Multichannel and Repeatable Self-Healing of Mechanical Enhanced Graphene-Thermoplastic Polyurethane Composites

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Polymeric materials have been used in a variety of fields, including transport industries (cars, ships, and aircrafts), defense industries, civil engineering, electronics, etc. However, these materials are susceptible to failure after fracture or damage, which leads to a sharp decrease in their sustainability, safety, and lifetime. Thus, exploration of self-healing polymeric materials that can repair themselves after mechanical damage is in high demand.

For decades, scientists and engineers have paid great attention to developing self-healing polymeric materials to improve the safety, lifetime, energy efficiency, and environmental impact of man-made materials.[1] In most cases, microcontainers, such as hollow fibers,[2–4] particles,[5] and microcapsules,[6–8] which store healing agents, are embedded in the polymer matrix to form self-healing polymeric composites. Once a crack is formed, the healing agent would be released into the crack place due to the capillary effect, and then re-bond the crack. This kind of self-healing materials can heal themselves spontaneously and timely, but they can be healed only once at the same location because of exhaustion of the healing agents. To overcome this limitation, Toohey et al. designed in 2007 a repeatable self-healing material by replacing the conventional microcontainers with microvascular networks.[9] In this self-healing system, the healing agent could be delivered to the crack area via a three-dimensional microvascular network which was embedded in the epoxy matrix and thus the polymeric material could be healed repeatedly. On the other hand, Wudl and co-workers developed a reversible polymer that also exhibited multiple cycles of crack mending with simple thermal treatment.[10] Then, a new type of self-healing materials, the synthesized reversible polymers, which can be self-healed owing to the physical and/or chemical interactions at the broken interfaces have been designed recently.[1,11–15] Though research on these two types of self-healing materials has made great advances, some critical problems that hinder their practical applications still remain. For example, self-healing materials with embedded microcontainers may have compromised mechanical strength.[2,13,16–20] And reversible polymers are also unsatisfactory with respect to their poor mechanical properties and high cost. More importantly, all polymeric materials can just be healed via only one approach, which severely limits their possible applications in many cases. Thus, developing novel self-healing materials, which not only possess enhanced mechanical properties without sacrificing their healing efficiencies but also can be healed repeatedly via multi-channels still remains a great challenge.

Graphene materials, 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 composite materials because of their ultrahigh mechanical strength.[21–25] Furthermore, they also have some remarkable properties, including super chemical stability, outstanding electrical and thermal conductivity,[26–30] good microwave and infrared (IR) absorbing capacity,[31–34] which endows them with a strong response to IR light, electricity and electromagnetic waves, etc. These properties prompt us to believe that integrating graphene materials with appropriate polymeric materials might generate some novel self-healing materials, which not only have enhanced mechanical properties but also can be healed via multi-channels. To the best of our knowledge, no such study has been reported so far.

Herein, we report a novel self-healing material fabricated with few-layer graphene (FG) and thermoplastic polyurethane (TPU). Different from the conventional self-healing polymeric materials, in addition to its enhanced mechanical property, this FG-TPU self-healing material can be healed repeatedly via different methods including infrared (IR) light, electricity and electromagnetic wave with excellent healing efficiencies higher than 98%.

FG was prepared by the modified arc-discharge method as described in our previous work.[35] FG-TPU composites were fabricated through a simple mechanical mixing and subsequent removal of the solvent (more details are in the Supporting Information), and then they were cut into strips of ~ 45 mm × 10 mm × 0.16 mm by scalpel. Pristine TPU strips with the same size of the FG-TPU strips were obtained in a similar way for comparison. Before healing, a 5 mm fracture was cut in the middle of the strip along the traverse direction, and then the fractured sample was healed by IR light, electricity, or electromagnetic wave. Healing performances were evaluated with the healing efficiency, the optimal healing time and the lowest voltage. Healing efficiency is calculated as the ratio of the tensile strength of the healed and the virgin sample, and

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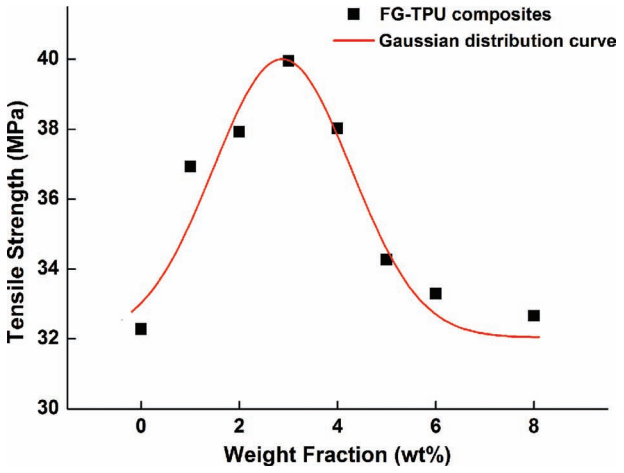

Figure 1. Tensile strengths of the FG-TPU composites with different FG loadings.

the optimal healing time for each case is defined as the shortest time required to achieve the best healing efficiency under the given conditions (such as loading of FG, light strength, electromagnetic wave frequency/power). For the case using electricity, the lowest voltage is defined as the minimum voltage for the sample to be healed with the best healing efficiency in 3 minutes.

Graphene materials are often used as fillers in fabricating mechanical enhanced composite materials because of their outstanding mechanical property. Indeed, as shown in **Figure 1**, while there is an optimized weight fraction of FG in the TPU matrix, the tensile strengths of the FG-TPU composites are overall enhanced partially due to the well-dispersed graphene sheets in the matrix. In contrast, the conventional self-healing materials may showed compromised or poor mechanical strength due to the limitation of their healing mechanisms.[2,13,16–20] The enhanced mechanical property partially highlight the potential of FG-TPU composites for practical applications.

The self-healing performances of the FG-TPU composites were investigated using three different methods including IR light, electricity and electromagnetic wave. For IR light healing, the fractured samples were positioned under a conventional IR lamp, and the power density delivered to the samples was ~ 0.2 W/cm^2. As shown in **Figure 2**a, the healing efficiencies of the FG-TPU samples with different FG loadings are all as high as 99%. The representative load-displacement curves for the virgin and the healed samples also indicated that the FG-TPU samples can be healed completely (see Supporting Information, Figure S1). The time to achieve such high healing efficiencies is all in the range of several minutes for all the samples with different FG loadings as shown in Figure 2d. On the contrary, the healed pure TPU samples broke immediately upon loading and offered zero healing efficiency even after longer healing. The results indicate clearly that the addition of FG remarkably improved the healing performances of TPU, and it is believed that two important intrinsic properties of graphene lead to these results. Firstly, Graphene has good IR absorbing capacity,[31,32] and the addition of FG could make the TPU composites show strong IR absorption, which is totally different from the original IR transparent TPU matrix (see Supporting Information, Figure S2). Secondly, the excellent thermal conductivity of graphene would make it efficiently transfer the Joule energy from the IR absorption into the TPU matrix. Thus, in the healing process, FG works as a nanoscale heater and transfer unit to generate the required energy and then transport the energy to the matrix efficiently. Therefore, once exposed to IR light, the FG-TPU samples were heated rapidly and homogeneously, and then the TPU chains at the broken interface diffused and re-entangled again to heal the fracture. Interestingly,

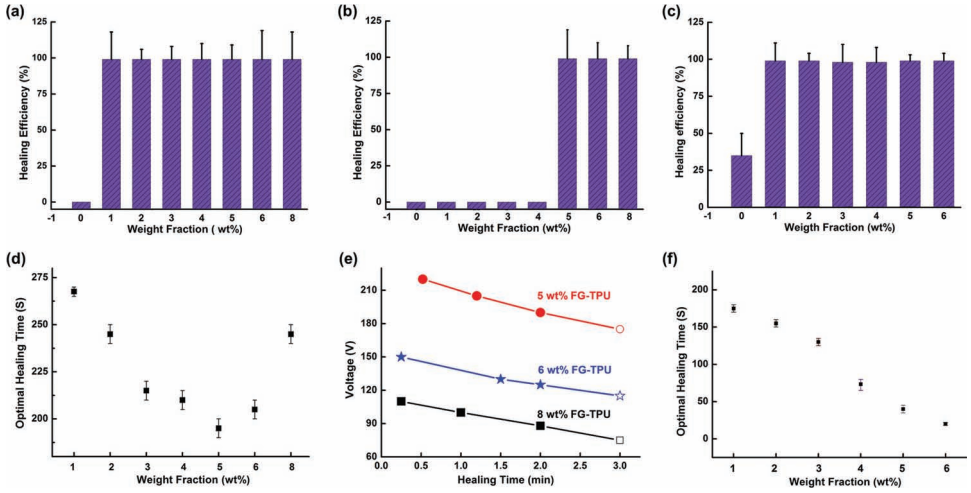

Figure 2. The healing performances of the FG-TPU samples with different FG loadings under the three healing processes. a) The IR light healing efficiencies of the pure TPU and the FG-TPU samples with different FG loadings at the optimal healing time. b) The electrical healing efficiencies of the pure TPU and the FG-TPU samples with different FG loadings at the optimal healing time. c) The electromagnetic wave healing efficiencies of the pure TPU and the FG-TPU samples with different FG loadings at the optimal healing time. d) The optimal healing time of the FG-TPU samples with different FG loadings. e) The relationship between the applied voltage and the healing time for the FG-TPU samples with different FG loadings. f) The optimal healing time of the FG-TPU samples with different FG loadings.

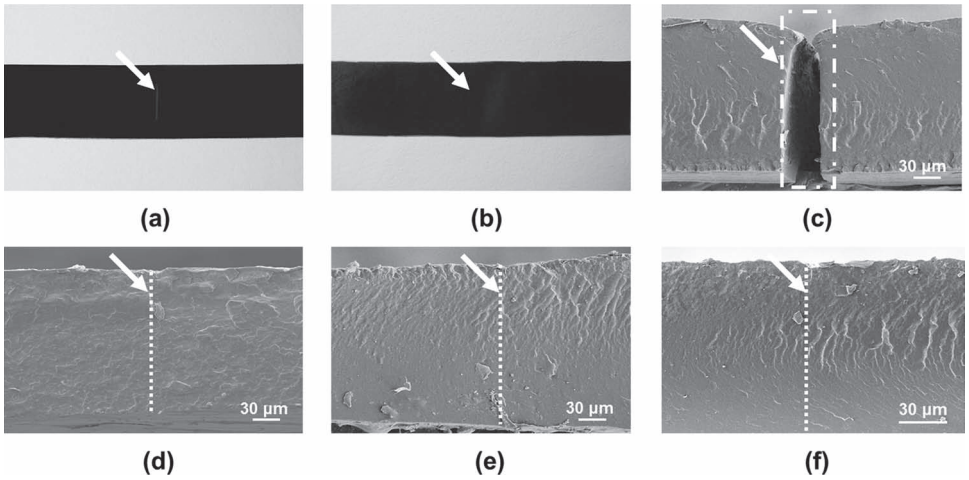

Figure 3. Optical and SEM images of the fractured sample with 6 wt% FG loading before and after healing. a,b) The optical images of the fractured sample before a) and after b) IR light healing. c-f) The cross-sectional SEM images of the fractured samples before c) and after IR light d), electricity e), electromagnetic wave f) healing, respectively.

the optimal healing time does not decrease linearly with the increasing of the FG loadings in the composites. The FG-TPU composites show the shortest healing time when the loading of FG reached 5 wt% as shown in Figure 2d. This result may be caused by the interplay among the IR light absorbing capacity, possible blocking of graphene sheets for the matrix molecules to move and the intrinsic re-stacking of graphene sheets.

The obviously increased electrical conductivities of the FG-TPU composites make it also applicable to investigate their electrical self-healing performances. In each case, we applied different voltages to the fractured FG-TPU samples according to the different electrical conductivities of them (see Supporting Information, Table S1) and the samples with more than 5 wt% FG could be healed with the healing efficiencies higher than 98% in 3 minutes (Figure 2b). In contrast, the pure TPU and the FG-TPU samples with 4 wt% or fewer FG loadings cannot be healed at 220V within hours and thus exhibit zero healing efficiency because of their poor electrical conductivities. The healing behaviors for these materials with different FG loadings were further studied, and the results are summarized in Figure S3 and 2e. As shown in Figure S3, under the defined healing time such as 3 minutes, the lowest voltages for the samples reduced with FG loadings increasing as expected. The FG-TPU samples with 5, 6, and 8 wt% of FG can be healed efficiently with excellent healing efficiencies by applying voltages of 175, 115 and 75V in 3 minutes, respectively. On the other hand, under the same FG loading, to achieve the same healing efficiency, shorter healing time is needed with the applied voltage increasing (Figure 2e). The required time to achieve the optimal healing is quite sensitive to the applied voltages. For example, most of the samples with 8 wt% FG loading need 3 minutes at 75 V to be completely healed, but only need 15 s at 110 V to achieve the same healing efficiency. The rapid healing behaviors were explored by in situ observation of the healing processes for 8 wt% FG-TPU samples (see Supporting Information, Movie S1 and S2). The results also show that the healing time reduce with the increasing of applied voltage. When voltage of 100 and 110 V was applied, the samples can be healed in a few seconds and the best healing efficiency can be achieved in 20 and 15 s, respectively. Note that nearly all the self-healing materials embedded with micro-containers and most of the self-healing materials healed by reversible chemical and/or physical interactions reported so far need hours to achieve efficient healing.[1,6,8–11,14,36–40] Obviously, these results demonstrate that the FG-TPU self-healing healing system has significant advantages in terms of healing time (see Supporting Information, Figure S4). This result means that when the FG-TPU composites are cracked, they can be healed in few seconds and hence significantly decrease the danger and loss. The high healing efficiency combined with the controllable healing voltage and the extremely short time, indicates that the FG-TPU composites can be used in various fields, especially in hazardous environments.

Graphene materials also has an ability to absorb electromagnetic wave efficiently.[33,34] Thus, we carefully investigated the electromagnetic wave healing behaviors of the FG-TPU samples by exposing them to a 800 W domestic microwave oven operating at 2.45 GHz. The healing performances of the FG-TPU samples were shown in Figure 2c and f. From Figure 2c, we can clearly see that all the FG-TPU samples with different FG loadings can be healed with healing efficiencies of 98% or more. However, the pure TPU samples can only be partly healed even after much longer exposure. Figure 2f shows that the optimal healing time of the FG-TPU samples reduces with the loading of FG decreasing, and for the samples with 8 wt% or more FG loadings the healing time is so short that we can not measure it. We suggest that this phenomenon should be attributed to the strong microwave absorbing capacity and the high thermal conductivity of FG. The outstanding healing performances indicate that all the FG-TPU samples can be successfully healed by electromagnetic wave rapidly. To the best of our knowledge, so far there is no report yet for self-healing polymeric materials using electromagnetic wave.

Optical and scanning electron microscopy (SEM) images were used to monitor the healing behaviors of the FG-TPU composites. Typical optical images for the fractured sample before and after IR light healing are shown in **Figure 3**a and b. Comparison of the two optical images shows clearly that the fracture in the FG-TPU sample disappeared after healing.

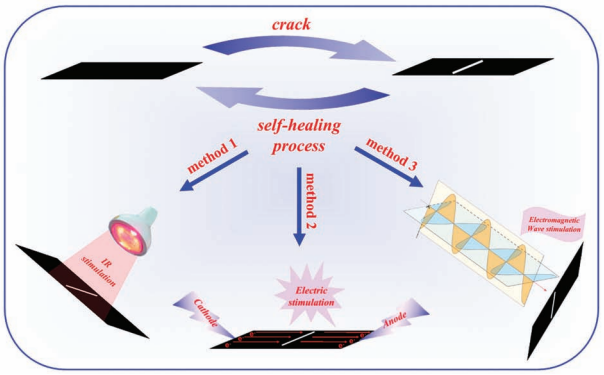

Figure 4. The healing concept. The FG-TPU composites were healed by IR light, electricity and electromagnetic wave with high healing efficiencies.

More detailed and convincing evidences for the healing of the fracture interface can be observed from the cross-sectional SEM characterization as shown in Figure 3c–f. From the SEM images, we can clearly see that the obvious fracture of the cut-off sample shown in Figure 3c vanishes completely after the healing process (Figure 3d–f, for IR light, electrical and electromagnetic wave healing respectively).

Healing repeatability is also very important for the self-healing polymeric materials, and to date only the polymeric materials, which were healed by embedding microvasculars or by reversible mechanical/physical interactions at the fracture interfaces can be healed repeatedly. But for the former, the method to fabricate the microvascular in the polymer matrix is still a little complex though A. P. Esser-Kahn has proposed a relatively simple method recently,[41] and the latter is always limited to few materials involved particular reaction and the fresh fracture. We also studied the self-healing repeatability of the FG-TPU composites. To demonstrate the repeatability of the healing performance, the FG-TPU composites with 5 wt% loading of FG were selected for the cycling test, because at this loading the healing can be achieved via all the three methods. By using IR-light healing, the FG-TPU samples could be healed for more than 20 times and the healing efficiencies in each healing cycle keep at 99% (see Supporting Information, Figure S5). The FG-TPU samples could also be healed for 2 and 5 times by electricity and electromagnetic wave respectively with the healing efficiencies still as high as 99%. This result suggests that this self-healing polymeric material with the increased reliability and service life may have a great potential to be used in a wide variety of applications ranging from microelectronics to aerospace.

Though the three self-healing processes use different external stimuli (**Figure 4**), it should be always the case that well dispersed graphene sheets convert the energy absorbed from IR light, electricity or electromagnetic wave into thermal energy and transfer it to the TPU matrix efficiently (see Supporting Information, Figure S6 and S7). Then the temperature of the whole FG-TPU composites increased rapidly and the self-healing of the FG-TPU composites are accomplished by the wetting, diffusion and re-entanglement of the TPU chains at a temperature above the T_g of TPU (see Supporting Information, Figure S8).[42] As discussed above, the excellent IR absorption and the efficient energy transfer of graphene are the cause of the light healing.[31] For the electrical healing, due to the efficient dispersion of FG in the matrix, the percolation state could be achieved at low loading of FG, which then act as the conducting networks to transfer the electrical energy into Joule-heating.[27,43] Moreover, upon the formation of fracture, the resistance in the fractured area should be higher than that in other parts of the composites. According to the equation $Q = I^2Rt$ (where Q is heat, I is the current, and R is the resistance), once an appropriate voltage is applied, more heat will be generated at the fractured area and thus a more efficient healing could be achieved.[44] Thus, as discussed above, the electrical healing can achieve high healing efficiency in the shortest healing time. For electromagnetic wave healing, it is well known that the large area conjugated π- structure of graphene will make it a giant electric dipole under microwave absorb and transform microwave into heat in the form of dipoles distortion.[33,34] Therefore, once positioned the FG-TPU composites under the electromagnetic wave environment, the well dispersed FG will act as the nanoscale heater in absorbing the energy from electromagnetic wave and then transfer it to the matrix molecules homogeneously and efficiently in the form of thermal energy.

In summary, a novel self-healing material based on graphene material was prepared via a simple method. These FG-TPU composites exhibit improved mechanical properties and could be healed effectively and rapidly by three different methods. Furthermore, they also can be healed repeatedly without any downgrading of healing efficiencies. These results, together with the wide applicability of the matrix material, indicate that FG-TPU composites can act as a promising self-healing material and find wide applications in transport industries, construction industries, electronics, and so on. Due to the simple approach, other matrix materials other than TPU are expected to demonstrate similar properties, and thus our results may have even wider implications for applications in industry.

Supporting Information

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

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