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Synthesizing UV Curable Silicon Acrylate Resins for SLA Type 3D Printers and Characterization of Mechanical, Thermal and Morphological Properties

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Abstract
This study includes synthesizing of silicon acrylate resin and characterization of SLA printed samples which are prepared for different rate of weights of silicon acrylate/epoxy acrylate.
First of all, acrylate functional PDMS is synthesized by reaction of hydroxyl-terminated polydimethylsiloxane with acrylate functional structure. Different rate of weights as 10%, 20%, 40%, 60%, and 80% for acrylate functional PDMS are added into epoxy acrylate resins. In addition pure (100%) acrylate functional PDMS samples are printed. Mechanical properties of SLA printed samples are characterized by tensile and hardness tests. The glassy transition temperature of the samples is tested by DSC. Fracture surfaces of specimens are investigated by SEM and density characterization is performed. The structure of the synthesized silicone acrylate resin is illuminated by FT-IR analysis.

1. Introduction

The manufacturing of 3D objects by stereolithography is based on the spatially controlled solidification of a liquid resin by photo-polymerization. Pattern is illuminated on the surface of a resin above the building table as UV light by projector with a computer-driven building stage. Eventually the resin in the pattern was cured to a defined thickness as resin amount of resin on the table (Ferry et al., 2010: 6122), (Wu et al., 2018: 1512). Then the building table was moved down and the cured layer was resurfaced by resin. The process was repeated until test specimens are printed. Nearing 30 years since its introduction, 3D printing technology is set to revolutionize research and teaching laboratories. With a B.S. in engineering physics from the University of Colorado, Hull started work on fabricating plastic devices from photopolymers in the early 1980s at Ultra Violet Products in California. The lengthy fabrication process (1–2 months) coupled with the high probability of design imperfections, thereby, requiring several iterations to perfect, provided Hull with the motivation to improve current

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methods in prototype development. In 1986, Hull obtained the patent for stereolithography and would go on to acquire countless more patents on the technology (Hull, 1986) (Hull, 1990). In 1986, he established 3D Systems and developed the .STL file format, which would "complete the electronic 'handshake' from computer aided design (CAD) software and transmit files for the printing of 3D objects". Hull and 3D Systems continued to develop the first 3D printer termed the "Stereolithography Apparatus" as well as the first commercial 3D printer available to the general public, the SLA-250 (Hull, 1992).

There are some researches on photolithography and optical 3d printing with photopolymers in literature (Montgomery et al., 2018: 363) (Miezinyte et al., 2019: 382). Especially Waters and Bernhardt (2017: 49) focused on the effects of curing parameters on compressive strength and hardness properties while maintaining surface quality for stereolithographic test specimens. They achieved the highest compressive strength at 25μm layer thickness. Also they observed that curing temperatures above 100^{o}C resulted in degraded surface quality.

Polydimethylsiloxane (PDMS) is used in range of applications owing to its unique features, such as high thermal and oxidative stability, weather and chemical resistance, and low surface tension (Hwang, 2011: 656). Researchers are used acrylate-functional polydimethylsiloxane (AF-PDMS) at coating studies (Kim, 2003: 2236). Mazurek et al. synthesized AF-PDMS copolymers with using methacrylic acid as solvent for coating investigations in 2000. In addition researchers are examined abrasion properties of AF-PDMS with low surface energy (Sonnenschein, 2008: 127). Williams is investigated morphological properties of silicon acrylate copolymers which are prepared by photopolymerization.

In this study, AF-PDMS is synthesized by using hydroxyl -terminated PDMS and acryloyl chloride reaction with triethylamine as a catalyzer. Obtained AF-PDMS is combined with Bis-GMA/HDDA mixture by different rate of weights and finally 1% photoinitiator added. Tensile test specimens are prepared by SLA type 3d printer and mechanical, morphological and thermal characterizations are investigated. In addition synthesized and commercial AF-PDMS are compared for structural properties by FT-IR spectroscopy.

2. Experimental

2.1. Materials

Bisphenol A-glycidyl methacrylate (Bis-GMA): This material also known as "epoxy acrylate" is the main structure of test specimens. Synthesized acrylate functional PDMS was added with different rate of weights as 20%, 40%, 60% and 80%, into the Bis-GMA/HDDA to prepare UV curable SLA resin. Bis-GMA is a quite rigid material and it has an important usage as dental filling material for this reason (Michelsen at all, 2003).

Hydroxyl-terminated polydimethylsiloxane (Tegomer® H-Si 2315): Hydroxyl-terminated polydimethylsiloxane (HT-PDMS) is the main structure of synthesized acrylate functional PDMS.

Acryloyl chloride: Acryloyl chloride is reacting with HT-PDMS and turns PDMS to acrylate functional and UV curable.

Triethylamine (TEA): This is the catalyzer of the reaction between HT-PDMS and Acryloyl chloride.

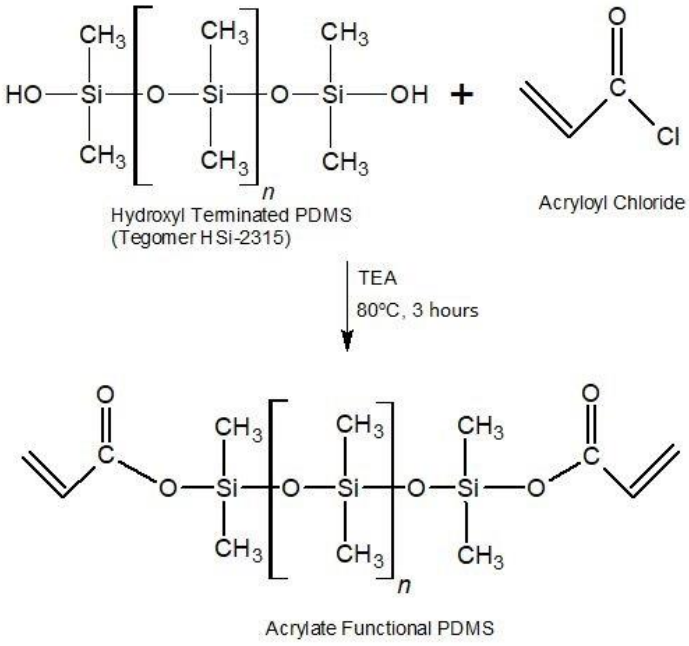
Hexanediol diacrylate (HDDA): HDDA is the reactive solvent of the SLA printed resin. It was decreased viscosity and also structure soluble.

Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure® 819): Irgacure® 819 is a versatile photo initiator for radical polymerization of unsaturated resins upon UV light exposure. Single bonds around the phosphor opens with UV light and react to other end groups.

2.2. Synthesizing of AF-PDMS

HT-PDMS, reactive solvent and 1% rate of weight triethylamine were combined in 1 liter 3-necked flask and dropping funnel contained acryloyl chloride was connected at one neck of the flask for adding to the mixture drop by drop until reaction. Reaction was performed at 80 ^{0}C for 3 hours. Reaction confirmed by FT-IR Spectroscopy.

Figure 1. Synthesizing reactions of AF-PDMS



2.3. SLA printing of test specimens

In this study AF-PDMS were added into UV curable resin which is contained Bis-GMA 50%, HDDA 50% and Irgacure® 819 1%, with significant rates of weights for printing process and specimens were printed of 0.1 mm thickness for each layer. Resolution of the image of UV light was 1920x1200 and gained from DLP projector. Size of building area was 200x120 mm. The building table was lifted 50 mm at every layer curing process to get resin properly on model for next layer.

2.4. Mechanical tests

Tensile test, abrasion test and hardness measurement were performed for mechanical characterizations. Tensile tests were occurred with Zwick® model tensile test machine at 5 mm/min deformation speed. Contacted extensometer was used to measure elongation. Tensile test specimens were prepared according to ASTM D638-02a type-IV (test specimens for polymer materials). Hardness tests were made with Zwick® model and Shore hardness tests was performed as a Shore A and Shore D scale. Standards of hardness are ASTM D2240, DIN 53505 and ISO 868. Abrasion tests were occurred by Devotrans® model abrasion test device. Abrasion tests were applied for two different rates of PDMS contained specimens as 20% and 40% due to flexibility of higher rates of PDMS contained samples were obstacle for abrasion. The test was performed at 100, 250 and 500 cycles with a load of 250 grams. Finally density measurement was occurred for all different rates of PDMS contained samples.

2.5. Morphological test and FT-IR analysis

SEM investigations were performed for two specimens that contained different rate of weights of acrylate functional PDMS as 20% and 60% at 5000x zoom rate. The effect of AF-PDMS ratio on fracture character was investigated by examining fracture surfaces. Transform infrared spectroscopies were occurred by FT-IR-4700 type-A model spectroscopy device.

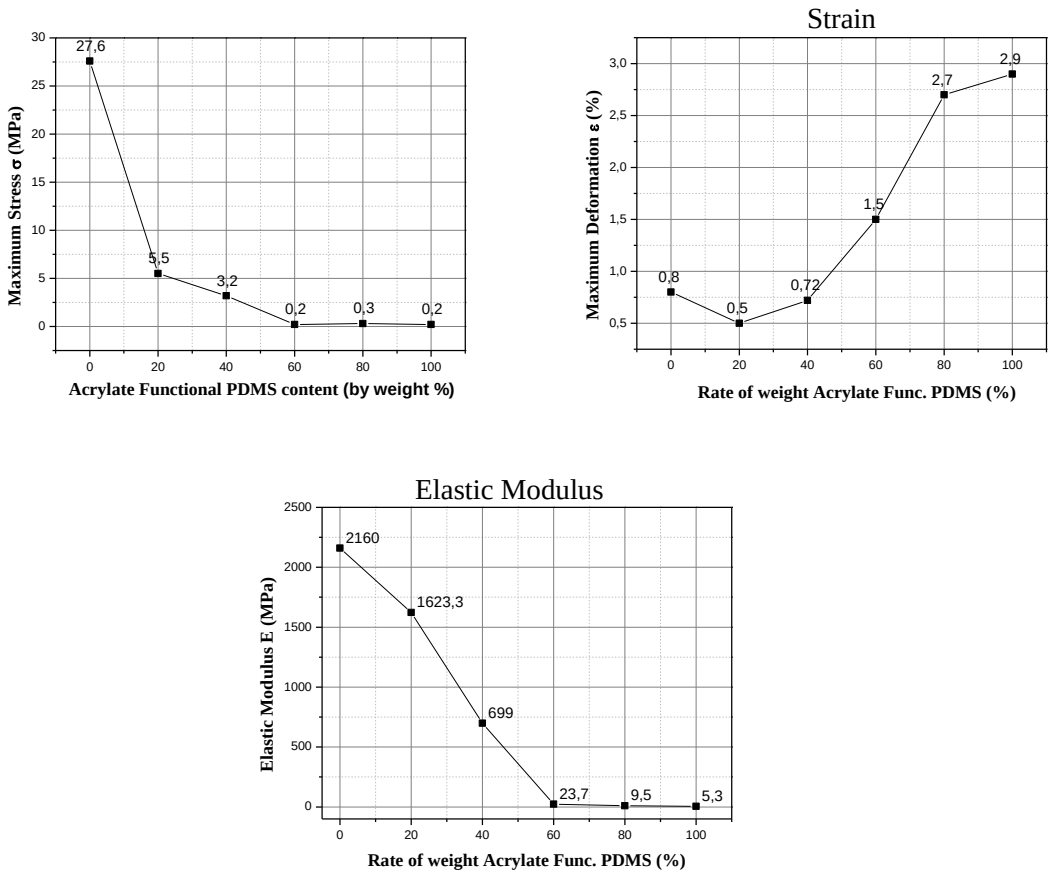
2.6. Thermal analysis

Differential Scanning Calorimeter (DSC) analysis was performed for four different samples to investigate the effect of AF-PDMS ratio on glassy transition temperature.

3. Results and Discussion

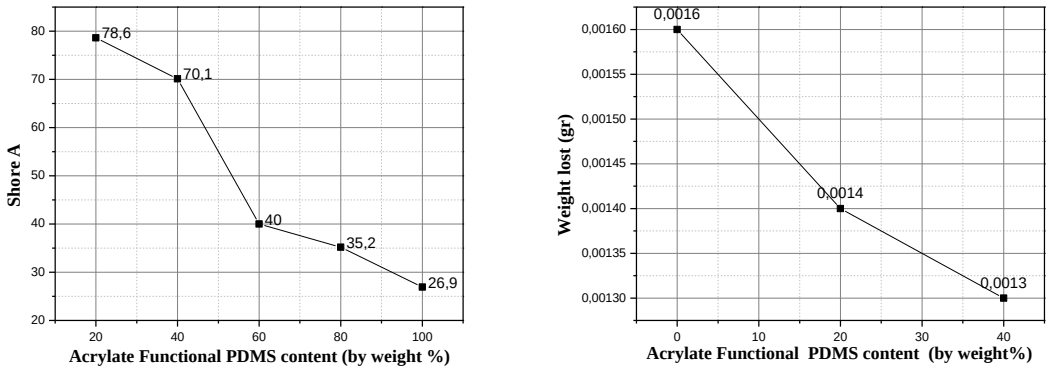
3.1. Mechanical properties

Figure 2. Tensile test results



As shown in the Figure 2 stress and elastic modulus values decreased with increasing acrylate-functional weight of rate. On the other hand strain value increased at the same situation. This result was expected before the study due to flexibility of PDMS material. An effectual decreasing is observed between pure Bis-GMA/HDDA and 20% AF-PDMS contained resin as approximately 80% for stress values. This result is also shown us that SLA resin structure and synthesized AF-PDMS are successfully combined each other. Another significant difference observed for strain value. Strain increased 83% with increasing PDMS rate 20% to 80%. Most effective changing observed for elastic modulus as 170% between 20% and 80% PDMS rate of weight.

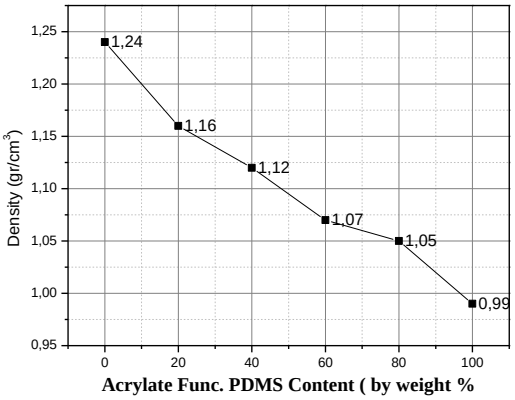
Figure 3. (a) Hardness and (b) abrasion test results



(a) (b)

As shown in the Figure 3 (a), hardness values decreased with increasing AF-PDMS rate approximately 66% due to flexibility. There is no significant difference for abrasion results in Figure 3 (b). In addition abrasion tests are not performed for over 40% PDMS contained samples due to galling to abrasive tool.

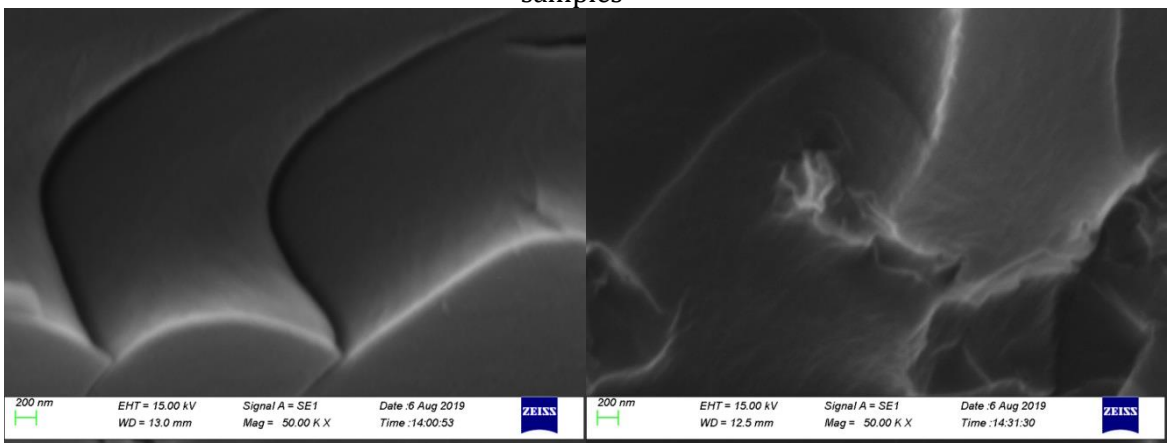
Figure 4. Density test results



Similarly with abrasion, density values were close to each other.

3.2 SEM and FT-IR results

Figure 5. SEM results of fracture surfaces for (a) 20% and (b) 60% AF-PDMS contained samples



(a) (b)

SEM pictures showed that the sample containing 20% PDMS showed brittle fracture (figure 5-a) while ductile fracture was observed in the sample containing 60% PDMS (figure 5-b). These results support the increased flexibility of the material with increasing PDMS rate, similar to the previous results.

Figure 6. FT-IR spectroscopy for acrylate functional PDMS

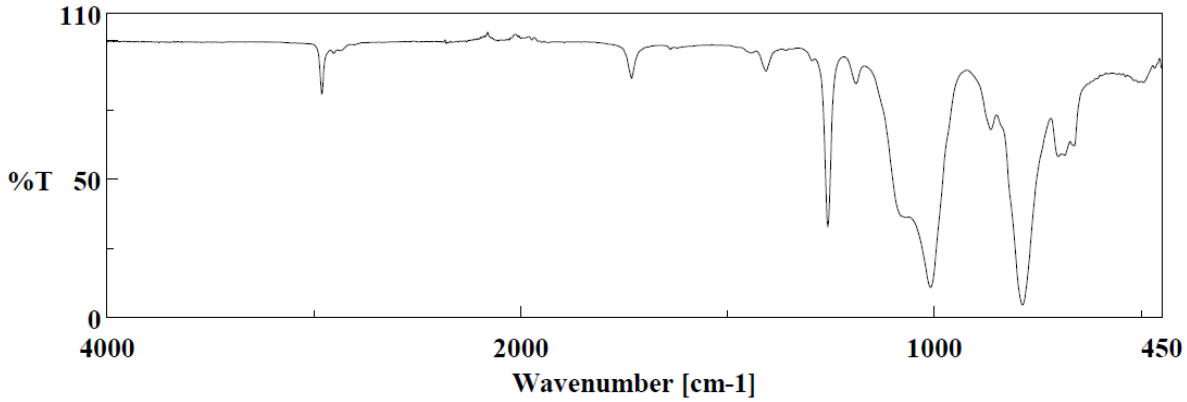


Figure 7. FT-IR spectroscopy for Tegomer® RC-1002

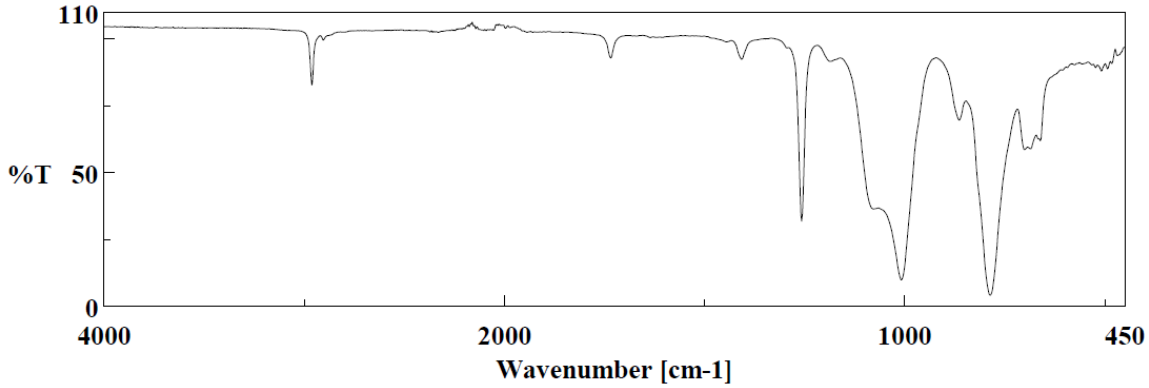
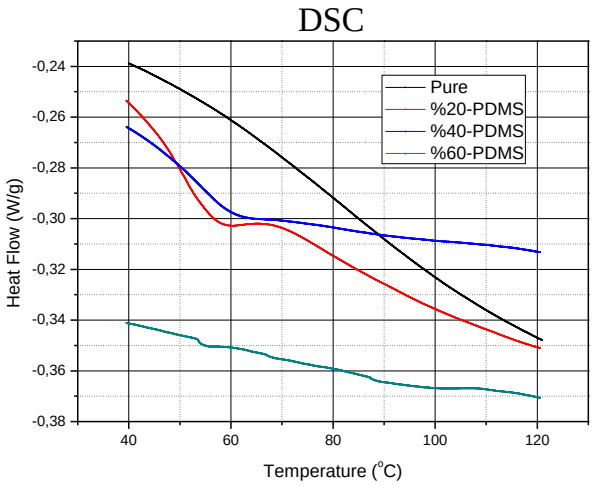


Figure 6 and Figure 7 show that commercially produced acrylate functional PDMS and synthesized acrylate functional PDMS have the same FT-IR spectroscopy pattern. This result proves that AF-PDMS has been synthesized successfully.

3.3. Thermal characterizations

Figure 8. DSC test results.



Comparison of the DSC results for 20%, 40% and 60% AF-PDMS contained specimens with pure Bis-GMA/HDDA mixture resin are given at Figure 8. The results shown as glassy transition temperatures are between 57 ^{0}C and 60 ^{0}C for all three of PDMS contained resins.

4. Conclusions

In this study, silicon acrylate (AF-PDMS) resin was synthesized and test specimens were produced by SLA type 3d printer by adding silicon acrylate into BisGMA/HDDA mixture with different rate of weights as 20%, 40%, 60% and 80%. Synthesized AF-PDMS was confirmed by FT-IR spectroscopy and mechanical, thermal and morphological properties of test samples were examined by tensile, hardness, abrasion, density, DSC and SEM tests.

According to the results, abrasion resistance, hardness, density, stress and elastic modulus values are decreased with increasing AF-PDMS rate. On the other hand strain value is increased at the same situation. In SEM images, it was seen that the material became ductile by increasing the silicon acrylate ratio. In addition, glassy transition temperature is decreased with increasing AF-PDMS rate. According to these results, synthesized resins and obtained samples are promising in soft tissue studies to be performed in SLA type printers.

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