

Preparation and Property Study of Graphene Oxide Reinforced Epoxy Resin Insulation Nanocomposites with High Heat Conductivity

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Abstract. In this paper, graphene oxide reinforced epoxy resin nanocomposites were successfully prepared. Compared with unmodified epoxy resin, the heat conductivity of the graphene oxide reinforced epoxy resin nanocomposites had been improved while keeping the insulation performance. The tensile strength was investigated at both room temperature (300 K) and liquid nitrogen temperature (77 K). And the fracture surfaces were examined by scanning electron microscopy (SEM). Results showed that the materials had excellent mechanical properties, which could be advantages for the applications as insulating layer in low temperature superconducting magnets.

1. Introduction

Epoxy resins have good electrical insulation properties, advantageous heat and chemical resistance, high elastic modulus, low density, strong bond ability, and convenient manufacturing process[1, 2], which allow them to be widely employed as adhesives, sealants, and matrices of insulation material of superconducting magnets[3]. For example, in the International Thermonuclear Experimental Reactor (ITER), epoxy resin has been applied as insulation material of the superconducting magnets[4, 5]. In order to meet the requirements for this application, high thermal conductivity and insulation properties are needed. However, epoxy resin, taking an example of EP 231, exhibits a low thermal conductivity of about $9.82\text{--}25.82 \times 10^{-3} \text{ W/m-K}$ at the temperature of 6 K-16 K, which limits its applications. In this case, development of epoxy resins with high thermal conductivity and insulation properties is urgently needed especially for cryogenic applications.

In order to obtain desired properties, one approach is the addition of rigid micro- or nano- fillers to a polymer[6, 7]. It is demonstrated that employing rigid fillers with a high thermal conductivity can effectively increase the thermal conductivity of the composite at lower loadings[8, 9]. As we know there is a number of materials with high thermal conductivity. Among them, oxide graphic (GO) has



attracted more and more interest to the researchers for its high thermal conductivity and insulation property [10, 11]. Therefore, GO is an attractive filler to tune the thermal conductivity of epoxy resin.

In this work, the oxide graphic/epoxy (GO/EP) nanocomposites were prepared with 0.5 wt% mass fractions of GO. Thermal conductivity was investigated within the temperature range of 6–16 K. The tensile properties of the nanocomposites were investigated at room temperature (300 K) and liquid nitrogen temperature (77 K). The fracture surfaces were examined by scanning electron microscopy (SEM).

2. Experimental

2.1. Preparation of GO/Epoxy Nanocomposites

Epoxy resin and curing agent were mixed in a 250 ml beaker by the mass ratio of 100: 24. Then the GO powders were dispersed into the blends according to the mass fraction of 0.5 wt% and ultrasonicated for 120 min. Then the mixture was degassed by a vacuum pump at 45 °C for 1 h and tenderly poured into a preheated mould. The sample was gelled at 80 °C for 24 h and cured at 130 °C for 12 h, then cooled naturally with the oven to RT. Finally, the double-bell samples were removed from the mould and used for further characterization.

2.2. Characterization

In order to test the microstructure of the GO and the fracture morphology of the GO/EP after the tensile test, scanning electron microscope (SEM) experiments were carried out on a HITACHIS-4300 SEM. The fracture surfaces were gold functionalized prior to improve its conductivity. X-ray diffraction (XRD) analysis of GO was characterized using Bruker AXS D8 Focus Diffractometer with Cu K α radiation. Tensile test was carried out by using a MTS-SUNS CMT 5000 test machine at both RT and 77 K with a cross-head speed of 1 mm/min. The GO/EP specimens of tensile test were prepared according to the ASTM standard D638. At least 5 samples were tested to establish reproducibility.

3. Results and Discussion

3.1. GO

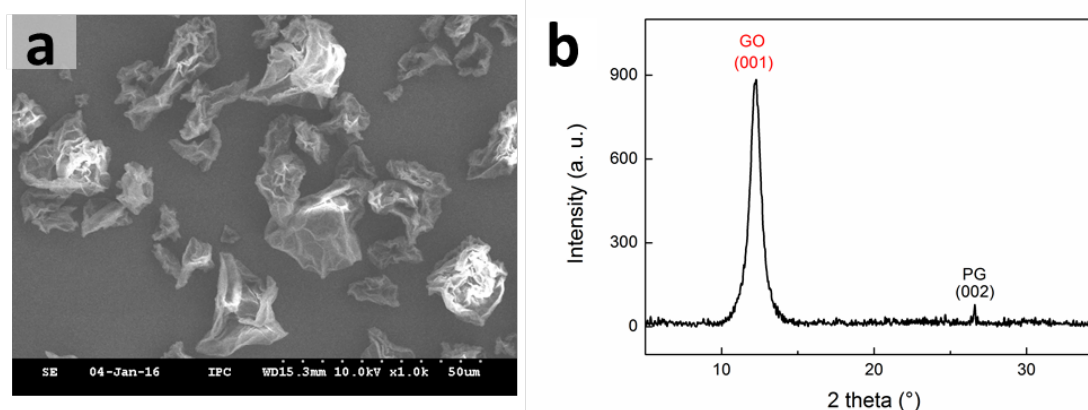


Fig. 1 The properties of the GO: (a) SEM and (b) XRD pattern.

Before the GO was used as filler of the epoxy composite materials, its oxidation degree and layer structure were tested. From the Fig. 1 (a), it can be observed that the GO has a fold sheet structure, which has a low number of layers, and a good dispersion. Although the sizes of the lamellas are not uniform, they are large enough to be used as fillers of composite materials. The XRD pattern of the GO is shown in Fig. 1 (b). It exhibited a strong peak at $2\theta = 12.17^\circ$, which is the (0 0 1) diffraction

peak of GO. According to Bragg equation, the value of 2θ corresponded to an interlayer spacing is about 0.73 nm[12, 13]. The increased-spacing was attributed to the presence of oxygen functionalities in the gallery spacing of GO. It proves that the GO has been stripped completely. This peak is a typical characteristic peak of graphene oxide as previously reported[14]. The peak at $2\theta = 43.02^\circ$ is the (0 0 2) diffraction peak of the precursor graphite (PG), corresponding to the carbon which is not oxidized.

3.2. GO/EP

The mass fraction of GO in the GO/EP composite material we made is 0.5 wt%. The performances we mainly concerned are thermal conductivity, mechanical properties and dielectric constant.

3.2.1 Thermal conductivity

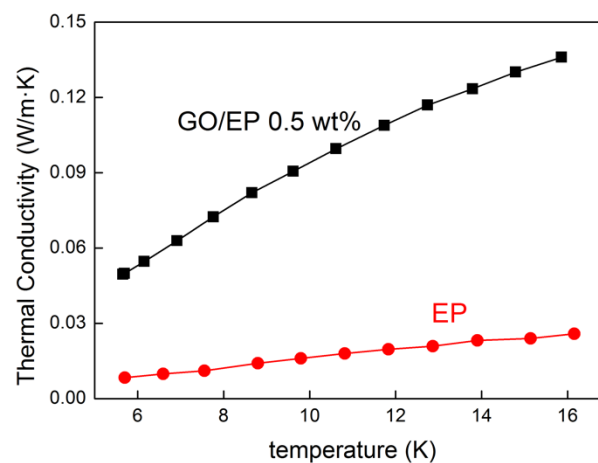


Fig. 2 The thermal conductivities of EP and GO/EP at low temperature

Fig. 2 shows the results of the thermal conductivity tests. At around 6 K, the thermal conductivity of pure EP 231 is about 9.82×10^{-3} W/m·K, which increases to 25.82×10^{-3} W/m·K with the temperature raised to 16 K. When the GO was added into the material as the mass fraction of 0.5 wt%, the thermal conductivity of the GP/EP composite material is increased to 54.63×10^{-3} W/m·K and 136.01×10^{-3} W/m·K at the same temperature, respectively, which indicated that the introduction of the GO obviously improves the performance of the thermal conductivity of the material. Moreover, with the increasing of the temperature, the value of the thermal conductivity of the GO/EP rises faster than pure EP, which can be contributed to the high thermal conductivity of the graphene oxide. When the GO was added into EP, it will affectively promote the spread of heat within the materials. And the effect could be more remarkable while the GO get any contact with each other.

3.2.2 Mechanical properties

Tensile properties of EP and GO/EP composite materials were measured at both 77 K and RT. The stress–strain curves are shown in Fig. 3. At RT, the stress–strain curves show large plastic deformation prior to failure of the specimens of both EP and GO/EP composite, and the materials show ductile behaviour. When the temperature decreases to 77 K, the materials show a brittle behaviour and a increased strength. The tensile strength and modulus of elasticity of EP and GO/EP composites are shown in Fig. 4.

What is the most obviously is that both the tensile strength and modulus of elasticity of EP and GO/EP materials at 77 K are much higher than those at RT. When the temperature decreased to 77 K, because of the epoxy matrix materials have a flexible chain structure and high thermal contraction property, the networks of molecular chains shrink and the intermolecular forces become stronger[15],

thus a larger load will be needed to break the matrix. As a result, the strength and modulus of elasticity of both EP and GO/EP composite materials is significantly improved when temperature is decreased to 77 K.

Moreover, compared with unmodified epoxy resin material, the tensile strength and modulus of elasticity of the GO/EP at 77 K is very close to that of the unmodified EP. When the temperature arises to RT, the GO/EP has a higher tensile strength and a slightly lower modulus of elasticity than unmodified EP. Based on these phenomenon, it can be inferred that at low temperature, the performance of the epoxy matrix is still playing a leading role to affect the mechanical properties of the composite material which was added a 0.5 wt% mass fraction of GO. It can be indicated that the GO at this content has no obvious advantages to the mechanical performances of the GO/EP composite materials. This property of adding GO without affecting the mechanical properties of the composite material is exactly we expected and needed.

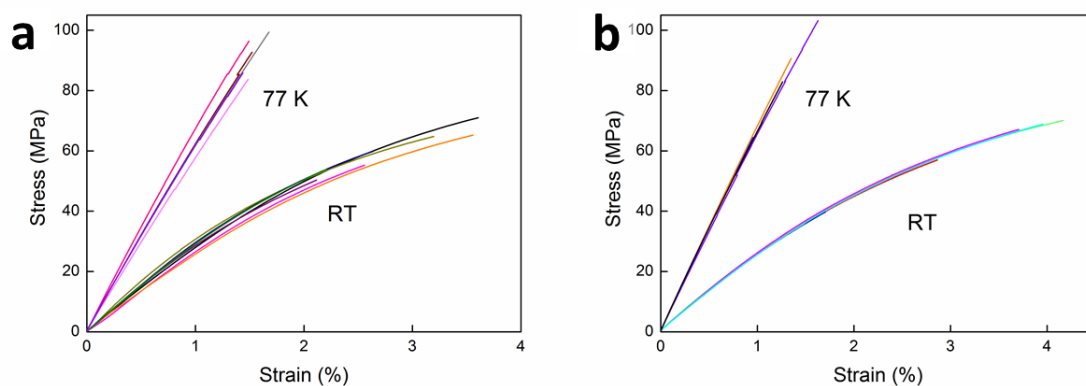


Fig. 3 The tensile test stress-strain curves at 77k and RT: (a) EP and (b) GO/EP.

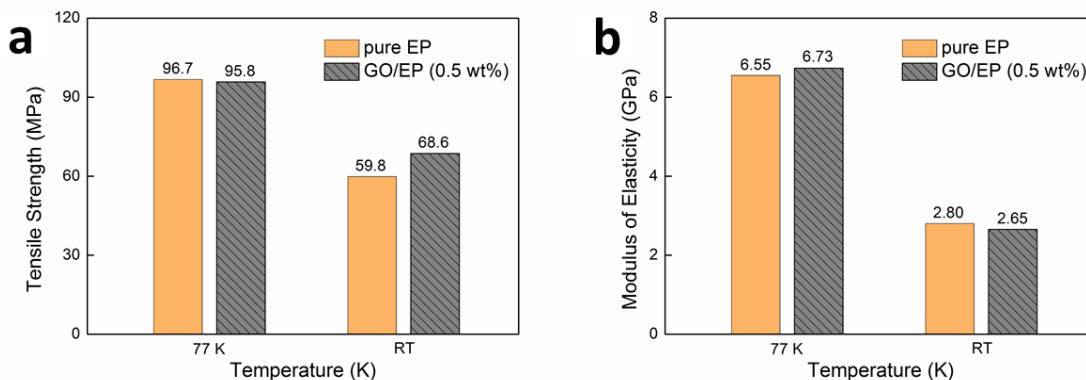


Fig. 4 Mechanical performances of EP and GO/EP composite materials:

(a) Tensile strength and (b) modulus of elasticity.

The fracture surfaces of broken samples of EP and GO/EP composite after tensile test at RT and 77 K are shown in Fig. 5. It can be observed that the fracture of the materials is brittle, and the fracture surfaces at 77 K (Fig. 5b and 5d) have more cracks and are rougher than that at RT (Fig. 5a and 5c), which means that the tensile fracture at 77 K need more energy to damage the internal combination of epoxy resin. This phenomenon conforms to the results of the tensile test. From Fig. 5e and 5f, it can be observed that the surface of the pulled out GO is attached with the matrix. This indicated that the strong interfacial bonding between the GO and the epoxy matrix which is an important guarantee of the mechanical properties of composite materials.

The two components of this composite material are both insulators, and by measuring the electrical conductivity or testing the composite with a multimeter, the results all proved that the nanocomposite is a insulation material.

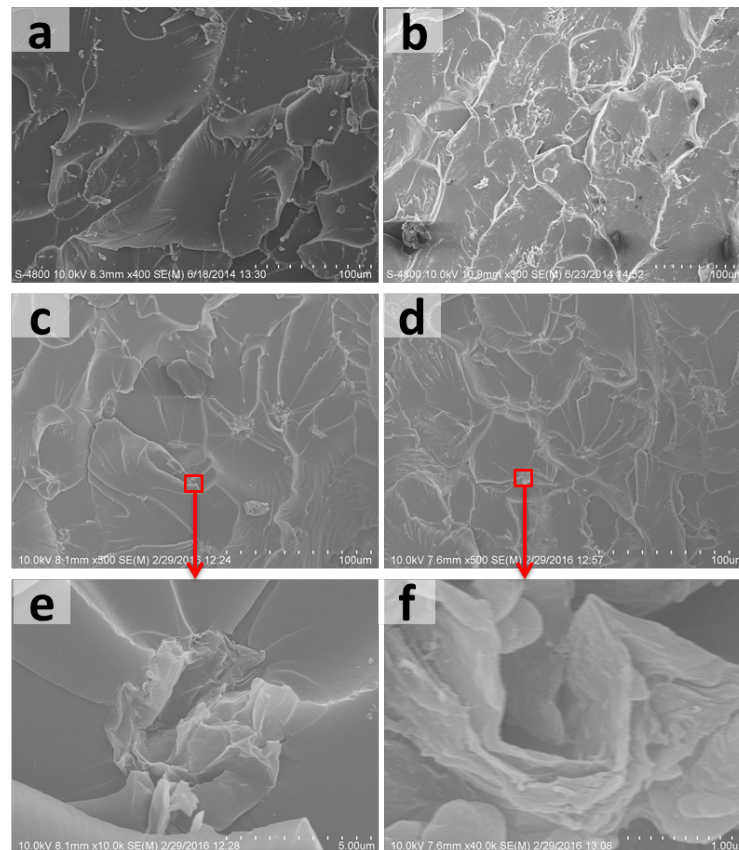


Fig. 5 SEM images of the fracture surface of EP and GO/EP after tested at RT and 77 K:

(a) EP, RT; (b) EP, 77 K; (c) GO/EP, RT; (d) GO/EP, 77 K;
(e) the pulled out GO/EP, RT; (f) the pulled out GO/EP, 77 K.

4. Conclusion

In this study, a GO/EP composite material with a 0.5 wt% mass fraction of GO was successfully prepared. Comparing with unmodified EP, the GO/EP material has a higher thermal conductivity at low temperatures. Meanwhile, it remains similar mechanical properties at both RT and 77 K while keeps the insulation characteristic. It can be expected that this material will have excellent applications in the field of cryogenic insulation.

Acknowledgments

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