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## In situ polymerization and mechanical reinforced, thermal healable graphene oxide/polyurethane composites based on Diels-Alder chemistry

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**Abstract:** The covalent bonding graphene oxide/polyurethane (GO/PU) composites with significant reinforcement and thermal healable property were developed via *in situ* polymerization based on Diels-Alder (DA) chemistry. The PU prepolymer was prepared with GO, 4,4-diphenylmethane diisocyanate, poly(tetramethylene glycol) and blocked by furfuryl alcohol firstly. Then the prepolymer was cross-linked by bifunctional maleimide via DA chemistry. SEM shows that the GO was dispersed uniformly in the PU matrix. The DA and retro-DA reactions were characterized by Fourier transform infrared spectra and differential scanning calorimetry separately. Tensile tests showed that with the incorporation of 0.1 wt% of GO, the tensile modulus of GO/PU composites increased from 9.80 MPa to 21.95 MPa, and the tensile strength and elongation at break of the GO/PU composites increased by more than 367% and 210%, respectively. Furthermore, the composites possessed thermal healable ability which was inspected by atomic force microscope and strain-stress test. The healing efficiency of 78% in average was achieved which was determined by recovery of breaking stress and the healing mechanism was tentatively proposed. Therefore, the covalent bonding self-healing GO/PU composites could be used for smart materials and structural material.

### Introduction

Polymeric materials have been used in a variety of fields, including sporting goods, biomedical, microelectronics, transportation, and aerospace, etc. In order to reinforce polymers and enlarge their application scope, inorganic materials such as carbon nanotube (CNT),<sup>1,2</sup> graphene,<sup>3,4</sup> glass fiber,<sup>5</sup> ceramic oxide<sup>6,7</sup> and nanosilica<sup>8-10</sup> were incorporated as fillers into polymer matrices. With no doubt, once the inorganic fillers were overloaded, microcracks would occur especially around the interface of inorganic fillers or processed structures. The propagation and coalescence of the microcracks might lead to the failure of the materials. Consequently, development of smart materials with self-healing property has received mass research attention in the past decades.<sup>11</sup> In general, self-healing materials could be classified into “autonomous” systems and

“stimuli-responsive” systems.<sup>12</sup> “Autonomous” systems heal themselves spontaneously and timely, but they can be healed only once at the same location because of exhaustion of the healing agents. “Stimuli-responsive” systems involve external factors to trigger the healing process, which is most accomplished by a bond-breaking and bond-rebuilding process.<sup>13</sup> Stimulus such as thermal,<sup>14-20</sup> electrical<sup>21,22</sup> and photo<sup>23-25</sup> have been reported by scientists. The temperature-dependent reversible covalent cross-linking of polymers or block copolymers, such as Diels-Alder (DA) chemistry (the schematic representation is shown in Fig. 1), which can be healed without any catalysts or healing agents has attained significant achievements recently.<sup>12</sup>

Graphene, the two-dimensional sp<sup>2</sup>-hybridized carbon, is the world's thinnest, strongest, and stiffest material, as well as being an excellent conductor of both heat and electricity. It is attractive to apply graphene into the polymer matrix. Yet, pristine graphene materials are unsuitable for direct intercalation because of the pronounced tendency to agglomerate in polymer matrix.<sup>26</sup> In contrast to pristine graphene, there are plenty of oxygen-containing groups on the graphene oxide (GO) sheets surface, such as hydroxyl and epoxy groups on their basal planes, as well as carbonyl and carboxyl groups located at the sheet edges, which not only allow the good dispersion of GO in matrix, but also provide active sites to form chemical bonds, acting as an ideal interface between the graphene nanosheets and polymers.<sup>27,28</sup>

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Very recently, some works have been reported concerning the construction of chemical bonding between GO sheets and polymer matrices to get the self-healing materials.<sup>29-32</sup> However, the healing mechanism in these systems were usually non-covalent bond i.e. hydrogen-bond<sup>29, 31</sup> or metal-ligand coordination<sup>32</sup> and the mechanical properties are poor. To our best knowledge, covalent bonding self-healing GO and polymer composites based on DA chemistry haven't been reported before.

In this work, the polyurethane (PU) prepolymer was prepared *in situ* on to the surface of GO to obtain GO/PU composites with furfuryl alcohol as end group. The as-prepared GO/PU was then covalently cross-linked by bifunctional maleimide via DA reaction. The structure, morphology, thermal stability and mechanic strength of the resultant composites were comprehensively investigated. At last, the thermal healing property was also studied.

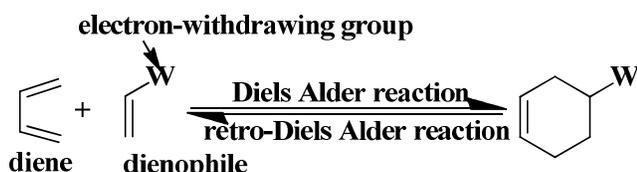


Fig. 1 The schematic representation of thermally reversible Diels-Alder reaction.

## Experimental

### Materials

Graphite powder, 4,4-diphenylmethane diisocyanate, (MDI, 99%), furfuryl alcohol (FA) and N,N'-(4,4'-diphenylmethane)bismaleimide (BMI) were supplied by Aladdin and used as received, poly(tetramethylene glycol) (PTMG,  $M_n = 2000$  g/mol) was purchased from Aladdin and used after 2 hours drying under vacuum at 110 °C. Dimethyl formamide (DMF) was dried with the molecular sieves for 24 h and freshly distilled before use. The chemicals included potassium permanganate ( $KMnO_4$ ), sodium nitrate ( $NaNO_3$ ), concentrated sulfuric acid (98%) and hydrochloric acid were all reagent grade purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

### Preparation of iGO-PU-DA composites

The procedure for preparing GO nanosheets functionalized polyurethane is presented in Scheme 1. The specific synthesis routes are described as follows: first of all, the graphene oxide is produced following Hummers' method<sup>33</sup>. Second, *in situ* polymerization of MDI, PTMG and FA in the presence of GO nanosheets is in turn completed. Briefly, the preparation of the sample containing 0.1 wt% GO is as follows: 6.1 mg of GO is dispersed in 50.0 g of DMF with the assistance of ultra-sonication at room temperature. Then, 1.5 g of MDI was added into the above GO suspension at 80 °C for 2 h in  $N_2$  atmosphere (denoted as iGO). Afterwards, 4.0 g of PTMG was added into the flask and the mixture was stirred at 80 °C for another 2 h. The 0.8 g FA was added into the system and stirred at 80 °C for another 2 h to *in situ* prepare polyurethane prepolymer on the graphene oxide nanosheets (denoted as iGO-PU-FA). Third, 2.86 g BMI was introduced into the homogeneous mixture which was stirred under  $N_2$  at 60 °C for 24 h. Then, the mixture was poured into pre-heated molds made from Teflon. Finally, covalent cross linked composites based on DA chemistry (denoted as iGO-PU-DA) were obtained via *in situ* polymerization. Other samples containing 0.5 wt% and 1.0 wt% GO were synthesized by the same procedure. All the final composites with different GO contents were labeled iGO-PU-DA-1, iGO-PU-DA-2 and iGO-PU-DA-3, respectively. As a comparison, the thermal healable crosslinked polyurethane was

prepared with the same process but without the addition of GO and named as PU-DA. The compositions of various GO/PU are shown in Table 1.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded with Bruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range of 4000–400  $cm^{-1}$ . Differential scanning calorimetry (DSC) was performed on Q20-1173 DSC thermal system (TA instruments, New Castle, USA) with a heating rate of 10 °C  $min^{-1}$  and ranging from 30 °C to 180 °C. Nitrogen gas was purged at a flow rate of about 50  $mL min^{-1}$ . Thermal gravity analysis (TGA) was made on a TA SDTQ600 thermo-gravimetric analyzer; the microbalance has a precision of  $\pm 0.1 \mu g$ . Samples of about 10 mg were placed into 70  $\mu L$  alumina pans. The samples were heated from 30 °C to 800 °C under a nitrogen flow of 100  $mL min^{-1}$ . Scanning electronic micrographs (SEM) were recorded with a Nova NanoSEM 450. The Raman spectra were measured by LabRAM HR Raman Spectrometer (HORIBA Jobin-Yvon, France) with a laser at the excitation wavelength of 632.8 nm and 15.7 mW power irradiation. The collection time for each spectrum was 60 s. The scattered light was detected with a thermoelectric cooled (-70 °C) charge coupled device detector (CCD). All the measurements were carried out directly over the sample. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/Max 2500) with monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a scanning rate of 2°  $min^{-1}$ . Tensile tests experiments were conducted on a RGM-4100 (Reger Instrument co., LTD, China) at room temperature with a cross-head speed of 5  $mm min^{-1}$ . The specimens were dumbbell-like (35  $mm \times 6mm \times 0.1-0.5$  mm). Atomic Force Microscopes (AFM) were recorded with MFP-3D<sup>TM</sup> (Asylum Research, USA) and operated in air in AC mode.

Table 1

Recipes for the preparation of the composites with different contents of GO.

Samples	Polyurethane (g)				GO (mg)
	MDI	PTMEG2000	FA	BMI	
PU-DA	1.00	4.00	0.392	0.716	0
iGO-PU-DA-1	1.00	4.00	0.392	0.716	6.11
iGO-PU-DA-2	1.00	4.00	0.392	0.716	30.54
iGO-PU-DA-3	1.00	4.00	0.392	0.716	61.08

## Results and discussion

### Characterization of GO, iGO, iGO-PU-FA and iGO-PU-DA

Firstly, GO was characterized by SEM, XRD and Raman. The SEM image in Fig. 2a shows paper-like wrinkles and the (002) reflection of GO appears at  $2\theta = 10.68^\circ$  as can be seen in Fig. 2b, suggesting that the interlayer distance increased to 0.83 nm, which is the typical separation of the layered GO. It indicated that the graphite had been successfully exfoliated during the chemical modification process. As shown in Fig. 2c, the Raman spectrum of graphite shows a prominent G peak at 1575  $cm^{-1}$  while the spectrum of GO displays an obvious D band at 1325  $cm^{-1}$  indicates the reduction in size of the in plane  $sp^2$  domains, possibly due to the extensive oxidation.

The distribution of GO sheets in the composites affect the properties of the polymer composites especially the mechanical

property.<sup>34, 35</sup> So the investigation of the distribution is carried out using by SEM on the cryogenically surface. It is seen that primary GO sheets are well dispersed in the polymer matrix at low content (0.1 wt%). However, particles were slightly agglomerated at high contents (0.5 wt%, 1.0 wt%).

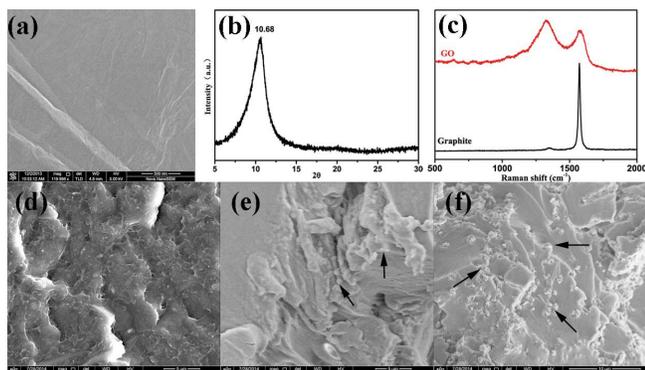
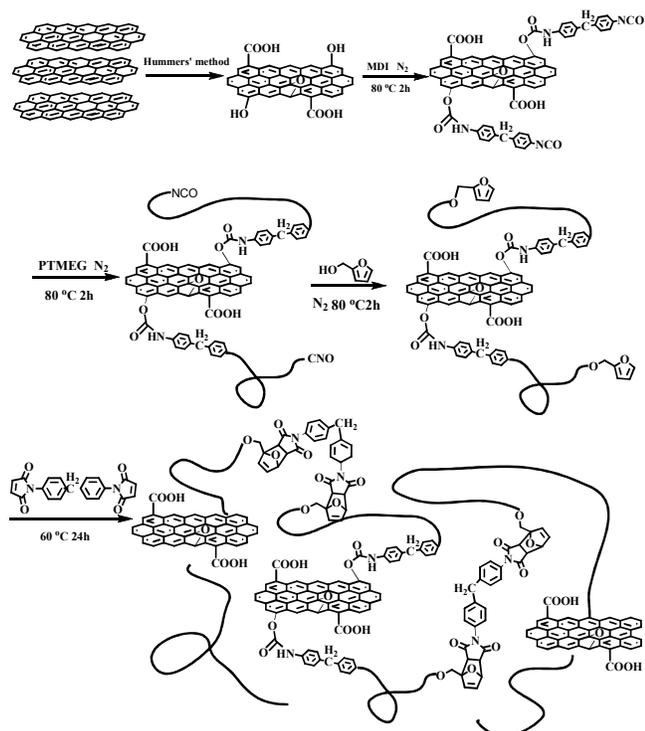


Fig. 2 (a) SEM image of GO; (b) XRD pattern of the GO; (c) Raman spectra of the GO and the pristine graphite and the SEM images of the cryogenically fracture surfaces of films for (d) iGO-PU-DA-1, (e) iGO-PU-DA-2 and (f) iGO-PU-DA-3.



Scheme 1 The synthetic procedures of iGO-PU-DA.

The procedure for preparing GO nanosheets functionalized polyurethane is presented in Scheme 1. Basically, the GO obtained by Hummer's method was modified by MDI at first and iGO was then reacted with PTMG resulting in the NCO-terminated PU. Then FA was added into the system to get iGO-PU-FA. Finally after reacting with BMI by DA reaction, iGO-PU-DA was obtained.

After GO was modified by functional molecule and polymer, obvious variation of characteristic peaks can be identified in the FTIR spectra. Fig. 3a shows the FTIR spectra of GO and iGO. In order to remove the unreacted MDI, iGO was filtered and washed twice by additional methylene chloride after the preparation, and

dried under vacuum. Upon treatment with MDI, the C=O stretching vibration at  $1733\text{ cm}^{-1}$  in GO becomes obscured by the appearance of a stronger absorption at  $1708\text{ cm}^{-1}$  that can be attributed to the carbonyl stretching vibration of the carbamate esters of the surface hydroxyls in iGO. The new band at  $1549\text{ cm}^{-1}$  originates from carbamate esters and corresponds to the coupling of the C–N stretching vibration with the CNH deformation. Besides, the characteristic absorption peak of –NCO group and *p*-phenylene at  $2270\text{ cm}^{-1}$  and  $815\text{ cm}^{-1}$  were clearly shown in the spectrum separately which indicated the successful modification of MDI on GO. Meanwhile, there are abundant oxygen-containing groups such as O–H ( $3310\text{ cm}^{-1}$ ), carboxyl C=O groups ( $1708\text{ cm}^{-1}$ ), C–O ( $1057\text{ cm}^{-1}$ ) and so on in the FTIR spectrum of iGO, so GO was not reduced obviously during the modification.

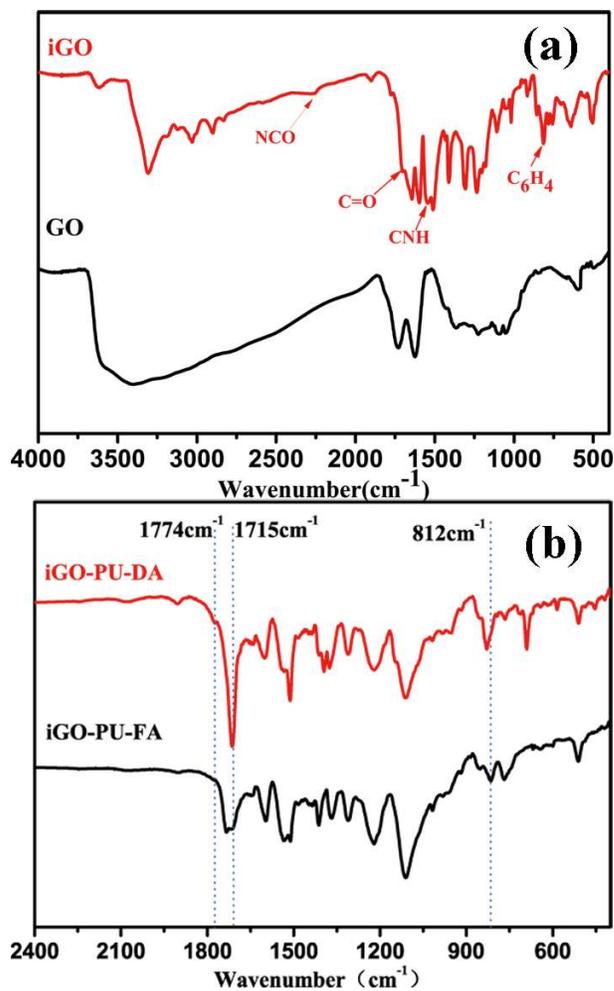


Fig. 3 FTIR spectra of (a) GO and iGO; (b) iGO-PU-FA and iGO-PU-DA.

The FTIR spectra of iGO-PU-FA and iGO-PU-DA are shown in Fig. 3b. The characteristic absorption peak of –NCO group at  $2270\text{ cm}^{-1}$  appeared in the spectra of iGO was completely disappeared in spectrum of iGO-PU-FA and iGO-PU-DA. The result indicated that all the –NCO groups were completely consumed in the following synthesis of iGO-PU-FA and iGO-PU-DA. The peak at  $812\text{ cm}^{-1}$  confirmed that the furan ring was successfully grafted in the iGO-PU-FA composites.<sup>36</sup> Furthermore, in the spectrum of iGO-PU-DA, around  $1715\text{ cm}^{-1}$  ascribing to C=O band of BMI was observed. Meanwhile, the peaks at  $1774\text{ cm}^{-1}$  in the spectrum of iGO-PU-DA can be ascribed to C=C which was specific to the DA adduct.<sup>37</sup>

Simultaneously, the intensity of  $812\text{ cm}^{-1}$  peak in the spectrum of iGO-PU-DA decreased compared with that of iGO-PU-FA, which can be ascribed to that the furan ring was reacted by BMI. Therefore, the novel PU/GA composites based on DA chemistry was successfully developed as expected.

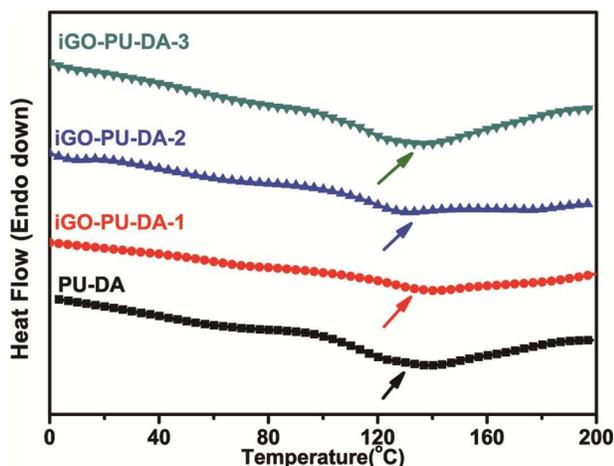


Fig. 4 DSC curves of PU-DA and iGO-PU-DAs.

The DA chemistry was successfully applied in the novel composite which is verified by the characteristic peak of retro-DA (rDA) reaction as shown in Fig. 4. The DSC curves of PU-DA and iGO-PU-DAs exhibit significant endothermic peaks at 130-150 °C which was predominately attributed to the rDA reaction. And it should be noticed that introducing GO into the composites doesn't have significant effect on the endothermic peak which might be due to the nature of the Diels-Alder chemistry of furan-maleimide system<sup>12</sup>. The significant endothermic peak at 130-150 °C indicates the successful synthesis of the GO/PU composites by Diels-Alder reaction and provides the thermal healing property of all the composites because of the thermal reversibility of the Diels-Alder chemistry.<sup>38, 39</sup>

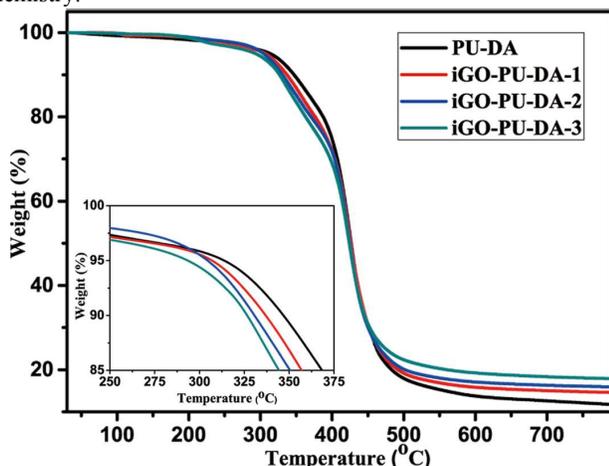


Fig. 5 TGA curves of PU-DA and iGO-PU-DAs.

Besides, the thermal stability of PU-DA and iGO-PU-DAs were assessed by TGA under a nitrogen atmosphere between 30 °C and 800 °C as shown in Fig. 5. It can be seen that the decomposition of pure PU and iGO-PU-DAs took place in a single step and it started at around 300 °C. From the inset figure we can see that the temperature at 5% weight loss ( $T_5$ ) decreased slightly with increasing GO compared with that of pure PU. However, all these composites possess excellent

thermal stability and keep the  $T_5$  higher than 300 °C. In short, the thermal stability showed no significant change with the addition of GO in PU matrix which is consistent with the result reported by Li et al.<sup>40</sup> Also, It can be seen that with the addition of GO the char yields at 800 °C increased slightly.

### Mechanical properties of the iGO-PU-DA composites

It was expected that the mechanical properties of the polymer would be enhanced due to the large aspect ratio of GO, covalent bonding between GO and PU matrix and good dispersion of GO in the matrix. The mechanical properties of GO/PU composites are shown in Fig. 6 and summarized in Table 2. From the typical stress-strain curves shown in Fig. 6 we can see that with the addition of GO, the Young's modulus ( $21.95 \pm 2.56$  MPa) and breaking strain ( $449 \pm 16\%$ ) increased twice and the breaking stress ( $8.01 \pm 0.71$  MPa) even increased nearly 4 times at a GO loading of only 0.1 wt%. The reason should be that the good dispersion and covalent linking of GO sheets promote the transfer of load in the composites.<sup>35</sup> The films of iGO-PU-DA-2 and iGO-PU-DA-3 showed higher Young's modulus but the breaking stress and breaking strain decreased slightly. Specially, the Young's modulus increased by ca. one order of magnitude when the weight percentage of GO changed from 0.1% to 1.0%, while the breaking strain decreased from 449% to 54% and the breaking stress decreased from 8.01 MPa to 7.09 MPa. This can be ascribed that the composite with higher GO loading brings about the concentration of stress at GO sheets and lead to the break of the films at the stretching process. On the other hand, the GO sheets in the composites disturb the orientations of polymer chain at high elongations at the same time.<sup>41</sup>

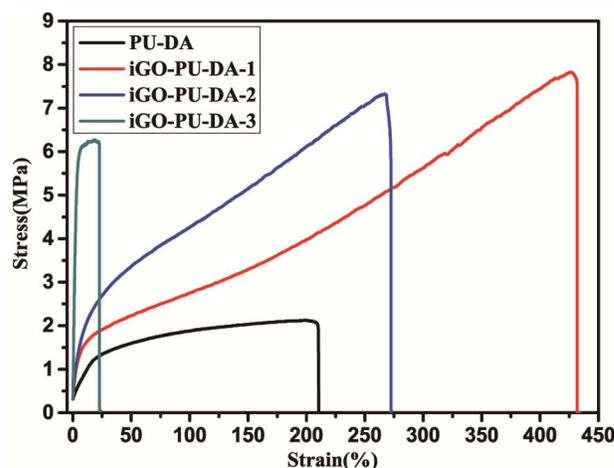


Fig. 6 Stress-strain curves of PU-DA and iGO-PU-DAs films (25 °C).

Table 2 Summary of the mechanical properties of the composite samples at different GO content. The average values were obtained from more than 3 samples.

Sample	Young's modulus (MPa)	Strain-at-break (%)	Stress-at-break (MPa)
PU-DA	$9.80 \pm 1.30$	$213 \pm 33$	$2.16 \pm 0.29$
iGO-PU-DA-1	$21.95 \pm 2.56$	$449 \pm 16$	$8.01 \pm 0.71$
iGO-PU-DA-2	$28.61 \pm 4.22$	$282 \pm 81$	$7.19 \pm 1.22$
iGO-PU-DA-3	$209.01 \pm 34.61$	$54 \pm 30$	$7.09 \pm 0.58$

### The healing test

In order to introduce surface defects, the respective films were treated with a spatula and the typical healing behavior of iGO-PU-DA-2 is shown in Fig. 7. After being scratched with a spatula, the film surface was analyzed using AFM (Fig. 7a). As can be seen, defined scratches (Scratch (a): 1.55  $\mu\text{m}$  depth, 15  $\mu\text{m}$  width.) were created. Afterwards, iGO-PU-DA-2 film was heated for 4 h at

150  $^{\circ}\text{C}$ , allowed to cool down slowly to 65  $^{\circ}\text{C}$ , and re-crosslinked for 24 h at 65  $^{\circ}\text{C}$ . After the rDA reaction at 150  $^{\circ}\text{C}$  (Fig. 7b), the scratch decrease to 0.98  $\mu\text{m}$  depth. With the subsequent crosslinking at 65  $^{\circ}\text{C}$  (Fig. 7c), profilometry revealed that the scratch almost disappeared completely and the depth was 0.05  $\mu\text{m}$ . The result shows that the GO/PU composites could be healed by the thermal reversible DA reaction.

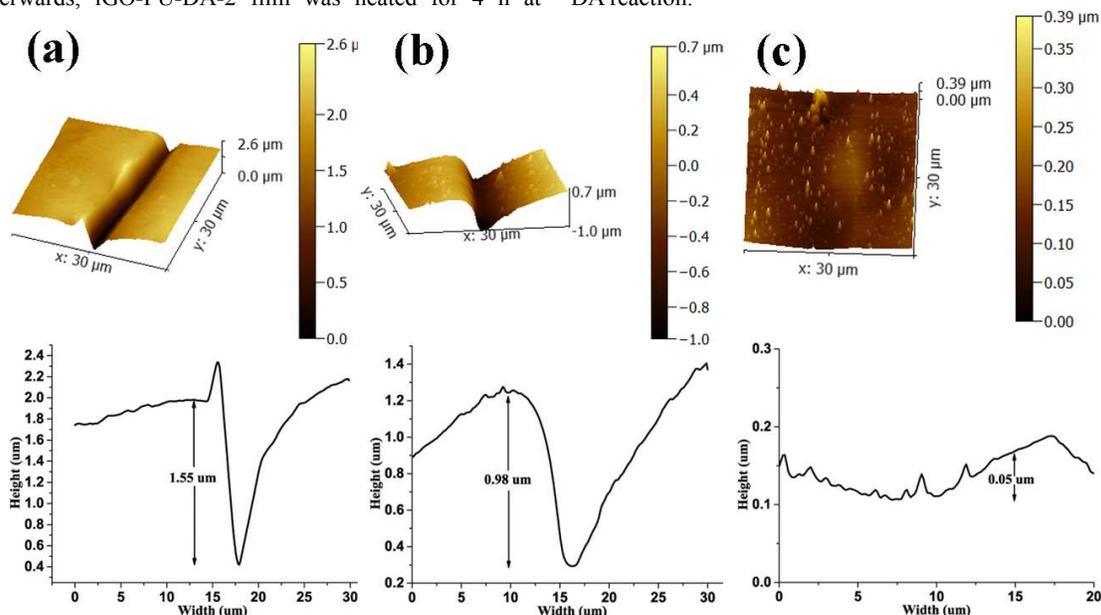


Fig. 7 Profilometry measurements by AFM of (a) scratching with a spatula, (b) after heating for 4 h at 150  $^{\circ}\text{C}$ , (c) subsequent heating for 24 h at 65  $^{\circ}\text{C}$ .

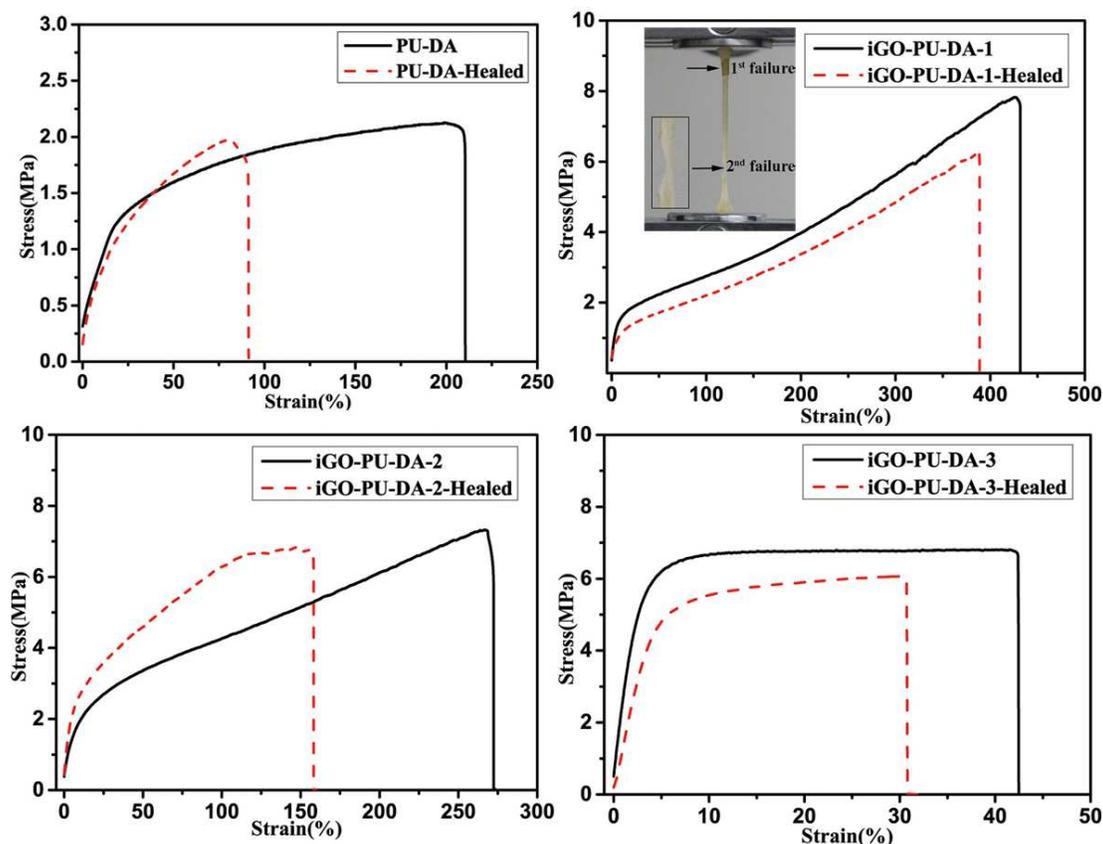


Fig. 8 Stress-strain curves of PU-DA and iGO-PU-DAs films before and after thermal healing: (a) PU-DA, (b) iGO-PU-DA-1, (c) iGO-PU-DA-2, and (d) iGO-PU-DA-3.

The healable behaviors of PU-DA and iGO-PU-DAs films were subsequently investigated by measuring the healing efficiency which is defined as the ratio of the recovered breaking (tensile) strength to the original strength. The original samples were first torn by the tensile test machine with a head speed of 5 mm min<sup>-1</sup>. Then the two broken surfaces were immediately reunited, subjected to a gentle pressure and stored at 150 °C for 4 hours followed by 24 h at 65 °C without any continuous pressure. The detailed data of the mechanical properties of the healed films at different GO contents are shown in Table 3. After the thermal healing process the Young's Modulus, breaking strain and breaking stress of the healed samples recovered significantly. The recovery of the mechanical properties should be ascribed to recombination of the 3D network formed by the Diels-Alder of the free furan-maleimide groups which were generated by the stretch process before as the interaction of the DA bond is much weaker than the other covalent bond.<sup>12</sup>

Table 3 Summary of the mechanical properties of the composite samples after the healing test. The average values were obtained from more than 3 samples.

Sample	Young' Modulus (MPa)	Strain-at-break (%)	Stress-at-break (MPa)
PU-DA	11.15±1.02	103±17	2.14±0.19
iGO-PU-DA-1	15.59±5.18	275±97	5.70±1.96
iGO-PU-DA-2	37.33±11.22	132±34	5.00±1.65
iGO-PU-DA-3	111.33±16.54	30±13	5.21±0.61

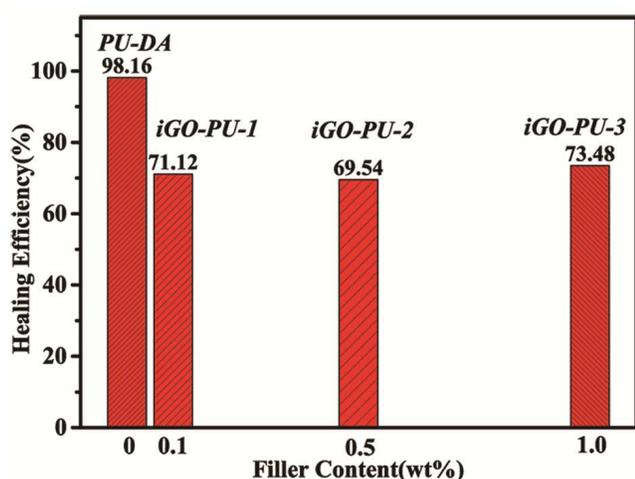


Fig. 9 Healing efficiency of PU-DA and iGO-PU-DAs films determined by recovery of breaking stress.

Fig. 8 shows the typical stress-strain curves before and after the healing tests of PU-DA and iGO-PU-DAs films. Here, healing efficiency is represented by the ratio of the breaking (tensile) strength of the healed sample to that of the original sample. And the healing efficiencies estimated from the experiments are presented in

Fig. 9 which is 98.16%, 71.12%, 69.54% and 73.48% respectively. Comparing with other samples, the pure PU-DA showed the highest healing efficiency. The reason should be that without the addition of GO, the polymer chain motion of the pure PU-DA is much easier to take place which will promote the Diels-Alder reaction of the furan-maleimide groups. With the addition of GO, the healing efficiency dropped distinctly which were around 70% for all the iGO-PU-DAs. The main reason could be that the addition of GO disturb the molecular motion and recombination of the furan-maleimide groups. GO sheets that are covalently linked with the polymer matrix usually increase the cross-link density of the matrix and result in decreased mobilities of GO sheets and polymer segments. In addition, the defect formed during the first stretch process accelerated the fracture of the films as well which is shown in inset digital photo of Fig. 8b. Therefore, *in situ* polymerization of GO/PU and introducing DA chemistry into the composites not only improve the mechanical properties but also decorate the thermal-healing ability to the novel composite material.

## Conclusion

In summary, a novel covalent bonding graphene oxide/polyurethane composite was successfully developed by *in situ* polymerization and Diels-Alder chemistry for the first time. All these composites with different GO contents show significant mechanical reinforcement and thermal healable property. Owing to the well dispersion and strong covalent bonding interactions with the polymer matrix great improvements in mechanical properties have been achieved for GO/PU composites. The result showed that with the incorporation of 0.1 wt% of GO, the tensile modulus of GO/PU composites increased from 9.80 MPa to 21.95 MPa, the tensile strength and elongation at the break of the GO/PU composites increased by more than 367% and 210%, respectively. Additionally, the composites showed excellent thermal healable ability with efficiency of 78% in view of breaking stress. Therefore, the ingeniously architecture design can widen the application of conventional composites.

## Acknowledgements

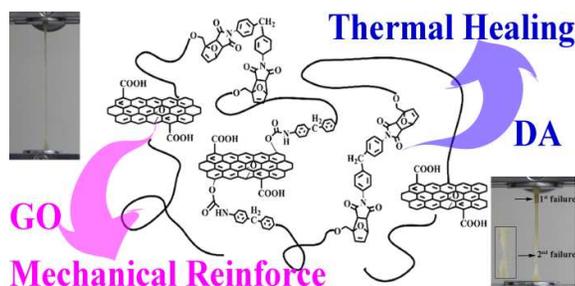
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Table of contents entry



The covalent bonding graphene oxide/polyurethane composites with significant mechanical reinforcement and thermal healable capability were developed via *in situ* polymerization based on Diels-Alder chemistry.