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FORMULATION AND TESTS OF HYBRID PHOTOCURABLE RESINS FOR ADDITIVE MANUFACTURING

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Abstract. Additive manufacturing (AM) is one of 4.0 industry cornerstones, furthermore, the AM enables and propels new business generation in several economic sectors. The raw materials development for different additive manufacturing processes, such as vat photopolymerization (VP), contributes to a better strength of the printed parts and expanding, even more, the AM employment possibilities. This paper aims to formulate and testing hybrid resins (with acrylic and epoxy monomers), for additive manufacturing by VP. Initial tests using commercial resins were carried out to verify the mechanical properties correspondence between molded and 3D printed materials. Hybrid resins were formulated and then test specimens were molded and 3D printed by vat photopolymerization. The specimens were subjected to tensile, compression, and flexural tests. The initial tests result evinced satisfactory proximity between the mechanical resistance of the molded and the printed photopolymerizable resins. Among the tested formulations, the printed resin with the highest average resistance reached 53 MPa in tension, 102 MPa in compression, 101 MPa in bending. The results obtained with the formulated raw materials encourage the hybrid resins usage for final product fabrication, it also motivates new compositions development focused on the printed parts resistance, expanding, even more, the applicability and business possibilities with AM.

Keywords: 3D printing, photopolymerization, hybrid resins, 4.0 industry

1. INTRODUCTION

Industry 4.0 has the additive manufacturing as one of its pillars. Some internet grounded technologies (e.g. internet of things, big data analytics, and cloud computing) are pointed out as bases of the fourth industrial revolution (Butt, 2020), but the AM is the main manufacturing processes highlighted by Industry 4.0 researchers (Haleem and Javaid, 2019; Butt, 2020; Forcina and Falcone, 2021). The literature about AM and the fourth industrial revolution also identifies the mechanical strength of 3D printed materials as one of the points to be improved focusing the Industry 4.0 productive processes development (Haleem and Javaid, 2019; Ashima et al., 2021).

Some applications for AM, such as customization, design development, and complex geometries fabrication (Haleem and Javaid, 2019), and also product fabrication at the point-of-demand (Gibson et al., 2021), enable new business opportunities in several production and service sectors. Customized orthosis made by additive manufacturing, as discussed by Wang et al. (2020), may provide a better fit and comfort for the patient than other commercial options, in this way the AM employment enables add value for the products on the orthosis market. The 3D printers by digital light processing (DLP) have been commonly utilized in odontology and it allows the dentist in-office quickly fabrication surgical templates and dental casts (Yao et al., 2020). Another AM application is complex geometries manufacture, sometimes unviable/impossible by conventional fabrication processes, like hot stamp tooling with curved

internal cooling channels that in some applications can speed up and increase the productivity of the stamping (Chantzis *et al.*, 2020; Muvunzi *et al.*, 2020). Gibson *et al.* (2021) provide other examples and explain how the 3D printing attributes offer opportunities for new business types, in addition, it is emphasized the importance of new materials development for increasing, even more, the AM usage.

Beginning in the first half of the 1980s, the additive manufacturing technologies by vat photopolymerization (VP) has been evolving and nowadays it is possible to obtain parts with AM by VP in ceramic (Amaral *et al.*, 2020), metal (Nguyen *et al.*, 2020) and composites (Medellin *et al.*, 2019; Asif *et al.*, 2020). These 3D printing technologies stand out in terms of geometric accuracy, being common equipment capable of printing parts with less than 30 μm layer thicknesses (Ahrens, 2017), it is also frequently cited the relatively high printing speed of VP compared with other AM technologies (Xu *et al.*, 2020; Lovo *et al.*, 2020; Zhao *et al.*, 2021). However, the photopolymeric properties required of the raw materials are a limitation for the vat photopolymerization processes (Ahrens, 2017; Westbeek *et al.*, 2020).

The development of raw material for VP is focused on recent academic researches. Chen *et al.* (2020) proposed some formulations and carried out mechanical tests with acrylic resins for digital light processing (DLP) 3D printing. Peerzada *et al.* (2020) analyzed and discussed VP resins compositions based on epoxy monomers and oligomers. Reinforcement fillers are also added to the photopolymeric formulations in order to increase the mechanical strength of printed materials (Medellin *et al.*, 2019; Dong *et al.*, 2021), some examples of these reinforcements are cellulose nanocrystals (Li *et al.*, 2019), short carbon fibers (Asif *et al.*, 2020), graphene (Li *et al.*, 2018), and silica (Dong *et al.*, 2021).

Hybrid photosensitive resins, composed of two or more molecular structure types of monomers (*e.g.* acrylate, epoxy, and vinyl ether) (Gibson *et al.*, 2021), are another interesting possibility of VP raw materials (Lantean *et al.*, 2018; Quan *et al.*, 2020). The hybrid photopolymer formulations allow combining characteristics inherent to the different components (Quan *et al.*, 2020), such as the high polymerization rates of acrylates with the low shrinkage and good thermal performance of epoxy (Lantean *et al.*, 2018). Also, the potential recycling capability (Chen *et al.*, 2021), and the mechanical behavior of printed parts (Lantean *et al.*, 2018; He *et al.*, 2021), contribute to the interest in hybrid resins as VP raw materials.

In this way, the purpose of this article is to formulate and testing hybrid resins (with acrylic and epoxy monomers), for vat photopolymerization 3D printing.

2. MATERIALS AND METHODS

In the present work it was utilized, molded and 3D printed by VP, specimens of different photopolymeric resins formulations. Both for molded parts polymerization and printed parts post-curing, it was applied an ultraviolet (UV) light polymerization unit model 520 (Exakt®) with 30W power.

Molds were confectioned using the material silicone P364 by Fillepoxi®, for the production of the molded photopolymer specimens. Using these molds enables testing with reduced amounts of resin compared to the volumes of material needed to fill a 3D printer vat.

A prototype DLP 3D printer was applied to make the specimens produced by VP. The AM machine utilized employs, as the light energy source, a projector X2 (Infocus®) with a native resolution of 800x600 pixels, luminous flux up to 1800 lumens, and without the UV filter. It was adopted the top-down configuration for the prototype equipment construction, with a spreading system like explained by Camargo *et al.* (2021). In addition, the 3D printer has the build volume of 70 mm x 50 mm x 50 mm (height) and it uses a precision linear actuator KR 33 (THK®), which allows a layer minimum thickness of 20 μm . Figure 1 shows the printing region of the AM machine utilized.

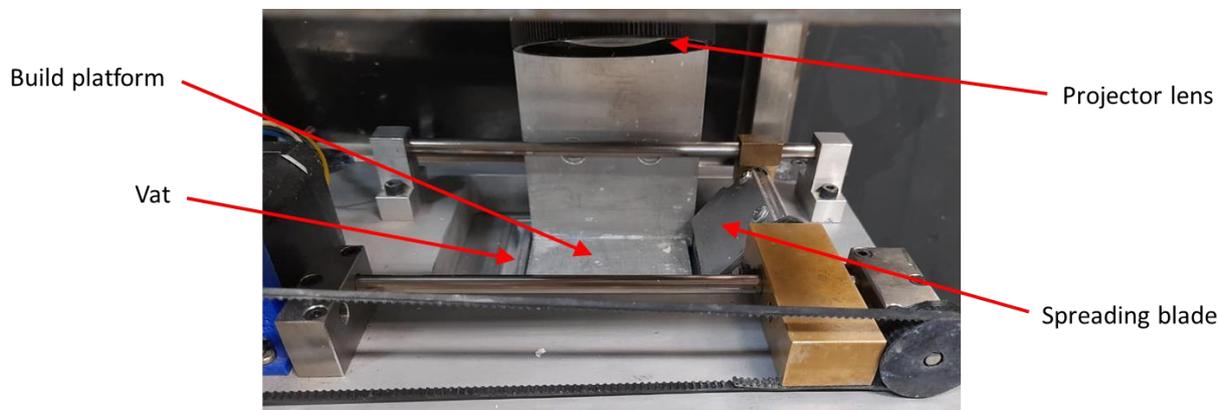


Figure 1. AM machine printing region.

In this work, it was employed (for specimens geometry, speed test, specimens number, apparatus, procedures, etc.), the following standards: ASTM D638 for tensile tests with specimens type IV, ASTM D695 for compression tests, and ASTM D790 for flexural tests with 40 mm of span. For all mechanical tests, it was utilized the universal testing machine Bionix (MTS®), with a load cell of 15.0 kN.

2.1 Molded vs. 3D printed photopolymers

Initial tests using two commercial resins were carried out to verify the mechanical properties correspondence between molded and 3D printed photopolymeric materials. The raw materials LS600 by Envisiontec® and Suen Ching by XRC® were utilized for this work first step.

Tensile, compression, and bending specimens were made in the silicone molds, with LS600 and Suen Ching resins, and the photopolymers were cured by exposure to UV light for 6 hours in the Exakt curing equipment. Also, with the two commercial raw materials, it was printed specimens for tensile, compression, and flexural tests, with 0.1 mm layer thickness. The printed parts were post-cured in the UV light for 2 hours.

The specimens (molded and made by AM) were tested, with a speed of testing 1.25 mm/min for tensile and 1.75 mm/min for compression and bending, on the universal testing machine. Room temperature was maintained at 20°C and air humidity between 50% and 60%.

2.2 Hybrid resins formulations

The previous work step demonstrated the mechanical properties correspondence between molded and printed photopolymers and thus the applicability usage of molds for VP raw materials development. In this way, for the present step, silicone molds were employed to produce the specimens of mechanical tests (tensile, compression, and flexural).

For resins formulations it was utilized acrylic monomers 2-Hydroxyethyl methacrylate (HEMA), photoinitiator for acrylic Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), epoxy monomers 3,4-Epoxyhexylmethyl 3,4-epoxycyclohexanecarboxylate (ECC), and photoinitiator for epoxy Triarylsulfonium hexafluorophosphate salts, mixed 50% in propylene carbonate (THS solution), all purchased from Sigma-Aldrich®. Five compositions were proposed, as presented in Table 1.

Table 1. Hybrid resins formulations.

Formulation	Composition (w/w%)
A	HEMA 98.0%; BAPO 2.0%
B	HEMA 73.5%; BAPO 1.5%; ECC 24.0%; THS solution 1.0%
C	HEMA 49.0%; BAPO 1.0%; ECC 48.0%; THS solution 2.0%
D	HEMA 24.5%; BAPO 0.5%; ECC 72.0%; THS solution 3.0%
E	ECC 96.0%; THS solution 4.0%

Each formulation was prepared, kept under vigorously shake with a magnetic stirrer for 24 hours, next placed in the silicone molds, and then placed in the UV light cure equipment by 24 hours for polymerization.

For the mechanical tests, it was applied 1.25 mm/min speed testing for tensile and 1.75 mm/min for compression and bending. Room temperature and air humidity were maintained respectively at about 20°C and 55%.

2.3 Hybrid resins formulation refinement

Based on the results of the preceding step, it was proposed a formulation refinement. In this sense, it was chosen a composition in order to obtain the resultant photopolymer with about acrylate 90% and epoxy 10% (weight percentage). This formulation (named "F") is detailed in Table 2. The components were mixed with a magnetic stirrer for 24 hours vigorously.

Table 2. Hybrid resin refined formulation.

Formulation	Composition (w/w%)
F	HEMA 88.2%; BAPO 1.8%; ECC 9.6%; THS solution 0.4%

Tensile, compression, and bending specimens were made both molded and with AM by DLP. The molded specimens were photopolymerized in the UV cure equipment by 24 hours. The specimens produced by DLP were printed with 0.1 mm layer thickness and post-cured for 8 hours in the UV light.

Mechanical tests of the molded and 3D printed refined formulation material were carried out, (at 20°C room temperature and 50% air humidity), and It has been used 1.25 mm/min speed testing for tensile and 1.75 mm/min speed testing for compression and bending.

3. RESULTS AND DISCUSSION

3.1 Molded vs. 3D printed photopolymers

Mechanical test results with the commercial resins (LS600 and Suen Ching), both molded and 3D printed specimens, were compiled to compare the strengths obtained by the two manufacturing methods. The comparative chart is shown in Figure 2.

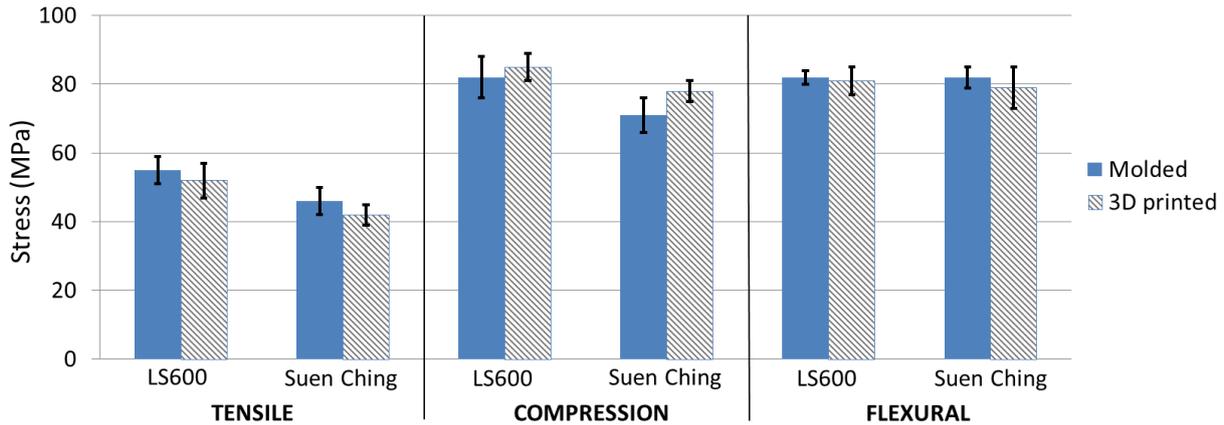


Figure 2. Molded vs. 3D printed photopolymers mechanical properties.

Observing the graph in Figure 2, it is possible to verify that in the tensile and compression tests, for the same resin, the average resistance difference between printed and molded materials did not reach 10%. Also, in compression tests, a trend of higher average strength was found in the printed parts, probably due to a greater ease of light penetration in the printing layers than in the total thickness of the compression specimens polymerized in mold. In bending tests the difference between the average strengths was even lower, it did not reach 4%.

Given the comparison of the results in traction, compression and flexion, it is confirmed a satisfactory closeness between the mechanical resistance of a resin light-cured in silicone mold and the same resin light-cured layer by layer with a 3D printer. Thus, the molds application is suitable for the formulation and characterization activities of raw materials for AM by VP, enabling tests with resources saving by using reduced resin amounts compared to the necessary volumes to fill the AM machines vat.

3.2 Hybrid resins formulations

The five proposed formulations presented mechanical properties significantly distinct from each other, due to the resins differences composition. In the Figure 3 graphs, the average curves obtained in the tensile, compression and flexural tests with the five photopolymers molded.

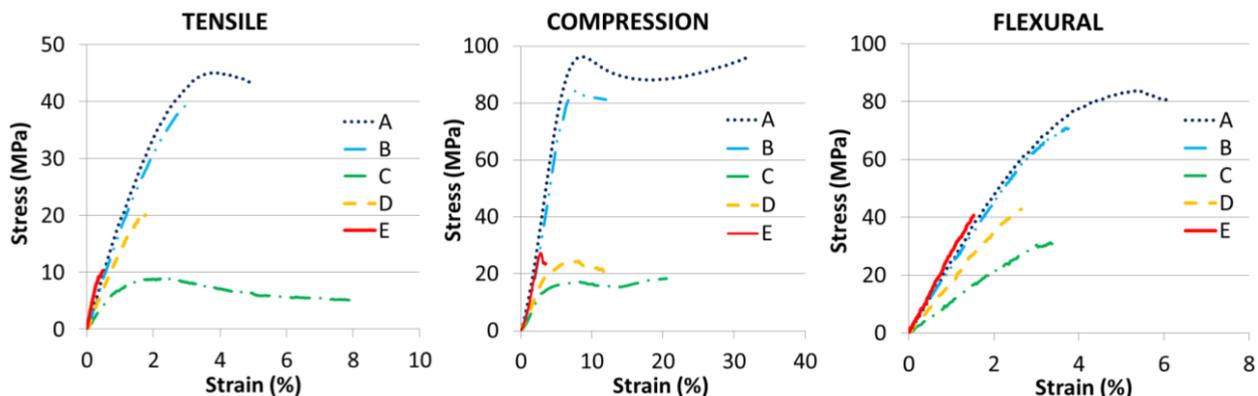


Figure 3. Average curves of mechanical tests with the five resins formulations.

Formulation A had the highest strength values among the five tested compositions (on average 45 MPa in tension, 96 MPa in compression and 84 MPa in bending), on the other hand, Formulation C had the lowest mechanical strength. The Formulation E obtained high elastic modulus (for a polymeric material), about 3.0 GPa, however, it presented considerable brittle behavior with less than 1% maximum strain in tensile tests.

Analyzing the mechanical tests results with the five formulations, for the adopted components and conditions, it is observed that the 25 wt% or more addition of epoxy monomer to an acrylic resin do not imply in strength gains. However, based on the literature information (Gibson *et al.*, 2021) and the obtained results, it was proposed a hybrid resin formulation with less than 25 wt% of epoxy monomer.

3.3 Hybrid resins formulation refinement

Mechanical tests results with the Formulation F (refined hybrid resin formulation), for molded and 3D printed specimens, is shown in Figure 4.

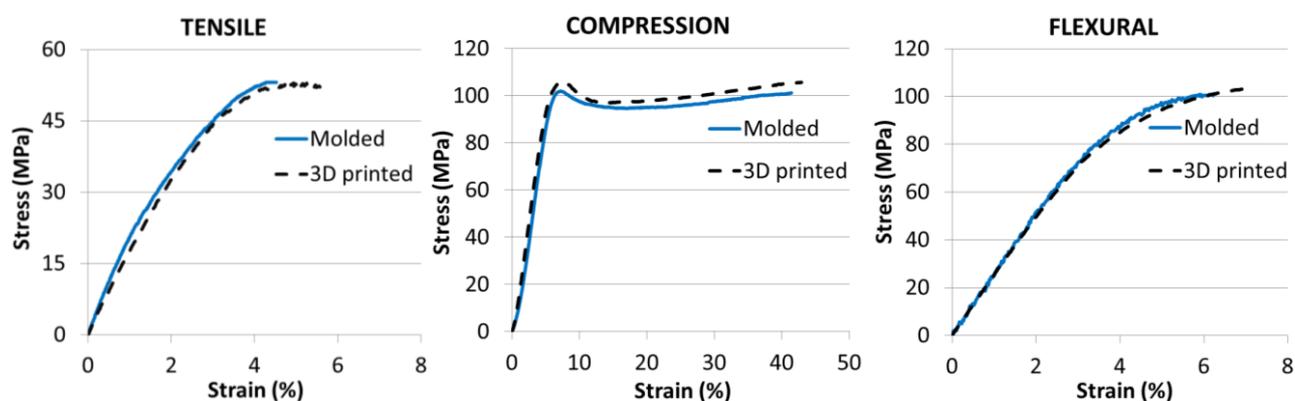


Figure 4. Average curves of mechanical tests with the refined hybrid resin formulation.

Formulation F reached the average resistance of 53 MPa in tension, 102 MPa in compression, 101 MPa in flexural, and more than 4% maximum strain in tensile tests. The mechanical strength values of Formulation F are higher than the obtained with Formulation A. In this way, it was demonstrated the possibility of obtaining a resin composed by two types of monomers (hybrid resin) with greater mechanical strength compared to resins consisting of only one of these monomers.

It is possible to verify by Figure 4 graphics the proximity between the average curves obtained with molded and printed specimens tests. Also, it is observed a slightly higher ductility of Formulation F processed by DLP compared of the same material photopolymerized in mold.

4. CONCLUSIONS

Comparative tests evinced a satisfactory proximity between the mechanical resistances of molded and printed by DLP photopolymers. Therefore, the silicon molds are a valuable tool for the development of new photopolymeric resins for AM by VP, permitting the formulation and tests activities without requiring the material volumes to fill the 3D printers vat, enabling research resources saving.

The five compositions proposed in hybrid resins formulations step presented great variations between their mechanical strength values, due to the differences of utilized monomers ratios. It was realized that, for the components and conditions applied for the present work, the addition of 25 wt% or more epoxy monomer to an acrylic resin do not implied in mechanical strength gains for the formulated materials.

The refined hybrid resin composition (Formulation F) had the highest strength among the proposed formulations, and it was observed the feasibility of obtaining a hybrid resin (composed by two types of monomers) with higher mechanical strength than the resins consisting of only one of these monomer types. In this way, the results obtained with the Formulation F encourage the hybrid resins usage for final product fabrication, it also motivates new compositions development focused on the printed parts resistance, expanding, even more, the applicability and business possibilities with AM.

5. ACKNOWLEDGEMENTS

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