Preparation of functionalized graphene/thermal conductive polyurethane films

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Abstract. Graphene/polymer composites have been widely used as thermal conductive materials in electronic equipment. However, the development of advanced graphene thermal conductive composites faces many problems, such as easy agglomeration, high interfacial thermal resistance and poor mechanical properties. In our work, new graphene-based polyurethane thermal conductive composites based on octadecylamine (ODA), graphene and thermoplastic polyurethane were prepared. The thermal conductivity (λ) of the composites reached 1.46 W/(mK) with loading 20wt.% mRGO, which was increased by 326.02% compared with that of TPU.

1. Introduction
With the development of miniaturization and integration of electronic devices, efficient heat dissipation during equipment operation can prevent local temperature overheating, slow down the operation speed and reduce the service life of equipment. Polymers are considered as substrates for thermal conductive materials due to their excellent properties of easy machining, light weight and low density. However, most of the polymer intrinsic thermal conductivity is extremely low, about 0.1 ~ 0.5 W/(mK). Therefore, adding thermal conductive filler to polymer matrix to improve the thermal conductivity of polymer has been widely studied.

Graphene is a two-dimensional lamellar structure composed of sp² hybridized carbon atoms. Its basic structural unit is a honeycomb lattice formed by six carbon atoms. The thickness of single-layer graphene is only 0.335nm, making it the thinnest two-dimensional material found so far. Because of its high aspect ratio, graphene is an ideal filler material. Compared with typical inorganic fillers, graphene can achieve significant improvements in thermal and mechanical properties of composite materials under lower loads. Therefore, graphene is widely used in the research and development of polymer-based thermal management materials.

In this paper, ODA is used to perform non-covalent functional modification of graphene oxide so that it has strong interaction without destroying the crystal structure of graphene. The amino group of mRGO may form hydrogen bonds with polyurethane, thereby improving the dispersion of mRGO in the polyurethane matrix and forming an effective thermal network. Therefore, the thermal conductivity of the polyurethane composite film can be greatly improved. The method is simple, gentle, green and economical, and suitable for large-scale applications.
2. Experimental

2.1. Preparation of GO water dispersion
Using natural flake graphite as raw material, graphene oxide was synthesized by the modified Hummers method. In a typical process, 2.0 g of graphite powder is put into concentrated H$_2$SO$_4$ (100 ml) and stirred in a 500 ml beaker. KMnO$_4$ (12.0 g) is slowly added to the mixture and the temperature of the solution is kept below 10°C. After that, the mixed solution was stirred at 40°C for 2 hours. Then, 150 ml of DI water was added dropwise to the reaction mixture so that the temperature did not exceed 100°C. After the mixture was stirred to room temperature, 10 ml of 30 wt.% H$_2$O$_2$ was added dropwise to the mixture, and the color of the mixture became golden yellow. Metal ions were removed with 5% HCl solution (30 ml). The obtained golden-yellow mixture was washed repeatedly with DI water until the pH of the solution was 6-7, followed by low-frequency ultrasound for 2 hours to obtain a 1 mg/ml GO solution.

2.2. Preparation and reduction of ODA modified GO
Take 100mg of ODA, dissolve it in 50ml absolute ethanol, add 100ml 1mg/ ml GO dispersing solution, stir it at room temperature for 12h. The solution was suction filtered with absolute ethanol and deionized water to remove excess ODA, and lyophilized to obtain ODA modified GO powder.

Prepare 1L of 1mg/ml ODA-GO aqueous solution, add 10g of ascorbic acid, and stir at 80°C for 12 hours. After that, it was washed repeatedly with deionized water and freeze-dried to obtain reduced mRGO.

2.3. The Composite Preparation
Different mass fractions of PU and mRGO were added to the DMF organic solvent, the electronic stirrer speed was set to 500 rpm/min and stirred for 180 minutes, and vacuum degassed for 30 min.

Pour the prepared PU solution onto the glass template of fixed size, in which the inner size of the glass plate mold is 100 mm×100mm×1mm (length×width×thickness), use clean glass rod to slowly flatten the film, and then place the glass plate containing polyurethane solution in an 80°C oven for drying for 12h.

Take out the glass plate, uncover the film, and place the prepared PU film in a dry environment for later use.

3. Results and discussion

3.1. SEM characterization of mRGO/TPU composite film
As shown in Figure 1, when the content of mRGO is low, especially in the TPU composite materials with 5%mRGO and 10%mRGO, mRGO has good dispersion in the composite material and is covered by TPU, so a good heat transfer network cannot be formed, resulting in a large thermal resistance at the interface of the composite material. Therefore, when the mRGO content of the modified filler is low, the thermal conductivity of the composite material is poor. As can be seen from Figure 1(d) and (e), with the increase of mRGO content, thermal conductive fillers in the cross section of the composite material pile up together and contact with each other to form a good thermal conductivity path. Therefore, the thermal conductivity is relatively high, which is consistent with the following thermal conductivity test results.
3.2. Thermal stability of mRGO/TPU composite films
Thermal conductive composite films can withstand great temperature difference during use, so it is necessary to study their thermal stability. As shown in Figure 2, both pure polyurethane and composite materials have two weight loss ranges. 220-320°C is the decomposition of hard segment carbamate in polyurethane, while 350-460°C is the decomposition of soft segment polyols in polyurethane. It can be seen that with the addition of modified mRGO, the modified mRGO would begin to decompose at 120°C, so the decomposition temperature of the composite film would be lower than that of the pure TPU film. However, with the increase of the mass fraction of packing, the T50% of composite film would increase corresponding, reflecting that filler would improve the thermal stability of TPU composite film.

| Table 1 TGA data of composite films |
|-------------------------------------|
| Pure-TPU | 5% mRGO | 10% mRGO | 15% mRGO | 20% mRGO |
| T50% (°C) | 386 | 386 | 390 | 392 | 394 |
| Residue (%) | 5.0 | 4.9 | 6.9 | 9.2 | 12.0 |

3.3. Thermal conductivity of mRGO/TPU composite film
In order to prepare a heat conduction network with a close connection, the most common method is to add enough heat conduction filler to the matrix. Generally, poor interface combination between thermal conductive filler and polymer matrix will result in large interface thermal resistance and poor dispersion of thermal conductive material, which will increase phonon scattering and reduce phonon transmission efficiency, thus resulting in low thermal conductivity.
Figure 3 shows the thermal conductivity and thermal enhancement efficiency of mRGO/TPU composite film. It can be seen from the Figure that the thermal conductivity of the composite film increases with the increase of mRGO content. Compared with pure TPU film, under the low filling amount, the thermal conductive filler in matrix in the shape of "detached island", between each other is polyurethane apart, can't touch each other, so the low thermal conductivity, packing heat enhancement effect is not obvious, at this point, 5wt.% of the compound thin film thermal conductivity is 0.41W/(m·K), than the thermal conductivity of pure TPU 0.34W/(m·K) increased by 19.88%. When mRGO content reaches 10wt.%, due to the mutual contact between mRGO, the filler in the composite film begins to change from "island" form to form part of thermal conductivity link. With the further increase of mRGO content, a complete thermal conductivity network begins to form inside the film, so the thermal conductivity of the film is greatly improved. When mRGO quality score is 20wt.%, the thermal conductivity of composite film is 1.46W/(m·K), thermal conductivity enhancement effect was 326.02%.

4. Conclusion
After ODA modification of GO, mRGO can be uniformly dispersed in the polyurethane matrix due to the alkyl amine chain grafted on mRGO and the hydrogen bond between mRGO and TPU. The composite film is composed of mRGO and thermoplastic polyurethane and is manufactured by a simple casting process. mRGO/TPU composite film under the content of 20 wt.% mRGO can achieve 1.46W/(m·K) of the thermal conductivity, which was increased by 326.02% compared with that of pure TPU. The composite film can be prepared simply and is expected to be an advanced heat dissipation material.

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