Acrylate-based photosensitive resins for digital light processing (DLP) 3D printing generally suffer from large volumetric shrinkage, insufficient functionality conversion and heterogeneous networks. Based on thiol-ene click chemistry, we developed a series of thiol-ene-acrylate ternary formulations and systematically studied the effects of each composition on the photopolymerization kinetics and thermomechanical properties. The ternary systems exhibit very low viscosity (< 0.15 Pa·s) and sufficient thermal storage stability. The mechanical properties of the networks can be adjusted by simply altering the components ratio. With optimal parameters, the thiol-ene-acrylate ternary system can be applied to DLP 3D printing to fabricate delicate objects.

Keywords: 3D Printing, Thiol-ene-acrylate, Photopolymerization

1. Introduction

3D printing is an additive manufacturing method for constructing 3D objects based on digital models. It has drawn tremendous attention from both academia and industry with its potential applications in various fields, such as the aerospace, automotive, medical, and pharmaceutical domains [1-5]. The digital light processing (DLP) 3D printing technology, which involves photopolymerization of liquid photosensitive resin via selective exposure to light, is quite attractive due to its unique advantages including high fabrication accuracy, rapid fabrication speed, and high-quality surface finish [6,7]. Therefore, it is highly desired to develop photosensitive resins for DLP 3D printing with fast printing speed and high printing accuracy as well as desired mechanical properties.

Currently, acrylic and epoxy resins, which allow photopolymerization via free radical or cationic mechanism, are still the most popular materials used in photosensitive resins for DLP 3D printing [8]. However, in chain growth polymerization of multifunctional acrylates, early gelation generally leads to heterogeneous matrices with low cross-linking density and insufficient functionality conversion. The rapid progress of acrylate photopolymerization also leads to a large polymerization shrinkage stress during layer by layer fabrication, resulting curling and other deformation problems to reduce printing accuracy [9]. On the other hand, the epoxy resin system suffers from brittleness issue, and its slow curing speed is also difficult to meet the requirements of DLP rapid prototyping [8].

Thiol-ene systems are promising alternatives that form highly uniform cross-linked networks via a free radical step-growth process [10,11]. Compared to acrylates, the delayed onset of the gel point endows thiol-ene photopolymerization with low shrinkage and high functionality conversion [12]. Also, the fast polymerization rates of thiol-ene reactions can increase the printing speed and decrease amount of photoinitiator, which reduces the cost and alleviates the yellowing and migration problem of the residual photoinitiators.

Compared to thiol-ene binary systems, the thiol-ene-acrylate ternary systems, undergoing a mixed step-chain growth mechanism, present an even greater opportunity for fabricating networks with a tailored set of properties [13]. Moreover, higher monomer conversion, synergistic mechanical properties, lower shrinkage and better bioavailability have been proven for the ternary systems [14-16]. However, currently only very few
studies applying thiol-ene-acrylate resins to 3D printings [17].

In this paper, a series of thiol-ene-acrylate photosensitive formulations with different monomer ratios were designed and prepared (Fig. 1). The effects of each composition on the photopolymerization kinetics, thermomechanical properties and storage stability were systematically studied. The feasibility of DLP 3D printing based on the prepared ternary systems was also investigated.

Fig. 1. The structures of the monomers in the thiol-ene-acrylate ternary systems.

2. Experimental

2.1. Materials

Pentaerythritol tetrakis(3-mercaptopbutylate) (PETMP) was obtained from Tokyo Chemical Industry and bis (2,4,6-trimethylbenzoyl)phenyl phosphine oxide (Irgacure 819) was supplied by BASF Chemical Reagent Co., Ltd. Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) was purchased from Adamas Reagent Co., Ltd. Ethoxy trimethylolpropane triacrylate (TMPTA3EO) was obtained from Jiangsu Kailin Ruiyang Chemical Co., Ltd All the materials were used as received.

2.2. Preparation of photosensitive samples

The preparation was conducted in a yellow light room. Appropriate amounts of TMPTA3EO and TTT (90-10,80-20,70-30) were charged into a glass vial and mixed with magnetic stirrers. Then different amounts of PETMP (0 wt%, 10 wt%, 20 wt%, 30 wt%) were added to different proportions of the formulations, followed by addition of 0.3 wt% phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure 819) as photoinitiator and 0.035 wt% 1,2,3-benzenetriol as inhibitor in all samples and stirred at room temperature for 2 h until the solid samples were completely dissolved to obtain a homogeneous photosensitive resin (Table 1).

2.3. Thermal stability

The thermal stability of the formulations was evaluated using the viscosity values measured by a rheometer (TA Discovery DHR-3) equipped with a cone plate geometry of 40 mm diameter. All samples were stored at 60 °C for 4 weeks and the measurements were conducted each week with shear rates ranging from 0.1 to 100 s⁻¹ at 25 °C.

2.4. Polymerization kinetics study

A Fourier transform infrared spectrometer (FT-IR, Nicolet 6700, Thermo Fisher Scientific, 500-4000 cm⁻¹ wavelength range) was used to study the functional group conversions of each formulation. An external light source (Omic Cure S1000 series) with a light intensity of 22.5 mW/cm² at 365 nm was used to initiate polymerization. The conversions of the functional groups were calculated by using the following equation (1):

\[
\text{Conversion} = \left(1 - \frac{A_1}{A_0}\right) \times 100\% \quad (1)
\]

where \(A_1\) corresponds to the area of the characteristic absorbance peaks of the double bond of acrylates (peak at 819 cm⁻¹), the thiol (peak at 2570 cm⁻¹) or the double bond of allyl (peak at 3083 cm⁻¹) group at time \(t\), and \(A_0\) represents the initial area of the corresponding peaks.

2.5. Volume shrinkage measurements

To confirm the volume shrinkage of samples before and after photocuring, the density values were tested by a high-precision electronic hydrometer (DH-120T), and the curing shrinkage was calculated using the following equation (2):

\[
\text{Volume Shrinkage} = \frac{\rho_2 - \rho_1}{\rho_1} \times 100\% \quad (2)
\]

where \(\rho_1\) and \(\rho_2\) are density values of samples before and after photocuring.

2.6. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed to obtain tan \(\delta\) and storage modulus \(E\) versus temperature curves using a Q800 DMA (TA Instruments, American). The 3D printed dumbbell-shaped objects (15 mm × 4.3 mm) were measured in film tensile mode with a heating rate of 3 °C/ min and a frequency of 1 Hz from -40 °C to 140 °C.

2.7. DLP 3D printing and scanning

The prepared photosensitive resins were printed using a mini-fab DLP printer (Wuxi Jiangsu 3D Technology Co., Ltd.) at 415 nm wavelength after adjusting exposure time and printing speed until the complete models or testing samples were printed.
The printed objects were immersed in absolute ethanol (1-2 min) to wash off the uncured liquid resin on the surface. It was placed again under a 405 nm LED light for post-curing for 3-5 min until the resin was fully cured. The printed objects were scanned using a 3D scanning machine (OpenTechnologies S.R.L) and then fitted with the digital model of the initial STL file to obtain the fitted data.

3. Results and discussion

3.1. Viscosity of the ternary systems

Viscosity of the photosensitive formulation is one of the important parameters to judge whether the resin is suitable for DLP 3D printing. The viscosity of the resin directly affects the printing speed. The higher the viscosity, the longer the waiting time of the recoating process, and the longer the printing time. The viscosity of the photosensitive resins with different thiol contents in the ternary system was tested by a rotary viscometer. As shown in Fig. 2, with the increase of thiol content, the viscosity of the resin increases gradually. The formulation of the same thiol content decreases with the decrease of the ratio of TMPTA3EO/TTT, that is, the larger the TTT ratio, the greater the viscosity due to the rigid structure of TTT. The maximum viscosity of the thiol-ene-acrylate ternary system with different PETMP content is less than 0.15 Pa·s at room temperature, less than that of the commercial resins for DLP 3D printing (0.4-1.5 Pa·s).

3.2. Thermal storage stability

Besides viscosity, the thermal stability of the photosensitive resin is another important parameter of 3D printing, which influence the storage and transportation of materials. This is especially true for thiol-based formulations which generally suffer from poor thermal storage stability [18]. We added 0.035 wt% 1,2,3-benzenetriol as inhibitor to the formulations which were placed in an oven at 60 °C, and measured the viscosity change within 4 weeks by a rotational rheometer. As shown in Fig. 3, marginal change of the viscosity was observed in the absence of the thiols because the possibility of copolymerization between acrylate and ene, and the homopolymerization of acrylates is very low under the testing condition. With the increase of thiol content, the increase of resin viscosity became obvious. The premature polymerization might be caused by the decomposition of peroxide impurities of thiols or the generation of radicals through a ground-state charge transfer complex formed between the thiol and ene components in the mixture [10]. On the whole, even after being placed at 60 °C for 4 weeks, the resin still maintained good fluidity and the viscosity was less than 1 Pa·s.

The printed objects were immersed in absolute ethanol (1-2 min) to wash off the uncured liquid resin on the surface. It was placed again under a 405 nm LED light for post-curing for 3-5 min until the resin was fully cured. The printed objects were scanned using a 3D scanning machine (OpenTechnologies S.R.L) and then fitted with the digital model of the initial STL file to obtain the fitted data.

Table 1. Ternary formulations, the conversion of the functional groups and thermo-mechanical property data.

| Formulation | TMPTA3EO/TTT | PETMP Wt % | Conversion | $T_g$ (℃) | $E^\prime (T_g +50$ ℃) (MPa) |
|-------------|--------------|------------|------------|-----------|-------------------------------|
| Acrylate    | Ene          | Thiol      | %          |           |                               |
| 90/10-0     | 90/10        | 0          | 51         | 16        | 79.4                          |
| 90/10-10    | 10           | 52         | 28         | 56        | 67.5                          | 68.77 |
| 90/10-20    | 20           | 61         | 29         | 55        | 58.8                          | 46.64 |
| 90/10-30    | 30           | 68         | 29         | 56        | 54.1                          | 43.70 |
| 90/10-40    | 40           | 76         | 51         | 62        | 39.8                          | 38.71 |
| 80/20-0     | 80/20        | 0          | 40         | 11        | 72.8                          | 194.06 |
| 80/20-10    | 10           | 57         | 17         | 61        | 71.6                          | 83.96 |
| 80/20-20    | 20           | 58         | 17         | 52        | 67.1                          | 71.27 |
| 80/20-30    | 30           | 68         | 29         | 59        | 52.8                          | 53.66 |
| 80/20-40    | 40           | 74         | 41         | 60        | 51.1                          | 53.74 |
| 70/30-0     | 70/30        | 0          | 45         | 9         | 75.3                          | 235.0 |
| 70/30-10    | 10           | 51         | 14         | 51        | 67.1                          | 107.44 |
| 70/30-20    | 20           | 68         | 23         | 67        | 54.0                          | 59.93 |
| 70/30-30    | 30           | 71         | 31         | 66        | 53.6                          | 42.57 |
undergo a mixed step-chain growth mechanism and when the thiol content is 40 wt%, the final double bond conversion of the acrylate can reach 76%. Meanwhile, the ene monomers copolymerize with thiols via stepwise polymerization mechanism, leading to the increased double bond conversion from 16% to 51%. Samples of different TMPTA3EO/TTT ratios showed similar patterns (Table 1). Since the content of thiol groups in the samples varied all the time, the conversion of thiol groups has no obvious regularity.

3.3. Polymerization kinetics

The photopolymerization kinetics of thiol-ene-acrylate ternary system were investigated by real-time FT-IR. As shown in Fig. 4, for the thiol-free sample, under irradiation, the free radicals generated from the photodecomposition of the photoinitiators induce the homopolymerization of the acrylates via chain growth mechanism with the final double bond conversion of 51%. Theoretically, the ene monomer hardly reacts. When adding the thiol monomers to the formulation, the acrylates

Fig. 2. Viscosity of the photosensitive resin (a) TMPTA3EO/TTT=90/10, (b) 80/20, (c) 70/30 with different PETMP content.

Fig. 3. Viscosity of photosensitive resin (a) TMPTA3EO/TTT=90/10, (b) 80/20, (c) 70/30 with different PETMP content at different times when placed at 60 °C for 4 weeks.
3.4. Thermo-mechanical properties of the printed objects

The thermo-mechanical properties of the 3D printed dumbbell-shaped objects based on thiol-ene-acrylate ternary systems were analyzed by DMA, and the results are shown in Fig. 6 and Table 1. In the absence of the thiols, a broad temperature transition and a relatively high $T_g$ of 75.3 °C were observed. This can be attributed to the sole homopolymerization of acrylates via chain growth mechanism which generally leads to early gelation and heterogeneous networks. With the increase of the thiol content, the half-peak width regions become narrow and the $T_g$ decreases. The increased proportion of the thiol-ene and thiol-acrylate polymerization via step-growth mechanism can provide more homogeneous networks and therefore narrower half-peak width. The decreasing $T_g$ can be explained by the formation of flexible thioether linkages within the matrices, which also leads to the decreased storage modules. By simply altering the components ratio, the mechanical properties of 3D printed objects can be adjusted to meet the application requirement.

3.5. DLP 3D printing and Scanning

Considering that the formulation 70/30-30 provides the best comprehensive performance
including the lowest shrinkage (8.67%, Fig. 5) and the relatively uniform of the crosslinked network, such photosensitive resin was selected for DLP 3D printing to fabricate delicate articles such as a dog, a hollow polyhedron and a mini Eiffel Tower (Fig. 7). The hollow shapes within the Eiffel Tower, observed via an ultra-depth microscope, indicate the high printing precision.

4. Conclusion

In conclusion, a series of thiol-ene-acrylate ternary formulations were designed and prepared, and the compact of each composition on the photopolymerization kinetics and thermomechanical properties was systematically studied. The ternary systems exhibit very low viscosity (< 0.15 Pa·s) and sufficient thermal storage stability even being placed at 60 °C for 4 weeks (< 1 Pa·s). The increased thiol content leads to faster photopolymerization, narrower half-peak width regions, lower \( T_g \) and storage modules. Compared to binary thiol-ene system, higher 3D printing resolution can be obtained based on thiol-ene-acrylate ternary system.

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