Chinese Journal of Polymer Science Vol. 35, No. 6, (2017), 728−738

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2017

Thermo-reversible MWCNTs/Epoxy Polymer for Use in Self-healing and Recyclable Epoxy Adhesive*

Ya-kun Guo[a], Han Li[b], Peng-xiang Zhao[a], Xiao-fang Wang[a], Didier Astruc[c] and Mao-bing Shuai[a**]

[a] *Institute of Materials, China Academy of Engineering Physics, Jiangyou 621908, China*
[b] *Department of Materials, Southwest University of Science and Technology, Mianyang 621010, China*
[c] *Institut des Sciences Moleculaires, University Bordeaux, 351 Cours de la Liberation, Talence Cedex 33405, France*

Abstract A self-healing and recyclable carbon tube/epoxy adhesive was prepared by epoxy monomer with Diels-Alder (DA) bonds, diethylenetriamine and polyethyleneimine modified multi-wall carbon nanotubes (MWCNTs). The self-healing and recyclable ability was attained by thermally reversible Diels-Alder reaction between furan and maleimide in the epoxy monomer. By controlling the molar ratio of furfuryl glycidyl ether and 4,4′-methylenebis(*N*-phenylmaleimide), the glass transition temperature and mechanical properties of MWCNTs/epoxy adhesives were varied. The self-healing properties of MWCNTs/epoxy polymers were evaluated by lap shear experiment and the results showed that the MWCNTs/epoxy adhesives exhibited enhanced mechanical properties and excellent self-healing ability under heat stimulus. The healing efficiency was related to the molecule mobility and the conversion of DA reaction between furan and maleimide. The MWCNTs/epoxy adhesives also displayed excellent recyclable ability by transforming into soluble polymer under heating. These materials offer a wide range of possibilities to produce materials with healing and recyclable ability and have the potential to bring great benefits to our daily lives by enhancing the safety, performance, and lifetime of products.

Keywords Self-healing; Recyclable; Epoxy adhesives; MWCNTs; Diels-Alder reaction

Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s10118-017-1920-y.

INTRODUCTION

Epoxy resin, as the most commonly used thermosetting resin, has been widely used in fibre-reinforced composite materials, coatings, adhesives, electronics, and aerospace, due to its high tensile strength, low shrinkage, good chemical and corrosion resistance[1−3]. However, they are susceptible to damage under stress due to its brittleness, which leads to a sharp decrease in their sustainability, safety, and lifetime[4, 5]. Crack damages, even at its microscopic scales, would lower the mechanical properties. Thus, exploring self-healing polymeric materials that can repair themselves after mechanical damage is in high demand.

In the past decades, scientists have paid great attention to develop self-healing polymeric materials[6−8]. The methods include extrinsic self-healing and intrinsic self-healing[9]. Intrinsic self-healing, due to reversible covalent or noncovalent bonds present in the polymeric matrix, has attracted a lot of interest[10, 11]. Diels-Alder

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51573172, 11405149 and 51401187), the Science and Technology Planning Project of Sichuan Province (No. SCXSDTR15001) and Director's Funds of China Academy of Engineering Physics (No. SJZ201506).
** Corresponding author: Mao-bing Shuai (帅茂兵), E-mail: shuaimaobing@caep.cn
Received November 15, 2016; Revised December 8, 2016; Accepted December 15, 2016
doi: 10.1007/s10118-017-1920-y

(DA) reaction between furan and maleimide moieties has been the most promising method for intrinsic self-healing polymer, because it could form strong dynamic covalent bonds and be repeatedly healed through only the application of heat[12–18]. For instance, Bai *et al.*[19] and Kuang *et al.*[20] have prepared a cross-linked epoxy system based on the diglycidyl ether of bisphenol A (DGEBA) and a new diamine cross-linker which processes DA bond in its molecule. Tian *et al.*[15] and Min *et al.*[21] reported the self-healing and recyclable epoxy polymer prepared with the thermal reversible epoxy monomer with DA bonds. But the epoxy polymer based on thermal reversible epoxy monomer was brittle[21]; the mechanical property and the toughness need to be further improved.

Carbon nanomaterials, which show good compatibility with polymeric materials due to their large π-conjugated system, have been widely used as efficient fillers in fabrication of mechanical enhanced self-healing polymer materials because of their ultrahigh mechanical strength[22–25]. For example, Kuang *et al.*[24] have reported that the Young's modulus and toughness of self-healing rubber were enhanced by 200%–300% *via* adding 5 wt% furfurylamine (FA) modified multi-wall carbon nanotube (MWCNT) into the rubber substrate. Meanwhile, the healing efficiency also increased with the increase of MWCNT-FA content. Li *et al.*[25] reported that by incorporating 0.1 wt% covalently bonded graphene oxide (GO) into polyurethane polymer, the mechanical properties and thermally healable capability increased significantly by DA reaction. Despite these advances, to the best of our knowledge, few reports are available until now about the use of MWCNT as functional nanofiller for high-performance self-healing epoxy adhesive.

Here, we report a self-healing and recyclable carbon tube/epoxy adhesive with enhanced mechanical properties by incorporating the polyethyleneimine (PEI) modified MWCNTs into epoxy adhesive with DA bonds. The preparation process is illustrated in Scheme 1. The thermally reversible epoxy monomer was synthesized by furfuryl glycidyl ether (FGE) and 4,4′-methylenebis(*N*-phenylmaleimide) (DPMBMI). MWCNTs were modified by PEI, a branched polymer with plentiful amine groups on its molecular chains, by covalent linkage. MWCNTs/epoxy adhesive was prepared by mixing the epoxy monomer with DA bonds, diethylenetriamine (DETA) and PEI modified MWCNTs and cured at 25 °C for 96 h and 60 °C for 12 h. Different from the conventional self-healing polymeric materials, this MWCNTs/epoxy self-healing adhesive not only possesses enhanced mechanical properties but also can be multiple self-healing and recyclable.

EXPERIMENTAL

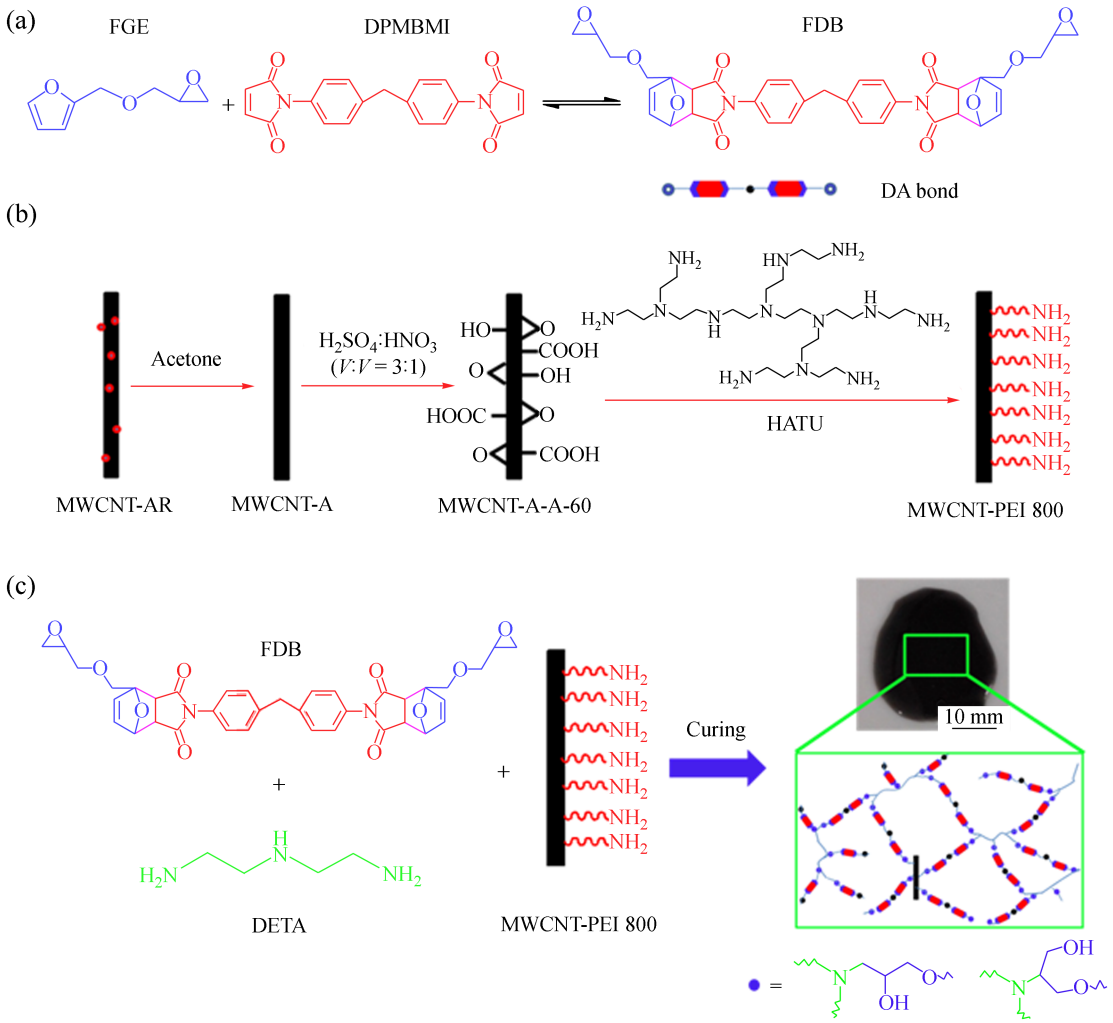
Materials

Furfuryl glycidyl ether (FGE, 97 wt%) and 4,4′-methylenebis(*N*-phenylmaleimide) (DPMBMI, 95 wt%) were purchased from J&K Scientific Ltd. Polyethyleneimine (PEI, M_w = 800), diethylenetriamine (DETA, A.R.) and 1-(bis(dimethylamino)methylene)-1*H*-1,2,3-triazolo(4,5-b)pyridinium 3-oxid hexafluorophosphate (HATU) were purchased from Aladdin Reagent Ltd. Sulfuric acid (H_2SO_4, A.R. 95 wt%–98 wt%), nitric acid (HNO_3, A.R. 67 wt%), *N*,*N*-dimethylformamide (DMF, A.R.) and all the other solvents were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Multi-wall carbon tubes (MWCNTs, Brand JCMT-999-11-10) were bought from Nanjing Jicang Nano. Tech. Ltd. The technical parameters are shown in Table S1 (in supporting information, SI). All solvents and the above reagents were used as received without further purification.

Synthesis of Thermally Reversible Epoxy Monomer

2,2′-(Methylenebis(4,1-phenylene))bis(4-((oxiran-2-ylmethoxy)methyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione) (FDB) was synthesized by a one-step method according to Min *et al*[21]. The detailed experimental procedure is described as follows: 14.28 g (0.04 mol) of DPMBMI was dissolved in 100 mL of anhydrous tetrahydrofuran (THF). The solution was charged into a 250 mL three-necked round-bottom flask equipped with magnetic stirring, a condenser and a thermometer. 12.32 g (0.08 mol) of FGE was then slowly dropped into the solution by a constant dropping funnel. Afterward, the solution was refluxed at about 66 °C for 24 h under a N_2 atmosphere and then cooled down to room temperature. The reaction solution was dropped into

a large excess amount of diethyl ether. The precipitate was filtered and then dried under vacuum at room temperature. The obtained powder was dissolved in 10 mL of acetone and poured into 1000 mL of diethyl ether again. Finally, the precipitate was filtered and dried under vacuum at room temperature to obtain the light yellow powder product.



Scheme 1 Schematic diagram showing the overall processing required for the preparation of MWCNTs/epoxy adhesives: (a) Synthesis of 2,2′-(methylenebis(4,1-phenylene))bis(4-((oxiran-2-ylmethoxy)methyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione) (FDB); (b) The modification process of MWCNTs by PEI 800; (c) Preparation of MWCNTs/epoxy adhesives embedded with DA bonds

Modification of MWCNTs by PEI 800

Oxidation of MWCNTs

To remove the commercial sizing, the commercially received carbon tubes (MWCNT-AR) were first refluxed in acetone for 48 h and then dried in a vacuum oven at 80 °C overnight. The washed MWCNTs were denoted as MWCNT-A. Subsequently, a mixture consisting of concentrated sulfuric acid and concentrated nitric acid with a volume ratio of 3:1 was poured into a three-necked flask and heated to 60–65 °C. MWCNT-A was then soaked in the acid mixture and the reaction was carried out for 60 min[26, 27]. Accordingly, the obtained products were named as MWCNT-A-A-60.

Modification of MWCNTs with polyethyleneimine

0.1 g of PEI 800 was added into 50 mL of anhydrous DMF in a glass vial. HATU (5 mg) was then added into diluted PEI solution and 1 g of MWCNT-A-A-60 was added. The vial was placed in oil bath and maintained at 120 °C for 12 h. The final modified MWCNTs were obtained and denoted as MWCNT-PEI 800.

Preparation of the Epoxy and MWCNTs/Epoxy Adhesives with DA Adduct

Epoxy adhesives with different furan and maleimide molar ratio were synthesized from the curing reaction of the mixture of FDB and FGE with DETA. First, FDB was mixed with FGE to form uniform mixture by changing the molar ratio of furan and maleimide (F/M). The F/M ratio was set to 1/1, 1.25/1, 1.5/1, 1.75/1, 2/1 or 2.5/1, and the obtained mixtures are designated as FDB-1, FDB-2, FDB-3, FDB-4, FDB-5 and FDB-6. Then the epoxy adhesives were prepared by mixing the mixture of FDB and DETA and cured at 25 °C for 96 h and 60 °C for 12 h. The epoxy adhesive prepared by FDB-1 and DETA needed some 1,2-dichloroethane (CH_2Cl_2) in order to dissolve the FDB-1 power. The accordingly epoxy adhesives were designated as EP-1, EP-2, EP-3, EP-4, EP-5 and EP-6. The MWCNTs/epoxy adhesives were prepared according to the above process except for adding MWCNT-PEI 800 into DETA curing agent first. The obtained MWCNTs/epoxy adhesives were designated as CNT-EP-1, CNT-EP-2, CNT-EP-3, CNT-EP-4, CNT-EP-5 and CNT-EP-6.

Measurement and Characterization

The chemical composition and molecular structure of FGE, DPMBMI, the mixture of FGE and DPMBMI before refluxing and refluxing for 24 h were characterized by Fourier transform infrared spectrometer (FTIR, Bruker Vertex 70). The mixture solution in acetone (0.02 g/mL) was coated on the surface of a KBr tablet, and then the FTIR spectrum was collected after the tablet had been dried at room temperature. The spectra were recorded in the range of 4000–400 cm^{-1}. ^1H and ^{13}C nuclear magnetic resonance (^1H- and ^{13}C-NMR) spectra were obtained on a Bruker Advance 600 MHz spectrometer with tetramethylsilane (TMS) as internal standard using DMSO-d_6 as the solvent. The curing reaction of FDB and DETA, the thermal reversible reaction of FDB and epoxy adhesive was monitored by *in situ* FTIR spectra (Bruker Vertex 70). The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Mettler Toledo DSC 3+ STAR^e System). The surface chemical composition of MWCNTs was characterized by X-ray photoelectron spectroscopy (XPS), which was recorded on an Axis Ultra spectrometer (ESCALAB 250) with a monochromated Al Kα X-ray source (1486.7 eV) operating at 15 kV. For hydrocarbons, the C1s line centered at 284.8 eV was taken as the indicator to calibrate the binding energy for XPS measurements. Raman spectra of MWCNTs were recorded using a HORIBA Scientific XploRA PLUS spectrometer with laser excitation source of 532 nm. The morphology of MWCNTs and their dispersion in epoxy adhesive was characterized by transmission electron microscopy (TEM, FEI TITAN). The fractured planes of epoxy adhesive and MWCNTs/epoxy adhesive were observed by field emission scanning electron microscopy (FESEM, FEI Helios Nanolab 600i). Prior to observation, the samples were sputter-coated with gold. The self-healing property was measured by lap shear strength in accordance with ISO 9664–1995. The bonded area was 25 mm × 12.5 mm. The thickness of epoxy adhesive and MWCNTs/epoxy adhesive was about 300 μm controlled by glass beads. Five specimens were tested for each set of conditions and the mean values and their standard deviations were calculated. The recyclable property was evaluated by solubility experiment.

RESULTS AND DISCUSSION

Preparation of Thermo-reversible Epoxy Adhesive and MWCNTs/Epoxy Adhesive

Epoxy resin (FDB) with two DA covalent bonds and two oxirane groups was synthesized by [4+2] cycloaddition of FGE with DPMBMI in refluxed THF (66 °C) for 24 h[21]. FTIR (Fig. S1 in SI) and NMR spectroscopy (Figs. S2–S4 in SI) confirmed that significant DA adduct have been formed and the conversion was about 90%. The thermo-reversible of FDB was tested by *in situ* FTIR (Fig. S5 in SI) and ^1H-NMR (Fig. S6 in SI) spectra. The results identified DA reaction with thermal repeatability. Epoxy adhesives with different furan and maleimide molar ratio were synthesized from the curing reaction of the mixture of FDB and FGE with DETA. The curing reaction of FDB-1 and DETA (with stoichiometric ratio of 1:1) was monitored by *in situ* FTIR

spectrometer and the spectra are shown in Fig. 1. As is shown in Fig. 1, the peaks attributed to the epoxide groups at 903 cm^{-1} (oxirane ring breathing) gradually decreased, indicating that epoxide groups have reacted with amine groups of DETA to form epoxy networks. A characteristic peak of hydroxyl groups emerges at 3396 cm^{-1} as a result of this reaction. Besides, the DA reaction of furan and maleimide groups in the cured sample is also proved by the existence of the peak at 1776 cm^{-1}. The curing reaction mechanism was illustrated in Fig. S7 (in SI).

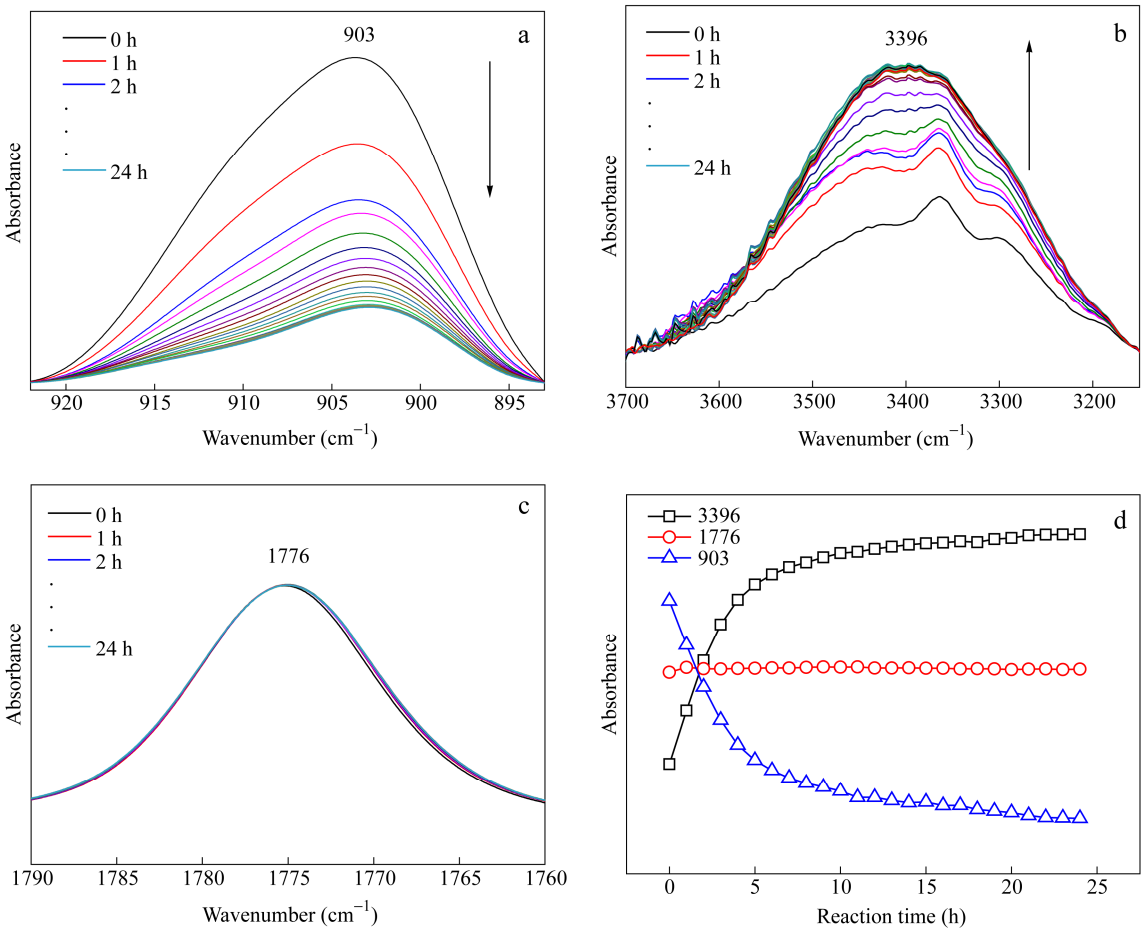


Fig. 1 *In situ* FTIR spectra of FDB and DETA: (a) epoxide group, (b) hydroxyl group, (c) DA peak (C=C), (d) the absorbance intensity change of the above characteristic peaks with reaction time

In order to reveal how the DA bonds behave under thermal stimulus, *in situ* heating FTIR spectra and DSC of the cured EP-1 polymer were recorded (Fig. 2). From Fig. 2(a), it can be seen that the peaks at 1776 cm^{-1} (C=C in DA adduct) and 1191 cm^{-1} (C—C in DA adduct) decrease gradually with increasing temperature, which indicates that the DA adduct in the epoxy adhesive has been decomposed. Accordingly, the peaks at 1018 cm^{-1} (ring breathing and ether linkage in furan ring) and 1149 cm^{-1} (absorption of C—N—C in maleimide ring) increase until to 120 °C, and then decrease due to the self-polymerization of maleimide or furan[15]. The thermal reversibility of epoxy adhesives was also evaluated by DSC curves (Fig. 2b). The first heating trace shows a glass transition at *ca.* 94.18 °C and an endothermic peak at 127 °C as a result of the retro-DA (rDA) reaction. Because there is not enough time for the recovered furan and maleimide moieties to be reconnected during the subsequent cooling and reheating processes, the consecutive cooling and second heating processes exhibited nearly flat curves. The rDA reaction mechanism is shown in Fig. S8 (in SI).

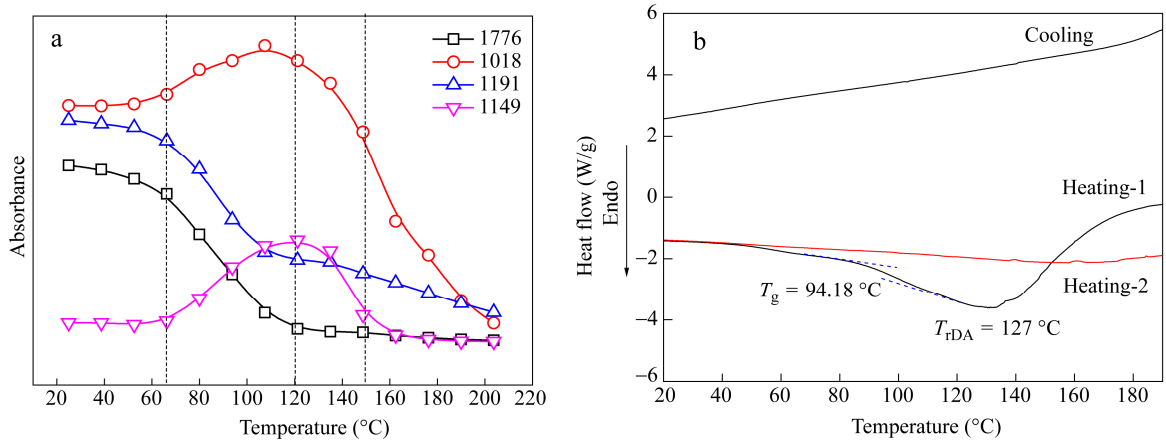


Fig. 2 (a) *In situ* FTIR spectra of different peaks between 25 and 200 °C; (b) DSC result of the cured epoxy polymer EP-1 reacted at 25 °C for 96 h and 60 °C for 12 h (N_2 atmosphere, 10 K/min)

In the above discussion, the thermal reversibility of the epoxy adhesive is verified. In order to prepare self-healing and recyclable epoxy adhesive with enhanced mechanical property, PEI modified MWCNTs were introduced. The MWCNTs were firstly washed by acetone to remove the impurities, then soaked in strong acid for 60 min to graft oxygen groups and finally treated with 10 wt% branched PEI 800 to obtain functionalized MWCNTs (as exhibited in Scheme 1b). The modification of MWCNTs is measured by Raman spectroscopy (Fig. S9 in SI), XPS spectra (Figs. S10 and S11 in SI) and TEM images (Fig. S12 in SI), which identified that active chemical groups have been efficiently introduced onto the surface of MWCNTs. Then, MWCNTs/epoxy adhesives were prepared by filling 1 wt% MWCNT-PEI 800 into the epoxy polymer with different F/M ratio. The dispersion of MWCNT and MWCNT-PEI 800 in epoxy polymer was observed by TEM, and the images are shown in Fig. 3.

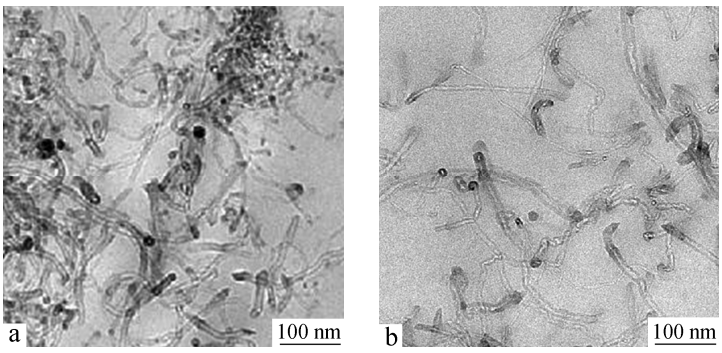


Fig. 3 TEM images of epoxy adhesive filled with (a) MWCNTs and (b) MWCNT-PEI 800

It can be seen that the MWCNT-PEI 800 were dispersed uniformly in epoxy adhesive. This phenomenon is the result of the increased interfacial bonding between PEI modified MWCNTs and epoxy matrix[26]. Good dispersion of MWCNT-PEI 800 in the epoxy matrix reduces the stress concentration and enhances uniformity of stress distribution. As a result, PEI modified MWCNTs/epoxy composites show better mechanical properties compared to the pure epoxy polymer. These experimental findings are in agreement with the available data in the literature[28].

Mechanical Properties of Epoxy Adhesive and MWCNTs/Epoxy Adhesive

The T_g of epoxy adhesive and MWCNTs/epoxy adhesive with different F/M ratio was determined by DSC and the results are shown in Fig. 4 and Table S2 (in SI). The T_g of epoxy polymer with different F/M ratio were

94.18, 68.45, 45.99, 38.75, 35.65 and 25.29 °C, and the T_g of MWCNTs/epoxy polymer were 97.23, 72.88, 57.43, 44.24, 38.72 and 27.45 °C, which decreased drastically with increase of the ratio of F/M. The decrease of T_g is attributed to the reduction of cross-link density. Meanwhile, the addition of MWCNT-PEI 800 to epoxy polymer made some increase of T_g because of the hinder effect[29].

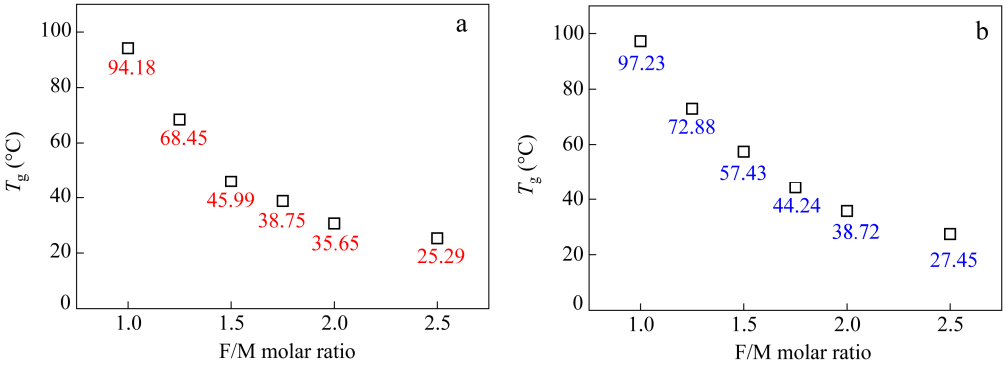


Fig. 4 T_g value of (a) epoxy adhesive and (b) MWCNTs/epoxy adhesive with different F/M ratio

The shear properties of epoxy polymer and MWCNTs/epoxy adhesive are shown in Fig. 5. It can be seen that the shear strength first increases and then decreases with the increase of F/M ratio. The maximum value is obtained at the F/M = 1.5. The lower shear modulus of F/M = 1.0 and 1.25 than that of F/M = 1.5 is attributed to the interfacial fracture mode. Above 90% and 72% of the epoxy and MWCNTs/epoxy adhesive with F/M = 1.0 and 1.25 were interfacial fracture, while most of epoxy and MWCNTs/epoxy adhesives with F/M = 1.5–2.5 were cohesive fracture. Cohesive fracture is conducive to absorb a lot of stain energy and increase the shear strength. The decrease in shear strength of F/M = 1.5 to 2.5 is coincided with the decrease of their T_g, which is attributed to the decrease of cross-linking density of epoxy polymer. The shear data indicate that the mechanical properties, T_g and cross-link density of epoxy adhesive could be controlled by changing the molar ratio of furan and maleimide.

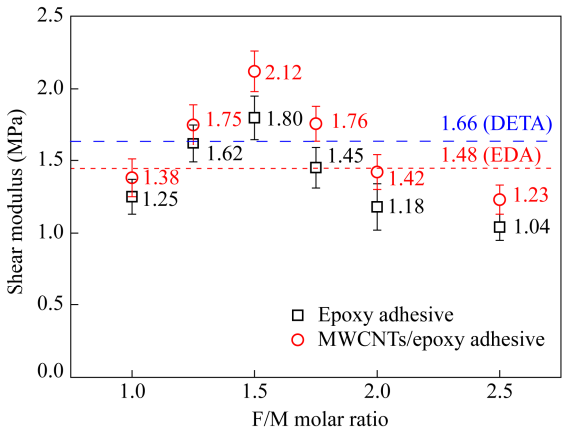


Fig. 5 Shear strength of epoxy and MWCNTs/epoxy adhesives with different F/M ratio

The fractured planes of epoxy adhesive and MWCNTs/epoxy adhesive were observed by SEM and the images are shown in Fig. 6. It can be seen that the fractured plane of epoxy adhesive was smooth and with a river shape, which meant that a brittle fracture happened. After filling with the PEI modified MWCNTs, a rough surface was observed, which indicated that a lot of stain energy was absorbed by PEI modified MWCNTs.

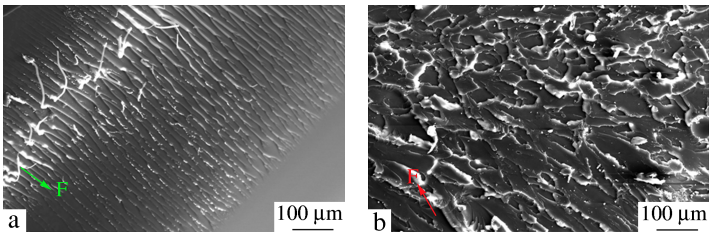


Fig. 6 SEM images of (a) epoxy adhesive and (b) epoxy adhesive filled with MWCNT-PEI 800

Self-healing Properties of Thermo-reversible MWCNTs/Epoxy Adhesive

The self-healing behaviour of MWCNTs/epoxy adhesives was analysed by lap shear experiment with a tensile testing machine. First, the bonded samples were torn into two pieces. Immediately after that, the broken surfaces were put into contact under 1 kN load and healed under different conditions (Fig. S13 in SI). The healing conditions were 25 °C for 7 days, 70 °C for 24 h or 120 °C/30 min and 70 °C for 24 h. In the first healing condition (25 °C for 7 days), the cleaved DA bond could not be bonded together due to the low temperature. Hence, the healing is originated from viscous flow and entanglement of molecule chains. In the second healing condition (70 °C for 24 h), the cleaved DA bond could reform together and heal the fracture planes. So the healing efficiency is originated from the effect of viscous flow and DA reaction. Under the third healing condition (120 °C/30 min and 70 °C for 24 h), the specimens were heated up to a temperature above the cleaving temperature so that the unbroken bonds could separate into two individual molecules. This allowed for a greater chance to heal the fracture planes when undergoing the DA reaction since polymer cannot return the crack faces into its exact prior condition to allow the formation of identical bonds. Therefore, the healing efficiency is produced by the viscous flow and higher DA healing effect. The healing efficiencies under different healing condition are shown in Fig. 7 and Table S3 (in SI).

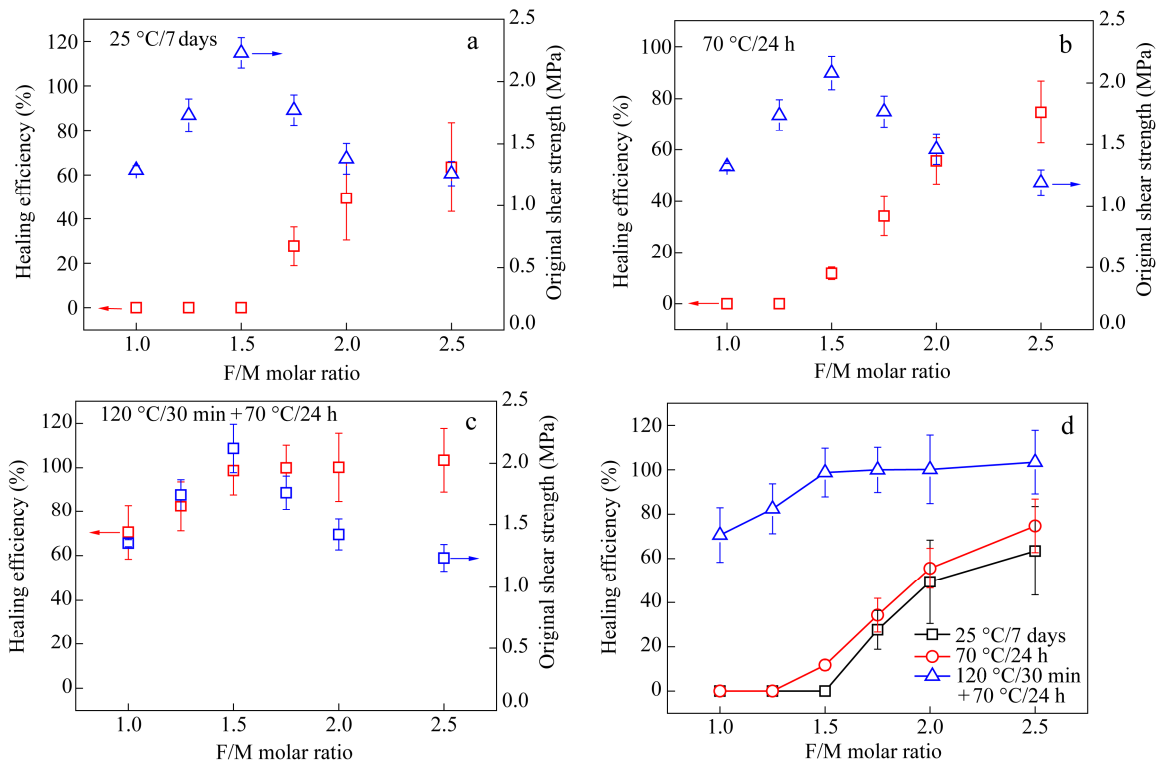


Fig. 7 The healing efficiency of MWCNTs/epoxy adhesives with different F/M molar ratio at different healing conditions

As is shown in Figs. 7(a)–7(c), the healing efficiency increases with the increase of F/M molar ratio under different healing conditions, which indicates that decreasing T_g (*i.e.*, increasing the molecule mobility) helps to increase the healing efficiency. For example, average healing efficiency of 103.4% ± 14.3% was achieved for the molar ratio of F/M = 2.5 system, which has a room temperature T_g, whereas a healing efficiency of 0 is observed for the molar ratio of F/M = 1 system (T_g = 97.23 °C). Compared with the healing efficiency under different healing conditions, it can be seen that the healing efficiency increases with the healing temperature. At 25 °C, the MWCNTs/epoxy adhesives with high T_g presented no healing efficiency (For example, MWCNTs/epoxy adhesives with F/M = 1.0 and 1.5). When the healing temperature was increased to 70 °C, the healing efficiency of MWCNTs/epoxy adhesives with F/M = 1.5–2.5 increased. Increasing the healing temperature to 120 °C, all the epoxy adhesives present better healing efficiencies. Lafont *et al.* also observed a temperature-dependence to healing of thermoset rubbers containing disulfide bonds[30]. The relationship of healing efficiency with temperature and T_g results from the amount of time the specimen remains in a viscous state. Higher temperature and longer time are conducive for the healing of epoxy polymer with low T_g, because it increases the probability that a maleimide and furan will come into contact and subsequently react to form DA bond. Time required for full recovery of properties decreases with increasing temperature and increases with increasing T_g. Chain and network flexibility is also important in decreasing time to achieve full recovery, although the importance of mobility on recovery time becomes much less pronounced as the healing temperature increases. From the above discussion, it is reasonable to think that the healing efficiency is influenced not only by the viscous flow of molecular chain but also by the contact chance between furan with maleimide and the conversion of DA reaction. Therefore, the healing efficiency of MWCNTs/epoxy adhesives with different F/M ratio at different healing conditions represents the total healing efficiency of viscous flow and DA reaction.

To explore this behavior further, we combined the results for specimens with varied T_g values in Fig. 4(b) with the data set of Fig. 7(d). Healing efficiency was plotted versus $T - T_g$, where T is the testing temperature and the results are given in Fig. 8. Data from Fig. 8 show an increase in healing efficiency with increasing $T - T_g$ (decreasing T_g); however, the specimens tested at a higher temperature display strong deviation from this behavior. Specimens with high T_g vitrify at low temperatures and need more time to be in a mobile state. When $T > T_g$, furans have significantly more mobility and are more likely to bond with maleimides at the interface. Therefore, increasing the temperature or decreasing the T_g should both result in increased bonding at the interface. However, since furans and maleimides are bonded through a thermo-reversible reaction, there is a competing phenomenon of decreasing equilibrium Diels-Alder adduct with increased temperatures. As a result, lowering T_g is a more effective way of increasing healing efficiency.

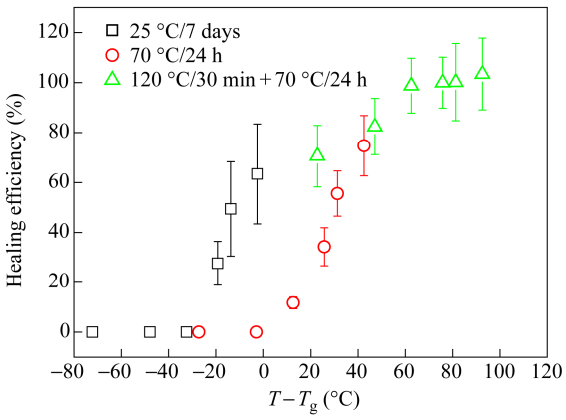


Fig. 8 Healing efficiency as a function of $T - T_g$ where T is the testing temperature

Recyclable Properties of Thermo-reversible Epoxy Adhesive and MWCNTs/Epoxy Adhesive

In addition to self-healing property, the re-solubility is also meaningful to the crosslinked epoxy adhesives. The

cross-linked epoxy adhesives and MWCNTs/epoxy adhesives were insoluble in dimethyl sulfoxide (DMSO) at 25 °C (Fig. 9a) and became readily soluble after being heated at 120 °C (Fig. 9b). Therefore, the FDB could be utilized as a new class of thermally reversible cross-linked polymers which reserve its properties at low temperatures and show removability and solubility at high temperatures and this means that the resins could be reused and recycled.

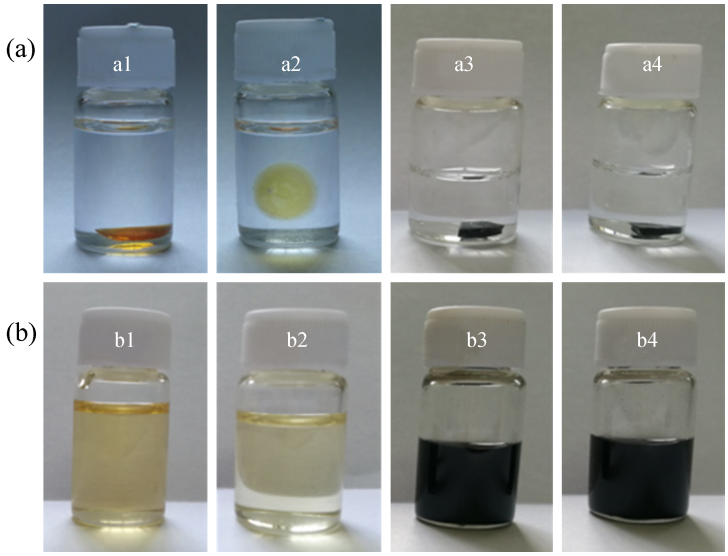


Fig. 9 Epoxy adhesives and MWCNTs/epoxy adhesives with different F/M ratio in DMSO: (a) 24 h at 25 °C, (b) 30 min at 120 °C; 1: EP-1, 2: EP-3, 3: CNT-EP-1, 4: CNT-EP-3

CONCLUSIONS

A self-healing and recyclable carbon tube/epoxy adhesive with enhanced mechanical property was prepared by epoxy monomer with DA bonds, diethylenetriamine and polyethyleneimine modified MWCNTs. The T_g of epoxy adhesives and MWCNTs/epoxy adhesives decreased with the increase of the molar ratio of furfuryl glycidyl ether and 4,4′-methylenebis(*N*-phenylmaleimide). The shear strength first increased and then decreased with the F/M ratio, and a maximum value was obtained at F/M of 1.5. The healing efficiency increased with increasing molar ratio of F/M and decreased with increasing T_g. The results indicated that the healing temperature and molecular mobility play an important role in the formation of DA adducts, as DA bond formation is effectively halted upon vitrification of the polymer network. In the future, the effect of MWCNTs on the self-healing and recyclable properties of epoxy adhesives under far-IR heating will be studied.

REFERENCES

1 Goodman, S.W., “Handbook of thermoset plastics”, access online *via* Elsevier, 1999, p. 23
2 Blaiszik, B.J., Kramer, S.L.B., Olugebefola, S.C., Moore, J.S., Sottos, N.R. and White, S.R., Annu. Rev. Mater. Res., 2010, 40: 179
3 Wu, D.Y., Meure, S. and Solomon, D., Prog. Polym. Sci., 2008, 33: 479
4 Diesendruck, C.E., Sottos, N.R., Moore, J.S. and White, S.R., Angew. Chem. Int. Ed., 2015, 54: 2
5 Stoddart, A., Nat. Rev. Mater., 2016, 1: 16004
6 Huang, L., Yi, N.B., Wu, Y.P., Zhang, Y., Zhang, Q., Huang, Y., Ma, Y.F. and Chen, Y.S., Adv. Mater., 2013, 25: 2224
7 White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N. and Viswanathan, S., Nature, 2001, 409: 794

8 Roy, N., Bruchmann, B. and Lehn, J.M., Chem. Soc. Rev., 2015, 44(11): 3786
9 Hager, M.D., Greil, P., Leyens, C., Zwaag, S.V.D. and Schubert, U.S., Adv. Mater., 2010, 22: 5424
10 Yang, Y. and Urban, M.W., Chem. Soc. Rev., 2013, 42: 7446
11 Kloxin, C.J. and Bowman, C.N., Chem. Soc. Rev., 2013, 42: 7161
12 Pratama, P.A., Sharifi, M., Peterson, A.M. and Palmese, G.R., ACS Appl. Mater. Interfaces, 2013, 5: 12425
13 Zeng, C., Seino, H., Ren, J., Hatanaka, K. and Yoshie, N., Macromolecules, 2013, 46: 1794
14 Rivero, G., Nguyen, L.T.T., Hillewaere, X.K.D. and Du, P.F.E., Macromolecules, 2014, 47: 2010
15 Tian, Q., Yuan, Y.C., Rong, M.Z. and Zhang, M.Q., J. Mater. Chem., 2009, 19: 1289
16 Heo, Y.S. and Sodano, H.A., Adv. Funct. Mater., 2014, 24: 5261
17 Liu, Y.L. and Chuo, T.W., Polym. Chem., 2013, 4: 2194
18 Barthel, M.J., Rudolph, T., Teichler, A., Paulus, R.M., Vitz, J., Hoeppener, S., Hager, M.D., Schacher, F.H. and Schubert, U.S., Adv. Funct. Mater., 2013, 23: 4921
19 Bai, N., Saito, K. and Simon, G.P., Polym. Chem., 2013, 4: 724
20 Kuang, X., Liu, G.M., Dong, X. and Wang, D.J., Macromol. Mater. Eng., 2016, 301: 535
21 Min, Y.Q., Huang, S.Y., Wang, Y.X., Zhang, Z.J., Du, B.Y., Zhang, X.H. and Fan, Z.Q., Macromolecules, 2015, 48: 316
22 Byrne, M.T. and Gun'ko, Y.K., Adv. Mater., 2010, 22(15): 1672
23 Schwenke, A.M., Hoeppener, S., Ulrich, S. and Schubert, U.S., Adv. Mater., 2015, 27(28): 4113
24 Kuang, X., Liu, G.M., Dong, X., Liu, X.G., Xu, J.J. and Wang, D.J., J. Polym. Sci., Part A: Polym. Chem., 2015, 53: 2094
25 Li, J.H., Zhang, G.P., Deng, L.B., Zhao, S.F., Gao, Y.J., Jiang, K., Sun, R. and Wong, C.P., J. Mater. Chem. A, 2014, 2: 20642
26 Tang, X.Z., Yu, B., Hansen, R.V., Chen, X.L., Hu, X. and Yang, J.L., Adv. Mater. Interfaces, 2015, 2: 1500122
27 Peng, Q.Y., He, X.D., Li, Y.B., Wang, C., Wang, R.G., Hu, P.G., Yan, Y.D. and Sritharan, T., J. Mater. Chem., 2012, 22(13): 5928
28 Montazeri, A., Javadpour, J., Khavandi, A., Tcharkhtchi, A. and Mohajeri, A., Mater. Design, 2010, 31: 4202
29 Yang, K., Gu, M., Guo, Y., Pan, X. and Mu, G., Carbon, 2009, 47: 1723
30 Lafont, U., van Zeijl, H. and van der Zwaag, S., ACS Appl. Mater. Interfaces, 2012, 4(11): 6280