MethacrylPhenyl POSS modified UV-curing materials for three-dimensional printing

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Abstract

Ultraviolet curing three dimensional printing (3DP), as an additive manufacturing technology, possesses relatively higher forming precision and faster forming speed, However, its low mechanical properties limit its applications. In this work, the morphology and properties of epoxy acrylate matrix 3DP materials modified by MethacrylPhenyl polyhedral oligomeric silsesquioxanes (MP-POSS) at different loadings (wt% = 0, 1, 3, 5, 7) were studied. The XRD and FTIR analysis indicated that MP-POSS chemically incorporated into the hybrid materials by copolymerization. The morphological analysis showed that POSS rich particles appeared when POSS loading was 5 wt%, the mean diameter of POSS rich particles increased with the increasing of POSS loadings, and the POSS rich particles agglomerated obviously when POSS loading reached 7 wt%. The tensile strength and the impact strength of the nanocomposites with 5 wt% POSS were increased to 48.9 MPa and 12.8 kJ/m² which were 150.9% and 162.1% compared with the unfilled materials. Analyzed with the SEM images of fracture surfaces, the mechanical properties may depend on the synergistic effect of reactive POSS nanocages and unreactive POSS rich particles. TGA and DTG curves showed the enhancement of the thermal stability of the nanocomposites at the later period of degradation process.

Keywords UV-curing · 3DP materials · Mechanical properties · Microstructure

1 Introduction

Nowadays, three-dimensional printing (3DP) as an additive manufacturing method has become a hot spot in our society. Ultraviolet (UV)-curing 3DP which is based on the process of photo polymerization has the best molding precision and the fast forming speed in the field of 3DP, however, because most of the UV-curing materials are polymers, their poor mechanical and thermal properties restrict their applications in some fields like construction and mechanical industry [1–3].

The epoxy acrylate (EA), with some excellent properties like solvent resistance, good adhesion properties and relatively high mechanical strength, has been one of the most important and extensively used acrylate monomer in UV-curing systems [4]. In the last few years, the incorporation

of nano-fillers has become an effective method to improve the thermal stability and mechanical properties of EA networks [5–7].

Polyhedral oligomeric silsesquioxanes (POSS) is a sort of organic–inorganic hybrid nanomaterial constituted of a shell-core structure with general formula: $R_n(SiO_{1.5})_n$, where n ($n = 8, 10$ or 12) is the number of silicon atoms of the cage and the R is a hydrogen atom or an organic functional group such as alkyl, alkylene, acrylate, hydroxyl, or epoxide unit. These functional groups make it easier to incorporate with polymers or other classes of materials attached with functional groups, and finally improve some properties of composites, such as thermal stability, electrical properties, flame retardant as well as mechanical strength [8, 9]. During the last thirty years, POSS have been used as a novel class of nanofillers for its changeable

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functional groups, well chemical compatibility and unique cage structure [10]. The effect of POSS depends on several factors: whether the POSS is miscible with the polymer, the type of polymer being modified, properties of the POSS, and whether it is chemically bonded in polymer chains [11]. An essential factor in optimizing the properties of a POSS-polymer system is the thermodynamic interaction between the vertex R group and polymer matrix. The degree of dispersion of POSS in the matrix contributes to the level of property modification [12].

Chemical co-polymerization or physical blending are two common ways for POSS cages to be introduced into polymer systems [13]. Traditionally, co-polymerization which is the most common approach used to obtain polymer/POSS nanocomposites. The incorporation of POSS monomer into polymers by this way have better miscibility and other properties [14]. While nanocomposites obtained by physical blending own the advantages of being inexpensive and easy to scale up at industrial level [15].

In this study, in order to improve the dispersion of POSS and make POSS chemically bonded in polymer chains, MP-POSS was introduced into the EA matrix UV-curing 3DP system. The microstructure and morphology of EA/MP-POSS were investigated by FTIR, XRD and SEM. The thermal stability was tested by TGA, the mechanical properties of

the EA/POSS 3DP specimen were investigated employing tensile and impact strength.

2 Experimental procedure

2.1 Materials

Experimental Materials and their resources were shown in Table 1.

2.2 Sample preparation

As shown in Fig. 1, to make the MP-POSS disperse in the liquid UV-curing resin more uniformly, the study took two steps to blend different components together. Firstly, MP-POSS in different proportion was added into the mixture of NVP (as POSS dispersant) and DPGDA with an ultrasonic bath for 1 h. Then EA and DPGDA were added to another beaker. The mixture was vigorously stirred by a magnetic stirring apparatus at 60 °C until it became transparent. Secondly, the above two components were blended by a planetary ball mill at a speed of 400 rpm for 8 h. The final mixture was ultrasonicated for 30 min to remove the air bubbles. The specific formulations were shown in Table 2.

Table 1 Experimental materials

Material	Specification	Source
Epoxy acrylate (EA)	HS9103	Guangdong Tianyi Co
Dipropylene glycol diacrylate (DPGDA)	AgiSyn™2833	Royal DSM
N-Vinyl-2-pyrrolidone (NVP)	MAK706	Shanghai Aladdin Chemicals Co
Photoinitiator 819	Irgacure819	Japanese TCL Co
MP-POSS	MA-0734	Hybrid Plastics
Flatting agent	BYK331	BYK Co
Defoamer	ST108	Dow Corning Co

Fig. 1 Schematic illustration of 3DP samples preparation

Table 2 Formulations of 3DP materials

Sample	EA (wt%)	DPDGA (wt%)	NVP (wt%)	POSS (wt%)	819 (wt%)	assistant (wt%)
#1	40	47	8	0	3	2
#2	40	47	8	1	3	2
#3	40	47	8	3	3	2
#4	40	47	8	5	3	2
#5	40	47	8	7	3	2

200 g prepared uncured 3DP materials with (wt% = 0, 1, 3, 5, 7) MP-POSS filled were put into the LCD resin tank in proper sequence, set the curing layer thickness of 0.05 mm and the exposure time of 6S, the resins were solidified into dumbbell shaped plates and rectangle plates layer by layer under ultraviolet light from the projection area, which were prepared for the subsequent tensile and impact strength test. The curing reaction process of the 3DP materials was shown in Fig. 2.

2.3 Characterizations

2.3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy spectra of MP-POSS, uncured EA/POSS, and EA/POSS nanocomposites were obtained between 4000 and 400 cm^{-1} with a NEXUS670 FTIR spectrometer from Nicolet. Samples were milled into fine powders by a planetary ball mill and doped with KBr.

2.3.2 X-ray diffraction (XRD)

The MP-POSS and the UV-cured samples with (wt% = 0, 1, 3, 5, 7) POSS filled which were milled into powders by a planetary ball mill were scanned at a speed of 4 $^{\circ}\text{C}/\text{min}$ at ambient temperature using an X-ray diffractometer (DX-2600) at a generator voltage of 35 kV and a current of 25 mA and the data were collected from 5 $^{\circ}$ to 45 $^{\circ}$ intervals.

2.3.3 Transmission electron microscope (TEM)

TEM was carried out on a JEM-1200EX microscope at 60 kV. EA/MP-POSS nanocomposites at different loadings were cured by a portable UV curing machine. Then the samples were cut to 70 nm with a Weiyong ultramicrotome.

2.3.4 Scanning electron microscopy (SEM)

Hitach S3400 scanning electron microscopy was used to observe the tensile and impact fracture of POSS filled printing samples. All the samples were coated with thin layers of gold to make the surface conductive.

2.3.5 Tensile strength testing

Tensile tests were carried out according to ASTM D 638 at 25 $^{\circ}\text{C}$. Three printed dumbbell-shaped specimens as a group with thicknesses of 4 mm were tested for different POSS additions, and the average value is reported. The performed tests were conducted on a 5-kN CMT5105 electronic universal testing machine at a crosshead speed of 5 mm/min.

2.3.6 Impact strength testing

The impact resistance of the composites was evaluated on an impact tester machine. According to ASTM D 256, Izod impact tests were performed with an energy level of 0.5 J at room temperature. Five unnotched impact test specimens with dimensions of 80 $\times$ 10 $\times$ 4 mm^3 were examined for each set of nanocomposites.

2.3.7 Thermal gravimetric analysis

The cured specimens with different POSS contents were milled into powders by a planetary. The thermal stability of the powders in nitrogen atmosphere were measured using a NETZSCH Simultaneous TG analyzer (STA449C). Samples (2–5 mg) were loaded in aluminium pans, heated to 600 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}/\text{min}$) with the nitrogen flow rate of 20 ml/min.

Fig. 2 Chemical incorporation of MP-POSS cages into epoxy acrylate chains

3 Results and discussion

3.1 FRIR analysis

Fourier transform infrared spectroscopy (FTIR) is an effective method of investigating specific interactions during polymerization process. Figure 3 showed the FTIR spectra of the MP-POSS, UV-cured and uncured 1% mass MP-POSS modified EA matrix 3DP materials. Before UV-curing, the MP-POSS and uncured EA/POSS can be characterized by the stretching vibration band of carbon-carbon double bonds at 1630 cm^{-1} and the peak of carbon hydrogen bonds linked to carbon-carbon double bonds at 810 cm^{-1} . As can be seen from the curve of cured EA/POSS nanocomposites the carbon-carbon double bonds at 1630 cm^{-1} and 810 cm^{-1} both disappeared. However, the Si-O-Si stretching vibration bond of MP-POSS which is shown at 1100 cm^{-1} can also be found from the curve. These facts indicate that MP-POSS nanocages have chemically incorporated into the hybrid materials and formed across-linked network between MP-POSS and EA [16].

3.2 XRD analysis

The X-ray diffraction (XRD) diagrams of the EA, MP-POSS, and EA/MP-POSS hybrid nanocomposites were shown in Fig. 4. EA showed a typical amorphous pattern with a wide region and maximum intensity at 2θ angles of 20° , MP-POSS exhibited the strongest reflections at 2θ angles of 7.6° , 8.8° , 10.7° , 17.5° , 18.4° , 19.1° , 20.0° and 24.4° . According to the previous works, the sharp and strong peak at $2\theta = 7^\circ$ is a typical peak also belongs to other POSS with

Fig. 3 FTIR spectra of the MP-POSS, uncured and cured EA-1%MP-POSS

Fig. 4 X-ray diffraction diagrams of the EA/MP-POSS nanocomposites

similar architecture, in addition the broad peak at $2\theta = 20^\circ$ is a typical feature peak of Si-O-Si linkages [17, 18]. It can be observed from the curves of EA modified by MP-POSS (wt% = 1, 3, 5, 7), except the green curve, other hybrid materials were completely amorphous and diffraction peaks of MP-POSS have been completely disappeared. The green curve showed a strong peak at 24.4° corresponding to (111) reflection peak of MP-POSS which may be on account of the mass of POSS was beyond the critical point and resulted in the aggregation of MP-POSS. The XRD result indicated that MP-POSS nanocages have chemically incorporated into the hybrid materials and formed a cross-linked network between MP-POSS and EA, which was consistent with the results of FTIR analysis.

3.3 Morphological analysis

The morphology of MP-POSS monomers in the EA matrix was investigated by TEM (Fig. 5). It can be seen from the figure that MP-POSS particles can hardly be observed at 1% MP-POSS addition. When the addition amount was 3%, MP-POSS nanoparticles were uniformly dispersed in the matrix of 3DP materials with a particle size of 30–50 nm. The number and particle size of MP-POSS nanoparticles increased with the increase of MP-POSS addition. The agglomeration of MP-POSS particles occurred when the addition of MP-POSS reached 7%, which was mainly due to the increasing insolubility of MP-POSS in the 3DP resin. According to the like dissolves like theory, the good dispersion of MP-POSS in the EA matrix was mainly depended on the groups at its apex, the phenyl group and methacryloxy

Fig. 5 TEM images of EA/MP-POSS nanocomposites at different loadings. **a** 1%MP-POSS **b** 3%MP-POSS **c** 5%MP-POSS **d** 7%MP-POSS

group were both nonpolar groups which had the similar polarity with the groups of EA and DPGDA.

3.4 Mechanical properties

As shown in Fig. 6, the tensile strength of the nanocomposite increased with the increasing content of MP-POSS, but it acted the opposite when the POSS content was 7 wt%. The addition of 5 wt% POSS to the EA matrix 3DP material increase the tensile strength from 32.4 MPa to

a maximum of 48.9 MPa. The tensile result may depend on the synergistic effect of reactive POSS nanocages and unreactive POSS rich particles. The reactive part can increase the rigidity of polymer chain while the unreactive part can act as nano particle reinforcement which was dependent on the dispersion state and interface binding strength [19, 20].

To further investigate the reinforce mechanisms, the fracture surfaces of the broken specimens after the tensile

Fig. 6 Tensile strength of nanocomposites with different contents of MP-POSS

test were examined with scanning electron microscopy. As shown in Fig. 7, It was observed that the tensile yield tearing appeared on the fracture surface, and with the increase of POSS content, tensile yield tearing became more predominant. When POSS content was 5 wt%, tensile yield tearing disappeared while the broken steps and POSS particles were observed, and when the POSS content was up to 7 wt%, the particle size and the depth of broken steps were significantly increased. Si EDS map of Fig. 6d showed that there was uniform dispersion of POSS at the sub-micrometric level. The phase separation of POSS rich particles with the increase of POSS content has also been reported in other studies [21, 22].

Curing degree is one of the most important factors that affect the strength of UV-curing 3DP materials. As shown in Fig. 8, reactive molecules were EA, DPGDA, reactive POSS which participated in UV-curing reaction, the different micro structure of A, B, C regions directly affect the diffusion of photo-initiator and finally affect the curing behavior of the system. The A region was a homogeneous reaction molecular system, and the photo-initiator molecules can be diffused uniformly, thus ensuring the normal curing reaction. The B region was a relatively dense interface phase, and the photo-initiator molecules are difficult to diffuse, thereby reducing the curing degree. The active molecules in the C region were surrounded by POSS particles, the curing reaction would be subjected to a greater

hindrance effect, therefore the interfacial strength would be obviously lower compared with the B region.

Figure 9 showed the tensile fracture surface after etched by acetone. The 3DP materials were etched by acetone to observe the POSS particles more clearly. It can be appreciated from the micrographs that the discrete spherical POSS-rich particles with the size about 30–50 nm were dispersed in the EA matrix uniformly when the POSS content was 5 wt%, most of the POSS particles were still partially embedded in the EA matrix. However, when the content of the MP-POSS attached 7 wt%, The agglomerations of POSS-rich particles which were completely bared can be clearly observed, which was consistent with the discussion above.

As shown in Fig. 10, acted like the tensile strength, the impact strength of the nanocomposite increased with the increasing content of MP-POSS, it obtained the most dramatic increase in the impact strength with the addition of 5 wt% MP-POSS (from 7.9 to 12.8 kJ/m²), and it demonstrated considerable changes when POSS content arrived 7% which mainly because of the agglomerating of POSS particles. The impact strength was also depended on the synergistic effect of reactive POSS nanocages and unreactive POSS rich particles. POSS nanocages can effectively absorb the energy acting on the polymer chain and share the impact load, while homogeneous POSS particles can branch and deflect cracks by deflection, blocking, or crack bridging to prevent crack propagation [23–25].

The impact fracture surface of the broken specimens were examined with scanning electron microscopy. The fracture surface of neat specimen was rough and some brittle fracture patterns were clearly observed. As shown in Fig. 11b–d, it can be seen that the addition of POSS made the brittle fracture patterns of the 3DP material disappear and produced the dendrimer impact crack, with the increase of the content of POSS, the branching degree and the branching pattern of the impact crack were more obvious. However, as the amount of addition further increased to 7 wt%, the impact pattern became blurred again.

3.5 Thermal gravimetric analysis (TGA)

Figure 12 were the TGA and DTG curves of nanocomposites containing different contents of MP-POSS in nitrogen atmosphere. No significant weight loss below 100 °C was observed in the TGA curves, which indicated that

Fig. 7 SEM images of tensile fracture surface of EA/MP-POSS nanocomposites at different loadings

Fig. 8 Schematic diagram of the dispersion of POSS particles in the EA matrix

Fig. 9 SEM images of the tensile fracture surface etched by acetone

Fig. 10 Impact strength of nanocomposites with different contents of MP-POSS

the samples were completely anhydrous [26]. As can be seen from the Fig. 12 there was obvious weightlessness between 340 and 460 °C, which was mainly caused by polymer chain breakage and polymer thermal decomposition. With the increase of POSS content, although the initial decomposition temperature was slightly turned lower, but the thermal degradation speed was obviously decreased in the late stage of degradation. The spatial chain resistance and interaction with polymer chains caused by the incorporation of POSS nanocages may lead to restrictions on polymer chain mobility during thermal degradation and made a slight increase in thermal stability [27].

In addition, POSS may cause a decrease in the thermal conductivity of the nanocomposite and also hinder the outward diffusion of thermal degradation products. The char yield increased with the increasing POSS content, because of the increased yield of silica and carbon produced by thermal degradation of POSS. Therefore, the higher POSS content lead to the higher the yield.

4 Conclusions

- (1) This paper mainly studies the application of MP-POSS in EA based 3DP system. MP-POSS had good compatibility and dispersibility in the system

under the action of dispersant N-vinylpyrrolidone. The dissolved MP-POSS can participate in the light curing reaction of the system under the action of photo-initiator, and the other components in the system form a network crosslink structure by chemical bonding. When the amount of POSS addition reaches a certain value (about wt% = 3), some POSS can not be fully dissolved in the system. The insoluble part can not participate in the photo polymerization reaction which will be distributed in the form of POSS rich particles in the system and the particle size increased with the increase of the amount of POSS.

- (2) The addition of POSS made the mechanical properties of the EA matrix 3DP material greatly improved. When the amount of POSS is added (wt% = 5), the reinforcing effect of the material was the most obvious. The tensile strength is up to 48.9 MPa and the impact strength reaches 12.8 kJ/m² which were 150.9% and 162.1% respectively compared with the original material. This depended mainly on the synergistic effect of POSS molecules which were incorporated to the polymer chains and the POSS particles in the form of physical blending. When the particle size of POSS particles increases to a certain value, POSS particles will cause the formation of defects in the system to lead to the stress concentration, and increase the brittleness of the material to decrease the strength.
- (3) The addition of POSS greatly changed the tensile and impact fracture morphology of the EA matrix 3DP materials. With the increase of POSS loading, tear patterns and broken steps can be observed gradually on the SEM images of tensile fracture surface, the appearance and deepening of dendritic impact crack were showed on the SEM images of tensile fracture surface. The TGA curves showed that, with the increase of POSS content, although the initial decomposition temperature was slightly turned lower, but the thermal degradation speed was obviously decreased in the late stage of degradation.

Fig. 11 SEM images of impact fracture surface of EA/MP-POSS nanocomposites at different loadings

Fig. 12 TGA and DTG curves of EA/MP-POSS nanocomposites in nitrogen atmosphere

Compliance with ethical standards

Competing interests The authors declare that they have no competing interests

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