Efficient intrinsic self-healing epoxy acrylate formed from host-guest chemistry

Zhen Hu[a,*], Yingying Liu[a], Xirong Xu[a], Weihao Yuan[a], Lei Yang[a], Qian Shao[b], Zhanhu Guo[d,**], Tao Ding[c,***], Yudong Huang[a,****]

[a] School of Chemistry and Chemical Engineering, MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, Harbin Institute of Technology, Harbin, 150001, China
[b] College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China
[c] College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, China
[d] Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37996, USA

HIGHLIGHTS

- Host-guest chemistry is introduced to the crosslinking points of epoxy acrylate to fabricate intrinsic self-healing polymer.
- The host-guest strategy and UV curing technology endow the epoxy acrylate excellent self-healing and mechanical properties.
- The present strategy can be used to modify the main chain and cross-linking structures of various polymers.

ARTICLE INFO

ABSTRACT

As epoxy resins have been widely applied in advanced composites, the self-healing performances are urgently needed to improve the service reliability and extend service time. In the present study, host-guest chemistry is directly introduced into the crosslinking structure of epoxy acrylate for the first time to endow the composite with self-healing behaviors. In order to implement the above strategy, a β-CD/azobenzene inclusion complex (6-GMA-β-CD/AAAB) containing double C=C bonds is designed and synthesized. By facile ultraviolet (UV) curing process, the epoxy acrylate is crosslinked by 6-GMA-β-CD/AAAB complex via free radical copolymerization. Benefited from the advantage of the reversible dynamic host-guest interactions, the obtained epoxy films exhibit excellent self-healing and mechanical properties. In the present work, the tensile strength of a damaged sample (SHE-5) is restored to 63.3% (9.37 MPa) of the original values (14.80 MPa) under moderate heating stimulus. The present host-guest strategy offers a paradigm toward the practical applications of smart thermosetting composites in engineering.

1. Introduction

Owing to the excellent mechanical properties, chemical resistance and thermal stability, epoxy is considered to be the most widely applied resin matrix in advanced composites [1,2]. During the service period, epoxy matrix composites are usually exposed to extreme conditions (ultraviolet, atom oxygen, ect), which would cause micro damages deep inside the composites. To repair these indetectable cracks, the integration of self-healing ability to the composites has been considered

to be challenging and important strategy to prolong their lifetime [3–6].

There are two main processes to endow the epoxy composites with self-healing ability: intrinsic or extrinsic. The extrinsic self-healing incorporates capsules [7–10] or vascular systems [11,12] into the epoxy matrix. The external force caused cracks would break the microcontainers, leading the release and following polymerization of the healing agents in the damage site. As the healing agents will eventually run out, the extrinsic self-healing can be only achieved for limited

times. To accomplish repeatable self-healing, reversible dynamic bonds are introduced into the epoxy. During the last decade, researchers have done pioneering works and introduced several dynamic bonds to epoxy, including Diels-Alder bond [13–17], ester exchange [18–20] and disulfide exchange [21,22]. Different from extrinsic autonomous self-healing, the intrinsic strategy relies on external stimuli to trigger the recombination of the cross-linking structure in the damage sites.

Noncovalent reversible interactions can spontaneously occur under mild stimulus, which play important roles in the construction of supermolecules as well as self-healing composites [23–26]. Host-guest interactions, the most typical supramolecular binding, can automatically form highly selective recognition between host and guest moieties. This amazing property gives us inspiration for the fabrication of high efficient self-healing composites [27–29]. In fact, several types of self-healing polymers have been prepared via host-guest chemistry, including poly (acrylic acid) [30], polyethylene glycol [31], polyethylenimine [32], poly (glycidyl methacrylate) [33], etc. However, the host-guest chemistry based self-healing polymers mainly focus on the hydrogels with low mechanical strength. Efforts should be focused on the fabrication of self-healing thermosetting resin with superior mechanical strength to meet the requirement of advanced applications. Owing to their ease of functionalization and low cost, cyclodextrins (CDs) are usually applied as host molecular to form networks in the preparation of self-healing materials. The mechanical properties, stimuli-responsive performances, as well as self-healing behaviors of the materials can be tailored by an appropriate selection of specific guests [34–38]. Previous researches have shown that the association constant (K_a) of azobenzene (Azo) with β-CD is ~10000 M^{-1} [39]. This relatively strong inclusion effects will lead to excellent healing effects. More interesting, it is well known that Azo can be reversibly included and excluded by the cavity of β-CD under UV–vis stimulation, which could be used to construct light responsive 3D networks in thermosetting polymers. For intrinsic self-healing epoxy, besides the reversible dynamic bonds, polymer chains should also have sufficient mobility to flow into the damage sites for forming new crosslinking structures [40]. Benefit from the light responsive behaviors of β-CD/Azo inclusion complex, UV light can be used to de-crosslink the epoxy 3D networks. This process increases the content of combinable host-guest pairs and the polymer chain motilities at the crack sites, which greatly satisfies the requirements to achieve effective self-healing [41,42]. In fact, host-guest self-healing epoxy resin has been fabricated using CD/graphene as macro-cross-linker in our previous works [43]. However, the host moieties (CDs) anchored on the graphene could not move freely and were not covalently linked to the polymer chains of epoxy resin. Due to the steric hindrance of graphene, the re-binding of host and guest may be hindered and the self-healing properties of the resin would be affected. In order to systematically study self-healing epoxy resin based on host-guest chemistry, it is necessary to carry out further research.

In this work, self-healable epoxy acrylate driven by supramolecular complexation of Azo and β-CD is designed and fabricated. Vinyl CDs (6-GMA-β-CD), using as host moieties, can form stable inclusion complex with acrylamido azobenzene (AAAB). This bifunctional complex can be incorporated into the epoxy crosslinking structure via copolymerization as the healable element. Benefit from the strong, reversible and light-responsive host-guest bindings, the 6-GMA-β-CD/AAAB complex crosslinkers can "turned on" or "off" the epoxy 3D networks, endowing the resin with excellent intrinsic self-healing properties as well as mechanical performances.

2. Experimental section

2.1. Materials

The bisphenol A epoxy diacrylate (M_n: 452; viscosity: 15000–25000 mPa s) and the 1-hydroxycyclohexyl phenyl ketone (photoinitiator184, λ_{ex} = ~330 nm) were supplied by Lihou Guangzhou Trade Company Limited. The *p*-toluenesulfonyl chloride and β-cyclodextrin were purchased from Energy Chemical Technology Co., Ltd. Ethylenediamine, glycidyl methacrylate, *p*-aminoazobenzene, acryloyl chloride and other conventional reagents were obtained from Aladdin Reagent Company Limited.

2.2. Synthesis of acrylamido-azobenzene (AAAB)

Acryloyl chloride (0.8 mL) was slowly added under stirring to *p*-aminoazobenzene (1.97 g) in benzene (20 mL) at 20 °C. The above mixture was refluxed at 60 °C for 3 h. After the reaction, the solution was filtered and dried. The obtained solid was washed with pure water and recrystallized by ethanol twice to yield AAAB powder (Yield: 56.3%). FTIR: 985, 1555, 1600, 1670, 3070, 3135, 3200, 3280 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.96, 7.75, 7.51, 6.50, 5.81–6.32 ppm. ^{13}C NMR (100 MHz, CDCl$_3$, δ): 163.5, 152.7, 149.3, 140.3, 130.8, 129.0, 124.1, 122.8, 128.6, 120.1 ppm. ESI-MS *m/z*: 252.32 for [M + H] $^+$. The detailed spectra were presented in Fig. S1.

2.3. Synthesis of amino β-CD (6-EDA-β-CD)

The toluenesulfonyl chloride (*p*-TsCl) modified β-CD (6-OTs-β-CD) was successfully prepared according the route described in Ref. [36]. The characterization spectra were presented in Fig. S2. Then, the 6-OTs-β-CD (5.0 g) was added into ethylenediamine (30 mL, EDA). The solution was reacted at 75 °C with stirring for 4 h. The solution was cooled and added into acetone to obtain white precipitate. The above precipitate was redissolved in a mixed solvent of CH$_3$OH and water (volume ratio = 1:3), which was precipitated with acetone to give the 6-EDA-β-CD (Yield: 67.9%) as white solid. FTIR: 580, 941, 1031, 1154, 1663, 2926, 3365 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 2.66–2.82 (CH$_2$ of EDA moieties), 3.32–3.64 (H-2 ~ H-6 of β-CD), 4.43 (OH-6 of β-CD), 4.83 (H-1 of β-CD), 5.68 (OH-2 and OH-3 of β-CD) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, δ): 41.3, 50.8 (C of EDA moieties), 60.7 (C-6 of β-CD), 72.0–73.5 (C-2, C-3 of β-CD), 82.5 (C-4 of β-CD), 102.2 (C-1 of β-CD), ppm. ESI-MS *m/z*: 1163.12 for [M + H] $^+$. The detailed spectra were presented in Fig. S3.

2.4. Preparation of inclusion complex 6-GMA-β-CD/AAAB

A mixture of 1.0 equivalent 6-EDA-β-CD, 1.5 equivalent of glycidyl methacrylate (GMA), a small amount of hydroquinone, and dimethylformamide (DMF, 60 mL) was added into a 200 mL round-bottomed flask. The reaction was proceeding for 6 h at 60 °C before being cooled to 20 °C. The raw product was precipitated from DMF after adding 200 mL acetone. The obtained solid was washed with acetone for 3 times, and 6-GMA-β-CD (Yield: 71.3%) was obtained after drying in vacuum. FTIR: 586, 941, 1038, 1160, 1405, 1560, 1712, 2930, 3358 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.77–1.88 (CH$_3$ of GMA moieties), 2.54–2.82 (CH$_2$ of EDA and GMA moieties), 3.32–3.64 (H-2 ~ H-6 of β-CD), 4.45 (OH-6 of β-CD), 4.82 (H-1 of β-CD), 5.64 (OH-2 and OH-3 of β-CD), 5.86–6.05 (CH$_2$ of GMA moieties) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, δ): 16.7 (C of CH$_3$), 44.5, 45.8 (C of CH$_2$), 60.1 (C-6 of β-CD), 68.9 (C of CH–OH), 73.1–74.8 (C-2, C-3 of β-CD), 82.4 (C-4 of β-CD), 102.9 (C-1 of β-CD), 123.5, 135.2 (C of C=C), 159.6, 161.8 (C of C=O). ESI-MS *m/z*: 1305.66 for [M + H] $^+$. The detailed spectra were presented in Fig. S4.

The 6-GMA-β-CD (1326 mg, 1 mmol) and AAAB (252 mg, 1 mmol) were dissolved in DMF (100 mL). The above solution was placed in dark with moderate stirring for 1 day. Then, the solution was dried in vacuum to get inclusion complex 6-GMA-β-CD/AAAB.

2.5. Preparation of self-healable epoxy acrylate films

Butyl acrylate (4.0 g, 4.49 mL) and a certain proportion of 6-GMA-β-CD/AAAB complex were mixed with epoxy acrylate (6.0 g) under

stirring for 30 min. Then, the photoinitiator184 (0.4 g) was added into the viscous mixture solution. The epoxy acrylate films were prepared by blade-casting and 20 min UV curing process at 20 °C (Light source: 500 W high-voltage mercury lamp).

2.6. Characterization

The chemical structures of the synthesized compounds in the present study were characterized by Fourier transform infrared spectra (FT-IR, Bruker, Tensor 27), ultravioletvisible spectra (UV–vis, Beijing Purkinje General Instrument Co., Ltd), ^{1}H NMR and ^{13}C NMR (Bruker, AVF400, 400 MHz), and mass spectra (Fisons Platform spectrometer with electrospray ionization). The structure and morphology of the epoxy acrylate films were detected by FT-IR and scanning electron microscope (SEM, S-4800, Hitachi Instrument).

The thermal properties of epoxy acrylate films were analyzed by thermogravimetric analyzer (TGA, Netzsch STA449C) and dynamic mechanical analysis (DMA, 01Db-metravib-DMA25 apparatus). Instron Universal Testing Machine (Model 4302) was used to determine the mechanical performances of the samples with a cross-head speed of 1 mm/min. To characterize the self-healing behaviors, a razor blade was used to cause damage to the films. The damaged films were irradiated by UV light (hand-held ultraviolet lamp, 40 W, λ = 365 nm) before the self-healing process, which would disconnect the light sensitive host-guest interactions between AAAB and 6-GMA-β-CD. Subsequently, self-healing was triggered by elevating the temperature to 120 °C in dark to recombine the crosslinking structure. An optical microscope equipped with a digital camera (Meiji Techno Co., Ltd, Japan) was used to get the visual images of the damage sites.

3. Results and discussion

Fig. 1 shows the preparation process of the self-healable epoxy acrylate by using host-guest chemistry. Both of the 6-GMA-β-CD and AAAB contain C=C unsaturated bonds, which are necessary for the radical copolymerization during the curing process. Prior to UV curing, guest monomers (AAAB) and host monomers (6-GMA-β-CD) are dissolved in DMF to form inclusion complexes. The self-healing epoxy acrylate films are prepared by UV curing of the epoxy diacrylate with inclusion complex using the 1-hydroxycyclohexyl phenyl ketone as photoinitiator. The obtained resins with 6-GMA-β-CD/AAAB complex of 3, 5, and 7 wt % are described as SHE-3, SHE-5, and SHE-7, respectively. It is also worth noting that the UV curing process would cause the dissociation of 6-GMA-β-CD/AAAB complex. However, the host and guest moieties can't dissociate or move freely in the viscous

prepolymer solution. Furthermore, the UV curing process is in the undisturbed status, which makes the complexes fix in their original positions. Therefore, the excluded 6-GMA-β-CD/AAAB complex could be recombined in subsequent dark environments. As shown in Fig. S5a-d, the UV curing process provides the facile and rapid manufacturing of yellow and transparent SHE films as well as colorless pristine epoxy acrylate films. Fracture surfaces of epoxy acrylate films containing different contents of 6-GMA-β-CD/AAAB are examined by SEM (Fig. S5e-h). The fracture surface of pristine epoxy represents smooth and clean, indicating the brittle failure of the resin. With the increasing of the 6-GMA-β-CD/AAAB content, the fracture surfaces show increasing tortuosity and roughness. It seems that some polymer chains are pulled out when the film is damaged, indicating the presence of healable components in the crack sites [44,45].

The association effect is study by UV/Vis spectroscopy to confirm host-guest interaction between 6-GMA-β-CD and AAAB (Fig. 2a). In the present study, DFM was selected as the measurement solvent. As the DMF has relatively strong UV absorption at 200–300 nm, the UV–vis spectra of 6-GMA-β-CD/AAAB present high value at 300 nm. The AAAB (25 μM) displays a characteristic absorption of Azo groups at 357 nm. With the addition of 6-GMA-β-CD, the peak intensity of Azo in AAAB clearly decreases gradually, indicating the Azo groups have been encapsulated by the hydrophobic cavities of β-CD. By varying the 6-GMA-β-CD concentration from 5 to 25 μM, the absorbance of Azo decreases linearly, indicating the concentration-dependent manner of AAAB encapsulation. The chemical structures of SHE films are monitored by FT-IR spectroscopy. In Fig. 2b, the absorption located at 1723, 1507, 1035 cm^{-1} can be can be assigned to characteristic peaks of C=O, Ph C=C, C—O groups of epoxy acrylate, respectively. In the FT-IR spectra of SHE films, the variations in the intensity of the absorption peaks give us clue to detect the groups' evolution involved in the UV curing process. In SHE films, stronger characteristic absorption peaks at 3441 and 1605 cm^{-1} appears, mainly ascribed to the O—H groups in β-CD and N=N groups in AAAB, respectively. The gradual increase in intensity of these two absorptions indicates that the 6-GMA-β-CD/AAAB complex is incorporated to the resin network to form reversible cross-linking structure.

The thermal behaviors of the prepared SHE films are investigated, for the purpose of determining the optimum self-healing temperature. As observed in the TGA curves (Fig. 3a), all samples reveal similar thermal degradation behaviors and the onset decomposition temperatures are 391, 390, 385, and 383 °C for pristine epoxy, SHE-3, SHE-5, and SHE-7, respectively. The results confirm that the main chain structure of bisphenol A epoxy resin remains unchanged. The slight reduction in thermal stability can be attributed to the presence of
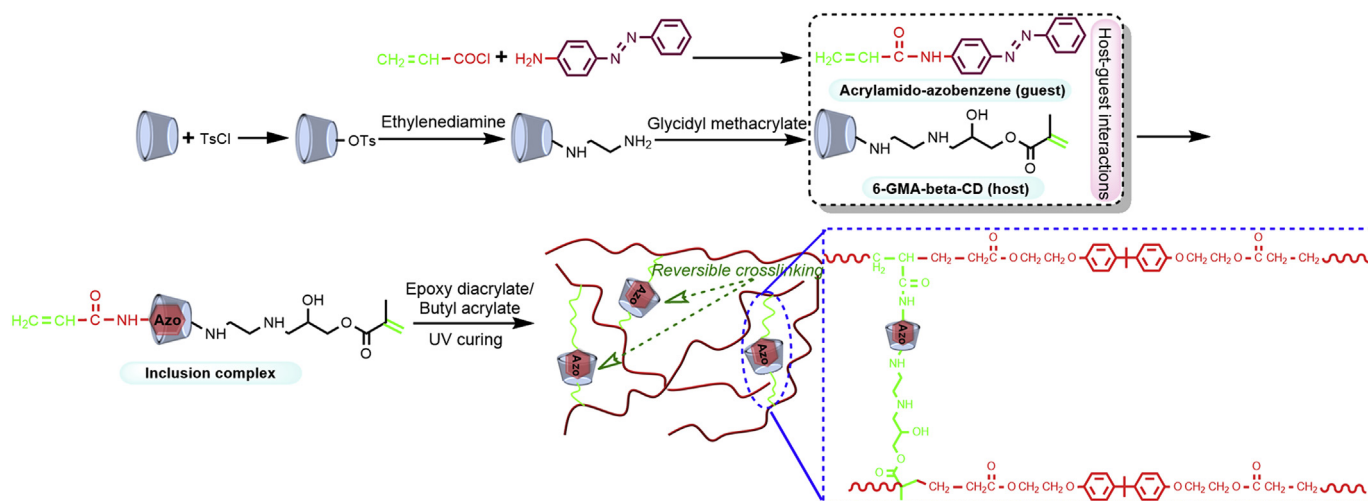

Fig. 1. The preparation scheme of the self-healing epoxy acrylate based on host-guest chemistry.
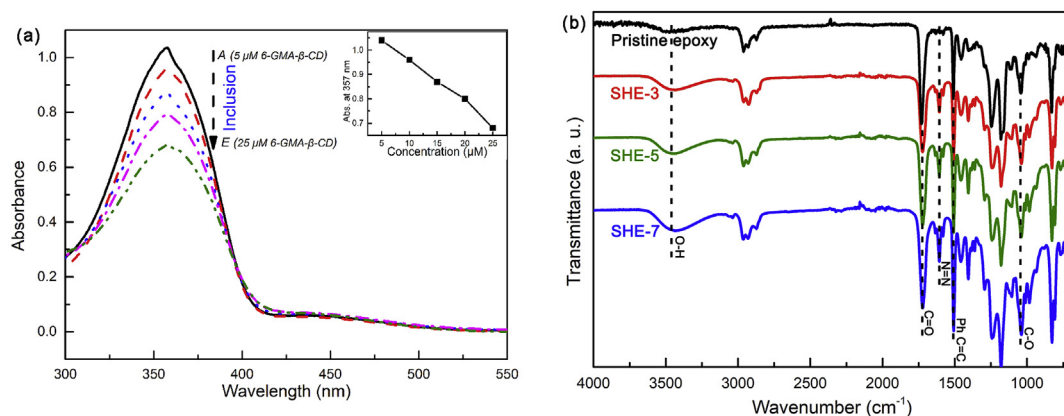
Fig. 2. (a) UV–vis spectra of AAAB (25 μM) and 6-GMA-β-CD/AAAB at different molar ratios from 5:1 to 1:1. The inset represents the relationship between 357 nm absorbance of AAAB and the concentration of 6-GMA-β-CD. (b) FTIR spectra of the self-healable epoxy acrylate films.

reversible host-guest interactions in the crosslinking sites, which are obviously less stable than the covalent bonds. Although the host-guest inclusion can be achieved spontaneously at room temperature, self-healing of thermosetting resins still requires the polymer chains have certain mobility. Consequently, the healing temperature is closely related to the T_g of the composites, and a healing temperature higher than T_g is necessary for ensuring the mobility of polymer chains and reforming of cross-linking structures. The T_g of the SHE films are measured according to DMA tests. As shown in Fig. 3b, the T_g of pristine epoxy acrylate is 54.2 °C, lower than the traditional epoxy resin. This is due to the fact that the cross-linking structure of epoxy acrylate is consisted of soft-segment chains, which offers more flexibility for the resin and decreases the T_g. The results also reveal that the degree of cross-linking based on host-gust interactions has only a weak effect on the T_g. With the addition of 6-GMA-β-CD/AAAB complexes, the T_g decreases from 54.2 to 54.1, 53.0, and 51.1 °C for SHE-3, SHE-5, and SHE-7, respectively. Based on the TGA and DMA results, the self-healing condition is set to 120 °C in dark in present study, which would provide the polymer chains certain mobility to make it possible to re-connect the broken bonds.

The essence of the intrinsic self-healing is chain movement and re-combination. However, the 3D crosslinking structure of epoxy acrylate prevents molecular motion of the chains and thereby has important influences on the mechanical properties and self-healing behaviors of the materials. In the present study, monofunctional monomer (butyl acrylate) is used as one of the main components to adjust the cross-linking density of epoxy acrylate. The adding of butyl acrylate ensures the epoxy acrylate has considerable mechanical properties and also endows the material with self-healing behaviors. It is worth investigating healing properties of the SHE films copolymerized with

different content of 6-GMA-β-CD/AAAB complexes (Fig. 4a). For each sample, fresh cracks are made on the film surfaces and the samples are treated under 120 °C for 5–20 min. As shown in Fig. 4a, the damages reveal no healing for SHE-3 at first 10 min treatment. Although the damages of SHE-3 represent evident healing after 20 min heating, obvious cracks are still can be observed. It is believed that the healing process is driven by surface tension induced viscoelastic reflow. For thermosetting resin, the ability of flowing mainly depends on the internal crosslink density and external temperature. As SHE-3 having the lowest reversible crosslinking structure, the healing is difficult to achieve under the present experimental conditions. For SHE-5 and SHE-7, the scratch width is obviously reduced at first 5 min, and the cracks are almost completely healed after 20 min. These results indicate more reversible crosslink density offers more mobility, which make the resins present improved healing properties. Furthermore, higher content of 6-GMA-β-CD/AAAB complexes brings stronger host-guest bindings at the damage sites, resulting in better self-healing performances.

The stress-strain curves of the samples are tested for quantitative analysis. In this work, the ratio of self-healed tensile strength to initial strength is regarded as the self-healing efficiency. As can be seen from Fig. 4b and Table 1, both of the original strength and healing efficiency of the SHE films depend on the content of the 6-GMA-β-CD/AAAB complexes present in the epoxy materials. The epoxy acrylate films with the highest 6-GMA-β-CD/AAAB complexes concentration (7 wt%) show the worst tensile strength (4.47 MPa) and best self-healing efficiency (74.0%). The results indicate that the initial strength and healing efficiency are two sides of a coin. Although the host-guest interactions make main contribution to the restoration of the mechanical strength, too many complexes significantly reduce the mechanical properties of the material. However, the right balances between initial strength and
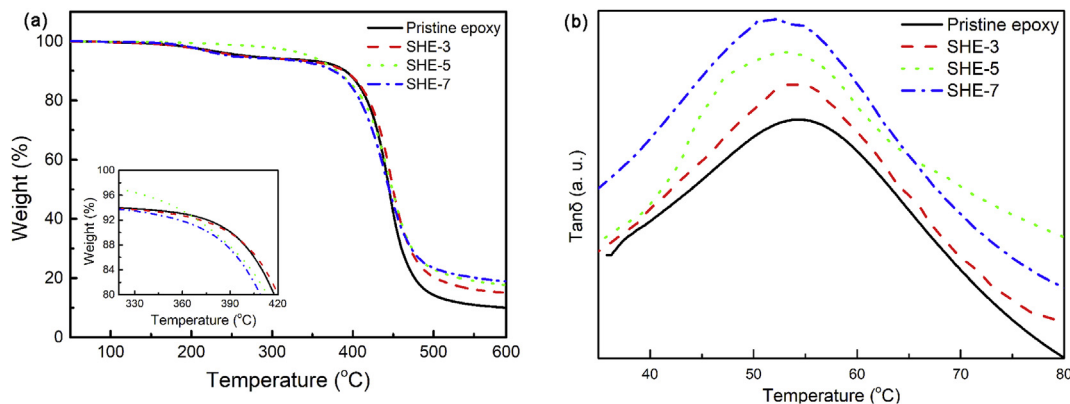

Fig. 3. (a) TGA curves and (b) DMA curves of pristine and self-healable epoxy acrylate films.
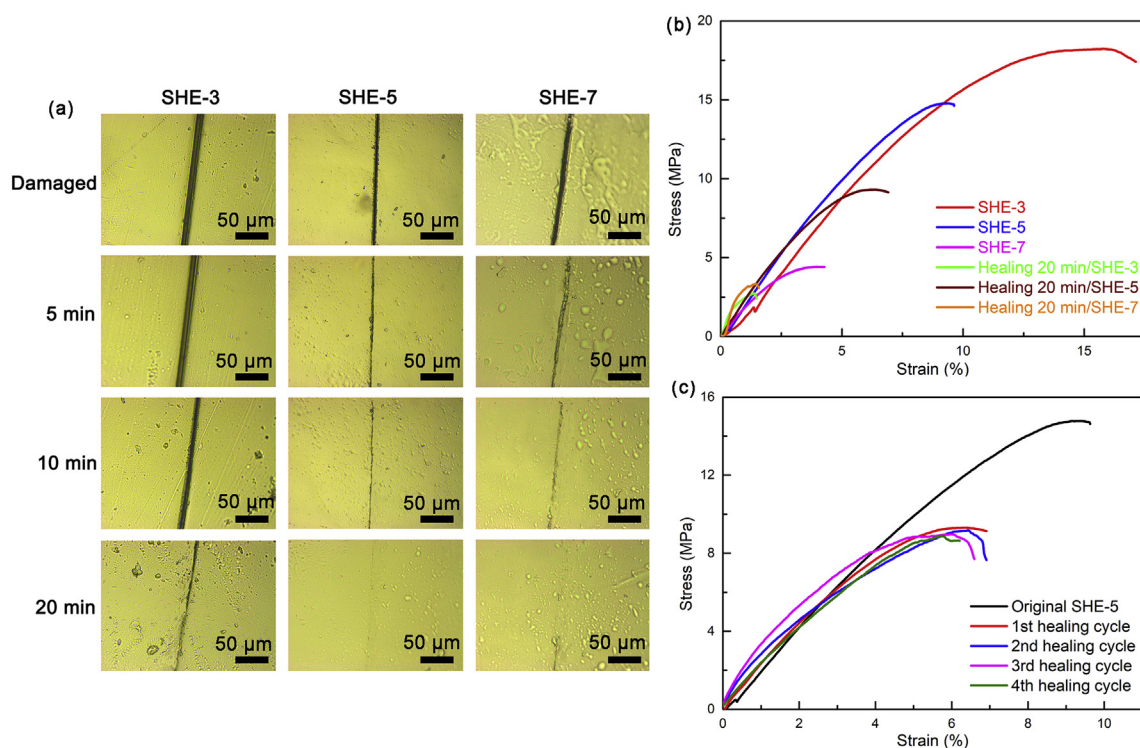
Fig. 4. (a) Optical microscope images of SHE films before and after the self-healing process. (b) Stress-strain curves of SHE films with different contents of 6-GMA-β-CD/AAAB complexes. (c) Stress-strain curves of SHE-5 films after multiple healing cycles.

Table 1
Tensile stress and self-healing efficiency of the SHE films as a function of the healing time.

Samples	Tensile stress (MPa)/Self-healing efficiency (%)		
	5 min	10 min	20 min
SHE-3	–	–	2.78/15.3
SHE-5	3.49/23.6	5.61/37.9	9.37/63.3
SHE-7	2.13/47.8	2.97/66.6	3.31/74.0

healing efficiency can be struck by adjusting the content of 6-GMA-β-CD/AAAB complexes. Encouragingly, SHE-5 reveals the maximum recovered tensile strength (9.37 MPa) and relatively high healing efficiency (63.3%) after 20 min healing at 120 °C. From the results shown in Table 1, it can be also noted that longer healing time makes the healing more effective. However, the healing efficiency has changed little by continuously extending the processing time, indicating the healing is quickly achieved in 20 min. Fig. 4c presents the stress-strain curves of repeatedly healed SHE-5 films. Obviously, the elongation at break and tensile strength of the SHE-5 films could be greatly restored. The few declines in healing efficiency with healing cycles could attribute to the heterogeneity of reversible recombination of host-guest moieties at the damage sites.

In this work, host-guest interactions are applied for building up self-healing epoxy acrylate via supramolecular 3D networks. When external mechanical stress is applied, these supramolecular weak bonds will be preferentially failed and cause micro damages. Previous studies have already proved that the amount of combinable fictional groups and the chain mobility greatly affect the intrinsic self-healing behaviors [5,6,40,46]. Thanks to the light responsive nature of 6-GMA-β-CD and AAAB, prior UV irradiation process makes β-CD exclude the AAAB from its cavity to disconnect the connection between the host and guest molecules. This step ensures sufficient quantity and mobility of the host-guest moieties essential for the following self-healing. The epoxy further gains mobility while being heated up to above T_g, which supports a reflow of the polymer chains. Consequently, the dissociated host-guest interactions are able to spontaneous recombine and self-healing is achieved. The schematic illustration of the self-healing mechanism based on host-guest chemistry is shown in Fig. 5. There are several pioneering researches report intrinsic self-healing epoxy acrylate via reversible interactions, such as Diels-Alder chemistry [47], thiol-disulfide reactions [48,49], alkoxyamine-based reactions [50]. For a better evaluation, the current works are compared with others. Compared with above references, the present SHE-5 film shows the highest initial strength (14.80 MPa) and relatively high healing efficiency (63.3%). It is also worthwhile pointing out that the present strategy can be used to modify the main chain and cross-linking structures of various polymers, which should be valuable for design and
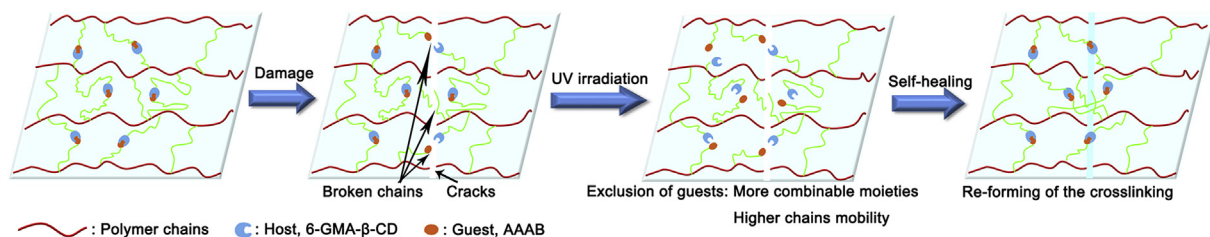

Fig. 5. Schematic illustration of the self-healing mechanism based on host-guest chemistry.

preparation of novel smart materials such as degradable thermosetting composites, shape-memory composites, and controlled release drug carriers.

4. Conclusions

In this work, the self-healable epoxy acrylate is designed and prepared by crosslinking the epoxy acrylate chains with host-guest inclusion complexes (6-GMA-β-CD/AAAB). The obtained epoxy acrylate films show a flexible range of tensile strength of 4.47–18.2 MPa corresponding to different 6-GMA-β-CD/AAAB. Benefit from the light responsive behaviors of 6-GMA-β-CD/AAAB, the crosslinking points can be unlocked by UV irradiation to increases both the combinative bonds' quantity and the chain mobility, endowing the epoxy better self-healing abilities. In order to trigger the spontaneous host-guest interactions, moderate heating is used to further increase the chain mobility at the crack area. Consequently, the damaged chains are able to recombine via host-guest chemistry, endowing the SHE-5 films with relatively excellent restored tensile strength (9.37 MPa) and healing efficiency (63.3%). The reversible dynamic nature of the host-guest chemistry allows healing to occur over multiple cycles. The present work confirms that it is possible to achieve macroscopical self-healing via host-guest interactions, which is very helpful for preparing smart thermosetting composite for practical applications.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.01.010.

References

[1] Z. Hu, C. Song, Q. Shao, J. Li, Y. Huang, One-step functionalization of graphene by cycloaddition of diarylcarbene and its application as reinforcement in epoxy composites, Compos. Sci. Technol. 135 (2016) 21–27.
[2] M.D. Reale Batista, L.T. Drzal, Carbon fiber/epoxy matrix composite interphases modified with cellulose nanocrystals, Compos. Sci. Technol. 164 (2018) 274–281.
[3] B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, Self-healing polymers and composites, Annu. Rev. Mater. Res. 40 (2010) 179–211.
[4] N.K. Guimard, K.K. Oehlenschlaeger, J. Zhou, S. Hilf, F.G. Schmidt, C. Barner-Kowollik, Current trends in the field of self-healing materials, Macromol. Chem. Phys. 213 (2012) 131–143.
[5] Y. Yang, M.W. Urban, Self-healing polymeric materials, Chem. Soc. Rev. 42 (2013) 7446–7467.
[6] Y. Yang, X. Ding, M.W. Urban, Chemical and physical aspects of self-healing materials, Prog. Polym. Sci. 49–50 (2015) 34–59.
[7] L. Gao, J. He, J. Hu, C. Wang, Photoresponsive self-healing polymer composite with photoabsorbing hybrid microcapsules, ACS Appl. Mater. Interfaces 7 (2015) 25546–25552.
[8] W. Guo, Y. Jia, K. Tian, Z. Xu, J. Jiao, R. Li, et al., Uv-triggered self-healing of a single robust sio2 microcapsule based on cationic polymerization for potential application in aerospace coatings, ACS Appl. Mater. Interfaces 8 (2016) 21046–21054.
[9] X.K.D. Hillewaere, R.F.A. Teixeira, L.-T.T. Nguyen, J.A. Ramos, H. Rahier, F.E. Du Prez, Autonomous self-healing of epoxy thermosets with thiol-isocyanate chemistry, Adv. Funct. Mater. 24 (2014) 5575–5583.
[10] H. Jin, C.L. Mangun, D.S. Stradley, J.S. Moore, N.R. Sottos, S.R. White, Self-healing thermoset using encapsulated epoxy-amine healing chemistry, Polymer 53 (2012) 581–587.
[11] K.R. Hart, N.R. Sottos, S.R. White, Repeatable self-healing of an epoxy matrix using imidazole initiated polymerization, Polymer 67 (2015) 174–184.
[12] R. Luterbacher, R.S. Trask, I.P. Bond, Static and fatigue tensile properties of cross-ply laminates containing vascules for self-healing applications, Smart Mater. Struct. 25 (2016) 015003–015012.
[13] N. Bai, K. Saito, G.P. Simon, Synthesis of a diamine cross-linker containing diels-alder adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer, Polym. Chem. 4 (2013) 724–730.
[14] X. Kuang, G. Liu, X. Dong, X. Liu, J. Xu, D. Wang, Facile fabrication of fast recyclable and multiple self-healing epoxy materials through diels-alder adduct cross-linker, J. Polym. Sci. Polym. Chem. 53 (2015) 2094–2103.
[15] X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen, S.R. Nutt, et al., A thermally remendable cross-linked polymeric material, Science 295 (2002) 1698–1702.
[16] Y. Min, S. Huang, Y. Wang, Z. Zhang, B. Du, X. Zhang, et al., Sonochemical transformation of epoxy–amine thermoset into soluble and reusable polymers, Macromolecules 48 (2015) 316–322.
[17] Q. Tian, Y.C. Yuan, M.Z. Rong, M.Q. Zhang, A thermally remendable epoxy resin, J. Mater. Chem. 19 (2009) 1289–1296.
[18] F.I. Altuna, V. Pettarin, R.J.J. Williams, Self-healable polymer networks based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution, Green Chem. 15 (2013) 3360–3366.
[19] A. Ghazi, E. Ghasemi, M. Mahdavian, B. Ramezanzadeh, M. Rostami, The application of benzimidazole and zinc cations intercalated sodium montmorillonite as smart ion exchange inhibiting pigments in the epoxy ester coating, Corros. Sci. 94 (2015) 207–217.
[20] R. Long, H.J. Qi, M.L. Dunn, Modeling the mechanics of covalently adaptable polymer networks with temperature-dependent bond exchange reactions, Soft Matter 9 (2013) 4083–4096.
[21] M. Hernández, A.M. Grande, W. Dierkes, J. Bijleveld, S. van der Zwaag, S.J. García, Turning vulcanized natural rubber into a self-healing polymer: effect of the disulfide/polysulfide ratio, ACS Sustain. Chem. Eng. 4 (2016) 5776–5784.
[22] U. Lafont, H. van Zeijl, S. van der Zwaag, Influence of cross-linkers on the cohesive and adhesive self-healing ability of polysulfide-based thermosets, ACS Appl. Mater. Interfaces 4 (2012) 6280–6288.
[23] Y. Chen, Z. Guan, Multivalent hydrogen bonding block copolymers self-assemble into strong and tough self-healing materials, Chem. Commun. 50 (2014) 10868–10870.
[24] P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, Self-healing and thermoreversible rubber from supramolecular assembly, Nature 451 (2008) 977–980.
[25] L.R. Hart, J.L. Harries, B.W. Greenland, H.M. Colquhoun, W. Hayes, Healable supramolecular polymers, Polym. Chem. 4 (2013) 4860–4870.
[26] S. Basak, J. Nanda, A. Banerjee, Multi-stimuli responsive self-healing metallo-hydrogels: tuning of the gel recovery property, Chem. Commun. 50 (2014) 2356–2359.
[27] Z. Hu, C. Wang, F. Zhao, X. Xu, S. Wang, L. Yu, et al., Fabrication of a graphene/c60 nanohybrid via gamma-cyclodextrin host-guest chemistry for photodynamic and photothermal therapy, Nanoscale 9 (2017) 8825–8833.
[28] Z. Hu, D. Zhang, L. Yu, Y. Huang, Light-triggered c60 release from a graphene/cyclodextrin nanoplatform for the protection of cytotoxicity induced by nitric oxide, J. Mater. Chem. B 6 (2018) 518–526.
[29] M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, Redox-responsive self-healing materials formed from host-guest polymers, Nat. Commun. 2 (2011) 511–516.
[30] U. Gulyuz, O. Okay, Self-healing poly(acrylic acid) hydrogels with shape memory behavior of high mechanical strength, Macromolecules 47 (2014) 6889–6899.
[31] Q. Yan, A. Feng, H. Zhang, Y. Yin, J. Yuan, Redox-switchable supramolecular polymers for responsive self-healing nanofibers in water, Polym. Chem. 4 (2013) 1216–1220.
[32] Y.-F. Wang, D.-L. Zhang, T. Zhou, H.-S. Zhang, W.-Z. Zhang, L. Luo, et al., A reversible functional supramolecular material formed by host–guest inclusion, Polym. Chem. 5 (2014) 2922–2927.
[33] T.-W. Chuo, T.-C. Wei, Y.-L. Liu, Electrically driven self-healing polymers based on reversible guest-host complexation of β-cyclodextrin and ferrocene, J. Polym. Sci. Polym. Chem. 51 (2013) 3395–3403.
[34] T. Kakuta, Y. Takashima, M. Nakahata, M. Otsubo, H. Yamaguchi, A. Harada, Preorganized hydrogel: self-healing properties of supramolecular hydrogels formed by polymerization of host-guest-monomers that contain cyclodextrins and hydrophobic guest groups, Adv. Mater. 25 (2013) 2849–2853.
[35] K. Miyamae, M. Nakahata, Y. Takashima, A. Harada, Self-healing, expansion-contraction, and shape-memory properties of a preorganized supramolecular hydrogel through host-guest interactions, Angew Chem. Int. Ed. Engl. 54 (2015) 8984–8987.
[36] K. Guo, D.L. Zhang, X.M. Zhang, J. Zhang, L.S. Ding, B.J. Li, et al., Conductive elastomers with autonomic self-healing properties, Angew Chem. Int. Ed. Engl. 54 (2015) 12127–12133.
[37] Y. Takashima, K. Yonekura, K. Koyanagi, K. Iwaso, M. Nakahata, H. Yamaguchi, et al., Multifunctional stimuli-responsive supramolecular materials with stretching, coloring, and self-healing properties functionalized via host–guest interactions, Macromolecules 50 (2017) 4144–4150.
[38] C. Yu, C.-F. Wang, S. Chen, Robust self-healing host-guest gels from magnetocaloric radical polymerization, Adv. Funct. Mater. 24 (2014) 1235–1242.
[39] M.V. Rekharsky, Y. Inoue, Complexation thermodynamics of cyclodextrins, Chem. Rev. 98 (1998) 1875–1917.
[40] D. Habault, H. Zhang, Y. Zhao, Light-triggered self-healing and shape-memory polymers, Chem. Soc. Rev. 42 (2013) 7244–7256.
[41] Z. Hu, Q. Shao, Y. Huang, L. Yu, D. Zhang, X. Xu, et al., Light triggered interfacial damage self-healing of poly(p-phenylene benzobisoxazole) fiber composites, Nanotechnology 29 (2018) 185602–185613.
[42] Q. Shao, Z. Hu, X. Xu, L. Yu, D. Zhang, Y. Huang, Mussel-inspired immobilization of bn nanosheets onto poly(p-phenylene benzobisoxazole) fibers: multifunctional interface for photothermal self-healing, Appl. Surf. Sci. 440 (2018) 1159–1165.
[43] Z. Hu, D. Zhang, F. Lu, W. Yuan, X. Xu, Q. Zhang, et al., Multistimuli-responsive intrinsic self-healing epoxy resin constructed by host–guest interactions, Macromolecules 51 (2018) 5294–5303.
[44] Z. Hu, Q. Shao, M.G. Moloney, X. Xu, D. Zhang, J. Li, et al., Nondestructive functionalization of graphene by surface-initiated atom transfer radical polymerization:

an ideal nanofiller for poly(p-phenylene benzobisoxazole) fibers, Macromolecules 50 (2017) 1422–1429.

[45] Z. Hu, Q. Shao, X. Xu, D. Zhang, Y. Huang, Surface initiated grafting of polymer chains on carbon nanotubes via one-step cycloaddition of diarylcarbene, Compos. Sci. Technol. 142 (2017) 294–301.

[46] D.Y. Wu, S. Meure, D. Solomon, Self-healing polymeric materials: a review of recent developments, Prog. Polym. Sci. 33 (2008) 479–522.

[47] Q. Tian, M.Z. Rong, M.Q. Zhang, Y.C. Yuan, Synthesis and characterization of epoxy with improved thermal remendability based on diels-alder reaction, Polym. Int. 59 (2010) 1339–1345.

[48] J. Canadell, H. Goossens, B. Klumperman, Self-healing materials based on disulfide links, Macromolecules 44 (2011) 2536–2541.

[49] M. Pepels, I. Filot, B. Klumperman, H. Goossens, Self-healing systems based on disulfide–thiol exchange reactions, Polym. Chem. 4 (2013) 4955–4965.

[50] Z.P. Zhang, M.Z. Rong, M.Q. Zhang, Room temperature self-healable epoxy elastomer with reversible alkoxyamines as crosslinkages, Polymer 55 (2014) 3936–3943.