

A Rapid and Efficient Self-Healing Thermo-Reversible Elastomer Crosslinked with Graphene Oxide

Chao Wang, Nan Liu, Ranulfo Allen, Jeffrey B.-H. Tok, Yinpeng Wu, Fan Zhang, Yongsheng Chen, and Zhenan Bao*

Most natural biomaterials have an innate ability to self-heal or self-repair upon encountering damages. For example, a minor wound on human skin can be completely healed over time, while a more severe damage will lead to scar, but still nonetheless able to retain primary sensory functionalities. This self-healing ability has recently been shown to extend material lifetime, safety and other desired parameters in numerous applications.^[1–8] For these purposes, many synthetic self-healing polymers have thus been developed.^[9–12] Most reported self-healing polymers are designed based on reversible bonds, including non-covalent or dynamic covalent bonds.^[13] These bonds are able to reversibly associate and dissociate upon the input of external energy, such as heat^[14–18] or light.^[19–24] Since their bond strengths are weaker than covalent bonds, they tend to break first upon damaging. However, with heat or light irradiation, these dynamic bonds at the fractured/damaged areas can be re-established, thus driving the polymer chains to contact, diffuse and re-entangle above the glass transition temperature (T_g), hence leading to mechanical healing of the material.^[1]

A few examples of materials have shown the ability to spontaneously self-heal at ambient conditions. Moore and White have embedded microcapsules into polymers to allow for self-healing upon cracking the microcapsules. However, the healing process requires healing agents, e.g. monomers and catalysts, and is a singular event.^[25] Some gel systems have also been demonstrated to self-heal at room temperature, but they require a large amount of solvent and lack sufficient mechanical strength for application.^[26–28] Sun and coworkers demonstrated the healing of polyelectrolyte film (PET) at room temperature, but this process requires the assistance of water.^[29]

For practical applications, self-healing polymers with good elasticity and spontaneous self-healing capability are highly desirable towards replacement of conventional rubber materials as protective coatings, sealing agents, etc. However, elastic self-healing polymers are still rare. One promising approach

towards spontaneous self-healing material is amorphous polymers based on hydrogen bonding network, which is able to associate and dissociate reversibly at room temperature.^[30] However, most of these polymers generally have very poor mechanical properties and are not suitable for practical applications. To address this problem, Leibler and coworkers pioneered the design of a self-healing polymer with a high density of hydrogen bonds and covalent cross-linking sites.^[31,32] However, as the T_g of the described polymer was too high for spontaneous self-healing, addition of a plasticizer was required. We have recently used chemically-compatible nickel microparticles as fillers to enhance the mechanical properties of the hydrogen-bonded polymers and successfully obtained a conductive composite with autonomous and repeatable self-healing capability at room temperature and touch-sensing capability.^[2] In addition, Guan and coworkers recently reported a strategy for self-healing polymer by generating covalently linked hard crystalline polystyrene domains to soft polymers, hence creating a self-healing thermoplastic rubber.^[33] However, in the last two examples, a rather high volume percentage of fillers or crystalline domains were required in order to obtain a solid material, which subsequently greatly reduces the density of dynamic hydrogen bonds, thus restricting the movement of the polymer chains bearing hydrogen bonds. This effect usually results in a slow mechanical healing speed (typically over one day for complete mechanical healing). Hence, developing materials that possess parameters including adequate mechanical strength, spontaneous self-healing capability and fast self-healing speed, still remain a daunting challenge.

Here, we describe an elastic nanocomposite material with the ability to rapidly self-heal at room temperature by combining the unique features of hydrogen-bonded polymer and graphene oxide (GO) as a macro-crosslinker. Importantly, it also possesses mechanical strength comparable to commercial rubbers. Incorporation of GO enabled our composite with good mechanical strength; while the hydrogen bonding network within the polymer chains provide self-healing capability. GO is the oxidized form of graphene^[34–45] and has been established for its high-mechanical strength, large surface area and its ease for chemical modifications.^[46–50] The advantage of using GO instead of other typical crosslinkers is that only a small amount of GO is needed to achieve a dramatic improvement in the mechanical property of the composite, due to the multiple reactive sites on GO and its high mechanical strength. As a result, the density of available hydrogen bond sites (highly critical for self-healing) is not significantly reduced (**Figure 1**). In specific, we observed that by adding as little as <2 wt% of GO to the polymer, we obtained an elastic material (elastomer) with similar mechanical property to that of conventional rubbers,

Dr. C. Wang, Dr. N. Liu, R. Allen, Dr. J. B.-H. Tok,
Prof. Z. Bao
Department of Chemical Engineering
Stanford University
381 North South Mall, Stanford, CA, 94305, USA
E-mail: zbao@stanford.edu

Y. Wu, F. Zhang, Prof. Y. Chen
The Key Laboratory for Functional Polymer Materials
and Centre for Nanoscale Science and Technology
Institute of Polymer Chemistry
College of Chemistry
Nankai University
Tianjin, 300071, China



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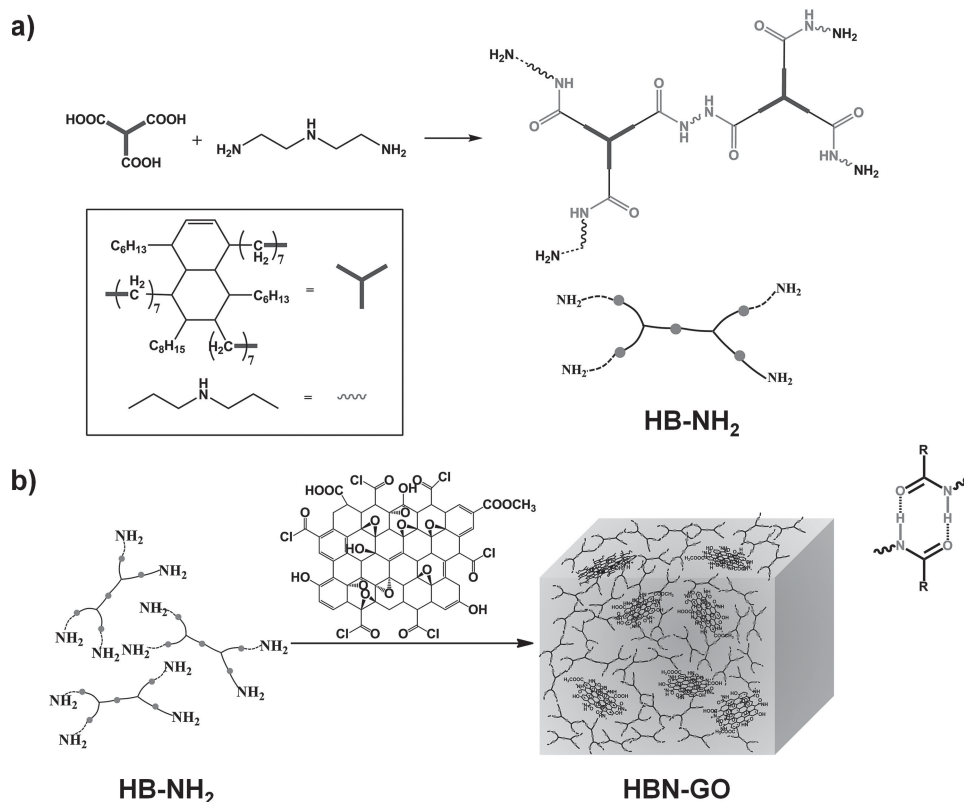


Figure 1. a) Synthetic route of HB-NH₂; b) Schematic illustration of the synthesis of the self-healing nanocomposite (HBN-GO)

while possessing a very fast healing speed at room temperature. Our obtained nanocomposite displayed a fast spontaneous self-healing and can heal up to 50% of its pristine extensibility in ~ 1 min in the absence of any healants, plasticizer, solvents, or external energy, while complete mechanical healing can be completed in ~ 1 hr.

The synthesis of the nanocomposite is described in detail in the Materials section. Briefly, amine-terminated randomly branched oligomer (HB-NH₂) was afforded as a viscous material by adding a tri-acid to a diethylene triamine at high temperature (Figure 1a). Next, commercially available GO nanosheets were treated with thionyl chloride, and the generated carbonyl chloride groups (GO-COCl) were confirmed via X-ray photoelectron spectroscopy (XPS) (Figure S1). Upon subsequent addition to HB-NH₂, GO-COCl will covalently cross-link to the oligomer (through the formation of amide bonds) to produce a black elastic material. Again, the formation of covalent amide binds are confirmed by XPS, which displays strong N1s peaks for the GO sample after reacting with HBN (Figure S1). Even though the extent of crosslinking by GO-COCl is difficult to quantify, it should be noted that direct mixing of HB-NH₂ with unmodified graphene oxide can only lead to viscous liquid-like materials instead of a solid material with GO-COCl, confirming the presence of covalent cross-linking between the polymer and graphene. In addition to GO, the polymer matrix is different from those previously used by Leibler^[31] and our previous work^[2] in that: (i) instead of urea groups, amide groups, which have weaker hydrogen bonds but more dynamic (i.e. can break

and re-form at a faster speed), are used; (ii) the polymer has a more branched structure due to the use of the tri-acid instead of a mixture of tri- and di-acid as the starting material for the polymer network; and (iii) addition of a small amount of GO resulted in a higher elasticity.

To investigate the influence of GO as a filler within the polymer, we proceed to synthesize three HBN-GO composites with different weight percentages of GO at 1, 2 and 4 wt%; which we termed HBN-1% GO, HBN-2% GO, HBN-4% GO, respectively. For all the three materials synthesized, we did not observe any crystalline patterns from our obtained GIXD results, indicating that all the three materials are amorphous (Figure S3), typical for randomly branched polymers. The periodic pattern at 0.42 nm corresponds to the slight π - π packing of 2-D GO sheets. Cross-section images show that majorities of the GO nanosheets were well dispersed in the polymer matrix for all the three composite samples with different GO wt% (Figure S4). Furthermore, we observed that the amount of GO nanosheets increased correspondingly with increasing weight percentages of GO. In addition, no large aggregations of the GO nanosheets were observed, even when the amount of GO was at 4 wt%. The high resolution SEM image of HBN-2% GO sample showed that the dispersion of the GO nanosheets was uniform with polymer coated on their surfaces (Figure 2a). Last, since the increase in GO components results in more cross-linking sites, the T_g values of the resulting composites have also changed as confirmed by their DSC results (Figure 2b). In specific, the composite of 1 wt% GO has a T_g of -5 °C, while

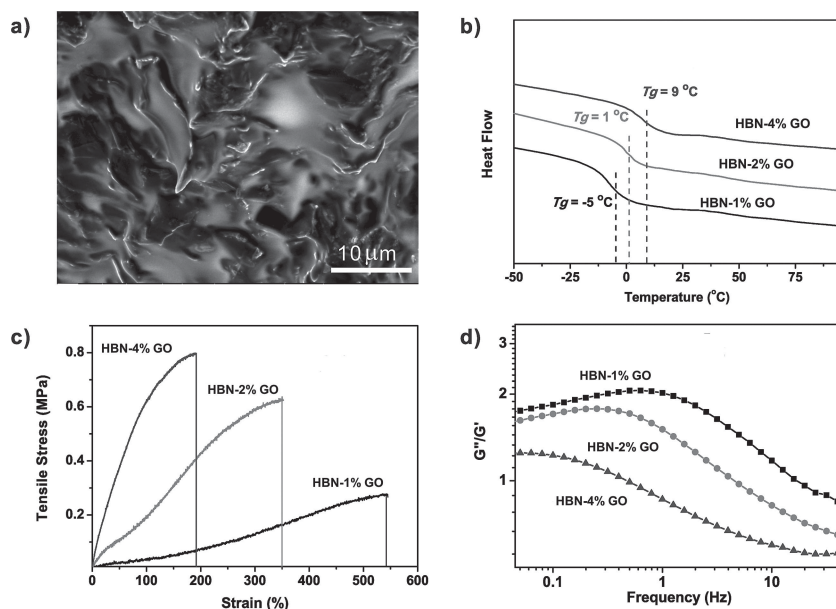


Figure 2. a) A cross-sectional SEM image of the HBN-4%GO nanocomposite; b) DSC isotherms of the self-healing composites with different GO percentages; c) Strain-stress curves of the self-healing nanocomposite with different graphene oxide composition; d) The ratios between loss modulus (G'') and storage modulus (G') of the materials at different frequencies.

the T_g of HBN-2% GO and HBN-4% GO increased to 1 °C and 9 °C, respectively. The obtained T_g values of all these materials are well below ambient temperature, indicating that they have potential for self-healing at room temperature.

Since there is a high number of hydrogen bonding networks in the composites, the material can be reversibly molded into various shapes at elevated temperatures, which is termed as a 'thermo-reversible' property. All the HBN-GO nanocomposites behaved similarly to typical rubbers, such as poly(dimethyl siloxane) (PDMS), at room temperature, and can quickly reverted to their original dimensions under several seconds after being stretched to double its original length. Detailed mechanical properties of the composites were measured via tensile-strain tests. As shown in Figure 2c, the static stress-strain curves of all the HBN-GO nanocomposite materials resembles that of classical rubbery materials with a large elastic deformation region up to 540%. The key parameters of the mechanical properties are summarized in Table 1. The values of the Young's modulus and maximum strain are comparable to conventional rubber (e.g. soft PDMS, with an $E' = \sim 0.1$ MPa). The mechanical properties of the composites can also be systematically tuned by varying the amount of GO. Figure 1 shows

that the Young's modulus increased by ca. one order of magnitude when the weight percentage of GO change from 1% to 4%, while the maximum strain decreased from 540% to 190%. When the samples were left in open air to fully equilibrate with moisture, the modulus can drop by around 20–30%. This result is similar with previously-reported self-healing elastic materials based on hydrogen bonds.^[33] The addition of GO increased the elasticity of the composite, as evident from the results obtained via rheological tests of the composites. The ratio between loss modulus (G'') and storage modulus (G') is an indication of the elasticity of the material, in which a higher G''/G' value indicates a lower elasticity. As shown in Figure 2d, we observed that the G''/G' ratios decreased with the corresponding increase in GO amounts (when measured at all frequencies), confirming that the elasticity of our nanocomposite material is indeed enhanced upon an increase in GO cross-linkers.

Unlike conventional rubbery materials, our nanocomposite materials are able to self-heal since they contain a high number of mobile hydrogen bonding sites in the networks (the density of amide is around 1 mmol/g). It was recently reported that the hydrogen bond density, as governed by their density on the polymer side chains, were critical in mediating the self-healing when two separate hydrogel pieces were placed in close contact^[51]. Specifically, the flexible side chains allowed the functional moieties at the interface between the two hydrogel pieces to rapidly re-establish hydrogen binding networks, which led to an increase in the healing speed. We believe our reported self-healing nanocomposite behaves through a similar mechanism, in which the polymers are randomly branched and are low in its molecular weight, enabling the polymer chains to be mobile while the required mechanical properties are tuned by the incorporation of GO. Upon a mechanical damage event, the weaker hydrogen bonds are more likely to break as opposed to the stronger covalent bonds. Once the exposed damaged surfaces are returned into contact, the 'broken' hydrogen bonds at the interfaces can be re-established, thus driving the polymer chains to rearrange, diffuse, and heal above T_g . Again, our nanocomposite materials have a high density of hydrogen bonding network to enable this efficient and fast healing capability. Both its amorphous structure and low T_g allow the polymer chains to diffuse and

Table 1. Summary of the mechanical properties of the nanocomposite samples at different GO composition. The average values were obtained with 3 samples.

Sample	Young's Modulus (MPa)	Strain-at-break (%)	Stress-at-break (MPa)	1 min healing (%)	1 h healing (%)
SHP-1% GO	0.086 ± 0.010	530 ± 45	0.26 ± 0.05	60 ± 3	98 ± 5
SHP-2% GO	0.23 ± 0.02	336 ± 18	0.58 ± 0.06	36 ± 2	85 ± 3
SHP-4% GO	0.85 ± 0.09	191 ± 10	0.80 ± 0.02	21 ± 1	53 ± 3

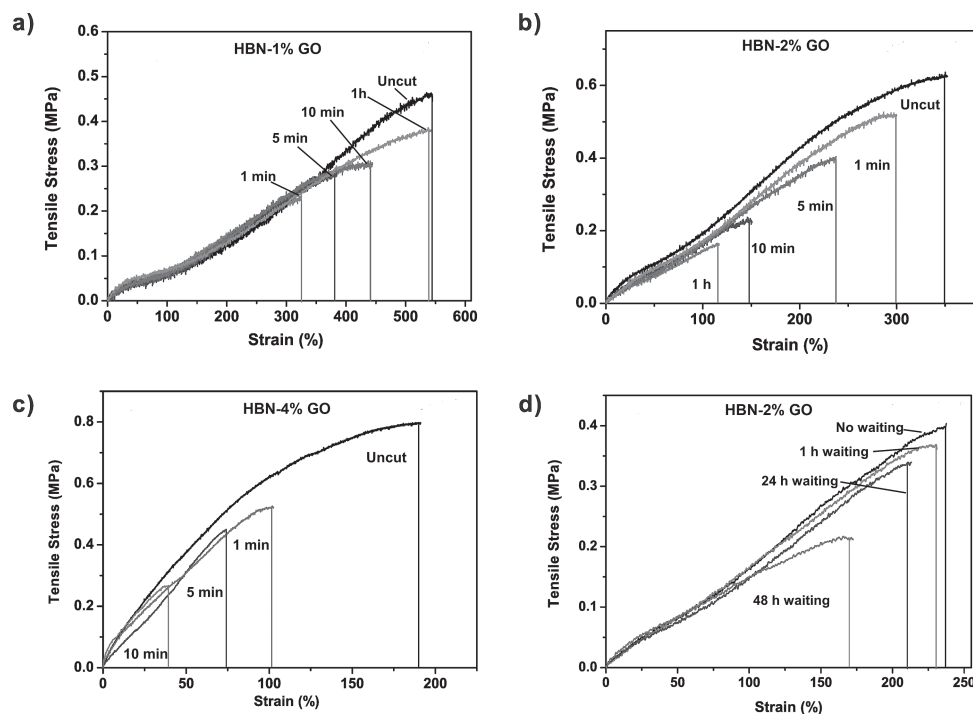


Figure 3. Strain-stress curves of the self-healing composites with GO at a) 1 wt%, b) 2 wt% and c) 4 wt% upon different healing time at room temperature; d) Strain-stress curves of the HBN-2% GO samples of 10 min healing at different waiting time. The waiting was performed at approx. 0% relative humidity.

mix at room temperature, and be able to self-heal at room temperature without the need of any plasticizer, solvent, healing agents or external stimuli. To demonstrate this effect, we proceeded to first cut our nanocomposite material into two separate pieces with a razor blade. Subsequently, we brought the two cut pieces gently back into contact. We observed that the two individual cut pieces were able to spontaneously self-heal under ambient conditions without any other treatment in less than 60 sec. In addition, our obtained stress-strain curves for our GO-incorporated polymer showed characteristic rubber behavior and resembled values similar to the original uncut samples. In specific, we observed that HBN-1% GO has the fastest healing speed. As shown in **Figure 3a**, after bringing the two cut pieces back in contact for ~1 min, the HBN-1% GO sample can be healed to ~60% of its original tensile strength prior to cutting. In addition, complete healing of the mechanical properties can be obtained in 1 hour. Increasing the amount of GO allows for more covalent cross-linking and more restricted movement of polymer chains, which may explain the observed trend for increased time for the self-healing process. Both the samples in HBN-2% GO and HBN-4% GO also possess fast self-healing capabilities, in which they are able to recover 36% and 20% of their original extensibilities, respectively, in ~1 min. The healing speed for all our GO composites is significantly shorter than other previously described hydrogen bonding self-healing polymers, which generally need more than 10 hours heal to 90% of its original tensile strength. Even though our previously reported self-healing conductive composites had a quick healing speed but they were not elastic.^[2]

For self-healing materials that rely on hydrogen bonds, a major disadvantage is the rapid drop in its self-healing efficiency when the two damaged surfaces are left apart for as short as several hours, even at low humidity conditions.^[31,33] To investigate the decay of self-healing efficiency over time, several samples of HBN-2% GO were cut and left apart in nitrogen glovebox for different durations, and their self-healing efficiencies were subsequently tested after being healed for 10 minutes. As shown in **Figure 3d**, the self-healing capability only dropped to ~90% efficiency after the two fractured surfaces were left apart for 24 h, and dropped further to ~50% after 96 h. In comparison, for several related self-healing systems previously reported,^[31] the self-healing efficiency dropped to ~50% after the two fractured surfaces were left apart for 18 h. Furthermore, in the self-healing side chain polymer system,^[33] the self-healing efficiency dropped to ~50% after the two fractured surfaces were left apart for 10 h. Hence, our self-healing composite shows a significantly slower decay rate in its self-healing efficiency, and we again attribute this property to the high density of available hydrogen bonding sites within our nanocomposite materials. Another reason could again be attributed to the graphene component, which can increase the Young's modulus of the composite and, at the same time, decrease the recombination speed, leading to the slow decay of self-healing efficiency.

To investigate the physical details of the self-healing behaviors of HBN-2% GO samples, we monitored the healing process using both optical microscope and SEM. Again, we first cut our nanocomposite material into two separate pieces with a razor blade, followed by bringing the two cut pieces gently

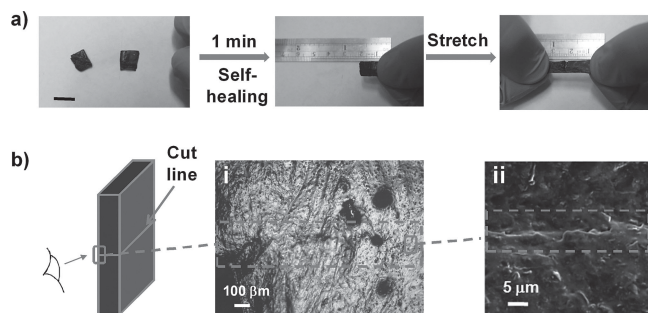


Figure 4. a) Stretching of the SHP-GO 2% sample after cut and subsequent 1 min self-healing at room temperature. The sample can be stretched to 100% after only 1 min of healing while retaining a modulus similar to pristine sample. b) (i) Optical microscope images and (ii) SEM images of the cross-section of the interface, i.e. cut line.

back into contact to heal. First, the obtained optical microscope images indicated that physical healing of the damaged surfaces occurred in ~ 12 h (Figure 4b), with the exception at the edges (in which we attribute to poor contact at the edges). Second, SEM images confirmed that the physical interface between the damaged surfaces sufficiently healed such that the gaps were indiscernible (Figure 4bii), thus lending strong evidences to the efficiency in the overall self-healing process. Besides its physical property, we also measured their mechanical property. We observed that when the two cut pieces were brought together for a mere ~ 1 min, the resulting healed sample can be subsequently subjected to 100% strain. Furthermore, it was also able to revert to its original dimension after stretching (Figure 4a).

To confirm the role of GO, we prepared a control sample with similar mechanical property as our graphene composites. Instead of using 1 wt% of GO, the control sample (named HBN-diacid) was prepared by reacting HB-NH₂ with adipic acid (a diacid). In this case, 8 wt% of diacid was needed in order to achieve a similar Young's modulus (~ 0.09 MPa) to the GO composite. Therefore, a much higher number of covalent bonds is present in our composite and, hence, is expected to restrict the movement of the polymer chains (see Experimental Section for its structure and information about its preparation). As a result, HB-diacid showed a much lower self-healing efficiency after the same healing time. When compared to HBN-1% GO, which can heal up to 80% of its initial extensibility in 10 min, HBN-diacid was able to heal to only $\sim 50\%$. We attribute this observation to the presence of larger amount of covalent cross-linking sites present in HBN-diacid (~ 0.5 mmol/g), in which they have greatly reduced the flexibility and dynamic property of the polymer chains and, hence, decreased its self-healing capability. Therefore, using GO as a reactive high surface area filler can greatly increase the material's mechanical properties, and also in preserving its self-healing efficiency.

In conclusion, we have described a self-healing thermoreversible elastomer based on GO nanocomposites. In contrast to previously reported self-healing systems, our HBN-GO system allows for both rapid and efficient self-healing (in only several minutes) at room temperature, without the need for any external stimuli (e.g. heating or light exposure), healing

agents, plasticizers or solvents. It should be noted that the mechanical property of nanocomposites can be further tuned by adding small molecule cross-linkers (like adipic acid or other diacid, triacid, etc.) and further cross-linking. At higher cross-linking density, the nanocomposite exhibited higher modulus and lower extensibility. These self-healing elastomers should be useful toward applications such as protecting barrier for electronic wires and devices, sealing layer for gas systems, etc. Our described concept of using GO as both cross-linkers and fillers to derive highly efficient self-healing materials will also be applicable to a wide range of other supramolecular systems, e.g. metal coordination bond or dynamic covalent bond containing functional polymers. Last, when combined with electrical fillers, these elastomers should also display electrical conductivities that are useful towards stretchable self-healing conductive wires.

Experimental Section

Synthesis of HB-NH₂: Trimer acids (41.5 g, Emery 2045, Emery Oleochemicals, 0.137 mol of COOH) were mixed with 16 g of DETA (0.155 mol). The mixture was stirred at 120 °C in Ar for 2 h until a homogeneous dispersion was attained. The temperature was then increased to 160 °C and the mixture was stirred for an additional 24 h. The products were cooled down to room temperature, and subsequently dissolved in 150 mL of chloroform. It was then washed with 500 mL of a mixture of methanol and water (1:2 by volume) 3 times. The organic layer was pooled and the HB-NH₂ product was obtained by removing the solvent under vacuum. ¹H NMR (500 MHz, d-chloroform): 3.32 (m), 2.79 (m), 2.72 (m), 2.65 (m), 2.35 (m), 1.60 (m), 1.22 (m), 0.85 (m).

Preparation of self-healing composites: GO was prepared according to Hummer's methods. Briefly, GO powder was mixed with excessive amount of thionyl chloride. The mixture was kept stirring at 70 °C for 12 h in a flask equipped with a water-condenser. GO modified with carbonyl chloride (GO-COCl) was obtained by evaporating thionyl chloride under vacuum, and then dispersed in anhydrous DMF. The dispersion was added dropwise into the DMF solution of HB-NH₂. The resulted mixture was heated at 90 °C for 24 h, and then drop-casted on a glass at 80 °C for 30 mins to evaporate the solvents. The film was then peeled off from the glass and molded onto samples for testing.

Preparation of HB-GO-ester: GO-COCl was mixed with excessive amount of methanol and triethylamine and stirred at 60 °C for 5 h. The solvent was then removed under vacuum to yield GO terminated with ester. GO-ester was dispersed in DMF and mixed with HB-NH₂. Resulting mixture was dropped casted onto a glass at 80 °C to remove DMF, and the obtained film was peeled off from glass and molded onto samples for testing.

Preparation of HB-diacid: HB-NH₂ (1 g) was added to 80 mg of adipic acid (0.54 mmol) and stirred at 140 °C in Ar for 1 hr. The obtained HB-diacid was then molded onto the samples for testing.

Mechanical tests: Mechanical tensile-stress experiments were performed using an Instron 5848 Microtester, using ASTM D638 normalized samples as references. We tested three samples for each volume fraction. Tensile experiments were performed at room temperature (25 °C) at a strain rate of 5 mm/min. Healing experiments were performed at room temperature by gently bringing severed samples together. Rheological experiments were carried out using a stress-controlled rheometer (TA Instruments Model AR-G2). Differential Scanning Calorimetry (DSC) experiments were performed using a Model Q2000 from TA Instruments (USA). The temperature range is -50 to 150 °C, at a heating and cooling speed of 20 °C/min. The waiting procedure after cutting was performed in a nitrogen glovebox with a very low humidity (approx. < 1 ppm H₂O, 0% relative humidity).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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