



# Supramolecularly toughened and elastic epoxy resins by grafting 2-ureido-4[1H]-pyrimidone moieties on the side chain

Peng Zhang, Lei Kan, Xinyue Zhang, Rui Li, Chuanqi Qiu, Ning Ma, Hao Wei\*

Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

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## ABSTRACT

Multiple hydrogen bonds have been widely used to form a supramolecular network and endow materials with enhanced mechanical strength, good elasticity, and/or self-healing properties. In this study, 2-ureido-4[1H]-pyrimidone (UPy) compounds were synthesized and chemically grafted onto the side chain of epoxy resins. The UPy-modified epoxy resin demonstrated substantial improvements in toughness and elasticity compared with unmodified epoxy resin as proven by a tensile test and distortion test. The breaking elongation of the UPy-modified epoxy resin was 5 times higher than that of unmodified epoxy resin under a tensile test. In addition, the fracture mechanism of the modified epoxy resin matched with the ductile fracture rather than the brittle fracture of unmodified epoxy resins. The introduction of quadruple hydrogen bonds by chemical modification may provide a simple and effective way to design and prepare highly flexible thermosetting resin materials.

## 1. Introduction

As thermosetting polymeric materials, epoxy resins have shown excellent advantages in dimensional stability, chemical resistance, electrical insulation, and improved thermomechanical properties [1–3]. Epoxy resins have been widely used as adhesives [4–7], coatings [8–10], and composite matrices due to such benefits [11–15]. Generally, epoxy resins have a crosslinked network structure with covalent crosslinking, providing an insoluble thermoset with low fracture extensibility and high brittleness because of the crosslinked structure. Many research teams have demonstrated that high crosslinking density reduces the fracture toughness of original epoxy resin due to internal stresses produced during the curing process [17–19]. In highly crosslinked density epoxy resins, the forces that hinder crack generation are very small, and pore growth due to plastic deformation is limited [20]. Therefore, much effort has been devoted to toughening cured epoxy for extended applications [16].

The small impact resistance of epoxy resins requires functional modification; thus, significant attention has been paid to epoxies toughened with micrometer-sized liquid rubbers, core-shell rubber particles, and thermoplastic particles and nanoparticles [21,22]. For example, Ma et al. [23] reported that thermoplastic polystyrene grafted with epichlorohydrin (g-PS) could act as an effective toughener for cured epoxy. Chen Y. et al. [24] used epoxy-block-silicone copolymers

and hydroxyl-terminated silicone oligomers to modify bisphenol-A type epoxy resin via physical blending and chemical grafting. Rubbery toughening agents added to the epoxy resin matrix often lead to impressive toughening; however, the glass transition temperature ( $T_g$ ), strength, and other desirable properties may deteriorate. A significant need to develop alternative toughening approaches thus remains, despite the remarkable results already achieved, to increase the fracture resistance of brittle epoxies with other desirable physical and mechanical properties.

Chemical grafting is an effective method for binding functional moieties onto molecular chains of epoxy resin to realize chemical modification. Na T. et al. [25] developed a new type of epoxy monomer, 1,5-bis(4-fluorobenzoyl)-2,6-diglycidyl ether naphthalene, through a three-step procedure involving Friedel-Crafts acylation, demethylation, and a nucleophilic reaction. New curing agents and curing agent catalysts can be prepared according to functional and technical requirements of the materials, such as efficient reprocessing and internal self-healing. Wang D. et al. [26] demonstrated a facile methodology to prepare reversibly crosslinked epoxy with efficient recycling and multiple self-healing capacities based on a diamine Diels–Alder adduct crosslinker and a commercial epoxy oligomer. Mirmohseni-Namin A. [27] et al. used an inorganic ultra-accelerator to enhance the toughness and tensile strength of an epoxy-diamine system. In their study, the toughness of the cured material was significantly improved,

\* Corresponding author.

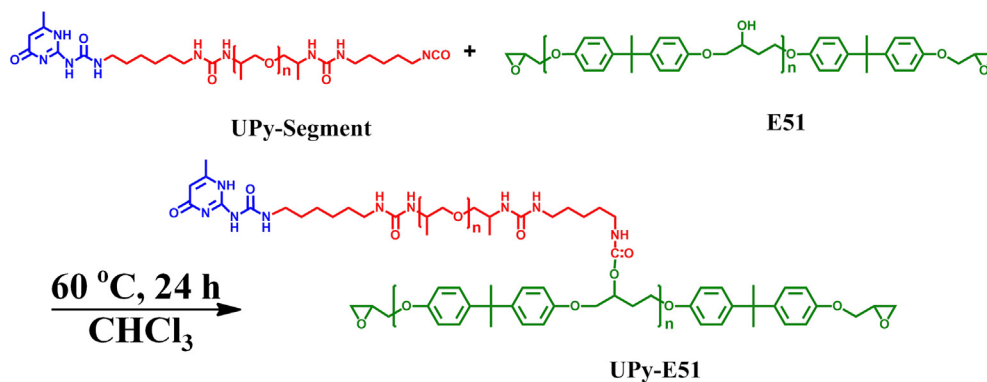
E-mail addresses: [nma@hrbeu.edu.cn](mailto:nma@hrbeu.edu.cn) (N. Ma), [weihao7512@126.com](mailto:weihao7512@126.com) (H. Wei).

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**Scheme 1.** Synthesis route of modified bisphenol-A resin with UPy-grafted segment.

but its synthesis process was relatively complicated.

In recent years, supramolecular polymers [28–31] have attracted the attention of many research groups as polymers with excellent properties. Xu and Zhang et al. [32] developed a new method of supramolecular polymerization at the water-oil interface to prepare the supramolecular polymer. Cates et al. [33] described a theoretical simulation in which supramolecular polymers can relax via dissociation and association of hydrogen bonds. The non-covalent interactions of supramolecular polymers with multiple hydrogen bond units have become important in the design and preparation of new supramolecular structures [34–37]. 2-Ureido-4[1H]-pyrimidone (UPy) compounds were developed by Meijer and have proven to be good candidates for hydrogen bonding assembly [38–40]. Guan et al. [41,42] reported a biomimetic design of a modular polymer with high modulus, toughness, resilience, adaptive mechanical properties and a supramolecular block copolymer with multiphase self-healing property. Our group reported a modified epoxy resin with high impact resistance by introducing quadruple-hydrogen-bonded UPy-containing supramolecular polymers with a physical blending process. A significant improvement of 300% in impact resistance of the supramolecular polymer-incorporated epoxy resin was obtained under a supramolecular polymer content of 10 wt% [43]. In the present work, we anticipate that the UPy groups can be introduced into the side chain of the epoxy resin via chemical grafting, and quadruple hydrogen bonds between molecular chains will promote a toughening effect of epoxy resin. It is hoped that this simple and effective method can be used to design and prepare highly flexible thermosetting resin materials.

## 2. Experimental and materials

### 2.1. Materials

The epoxy resin matrix used in this study was bisphenol-A glycidyl ether epoxy resin (E-51) with an epoxy value of 0.51, purchased from Kukdo Chemical (Kunshan, China). Poly(propylene glycol) bis(2-aminopropyl ether) (average  $M_n \sim 2000$ ) and poly(propylene glycol) bis(2-aminopropyl ether) (average  $M_n \sim 400$ ) were purchased from Aladdin (Shanghai, China). 2-Amino-4-hydroxy-6-methylpyrimidine and 2-amino-6-methyl-4-hydroxypyrimidine (98%) were obtained from SAFC (Shanghai, China). Butyl isocyanate (BI) was purchased from Aladdin (Shanghai, China). Hexamethylene diisocyanate (HDI) was purchased from Hubei Jusheng Technology Co., Ltd. (Tianmen, China). Hexane (AR) and chloroform (AR) were of analytical grade and obtained from Guangfu Fine Chemical Co., Ltd. (Tianjin, China).

### 2.2. Instruments

Fourier transform infrared (FT-IR) spectra of the samples were recorded with a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. All

spectra were acquired at a resolution of  $4\text{ cm}^{-1}$  with 8 scans.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. Scanning electron microscopy (SEM) with energy dispersive spectrometry was carried out on a FEI Sirion field emission scanning electron microscope. Each sample was taped to the copper sheet with conductive tape and then sprayed with gold. Mechanical tensile testing of samples was performed on an Instron 3365 Electronic Rally. Test samples measured  $30\text{ mm} \times 10\text{ mm} \times 2\text{ mm}$ . Dynamic mechanical analysis (DMA) was conducted in multi-frequency-strain mode using a TA Q800 instrument at a frequency of 1 Hz and a heating rate of  $3\text{ }^{\circ}\text{C}/\text{min}$  in a temperature range of  $-80$  to  $120\text{ }^{\circ}\text{C}$ ; sample dimensions were  $25\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$ . Differential scanning calorimetry (DSC) was conducted in heat-cool-heat mode using a TA Q200 instrument at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  in the temperature range of  $-80$  to  $150\text{ }^{\circ}\text{C}$ . Thermo Gravimetric Analyzer (TGA) was conducted using a TA Q50 instrument at a heating rate of  $20\text{ }^{\circ}\text{C}/\text{min}$  in the temperature range of ambient temperature to  $800\text{ }^{\circ}\text{C}$ . Gel Permeation Chromatography (GPC) was conducted using the Waters 1515 HPLC to determine the molecular weight of the synthesized product. Viscosity of the samples was recorded with TA-DHR-1, TA-DHR-2, and a rotational viscometer (NDJ-1B). A TCJ Elastic impact tester was used to evaluate the impact resistance of materials; sample dimensions were  $1.5\text{ mm} \times 1.5\text{ mm} \times 1\text{ mm}$ . Optical photographs of samples were recorded on a Canon EOS 800D SLR camera. The modified resin was placed in a colorless, transparent sample bottle, and the twist test sample was prepared to a size of  $50\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$ .

### 2.3. Synthesis of modified bisphenol-A resin with UPy-grafted segment (UPy-E51)

The modified bisphenol-A resin with a UPy-grafted segment (the synthesis and characterization were shown in Scheme S2 and Fig S2) was prepared as shown in Scheme 1. The grafted segment (8.62 g, 0.010 mol) and bisphenol-A glycidyl ether (15.22 g, 0.039 mol) were added to a 250 ml three-necked round-bottomed flask. The resultant mixture was refluxed and stirred at  $60\text{ }^{\circ}\text{C}$  for 24 h. Reaction progress was monitored by FT-IR spectroscopy; see Fig. 1a. The results of FT-IR spectra confirmed that the reaction was completed. The vibrational absorption peak of the  $-\text{NCO}$  groups ( $2270\text{ cm}^{-1}$ ) and  $-\text{OH}$  groups ( $3330\text{ cm}^{-1}$ ) disappeared completely. Surprisingly, no other miscellaneous peaks appeared, indicating that the reaction product was the target product. In addition, the test of  $^1\text{H}$  NMR and GPC was completed. The test result of  $^1\text{H}$  NMR determined that the graft polymer (UPy-E51) was obtained successfully, as illustrated in Fig S5. The molecular weight of the UPy-E51 was determined by GPC, and the test results were shown below:  $M_n = 2663$ ,  $M_w = 2982$ ,  $M_p = 2082$ ,  $\text{PDI} = 1.12$ .

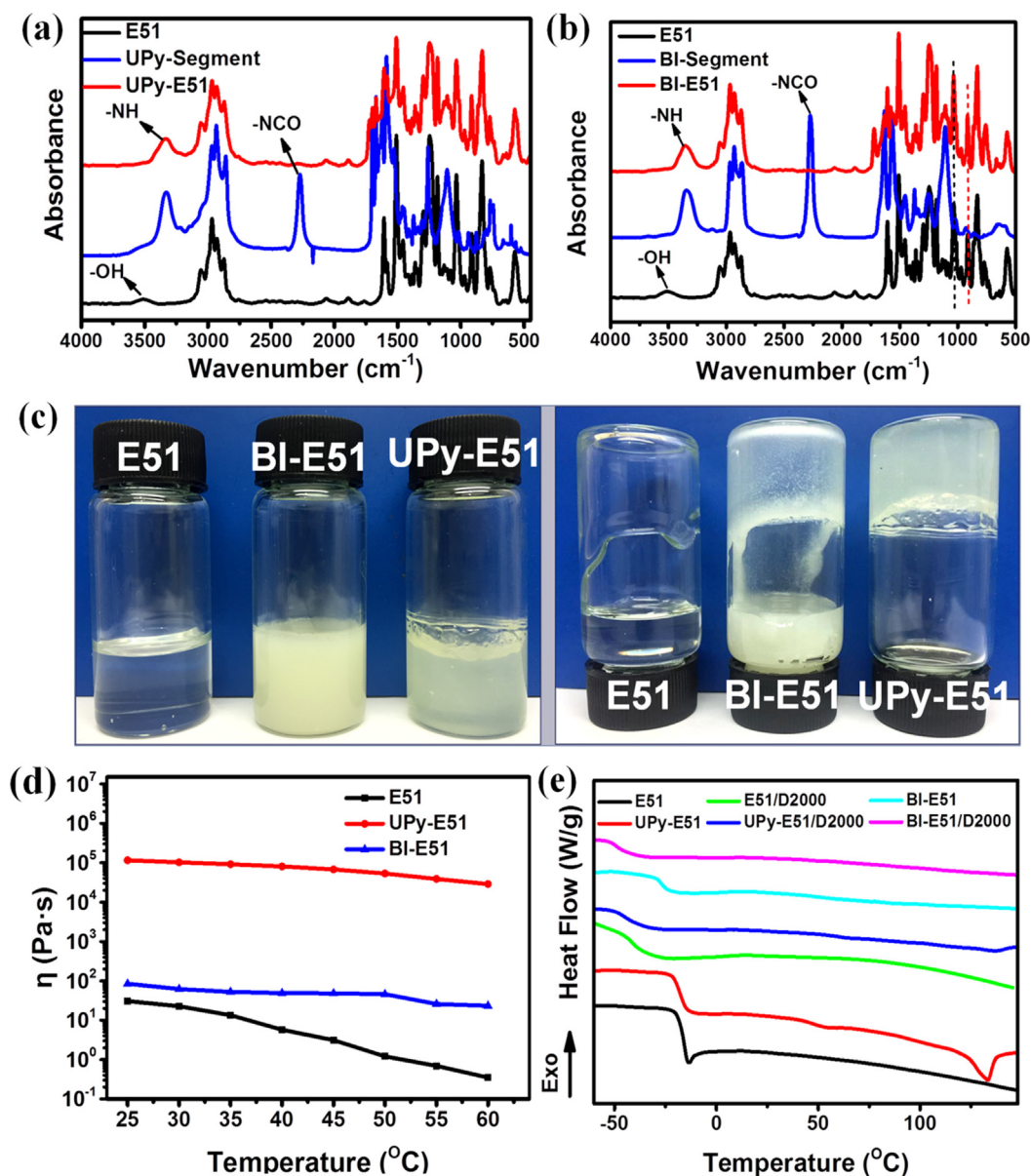


Fig. 1. Optical photographs of sample states, FT-IR spectra of neat and modified epoxy resins, and rheological behavior and DSC curves of samples: (a) IR transform infrared spectra of E51, UPy-segment, and UPy-E51; (b) IR transform infrared spectra of E51, BI-segment, and BI-E51; (c) optical photographs of E51, BI-E51, and UPy-E51; (d) viscosity curves with temperatures of E51, BI-E51, and UPy-E51; (e) DSC curves of E51, E51/D2000, UPy-E51, UPy-E51/D2000, BI-E51, and BI-E51/D2000.

#### 2.4. Synthesis of modified bisphenol-A resin with BI-grafted segment (BI-E51)

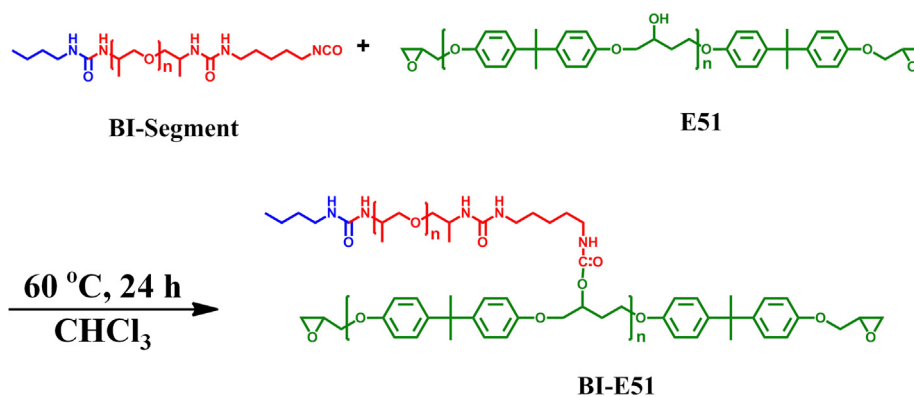
A modified bisphenol-A resin with BI-grafted segment (the synthesis and characterization were shown in Scheme S2 and Fig S2) was prepared as shown in Scheme 2. The grafted segment (6.68 g, 0.010 mol) and bisphenol-A glycidyl ether (26.08 g, 0.067 mol) were added to a 250 ml three-necked round-bottomed flask. The resultant mixture was refluxed and stirred at 60 °C for 24 h. Reaction progress was monitored by FT-IR spectroscopy, as indicated in Fig. 1b. FT-IR spectra results confirmed that the reaction was completed. The vibrational absorption peak of the -NCO groups (2270 cm<sup>-1</sup>) and -OH groups (3330 cm<sup>-1</sup>) disappeared completely. Again, the absence of miscellaneous peaks suggests that the reaction product was the target product. In addition, the test of <sup>1</sup>H NMR was completed. The test result of <sup>1</sup>H NMR determined that the graft polymer (BI-E51) was obtained successfully, as illustrated in Fig S5.

#### 2.5. Preparation of M-E51/D2000 material

The modified bisphenol-A glycidyl ether (M-E51) (UPy-E51, 13.8 g; BI-E51, 12.62 g) was dissolved in chloroform (50 mL). Poly(propylene glycol) bis(2-aminopropyl ether) (D2000) (25.5 g, 0.013 mol) was added as the curing agent into the M-E51 chloroform solution. The mixture was stirred for 30 min and poured into a 90-mm PP petri dish at room temperature for 24 h. The mixture was then heated at 80 °C for 4 h in a draught drying cabinet before being heated at 100 °C for 6 h. Finally, a fully cured modified resin material was obtained. The cured material prepared using the above method was a beige-white opaque solid.

### 3. Results and discussion

The modified epoxy resins were synthesized by tailoring the UPy-containing poly(propylene glycol) derivatives and BI poly(propylene



Scheme 2. Synthesis route of modified bisphenol-A resin with BI-grafted segment.

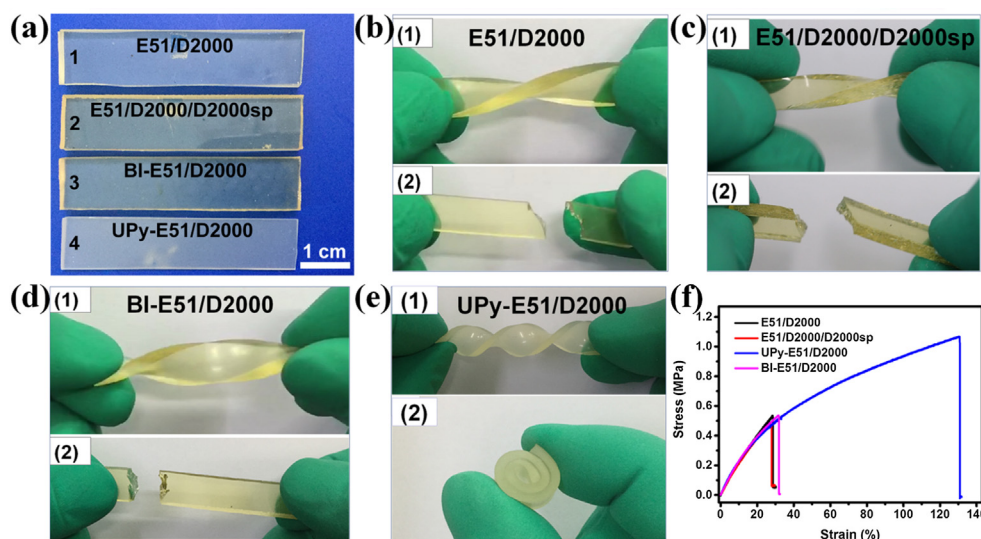


Fig. 2. Photographs of torsion test and tensile test of E51/D2000, E51/D2000/D2000sp, BI-E51/D2000, and UPy-E51/D2000 cured material: (a) state of test samples for four cured materials; (b), (c), (d), (e) distortion testing process and results for four cured materials; (f) stress-strain curves of E51/D2000, E51/D2000/D2000sp, BI-E51/D2000, and UPy-E51/D2000 cured materials.

glycol) derivatives onto E51 epoxies. Because the modified epoxy resin was synthesized by the reaction of isocyanate groups and hydroxyl groups, the reaction process could be monitored using FT-IR. Fig. 1a and b display the FT-IR spectra of modified epoxy resin (UPy-E51 and BI-E51), grafted segment (UPy-segment and BI-segment), and neat E51 epoxy resin. The absorption of  $-OH$  at  $3330\text{ cm}^{-1}$  of the E51 resin and the stretching vibration peak of  $-NCO$  at  $2270\text{ cm}^{-1}$  of the grafted segment disappeared in the FT-IR spectra of M-51, indicating that the reaction between  $-NCO$  and  $-OH$  was successful. Moreover, a stretching vibration peak of carbamate appeared at  $1735\text{ cm}^{-1}$  in the FT-IR of M-51 epoxy resins. The above results imply that the modified epoxy resin (UPy-E51 and BI-E51) was synthesized successfully.

As revealed in Fig. 1c, the pure E51 resin was a colorless and transparent liquid at room temperature, but the UPy-E51 and BI-E51 were light yellow, opaque, and viscous liquids at room temperature. To explore the effect of temperature on sample viscosity, conventional experiments were designed and a viscosity test was carried out with a rheometer. Sample bottles containing pure resin or modified resin were heated at  $80\text{ }^\circ\text{C}$  for 1 h, respectively. The viscosity of pure resin and BI-E51 reduced significantly, but the UPy-E51 failed to flow in the sample bottle similar to silicone grease. Fig. 1d presents curves of E51, BI-E51, and UPy-E51. The rheological measurement results indicate the viscosity of E51 and BI-E51 was very low at room temperature (merely 30 Pa s and 55 Pa s), but the viscosity of UPy-E51 was more than 100,000 Pa s. The viscosity of samples declined with an increase in temperature. At  $50\text{ }^\circ\text{C}$ , the viscosity of E51 declined to 1 Pa s, and that of BI-E51 declined to 45 Pa s. The viscosity of UPy-E51 was significantly reduced, but its viscosity was still much higher than that of E51 and BI-

E51. The UPy-E51 was obtained by introducing the UPy group to pure resin. The viscosity of resin and the difficulty of chain movement increased due to the existence of quadrupolar hydrogen bonding between the UPy groups.

The DSC test results indicate that the  $T_g$  of the modified matrix number reduced, as did the  $T_g$  of the cured material given the introduction of flexible chain segments in the molecular chain of the matrix resin (Fig. 1[e]). Two heat absorption peaks appeared on the DSC test curves of UPy-E51. The introduction of side chains with UPy group in the resin molecular chain increased the movement resistance of UPy-E51. The molecular chain starts to move with the increase of temperature. However, the movement range of the chain segment is limited because of the presence of quadruple hydrogen bond, so an endothermic peak occurs at  $50\text{ }^\circ\text{C}$ . As we all know, hydrogen bond is a reversible non-covalent bond. Hydrogen bond was dissociated with external stimulus (force, heat, etc). Endothermic peak of the quadrupolar hydrogen bonding appeared in the DSC curves of UPy-E51 and UPy-E51/D2000 at about  $130\text{ }^\circ\text{C}$ . Additionally, UPy-E51/D2000 for quadrupolar hydrogen bonding formed between the UPy groups.

TGA test was used to evaluate the heat resistance of M-E51/D2000 (as shown in the Fig S4). The thermal stability and thermal decomposition temperature of the M-E51/D2000 ( $T_d$  of the modified resin was about  $300\text{ }^\circ\text{C}$ ) did not change significantly compared with E51 according to the TGA curves of UPy-E51/D2000.

The UPy- and BI-modified epoxy resins, UPy-E51 and BI-E51, were cured with polyetheramine D2000 to prepare a crosslinked resin material. For comparison, pure E51 resin was cured with D2000 in the absence/presence of UPy-containing supramolecular polymer

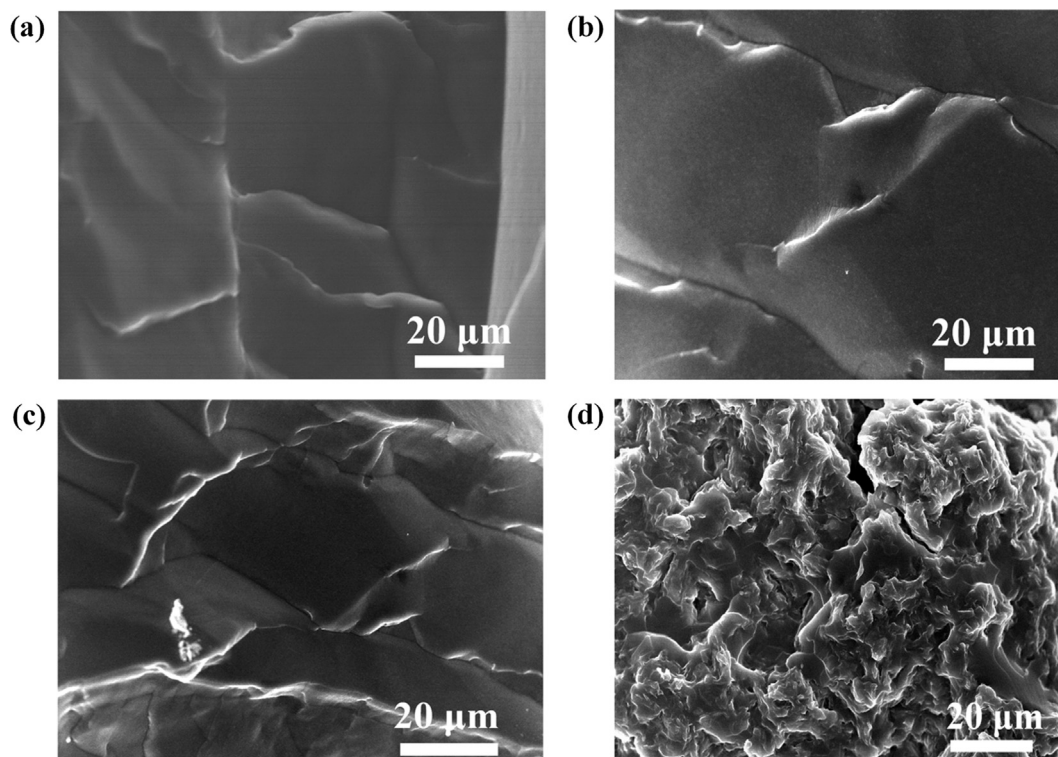


Fig. 3. SEM images of tensile fracture surfaces of (a) pure resin, (b) pure resin/D2000sp, (c) BI-E51, and (d) UPy-E51 cured materials.

(D2000sp). As shown in Fig. 2, the E51/D2000 (Fig. 2[a] 1), E51/D2000/D2000sp (Fig. 2[a] 2), and BI-E51/D2000 (Fig. 2[a] 3) were transparent, but the material was yellow due to the addition of light yellow D2000. The cured material of UPy-E51 exhibited less transparency and a beige color (Fig. 2[a] 4). Compared to pure resin, in the E51/D2000sp or BI-E51 cured material, a crystal-like region was formed during the curing process by the interaction between hydrogen bonds when the UPy group was introduced to UPy-E51. Therefore, UPy-E51/D2000 demonstrated excellent flexibility and toughness because the flexible side chain and UPy moieties were introduced in the epoxy resin.

A distortion test experiment was designed to verify our speculations, and the process and results of the distortion test are displayed in Fig. 2(b)–(e). Typically, the samples were slowly rotated by a certain angle until the material was destroyed. Samples fractured when pure E51 resin material was reversed  $720^\circ$  (Fig. 2[b]). The E51/D2000sp and BI-E51 cured material was not destroyed when twisted by  $720^\circ$  but was completely destroyed at a twist angle of  $900^\circ$  (Fig. 2[c] and [d]). Surprisingly, for the UPy-E51, the material maintained good integrity even at a twist angle of  $1080^\circ$  (Fig. 2[e]). The distortion test results illustrate that the UPy-E51 cured material showed superior flexibility compared with the other two cured materials. In addition, a flexural bending test was conducted to better demonstrate the excellent flexibility of the UPy-E51 cured material. The four materials of pure E51 resin, E51/D2000sp, BI-E51, and UPy-E51 were respectively folded in half. The pure E51 resin, E51/D2000sp, and BI-E51 cured material fractured when the folding angle reached  $170^\circ$ ; however, the UPy-E51 cured materials remained complete no matter how large the angle was (Fig. 2[e] 2). The above phenomenon manifested because internal stress could not be effectively released in the material distortion process for pure resin, pure resin/D2000sp, and BI-E51 cured material due to low crosslinking density. However, for UPy-E51, a soft segment was introduced into the resin molecular chain, and quadrupolar hydrogen bonds could form between the flexible segments so the material could maintain integrity of the crosslinked network structure when it was destroyed by external force.

A material's elongation at break is an important parameter for evaluating material flexibility. In this study, three cured materials were subjected to tensile tests using an electronic tensile machine, resulting in respective stress–strain curves; test results are presented in Fig. 2(f). The elongation at break of the UPy-E51 cured material improved by about 5 times compared with the unmodified resin cured material and BI-E51 cured material, and the tensile breaking strength increased from 0.5 MPa to 1.1 MPa. The elongation at break of the E51/D2000sp curing material was less than that of pure resin, and the breaking strength of the material was nearly unchanged. The elongation at break of the BI-E51 curing material increased slightly compared with the pure resin, and the breaking strength of the material was also nearly unchanged. These data indicate that the physical blending method pulled the system material, whereas stretch-breaking strength had little effect. This phenomenon presumably occurred because a soft segment with a UPy group was introduced into the UPy-E51 molecular chain. During the stretching process, formation of quadrupolar hydrogen bonds between the UPy groups consumed part of the energy. Remarkably, quadrupolar hydrogen bonds that formed inside the material played a role in physical crosslinking, and the introduction of flexible segments increased sliding resistance between them; thus, elongation at break and the tensile breaking strength of the material were improved simultaneously.

To study the fracture mechanism of the material, the tensile fracture surface was subjected to SEM testing as shown in Fig. 3(a)–(d). SEM photographs clearly indicate that the fracture surfaces of pure resin, pure resin/D2000sp, and BI-E51 cured material were smooth and exhibited obvious brittle fractures; the fracture surface of UPy-E51 was rough, showing a clear ductile fracture mechanism. The interactions of quadruple hydrogen bond could be formed between the UPy groups. A large number of cross-linking points and the aggregation area could be formed in the UPy-E51/D2000 with hydrogen bonds of UPy groups. The energy generated by external forces inside the material could be dissipated through the fracture of the quadruple hydrogen bond between the UPy groups and the friction of the side chain when the material was stretched. Thus the fracture mechanism of the UPy-E51/D2000 was

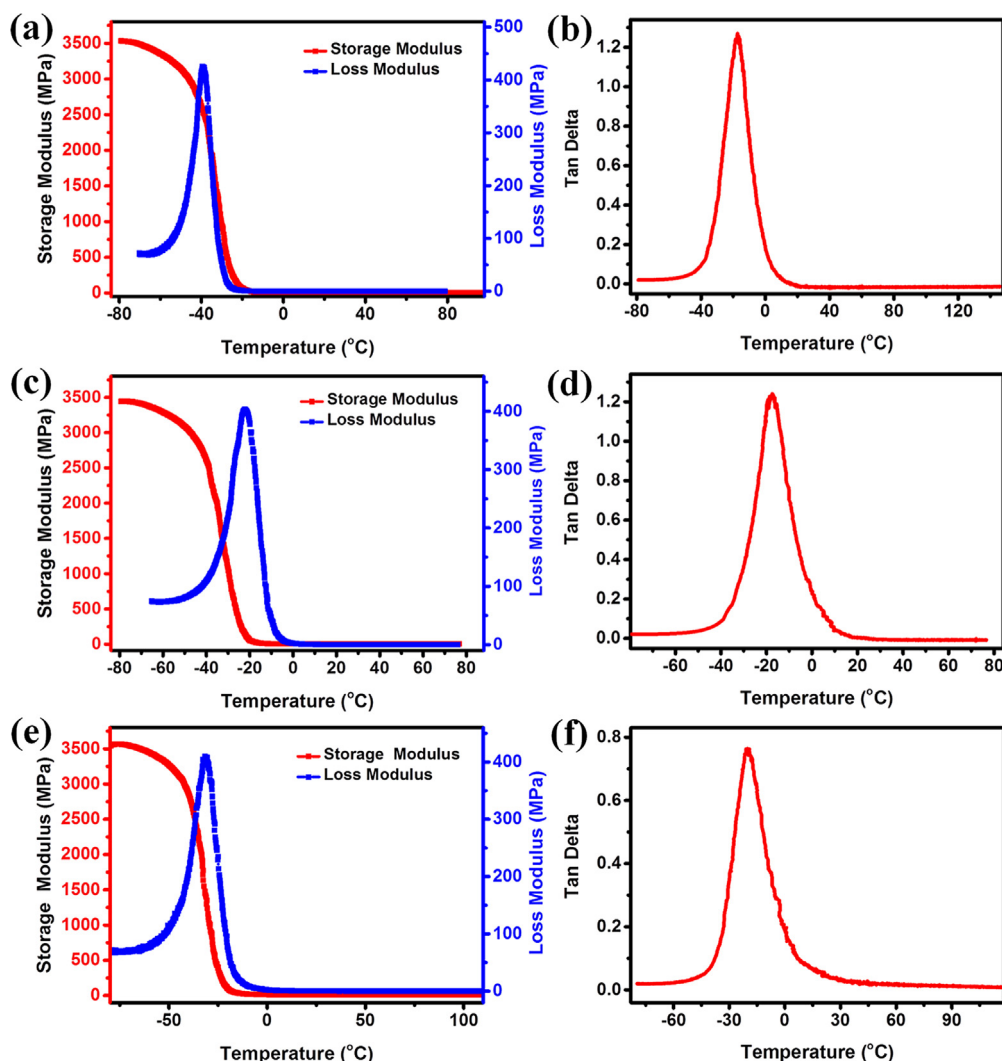


Fig. 4. Storage modulus, loss modulus and tan delta of (a, b) E51/D2000, (c, d) E51/D2000/D2000sp, and (e, f) UPy-E51/D2000.

ductile fracture. These results were fully anticipated, confirming that modifying resin via chemical grafting is an effective and feasible method. The following test samples were selected for E51, E51/D2000sp, and UPy-E51 cured material based on the above test results.

Dynamic mechanical analysis (DMA) provided specific information on the thermomechanical properties of the materials, including storage modulus ( $E'$ ; the elastic modulus of nanocomposites), loss modulus ( $E''$ ; energy dissipation associated with motion of polymer chains), and loss factor ( $\tan\delta$ ) within the measured temperature range. Data analysis with the storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss factor ( $\tan\delta$ ) for the E51/D2000, E51/D2000/D2000sp, and UPy-E51/D2000 materials is presented in Fig. 4. The  $E'$  for the E51/D2000, E51/D2000/D2000sp, and UPy-E51/D2000 materials declined with increasing temperature due to energy dissipation.

The storage modulus indicates the amount of elastic energy stored in the composite, which is correlated to mechanical properties and interfacial interaction. Compared with neat epoxy or compositions, the storage modulus of the UPy-E51/D2000 material was higher in the glassy-state region because the temperature provided sufficient energy for modified epoxy to undergo a conformation transition and promoted chain segment motion. The change in  $E'$  indicates that the stiffness of the modified resin material increased and was thus enhanced, consistent with the tensile test results.

The  $\tan\delta$  denotes the ratio of  $E''$  to  $E'$ , and the peak of  $\tan\delta$  is used to determine  $T_g$ . As shown in Fig. 4(b), (d), and (f), compared with neat

epoxy, the glass transition temperature of E51/D2000/D2000sp and modified epoxy hardly changed and revealed nearly no loss in thermodynamic properties of the modified epoxy resin.

Impact resistance is the ability of a sample to resist impact loads. The degree of damage to the product after an impact test indicates the toughening effect of the material. A TCJ Elastic impact tester was used to evaluate the impact resistance of materials in this study. The impact height of the test was 112 cm, and the mass of the impact hammer was 1000 g; results are shown in Fig. 5. The E51/D2000 and E51/D2000/D2000sp cured materials were slightly damaged after the impact test; however, the UPy-E51/D2000 material remained intact with no damage. After materials were impacted twice, the pure resin material was destroyed completely, and the composite material doped with D2000sp suffered serious damage. These materials each lost their use effect. However, only minor damage occurred for the modified resin cured material, which remained intact after three impacts.

The impact test results show that the flexible segment with the UPy group was introduced into the molecular segment of the epoxy resin, which can effectively absorb and dissipate energy of external damage to the material, effectively toughening the material and enhancing usability. We also tested material properties. Results illustrate the effectiveness of chemically modified resins in this study. We studied the toughening mechanism of modified resins as well. As depicted in Fig. 6, the resin reacted with the curing agent to form a crosslinked network. Without application of an external stimulus, the molecular chain

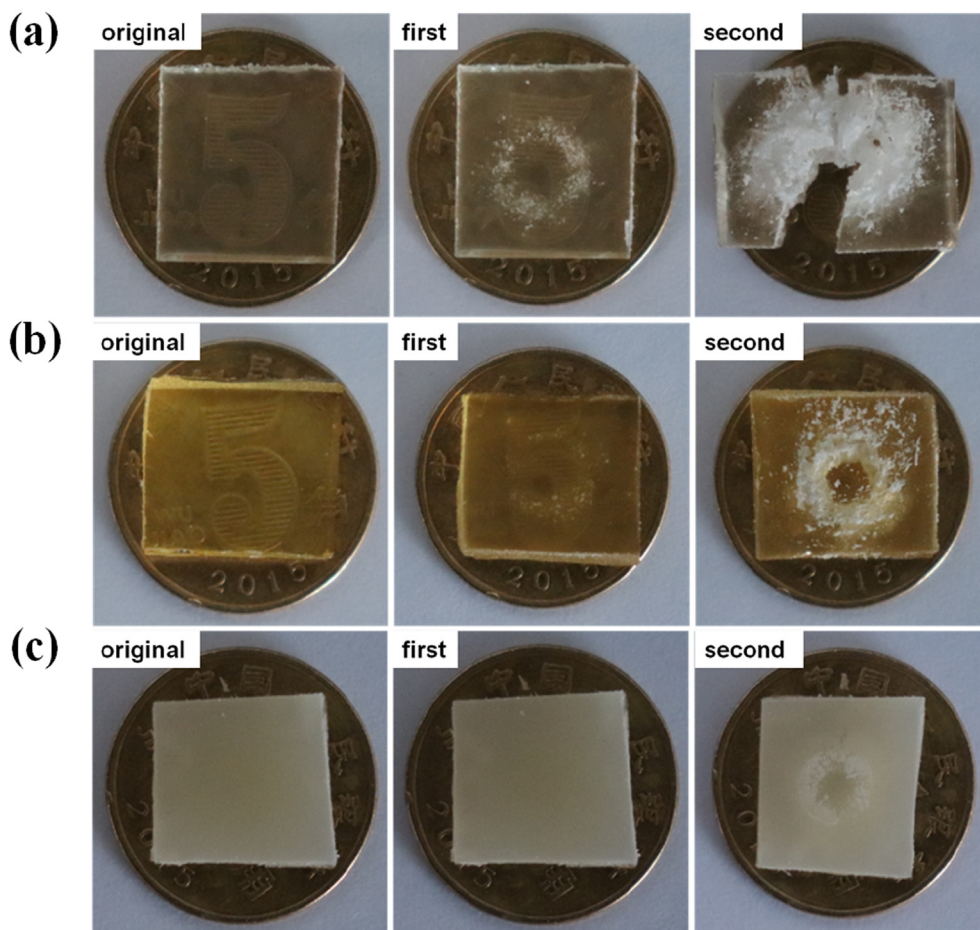


Fig. 5. Impact resistance of (a) E51/D2000, (b) E51/D2000/D2000sp, and (c) UPy-E51/D2000.

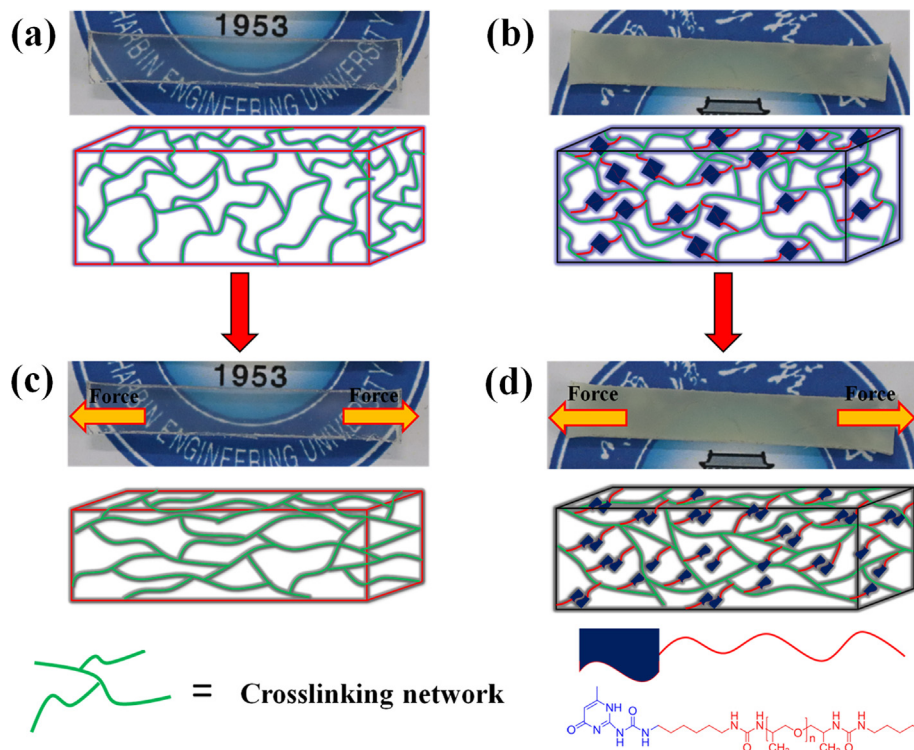


Fig. 6. Mechanism diagram of chemically modified resin toughening.

segments were in a twisted state. Under stimulation from external forces, the original molecular twist of the material could be resolved. The material was destroyed when stretched to a certain extent. As shown in Fig. 6(b) and (d), the molecular chain of the modified resin encountered a soft segment with the UPy group, and quadrupolar hydrogen bonds formed between UPy groups during material solidification. A bridge-like structure formed between internal crosslinked networks of the material due to quadrupolar hydrogen bonds. When the material was subjected to external stimuli such as pulling force, the four hydrogen bonds of the material were broken. The soft segment introduced into the resin molecular segment blocked segment movement, thereby toughening the modified resin.

#### 4. Conclusion

We successfully grafted a soft segment with a UPy group onto a resin molecular segment via a chemical method and prepared the modified epoxy resin M-E51. The elongation at break of the modified resin was 5 times that of the unmodified resin. The fracture tensile strength of the material increased from 0.3 MPa to 1.3 MPa. During the curing process, four hydrogen bonds formed between UPy groups. When the material was subjected to a pulling force, breakage of the four hydrogen bonds and introduction of the soft chain blocked movement of the crosslinking network, thus pulling the modified resin. Stretch-breaking strength and elongation at break increased simultaneously. The results of this study indicate that the chemically modified resin is an extension of resin modification technology and shows promise for a range of resin-related applications.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2019.04.001>.

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