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Original Paper

Effect of various reactive diluents on the mechanical properties of the acrylate-based polymers produced by DLP/LCD-type 3D printing

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ABSTRACT

The mechanical properties of the products obtained by 3D printing heavily depend on the choice of main resins and reactive diluents. In this study, we investigated the influence of different reactive diluents on the mechanical properties of the products derived from polyester acrylate (PEA), urethane acrylate (UA), and silicone acrylate (SiA) resins using DLP/LCD type 3D printing. As reactive diluents, 1,6-Hexanediol Diacrylate (HDDA), di(propylene glycol) diacrylate (DPGDA), trimethylolpropane triacrylate (TMPTA), and TMPTA10 were used in main resins. TMPTA10 was prepared in this study, which includes TMPTA, DPGDA and HDDA in its composition. While TMPTA is a reactive diluent with three acrylate functional groups, DPGDA and HDDA have two acrylate functional groups. Our results revealed that while the products with TMPTA reactive diluent significantly enhanced the ultimate tensile strength (UTS) and Young's modulus, they led to a decrease in Izod impact strength. To address this, TMPTA10 was formulated and incorporated into the main resins, resulting in improved Izod impact strength while maintaining or enhancing UTS and Young's modulus. Notably, the products prepared by using UA resin with TMPTA or TMPTA10, and PEA resin with TMPTA10 exhibited exceptional mechanical properties compared to the other products. These findings highlight the importance of reactive diluent selection in optimizing the mechanical performance of the products obtained by DLP/LCD type 3D Printing.

I. INTRODUCTION

Manufacturing procedures in many different industries have been transformed by three-dimensional (3D) printing, which provides unmatched design flexibility and customization [1-3]. Resin systems that are specifically formulated for a given application are essential to the success of 3D printing. In this instance, the mechanical properties of the products produced via 3D printing mostly determine their suitability for end-use applications [1, 4]. The mechanical performance of the products obtained by 3D printing is influenced by several factors, including main resins and reactive diluents [5, 6]. The major resins have a high viscosity, making them challenging to use alone. Reactive diluents are added to main resins to achieve the ideal viscosity for ease of use and improved mechanical performance [7-9].

The reactive diluents that was used in this study are di(propylene glycol) diacrylate (DPGDA), 1,6-Hexanediol Diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), and TMPTA10 (derivative of TMPTA). While DPGDA and HDDA are two functional acrylate monomers, TMPTA is a three-functional acrylate monomer. DPGDA provides flexibility and high strength due to its characteristic structure with ether bondings. HDDA has very high compatibility with almost all resins and present high rigidity [10-12]. TMPTA, besides its three-functional acrylate, offers high curing reactivity. Moreover, it is highly possible to provide more enhanced mechanical properties with the resin systems having reactive diluents with three-functional acrylate groups compared to those with two-functional acrylate groups [13, 14]. Despite its benefits, the resin systems with

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TMPTA have highly possibility to provide low impact resistance due to the providing highly crosslinking amounts [15, 17]. Because of this, the last reactive diluent, TMPTA10, was developed to reduce the decline in Izod impact resistance while maintaining or enhancing other mechanical properties. DPGDA, HDDA, and TMPTA reactive diluents constitutes of TMPTA10. After reviewing the literature, Kim and Seo [17] investigated the effects of several reactive diluents, such as hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA), and trimethylol propane triacrylate (TMPTA), on the mechanical characteristics of EB80 UV-cured commercial polyester acrylate resin by UV curing. They were able to achieve tensile strengths of 12.5 MPa, 14 MPa, and 18 MPa, respectively, with HDDA, TPGDA, and TMPTA. However, they did not investigate Young's modulus and Izod impact resistance values. Hevus et al. [18] employed furanic acrylate and methacrylate monomers as 3D printing reactive diluents. In comparison to HDDA, a common petroleum-based difunctional diluent, they found that furanic acrylate and methacrylate monomers exhibit noticeably better thermal and mechanical properties (glass transition temperature, Young's modulus, tensile strength, and fracture toughness). The impact of the contents of HDDA and Photocentric 27, which are difunctional acrylates, Photocentric 34, which are trifunctional acrylates, and PPTTA and PE(EO)nTTA, which are four functional acrylates, on mechanical characteristics was examined by Oezkan et al. [19]. The molecular weights of PPTTA and PE(EO)nTTA are higher than those of the other functional acrylates. They [19] reported that molecular weight and functionality both had an impact on mechanical properties. In light of this, in addition to the composition and capabilities of the reactive diluents, the main resins that can serve as the skeleton or backbone of the end product have become more significant in terms of overall mechanical properties. In this approach, in order to obtain novel photopolymerizable resin systems, it was also chosen to examine several commercial resins in addition to various reactive diluents.

Our research focuses on assessing the mechanical properties of products produced through DLP/LCD type 3D printing for different novel photopolymerizable resin system combinations that include HDDA, DPGDA, TMPTA, and TMPTA10 as reactive diluents and polyester, silicon, and urethane as the main resins. Our objective is to find the best resin-diluent combinations that strike a balance between printability and mechanical performance through extensive mechanical testing. Tensile, Shore D hardness, and Izod impact resistance with notched sample were used to characterize the mechanical properties. The ultimate tensile strength, Young's modulus, and elongation at break values were determined as a consequence of the tensile test. The findings showed that although the products using TMPTA reactive diluent greatly increased Young's modulus and ultimate tensile strength (UTS), they also caused a drop in Izod impact strength. In order to overcome this, TMPTA10 was developed and added to the main resins, improving Young's modulus and UTS while also improving Izod impact strength. Remarkably, when compared to the other products, the ones made with UA resin with TMPTA or TMPTA10 and PEA resin with TMPTA10 showed remarkable mechanical properties. These results emphasize how crucial it is to choose reactive diluents carefully in order to achieve the best mechanical performance of the products produced by DLP/LCD type 3D printing.

II. EXPERIMENTAL METHOD

2.1 Materials

EBECRYL® 350, EBECRYL® 284, and EBECRYL® 884 were used as commercial silicone diacrylate, aliphatic urethane diacrylate, and polyester acrylate main resins that were purchased from Allnex. As reactive diluents, 1,6-Hexanediol Diacrylate (HDDA), di(propylene glycol) diacrylate (DPGDA), trimethylolpropane triacrylate (TMPTA) were used. The other reactive diluent, TMPTA10 that consisting of HDDA (20%), DPGDA (20%), and TMPTA (10%) was prepared in our laboratory. The ratio of all reactive diluents that were used in main resins was 50% for 3D printing. The prepared resin systems were cured via Phrozen sonic mini resin DLP/LCD-type 3D printer. The photoinitiator utilized was bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO) (IRGACURE® 819).

2.2 Preparation of resin systems for DLP/LCD type 3D printer

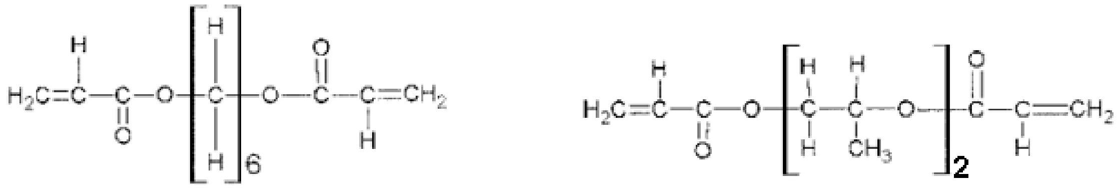
There were three main categories of acrylate-based resins used: polyester acrylate, silicon diacrylate, and urethane diacrylate. HDDA, DPGDA, TMPTA, and the prepared TMPTA10 were utilized as reactive diluents. Figure 1 presents the chemical structures of the reactive diluents that were used in this study. For every main resin, four resin systems were intended to be obtained. Therefore, these four distinct reactive diluents were mixed separately with each main resin. The weight adjustment for these resin systems was 1/1. The resin systems produced by these main resins and reactive diluents were mechanically stirred in a beaker for ten minutes. A 5% weight concentration of BAPO photoinitiator was added to the homogenous resin systems. Both mechanical and ultrasonic stirring methods were used simultaneously for one hour to mix the resin systems containing BAPO. A clean and uniform view of the resin systems was obtained after one hour of mechanical and ultrasonic stirring. When the clear and homogeneous resin systems were added to the resin tank of the DLP/LCD type 3D printer, the products were obtained during the curing process.

2.3 Characterization of Test Specimens

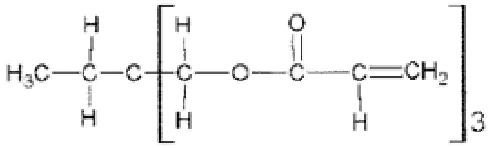
For the purpose of determining their mechanical properties, standard tensile tests were performed in compliance with ASTM D638 to ascertain the material's Young's modulus, ultimate tensile strength, and maximum elongation. The crosshead speed for the tensile tests was 5 mm/min. At room temperature, the tensile test was conducted using Zwick Z010 apparatus. The IZOD impact resistance was evaluated using notched samples in compliance with ASTM D 256. The Zwick B5113.30 test device was utilized, which had a 5.4 J hammer and a striking rate of 3.96 m/s. The samples' hardness values were ascertained using Durometer Hardness (Shore D hardness) in accordance with ASTM 2240. A Carl Zeiss Ultra Plus SEM (scanning electron microscope) operating at a voltage acceleration of 20 kV was used to analyze the fracture surface morphologies following the tensile test. Before the SEM analyses, the samples were sprayed with 2-4 nm of Au/Pd in an ion beam sputtering system utilizing a Quorum Q150R device.

III. RESULTS AND DISCUSSIONS

In this study, it was believed that TMPTA would increase the crosslinking density more than DPGDA and HDDA due to its trifunctional groups and high reactivity. As expected, the products with TMPTA reactive diluent significantly enhanced the ultimate tensile strength (UTS) and Young's modulus, according to our results. However, they led to a decrease in Izod impact strength. To resolve this problem, TMPTA10 was formulated and incorporated into the main resins, resulting in improved Izod impact strength while maintaining or enhancing UTS and Young's modulus. The incorporation of DPGDA and HDDA reactive diluents into the TMPTA10 formulation plays a major role in these results. It is because DPGDA has a special flexible structure due to its ether bonding. Thus, the crosslinking structure with DPGDA has also belonged to higher elongation at maximum besides high ultimate tensile strength. These improved mechanical properties for resin systems with DPGDA enhanced Izod impact resistance. Moreover, HDDA has an aliphatic structure, high reactivity, and high compatibility with almost all the resins. Notably, the products prepared by using UA resin with TMPTA or TMPTA10 and PEA resin with TMPTA10 exhibited exceptional mechanical properties compared to the other products. These findings highlight the importance of reactive diluent selection in optimizing the mechanical performance of the products obtained by DLP/LCD-type 3D printing. Figure 1 presents the chemical structures of the main reactive diluents that were used in this study.



1,6 Hexanediol diacrylate (HDDA) **Dipropylene glycol diacrylate (DPGDA)**



Trimethylol propane triacrylate (TMPTA)

Figure 1. The chemical structures of the reactive diluents that used in this study

For instance, in the case of PEA resin composites, samples containing TMPTA10 demonstrated an increase of 50% in UTS compared to those prepared with DPGDA or HDDA. Furthermore, Young's modulus showed an increase of 94% and 38%, respectively. Moreover, Izod impact strength was increased by the incorporation of TMPTA10, with an increase of 58% compared to the samples with HDDA and with an increase of 9.8% compared to those with DPGDA. However, the samples of PEA-TMPTA were not able to be achieved on the aluminum platform of the 3D printer when exposed to the digital light curing process.

In the case of UA resin systems, samples containing TMPTA demonstrated a significant increase in mechanical properties. UA-TMPTA samples exhibited increases of 60% and 67% in UTS compared to the samples with DPGDA and HDDA, respectively. Furthermore, Young's modulus showed impressive increases of 224% and 203%, respectively. However, there was a slight decrease in Izod impact strength compared to the samples with DPGDA and HDDA. This trend continued with the UA-TMPTA10 samples, which showed improvements in UTS, Young's modulus, and Izod impact strength compared to the samples with DPGDA and HDDA. It was able to obtain successful 3D-printed samples by using UA-TMPTA and UA-TMPTA10 resin systems in contrast to PEA-TMPTA. Considering SiA resin system, it showed high compatibility with HDDA. The samples with HDDA presented much improved mechanical properties compared to those with DPGDA. The results of SiA-DPGDA samples could be affected by the flexible nature of the SiA main resin and the DPGDA reactive diluent [20,21]. On the other hand, the SiA-TMPTA and SiA-TMPTA10 samples were not able to be achieved successfully. Evaluating mechanical properties in terms of the main acrylate resins, the resin systems with urethane acrylate were the most prominent compared to the polyester acrylate and silicon diacrylate resin systems. As expected, the lowest mechanical properties were obtained for SiA-based resin systems. The tensile stress-strain curves of the acrylate-based products are presented in Figure 2. A comparative view that presented the mechanical property trend of each acrylate-based sample is shown in Figure 3. Moreover, all mechanical values of the produced samples are given in Table 1.

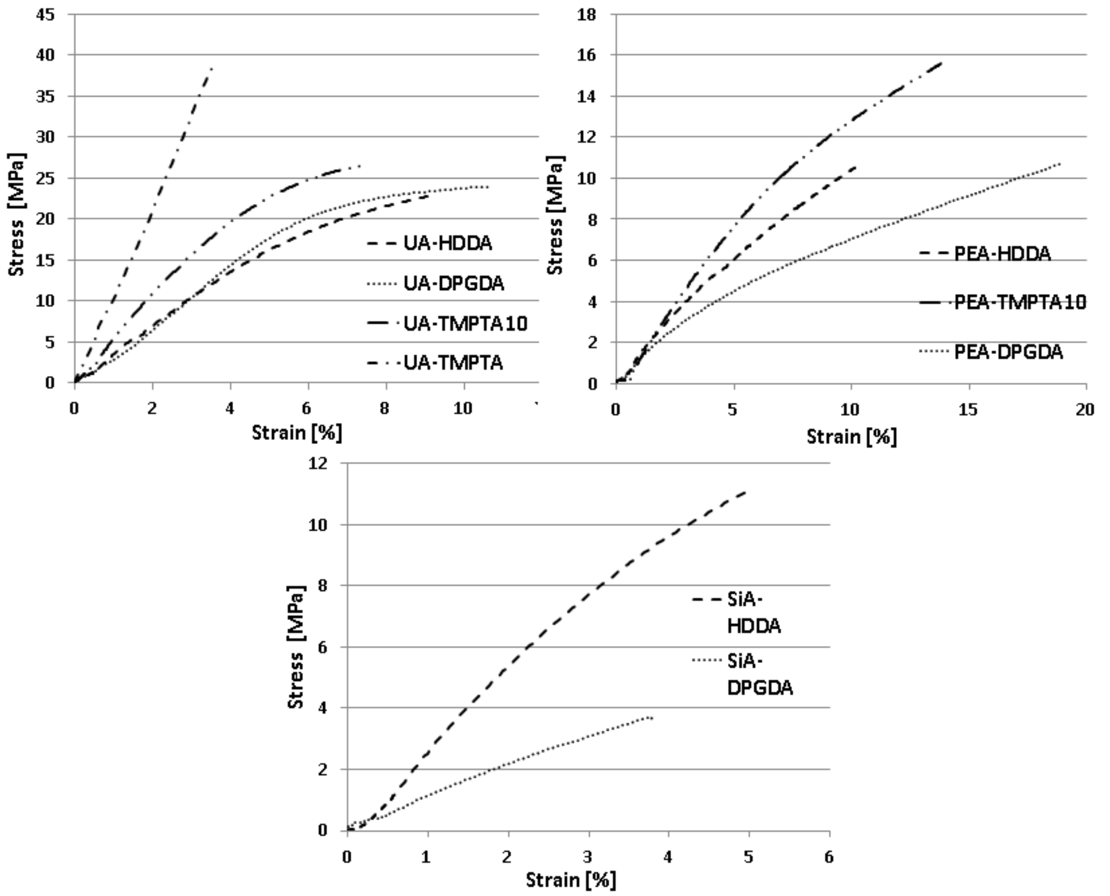


Figure 2. The average tensile stress-strain curves of the acrylate-based products

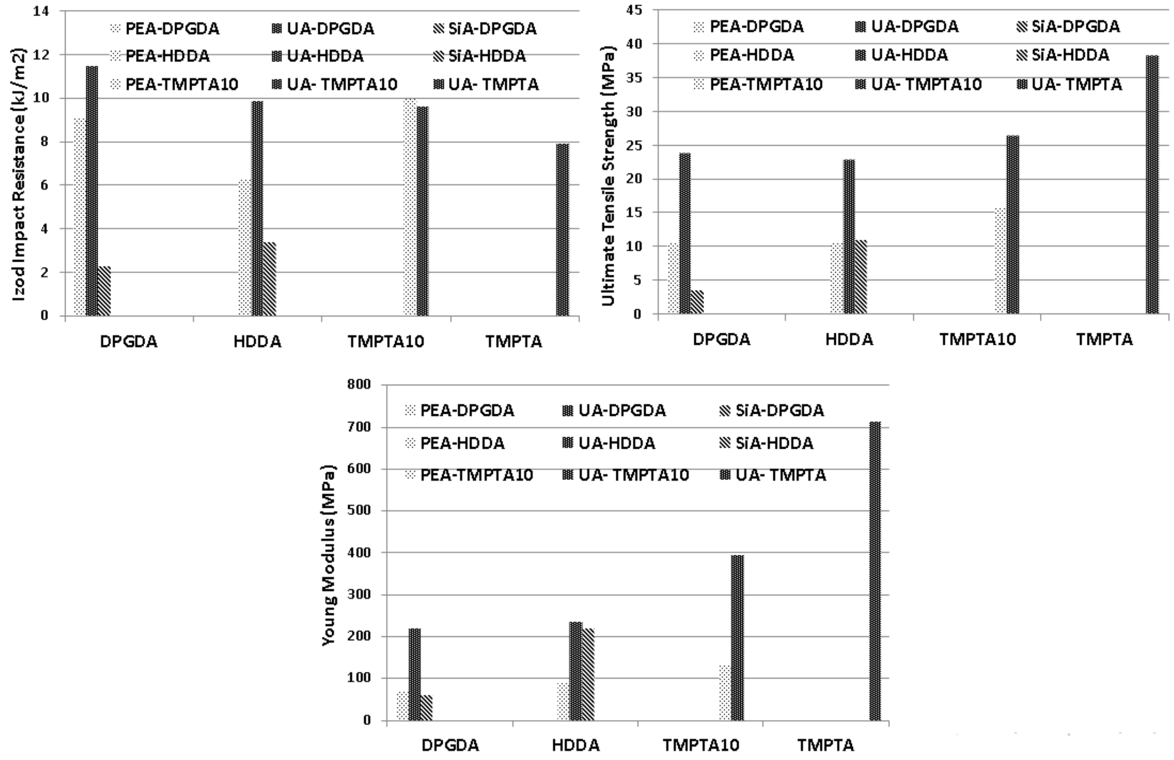


Figure 3. Comparative analysis of mechanical property trend of each acrylate-based sample

Table 1. The mechanical values of the nanocomposites

Sample	**Ultimate Tensile Strength** (MPa)	**Elongation at Break** (%)	**Young's Modulus** (MPa)	**Izod Impact** (kJ/m^2)	**Shore D Hardness**
PEA-DPGDA	10.73	18.99	67.58	9.1	56
PEA-HDDA	10.73	10.44	93.16	6.3	62
PEA-TMPTA10	15.80	14.14	132	10	64
PEA-TMPTA	**NA**				
UA-DPGDA	23.96	10.67	220.33	11.5	63
UA-HDDA	22.94	9.29	235.77	9.9	65
UA- TMPTA10	26.46	7.29	396.23	9.6	65
UA- TMPTA	38.37	3.53	713.52	7.9	69
SiA-DPGDA	3.72	3.77	61.26	2.3	34
SiA-HDDA	11.06	4.95	220.97	3.4	48
SiA-TMPTA10	**NA**				
SiA-TMPTA	**NA**				

Following the tensile test, Figure 4 shows the fracture surface morphologies of the PEA-HDDA, PEA-TMPTA10, UA-TMPTA, and UA-TMPTA10. In terms of mechanical properties, the PEA-HDDA had a poorer Izod impact resistance than the prominent samples, PEA-TMPTA10, UA-TMPTA, and UA-TMPTA10. SEM morphology in Figure 4 supported this condition with the overall smooth texture and river-line and textured microflow patterns of PEA-HDDA and UA-TMPTA. The fracture behavior of PEA-TMPTA10 and UA-TMPTA was more ductile compared to PEA-HDDA and UA-TMPTA. Moreover, it appeared that shear stresses had occurred on the PEA-TMPTA10 and UA-TMPTA10 fracture surfaces. These shear forces demonstrated the stronger interactions represented by PEA-TMPTA10 and UA-TMPTA10 [22, 23].

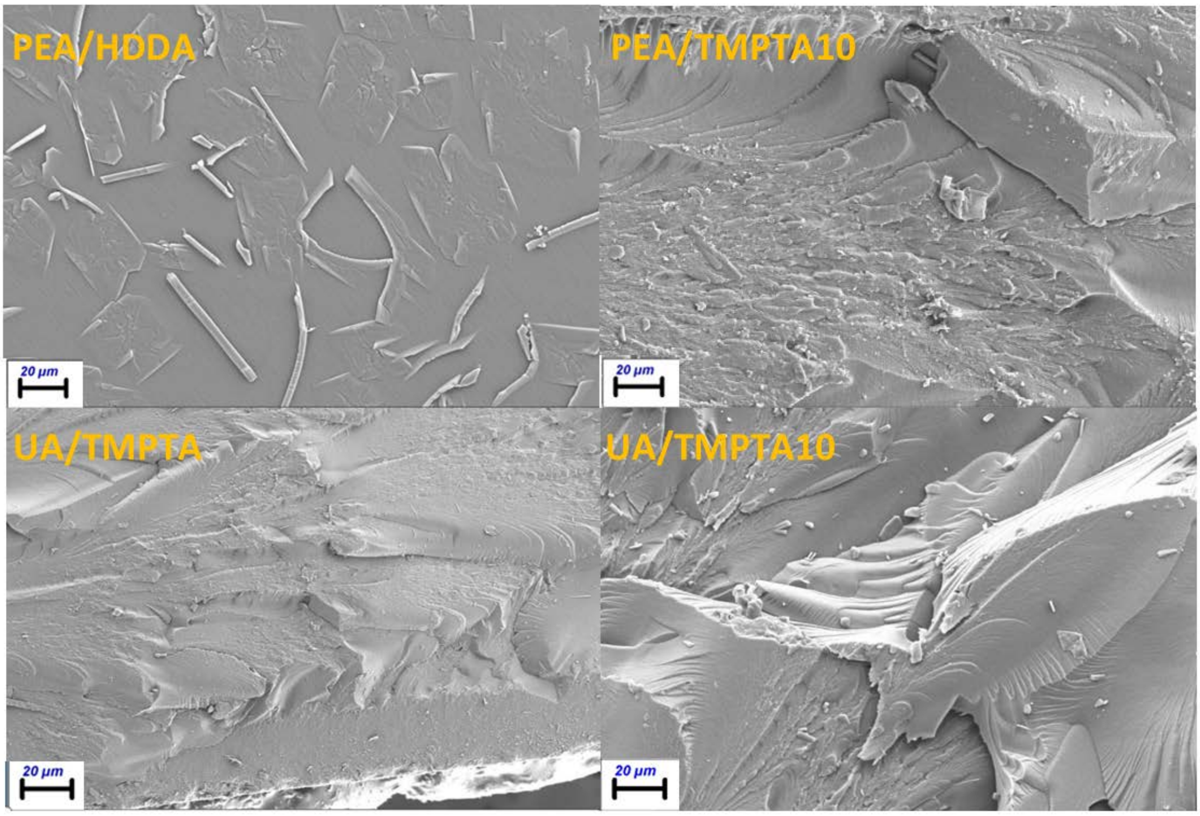


Figure 4. The fracture surfaces SEM morphologies of the PEA-HDDA, PEA-TMPTA10, UA-TMPTA, and UA-TMPTA10 after tensile test

IV. CONCLUSIONS

In conclusion, the results demonstrate the significant effect of reactive diluent selection on the mechanical properties and microstructural characteristics of 3D-printed resin systems. Samples prepared from the resin systems with TMPTA and TMPTA10 reactive diluents exhibited remarkable improvements in UTS and Young's modulus, highlighting their potential for enhancing the mechanical performance of resin systems. TMPTA reactive diluent can only be used for the urethane acrylate main resin due to its curing problem. Moreover, UA/TMPTA exhibited poor impact resistance despite its improved UTS and Young's modulus values. For this reason, the formulation of TMPTA10 was prepared as a new reactive diluent. The formulation of TMPTA10 addressed the brittleness and non-printability issues associated with the resin systems with TMPTA, resulting in improved Izod impact strength and successful 3D-printed resin systems while maintaining or enhancing other mechanical properties. While UA-TMPTA, UA-TMPTA10, and PEA-TMPTA10 presented the most improved mechanical properties, SiA-TMPTA, SiA-TMPTA10, and PEA-TMPTA could not be obtained by 3D printing. In brief, UA-TMPTA samples exhibited increases of 60% and 67% in UTS compared to the samples with DPGDA and HDDA, respectively. Furthermore, Young's modulus showed impressive increases of 224% and 203%, respectively. PEA-TMPTA10 demonstrated an increase of 50% in UTS compared to those prepared with DPGDA or HDDA. Furthermore, Young's modulus showed an increase of 94% and 38%, respectively.

Moreover, Izod impact strength was increased by the incorporation of TMPTA10, with an increase of 58% compared to the samples with HDDA and with an increase of 9.8% compared to those with DPGDA. Considering the SiA resin system, it showed high compatibility with HDDA. The samples with HDDA presented much improved mechanical properties compared to those with DPGDA, as mentioned. Considering the SiA resin system, it showed high compatibility with HDDA. The samples with HDDA presented much improved mechanical properties compared to those with DPGDA. These findings emphasize the importance of optimizing main resin-diluent formulations to achieve superior mechanical performance and structural integrity in 3D-printed parts. In the future, research may concentrate on optimizing processing parameters and investigating new additives to further improve the qualities of resin systems for cutting-edge uses across a range of sectors.

REFERENCES

1. Schittecatte L, Geertsen V, Bonamy D, Nguyen TT, Guénoun P (2023) From resin formulation and process parameters to the final mechanical properties of 3D printed acrylate materials. MRS Commun. https://link.springer.com/article/10.1557/s43579-023-00352-3
2. Cakir Yigit N, Karagoz I (2023) A review of recent advances in bio-based polymer composite filaments for 3D printing. Polym.-Plast Technol Mater. 62(9):1077-1095.
3. Karagöz İ, Bekdemir AD, Tuna Ö (2021) 3B yazıcı teknolojilerindeki kullanılan yöntemler ve gelişmeler üzerine bir derleme. Düzce Üniversitesi Bilim ve Teknoloji Dergisi 9(4):1186-1213.
4. Dawood A, Marti B, Sauret-Jackson V, Darwood A (2015) 3D printing in dentistry. Br Dent J. https://www.nature.com/articles/sj.bdj.2015.914
5. Gopinathan J, Noh I (2018) Recent trends in bioinks for 3D printing. Biomater Res 22.
6. Jagtap AR, More A (2021) Developments in reactive diluents: a review. Polym Bull 79:5667–5708.
7. Wu G, Zang H, Zhang H (2020) Preparation and performance of UV-curable waterborne polyurethane prepared using dipentaerythritol hexaacrylate/dipropylene glycol diacrylate monomers. J Macromol Sci Part A 57:927–934.
8. Keck S, Liske O, Seidler K, Steyrer B, Gorsche C, Knaus S, Baudis S (2023) Synthesis of a liquid lignin-based methacrylate resin and its application in 3D printing without any reactive diluents. Biomacromolecules 24:1751–1762.
9. Ligon SC, Schwentenwein M, Gorsche C, Stampfl J, Liska R (2015) Toughening of photo-curable polymer networks: a review. Polym Chem 7(2):257–286.
10. Khalina M, Beheshty MH, Salimi A (2018) The effect of reactive diluent on mechanical properties and microstructure of epoxy resins. Polym Bull 76:3905–3927.
11. Li G, Jiang S, Gao Y, Liu X, Sun F (2013) Synthesis and property of water-soluble hyperbranched photosensitive polysiloxane urethane acrylate. Industrial & Engineering Chemistry Research 52, 2220–2227.
12. Yu Y, Liao B, Jiang S, Li G, Sun F (2015) Synthesis and characterization of photosensitive-fluorosilicone–urethane acrylate prepolymers. Des Monomers Polym 18:199–209.
13. A Schuster M, Turecek C, Mateos A, Stampfl J, Liska R, Varga F (2007) Evaluation of biocompatible photopolymers II: further reactive diluents. Monatsh Chem 138:261–268.
14. Schuster M, Turecek C, Kaiser B, Stampfl J, Liska R, Varga F (2007) Evaluation of biocompatible photopolymers I: photoreactivity and mechanical properties of reactive diluents. J Macromol Sci Part A, 44:547–557.
15. Ali KMI, Khan MA, Zaman MM, Hossain MA (1994) Reactive diluent effect on properties of UV-cured films. J Appl Polym Sci 54:309–315.
16. Liu HB, Zhang WY, Lin F, Qing N, Xu L (2013) The influence of reactive diluents on the properties of UV dual cured polyurethane-modified epoxy monoacrylates films. J Appl Mech 477–478:1169–1174.
17. Kim DS, Seo WH (2004) Ultraviolet-curing behavior and mechanical properties of a polyester acrylate resin. J Appl Polym Sci 92:3921–3928.
18. Hevus I, Kannaboina P, Qian Y, Wu J, Johnson M, Gibbon LR, Scala JJL, Ulven C, Sibi MP, Webster DC (2023) Furanic (meth)acrylate monomers as sustainable reactive diluents for stereolithography. ACS Appl Polym Mater 5:9659–9670.
19. Oezkan B, Sameni F, Karmel S, Engstrøm DS, Sabet E (2021) A systematic study of vat-polymerization binders with potential use in the ceramic suspension 3D printing. Addit Manuf 47: 102225.

20. Liu H, Chen M, Huang Z, Xu K, Zhang X (2004) The influence of silicon-containing acrylate as active diluent on the properties of UV-cured epoxydiacrylate films. Eur Polym J 40:609–613.
21. Zheng Y, Chonung K, Jin X, Wei P, Jiang P (2007) Study on the curing reaction, dielectric and thermal performances of epoxy impregnating resin with reactive silicon compounds as new diluents. J Appl Polym Sci 107:3127–3136.
22. Idrees M, Yoon H, Palmese GR, Alvarez NJ (2023) Engineering toughness in a brittle vinyl ester resin using urethane acrylate for additive manufacturing. Polym 15:3501.
23. Uysal E, Çakır M, Ekici B (2019) Synthesizing UV curable silicon acrylate resins for SLA type 3D printers and characterization of mechanical, thermal and morphological properties. JESTEC 5:(1) 47-56.