

Self-healing Supramolecular Polymer Composites by Hydrogen Bonding Interactions between Hyperbranched Polymer and Graphene Oxide

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 Electronic Supplementary Information

Abstract A self-healing supramolecular polymer composite (HSP-GO) was designed and prepared *via* incorporation of modified graphene oxide to hyperbranched polymer by hydrogen-bonding interactions. The polymer matrix based on amino-terminated hyperbranched polymer (HSP-NH₂) was synthesized by carboxylation, Curtius rearrangement, and amination of hydroxyl-terminated hyperbranched polyester (HP-OH), while the modified graphene oxide was prepared by transformation of hydroxyl to isocyanate and further to carbamate ester. Spectroscopic methods were utilized to characterize the obtained polymer composites. Stress-strain test was selected to carefully study the self-healing property of HSP-GO. It is found that a small amount of modified graphene oxide (up to 2 wt%) improves the glass transition temperature (T_g), tensile strength, Young's modulus, and self-healing efficiency of the polymer composites. After healed at room temperature for 10 min, the addition of modified graphene oxide improves the self-healing efficiency to 37% of its original tensile strength. The experiment result shows that the self-healing efficiency is related to the density of hydrogen bonding site and the molecular movement.

Keywords Self-healing; Supramolecular polymer; Graphene oxide; Hydrogen bonding

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INTRODUCTION

Self-healing materials have an ability to identify and repair the damage during usage, which reduces the total cost in the long term service life and increases the useful life of materials. A variety of reports were proposed in the past years to obtain the self-healing polymer materials^[1, 2]. The design of these self-healing materials is mostly based on the reversible bonds, including dynamic covalent and non-covalent bonds^[3]. When the materials are damaged by outside force, the damage area can be self-healed under appropriate stimulation, such as heating^[4–8], changing pH^[9] or light stimulation^[10–12], which drives the polymer chains to move, touch, and get tangled, hence reaching to the previous state.

Commonly, the supramolecular polymers are obtained by reversible noncovalent assembly to connect the monomer units together. Different noncovalent forces, such as π - π interactions, metal-ligand interactions, electrostatic interactions and hydrogen bonding are employed to prepare supramolecular polymers^[13–17]. The supramolecular polymers with hydrogen bonding networks are very promising self-healing materials because the hydrogen bonds can be separated or reconnected reversibly at room temperature.

However, most of these polymers have very poor mechanical properties and are not suitable for practical applications^[18–20]. To solve this problem, Codier *et al.* reported the first self-healing hydrogen-bonded supramolecular elastomer, which was prepared by the characteristics of high flexibility of elastomer molecular chain and the dynamic network structure with multiple hydrogen bonds. However, the product needed to add a long chain (twelve carbon) alkane plasticizer to reduce the glass transition temperature (T_g)^[21]. Bao *et al.* introduced carbon black nanoparticles or silicon microparticles into the randomly branched hydrogen-bonding polymer to prepare the self-healing conductive composite material. They also used nickel ions as fillers to incorporate into the randomly branched hydrogen-bonding polymer. The obtained conductive composite material showed self-healing function at room temperature and could be used for artificial electronic skin^[22–24]. In the above cases, the mechanical properties of the supramolecular polymer are enhanced, but the incorporation of high volume fillers into the polymer system lowers the density of hydrogen bonds, limits the movement of molecular chain containing the hydrogen bonds, thus reduces the healing speed.

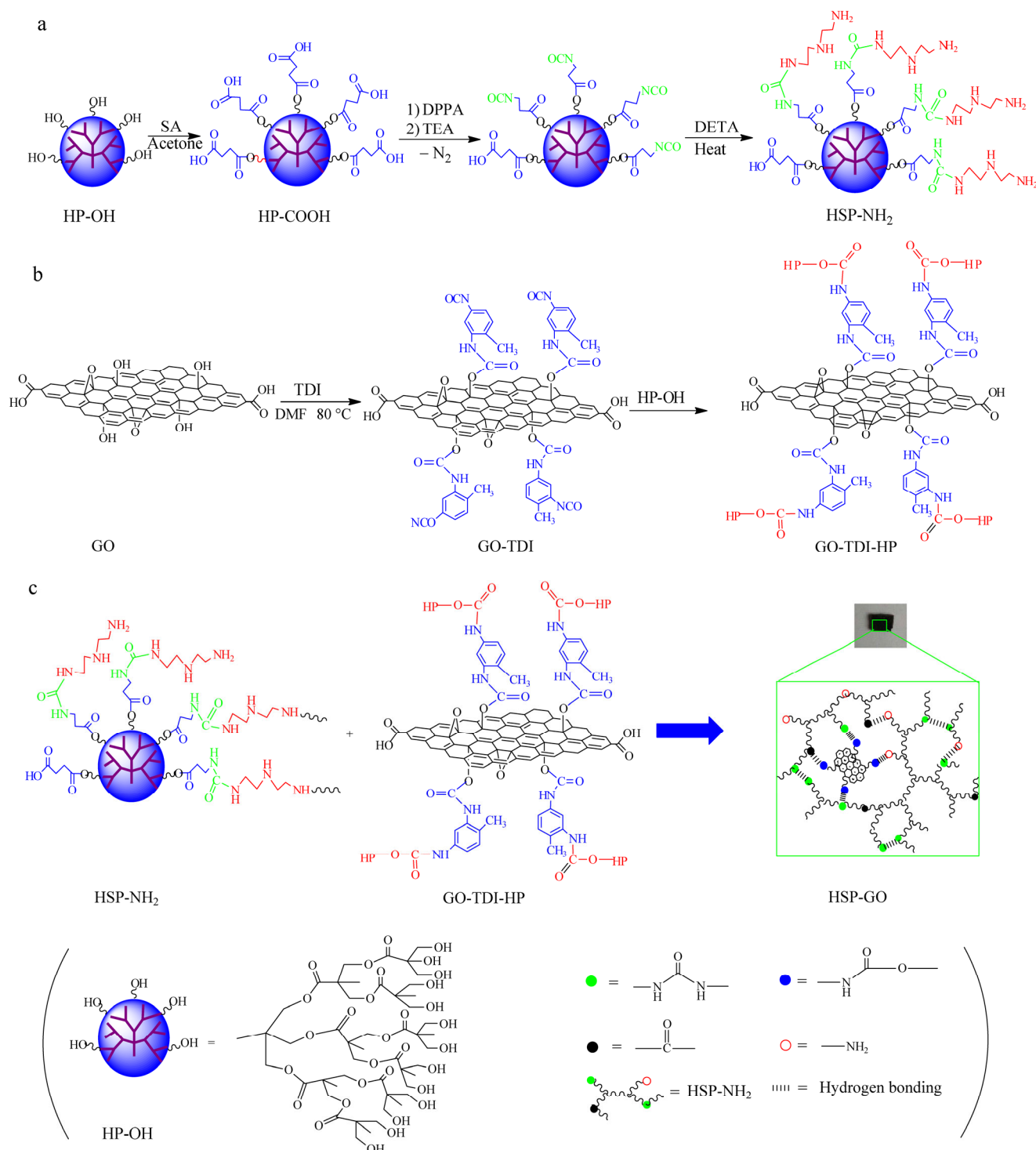
Graphene oxide (GO) has excellent properties, such as high mechanical strength, high surface area and ease for chemical modifications^[25–27]. It is attractive to add GO into the self-healing polymer structures because of its high

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mechanical properties and multiple reacting active sites. By this way, the density of hydrogen bonds is not significantly reduced. Some studies reported the construction of covalent composites materials^[28, 29]. However, to establish the hydrogen bonds between graphene and polymers by introducing the donor and acceptor to the surface of graphene oxide has not been reported so far.

In this work, we report a self-healing and elastic nanocomposite material with enhanced mechanical properties by introducing the modified graphene into the supramolecular polymer with hydrogen bonds. The preparation process is shown in Scheme 1. The supramolecular polymer based on amino-terminated hyperbranched polymer (HSP-NH₂) was synthesized by using the hydroxyl-terminated hyperbranched polyester (HP-OH),



Scheme 1 (a) Synthetic route to HSP-NH₂, (b) the modification process of GO, and (c) schematic illustration of the synthesis for self-healing composite (HSP-GO)

succinic anhydride (SA), diphenyl azidophosphate (DPPA), and diethylenetriamine (DETA) as the raw materials. The graphene oxide (GO) was modified by 2,4-tolylene diisocyanate (TDI) and HP-OH to offer the donor and acceptor of hydrogen bonds. The HSP-GO composites combine the unique features of supramolecular polymer and graphene oxide, which not only can rapidly heal at room temperature, but also, importantly, has high strength and elasticity as compared with other self-healing materials.

EXPERIMENTAL

Materials

Hydroxyl-terminated hyperbranched polyester (HP-OH) was obtained from Wuhan HyperBranched Polymer Reins Science and Technology Co., Ltd. Succinic anhydride (SA), diphenylphosphoryl azide (DPPA, 97%), and 2,4-tolylene diisocyanate (TDI) were purchased from Aladdin. Graphene oxide powders (GO) were brought from Nanjing XFNANO Tech Co., Ltd. Diethylenetriamine (DETA) and triethylamine (TEA) were obtained from Tianjin VAS Chemical Reagents Co. *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,4-dioxane, dichloromethane, ether, and acetone were obtained from Beijing Chemical Factory.

Instrumentation

Fourier transform infrared (FTIR) spectra were obtained by the KBr disk method at room temperature or at a high temperature *via* a Bruker V70 spectrometer fitted with a high temperature bracket. ¹H-NMR spectra were acquired in deuterated chloroform, acetone, and DMSO on a Bruker AV400 at a proton frequency of 400 MHz. Tetramethylsilane was used as an internal standard. Differential scanning calorimetry (DSC) measurements were carried out with a DSC204F1 apparatus (Netzsch Instruments, Selb/Bavaria, Germany). The XPS spectra were measured on a VG ESCALAB MK-II X-ray photoelectron spectrometer at 25 °C using Mg/K as X-radiation source. Scanning electron microscopy (SEM) was performed with a Nova Nano SEM 450. Rheological experiments were carried out using a stress-controlled rheometer (TA Instruments Model AR-G2). Tensile test experiments were conducted on a CMT4202 at room temperature with a stretch speed of 5 mm/min and the size of specimens was 20 mm × 4 mm × 2 mm.

Synthesis of Supramolecular Polymer Based on Amino-terminated Hyperbranched Polymer (HSP-NH₂)

HSP-NH₂ was synthesized according to the synthetic routes in Scheme 1. HP-OH (5 g, 4.17 mmol) was loaded into a three-necked flask and dissolved in acetone (80 mL). Then the succinic anhydride (5.15 g, 4.17 mmol) was added and refluxed at 65 °C for 8 h. The solution was cooled to room temperature and precipitated twice in ether, and the product was dried at 35 °C under vacuum. Viscous liquid carboxy-terminated hyperbranched polyester (HP-COOH) was obtained in a yield of 76%. Into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added HP-COOH (2.59 g, COOH content = 12.22 mmol) and 1,4-dioxane (8 mL). The mixture was stirred and heated to dissolve HP-COOH, and then cooled to room temperature under nitrogen. Then DPPA

(4.37 g, 15.89 mmol) and TEA (3.70 g, 28.11 mmol) were added at low temperature (about 10 °C). After stirring for 1.5 h in dark, the temperature was raised to room temperature and continued to react for 1.5 h. Then the reaction was allowed to proceed to 70 °C and stirred until no more bubbles emerged. DETA (1.41 g, 13.71 mmol) was added to the reaction system, and the system was stirred at 90 °C for another 3 h. After cooling down, the reaction solution was precipitated three times in acetone, and then the precipitate was washed twice with water, ether, and dried at 35 °C under vacuum. The brown HSP-NH₂ was obtained.

Graphite Oxide Functionalization

Preparation of GO with NCO group

In a typical procedure, GO (50 mg) was dispersed into anhydrous DMF (10 mL), stirring at room temperature for 48 h. Then, TDI (0.35 g, 2 mmol) was added and the mixture was allowed to stir under nitrogen at 80 °C for 12 h. After cooling to room temperature, the solid product was obtained by centrifugation. The products were washed three times with methylene chloride and dried under vacuum. Accordingly the products were named as GO-TDI^[30].

Grafting reactions of HP-OH with GO-TDI

A mixture of GO-NCO (50 mg) and HP-OH (3 g, 2.5 mmol) in anhydrous DMF (20 mL) was stirred at 80 °C for 8 h under nitrogen atmosphere. Then the reaction mixture was centrifuged to remove unreacted HP-OH and washed three times with acetone. The product was dried at 60 °C under vacuum and marked as GO-TDI-HP.

Preparation of Self-healing Composite (HSP-GO)

To investigate the influence of modified graphene oxide fillers within the HSP-NH₂, we synthesized the HSP-GO composites. The preparation of the sample containing modified graphene oxide is as follows. HSP-NH₂ was dissolved in DMSO and stirred at 25 °C under nitrogen atmosphere, GO-TDI-HP was added into the solution with weight percentage of 1 wt% and 2 wt%, respectively, which was termed as HSP-1%GO, HSP-2%GO. The solution was precipitated twice in acetone, the precipitate was dried under vacuum, and then brown HSP-GO composites were obtained.

RESULTS AND DISCUSSION

Preparation of HSP-NH₂ and HSP-GO Composites

The synthesis of HSP-NH₂ was carried out *via* two steps as shown in Scheme 1. In the first step, excessive succinic anhydride was used to react with the hydroxyl group of HP-OH for ensuring the transformation of every hydroxyl group to the carboxyl group. The next reaction *via* carboxyl-terminated hyperbranched polyester (HP-COOH) with DPPA generated the isocyanate group that reacted with DETA to introduce ureido groups and amino groups in the structure of HSP-NH₂. Figure 1 shows the FTIR spectra of HP-OH, HP-COOH and HSP-NH₂. By comparison, we found that SA reacted with hydroxyl groups of HP-OH as evidenced by the emergence of a new band at 1562 cm⁻¹ that was ascribed to the stretching vibrations of carboxyl groups. These carboxyl groups can further incorporate with ureido groups and amidogen groups *via* Curtius rearrangement and amination. In Fig. 1(c), the appearance of a stretching vibration

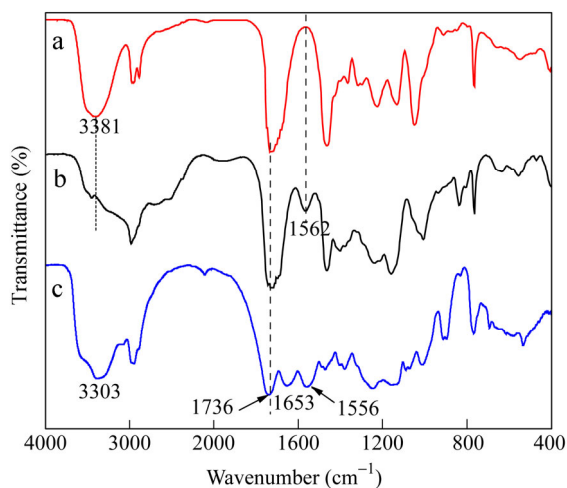


Fig. 1 FTIR spectra of (a) hydroxyl-terminated hyperbranched polyester (HP-OH), (b) carboxyl-terminated hyperbranched polyester (HP-COOH), and (c) amino-terminated hyperbranched polymer (HSP-NH₂)

peak at 3303 cm⁻¹ can be assigned to N—H bonds, while the peaks around 1653 cm⁻¹ are attributed to the stretching vibrations of C=O in the ureido. This result confirms the formation of HSP-NH₂. Further evidence of this reaction can also be identified by ¹H-NMR spectra as shown in Fig. S1 (in electronic supplementary information, ESI).

The association of hydrogen bonds was characterized by the FTIR spectra of HSP-NH₂ at different temperatures. As shown in Fig. 2, with increasing temperature, the C=O stretching signal of ureido shifts to higher wavenumber (from 1653 cm⁻¹ to 1665 cm⁻¹), while the N—H bending signal shifts to lower wavenumber (from 1565 cm⁻¹ to 1552 cm⁻¹). This phenomenon is due to the disassociation of hydrogen bonds with the increase of temperature, which results in the displacement of corresponding group of characteristic peaks. When the HSP-NH₂ was cooled to the room temperature, its FTIR spectra recovered to the original characteristic.

In the above discussion, the association of hydrogen bonds is verified. HSP-NH₂ based on hydrogen bonding interaction could associate and disassociate reversibly at room temperature. In order to enhance the mechanical strength of HSP-NH₂, modified graphene oxide was incorporated. Firstly, one isocyanate group of TDI was anchored onto the surface of GO, leaving the other one free. Then the hydroxyl groups of HP-OH and the residual isocyanate groups bridged the hyperbranched polyester and GO nanoplatelets together (as exhibited in Scheme 1b). When the GO was modified by organic isocyanates and polyester, the result could be identified by the FTIR spectra. Figure 3 shows the FTIR spectra of GO, GO-TDI and GO-TDI-HP, respectively. To remove unreacted TDI, GO-TDI was washed three times by methylene chloride and dried in vacuum. It can be found that the C=O stretching vibration of GO at 1732 cm⁻¹ disappears and a new band at 1708 cm⁻¹ appears (stretching of carbamate esters). In addition, there is an obvious absorption peak of —NCO groups at 2267 cm⁻¹ that proves the reaction between TDI and GO. The —NCO groups can further react with hydroxyl-terminated hyperbranched polyester, grafting

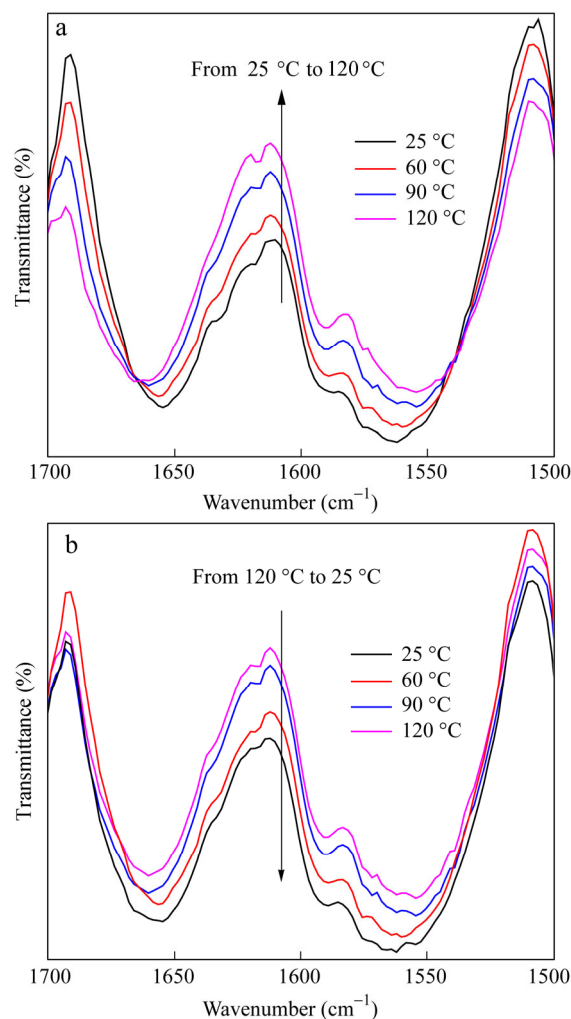


Fig. 2 FTIR spectra of HSP-NH₂ upon (a) heating from 25 °C to 120 °C and (b) cooling from 120 °C to 25 °C

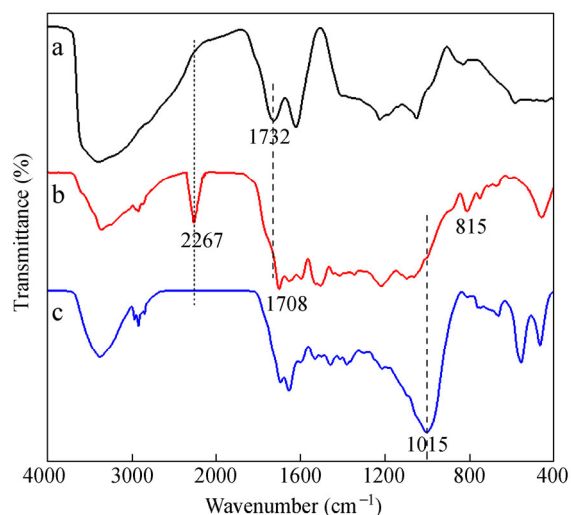


Fig. 3 FTIR spectra of (a) GO, (b) GO-TDI, and (c) GO-TDI-HP

polyester to GO. As shown in Fig. 3(c), the band at 2267 cm⁻¹ (—NCO groups) disappears and a new absorption of HP-OH emerges at 1015 cm⁻¹ (C—O absorption peak). Further evidence of the reaction can be identified by XPS spectra as

shown in Figs. S2 and S3 (in ESI). These results prove the successful modification of GO as expected.

Finally, HSP-GO composites were prepared by filling 1 wt% or 2 wt% modified graphene oxide, respectively, into amino-terminated hyperbranched polymer. The SEM images show the dispersion of modified graphene oxide in the supramolecular polymer (Fig. S4, in ESI). The images exhibit that most of the modified graphene oxide nanosheets are well dispersed in the polymer matrix for the HSP-1%GO sample. The stress concentration is reduced and the uniformity of stress distribution is enhanced when the modified graphene oxide nanosheets are well dispersed in the polymer matrix. Furthermore, the modified graphene oxide has carbamate esters and multiple reactive sites, which guarantee the density of hydrogen bond sites in composite materials. As a result, the HSP-GO composites show high mechanical strength as compared to the polymer matrix.

Mechanical Properties of HSP-NH₂ and HSP-GO Composites

The T_g s of HSP-NH₂ and HSP-GO composites with different contents of modified graphene oxide were tested by DSC (Fig. 4). HSP-NH₂ has T_g of -36 °C, while T_g s of HSP-1%GO and HSP-2%GO increase to -21 and -14 °C, respectively. The increased T_g is attributed to the hinder effect of modified graphene oxide nanosheets. However, T_g of the composite is lower than room temperature, which means that these composite materials have the possibility of self-healing at room temperature.

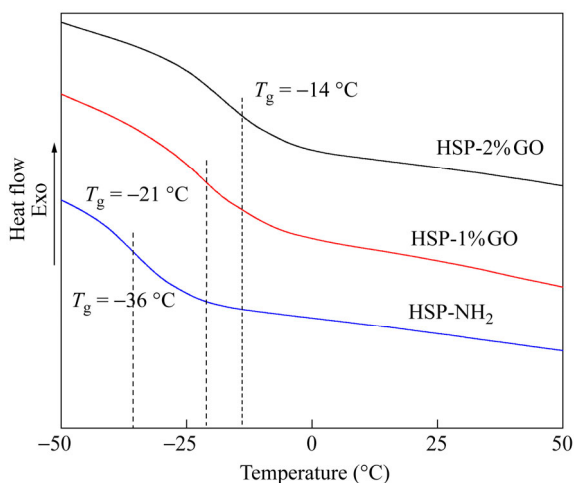


Fig. 4 DSC curves of HSP-NH₂, HSP-1%GO, and HSP-2%GO

We mold HSP-NH₂ and composites into samples at 90 °C. Similarly to common rubber, all the materials can be stretched and quickly return to its original length at room temperature. Detailed mechanical properties of HSP-NH₂ and HSP-GO composites are shown in Fig. 5. From the stress-strain curves of all materials, we find that HSP-NH₂ has large strain at break up to 306%, but the Young's modulus is lower than rubber. However, the mechanical properties of HSP-NH₂ can be changed by applying different amounts of modified graphene oxide. The parameters of mechanical properties are shown in Table 1. It can be seen that the breaking stress (0.38 MPa) increases twice and the Young's modulus

(0.36 MPa) even increases nearly 4 times with the loading amount of modified graphene oxide only 1 wt%. This may be owing to the excellent mechanical properties of GO and good dispersion in the polymer matrix. Compared with HSP-1%GO, HSP-2%GO showed a higher Young's modulus and breaking stress but the break strain decreased slightly. This can be ascribed to the fact that the modified graphene oxide sheets disturb the orientations of the polymer chains at high elongations, thus reducing the mobility of molecular chains.

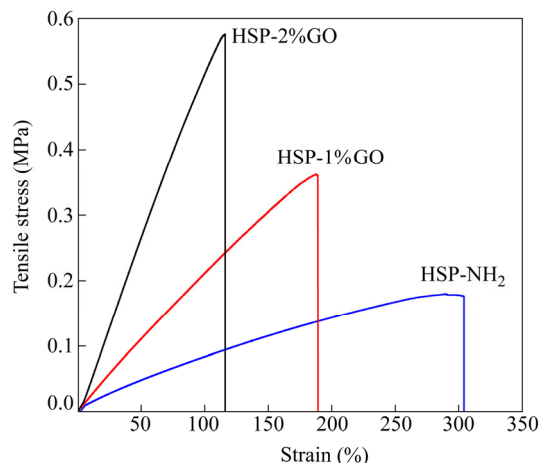


Fig. 5 Stress-strain curves of the HSP-NH₂, HSP-1%GO, and HSP-2%GO

Table 1 Summary of the mechanical properties of HSP-NH₂ and HSP-GO composites

Sample	Elastic modulus (MPa)	Strain at break (%)	Stress at break (MPa)
HSP-NH ₂	0.081 ± 0.006	306 ± 19	0.18 ± 0.02
HSP-1%GO	0.36 ± 0.04	188 ± 10	0.38 ± 0.04
HSP-2%GO	0.63 ± 0.07	118 ± 6	0.58 ± 0.03

The addition of modified graphene oxide can increase the elasticity of HSP-GO composites. According to the literature, the ratio between loss modulus (G'') and storage modulus (G') is an indication of the elasticity of material^[28]. The higher G''/G' value, the lower the elasticity of material is. As shown

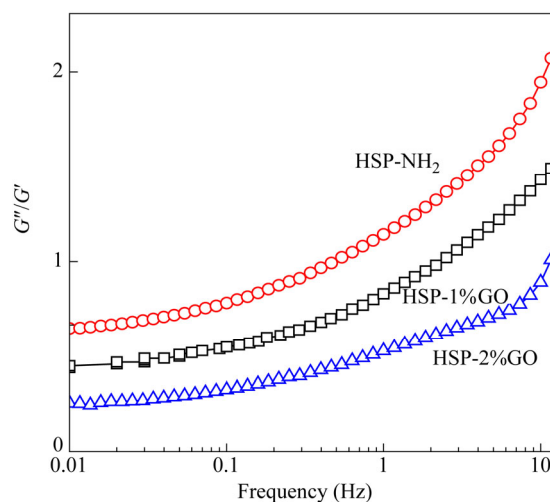


Fig. 6 The ratio of loss modulus (G'') and storage modulus (G') of the materials at different frequencies

in Fig. 6, the G''/G' values decrease with increasing the modified graphene oxide content, which proves the enhancement of elasticity of HSP-GO composites with increasing the content of modified graphene oxide.

Self-healing Properties of HSP-NH₂ and HSP-GO Composites

The supramolecular polymer based on amino-terminated hyperbranched polymer has self-healing ability due to the hydrogen bonding interaction. In order to investigate the behavior of HSP-NH₂ sample, we cut HSP-NH₂ into two separate pieces with a razor blade, then bringing the two pieces gently back into contact at room temperature for 30 min. It can be found that the interface between the two damage pieces almost completely disappears and the sample can be stretched without broken (Fig. 7).

The healing properties were further tested by measuring the self-healing efficiency, which was defined by the ratio between tensile strength of the mending sample and the sample original strength. Again, we cut the sample into two pieces and the pieces were brought together for some time at room temperature without other pressure. The recovery sample could be stretched again and recover to original length when the stress was released. Detailed self-healing properties of HSP-NH₂ and composites are shown in Fig. 8. The recovery of the sample strength is due to the self-complementary and mobile hydrogen bonding network site. When they were cut into pieces, the weaker hydrogen bonds on the section were broken and linked with other non-associated groups. Once they were combined together, the broken hydrogen bonds associated again, then driving

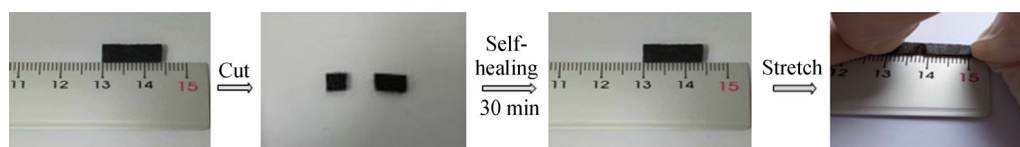


Fig. 7 Photographs of self-healing behavior of the sample HSP-NH₂ after cut and subsequent 30 min healing at room temperature

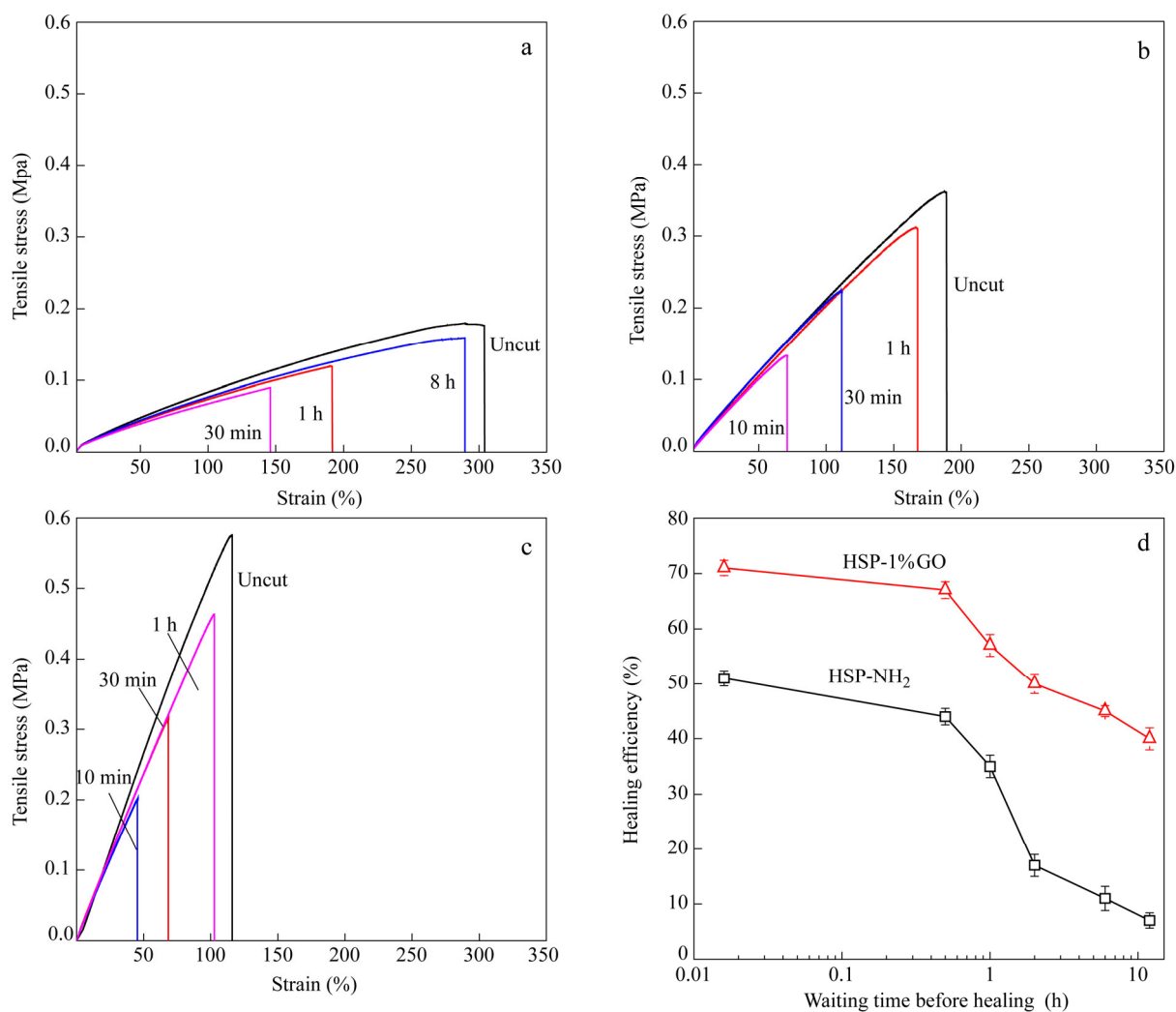


Fig. 8 Stress-strain curves of the HSP-NH₂ and HSP-GO composites upon different healing time at room temperature: (a) HSP-NH₂, (b) HSP-1%GO, and (c) HSP-2%GO; (d) Healing efficiency of HSP-NH₂ and HSP-1%GO samples for 30 min, healing with different waiting time (10 min, 30 min, 1 h, 2 h, 6 h and 12 h)

the molecular chains to move, touch, and get tangled for reaching to the previous state.

Figure 8(a) shows the stress-strain curves from healing test of HSP-NH₂. Longer healing time leads to higher efficiency. When the contact time is about 8 h, 90% self-healing can be achieved to its original tensile strength, but the healing rate is too low for the actual application. We cut the HSP-GO composites into two pieces and brought the pieces to contact. Two pieces mend quickly without other treatment and the healing time is shorter than that of HSP-NH₂. As shown in Fig. 8(b), after the two pieces contact for 10 min, the HSP-1%GO sample heals to 37% of its original tensile strength. When the contact time is 1 h, the repaired sample can almost reach original mechanical properties. With the addition of modified graphene oxide in HSP-NH₂, the HSP-2%GO sample can recover 30% of their original strength in 10 min. Compared with the HSP-1%GO sample, the time of self-healing process of HSP-2%GO increases. The main reason may be that the addition of modified graphene oxide disturbs the polymer chains movement, resulting in decreased healing rate of composite materials. The time of healing process for all the composites is significantly shorter than that for pure HSP-NH₂ because of many reactive sites on the modified graphene oxide surface. Importantly, we also introduce the donor and acceptor of hydrogen bond to the graphene oxide, ensuring a high density of hydrogen bonding network for rapid self-healing at room temperature.

Some reports showed that the self-healing efficiency of samples decreased rapidly when the samples were not mended completely but waited for some time^[31]. The self-healing efficiency relies on the non-associated groups in the damaged interface; the longer the waiting time before healing is, the less the free non-associated groups exist on the interface. In addition, the longer the waiting time before healing is, the lower the self-healing efficiency of the samples is. To investigate the decrease of self-healing efficiency with the lapse of waiting time, we cut HSP-NH₂ and HSP-1%GO into two pieces and waited for different time in nitrogen atmosphere, and the self-healing efficiency was tested after mending for 30 min. As shown in Fig. 8(d), the self-healing of HSP-NH₂ dropped to 40% while the two pieces were left apart for 30 min. In comparison, the self-healing efficiency of HSP-1%GO dropped to 40% when the pieces were left apart for 10 h. These phenomena indicate that HSP-1%GO has a lower descent rate of healing efficiency than HSP-NH₂, which is attributed to the loss of hydrogen bonds site in the composites. The other reason is that the graphene oxide can increase the Young's modulus of composites, leading to the slow descent of self-healing efficiency.

It is difficult to obtain direct spectrum evidence of an excess of non-associated hydrogen bonds at a cut surface because even reflectance infrared techniques probe and average over a depth comparable to the radiation wavelength, that is, a few micrometres^[21]. The dynamic re-association of the hydrogen bonds on the cut surface can be tested by temperature-jump experiment. The HSP-NH₂ sample is heated at 120 °C for 10 min and then quenched to 25 °C, and the evolution of infrared spectrum over time can be observed. Figure 9 shows the relationship between intensity ratio of free

N–H bending signals (1552 cm⁻¹) and associated N–H bending signals (1565 cm⁻¹) with increasing characteristic time. This explained that when excess free hydrogen groups were created by cutting or heating, they associated slowly, and the association time was compatible with the time during which healing was possible.

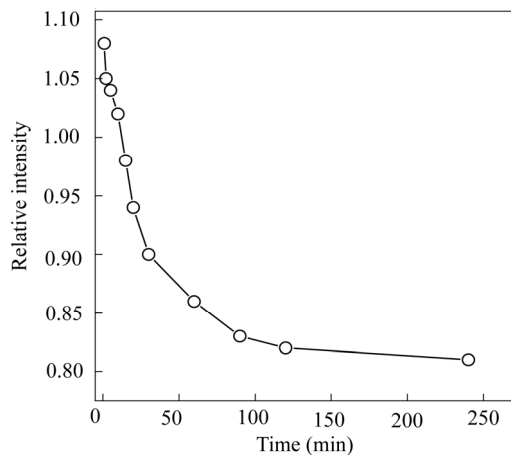


Fig. 9 The corresponding relative intensity of free N–H (1552 cm⁻¹) and associated N–H (1565 cm⁻¹)

CONCLUSIONS

In summary, a self-healing supramolecular polymer composite (HSP-GO) was prepared by supramolecular polymer matrix with hydrogen bonds and modified graphene oxide. The hydrogen bonds of HSP-NH₂ mainly stem from ureido groups and amino groups, which is possible for the observation of self-healing behaviors. However, the polymer has poor mechanical properties and slower healing rate. In contrast to pure HSP-NH₂, the HSP-GO composites allows for rapid and efficient self-healing at room temperature. The result shows that upon adding 1 wt% of modified graphene oxide, the efficiency of HSP-1%GO can improve 37% of original break strength. The self-healing efficiency is related to the density of hydrogen bonding sites and the molecular movement. It should be noted that the composites show a significant enhancement of mechanical properties by adding modified graphene oxide. Owing to their good dispersion and excellent mechanical properties, the composites exhibit higher modulus and lower tensile strain. These properties may make the materials have a good application prospects.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2025-y>.

REFERENCES

- Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-healing polymers and composites. *Annu. Rev. Mater. Res.* 2010, 40, 179–211.
- Hager, M. D.; Greil, P.; Leyens, C.; Zwaag, S. V. D. Self-healing materials. *Adv. Mater.* 2010, 22(47), 5424–5430.

- 3 Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. Using the dynamic bond to access macroscopically responsive structurally dynamic polymers. *Nat. Mater.* 2011, 10(1), 14–27.
- 4 Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science* 2002, 295(5560), 1698–1702.
- 5 Burattini, S.; Greenland, B. W.; Merino, D. H.; Weng, W.; Seppala, J.; Colquhoun, H. M.; Hayes, W.; Mackay, M. E.; Hamley, L. W.; Rowan, S. J. A healable supramolecular polymer blend based on aromatic π - π stacking and hydrogen-bonding interactions. *J. Am. Chem. Soc.* 2010, 132(34), 12051–12058.
- 6 Klukovich, H. M.; Kean, Z. S.; Iacono, S. T.; Craig, S. L. Mechanically induced scission and subsequent thermal remending of perfluorocyclobutane polymers. *J. Am. Chem. Soc.* 2011, 133(44), 17882–17888.
- 7 Zheng, P.; Mccarthy, T. J. A surprise from 1954: siloxane equilibration is a simple, robust, and obvious polymer self-healing mechanism. *J. Am. Chem. Soc.* 2012, 134(4), 2024–2027.
- 8 Chen, X.; Wudl, F.; Mal, A. K.; Shen, H.; Nutt, S. R. New thermally remendable highly cross-linked polymeric materials. *Macromolecules* 2003, 36(6), 1802–1807.
- 9 Liu, F.; Li, F.; Deng, G.; Chen, Y.; Zhang, B.; Zhang, J.; Liu, C. Y. Rheological images of dynamic covalent polymer networks and mechanisms behind mechanical and self-healing properties. *Macromolecules* 2012, 45(3), 1636–1645.
- 10 Ghosh, B.; Urban, M. W. Self-repairing oxetane-substituted chitosan polyurethane networks. *Science* 2009, 323(5920), 1458–1460.
- 11 Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. Optically healable supramolecular polymers. *Nature* 2011, 472(7343), 334–338.
- 12 Ling, J.; Rong, M. Z.; Zhang, M. Q. Effect of molecular weight of PEG soft segments on photo-stimulated self-healing performance of coumarin functionalized polyurethanes. *Chinese J. Polym. Sci.* 2014, 32(10), 1286–1297.
- 13 Lehn, J. M. Dynamers: dynamic molecular and supramolecular polymers. *Prog. Polym. Sci.* 2005, 30, 814–831.
- 14 Herbst, F.; Döhler, D.; Michael, P.; Binder, W. H. Self-healing polymers *via* supramolecular forces. *Macromol. Rapid Commun.* 2013, 34(3), 203–220.
- 15 Cuthbert, T. J.; Jadischke, J. J.; Bruyn, J. R. D.; Ragona, P. J.; Gillies, E. R. Self-healing polyphosphonium ionic networks. *Macromolecules* 2017, 50, 5253–5260.
- 16 Li, Y.; Li, J.; Chen, B.; Chen, Q.; Zhang, G.; Liu, S.; Ge, Z. Polyplex micelles with thermoresponsive heterogeneous coronas for prolonged blood retention and promoted gene transfection. *Biomacromolecules* 2014, 15(8), 2914–2923.
- 17 Wang, C.; Zhang, G.; Liu, G.; Hu, J.; Liu, S. Photo- and thermo-responsive multicompartement hydrogels for synergistic delivery of gemcitabine and doxorubicin. *J. Control. Release* 2017, 259, 149–159.
- 18 Zeng, Q.; Desai, M. S.; Jin, H. E.; Lee, J. H.; Chang, J.; Lee, S. W. Self-healing elastin-bioglass hydrogels. *Biomacromolecules* 2016, 17(8), 2619–2625.
- 19 Brocorens, P.; Linares, M.; Guyardduhayon, C.; Guillot, R.; Andrioletti, B.; Suhr, D.; Benjiamin, I.; Lazzaroni, R.; Bouteiller, L. Conformational plasticity of hydrogen bonded bis-urea supramolecular polymers. *J. Phys. Chem. B* 2013, 117(17), 5379–5386.
- 20 van Gemert, G. M. L.; Peeters, J. W.; Söntjens, S. H. M.; Janssen, H. M.; Bosman, A. W. Self-healing supramolecular polymers in action. *Macromol. Chem. Phys.* 2012, 213, 234–242.
- 21 Cordier, P.; Tournilhac, F.; Soulie-Ziakovi, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* 2008, 451(7181), 977–980.
- 22 Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. *Nat. Chem.* 2013, 5, 1042–1048.
- 23 Lopez, J.; Chen, Z.; Wang, C.; Andrews, S. C.; Cui, Y.; Bao, Z. The effects of cross-linking in a supramolecular binder on cycle life in silicon microparticle anodes. *ACS Appl. Mater. Interfaces* 2016, 8, 2318–2324.
- 24 Tee, B. C.; Wang, C.; Allen, R.; Bao, Z. An electrically and mechanically self-healing composite with pressure- and flexion-sensitive properties for electronic skin applications. *Nat. Nanotechnol.* 2012, 7(12), 825–832.
- 25 Wang, G.; Yang, J.; Park, J.; Gou, X.; Wang, B.; Liu, H.; Yao, J. Facile synthesis and characterization of graphene nanosheets. *J. Phys. Chem. C* 2008, 112, 8192–8195.
- 26 Wang, G.; Shen, X.; Yao, J.; Park, J. Graphene nanosheets for enhanced lithium storage in lithium ion batteries. *Carbon* 2009, 47, 2049–2053.
- 27 Pei, S.; Cheng, H. M. The reduction of graphene oxide. *Carbon* 2012, 50(9), 3210–3228.
- 28 Wang, C.; Liu, N.; Allen, R.; Tok, J. B. H.; Wu, Y.; Zhang, F.; Chen, Y.; Bao, Z. A rapid and efficient self-healing thermo-reversible elastomer crosslinked with graphene oxide. *Adv. Mater.* 2013, 25, 5785–5790.
- 29 Li, J.; Zhang, G.; Deng, L.; Zhao, S.; Gao, Y.; Jiang, K.; Sun, R.; Wong, C. *In situ* polymerization of mechanically reinforced, thermally healable graphene oxide/polyurethane composites based on Diels-Alder chemistry. *J. Mater. Chem. A* 2014, 2(48), 20642–20649.
- 30 Xu, C.; Wu, X.; Zhu, J.; Wang, X. Synthesis of amphiphilic graphite oxide. *Carbon* 2008, 46(2), 386–389.
- 31 Zhang, A.; Yang, L.; Lin, Y.; Yan, L.; Lu, H.; Wang, L. Self-healing supramolecular elastomers based on the multi-hydrogen bonding of low-molecular polydimethylsiloxanes: synthesis and characterization. *J. Appl. Polym. Sci.* 2013, 129(5), 2435–2442.