Environmental Material Research of Infrared Light Responsive Self-healing Graphene-based Thermoplastic Polyurethane

Yuehui Wang¹,²,* Zhimin Zhou¹,², Jiahao Zhang¹, Jinyuan Tang¹ and Peiyu Wu¹
¹Zhongshan Institute, University of Electronic Science and Technology of China, Zhongshan, Guangdong Province, P. R. China
²University of Material and Energy, University of Electronic Science and Technology of China, Chengdu 610054, China

*Corresponding author email: wyh@zsc.edu.cn

Abstract. Graphene-based thermoplastic polyurethane (G-TPU) composite materials were prepared and used for the fabrication of G-TPU film. The thermal conductivity and infrared radiation (IR) response and self-healing performances of the G-TPU film were studied. The experimental results reveal that the thermal conductivity of the TPU film was improved through the incorporation of graphene and increases with increasing of the graphene mass content. The G-TPU film displays a good IR thermal response characteristic. After heated by IR illumination, the temperatures of the G-TPU composite film incorporation of graphene of 0.2 wt% and 1.5 wt%, reach to 92.9 °C and 109.1 °C respectively. When the graphene mass content is in the range 0.6 wt% - 1.2 wt%, the crack on the G-TPU film can be completely healed via IR illumination.

Keywords: Graphene; Thermoplastic polyurethane; Infrared light responsive; Self-healing.

1. Introduction
Polymers and their composites have been applied in many fields due to their high mechanical performance. [1-4]. However, cracks might occur during processing and utilization, resulting in decrease of the performance and potential risk. In this case, self-healing polymers that can repair themselves in response to damage have aroused great interest in recent years, becoming a research hotspot of the functional polymer materials area [5-11].

Thermoplastic polyurethane (TPU) is a kind of polymer materials used widely in many fields due to its flexibility, abrasion resistance, resistance, and good processing performance [12-17]. Recently, literature reports revealed the self-healing property of TPU filled with graphene, silver and gold nanostructures, carbon nanotubes triggered by electric field, infrared radiation (IR), and microwave [18-21]. Many researches have been carried out to obtain TPU film with excellent self-healing property. However, some problems remain to be solved. We reported herein on IR thermal property of TPU filled with commercial graphene and the self-healing performance by IR illumination.

2. Experimental Approach
2.1. Materials
Graphene sheets with an average diameter of 8 µm was purchased from Jiacai Technology Co., Ltd., Chengdu, Sichuan, China; N, N-Dimethylformamide (DMF) was purchased from Jinan Shuangying
2.2. Preparation of Thermopolyurethane Film Containing Graphene

We have fabricated TPU film containing graphene (G-TPU) composite film and studied the electrical-thermal properties and tensile strength of the composite film [21]. Based on previous studies, we chose the initial TPU concentration of 25 wt% to prepare the mixed slurry of G-TPU because the rheological properties of the mixed slurry are suitable for Mayer rod coating in this case. 50 g TPU masterbatches were dissolved in 200 mL DMF. Graphene was added into TPU solution under vigorous stirring according to graphene mass contents of 0, 0.2, 0.4, 0.6, 1.0, 1.2, and 1.5 wt%, respectively, and the stirring process was performed in sonicator bath for 30 min. Then mixed solution was dispersed by a nanometer dispersing eMulsification machine for 60 min. The composite films were fabricated on release paper by Mayer rod and dried at 70 °C for 48 hr. G-TPU film was peeled off from the release paper for further testing.

2.3. Characterization

Thermal conductivity of the film was measured by a thermal conductivity analyser (DRL-III, Shanghai Qunhong Instrument equipment Co., Ltd., Shanghai, China). Thermal analysis of the sample was characterized by differential scanning calorimetry (DSC, DSC-60H, Shimadzu, Kyoto, Japan). Infrared thermal images were obtained by infrared thermal imager (Fluke Ti400, Fluke China Co., Ltd., Shanghai, China). Surface morphologies of the composite film before and after healed were observed by optical microscope (Leica DMI3000, Leica Co., Ltd., Germay). Universal tensile machine (GBH-1, Guangzhou International Standard packaging Equipment Co. Ltd., Guangzhou, China). We used a blade to make a 5 mm crack on the surface of the sample, and then put the sample under the infrared lamp for irradiation. After that, we measured the tensile strengths of the healed samples again.

3. Results and Discussion

Thermal analysis of DSC of the pure TPU (Fig.1 curve a) and the composite films with the graphene of 0.4 wt% (Fig.1 curve b) and 1.0 wt% (Fig.1 curve c), respectively, were investigated and shown in Figure 1. The results reveal that the crystalline melting of the pure TPU is at about 167 °C. The crystalline melting of the composite films with graphene of 0.4 wt% and 1.0 wt% moves to 175 °C and 187 °C, respectively, demonstrating that graphene has an effect on the thermal behavior of TPU. The total reaction heat of the pure TPU and G-TPU with graphene of 0.4 wt% and 1.0 wt% are -1.076, -0.4063, and -0.4011 mW·mg⁻¹, respectively, demonstrating that graphene improve the curing behavior of TPU.

![DSC curves](image)

**Figure 1.** DSC curves of pure TPU (a) and the composite film with the graphene of 0.4 wt% (b) and 1.0 wt% (c).
Thermal conductivity of polymer is one of the important parameter to reveal its thermal properties. In here, we studied the relationship between thermal conductivity of composite film and graphene mass content (Figure 2). The inset is an optical image of sample. The thermal conductivity of the pure TPU is about 0.249 W·m⁻¹·K⁻¹ and the thermal conductivity of the composite film gradually increases as the amount of graphene increases. When the graphene reaches 4 wt%, the thermal conductivity of composite film reaches 0.294 W·m⁻¹·K⁻¹, increasing by a factor of 1.18.

![Figure 2](image_url)

**Figure 2.** Relationship between thermal conductivity of composite film and graphene mass content. The inset is an optical image of sample.

Graphene materials are the excellent fillers for the reinforcement of polymer. Recently, graphene materials as thermal conversion agents were applied to self-healing polymer materials due to their outstanding response to IR light, electricity and electromagnetic waves, etc. [7,8, 16-21] We investigated IR thermal effect of the G-TPU composite film [21]. In here, we also investigated the response to IR light of G-TPU composite film with low mass content of graphene. Figure 3 shows relationship between temperatures of the composite films and the illumination time of the IR light (Figure 3a) and temperatures of G-TPU films heated for 50 seconds and turned off (Figure 3b). The inset in (Figure 3b) shows an optical image of the tested sample. Seen from Figure 3, the temperatures of the pure TPU film gradually increases as time of IR illumination increases and reaches to 51.6 °C after illuminated for 50 seconds. However, the temperatures of the G-TPU film increases rapidly and linearly before heated for 35 seconds, and then increases gradually thereafter. In addition, the graphene content is less than 1 wt%, the temperature of the composite film heated for 50 seconds increases slightly as the graphene content increases. The graphene content exceeds 1 wt%, the temperature of G-TPU composite film heated for 50 seconds increases gradually as the graphene content increases. The temperatures of G-TPU films with graphene of 0.2 wt% and 1.5 wt%, reach to 92.9 °C and 109.1 °C, increased by 1.8 times and 2.1 times, respectively. The experimental results demonstrate that the graphene has remarkable IR absorbing capacity and convert them into heat and transfer to the TPU matrices, so the composite film has good thermal conductivity. However, it's worth pointing out that at low graphene content, there was little relationship between the temperature change of the G-TPU film heated for 50 seconds via IR light and graphene mass content. The possible reason is that in this case, the effective thermal conduction channels in the G-TPU film are not formed and the IR heat absorbed by graphene cannot be transferred to the film quickly and effectively in the composite film, resulting in slightly low temperature change. As graphene content increases, more and more graphene sheets are uniformly distributed in the film, and more effective heat conduction channels are formed by overlapping with graphene sheets, so the temperature of the G-TPU film changes significantly.
Figure 3. (a) Relationship between temperature of the G-TPU films and the illumination time of the IR lamp and (b) temperatures of G-TPU films heated for 50 seconds. The inset in (b) shows an optical image of the tested sample.

Further, we studied the self-healing performance of the G-TPU film under IR light. Figure 4 displays an optical images (Figure 4a, a’) of the pure TPU film and the G-TPU film (Figure 4b, b’) before (Figure 4a, b) and after (Figure 4a’, b’) healed for 9 minutes via IR light. Seen from Figure 4, we marked out a crack on the surface of the composite film. After being irradiated by IR light, the crack of the pure TPU film is still visible, but the scratch of G-TPU film disappears, indicating that self-healing behavior of G-TPU film occurs.

Figure 4. Photos (a, a’) of the pure TPU film and the G-TPU film (b, b’) before (a, b) and after (a’, b’) irradiated for 9 minutes by IR light.

Figure 5 presents tensile strength of original composite films healed at 140 °C and 150 °C, respectively. Under IR light for 9 min. Seen from Figure 6, the mechanical property of G-TPU film self-healed deteriorates as the graphene content is less than 0.4 wt%. This may be related to the non-uniform distribution of graphene in TPU, leading to local stress points. When graphene content increases from 0.6 wt% to 1.2 wt%, the tensile strength of the G-TPU film healed exceeds the value of the original G-TPU film, indicating full self-healing performance and the improvement of mechanical property after heat-treated via IR light. As the graphene mass content reaches 1.5 wt%, the tensile strength of the self-healing G-TPU film is lower than that of original G-TPU. With the increase of the self-healing temperature, the tensile strength of the G-TPU film self-healed increases.
Figure 5. Tensile strength of G-TPU composite films before and after healed under IR light

Figure 6 shows the optical images of scratch sample healed at 140 °C and 150 °C, respectively, for different time via IR light. The crack on the surface of film gradually reduces as the time IR illumination increases and the weak trace can be observed by optical microscope after 9 min.

Figure 6. Optical images of a crack sample healed at 140 °C and 150 °C, respectively, for different time via IR light.

4. Conclusion
In summary, the G-TPU composite materials were prepared and used for the preparation of G-TPU film. The thermal conductivity and infrared radiation (IR) response and self-healing performances of the G-TPU film were studied. The experimental results reveal that the thermal conductivity of the TPU film was improved through the incorporation of graphene and increases with increasing of the graphene mass content. The G-TPU film displays a good IR thermal response characteristic. After heated by IR illumination, the temperatures of the G-TPU composite film incorporation of graphene of 0.2 wt% and 1.5 wt%, reach to 92.9 °C and 109.1 °C respectively. When the graphene mass content is in the range 0.6 wt% - 1.2 wt%, the crack on the surface of G-TPU film can be completely healed via IR illumination.
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