

Preparation and Properties of 3D Printing Light-Curable Resin Modified with Hyperbranched Polysiloxane

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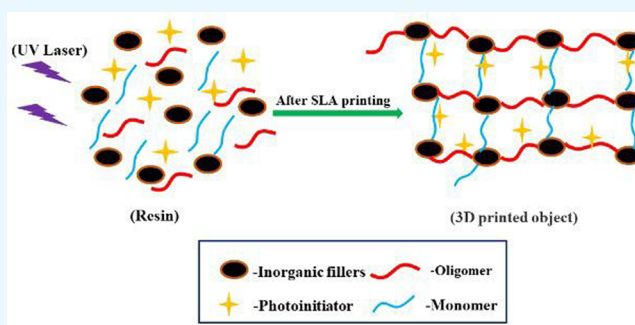
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ABSTRACT: A novel, hyperbranched polysiloxane (HBPSi) is successfully synthesized via hydrolysis using γ -methacryloxypropyl trimethoxysilane (A174) and deionized water, under catalyst-free conditions. Then, for the first time, the HBPSi are used to modify a 3D printing light-curing epoxy resin. Thermogravimetry results showed that the addition of HBPSi improved the heat resistance of the epoxy resin. Experimental results also show that the addition of HBPSi simultaneously improves tensile strength, elongation at break, and impact strength. In particular, a great increase in the toughness of 3D printing light-curing epoxy resin is observed, with 5 wt % HBPSi loading. These results indicate that the HBPSi containing OH- and Si-O-Si can be potentially effective at improving the performance of the 3D printing light-curing epoxy resin. This investigation suggests that the method proposed herein is a new approach to develop the performance of 3D printing light-curing epoxy resin for cutting-edge industries, especially those that simultaneously have outstanding thermal resistance and toughness.



1. INTRODUCTION

Three dimensional printing (3DP) technology has been a major breakthrough in the field of manufacturing technology in

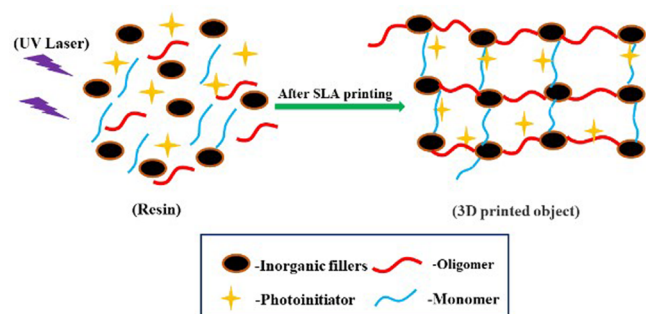


Figure 1. Curing mechanism of filler and resin blend.

the past 30 years.^{1–3} 3DP has changed the manufacturing concepts and models of traditional industries and solved some problems existing in the fields of national defense, aerospace, machinery manufacturing, biomedicine, and transportation. With the development of 3D printing technology, the manufacturing problems of complex parts have brought new changes in the manufacturing industry.^{4–8} Due to the advantages of high molding accuracy and fast speed,^{9–11} stereolithography (SLA) is currently the most well-known and widely used 3D printing technology, and it uses a liquid

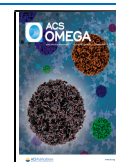
photosensitive resin as a raw material and includes active diluents, photoinitiators, and other additives. The resin used for light-curing 3D printing must have the characteristics required by general UV-curable coatings such as good stability and low volume shrinkage and also needs to have the advantages of low viscosity and fast curing speed.^{12–14} At the same time, dimensional accuracy and performance are closely related to light-curing resins. Therefore, the preparation of high-performance light-curing resins is a current research hotspot.

Epoxy resin is widely used in coatings, the aerospace industry, and other fields due to its wear resistance and chemical stability. However, there are large internal stresses after curing due to its high cross-linking density. On the other hand, it has a tendency to generate and propagate cracks and brittleness, which means that it is not resistant to impact.¹⁵ Consequently, it is desirable and favorable to modify the epoxy for these applications. At present, researchers focus on epoxy resin modification mainly in two aspects:¹⁶ one is the development of new epoxy resin polymers or curing agents,

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such as the introduction of new functional groups, benzene rings, and other structures; and the other is blended and copolymerization with heat-resistant polymer fillers, such as thermoplastic polymers, silicones, etc. Copolymerization uses the active groups in the molecules of the modified material to react with the epoxy groups and hydroxyl groups in the epoxy resin to form grafts or copolymers; meanwhile blending physically mixes the modified material with the epoxy resin to form new cross networks.¹⁷ This is shown in Figure 1, which has a better comprehensive performance system to improve the performance of epoxy resin. Li et al.¹⁸ used organic fluorine and a cathodic electrophoretic coating of epoxy acrylic resin synthesized with a cationic resin; due to the special nature of the fluorine atoms, the fluoropolymer had a spiral structure with a C–C backbone which was wrapped by F atoms, protecting the backbone from harsh environmental conditions and maintaining high stability. The results showed that the corrosion resistance and impact strength of the coating were improved compared with the previous epoxy acrylate coatings when the reaction temperature of the graft was 120 °C, the amination temperature was 100 °C, and the neutralization degree was 90%. Wang et al.¹⁹ et al. modified epoxy acrylate with polyethylene glycol (PEG) for UV curable 3D printing materials. The results showed that PEG can effectively improve the flexibility of epoxy acrylic acid materials, but the resin modified by PEG needed to undergo secondary curing to consolidate the esterification and cross-linking reaction when printing the sample. After the secondary curing, the tensile strength of the sample increased to 8 MPa, and the elongation increased to 30%.

Hyperbranched polymers are prepared by reactive monomer molecules AB_X ($X \geq 2$), which have a three-dimensional spherical structure^{20–22} and special properties different from linear polymers, which also have the advantages of good solubility in organic solvents, such as not easy to crystallize, low system viscosity, and no intermolecular chain entanglement. Hyperbranched polysiloxane (HBPSi) is one of the most widely used hyperbranched polymers. The commonly used preparation methods include hydrosilylation, hydrolysis polycondensation, atom transfer radical polymerization, and proton transfer polymerization.^{23–27} As widely used organic–inorganic hybrid polymeric materials, HBPSis possess attractive characteristics such as excellent chemical stability, thermal properties, and antiweatherability. Inspired by these properties, polysiloxanes are widely used in electronics, aerospace, and other industries.^{28–30} In addition, due to the Si–O–Si bond in the HBPSi molecular structure being long, the bond angle is large and easy to rotate, so the polymer presents a highly compliant state. At the same time, HBPSis accumulate a large number of active functional groups at the molecular ends, showing good compatibility with organic resins, so they have great potential in the modification of resins. By mixing HBPSis with organic resins, the resin matrix can retain the advantages of the HBPSi on the basis of retaining the original advantages, and a new modified resin can be obtained with excellent comprehensive performance. Niu et al.³¹ prepared a novel hyperbranched siloxane with double bonds and hydroxyl groups. These functional groups play an important role in forming blue luminescent materials. The epoxy functionalized polysiloxanes possess the virtue of epoxy resins and silicone resins. Epoxy groups could increase the adhesion of the polysiloxane. Wu et al.³² introduced an HBPSi into the bismaleimide resin system, where the active group

$CH_2=CH$ of the HBPSi terminal group reacted with the active double bond on bismaleimide, and a modified bismaleimide resin with high interfacial bond strength was obtained. This method not only improves the thermal properties of bismaleimide resin but also greatly optimizes the system toughness and curing process.

In the present work, we describe the synthesis of a novel HBPSi using γ -methacryloxypropyl trimethoxysilane as the monomer. The structure of the resulting polymers was characterized using 1H NMR, ^{29}Si NMR, and Fourier transform infrared (FTIR). Then, the influences of the HBPSi on thermal stability, mechanical properties, and toughening mechanisms of the epoxy acrylate (EA) were investigated in detail.

2. RESULTS AND DISCUSSION

2.1. Preparation of the Hyperbranched Polysiloxane (HBPSi). Figure 2 shows the reaction that occurred during the

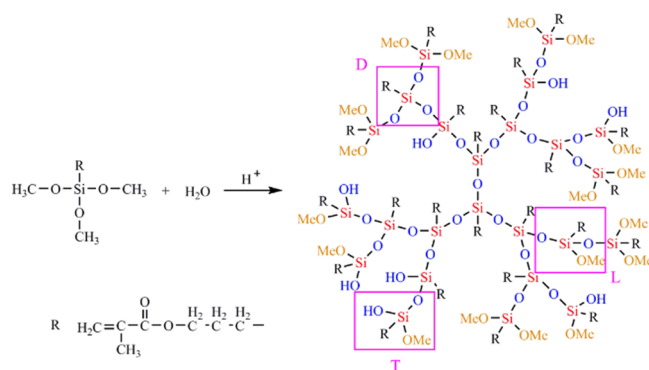


Figure 2. Synthetic route to a hyperbranched polysiloxane.

preparation process of the hyperbranched polysiloxane (HBPSi). The HBPSi was prepared from γ -methacryloxypropyl trimethoxysilane and distilled water by hydrolysis under acidic conditions. Silane coupling agent A174 and distilled water were added to the breaker at a molar ratio of (1.1:1, 1.2:1, 1.3:1, 1.4:1, and 1.5:1), the PH of the mixture was adjusted to 3 with 0.1 mol/L hydrochloric acid solutions and reacted at ambient temperature for 15 min. The reaction mixture was stirred for a certain time (1–5 h) at 50 °C, and then, a light pink transparent liquid with a certain viscosity was obtained by removing the hydrolysate and vacuum to remove methanol.

2.2. FTIR Characterization of HBPSi. The FTIR spectra of γ -methacryloxypropyl trimethoxysilane (A174) and the HBPSi are shown in Figure 3. Figure 3a shows the characteristic peak at 1015–1140 cm^{-1} for A174 belonging to $-Si-O-Si-$ groups, the stretching vibration absorption peak at 1635 cm^{-1} corresponded to $-C=C-$, and at 1726 cm^{-1} is the characteristic absorption peak of $-C=O$. The HBPSi (Figure 3b) holds major peaks around 1163 cm^{-1} for $-Si-O-C-$ and at 3468 cm^{-1} for silanol groups ($-Si-OH$), indicating that some alkoxy groups ($-OCH_3$) have been successfully transformed into siloxy groups ($-Si-O-$) and the desired reaction between H_2O and A174 occurred.

2.3. 1H NMR and ^{29}Si NMR of HBPSi. According to the 1H NMR spectra, Figure 4a, of the synthesized HBPSi, Generally speaking, the HBPSi has three different repeating units: dendritic, linear, and terminal units. The proton peak of the HBPSi is shifted to a certain extent compared with that of

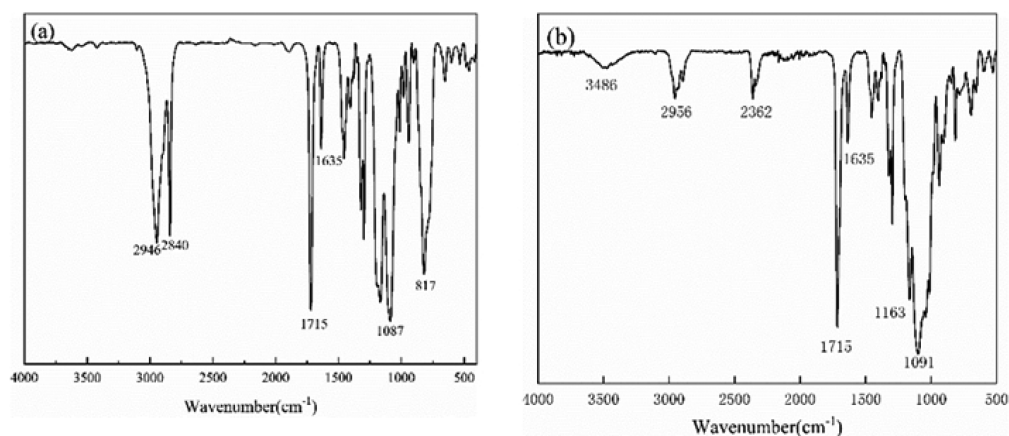


Figure 3. FT-IR spectrum of (a) γ -methacryloxypropyl trimethoxysilane and (b) hyperbranched polysiloxane.

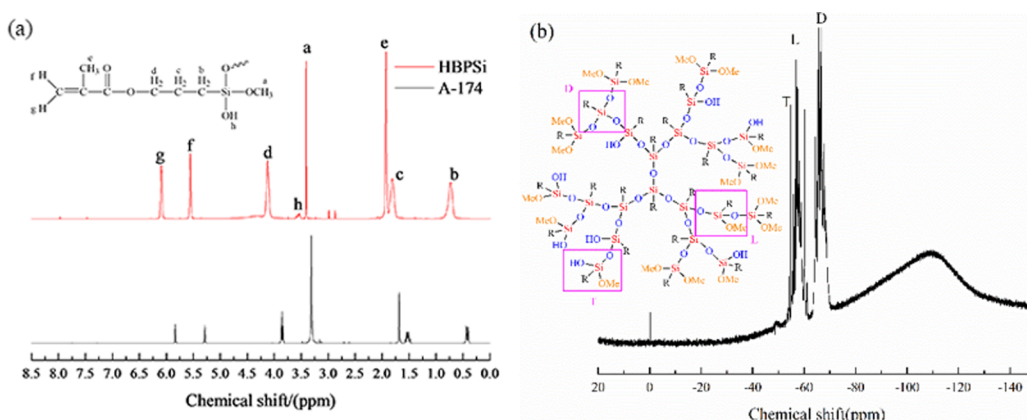


Figure 4. (a) ^1H NMR spectra of HBPSi and 3-methacryloxypropyltrimethoxysilane (b) and ^{29}Si NMR spectra of HBPSi.

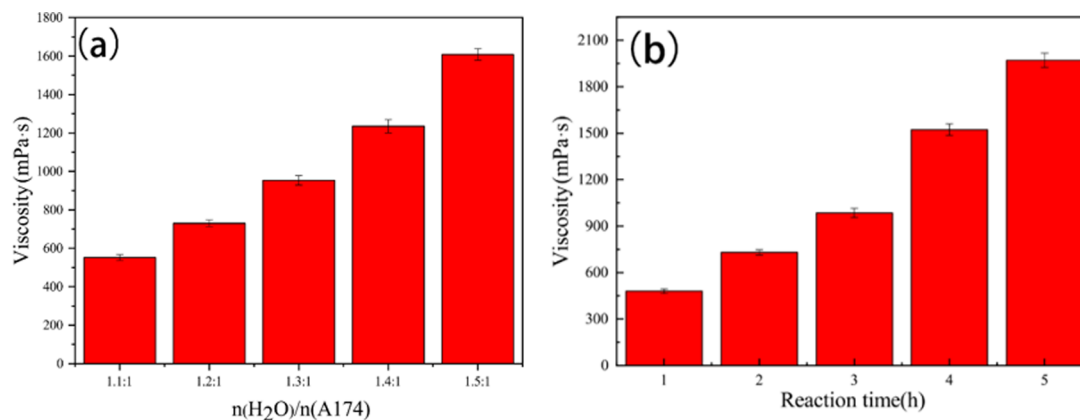


Figure 5. Effect of reaction conditions, (a) $n(\text{H}_2\text{O})/n(\text{A174})$ molar ratio and (b) different reaction times (1–5 h), on HBPSi viscosity.

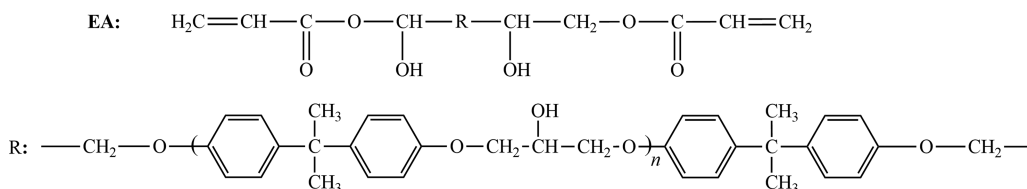


Figure 6. Structural formula of bisphenol A epoxy acrylate.

A174. The proton peaks at 5.56 (f) and 6.09 (g) ppm are hydrogen on $-\text{C}=\text{CH}_2$; the peaks belong to methylene ($-\text{CH}_2$) hydrogen at 0.73 (b), 1.81 (c), and 4.31–3.74 (d)

ppm, respectively; 3.41 (a) ppm is hydrogen on the $-\text{Si}-\text{OCH}_3$; 1.93 (e) ppm belongs to hydrogen on a methyl group ($-\text{CH}_3$) connected with double bonds. New proton peaks

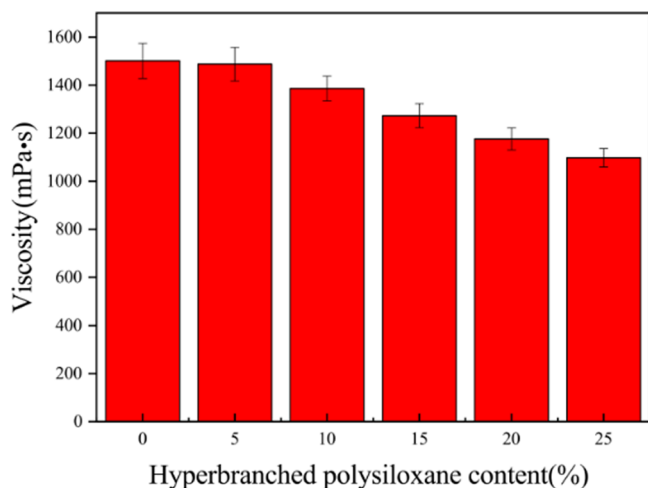


Figure 7. Effect of HBPSi content on the viscosity of 3D printing photosensitive resin.

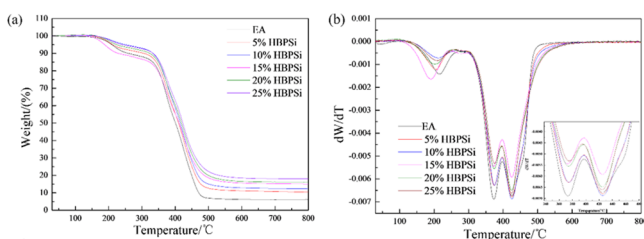


Figure 8. Influence curves of different HBPSi loading on the thermal stability of 3D photosensitive materials. (a) TG. (b) DTG.

Table 1. Data of Thermal Weight Loss of 3D Photosensitive Materials Modified with Different Content of HBPSi

	$T_{50\%}/^{\circ}\text{C}$	$T_{\text{max}1}/^{\circ}\text{C}$	$T_{\text{max}2}/^{\circ}\text{C}$	carbon yield
EA-0% HBPSi	400.67	372.67	424.33	6.23
EA-5% HBPSi	410.33	375.00	425.00	11.15
EA-10% HBPSi	415.33	375.83	426.50	12.86
EA-15% HBPSi	411.67	373.67	426.00	15.64
EA-20% HBPSi	419.17	375.17	426.17	16.57
EA-25% HBPSi	422.83	375.50	425.33	18.49

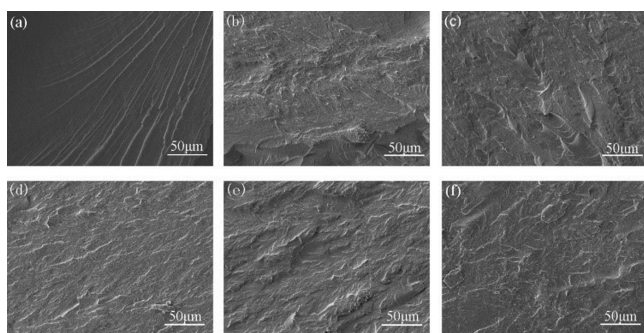


Figure 9. SEM images of tensile fracture surfaces of 3D photosensitive material modified with different content of HBPSi. (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20% HBPSi, and (f) 25% HBPSi.

appear at 3.56–3.53 (h) ppm compared with A174, because the methoxy group ($-\text{Si}-\text{OCH}_3$) of A174 is converted to the silanol hydroxyl group ($-\text{Si}-\text{OH}$), which is consistent with the results reported in the literature. Figure 4b shows the ^{29}Si NMR spectra of the HBPSi. It can be observed that there are

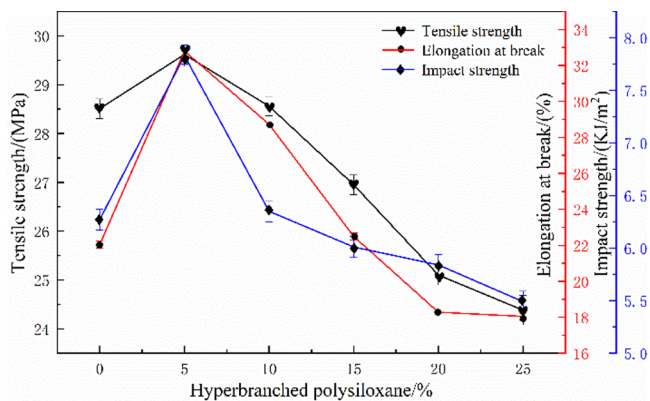


Figure 10. Effect of HBPSi content on the tensile strength, elongation at break, and impact strength of the 3D photosensitive material.

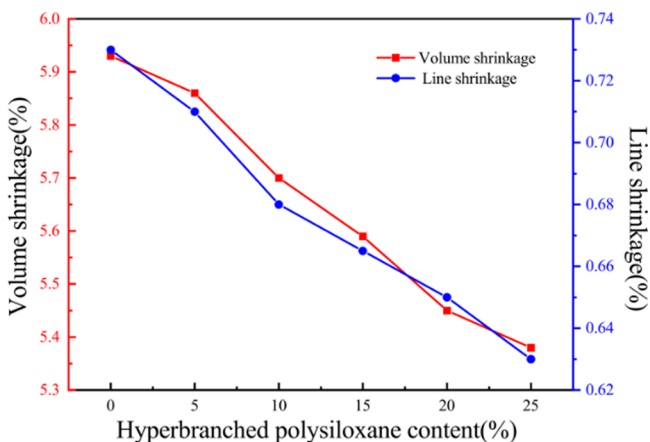


Figure 11. Effect of HBPSi content on the shrinkage of 3D photosensitive materials.

three different chemical shifts at -63.25 to -71.61 , -55.41 to -63.08 , and -52.45 to -55.41 ppm, which are branched unit (D), linear unit (L), and terminal unit (T), respectively. The integral ratio for them is 1.00:0.62:0.37. Furthermore, there are also some miscellaneous peaks, which are due to the prepared HBPSi existing in different chemical environments.

2.4. Viscosity of HBPSi. Figure 5a shows the results of viscosity at the effect of the molar ratio of A174/ H_2O , and the reaction time was 3 h. Figure 5b shows the influence of different reaction times on the viscosity of the HBPSi, maintaining a molar ratio of $\text{H}_2\text{O}/\text{A174}$ of 1.3:1. When the amount of H_2O was insufficient, the silane hydrolysis reaction in A174 was not sufficient and less silanol was produced. But when the amount of H_2O was excessive, the content of silanol generated by the hydrolysis of silane was excessive, which increased the hydroxyl groups and cross-linking density during the reaction. Subsequently the self-condensation phenomenon occurred, which caused the viscosity of the system to rise. On the other hand, if the reaction time was too long, the synthesized HBPSi will undergo self-condensation between hydroxyl groups, which will ascend the viscosity of the system. Due to the higher requirements for the viscosity of the resin system during the printing process, the molar ratio of $\text{H}_2\text{O}/\text{A174}$ was selected as 1.3:1, and the reaction time was maintained for 3 h, under the premise that the viscosity of the resin system was small and the performance of the synthesized hyperbranched polysiloxane was better. Therefore, the HBPSi

prepared under the conditions of a reaction time of 3 h and a molar ratio of 1.3:1 was selected to configure the resin.

2.5. Effect of HBPSi on the Viscosity of Bisphenol A Type Epoxy Acrylate (EA). Figure 6 provides the structure formula of bisphenol A type epoxy acrylate. Figure 7 gives the viscosity of the light-curing resin system under the effect of HBPSi content. It can be found that the viscosity of the light-curing resin system gradually decreased with the continuous increase of HBPSi content. When the addition amount of HBPSi reaches 25%, the resin viscosity was 1098 ± 38 mPa·s, which is reduced by 26.8% compared to that without the HBPSi. In this paper, the photocurable resin prepolymer was mainly composed of EA and urethane acrylate (PUA), which contains a large amount of hydroxyl and carbonyl groups, so hydroxyl bonds were easily formed between and within the molecule, resulting in a higher viscosity of the photosensitive resin. While there were also a large number of hydroxyl groups and carbonyl groups in the HBPSi molecules, which has a cavity structure in space, it is difficult to form hydrogen bonds between HBPSi molecules, and there was no entanglement between chains. So, the HBPSi had the same molecular weight. Compared with linear polymers, HBPSis have lower viscosity and better fluidity and achieved the effect of reducing the viscosity of the 3D printing light-curing resin system, which was beneficial to rapid light-curing molding and increased printing speed.

2.6. Thermal Stability of the HBPSi Modified EA. Figure 8a and b explain the thermogravimetry (TG) and differential TG (DTG) curves of the HBPSi modified photosensitive resin with different content. The thermal weight loss data are presented in Table 1. Figure 8a shows the main decomposition process of oligomers, photoinitiators, small molecule diluents, and modifiers between room temperature and 300 °C; these have not fully participated in the cross-linking and curing reaction. In the range of 300–500 °C, the decomposition process of the polyurethane chain end and epoxy acrylate segment occurred. It can be seen from Figure 8b that, with the increase of HBPSi content, the value of $T_{50\%}$ of the printed parts increased significantly until T_{max1} and T_{max2} when the increase slowed. When the addition amount of HBPSi reaches 25%, $T_{50\%}$ increases from 400.67 to 422.83 °C and the carbon residue rate increases from 6.23% to 18.49%, which due to the addition of the HBPSi will increase the content of Si in the composite material and form SiO₂ at high temperatures. At the same time, HBPSi itself has a large number of cavity structures, which can inhibit local cracking and expansion of the molded part, thereby achieving the effect of improving the thermal stability of the molded part.

2.7. SEM of Fracture Morphologies. In order to understand the mechanism of HBPSi interference comprehensively during the toughening process, scanning electron microscopy (SEM) was used to analyze the fracture surface of the printed sample. Figure 9 shows the tensile fracture morphologies of HBPSi (0%, 5%, 10%, 15%, 20%, and 25%) modified photosensitive materials with different additions. It can be observed from Figure 9 that, without HBPSi, the tensile fracture surface of the molded part is relatively smooth, with only very shallow fracture steps, and no obvious plastic deformation occurred due to sudden cracking, which is typical of a brittle fracture. When a small amount of HBPSi was added, the fracture surface became rough with obvious ductile recessed areas, and the molded part changed from brittle fracture to ductile fracture, indicating that the toughness of the

sample was increased. HBPSis contain a large number of flexible Si–O–Si chains and free volume cavities, which makes molecular chains in cross-linked networks easy to rotate and absorbs more energy under the action of external force. On the other hand, as a result of the HBPSis having a large amount of C=C bonds, the light-curing cross-linking density is increased, so as to achieve the effect of toughening the resin, but as the content of HBPSi continues to increase, the fracture surface appears brittle, which shows that adding more is not better. Therefore, by adding an appropriate amount of HBPSi, the mechanical properties of 3D printing photosensitive materials can be improved.

2.8. Tensile Strength, Elongation at Break, and Impact Strength of Formed Parts. The influence of different HBPSi contents on the tensile strength, elongation at break, and impact strength of molded parts is shown in Figure 10. As the amount of HBPSi increases, the tensile strength, elongation at break, and impact strength of the molded parts increase first and then decrease. When the addition amount of HBPSi is 5%, the maximum values are 29.62 MPa, 32.8%, and 7.83 kJ/m², which are 3.89%, 48.8%, and 25% higher than when HBPSi is not added. When the addition amount of HBPSi is greater than 5%, the tensile strength, elongation at break, and impact strength of the molded parts continue to decrease. Because HBPSi is a hyperbranched polymer with a three-dimensional cavity structure and contains more unsaturated C=C bond, there is no entanglement between the molecules, and it is not easy to crystallize; so, adding a small amount of HBPSi can appropriately increase the cross-linking density of the 3D printing photosensitive material and improve the mechanical properties of the molded part. However, when the amount added is too large, due to the low surface energy of the Si–O–Si bonds, the HBPSi will migrate to the surface during the photocuring process of the 3D printing photosensitive material, so that the silicon content on the surface of the printed material is higher than that in the interior layer by layer, leading to poor compatibility between the HBPSi and resin during the curing process. The corresponding tensile strength, elongation at break, and impact strength decrease. On the other hand, when the addition amount of HBPSi continues to increase, the end-group functional groups at the outer end of the HBPSi cannot completely react, resulting in a “suspension chain”, which leads to the increase of defects in the formed parts and the decline of mechanical properties. In order to improve the mechanical properties of the resin material, it is important to select the appropriate amount of HBPSi content.

2.9. Curing Shrinkage. In light-curing 3D printing, the curing shrinkage of the photosensitive resin itself has a great impact on the part. Before the photosensitive resin is cured, the resin mainly contains a variety of reactive monomers and oligomers. The force between objects is van der Waals force, and the distance between molecules is van der Waals distance. But when the resin is cured, the monomer and prepolymer react, the original van der Waals distance becomes the covalent bond distance, and the covalent bond is much less compared with the van der Waals distance. Hence, the entire system shrinks greatly. When the volume shrinks too much, shrinkage stress will inevitably occur, which will cause the shrinkage of layers to warp and other phenomena during the later curing. In order to reduce these phenomena, it is necessary to decrease the curing shrinkage rate of the photosensitive resin.

From the curve of the influence of different HBPSi additions on the volume shrinkage rate and linear shrinkage rate of molded parts (Figure 11), it can be seen that, with the increase of HBPSi content, the volume shrinkage rate and linear shrinkage rate of 3D printed molded parts gradually decrease. When the amount of HBPSi added is 25%, the volume shrinkage rate and linear shrinkage rate are both the minimum, which are 5.38% and 0.63%, respectively.

3. CONCLUSIONS

A friendly hyperbranched polymer was prepared by hydrolysis, which used silane coupling of methacryloxypropyl trimethoxysilane and distilled water as raw materials under acidic conditions. The chemical structure of the HBPSi was characterized by FTIR, ^1H NMR, and ^{29}Si NMR. Subsequently, the HBPSi was used as a refinement for an epoxy resin, it can simultaneously enhanced char yield, fracture toughness, and tensile strength. The TG and DTG results showed that the $T_{50\%}$ of the cured hybrid epoxy rose with increasing HBPSi content. At 5% HBPSi loading, the tensile strength, elongation at break, and impact strength were increased by about 3.89%, 48.8%, and 25%, and after 10–15%, there was a decrease of these properties. In summary, this study revealed that the easily and environmentally favorably synthesized HBPSi can act as a highly efficient toughener in a 3D printing light-curing epoxy resin.

4. EXPERIMENTAL SECTION

4.1. Materials. Epoxy acrylate (EA) was obtained from Shenzhen Kelifu Industrial Co, Ltd. Urethane acrylate (PUA) was supplied by the Zhongshan Bohai Fine Chemical Co, Ltd. Tripropylene glycol diacrylate and Trimethylol propane triacrylate were purchased Chengdu Sicheng New Material Co. Diphenylene (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), γ -methacryloxypropyl trimethoxysilane (A174), and absolute ethyl alcohol (AR) were obtained from Shanghai Yinchang New Material Co, Shandong Youso Chemical Co, and Tianjin Fuyu Fine Chemical Co, Ltd., respectively. Deionized water was synthesized by our laboratory.

4.2. Preparation of HBPSi Photosensitive Resin. The mass ratios of prepolymer EA to PUA and reactive diluent TPGDA to TMPTA were 8:2 and 7:3, respectively. The mass fraction of the reactive diluent was 35%, and the mass fraction of photoinitiator TPO was 5%. TPO was dissolved in the mixed solution of TPGDA and TMPTA in the dark and stirred magnetically for 20 min at 40 °C in a water bath. After the photoinitiator was completely dissolved, HBPSi was added with different mass fractions (0%, 5%, 10%, 15%, 20%, and 25%) under magnetic stirring at ambient temperature for 3 h. The well-stirred mixture of HBPSi, photoinitiator TPO, and diluent was poured into the weighed prepolymer, magnetically stirred at 1000 rpm at room temperature for 5 h, and allowed to stand in the dark for 24 h to remove air bubbles. Finally, a stable hyperbranched polysiloxane photosensitive resin was prepared and stored in the dark for future use.

4.3. Printing with the HBPSi Photosensitive Resin. The prepared mixtures were poured into the resin tank of the printer, and then, the parameters were set, and the digital model for printing was selected. After the process of printing finished, the resin sample was placed in absolute ethanol for 20 min and then taken out and stored away from light. Light-curing 3D printing parameters: main emission wavelength 405

nm, layer thickness 0.1 mm, UV laser power 58 W, and printing speed 40 mm/h.

4.4. Characterization. The synthesized HBPSi was characterized by ^1H NMR, ^{29}Si NMR, and FTIR spectroscopy.

A TGA/DSC produced by Mettler Toledo was used to analyze the thermal stability of HBPSi modified 3D printing photosensitive resin materials. Test conditions: under the protection of nitrogen (flow rate 80–100 mL/min), test temperature from room temperature to 800 °C, and rise rate 10 °C/min.

The morphological changes of the blank resin section and the HBPSi modified resin section after the tensile test were observed with a scanning electron microscope (SEM).

According to GB/T 1040.2-2006, a dumbbell-shaped sample with a size of 115 mm \times 25 mm \times 4 mm was printed and formed on an SLA-3D printer. A universal tensile material testing machine was used to test the mechanical properties of the molded parts. The tensile speed and measuring temperature were 50 mm/min and 25 °C, respectively. The tensile strength and elongation at break were calculated by formulas 1 and 2:

$$T_L = \frac{F}{bd} \quad (1)$$

Where, T_L represents the tensile strength (MPa), F is maximum load (N), and b and d refer to the sample thickness (mm) and width (mm), respectively.

$$E = \frac{L - L_0}{L_0} \times 100\% \quad (2)$$

Where, L and L_0 represent the fracture distance of the specimen (mm) and the original gauge length of the specimen (mm), respectively. E is the elongation at break of the specimen.

The sample with the size of 80 mm \times 10 mm \times 4 mm was printed and molded on an SLA-3D printer in accordance with GB/T 1043.1-2008. Five specimens were selected from each group and measured at room temperature. The impact strength could be calculated by using eq 3:

$$\sigma_i = \frac{W}{bc} \quad (3)$$

Where, σ_i represents the impact strength (kJ/m²), w is the power required for the specimen to be destroyed (J), b is the thickness of the sample (mm), and c represents the width of the sample (mm).

5. MOLDED PARTS

Using a photocured SLA-3D printer manufactured by Hong Kong Peopoly Moai, the hyperbranched polysiloxane modified epoxy resin material prepared in this paper was printed and



Figure 12. Resin-based molded parts.

molded. After molding, the surface was smooth, the structure was complete, and there were no obvious defects or residual resin (Figure 12).

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Author Contributions

L.N. led this research. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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