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Effect of modified calcium sulphate whiskers on free-radical/cationic hybrid photopolymers for 3D printing

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Abstract

This study presents and evaluates hybrid photopolymers applied to 3D printing. To obtain the hybrid system, epoxy acrylates (EA), epoxy resins and photoinitiators were compounded. As inorganic fillers are traditionally used to improve mechanical properties, calcium sulphate whiskers (CSW) were modified by acryloyl chloride and the effects of the modification on hybrid photopolymers were investigated. The viscosity and volume shrinkage of the hybrid system were also evaluated. Fourier transform infrared measurements showed that hybrid photopolymers had a higher conversion. Meanwhile, the mechanical properties showed that the tensile strength of the cured samples containing 7% modified CSW was increased by 28% compared to that of pure resin. Additionally, the improvement of interface interaction between modified whiskers and hybrid photopolymers was observed by a scanning electron microscope. Dynamic mechanical analysis showed that the hybrid system, with the addition of 7% modified whiskers, exhibited a higher storage modulus and crosslinking density. This work, the first to use modified CSW on 3D printing to enhance the tensile strength of hybrid photopolymers, demonstrates that the photocured samples can contribute to high accuracy and resolution.

1. Introduction

3D printing, also known as additive manufacturing (AM), is a type of rapid prototyping technology which can turn digital objects into physical objects based on specific digital design [1]. AM has become an accepted technology in the manufacturing industry in recent years because of its many advantageous properties, including its ability to achieve complex geometries, satisfy the demands of specific applications, consume lower amounts of energy and reduce waste in the curing process [2–4]. 3D printing has been widely used in the fields of electronic, microfluidics, medicine, biomaterials, MEMS and healthcare [5–11].

Stereolithography (SLA), one of the various 3D printing technologies, is based on the photocuring of liquid resins; it is one of the earliest developed technologies that shows higher accuracy than other technologies [12, 13]. However, several challenges exist in the development of 3D printing, including building speed, printing resolution, and multimaterial parts. Accordingly, the photopolymers used in 3D printing should have the outstanding properties of low viscosity and a high curing rate; additionally, the cured objects should exhibit better mechanical performance, low shrinkage and environmental friendliness [2, 13]. According to the different reaction mechanisms, photopolymerization can be divided into free radical photopolymerization and cationic photopolymerization [14]. Epoxy acrylates (EA) and epoxy resins are free radical resins and cationic resins, respectively, commonly used in the photocuring industry. EA has the advantages of a high curing rate, sufficient toughness and solvent resistance at room temperature; however, EA shows higher volume shrinkage because of its covalent bonds that replace the van der Waals during the curing process [15–18]. Acrylates polymerize via free radical propagation and epoxy resins, that are insensitive to oxygen; they can be ultraviolet (UV)-cured with photoacids via a ring opening pathway [19].

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In photocurable epoxy resins, the photoinitiator decomposes to give reactive intermediate which can abstract hydrogen atoms from a monomer. The mediate can form a Bronsted-acid and the acid propagates the cationic ring opening polymerization. The primary and secondary amines open the ring to form a hydroxyl group. Then, the amines are etherified with epoxy group to form a network [18].

Furthermore, the excellent heat resistance, adhesion and negligible toxicity of epoxy resins differentiates them from other polymers. Thus, it has been universally acknowledged that the hybrid resin system can utilize both the excellent properties of free-radical resin and cationic resin to solve the disadvantages of insufficient curing in the shadow and bottom of objects [4, 20, 21]. Although the incorporation of the two polymers appears to be a sound method to improve the desired properties, the application of pure resin is still limited by its poor mechanical properties. Adding inorganic fillers such as carbon nanotubes, calcium carbonate whisker and nano silica has been an largely successful approach for achieving sufficient properties in photopolymers [22–25]. In particular, it has been acknowledged that calcium sulphate whiskers (CSW) have the advantageous properties of a low cost, non-toxicity, high temperature resistance and high strength. To our knowledge, there are very few studies on the addition of CSW to photopolymers, and its compatibility with the liquid resin remains to be investigated. However, the high surface energy of whiskers results in poor interfacial adhesion between the whiskers and the hybrid resin [26–28]. Thus, the whiskers should be modified to improve the interfacial interactions between the matrix and fillers. Compared to other modification techniques, such as the use of surfactants or coupling agents, physical coatings are more convenient and effective [29]. Natural chitosan (CS) exhibits the properties of non-toxicity and biocompatibility and has reactive amino and abundant hydroxyl groups; thus, CS can be easily dispersed on the whisker surface.

Here, CS-coated whiskers were successfully modified with acryloyl chloride, to improve compatibility between fillers and photopolymers. The double bonds produced by the reaction can participate in the polymerization of the hybrid resin [30, 31]. Fourier transform infrared spectroscopy (FTIR) was conducted to characterize the groups on the surface of whiskers. The viscosity of the photopolymers and the volume shrinkage of hybrid UV-cured objects were investigated. The mechanical performance of the cured photopolymers were tested by dynamic mechanical analysis (DMA) and tensile testing. Thermogravimetric analysis (TGA) was adopted to evaluate the heat resistance of the CS that coats the surface of whiskers. The tensile fractured interfaces were observed by a scanning electron microscope (SEM).

2. Experiments

2.1. Materials
The EA resin was a commercially available product of Fangxin Resin Co., Ltd (China). Tipropylene glycol diacrylate (TPGDA) was provided by Qualipoly Chemical Co., Ltd (China). The aliphatic epoxy resin, H5001, which is highly tough, with an epoxide value of 0.5 was obtained by Chuzhou Huisheng electronic materials Co., Ltd (China). 4-vinyl-1-cyclohexene diepoxide (TT22), purchased from Tetrachem Co., Ltd (China), was used as a cationic monomer. The acryloyl chloride, CS, and N, and N-dimethylacetamide were commercially available products of Sinopharm Chemical Reagent Co., Ltd (China). Additionally, 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO), triaryl thionium salts and phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide (819) were used as photoinitiators in the hybrid systems obtained from Nanjing Jiaozhong Chemical Co., Ltd (China). CSW (average diameter: 1–3 μm) and (CSW") (average diameter: 3–10 μm) were purchased from Guangwei new material Co., Ltd (China).

2.2. Preparation
2.2.1. Comparison of different whisker sizes
Different sizes of whiskers were added to the hybrid photopolymers (4%, 7%, and 10%) to test the tensile strength and shrinkage of the photocured samples. The comparisons are shown in figure 1. It was apparent that the tensile strength and shrinkage of the samples involving CSW (average diameter: 1–3 μm) was higher than that involving CSW" (average diameter: 3–10 μm). Therefore, it was concluded that CSW (average diameter: 1–3 μm) was the optimal candidate.

2.2.2. Organic modification of CSW
The modified whiskers were prepared as follows: 1 g, 3 g and 5 g of CS was dissolved in a beaker containing 1,000 ml of acetic acid solution (5% w/v acetic acid), respectively. After stirring for 20 min, 5 g CSW was soaked into the solution of CS and stirred for 4 h at room temperature. The C-CSW was obtained by suction filtration and washed with alcohol. The filtered C-CSW was dried in the oven for 8 h. Finally, C-CSW was dissolved in 50 ml of dimethylacetamide solution, adding a determined quantity of triethylamine and acryloyl chloride depending on the content of CS coated on the surface of the whiskers. The mixed solution was stirred under a...
magnetic stirrer for 12 h; then, the modified CSW was obtained by a filter and dried in a vacuum oven for 8 h at 80 °C to remove excess water. These modified whiskers were named M-1-CSW, M-3-CSW and M-5-CSW, respectively. The production process of modified C-CSW (M-C-CSW) can be seen in scheme 1 and the samples with related acronyms in table 1.

2.2.3. Preparation of photopolymer
The hybrid photopolymer was formed from free radical resin (TPGDA:EA 1:1) and cationic resin (HS001:TT22 1:1) with a ratio of 4:1; TPO (1.5%) and triaryl thionium salts (2%) were selected as the free-radical photoinitiator and cationic photoinitiator, respectively. 819 (2%), added as a photosensitizer, resulted in UV–vis absorption of the photoinitiator shifting from 365 to 405 nm and made the blend suitable for a near-visible (405 nm) stereolithograph [28]. Then a certain amount of modified CSW was dispersed evenly by mechanical stirring and ultrasonic dispersing. The reinforcement mechanism of the whiskers is shown in scheme 2.

2.2.4. Samples preparation
A series of the hybrid photopolymer was prepared by adding different concentrations of M-C-CSW (1%, 4%, 7%, 10% and 15%). The composites of resins and whiskers were cured in a desktop SLA 3D printer with a wavelength of 405 nm (Peaking Dazzle-3D Tech Co., Ltd); the scanning speed of the laser was 2 m min⁻¹; the irradiation of the laser was 100 m W cm⁻². The model of the 3D printer is shown in figure 2. All cured samples

Table 1. Samples with related acronyms.

| Acronyms | Full name |
|----------|-----------|
| CSW      | calcium sulphate whiskers (diameter: 1–3 μm) |
| CSW‘     | calcium sulphate whiskers (diameter: 3–10 μm) |
| CS       | chitosan |
| EA       | epoxy acrylates |
| C-CSW    | chitosan coated calcium sulfate whiskers |
| M-C-CSW  | modified chitosan coated calcium sulfate whiskers |

Figure 1. Comparison of (a) tensile strength and (b) shrinkage rate with different whisker sizes.

Scheme 1. Synthetic route of modified chitosan-coated calcium sulphate whiskers (M-C-CSW).
were clamped by glass plates and post-cured at 80 °C for 1 h to remove internal stress. After cooling to room temperature, the testing samples were obtained.

2.3. Measurements and characterization

FTIR measurements of modified CSW were performed by a Nexus670 FTIR spectrometer (Nicolet, New York, USA). The powders of CSW were pressed into a pellet with a thickness of 2 mm, under 30 MPa pressure. Five different drops of deionized water were then dropped on the thin pellet, and the average value of five measurements was calculated as the water contact angle (WCA). Thermogravimetric analysis (TGA) of the different content of the modified C-CSW (M-1-CSW, M-3-CSW, M-5-CSW) were performed by a synchronous thermal analyzer (STA449 F3, Netzsch, Germany) at a heating rate of 10 °C min⁻¹ to 800 °C under air atmosphere. The viscosity of the hybrid photopolymer was tested from 15–60 °C by the rotatory viscometer (NDJ-79) (with a rate of 50 HZ and rotating speeds of 750 r/min, 75 r/min, and 7.5 r/min for M-1-CSW, M-3-CSW and M-5-CSW, respectively) to determine the optimum concentration of CSW. Mechanical properties of the samples were considered with the WZL-300B horizontal computer tensile tester according to ISO 527. The dumbbell-shaped samples were made by the 3D printer to test tensile strength, and the strain rate set to 50 mm min⁻¹. Five measurements were conducted for every sample. SEM was performed through a JSM-6510 SEM (JEOL Ltd, Tokyo, Japan) to observe the fracture surfaces of the specimens after tensile test; all fracture surfaces were coated with a thin gold layer. DMA was performed with a rotational rheometer (MCR302, Anton Paar China) from 25–120 °C at a heating rate of 3 °C min⁻¹. Shrinkage was calculated through the density of liquid resin (ρ₁) and that of the cured solid (ρ₂) by equation (1).
Shrinkage(%) = \frac{\rho_2 - \rho_1}{\rho_2} \times 100\%  \quad (1)

Real-time monitoring was performed to investigate the conversion of double bonds and epoxy groups. The liquid resin was coated on the KBr flake to form a film with a thickness of 25 \( \mu \text{m} \). During the curing process, the \textit{in situ} infrared spectra were recorded from 0–240 s.

### 3. Results and discussion

#### 3.1. Modification of CSW

Figure 2 illustrates the FTIR spectra of CS, CSW and M-C-CSW; the obvious peak at 1,622 cm\(^{-1}\) was assigned to the absorption bends of \(-\text{OH}\) from the surface of the CSW. The other obvious peak at 1,529 cm\(^{-1}\) corresponds to the characteristic absorption bends of double bonds, and can be attributed to the success of the acryloyl chloride modified C-CSW. A new peak was observed at 1,381 cm\(^{-1}\), due to the bending vibration of C–H on the surface of the CS.

The water contact angles (WCA) on the CSW, C-CSW and M-C-CSW powder samples were measured to study the extent of the hydrophobic character of the surface and the properties of fillers with the resin matrix. The WCA of pure CSW without any modifications was found to be 11.1\(^{\circ}\) (figure 3(a)); this indicates that the CSW was hydrophilic and the compatibility with resin was poor. As seen in figures 3(b) and (c), the WCA of C-CSW and M-C-CSW reached 33.5\(^{\circ}\) and 72.3\(^{\circ}\) respectively. The amino group and hydroxyl group on the surface of CS are polar groups, and are easily soluble in water. However, when acryloyl chloride reacted with the polar groups on the surface of the CS, the modified whiskers were hydrophobic. The change in WCA indicated that the M-C-CSW was successfully modified so as to exhibit a hydrophobic character, and the affinity with the resin matrix also increased\[29, 30\].

Figures 4(a) and (b) show the curves of TGA and their first derivative of the TGA curves (DTG) for different contents of chitosan (CS) coated on the surface of the calcium sulphate whiskers (CSW).

![Figure 3](image1.png)  
\(\theta=11.1\pm0.8^{\circ}\)  
\(\theta=33.5\pm1.2^{\circ}\)  
\(\theta=72.3\pm1.1^{\circ}\)

**Figure 3.** Water contact angles of (a) calcium sulphate whiskers (CSW), (b) chitosan-coated (C)-CSW and (c) modified (M)-C-CSW.

![Figure 4](image2.png)  
(a) Thermogravimetric (TG) analysis (conducted in air) and (b) first derivative of the TGA curves (DTG) for different contents of chitosan (CS) coated on the surface of the calcium sulphate whiskers (CSW).

![Figure 4](image3.png)  
(a) Thermogravimetric (TG) analysis (conducted in air) and (b) first derivative of the TGA curves (DTG) for different contents of chitosan (CS) coated on the surface of the calcium sulphate whiskers (CSW).
used to test the heat resistance of the different modified whiskers at different temperatures. Therefore, the more CS was coated on the CSW, the higher the heat resistance should be. Ultimately, these results demonstrated that CSW was successfully modified. Regarding the tensile strength and elongation at break of specimens containing different concentration of CS (Figure 5), the tensile strength of M-5-CSW reached a maximum value of 27.46 MPa; thus, it was concluded that M-5-CSW was the optimal candidate.

### 3.2. Hybrid photopolymers for 3D printing

UV-initiated hybrid polymers should have apparent viscosity, to satisfy the requirements of high printing resolution [32–34]. Different amounts of modified CSW were added to the hybrid resin, and the viscosity was measured from 15–60 °C to select the optimum addition. As shown in figure 6, the viscosity of the photopolymer composites gradually increased as the amount of modified whiskers increased. With 15% of M-C-CSW, the viscosity at 15 °C and 60 °C was 1270 mPa s and 53 mPa s, respectively, indicating that temperature has a great influence on viscosity. Thus, by changing the temperature, the viscosity can be adjusted to satisfy different printing requirements; the effect of CSW on viscosity is smaller than that of other inorganic fillers [31].

Upon photopolymerization, resin composites cause volume shrinkage and shrinkage stress, which leads to the warpage of the cured samples and affects the precision of the final objects. The main reason for the volume shrinkage was that the van der Waals bond became a covalent bond. Adding whiskers to the hybrid resin system was an effective method to reduce the volume shrinkage. Figure 7(a) shows the effect of hybrid resin on volume shrinkage according to different whisker content in the system. As whisker content increases, the shrinkage
volume of the cured resin decreased. The volume shrinkage of composites with M-C-CSW was significantly lower than that of CSW; the amino groups along the CS, which reacted with the epoxy resin, may lead to volume expansion of the photocurable resin \[35–38\]. When the addition amount was 15%, the volume shrinkage of the photocurable resin, CSW and M-C-CSW, was reduced by 11.3% and 11.6%, respectively, compared to pure resin. However, excessive whiskers can cause sedimentation during printing, which damages the structure of printed objects and does not satisfy the requirements of 3D printing. Figure 7(b) shows the test of volume shrinkage of the same batch of specimens after two months. At a very high loading (15%) of whiskers, the volume shrinkage after 2 months was 3.73%, which is 44% less than that of M-C-CSW, because the curing speed of epoxy resin is slow, and the reaction still occurs after prolonged exposure. Consequently, the hybrid system combined the respective advantages and demonstrated sufficient synergy effects on volume shrinkage of free-radical resin and cationic resin.

The function groups of the hybrid system were monitored by FTIR measurements. The conversion of epoxy groups was low, wherein attaining 100% was difficult. Therefore, here, the absorption peak at 1,723 cm\(^{-1}\) of C=O was selected as the internal standard. The absorption peaks at 1,636 cm\(^{-1}\) and 985 cm\(^{-1}\) of double bonds and epoxy groups of photopolymers were used to calculate the conversions (equations (2) and (3)) \[39\].

\[
x_C = \frac{A_{\lambda_{1636}}}{A_{\lambda_{1723}}} - \frac{A'_{\lambda_{1636}}}{A'_{\lambda_{1723}}} \times 100\%  \tag{2}
\]

\[
x_e = \frac{A_{\lambda_{985}}}{A_{\lambda_{1723}}} \times 100\%  \tag{3}
\]

\(A_{\lambda_{1636}}, A'_{\lambda_{1723}}, A_{\lambda_{985}}\) refer to the corresponding peaks before the samples are photocured; \(A'_{\lambda_{1636}}, A'_{\lambda_{1723}}\) and \(A'_{\lambda_{985}}\) are the corresponding peaks of samples which are partially cured; \(A_{\lambda_{1636}}, A'_{\lambda_{1723}}, A_{\lambda_{985}}\) refer to the corresponding peaks of samples which are fully cured. Figure 8(b) shows the determined relative conversions of C=C and epoxy groups of the hybrid photopolymers with the addition of 7% CSW and 7% M-C-CSW photopolymers. In general, the conversion of C=C was significantly higher than that of epoxy groups, indicating that the radical component curing rate and the degree of reaction were higher than the cationic component during the curing process. As shown in figure 8(b), in the first 50 s, the conversion rate of C=C and epoxy groups reached 80% and 78%, respectively. However, after 170 s, some double bonds were quickly consumed under UV light, and the conversion tended to be stable.

Figures 8(c) and (d) show the conversions of C=C and epoxy groups in hybrid photopolymers (pure resin and M-C-CSW addition of 4%, 7% and 10%). In the early stage of the reaction, the addition of whiskers quickly promoted photopolymerization. The trend of the conversion of C=C and epoxy groups was generally 4% > 7% > 10%, of whiskers addition, in the range of 40–240 s. The main reason for this is as follows: as the whisker content increased, the barrier to polymerization increased. The viscosity of the system also increased with the exposure time, such that the bonding probability of double bonds became weak, leading to a steady trend in the conversion. Meanwhile, the excessive addition of whiskers led to light shielding and the final conversion rate of the hybrid system was slow. Combining this with the results in figure 6, it can be seen that the
conversion of C=C influenced the volume shrinkage rate; the higher the conversion rate of C=C, the higher the shrinkage rate [38]. A 100% conversion rate of C=C and epoxy occurred at 180 and 220 s, respectively.

In conclusion, these results indicate that an appropriate amount of whiskers can promote the reaction rate and conversion of photocurable resin. Although the polymerization rates of free radicals and cationic photopolymers were different, the radical polymerization in the hybrid photopolymer can promote the polymerization of the cationic moiety [38]. Compared to other photopolymers applied to 3D printing, the photocuring rate of the hybrid composite was determined to be suitable for printing.

3.3. Mechanical properties of the photopolymers

The crosslink density $X_{LD}$ can be calculated by equation (4), where $R$ is the universal gas constant $8.3145 \text{ J mol}^{-1}\text{K}^{-1}$ and $T$ is the Kelvin temperature [40].

$$X_{LD} = \frac{E'}{3RT}$$

DMA was conducted to evaluate the effects of modified whiskers on the hybrid photopolymers. The changes in the storage modulus ($E'$ at 25 °C, $E'$ at $T_g + 50$ °C) and loss factor ($\tan \delta$) of the photopolymer are shown in figure 10. Various whiskers, as a function of temperature, and most dynamic mechanical properties are summarized in table 2. It can be seen from figure 9(a) and table 1 that the $T_g$ value of the photocurable resin with 7% M-C-CSW is lower than that of the pure resin, but higher than that of resin with 7% CSW throughout the entire investigated temperature range. At the same time, the storage modulus of 7% M-C-CSW composites reached the maximum value of 1,018 MPa at 25 °C and the composites had the largest crosslink density up to $8.93 \times 10^3$ mol m$^{-3}$. This is attributed to the following: the addition of whiskers reduced the molecular weight of the hybrid photopolymer system, such that the $T_g$ value was slightly lower than that of pure resin. Additionally, the surface of the M-C-CSW had a large number of C=C, leading to the production of crosslinking points such that the storage modulus improved.

Figure 8. (a) Real time Fourier Transform Infrared (FTIR) spectar of pure resin; (b) C=C and epoxy groups conversion of photopolymers containing 7% calcium sulphate whiskers (CSW) and 7% modified (M)-chitosan-coated (C)-CSW; (c,d) comparison of fillers with different content.
The DMA of the photocurable samples with different content of M-C-CSW were also compared (Figure 9(b) and Table 2). It can be seen that when the concentration of M-C-CSW was 7%, the storage modulus reached the largest value, due to the increase of the crosslink density (XLD). The storage modulus of the pure resin, of composites with 4% M-C-CSW and of composites with 10% M-C-CSW was reduced to a minimum value at 85 °C. However, when the addition of M-C-CSW was 7%, the storage modulus began to drop to a minimum at 95 °C. There was no significant difference in the Tg value between pure resin and composites with 4% M-C-CSW. Contrastingly, when the ratio was increased to 10%, the crosslink density was significantly reduced to $6.41 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, and the Tg of the system also decreased to 50 °C. Therefore, the Tg value depends on the crosslink density; the higher crosslink density, the larger the Tg value [18]. Addition of whiskers can expand the free volume of the composites, leading to an increase in the movement of the polymer chain, such that as the content increases, the glass transition temperature decreases [23, 38]. This indicates that the presence of 7% M-C-CSW led to a higher thermal ability and a larger photocuring degree; thus, these results all prove that the optimum content of M-C-CSW is 7% M-C-CSW.

As depicted in Figure 10(a), as the whiskers content increases, the tensile strength first increases and then decreases; it reaches a maximum value of 27.81 MPa with the content of 7% M-C-CSW. Meanwhile, the elongation at break was measured to be 12.5% in this case, with an improvement of 28% and 20% compared to the blank sample, respectively. With the addition of whiskers, the stress was transmitted from the substrate to the whisker, and the matrix dispersed most of the stress during tensile fracture. The tensile strength of the cured specimens with M-C-CSW was significantly higher than that of specimens containing CSW. These results demonstrated that C=C on the surface of the M-C-CSW participated in the reaction of the photopolymerization, such that the interfacial interaction between photopolymers and M-C-CSW was stronger than that between photopolymers and CSW. However, at the very high loading of 15%, the tensile strength dropped to 26.63 MPa, and the elongation at break decreased to 9%. Referring to Table 2, 15% M-C-CSW had a low crosslink density. It is thus noted that the mechanical properties often depend on the crosslink density of hybrid composites [41]. Thus, as the whisker content increases, the crosslink density decreases, which negatively influenced the mechanical properties.

Figure 11 presents the SEM images of the fracture surface of pure resin, CSW composites and M-C-CSW composites. As shown in Figure 11(a), the fracture surface was smooth and flat, indicating poor mechanical properties of the pure resin. It was observed that CSW tended to aggregate together, wherein the fracture surface was relatively smooth in (figure 11(b)); CSW have a large surface energy, limiting the compatibility of the whiskers with the matrix. In figure 11(c), it can be seen that the M-C-CSW were firmly combined with the resin matrix and the micro-fracture morphology was more complicated than that in figure 11(b). The specific surface

### Table 2. Dynamic mechanical analysis (DMA) of pure resin and different content of whiskers/photopolymers.

| Sample        | $T_g$ (°C) | $E'$ at 25 °C (MPa) | $E'$ at $T_g + 50$ °C (MPa) | $X_{LD}$ (× $10^3 \text{ mol} \cdot \text{m}^{-3}$) |
|---------------|------------|--------------------|-----------------------------|-----------------------------------------------|
| Pure resin    | 52.3       | 944.23             | 65.7                        | 7.02                                          |
| 7%CSW         | 49.9       | 821.21             | 63.2                        | 6.80                                          |
| 4% M-C-CSW    | 51.3       | 805.03             | 64.4                        | 6.90                                          |
| 7% M-C-CSW    | 51         | 1018               | 83.3                        | 8.93                                          |
| 10%M-C-CSW    | 50         | 835.21             | 59.6                        | 6.41                                          |

Figure 9. Dynamic mechanical analysis (DMA) curves of Pure resin, calcium sulphate whiskers (CSW)/photopolymers and calcium sulphate whiskers (M-C-CSW)/photopolymers.

The DMA of the photocurable samples with different content of M-C-CSW were also compared (Figure 9(b) and Table 2). It can be seen that when the concentration of M-C-CSW was 7%, the storage modulus reached the largest value, due to the increase of the crosslink density ($X_{LD}$). The storage modulus of the pure resin, of composites with 4% M-C-CSW and of composites with 10% M-C-CSW was reduced to a minimum value at 85 °C. However, when the addition of M-C-CSW was 7%, the storage modulus began to drop to a minimum at 95 °C. There was no significant difference in the $T_g$ value between pure resin and composites with 4% M-C-CSW. Contrastingly, when the ratio was increased to 10%, the crosslink density was significantly reduced to $6.41 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, and the $T_g$ of the system also decreased to 50 °C. Therefore, the $T_g$ value depends on the crosslink density; the higher crosslink density, the larger the $T_g$ value [18]. Addition of whiskers can expand the free volume of the composites, leading to an increase in the movement of the polymer chain, such that as the content increases, the glass transition temperature decreases [23, 38]. This indicates that the presence of 7% M-C-CSW led to a higher thermal ability and a larger photocuring degree; thus, these results all prove that the optimum content of M-C-CSW is 7% M-C-CSW.
Figure 10. (a) Tensile strength and (b) Elongation at break of specimens cured by a self-made model containing different concentration of whiskers.

Figure 11. Scanning electron micrographs of tensile fracture surface of (a) pure resin, (b), (d) photopolymers containing unmodified calcium sulphate whiskers (CSW) (b) and (c), (e) modified-CSW.
area produced by microcracks and the energy absorbed by the material were large, thus enhancing the macroscopic mechanical properties of the matrix. The different effects of adding CSW and M-C-CSW on the matrix resin can also be seen in figures 11(d) and (e). In figure 11(d), it can be seen that a high density of pores was formed between the whiskers and the resin matrix, such that the interface could be easily distinguished.

The appearance of ‘pores’ is attributed to the unmodified whiskers’ poor compatibility with the resin matrix. When the tensile fracture occurred, the whiskers were directly fractured and pulled out. Contrastingly, the M-C-CSW was homogenously distributed in the matrix and few pores can be found in figure 11(e). In conclusion, when the tensile fracture occurred, the whiskers resisted the stress concentration generated at the crack tip and consumed a certain amount of energy. As the interface compatibility between the resin matrix and whiskers increased, the mechanical properties of the cured specimens improved.

4. Conclusions

Here, a type of CSW coated with CS was effectively modified by acryloyl chloride. It was shown that C=C on the CSW surface can participate in photopolymerization, resulting in a significant improvement of interface adhesion and the mechanical properties of the composites. The free-radical/cationic hybrid photopolymers were compounded with epoxy acrylate resin, epoxy resin and modified whiskers. The increasing crosslink density caused an increase in mechanical properties. Experimental results demonstrated that the tensile strength of the sample with 7% M-C-CSW reached a maximum value of 27.81 MPa, exhibiting an increase of 28% compared to that of the control sample. The volume shrinkage of the cured composites with 15% M-C-CSW was 6.78%, a reduction of 11.6% compared to that of pure resin. After two months, the volume shrinkage of the same batch of specimens was 44% lower than that of the control sample. Additionally, the high thermal stability of the cured samples containing 7% M-C-CSW was demonstrated by TG and DTA measurements. SEM images showed the mechanism of reinforcement ability for whiskers. FTIR measurements showed that the hybrid photopolymers had a high conversion rate, and that an appropriate amount of whiskers can promote the curing speed of photocurable resin. Therefore, with their sufficient mechanical properties, fast curing rates and high final conversions, the free-radical/cationic hybrid photopolymers can effectively be used for 3D printing.

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