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Self-healing, recoverable epoxy elastomers and their composites with desirable thermal conductivities by incorporating BN fillers *via in-situ* polymerization

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ABSTRACT

Thiol-epoxy elastomers were firstly prepared by thiol-epoxide nucleophilic ring-opening reaction, and the micron boron nitride (*m*BN) fillers were then introduced into the above system *via in-situ* polymerization, finally to prepare the highly thermally conductive, self-healing and recoverable *m*BN/thiol-epoxy elastomer composites by hot-pressing method. Results revealed that the thiol-epoxide reaction was highly efficient and stable. The obtained *m*BN/thiol-epoxy elastomer composite with 60 wt% *m*BN fillers presented the optimal thermal conductivity (λ of 1.058 W/mK), excellent self-healing effect & efficiency which is achieved *via* transesterification reaction (Tensile strength after self-healing could maintain at more than 85% compared to that of original composites), wonderful recoverable performance (Tensile strength after post forming could maintain over 70% compared to that of original composites) and good thermal stability ($T_{heat\text{-}resistance\ index}$, T_{HRI} of 149.9 °C). And the improvement in λ value of the *m*BN/thiol-epoxy elastomer composites was beneficial to the promotion of the self-healing systems relying on thermal response.

1. Introduction

Polymer materials are widely applied in the fields of electronics, aerospace and electronic packaging because of their light-weight, excellent mechanical properties, good electrical insulation and easy-processing properties, *etc*., [1–4]. However, cracks and other forms of destruction & damage are also inevitably produced due to the influences of outer environmental factors, resulting in the performance degradation [5–9]. Modeled on the characteristics of organisms, self-healing polymer materials can timely repair local damage & micro-cracks, and also self-recover internal defects, in favor of improving the mechanical properties of the materials [10–15].

At present, self-healing materials are mainly divided into extrinsic and intrinsic self-healing materials. Extrinsic self-healing includes microcapsules, hollow-fibers and nanoparticles, *etc.*, [16–18]. To our knowledge, microcapsules were firstly applied in the self-healing composites reported by White [19], relying on the released healing agents from ruptured microcapsules. Dry [20] embedded the hollow-fibers containing healing agents in the polymeric matrix, and the self-healing was accomplished by released healing agents from ruptured hollow-fibers into the crack plane. Extrinsic self-healing can realize the positioning self-healing of the micro-cracks to a certain extent. However, the addition of healing agents may produce two phase interface, against the overall performances of the materials. Meantime, the corresponding healing efficiency is unsatisfactory and multiple healing can't be implemented [21]. Intrinsic self-healing can be achieved by reversible covalent bond or reversible non-covalent bond by designing the structure of polymers [22–24]. Deng [25] reported a self-healing organic gel based on reversible acylhydrazone bond. Klumperman [26] also prepared a self-healing system achieving multiple breakage and recombination *via* disulfide bond. The advantage of the intrinsic self-healing system is no additional catalysts and monomers. Such system

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can be self-healed independently under external effect or intermolecular interaction, and multiple healing can also be achieved in theory [27–29].

Certainly, the thermal initiation is one of the most common methods to accomplish the self-healing behaviors. Therefore, the increase of the thermal conductivities for the polymers would help to improve the self-healing efficiency and effect [30,31]. So far as we know, it is very difficult to fabricate the intrinsic thermally conductive polymers by designing molecular chain structure and/or adjusting the curing network [32–34]. Therefore, the addition of the fillers with highly thermally conductive coefficient (λ) into polymeric matrix is considered as the most simple and effective method [35–40].

Epoxy resins have been widely applied as the matrix of adhesives, coatings and advanced composites owing to their excellent comprehensive properties [41–45]. Nevertheless, the intrinsic low λ value, difficult self-healing and hardly reprocessing of cured epoxy resins have limited their broader application [46–49]. In our present work, the thiol-epoxy elastomers were firstly prepared by thiol-epoxide nucleophilic ring-opening reaction, to complete the self-healing behavior *via* transesterification reaction [50]. Furthermore, the micron boron nitride (*m*BN) fillers were introduced into the above system *via* in-situ polymerization, finally to prepare the highly thermally conductive, self-healing and recoverable *m*BN/thiol-epoxy elastomer composites by hot-pressing method. The molecular structures of the obtained thiol-epoxy elastomers were characterized by Fourier transform infrared (FTIR). And the corresponding thermal conductivities, self-healing & recoverable performance, tensile strength, glass transition temperature (T_g) and the thermal stabilities of the thiol-epoxy elastomers and *m*BN/thiol-epoxy elastomer composites were also analyzed and investigated. And the relationship between self-healing performance and thermal conductivities was also preliminarily explored and discussed.

2. Experiments

2.1. Materials

Trimethylolpropane triglycidyl ether (TMTGE), trimethylolpropane tris (3-mercaptopropionate) (TMMP) and 1, 5, 7-triazabicyclo[4.4.0] dec-5-ene (TBD) were all purchased from Sigma Aldrich Co., (Shanghai, China), and their structures were shown in Scheme 1. Micrometer boron nitride (*m*BN, mean diameter of 2–3 μm, specific area of 10–15 m^2/g) was supplied from Xuzhou Hongwu Nanomaterial Co., Ltd (Jiangsu, China). Ethyl alcohol (EtOH) was received from Tianjin Ganglong Chemical Group Co., Ltd (Tianjin, China).

2.2. Fabrication of the mBN/thiol-epoxy elastomer composites

Thiol-epoxy elastomers were firstly obtained by nucleophilic ring-opening reaction (Scheme 2) according to our previous work [50]. TMTGP (2.0 g, 6.62 mmol), TMMP (2.65 g, 6.62 mmol) and TBD (46 mg, 5 mol% of TMTGE) were well mixed in a beaker with stirring. And 0.235 g (5 wt%), 0.47 g (10 wt%), 0.94 g (20 wt%), 1.41 g (30 wt %), 1.88 g (40 wt%), 2.35 g (50 wt%) and 2.82 g (60 wt%) of *m*BN fillers was then added into the above solution with mechanical stirring, respectively. And the ethanol was then slowly dropped into the above mixtures to obtain the white solids. Finally, the above products were hot pressed at 10 MPa and 120 °C for 1 h, to obtain the *m*BN/thiol-epoxy elastomer composites.

2.3. Characterizations

FTIR (Fourier transform infrared) spectra of the samples were obtained from Bruker Tensor 27 equipment (Bruker Corporation, Germany).

DSC (Differential scanning calorimetry) analyses of the samples were carried out at 10 °C/min (nitrogen atmosphere) by DSC1 (Mettler-Toledo Corporation, Switzerland).

TGA (Thermal gravimetric analyses) of the samples were carried out at 10 °C/min (argon atmosphere) by STA 449F3 (NETZSCH Corporation, Germany).

SEM (Scanning electron microscope) morphologies of the samples were analyzed by VEGA3-LMH (TESCAN Corporation, Czech Republic).

Thermally conductive coefficient (λ) and thermal diffusivity (α) values of the samples were measured using TPS2200 Hot Disk instrument (AB Corporation, Sweden), according to standard ISO 22007-2: 2008, and the corresponding specimen dimension was 20 mm × 20 mm × 2 mm.

Tensile strength values of the samples were carried out at 500 mm/min by QJ211S (Qingji Corporation, China), according to standard ASTM D412.

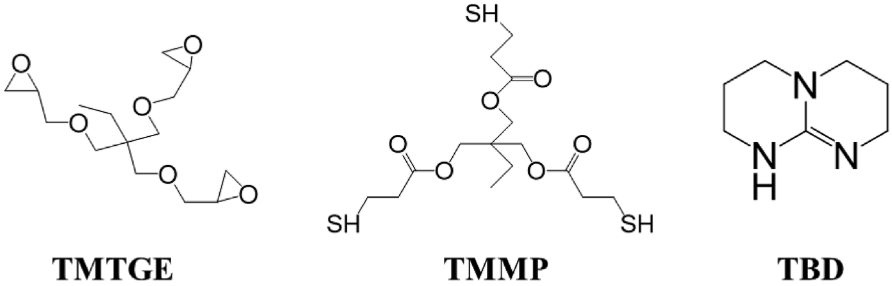
3. Results and discussions

3.1. Structural characterization of the thiol-epoxy elastomer

Fig. 1 presented the FTIR spectra of the monomers (TMMP and TMTGE) and target product (thiol-epoxy elastomer). The peak at 1130 cm^{-1} and 2970 cm^{-1} was corresponded to the absorption vibration of $-C-O$ and $-CH_3$, respectively. The peak at 910 cm^{-1} was ascribed to the absorption vibration of epoxy group. The peak at 1730 cm^{-1} and 2569 cm^{-1} could be assigned to the absorption vibration of $-C=O$ and $-SH$, respectively. After the nucleophilic ring-opening reaction, the two characteristic peaks of 2569 cm^{-1} and 910 cm^{-1} in the target products were disappeared, mainly attributed to the reaction of epoxy group and thiol group, which also proved that the desired target product (thiol-epoxy elastomer) was successfully obtained.

3.2. Thermal conductivities of the composites

Fig. 2 showed the λ and *α* values of the *m*BN/thiol-epoxy elastomer composites. Both the λ and *α* values of the obtained *m*BN/thiol-epoxy elastomer composites were increased with the increasing addition of *m*BN fillers. When the mass fraction of the *m*BN fillers was 60 wt%, the corresponding λ and *α* value was enhanced to 1.058 W/mK and 0.8479 mm^2/s, about 4 times and 6 times than that of pristine thiol-



Scheme 1. Chemical structures of the monomers.