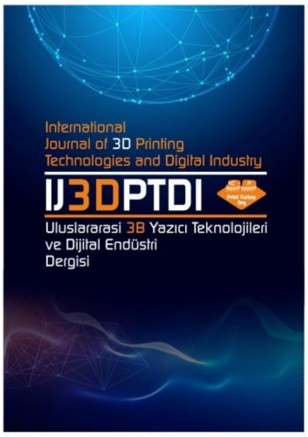

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THE EFFECT OF TRIACRYLATE MONOMER STRUCTURE ON VOLUME SHRINKAGE AND TENSILE PROPERTIES OF VAT POLYMERIZATION RESINS

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ABSTRACT

This study investigates the influence of triacrylate monomer structure on volume shrinkage, tensile properties, and viscosity of vat polymerization (VP) resins. The amount of triacrylate monomer kept constant as 20%wt. to prevent excessive volume shrinkage effect. Results indicated that ethoxylated and propoxylated triacrylate structures are beneficial to reduce the volume shrinkage of VP resins. However, these flexible chain structures led to a reduction in tensile properties and the elastic modulus of VP resins deteriorated up to 35% compared to trimethylolpropane triacrylate (TMPTA). There is no significant effect observed on VP resin reactivity according to the triacrylate type. Besides, ethoxylated triacrylate presented the best dilution effect on VP resin.

Keywords: VAT Polymerization, UV-curable resins, SLA, acrylate, photopolymerization, 3D Printing

1. INTRODUCTION

Three-dimensional (3D) printing is a method to produce solid elements based on the gradual assembling of materials. 3D printing is also called additive manufacturing (AM) or rapid manufacturing [1-2]. The history of AM dates back to the 1960s but the first commercial use of AM was realized by stereolithography (SLA) 3D printer from 3D Systems in 1987 [3]. After this milestone, several AM methods were developed and launched to the market. AM technologies were classified by the "American Society for Testing and Materials" (ASTM) [4] and classification is shown in Figure 1.

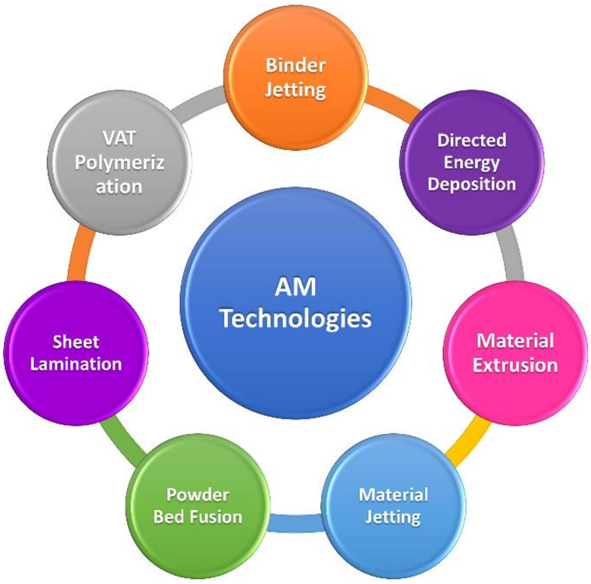


Figure 1. Types of 3D Printing Technologies (ASTM F2792-12a)

VAT polymerization (VP) is an additive manufacturing method, based on gradual solidification of photocurable resin material. In addition to the aforementioned classification of AM technologies, VP methods can be divided into three types; "laser stereolithography" (SLA), "digital light processing" (DLP), and "liquid crystal display" (LCD) [5]. Although all VP methods are following the same principles, they are differentiated according to the type of UV light source. SLA 3D printers utilize a UV laser and galvanometer to scan and cure each layer. The precision of the 3D printed part is determined by the beam size of the laser. DLP 3D printers utilize a UV light source created by a digital projector. A layer cured in one illumination and precision of the is part adjusted by projector's resolution. An LED array is used in LCD 3D printers as a UV light source. At this method, an LCD screen masks the UV light to cure the individual layer. The quality of the final part is directly related to the resolution of the LCD screen. Schematic representation of VP methods is shown in Figure 2.

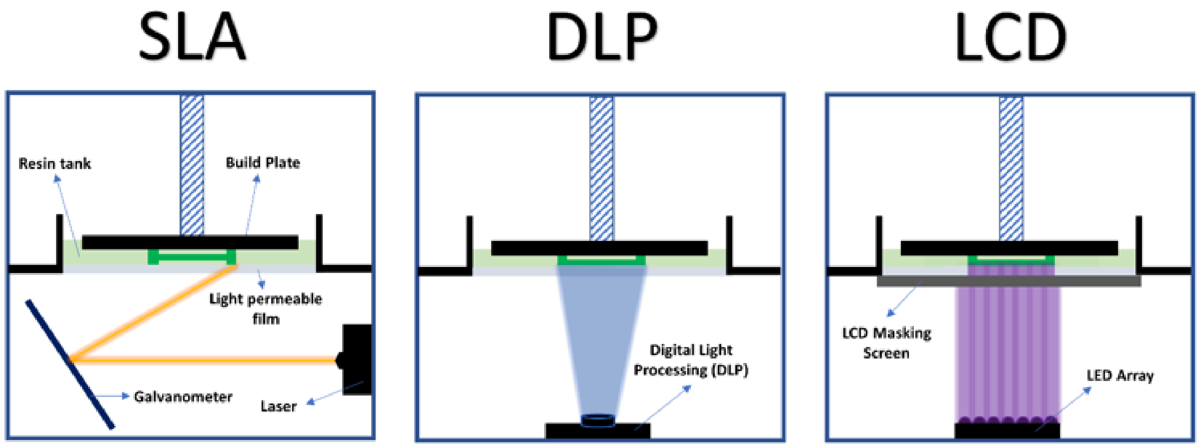


Figure 2. Schematic Representation of VP methods

VP resins are commercially used in numerous applications such as jewelry modeling [6-7], automotive part prototyping [8-11], dental modeling [12], footwear modeling [13-14], and so on. Simultaneously, researchers make an extensive effort to develop self-healing [15-16], shape-memory [17-18], and bio-based [19-21] VP resins. VP resins can be formulated by free radical curable (meth)acrylic materials [22-24], cationic curable epoxy-functional materials [25] or both free radical and cationic curable (meth)acrylate/epoxy mixtures [26]. In this article, (meth)acrylate-based VP resin is formulated. Acylate-based VP resins are the composition of (meth)acrylic monomers, (meth)acrylic oligomers, free radical photo-initiators, stabilizers, light absorbers, and other additives [27]. Acrylate-based resins exhibited high reactivity and fast curing compared to epoxy-based resins. However, acrylate-based presented high-volume shrinkage by contrast with epoxy-based resins [28].

One of the most common approaches to reduce volume shrinkage is the mixing of epoxy-based and acrylate-based resins. Shan et al. [29] reduced the volume shrinkage of 3D printed parts from 10.44% to 7.41% with the addition of epoxy resin. However, a high amount of epoxy resin led to a reduction of mechanical properties before post-curing. Besides, additional thermal post-curing is essential to cure the epoxy part of the resin mixture. Deng et al. [30] concluded that volume shrinkage of acrylate-based resins increases with the amount of monofunctional reactive diluent. Besides, acrylate oligomer content exhibited the opposite effect and led to the reduction of volume shrinkage. However high oligomer content caused the high viscosity and low reactivity.

Three functional acylate monomers are widely used as a crosslinker for acrylate-based VP resins. On the other hand, a high amount of these acrylates may lead to a significant amount of volume shrinkage. In this article, the effect of the type of three functional acrylate monomer on volume shrinkage is investigated.

2. MATERIALS AND METHOD

Trimethylolpropane triacrylate (TMPTA, commercial name Miramer M300) and Ethoxylated (3) Trimethylolpropane Triacrylate (EO3, commercial name Miramer M3130) were supplied by Miwon Specialty Chemicals (Ansan, South Korea). Propoxylated (3) Trimethylolpropane Triacrylate (PO3, commercial name SR492) was kindly provided by Sartomer-Arkema (Colombes Cedex, France). Figure 3. shows the chemical structures of triacrylate monomers. Isopropyl alcohol (IPA, technical grade) was purchased by Kempro Kimya, (İstanbul, Turkey).

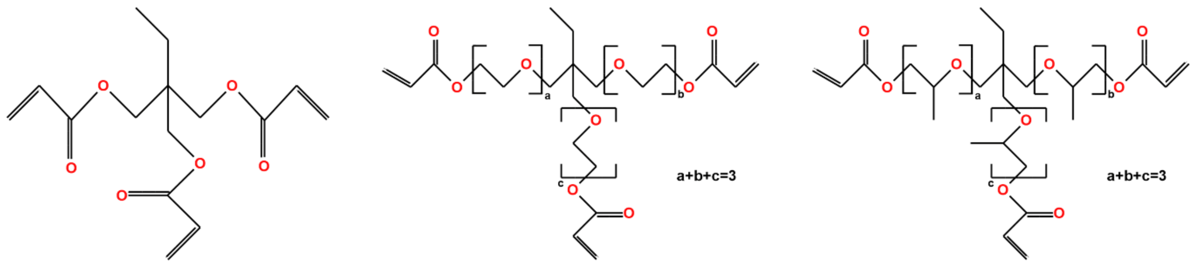
Table 1. Formulations of VP resins.

Abbreviations	TMPTA (% wt.)	EO3 (% wt.)	PO3 (% wt.)	Other Components* (% wt.)
TMPTA	20	-	-	80
EO3	-	20	-	80
PO3	-	-	20	80

*Other components are the mixture of acrylic monomers, oligomers, and a photoinitiator.

VP resin formulations are shown in Table 1 and prepared by prior mixing of urethane acrylate oligomers and acrylic monomers that have mono, di, or trifunctional groups at 50°C with a magnetic stirrer. After that, a phosphine oxide type photoinitiator (PI) was added and mixed until it completely dissolved.

“Anycubic Photon S LCD 3D printer” was utilized to produce test specimens which has a 405nm 50W UV LED array and a 2560 x 1440 (2K) HD LCD screen. 3D printed test specimens were washed with IPA and post-cured for 6 minutes via “Anycubic Wash&Cure Machine” which has 365 and 405nm 40W UV LED array with a rotatable platform to finalize the curing of 3D printed parts.



(a) (b) (c)

Figure 3. Chemical structures of triacrylate monomers, (a) Trimethylolpropane triacrylate (TMPTA), (b) Ethoxylated (3) Trimethylolpropane Triacrylate (EO3), (c) Propoxylated (3) Trimethylolpropane Triacrylate (PO3).

The tensile test was applied by using Devotrans GPSP/R Universal Tensile Tester according to the ASTM D638 with specimen type “V” as mentioned by Saraç et. al. [31] and 1mm/min test speed. Tensile test specimens were produced with 0.05 mm layer height. Layer curing time was set to 60 seconds for 10 layers and 10 seconds for the following layers.

The viscosity of VP resins was measured using Brookfield CAP 2000+ Cone&Plate Viscometer at 25°C. Volume shrinkage was calculated according to equation (1) where ρ_{liquid} and ρ_{solid} are the density of the VP resins before and after 3D printing, respectively. Figure 4. Shows the Anycubic Photon S LCD 3D Printer and the Anycubic Wash&Cure Machine.

$$Volume\ shrinkage\ (\%) = \frac{\rho_{solid} - \rho_{liquid}}{\rho_{solid}} \times 100 \quad (1)$$

Solid density was measured by using Mettler Toledo Precision Balance XPR204S Lab Scale equipped with a density kit. Liquid density was measured by using a pycnometer. Resin reactivity test applied using Photon S 3D printer. Firstly, the resin tank was taken off and a clear PET sheet was placed onto the LCD screen. Then, 2-3 grams of VP resin were poured onto the film. Screen activated 10 seconds using exposure test mode. The uncured resin was washed with IPA and cured film peeled off from the PET sheet. Cured film thickness was measured by using a micrometer.

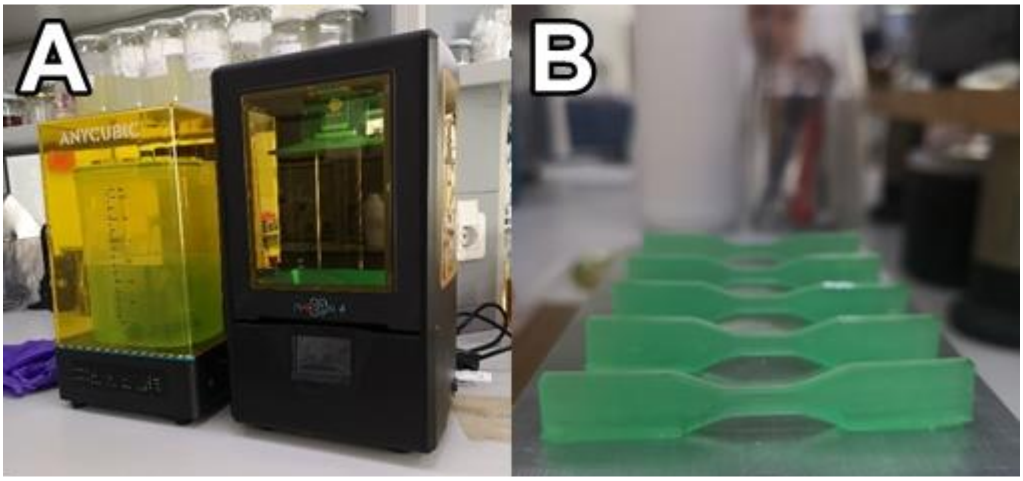


Figure 4. (A) “Anycubic Photon S 3D Printer” (right) and “Anycubic Wash&Cure Machine” (left) and (B) Tensile test specimens

3. RESULTS AND DISCUSSION

Before the production of test specimens, the reactivity of the VP resins was analyzed. Cured film thicknesses of VP resins were determined as 0.21mm according to the aforementioned method. Results indicated that the reactivity of VP resins was not affected significantly by the type of triacrylate monomer for 20%wt. addition. However, the reactivity of VP resins may differ for higher triacrylate monomer content due to the excessive crosslinking effect of the trifunctional monomers.

Figure 5. shows the viscosities of VP resins. TMPTA and PO3 exhibited the same viscosity while EO3 presenting a lower value. TMPTA and PO3 have the same dilution effect on VP resins. On the other hand, EO3 shows higher dilution efficiency, in other words, higher cutting power. EO3 may be led to better dilution owing to its flexible ethoxylated chemical structure.

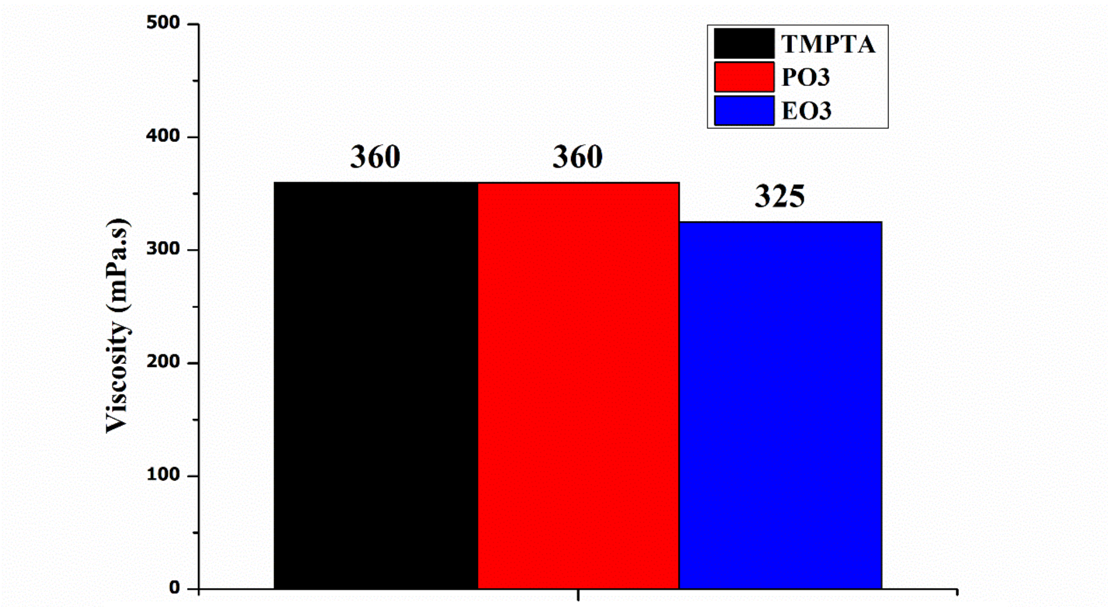


Figure 5. Cone&Plate viscosities of VP resins.

Figure 6. shows the tensile test results. TMPTA showed the highest stiffness compared to EO3 and PO3. The elastic modulus of TMPTA is almost 1.5 times higher than others. On the other hand, EO3 and PO3 exhibited almost 2 times higher elongation compared to TMPTA. Ethoxylated and propoxylated

triacrylates contributed to the elasticity of VP resins owing to their flexible chemical structures while TMPTA providing rigidity and stiffness.

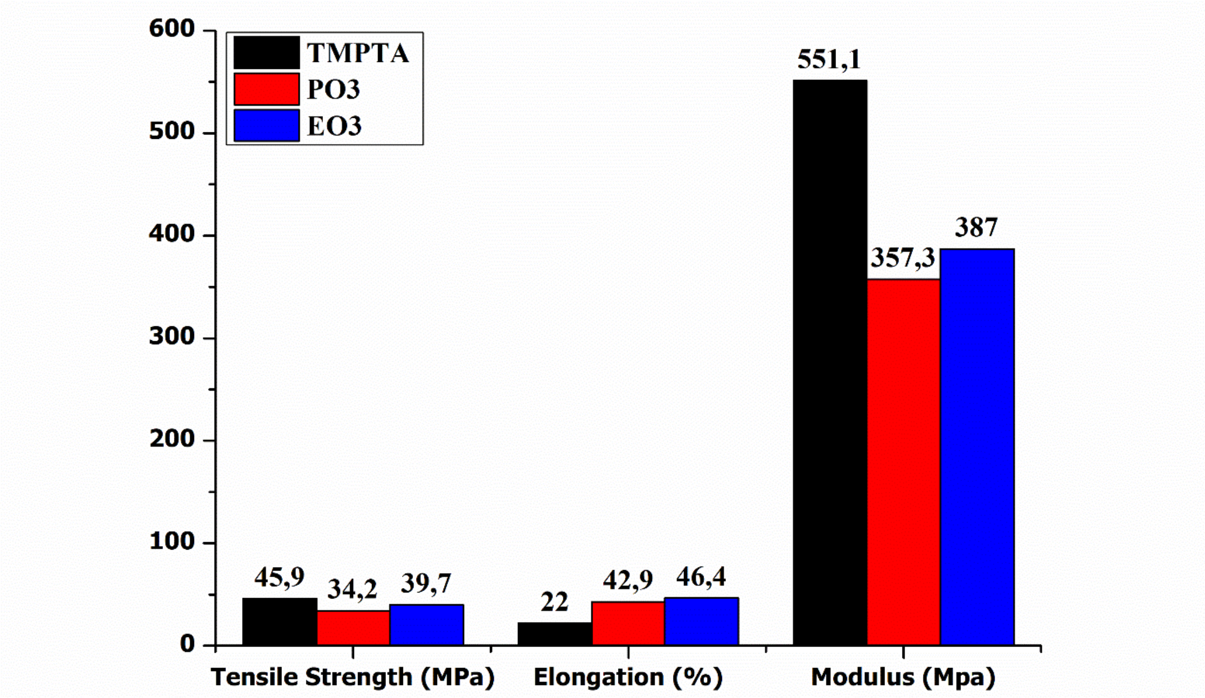


Figure 6. Tensile Properties of VP Resins

Table 2. shows the density and volume shrinkage values of VP resins. Solid densities of VP resins varied prominently compared to liquid densities. Thus, the volume shrinkage of VP resins differentiated according to the triacrylate structure. PO3 led to the lowest volume shrinkage while TMPTA presenting the highest volume shrinkage. Ethoxylated and propoxylated structures may limit the close packing of polymer chains after curing and lead to a decrease in shrinkage. This phenomenon may be observed more significantly for PO3 compared due to its spacer pendant propyl group.

Table 2. Density and volume shrinkage values of VP resins

Abbreviations	ρ_{solid} (g/cm^3)	ρ_{liquid} (g/cm^3)	Volume Shrinkage (%)
TMPTA	1.1836	1.0882	8.06
EO3	1.1762	1.0880	7.49
PO3	1.1686	1.0885	6.85

4. CONCLUSION

The effect of triacrylate type on the volume shrinkage, viscosity, and tensile properties was investigated in this article. Results concluded that triacrylate type has a significant effect on final VP resin properties except for the reactivity. Ethoxylated and propoxylated groups promote flexibility by increasing the elongation at break up to 210% and reduce shrinkage from 8,06% up to 6,85%. However, ethoxylated and propoxylated groups led to a dramatic reduction in elastic modulus up to 35% for PO3 compared to TMPTA. Mixtures of triacrylate monomers can be beneficial to obtain balanced results of volume shrinkage and elastic modulus.

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