm.

2.2.2. 3D Printing Parameters

After all this previous research about these two basic parameters (D and Power Rate), two solid cylinders of different composition of TPU (n=4) were 3D printed. The dimensions for sample A: 12.36±0.96 mm of diameter and 8.11±2.11 mm height. The dimensions for the sample B: 12.82±0.49 mm of diameter and 8.16±1.13 mm height.

The printing parameters used in the 3D printing process can be divided into two categories: (1) fixed parameters, and (2) variable parameters.

The considered fixed parameters are 6: (1) D; (2) SR or speed rate of the 3D printing tool-head; (3) TP or tip diameter of the nozzle; (4) LT or layer thickness of the 3Dprinting part (z height movement of the tool-head to change the layer); (5) time in isopropyl alcohol; and (6) PCT or post-curing temperature. Some considerations about the reasons for fixing them are also detailed.

(1) D: distance (D) between the UV source and the samples is fixed within a range between 40 and 50 mm, according to the preliminary curing test results.

(2) SR is fixed at 160 mm/min, a medium and common value for DIW. Future research could explore the influence of its variation but is not considered a key parameter in this first exploring research.

(3) TP is fixed at a diameter of 0.58 mm, also a very common value for Nordson standard syringe tips for DIW.

(4) LT is fixed at a height value of 0.35 mm, corresponding to a value considered optimal taking in account previous parameters as SR, TP and LT.

(5) time in isopropyl alcohol for removing any residual monomers (10 minutes).

(6) PCT is fixed at 70 ^{0}C, a standard value for polyurethanes.

The considered variable parameters are 3: PR, p or pressure applied in the syringe and t or time in the oven.

(1) PR: power rate of the UV light (considering the movement of the print-head is slow enough to keep the part enlightened during the process) was comprised between 10 % to 35 % of the maximum capacity of the device.

(2) p is allowed to vary between 0.5 and 2 Bar, to adjust the printing process to different viscosities of the sample. The more viscous the sample is the more pressure is needed to guarantee an optimal flux from the nozzle.

(3) t is not considered a key factor, and its value can vary within a large range without any special consequence on the properties of the samples. Time in the oven has been added in some samples trying to eliminate their remaining stickiness after the 3D printing process. Its value for every sample has been recorded, and probably further research should explore this factor.

2.2.3. Shore Hardness Test

Shore hardness is a measurement of the resistance of a sample to indentation. There are different scales based on ASTM D2240 testing standards [16]: A, B, C, D, DO, E, M, O, OO, OOO, OOO-S, and R. Each scale results in having values between 0 and 100, where higher values indicate that a material is harder. STM D2240-Durometer Hardness method was used [16]. For that, Shore Durometer Type A, 00 and 000, supplied by Baxlo, Instrumentos de Medida y Precisión, S.L., Spain. Shore A is the hardest, and Shore 000 the softest.

2.2.4. Warner-Bratzler Shear Test

Warner-Bratzler shear test is commonly used in the food industry as a standard characterization method. For example, it has been used to determine the best meat tenderness (toughness) for various types of meat. The Warner-Bratzler consists of a steel frame which is supporting a triangular shear blade. The texturometer Texture Analyser TA.XT.plus (Stable Micro Systems, Surrey, UK) was used with a 50N load cell. Maximum shear force (N) and area under the curve (J) was measured using the Warner-Bratzler probe. The speed is 1mm/s during 35 mm of cut. The height of sample was measured with a digital micrometer.

2.2.5. Statistical Analysis

Statistics were performed using MATLAB R19. Bulk and 3D printed TPU samples were assessed using paired sample T-Test to compare if the bulk and 3D printed TPU samples are equal by focusing on Shore and maximum forces values. Data are represented as mean ± SEM (Standard Error of the Mean). $p \leq 0.05$ (*), $p \leq 0.01$(**) and $p \leq 0.001$ (***). The null hypothesis states that the bulk and 3D printed TPU samples are equal. If the p-value is lower than 0.05, the hypotheses is rejected; and consequently, it is confirmed that the bulk and 3D printed TPU samples are not equal.

3. Results and Discussion

3.1. Curing Tests on TPU

The 3D printed samples manufactured for the preliminary study of the curing tests were different samples of A and B. There were four different outcomes from the curing tests (see Figure 3): (1) totally cured in which the sample is completely solidified at any point; (2) partially cured in which the sample contains an uncured area, commonly on a side; and (3) only cured at the center which is commonly when the area covered by the light is too small (implying the UV light is too close) and does not cure 100 % of the area of the cylinder; and (4) too cured. Table 1 summarizes the results. Then, the height H of the sample was also measured. Additionally, after the thermal treatment of the samples to eliminate the stickiness, a shrinkage between 15 % and 30 % was observed.

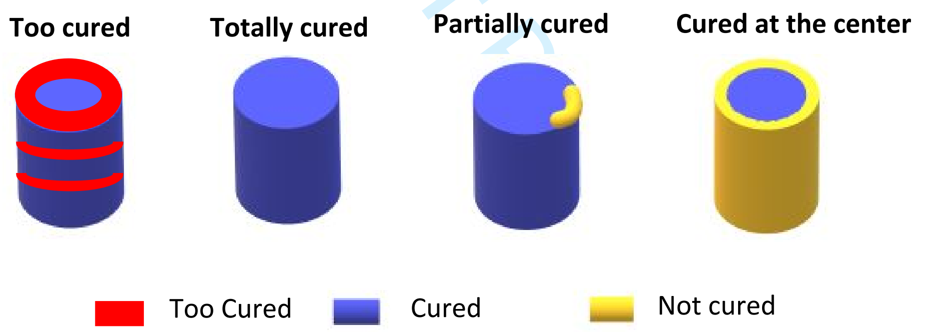


Figure 3. *Different outcomes of the curing tests.*

Table 1. *Qualitative results of the curing tests.*

Power Rate [%]	Sample Number	D [mm]	H [mm]	Curing
10	#1	0-10	4.85	Cured at the center
	#2	10-15	6.8	Cured at the center
	#3	15-20	5	Cured at the center
	#4	20-25	6.6	Cured at the center
	#5	25-30	6.1	Cured at the center
	#6	50	5.65	Partially cured
25	#7	0-10	4	Cured at the center
	#8	10-15	8	Cured at the center

	#9	15-20	6.5	Cured at the center
	#10	20-25	5.5	Partially cured
	#11	25-30	5	Partially cured
	#12	50	7	Totally cured
50	#13	0-10	4.5	Cured at the center
	#14	10-15	6.8	Partially cured
	#15	15-20	6.2	Cured at the center
	#16	20-25	5.6	Cured at the center
	#17	25-30	4.4	Partially cured
	#18	50	8	Totally cured
75	#19	0-10	2.2	Partially cured
	#20	10-15	3	Totally cured
	#21	15-20	4.6	Totally cured
	#22	20-25	4.25	Totally cured
	#23	25-30	5.5	Too cured
	#24	50	11	Too cured
100	#25	0-10	2.5	Totally cured
	#26	10-15	4.75	Totally cured
	#27	15-20	6.1	Totally cured
	#28	20-25	2.5	Too cured
	#29	25-30	3.4	Too cured
	#30	50	5.1	Too cured

As it can be seen, at about 50 mm away from the source, the polymer is nearly cured even for power rates where it is partially cured at other distances, indicating that to be totally cured, it does not require a very high irradiance but rather a full exposure of the piece to the UV radiation. Additionally, high irradiance could cure the tip (although the "shadowers" tips have been optimized, see Figure 2), which is something to consider, because if the tip is cured, the 3D printing process stops. Also, too much power rate can result in an excessively cured part, corresponding to an accelerated ageing of the 3D printed sample. Additionally, a higher distance achieves to cover the curing process of more parts of the 3D printed samples than shorter distances. In other words, short distance leaves some parts being uncured.

Therefore, it had been considered that the best option to follow on with more tests was to place the source at D= 40-50 mm distance and apply low-medium power rates (between 10% and 35%). However, low power rates can cause a partial curing of the sample, which it may be addressed afterwards with UV exposure out of the 3D printer. Anyway, this low Power Rate is going to prevent two major issues: clogging of the 3D printing tip and excessive curing.

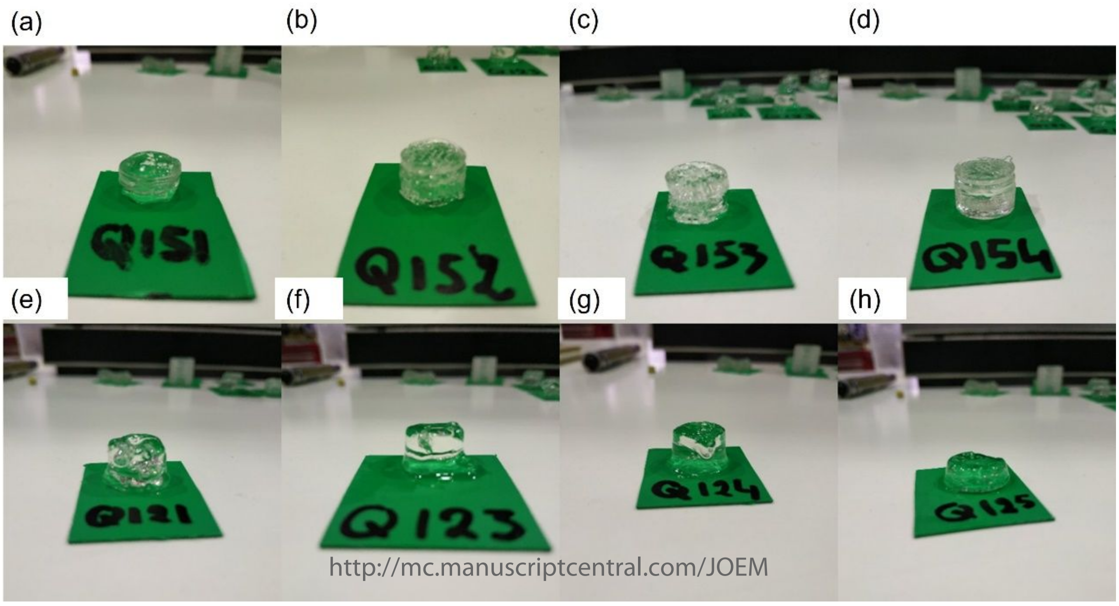
3.2. 3D Printed TPU Samples

After all the curing tests are finished and the optimal values for the two basic parameters (D and Power Rate) has been found, two solid cylinders of different composition A and B of TPU (n=4) were 3D printed. Table 2 summarizes every value used for the three variable parameters (PR, p or pressure applied in the syringe and t or time in the oven).

***Table 2**. 3D printing variable parameters of the TPU samples.*

Sample Name	Sample Number	Power Rate [%]	Pressure [Bar]	Time in the Oven [Hours]
B	#1	15	0.3	17
	#2	10	0.9	4
	#3	10	0.9	4
	#4	10	1.1	4
A	#5	10	0.9	68
	#6	15	0.9	66
	#7	25	1	3
	#8	35	1	3

Figure 4 shows the 3D printed samples. As can be seen, the 3D printing of this TPU is challenging due to several points. Firstly, the viscosity of the TPU makes very difficult to 3D print TPU



samples, while it also gives the material a sufficient shear strength not to collapse during the 3D printing process. Secondly, once the TPU samples are additively manufactured, their main issue is their sticky behavior. It seems that the softer the TPU samples are, the stickier is their behavior. In fact, despite the t and PCT factors, in some samples the removal of the stickiness wasn't achieved at 100%. Another major point to mention is the shrinkage which occurs after the thermal treatment and, for some applications, it can be a problem. This usually takes place with 3D printed ceramic parts after the sintering process. Despite these limitations, TPU is a promising material that can be used in different fields, and the results obtained warrant future further research. Additionally, its transparency – a characteristic scarcely found in the 3D printing world-, can make the difference for certain applications.

3.3. Shore Hardness Results

Shore hardness of bulk TPU samples was obtained. The reason was to compare it with Shore hardness of 3D printed samples. The aim was to analyze if, using the same liquid, the hardness was affected by a 3D printing process. The Shore hardness of the bulk TPU is 40±6.8 Shore A, 80±4.70 Shore 00 and 82±7 Shore 000.

The Shore hardness of the 3D printed TPU samples differs depending on the hard/soft segment ratio of both bulk TPU samples described previously (A and B). This might be due to a difference of density because 3D printed parts are known to have lower density in a general case. The values are summarized in Table 3. All in all, the less rigid segments proportion the sample has (minimum of 20% for samples type A), the softer is. Despite sample B is harder than A, both are softer than bulk TPU samples.

Table 3. *Shore hardness of the 3D printed TPU samples.*

3D Printed Sample	Shore A	Shore 00	Shore 000
A	0	39±4	65±6.5
B	11±1.5	57±4	71±4.5

Regarding its difference with bulk TPU samples, the p-value, by looking into the Shore 00, is 0.00001 and 0.0027, for A and B, respectively. This means that the bulk and 3D printed TPU samples are not equal since the null hypothesis is rejected.

And both bulk and DIW- 3D printed TPU are softer compared to typical Shore Hardness of TPU filaments, which is 26 Shore D [17]. This value might correspond 80 Shore A according to ISO 868 A [15]. To give some more detail related to commercial TPU filaments, Bioflex filament is 27 Shore D [18] or the TPU filament of Recreus filament varies from 70 Shore A to 95 Shore A [19].

3.4. Warner-Bratzler Shear Test

Warner-Bratzler shear test of bulk TPU samples was performed. The reason was to compare it with Warner-Bratzler shear test of 3D printed samples. The Warner-Bratzler shear test cutting profile can be seen in Figure 5. The maximum force measured is 544.27 N, near the limit that the machine can measure. Additionally, this value is still very high, but it is a good approaching in the finding of soft TPU. However, there is no possibility to compare with 3D printed TPU samples using FFF technology, because they are too rigid to be measured using this method.

In terms of the Warner-Bratzler shear test, Figure 5B shows the cutting profile of both samples A and B. The maximum forces are lower than bulk TPU samples (Figure 5A): 249±117 N and 326 ± 70 N for A and B, respectively.

Regarding its difference with bulk TPU samples, the p-value, by looking into the maximum force, is 0.015 and 0.13, for A and B, respectively. Therefore, regarding the sample A, the null hypothesis is rejected (p-value is lower than 0.05) and, consequently, the bulk and 3D printed TPU samples are not equal. However, p-value of the sample B is higher than 0.05 and, hence, the null hypothesis is not rejected. This means that both are more or less similar.

The samples type B need a higher force to be cut than type A. This is consistent with the proportions mentioned before. B-samples have a higher proportion of rigid parts than A-samples.

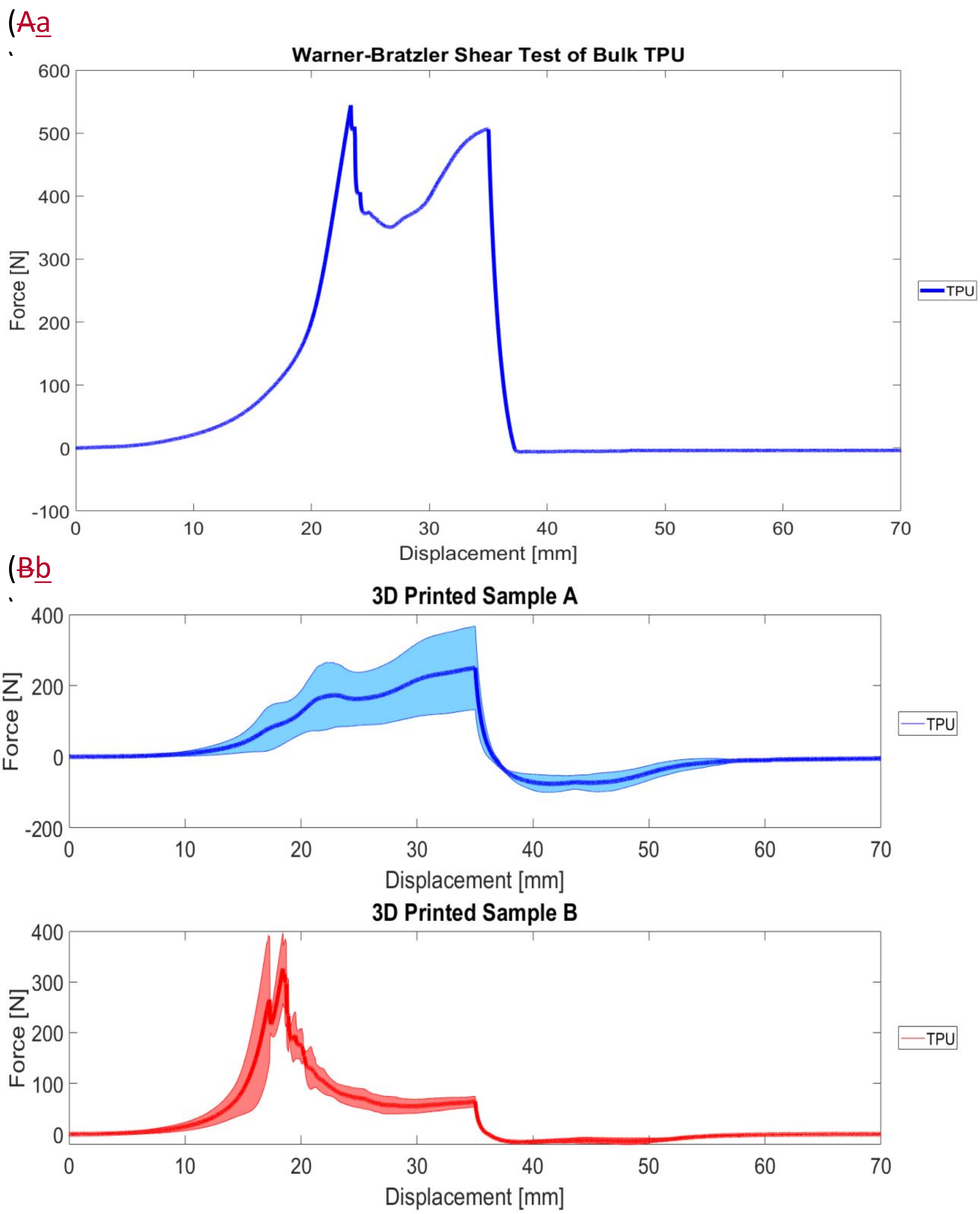


Figure 5. *(~~A~~a) Warner-Bratzler shear test of the bulk TPU sample. (~~B~~b) Warner-Bratzler shear test cutting profile of 3D printed samples.*

4. Conclusion

The present paper achieved to 3D print for the first time slurry-based TPU using DIW with UV light. Using this 3D printing technology with soft oriented TPU liquids makes sense in order to achieve lower hardness values compared to current solutions. More research must be done, and next works will be oriented on using other printing means apart of syringes, andsyringes and trying to correlate tackiness and softness. By now, this is a step forward in the state-of-the-art, not only in the AM field, but also in the discovery of TPU and soft materials that opens the door for future research studies. In this way, these materials could be used for the manufacturing of soft 3D printed parts, for example, in healthcare/bioprinting applications, as for example the manufacture of phantoms for preoperative surgical planning. Furthermore, in the future, slurry-based TPU could be used in hybrid multi-material 3D printers along with filaments or other materials, opening the possibilities of new technologies and applications in the AM field.

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Figure 1. (A) Ideal chemical structure of the synthesized hybrid TPU-acrylates. (B) FTIR-ATR spectra of the hybrid TPU-acrylates at different reaction times. Evolution of the polymerization reaction was monitored by following the decrease of the NCO peak at 2272 cm-1 (bottom-up observation, being the black spectra the beginning of the synthesis and the clear blue, the final).

Figure 2. a) CAD simulation of the tool-head assembly, made from specially designed and FFF 3D-printed components. Design of the shadow-generator pins has been optimized to protect the tip from clogging. b) Photopolymeric TPU being 3D-printed: parameter D is the distant between the UV light source and the sample.

Figure 3. Different outcomes of the curing tests.

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Figure 5. (A) Warner-Bratzler shear test of the bulk TPU sample. (B) Warner-Bratzler shear test cutting profile of 3D printed samples.

Soft 3D Printing of Thermoplastic Polyurethane: Preliminary Study

F. Fenollosa-Artes [1,2], L. Jorand [1], A. Tejo-Otero [1], P. Lustig-Gainza [1], G. Romero-Sabat [3], S. Medel [3], R. Uceda [1,2]

[1]Centre CIM, Universitat Politècnica de Catalunya (CIM UPC), Carrer de Llorens i Artigas, 12, 08028, Barcelona, Spain
[2]Universitat Politècnica de Catalunya. Departament of Mechanical Engineering. School of Engineering of Barcelona (ETSEIB). Av. Diagonal, 647. 08028, Barcelona, Spain
[3] Polymer Synthesis Unit, Leitat Technological Center, Carrer Innovació, 2, 08225 Terrassa, Barcelona

Abstract

Thermoplastic polyurethane (TPU) is a highly elastic linear polymer composed of soft segments, usually flexible polyester, or polyether. It is widely used in 3D printing technologies, being FFF the most common technique. However, stiffness and hardness values of 3D printed TPU in filament form are higher ~~that~~ than ~~it~~ would be desirable for some applications, which require softer parts. Therefore, it was seen necessary to find a new methodology for 3D printing soft TPU. In this way, the present study seeks to be the first research study ~~which~~ that focuses on the possibility of 3D printing TPU using DIW (Direct Ink Writing) technology with UV light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. Then, both bulk and 3D printed TPU samples were characterized in terms of shear strength using the Warner-Bratzler shear test and hardness using the Shore hardness test. It was seen that the 3D printed samples showed higher softness than bulk samples ~~as well as in comparison with~~compared to TPU filament. Finally, it was concluded that the 3D printing of TPU is challenging due to several points: (1) the viscosity of the TPU; (2) their main issue is their sticky behavior; and (3) the shrinkage which takes place after the thermal treatment and for some applications, it might be a problem. Despite that, TPU appears to be a promising material to be used in different industrial applications.

Keywords

3D Printing; additive manufacturing; thermoplastic polyurethane

Corresponding author

*ffenollosa@cimupc.org

Article Type

Original Article/Short Communication

1. Introduction

Since its discovery in 1937 by Otto Bayer, Polyurethane polymers (PU) have advanced until ~~becoming~~ they have become part of our everyday lives~~fe~~. Within Polyurethanes, Thermoplastic polyurethanes (TPUs) are usually randomly composed of linear polymer with flexible soft-chain (soft-domain) segments chemically bonded with low-mobile segments (hard-domain) that act as cross-linking points within the structure. The selection and hard/soft segment ratio can significantly affect the overall polymer behavior as well as ~~producing~~ produce its well-known versatility. Generally, it offers high elongation, low hardness (45-85 Shore A), moderate tensile strength (5-15 MPa), and elastic modulus (2400 N/mm^2) as well as excellent abrasion and tear resistance [1,2]. Additionally, it appears to have ~~an~~ excellent biocompatibility [3,4] and resistance against erosion, oil, and acid environment [5]. It can be used in combination with other polymers to change their mechanical properties, depending on the purpose. For instance, Pham [6] investigated the effect of polyamide (PA) 6 with TPUs.

TPU has mainly been ~~additive~~ additively manufactured [5] using material extrusion, powder bed fusion, and material jetting. Among these technologies, the most widely used is material extrusion, specifically FFF, since it is a cost-effective technology. For instance, Bates et al. [7] 3D printed TPU samples with the honeycomb structure using FFF technology. The material is selected due to its impact strength and abrasion resistance and therefore is used to create ~~energy absorbing~~energy-absorbing structures. Also, FFF technology is used to study the adhesion strength between soft TPU and ABS (Acrylonitrile Butadiene Styrene)/ASA (Acrylonitrile Styrene Acrylate) [8] aiming to further investigate the multi-material possibilities of 3D printing. It was found that TPU can adhere to both ASA and ABS, which allows them to be printed together in a ~~multi material~~multi-material 3D printer. According to this study, the adhesion strength was comparable to commercial adhesives. Another study [9] 3D printed a composite of TPU with glass fiber (GF) and showed that the addition of GF increases the mechanical properties of the TPU. Additionally, Hossain et al. [10] 3D printed for the first-time elastomeric PU using vat photopolymerisationphotopolymerization technology, in which the material is built and polymerized under UV light. In recent years, TPU was tried to be 3D printed using the Direct Ink Writing (DIW) technology. For instance, Valentine et al. [11] 3D printed TPU with added silver flakes using DIW for soft electronics development. Then, Ahmed et al. [12] developed a 3D printed TPU/CNPs strain sensor using the mentioned technology. Nevertheless, none of them used UV light, as it is sought in the present manuscript. Then, Dadbakhsh et al. [13] used SLS for the manufacture of TPU with an average hardness of 87 Shore A, with the aim of findingto find the importance of the powder morphology. Moreover, Plummer et al. [14] studied the recyclability of a the thermoplastic polyurethane powder for its use in laser sintering.

In the medical sector, the use of TPU in filament form for FFF is common. For example, Domínguez-Robles et al. [3] 3D printed TPU filaments containing levofloxacin (LFX) in various concentrations for the production of vaginal meshes. Then, Li et al. [15] additively manufactured medical grade TPU using FFF technology was found to have the potential to produce medical devices and surgical tools. Then, Esmaeili et al. [16] manufactured TPU composed of nanocrystalline hydroxiapatite hydroxyapatite (HA) nanopowder to construct artificial blood vessels. In case porous scaffolds were needed for a certain medical application, SLS could be used according to Yang et al. [17] as well as laser powder bed fusion (LPBF) [18].

But TPU filaments are not soft enough for certain applications, as trying to mimic living tissue hardness in surgical planning prototypes. Additionally, the FFF 3D printing of TPU is a challenge for several reasons: (1) sometimes the filament is not inserted into the hotend correctly, causing a jam in the knurled pulley of the extruder and the bearing; (2) an excessive filament friction producing a more pressure on the drive gear consequently more filament feed problems can happen as a result; (3) the need to be 3D printed at low temperatures; however, higher is the temperature, the lower is the pressure needs to be applied, but the possibility of breaking the filament also increases; (4) difficult to post-process; and (5) hotend intern pressure.

The solution explored to reach a higher softness is 3D printing special formulations for soft TPU using another material extrusion technology: DIW technology, as working with liquids should make it possible to avoid the feeding problems related with to soft filaments. An important point is the novelty of this research: it has not been found any previous mention about it the literature, which may be due to the intrinsic difficulty about of working with too soft materials in 3D printing. Hence, by taking everything into account, the aim of the present study is aims to present a soft TPU (softer than standard FFF TPU) to be processed by DIW technology using UV curing light. Firstly, the optimal 3D printing and curing parameters to print soft TPU are determined and then two different TPU formulations are 3D printed. And then, both bulk and 3D printed TPU samples are characterized in terms of shear strength using the Warner-Bratzler shear test and hardness using the Shore hardness test.

2. Materials and Methods

2.1. TPU Synthesis

Hybrid UV photocurable thermoplastic Polyurethane (TPU) - acrylate were manufactured following a pre-polymer solution method as follows: Polypropylene Glycol (PPG) with a molecular weight of 1000 g/mol and Tetrahydrofuran (THF) were introduced in a 100 mL 5-neck mini-reactor (Scharlab). The mixture was stirred at 260 rpm and heated to 60ºC in an Argon inert atmosphere to remove the possible presence of moisture. Once the set temperature was reached, Isophorone Diisocyanate (IPDI) was incorporated dropwise followed by three drops of Dibutyltin Dilaurate (DBTDL) as a reaction catalyst. The Polyol to isocyanate ratio was kept around 0.5:1 to ensure plenty of ~~isocyanate free~~isocyanate-free groups in the prepolymer for further functionalization. The reaction was monitored by FTIR-ATR (Fourier-Transform Infrared Spectroscopy in Attenuated Total Reflection mode) observing the NCO peak at 2272 cm-1(Figure 1B). Once the NCO peak was not further reduced due to complete reaction between PPG and IPDI (approximately 2 hours), ~~a~~ half of the theoretically required quantity of 1,4-Butanediol

(BDO) was introduced with a previously dispersed photoinitiator (Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide). When no more NCO peak reduction was observed from the FTIR spectra again, an acrylic molecule containing both a hydroxyl and a vinyl terminal was added and left to react. Finally, the rest of the BDO was introduced and the completion of the reaction was determined when no free isocyanate was observed. The final ideal chemical structure of the molecule and follow-up of the reaction by FTIR-ATR can be observed in ~~Figure~~ Figures 1A & 1B respectively. For example, regarding Figure 1A, each color corresponds to a chemical compound: (1) yellow to acrylic end-terminal (HEMA); (2) black to diisocyanate (IPDI); (3) red to polyol (PPG); and (4) green to chain extender (BDO). On the other hand, Figure 1B shows one color for each covalent bond, which is placed to the corresponding color in vertical. To procure a minimal shrinking effect on the UV post-curing process, the samples were left in a vacuum oven at 60ºC for at least 48h to eliminate the solvent from the product.

~~Two hybrid~~Two-hybrid TPU-acrylates with different hard/soft segment ~~ratio~~ ratios were synthesized by varying the polyol and isocyanate concentrations in the formulation: (1) sample A, 20:80 rigid and flexible (soft) segments, respectively; and (2) sample B, 35:65 rigid and flexible (soft) segments, respectively.

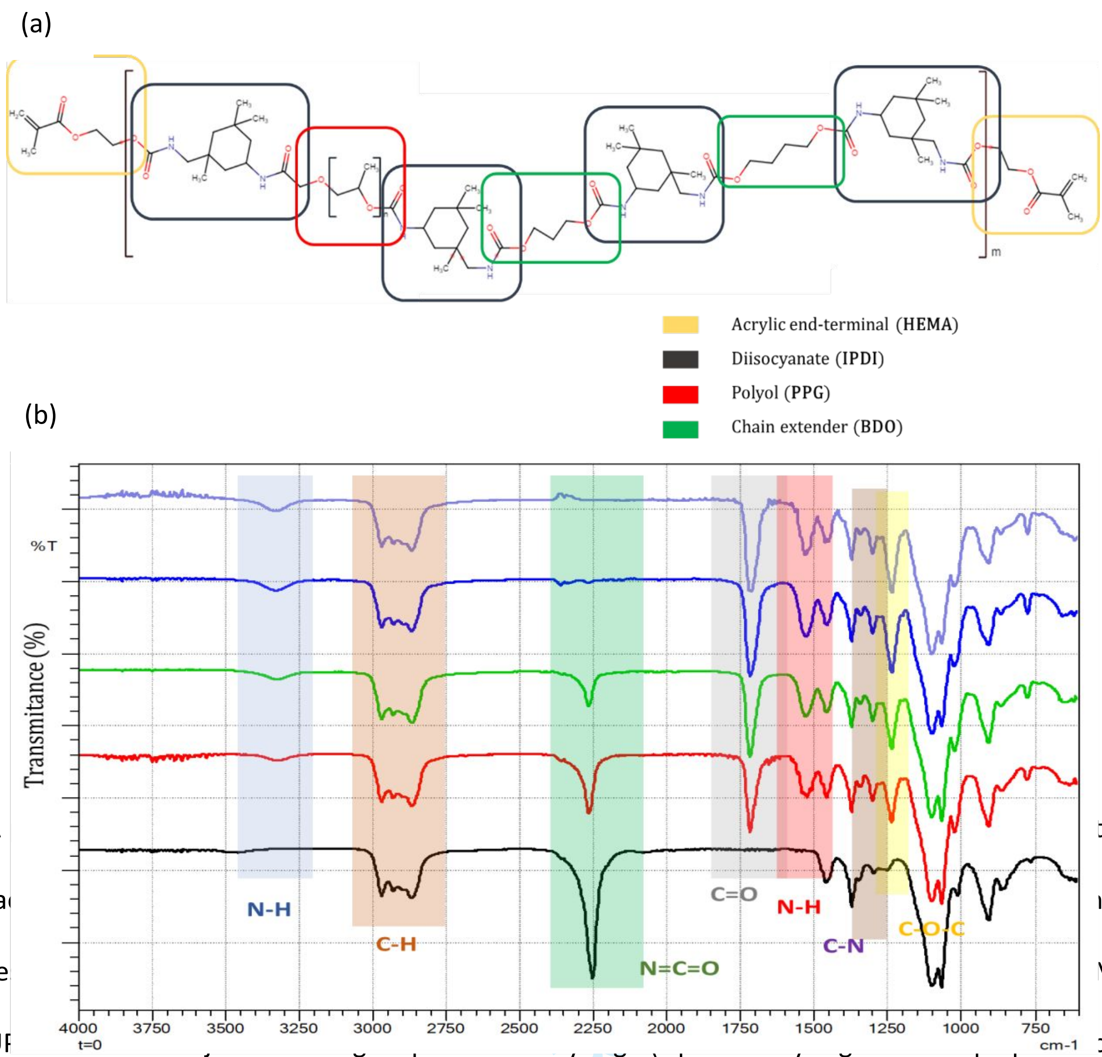

Figure 1. *(a) Ideal chemical structure of the synthesized hybrid TPU-acrylates. (b) FTIR-ATR spectra of the hybrid TPU-acrylates at different reaction times. Evolution of the polymerization reaction was monitored by following the decrease of the NCO peak at 2272 cm^{-1} (bottom-up observation, being the black spectra the beginning of the synthesis and the clear blue, the final).*

and an irradiation area of 3 mm ray. The led head unit is ~~a~~ an L14310 model with a mounted condenser lens E11923-110, producing radiation with a wavelength of 365 nm. To hold and fix this UV-light next to the printing tip, different tool parts were designed, and 3D printed in PLA filament material in a SIGMA BCN3D printer as can be seen in Figure 2. Additionally, a UV mask was also designed and placed in the tool for avoiding the tip ~~for~~ from being cured due to the UV light. Once a sample is 3D printed, it is left in an isopropanol bath ~~in order to~~to remove the TPU that is not cured. Then, the sample is placed for 2-3 hours at 70 ^{0}C in an oven from Memmert GmbH, Germany, so that the sticky part is removed.

(~~b~~a) (b)

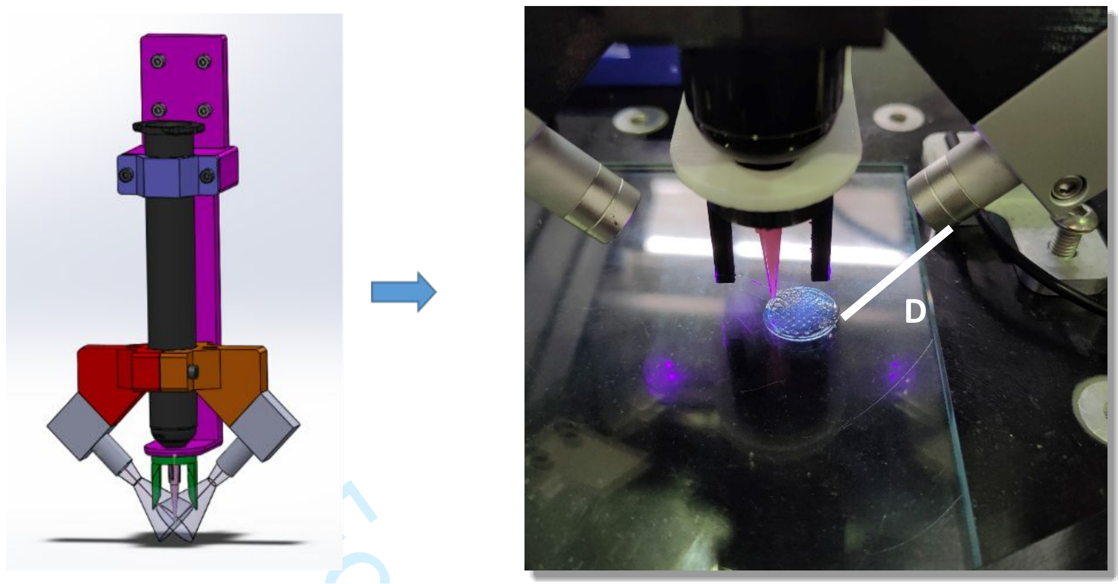

Figure 2. *a) CAD simulation of the tool-head assembly, made from specially designed and FFF 3D-printed components. Design of the shadow-generator pins has been optimized to protect the tip from clogging. b) Photopolymeric TPU being 3D-printed: parameter D is the distance between the UV light source and the the sample.*

~~a) b)~~

2.2.1. Curing Tests on TPU – Parameters

As not many research studies like this has been found (except from [10], where an elastomeric polyurethane (EPU) material is built and polymerized using ~~an~~ ultraviolet light, and [11,12] that 3D printed TPU but without using any UV light), it was necessary to do a preliminary curing study for the 3D printed TPU samples, so that the best parameter values for the TPU samples were achieved. Once these parameter values were obtained, the final TPU 3D printed parts were manufactured.

At first, two parameters were considered: (1) Power Rate, that is percentage of UV light power applied, which varies from 1 to 100 %; and (2) the distance D between the source and the 3D printed samples (see Figure 2). Both parameters are necessary to obtain the irradiance of the UV, that is the amount of energy that falls on a given surface, expressed in W/m² in the ISU, but mostly expressed in mW/cm². The maximum irradiance this source can provide is 14000 mW/cm² at 10 mm from the lamp and at the center of the irradiation area.

Distance D varies the irradiance with an inverse square law: irradiance is inversely proportional to the square of D. This means that the greater the distance to the sample, not only is the irradiance significantly less, but also much more uniform ~~with respect to~~concerning the distance to the center of the exposure's area. D is defined at approximate ranges, between 0 and 10 mm, between 10 and 15, then 15 to 20, 20 to 25, 25 to 30 mm, and finally 50mm.

2.2.2. 3D Printing Parameters

After all this previous research about these two basic parameters (D and Power Rate), two solid cylinders of different ~~composition~~ compositions of TPU (n=4) were 3D printed. The dimensions for sample A: 12.36±0.96 mm of diameter and 8.11±2.11 mm height. The dimensions for ~~the~~ sample B: 12.82±0.49 mm ~~of~~ in diameter and 8.16±1.13 mm in height.

The printing parameters used in the 3D printing process can be divided into two categories: (1) fixed parameters, and (2) variable parameters.

The considered fixed parameters are 6: (1) D; (2) SR or speed rate of the 3D printing tool-head; (3) TP or tip diameter of the nozzle; (4) LT or layer thickness of the 3Dprinting part (z height movement of the tool-head to change the layer); (5) time in isopropyl alcohol; and (6) PCT or post-curing temperature. Some considerations about the reasons for fixing them are also detailed.

(1) D: distance (D) between the UV source and the samples is fixed within a range between 40 and 50 mm, according to the preliminary curing test results.

(2) SR is fixed at 160 mm/min, a medium and common value for DIW. Future research could explore the influence of its variation but is not considered a key parameter in this first exploring research.

(3) TP is fixed at a diameter of 0.58 mm, also a very common value for Nordson standard syringe tips for DIW.

(4) LT is fixed at a height value of 0.35 mm, corresponding to a value considered optimal taking in into account previous parameters as SR, TP, and LT.

(5) time in isopropyl alcohol for removing any residual monomers (10 minutes).

(6) PCT is fixed at 70 ^{0}C, a standard value for polyurethanes.

The considered variable parameters are 3: PR, p, or pressure applied in the syringe and t or time in the oven.

(1) PR: power rate of the UV light (considering the movement of the print-head is slow enough to keep the part enlightened during the process) was comprised between 10 % to 35 % of the maximum capacity of the devicedevice's maximum capacity.

(2) p is allowed to vary between 0.5 and 2 Bar, to adjust the printing process to different viscosities of the sample. The more viscous the sample is the more pressure is needed to guarantee an optimal flux from the nozzle.

(3) t is not considered a key factor, and its value can vary within a large range without any special consequence on the properties of the samples. Time in the oven has been added in some samples trying to eliminate their remaining stickiness after the 3D printing process. Its value for every sample has been recorded, and probably further research should explore this factor.

2.2.3. Shore Hardness Test

Shore hardness is a measurement of the resistance of a sample to indentation. There are different scales based on ASTM D2240 testing standards [19]: A, B, C, D, DO, E, M, O, OO, OOO, OOO-S, and R. Each scale results in having values between 0 and 100, where higher values indicate that a material is harder. STM D2240-Durometer Hardness method was used [19]. For that, Shore Durometer Type A, 00 and 000, supplied by Baxlo, Instrumentos de Medida y Precisión, S.L., Spain. Shore A is the hardest, and Shore 000 the softest.

2.2.4. Warner-Bratzler Shear Test

Warner-Bratzler shear test is commonly used in the food industry as a standard characterization method. For example, it has been used to determine the best meat tenderness (toughness) for various types of meat. The Warner-Bratzler consists of a steel frame which is supporting a triangular shear blade. The texturometer Texture Analyser TA.XT.plus (Stable Micro Systems, Surrey, UK) was used with a 50N load cell. Maximum shear force (N) and area under the curve (J) ~~was~~ were measured using the Warner-Bratzler probe. The speed is 1mm/s during 35 mm of cut. The height of the sample was measured with a digital micrometer.

2.2.5. Statistical Analysis

Statistics were performed using MATLAB R19. Bulk and 3D printed TPU samples were assessed using paired sample T-Test to compare if the bulk and 3D printed TPU samples are equal by focusing on Shore and maximum forces values. Data are represented as mean ± SEM (Standard Error of the Mean). $p \leq 0.05$ (*), $p \leq 0.01$(**), and $p \leq 0.001$ (***). The null hypothesis states that the bulk and 3D printed TPU samples are equal. If the p-value is lower than 0.05, the ~~hypotheses~~ hypothesis is rejected; and consequently, it is confirmed that the bulk and 3D printed TPU samples are not equal.

3. Results and Discussion

3.1. Curing Tests on TPU

The 3D printed samples manufactured for the preliminary study of the curing tests were different samples of A and B. There were four different outcomes from the curing tests (see Figure 3): (1) ~~totally~~ cured in which the sample is completely solidified at any point; (2) partially cured in which the sample contains an uncured area, commonly on a side; and (3) only cured at the center which is ~~commonly~~ common when the area covered by the light is too small (implying the UV light is too close) and does not cure 100 % of the area of the cylinder; and (4) too cured. Table 1 summarizes the results. Then, the height H of the sample was also measured. Additionally, after the thermal treatment of the samples to eliminate the stickiness, a shrinkage between 15 % and 30 % was observed.

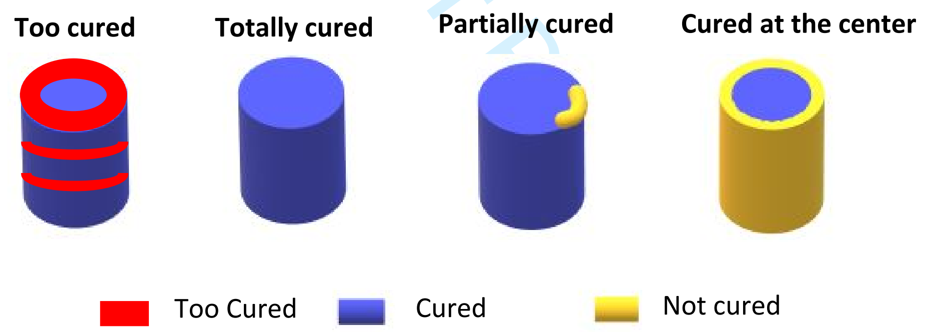

Figure 3. *Different outcomes of the curing tests.*

Table 1. *Qualitative results of the curing tests.*

Power Rate [%]	Sample Number	D [mm]	H [mm]	Curing
10	#1	0-10	4.85	Cured at the center
	#2	10-15	6.8	Cured at the center
	#3	15-20	5	Cured at the center
	#4	20-25	6.6	Cured at the center
	#5	25-30	6.1	Cured at the center
	#6	50	5.65	Partially cured
25	#7	0-10	4	Cured at the center
	#8	10-15	8	Cured at the center

	#9	15-20	6.5	Cured at the center
	#10	20-25	5.5	Partially cured
	#11	25-30	5	Partially cured
	#12	50	7	Totally cured
50	#13	0-10	4.5	Cured at the center
	#14	10-15	6.8	Partially cured
	#15	15-20	6.2	Cured at the center
	#16	20-25	5.6	Cured at the center
	#17	25-30	4.4	Partially cured
	#18	50	8	Totally cured
75	#19	0-10	2.2	Partially cured
	#20	10-15	3	Totally cured
	#21	15-20	4.6	Totally cured
	#22	20-25	4.25	Totally cured
	#23	25-30	5.5	Too cured
	#24	50	11	Too cured
100	#25	0-10	2.5	Totally cured
	#26	10-15	4.75	Totally cured
	#27	15-20	6.1	Totally cured
	#28	20-25	2.5	Too cured
	#29	25-30	3.4	Too cured
	#30	50	5.1	Too cured

As it can be seen, at about 50 mm away from the source, the polymer is nearly cured even for power rates where it is partially cured at other distances, indicating that to be totally cured, it does not require a very high irradiance but rather a full exposure of the piece to the UV radiation. Additionally, high irradiance could cure the tip (although the "shadowers" tips have been optimized, see Figure 2), which is something to consider, because if the tip is cured, the 3D printing process stops. Also, too much power rate can result in an excessively cured part, corresponding to ~~an~~ accelerated ~~ageing~~ aging of the 3D printed sample. Additionally, a higher distance achieves to cover the curing process of more parts of the 3D printed samples than shorter distances. In other words, a short distance leaves some parts being uncured.

Therefore, it had been considered that the best option to follow on with more tests was to place the source at D= 40-50 mm distance and apply low-medium power rates (between 10% and 35%). However, low power rates can cause ~~a~~ partial curing of the sample, which it may be addressed ~~afterwards~~ afterward with UV exposure out of the 3D printer. Anyway, this low Power Rate is going to prevent two major issues: clogging of the 3D printing tip and excessive curing.

3.2. 3D Printed TPU Samples

After all the curing tests are finished and the optimal values for the two basic parameters (D and Power Rate) ~~has~~ have been found, two solid cylinders of different ~~composition~~ compositions A and B of TPU (n=4) were 3D printed. Table 2 summarizes every value used for the three variable parameters (PR, p, or pressure applied in the syringe and t or time in the oven).

***Table 2**. 3D printing variable parameters of the TPU samples.*

Sample Name	Sample Number	Power Rate [%]	Pressure [Bar]	Time in the Oven [Hours]
B	#1	15	0.3	17
	#2	10	0.9	4
	#3	10	0.9	4
	#4	10	1.1	4
A	#5	10	0.9	68
	#6	15	0.9	66
	#7	25	1	3
	#8	35	1	3

Figure 4 shows the 3D printed samples. As can be seen, the 3D printing of this TPU is challenging due to several points. Firstly, the viscosity of the TPU makes it very difficult to 3D print TPU

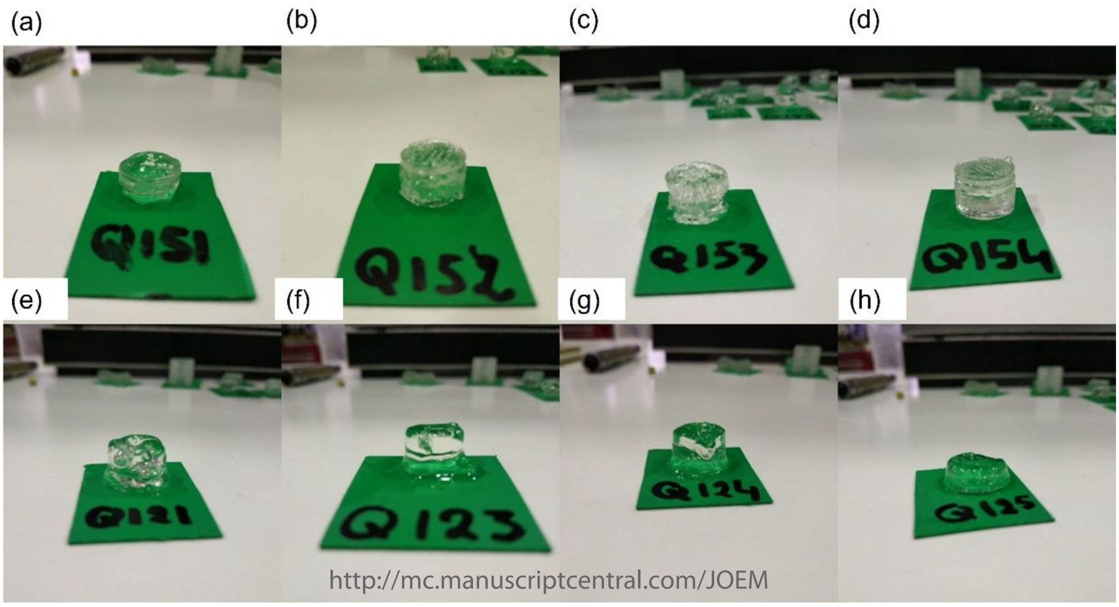

Figure 4. 3D printed TPU samples. Sample B: (A) Sample #1. (B) Sample #2. (C) Sample #3. (D) Sample #4. Sample A: (E) Sample #5. (F) Sample #6. (G) Sample #7. (H) Sample #8.

samples, while it also gives the material a sufficient shear strength not to collapse during the 3D printing process. Secondly, once the TPU samples are additively manufactured, their main issue is their sticky behavior. It seems that the softer the TPU samples are, the stickier is their behavior. In fact, despite the t and PCT factors, in some samples, the removal of the stickiness wasn't achieved at 100%. Another major point to mention is the shrinkage ~~which~~ that occurs after the thermal treatment and, for some applications, it can be a problem. This usually takes place with ~~3D printed~~3D-printed ceramic parts after the sintering process. Despite these limitations, TPU is a promising material that can be used in different fields, and the results obtained warrant future further research. Additionally, its transparency – a characteristic scarcely found in the 3D printing world-, can make the difference for certain applications.

3.3. Shore Hardness Results

Shore hardness of bulk TPU samples was obtained. The reason was to compare it with the Shore hardness of 3D printed samples. The aim was to analyze if, using the same liquid, the hardness was affected by a 3D printing process. The Shore hardness of the bulk TPU is 40±6.8 Shore A, 80±4.70 Shore 00, and 82±7 Shore 000.

The Shore hardness of the 3D printed TPU samples differs depending on the hard/soft segment ratio of both bulk TPU samples described previously (A and B). This might be due to a difference ~~of~~ in density because 3D printed parts are known to have a lower density in a general case. The values are summarized in Table 3. All in all, ~~the less rigid segments proportion~~the proportion of the less rigid segment the sample has (minimum of 20% for samples type A), the softer is. Despite sample B ~~is~~ being harder than A, both are softer than bulk TPU samples.

Table 3. *Shore hardness of the 3D printed TPU samples.*

3D Printed Sample	Shore A	Shore 00	Shore 000
A	0	39±4	65±6.5
B	11±1.5	57±4	71±4.5

Regarding its difference with bulk TPU samples, the p-value, by looking into the Shore 00, is 0.00001 and 0.0027, for A and B, respectively. This means that the bulk and 3D printed TPU samples are not equal since the null hypothesis is rejected.

And both bulk and DIW- 3D printed TPU ~~are~~ is softer compared to the typical Shore Hardness of TPU filaments, which is 26 Shore D [20]. This value might correspond to 80 Shore A according to ISO 868 A [15]. To give some more detail related to commercial TPU filaments, Bioflex filament is 27 Shore D [21] or the TPU filament of Recreus filament varies from 70 Shore A to 95 Shore A [22].

3.4. Warner-Bratzler Shear Test

Warner-Bratzler shear test of bulk TPU samples was performed. The reason was to compare it with the Warner-Bratzler shear test of 3D printed samples. The Warner-Bratzler shear test cutting profile can be seen in Figure 5. The maximum force measured is 544.27 N, near the limit that the machine can measure. Additionally, this value is still very high, but it is a good ~~approaching~~ approach in the finding of soft TPU. However, there is no possibility to compare with 3D printed TPU samples using FFF technology, because they are too rigid to be measured using this method.

In terms of the Warner-Bratzler shear test, Figure 5B shows the cutting profile of both samples A and B. The maximum forces are lower than bulk TPU samples (Figure 5A): 249±117 N and 326 ± 70 N for A and B, respectively.

Regarding its difference with bulk TPU samples, the p-value, by looking into the maximum force, is 0.015 and 0.13, for A and B, respectively. Therefore, regarding ~~the~~ sample A, the null hypothesis is rejected (p-value is lower than 0.05) and, consequently, the bulk and 3D printed TPU samples are not equal. However, a p-value of ~~the~~ sample B is higher than 0.05 and, hence, the null hypothesis is not rejected. This means that both are more or less similar.

The samples type B need a higher force to be cut than type A. This is consistent with the proportions mentioned before. B-samples have a higher proportion of rigid parts than A-samples.

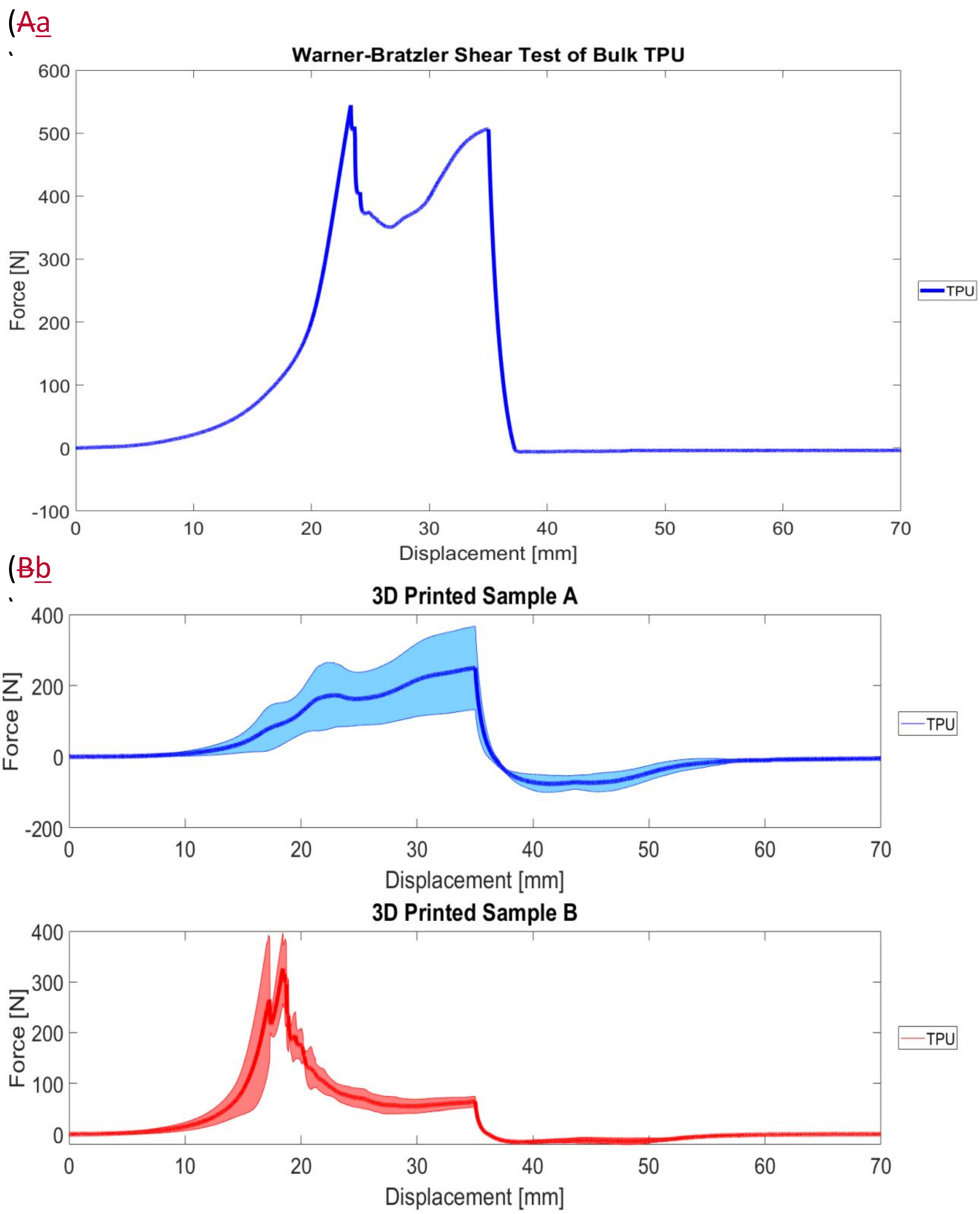

Figure 5. *(~~A~~a) Warner-Bratzler shear test of the bulk TPU sample. (~~B~~b) Warner-Bratzler shear test cutting profile of 3D printed samples.*

4. Conclusion

The present paper achieved to 3D print for the first time slurry-based TPU using DIW with UV light. Using this 3D printing technology with ~~soft oriented~~soft-oriented TPU liquids makes sense ~~in order to~~to achieve lower hardness values compared to current solutions. More research must be done, and next works will be oriented on using other printing means apart ~~of~~ from ~~syringes, and~~syringes and trying to correlate tackiness and softness. By now, this is a step forward in the state-of-the-art, not only in the AM field~~,~~ but also in the discovery of TPU and soft materials that ~~opens~~ open the door for future research studies. In this way, these materials could be used for the manufacturing of soft 3D printed parts, for example, in healthcare/bioprinting applications, ~~as~~ for example the manufacture of phantoms for preoperative surgical planning. Furthermore, in the future, slurry-based TPU could be used in hybrid multi-material 3D printers along with filaments or other materials, opening the possibilities of new technologies and applications in the AM field.

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