Synthesis and properties of near IR induced self-healable polyurethane/graphene nanocomposites

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Abstract

A series of self-healable polyurethane (SHPU)/modified graphene (MG) nanocomposites were synthesized from poly(tetramethylene glycol) (PTMG) and 4,4’-methylene diphenyl diisocyanate (MDI) with minute amounts (0–1 wt%) of MG which was chemically modified graphene oxide (GO) with phenyl isocyanate and reduced in the presence of phenylhydrazine.

MG gave dual effects of reinforcing filler and light absorption medium. That is, SHPU/MG nanocomposites showed significantly enhanced Young’s modulus and near infrared (NIR) absorption along with increased glass transition temperature ($T_g$). However, break strength and break strain decreased at high GO contents (MG075, MG100) implying that MG disturbs chain orientations.

The self-healing behavior of nanocomposites was done by intermolecular diffusion of polymer chains which was accelerated by thermal energy generated by NIR absorptions. The self-healing effect was most pronounced with 0.75 wt% MG (MG075) where the elastic strain energy was even greater than the fresh material up to over 200% strain. Further addition of MG (MG100) induced more light absorption, but physically disturbed the interchain diffusion to reduce the self-healing efficiency.

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1. Introduction

Polyurethanes (PUs) are a most versatile engineering material which is synthesized by a simple polyaddition reaction of polyol, isocyanate and chain extender. They find a variety of industrial applications including coatings, adhesives, sealants, elastomers (often abbreviated by CASE), primer, sports goods, medical devices, textile finish aside from the various foam products [1–3].

Graphene, atomically thin two-dimensional sheets of carbon, has emerged as the subject of enormous interest because of its exceptional micromechanical and electron transport properties. Graphene has a high basal plane elastic modulus, $E \approx 1$ TPa; ultimate strength, $\sigma_{\text{ultimate}} \approx 130$ GPa; and room temperature charge-carrier mobility, $\mu \approx 10,000$ cm$^2$/Vs $[4]$. Moreover, the perfect sp$^2$ carbon-network structures of the graphene materials ensure them to have excellent thermal conductivity and IR response $[5–8]$. With regard to the IR induced self-healing of polymer, fast heat transfer as well as high IR absorption is of prime importance since heat dissipated by IR at the surface should quickly transfer into the center to actuate the self-healing. In this regard, graphene is preferred over the carbon nanotube as well as carbon black $[9–10]$.

It is essential to highly exfoliate the graphite into layers to significantly enhance the mechanical and electrical properties of polymers at extremely small loading $[11–14]$. Oxidative exfoliation of natural graphite by acid treatment has been a most efficient method. However, the damage to graphene’s sp$^2$ carbon network would
severely affect the properties of graphene, such as mechanical [15], electrical [11], thermal [8], and optical absorption properties [6]. This can be solved by reducing graphene oxide (GO) which can restore sp² carbon network [5,11].

And owing to their hydrophilic nature, GO sheets can only be dispersed in aqueous media that are incompatible with most organic polymers. Exfoliation behavior of graphene oxide can be altered by changing the surface properties of GO sheets by way of chemical functionalization. The isocyanate treatment reduces the hydrophilic character of GO sheets by forming amide and carbamate ester bonds to the carboxyl and hydroxyl groups of graphene oxide, respectively. As a result, such isocyanate-derivatized graphene oxides no longer exfoliate in water but readily form stable dispersions in polar aprotic solvents such as N,N-dimethylformamide (DMF). These dispersions of isocyanate-derivatized graphene oxide allow GO sheets to be intimately mixed with many organic polymers, facilitating synthesis of graphene–polymer composites [11]. Also, the isocyanate treated GO can improve miscibility with polymer, especially PU which is synthesized from the same isocyanate groups. A number of studies regarding the polymer/graphene nanocomposites have been done, but most of studies focused on the improvement of mechanical property, electrical conductivity or gas barrier property [11–14,16–18].

Polymers with the ability to repair themselves after sustaining damage could extend the lifetimes of materials used in many applications [19,20]. When fractured, polymer can regain the physical properties of the original polymer [21] either autonomically [22], or in response to an external stimulus such as heat [23] or pressure [24]. Healable polymeric systems may for example contain encapsulated monomers and polymerization catalysts [22,25], or latent functionalities which are able to participate in thermally-reversible, covalent bond-forming reactions [23,26]. It has also been shown that non-covalent interactions, specifically hydrogen bonds [8] may be used to effect healing within a supramolecular polymer blend (albeit in the presence of a plasticising solvent) [24]. If the commodity PU is endowed with the ability to repair itself, vast applications will be opened up as functional polymer [27–29].

To the best knowledge of the present authors, the near IR (NIR) absorption of graphene has not been reported for self-healing of polymers in open literature. We synthesized PU/graphene nanocomposites to introduce the light induced self-healing by graphene as well as to reinforce the PU. To enhance the miscibility, graphene was chemically modified by phenyl isocyanate (pi-GO), and subsequently reduced in phenyl hydrazine to restore sp² carbon network. Mechanical, thermal, optical properties as well as the self-healing ability of the PU_modified graphene (MG) nanocomposites were measured.

2. Experimental

2.1. Raw materials

Polytetramethylene ether glycols (PTMG, Mn = 650 g/mol) and 1, 3-butadiol (1,3-BD, Aldrich) were dried and degassed at 80°C under vacuum for 3 h before use.

4,4’-Methylene diphenyl diisocynate (MDI, BASF), phenylhydrazine (Aldrich), phenyl isocyanate (Kanto Chem.) were used as received. Graphite powder (Conducting grade, 325 mesh) was purchased from Alfa Aesar.

2.2. Preparation of GO

Hummers’ method was used to prepare the GO [16,30–32]. The desired amounts of graphite (10 g) and NaNO₃ (7.5 g) were first put in a three neck flask and mixed thoroughly. Subsequently an appropriate amount of H₂SO₄ (621 g) was added and stirred in an ice water bath to absorb the heat of mixing. KMnO₄ (45 g) was then slowly added during the next 1 h, followed by cooling for the next 2 h. The mixture was allowed to stand for 5 days at 20°C with mild stirring. The liquid obtained was added to one liter of 5 wt% H₂SO₄ aqueous solution for 1 h with stirring. Then, 30 g of 30 wt% H₂O₂ aqueous solution was added and stirred for the next 2 h. Finally, the mixture was purified following the cyclic procedure which is well described in our earlier work.

2.3. Preparation of pi-GO

GO (675 mg) was loaded into a 500-mL round bottom flask equipped with a stirrer under nitrogen atmosphere. Anhydrous DMF (67.5 mL) was added to create an inhomogeneous suspension. Phenyl isocyanate (3.22 g) was then added and stirred for 7 days (Scheme 1). Then, the reaction mixture was poured into methylene chloride (675 mL) to coagulate the product. The product was filtered, washed with additional methylene chloride (675 mL), and dried under vacuum [33].

2.4. Synthesis of pi-GO/polyurethane nanocomposites

The overall reaction scheme for the synthesis of the composite is shown in Scheme 2. Molar excess of PTMG and 1,3-BD were reacted with MDI at 60°C for 1 h in a 500-mL four-necked flask with a mechanical stirrer, thermometer, condenser and a nitrogen injection tube. This reaction yields OH-terminated PU with theoretical molecular weight of 15,000, that were determined by the index of [OH]/[NCO] > 1. Then, the various compositions of pi-GO dispersed in DMF (1–2 mg/mL) (Table 1) were fed into a bial which was suspended in water of sonication bath operating in 40 kHz frequency. Reduction of the dispersed material was carried out with phenyl hydrazine (2.06–4.12 g) at 60°C for 24 h with stirring [34]. The nano-composite solution was then added dropwise to room-temperature methanol (600–1000 mL) with stirring [35]. Coagulated product was isolated by filtration and washed with methanol (400–800 mL). Composite was redissolved in DMF (70 g) with stirring and sonication, followed by casting and drying on a Teflon plate. Thickness of the dried film was approximately 0.4 mm.

2.5. Characterizations

Fourier transform infrared (FT-IR) spectroscopy (Mattson Satellite) was used to confirm the formations of OH
terminated PU and GO. Standard X-ray Photoelectron Spectroscopy (XPS) measurements were done using a VG-Scientific ESCALAB 250 spectrometer with an Al Kα X-ray source. Thermal properties of the cast films were determined using a Differential Scanning Calorimetry (DSC, Q100). The samples were first heated to 100 °C to erase their thermal history and then cooled to below −50 °C at 20 °C/min under nitrogen. Glass transition temperature ($T_g$) was measured during the second heating cycle at 10 °C/min. Morphology of the film was examined using a scanning electron microscopy (Zeiss FE-SEM SUPRA25). Sample was cryogenically fractured before viewing. Near infrared (NIR) light absorption spectra were obtained by FT–UV–VIS–IR Spectrometer (VERTEX 80). Tensile properties of the cast films were measured at room temperature with a Universal Testing Machine (UTM, Lloyd LRX) at a crosshead speed of 500 mm/min. Microtensile test specimens were prepared according to ASTM D 1822.

For quantitative healing test, nanocomposite film was scratched to a depth of 50–60% or cut using a razor blade in frozen state to avoid any accidental deformation of the film. And care was taken to ensure that heating and healing of the scratched or cut film occur mainly by the NIR absorption; experiment was done in darkroom at room temperature and effects of convection and radiation by heated lamp were possibly minimized by vertically placing the horizontal film below lamp at a distance of ca 20 cm while the lamp was continuously cooled by a fan. In case of cut, as soon as the film was cut, the ruptured edges were brought into close contact with but with no overlap in frozen state. Then, the film was exposed to NIR (HANA 0E17) for a certain time. The power density delivered to the sample was 20 mW/cm² as measured using a light intensity meter. The temperature was measured by infrared thermometer. The healed specimens were subjected to tensile test as above. Healing efficiency is defined using the modulus of toughness [19, 36] as:

$$\text{Healing efficiency (\%)} = \frac{\text{toughness}_{\text{healed}}}{\text{toughness}_{\text{original}}} \times 100 \tag{1}$$

Modulus of toughness is a measure of the strain energy required to break the material and corresponds to the area under the stress–strain curve [36, 37].

3. Results and discussion

3.1. Characterization of GO, pi-GO, PU

Fig. 1 shows that the characteristic absorption peak of NCO at 2,270 cm⁻¹ completely disappeared upon completing the OH terminated polyurethane forming reactions.
The formations of GO and pi-GO were confirmed by XPS. The C1s deconvolution spectrum of pristine graphite (a) shows a single peak at 284.61 eV, while that of GO (b) shows three different peaks at 284.7, 286.9, and 289.4 eV, corresponding to the C\text{=\text{C}}/C\text{=\text{C}} bonds in the aromatic rings, C (epoxy and alkoxy) groups, and C\text{=\text{O}} groups, respectively (Fig. 2) [16,32]. The atomic compositions of the three graphitic materials are given in Table 2. After oxidation, the oxygen content in GO increased from up to 35% suggesting the formation of C\text{=\text{O}} bonds. In addition to carbon and oxygen, sulfur was also detected on the surface of GO, which may be traced to their ions being physically trapped in the closed pores or covalently esterified with surface hydroxyls [38]. Upon treating the GO with phenyl isocyanate, carbamate and amide groups appeared.

### 3.2. Morphology and properties of PU/MG nanocomposites

#### 3.2.1. SEM

Fig. 3 shows the SEM morphology obtained from the cryogenically fracture surface of the PU/MG nanocomposites.

![Fig. 3. SEM images of the cryogenically fracture surfaces of films for (a) MG050, (b) MG075 and (c) MG100.](image)
It is seen that primary MG particles are well dispersed in polymer matrix at low contents (MG050, MG075). However, particles are agglomerated at high content (MG100).

3.2.2. DSC and UTM
Figs. 4 and 5 show thermal and mechanical properties of PU/MG nanocomposites while the detailed data are shown in Table 3. The $T_g$ of PU is increased with the addition of MG due to the restricted motion of PU chains in the presence of MG. The initial modulus monotonically increases with the addition and increasing amount of MG while the break strength and elongation at break increased with MG050 but decreased with MG075 and MG100. This suggests that the nanoparticles disturb the orientations of polymer chain at high elongations at high loadings [39].

3.2.3. NIR measurements
The NIR absorbance increases with addition of graphene [5]. Fig. 6 shows the NIR absorbance of the MG series where the NIR absorbance of PU (MG000) is increased over 10 times with MG050 due to existence of graphene which have many sp² carbons and it is further increased with MG075 and MG100 due to the increased content of MG viz. sp² carbon. It is mentioned that unfortunately the NIR absorbance for the MG075 and MG100 was over the instrument.

3.3. Tensile and healing tests
First, we assume that self-healing behavior of PU/MG nanocomposites will be done by intermolecular diffusion of polymer chains which is proportional to time and temperature. So, this intermolecular diffusion can be accelerated by thermal energy which is generated by NIR absorptions.

Fig. 7 is photographs showing that the PU/MG nanocomposite film bended by 180° largely recovers the deformation upon exposure to the NIR, or the cryogenically cut film is healed or rebonded by NIR irradiation. Fig. 8 and Table 4 shows the temperature and healing efficiency changes of the MG000 film with the irradiation time. Temperature of the film increases from 25 °C to a steady value of about 30 °C in about 1 h. The steady state is established as the rate of heat generation by NIR absorption becomes equal to the rate of heat loss by the interface heat transfer. As the heat generation within the film increases heat loss at the surface increases according to

$$q = h(T_s - T_\infty)$$

where $q$ is the heat flux, $h$ the heat transfer coefficient, $T_s$ the surface temperature, and $T_\infty$ the ambient temperature.

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As the irradiation time increases, $T_s$ should increase to give an increased $q$ until it becomes equal to the rate of heat generation by irradiation, and the time is ca. 0.5 h in the present experiment. On the other hand, the healing efficiency increases slowly up to about 2 h beyond which it increases rapidly. The time lag between the temperature and healing efficiency rises is an indication of slow intermolecular diffusion of polymer chains.

If MG000 which absorbs little amount of NIR is exposed to NIR excessively, it can be healed enough due to continuous NIR energy though its amounts are small. Maybe any polymers which can absorb NIR even though its amounts are very small can be healed enough on excessive NIR exposure. So, we determined NIR irradiation time for 2 h to clearly observe self-healability of MG series.

The stress–strain behaviors of the nano-composite were measured for the irradiation time of 2 h (Fig. 9 and Table 4). Even at low strain, the elastic strain energy (area under the $s$–$s$ curve) of the healed film (MG(12)) is significantly reduced for MG000 while it is mostly recovered with the addition of MG. Surprisingly with MG075, the elastic strain energy even increased over the fresh film upon NIR irradiation, which needs further investigation to clarify the mechanism. MG absorbs NIR and augments the film temperature in proportion to its content but the thermal equilibrium is established at ca 30–33°C regardless of its content (Table 5), while the interchain diffusion becomes less plausible at higher content so that an optimum content seems to exist, which is MG075 for the present work. The healing efficiency which is in the order of MG050 < MG100 < MG000 < MG075 again assures this.

### 4. Conclusions

PU/graphene nanocomposite were prepared to reinforce and augment the NIR absorption of polyurethane (MG000), graphite was oxidized and chemically modified with phenyl isocyanate and reduced in the presence of phenylhydrazine to form modified graphene (MG). With the addition of MG, glass transition temperature and initial modulus of the PU increased while break strength and elongation at break showed an increase at low (MG050) and decrease at high content (MG075, MG100) implying
that the GO could disturb chain orientations at high loadings and high elongations.

MG significantly enhanced the NIR absorbance leading to a self-healable PU/MG nano-composite, where the effect was most pronounced with MG075 which showed elastic strain energy greater than the fresh material up to ca 250% strain. However, at high content MG disturbs inter-chain diffusion to give a decrease of self-healing efficiency as compared with the appropriate amount of loading. It is expected that the self-healable polyurethane would expand its vast applications as a functional polymer.

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References