

ELECTRICAL, MECHANICAL AND THERMAL PROPERTIES OF SEMICONDUCTIVE SHIELD MATERIALS PREPARED WITH GRAPHENE NANOSHEETS

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In this paper, graphene nanosheets (GNS) was synthesized with an improved Hummers' method and the prepared sample was characterized using X-ray diffraction (XRD) and transmission electron microscope (TEM). The current research was mainly focused on the preparation a new-type semiconductive shielding material used in crosslinked polyethylene (XLPE) cable, by adding the GNS and conductive carbon black (CB) into ethylene/vinyl acetate copolymer (EVA). The results showed that the electrical and thermal properties of the composite EVA/CB-GNS was dramatically improved at low GNS loading. GNS reduce the content of conductive filler and improve the smoothness of semiconductive shielding layer of power cable. Meantime, the CB improved the dispersability of GNS in EVA. The volume resistivity of EVA/CB-GNS was decreased to 32.6 $\Omega \cdot \text{cm}$, only by adding 1.5wt% GNS and 18wt% CB. The tensile strength and elongation at break of EVA/18CB-1.5GNS was 12.1Mpa and 238.6% respectively, which met the requirements of National Machinery Industrial Standard of China JB/T 10738-2007.

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1. Introduction

The application of power cable with shielding layer in power transmission system is more and more popular. Due to discontinuous geometry of the conductor, there are air gaps exist between the insulation layer and the conductor. Without a shielding layer, excessive potential gradient may cause partial discharges within these gaps that might injure the insulation layer [1]. In general, the preparation of shielding materials for XLPE cable mainly adopts adding CB into EVA matrix to obtain conductive composites. To reduce volume resistivity of the composites lower than 100 $\Omega \cdot \text{cm}$, the CB content varies from 15wt% to 50wt% [2]. However, the high content of CB is harm to the smoothness and extrusion procession performance of shielding layer [3].

Graphene is a two-dimensional and conjugated honeycomb carbon network, which shows many unique and fascinating properties such as giant electron mobility, high thermal conductivity, excellent mechanical flexibility and large specific surface area [4]. Graphene has attracted considerable attention in view of its potential to significantly enhance the electrical conductivity of host polymers with a low loading [5, 6]. Therefore, if the graphene can be utilized in the shielding material, it is promising to increase the electrical property to a desirable level at lower filler concentration, so that the surface smoothness and extrusion performance can be improved.

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However, a huge challenge still lies in the development of highly conductive graphene-based polymer composites because of the agglomeration tendency of GNS and high contact resistance between GNS in the matrixes [7, 8]. To improve the dispersion of graphene, a great deal of efforts has been made by the organic group functionalization strategy [7, 9]. Although the homogeneous dispersion is achieved, these functional groups also damage the electronic conjugation of graphene and the electrical conductivity of these composites is still far below an expected level.

In this work, graphene has been utilized in the shielding material to replace a part of CB, and the composite EVA/CB-GNS has been synthesized. A three-dimensional conductive network can be formed due to the synergistic effect between CB and GNS, so that the electrical property of the composite was significantly enhanced at low GNS content. In addition, the EVA/CB-GNS was characterized by scanning electron microscope (SEM) and differential scanning calorimeter (DSC), and its mechanical property was also tested.

2. Experiments

2.1 Raw materials

The ethylene/vinyl acetate copolymer (EVA-260) was obtained from E. I. Du Pont Company; Conductive carbon black (LHJ-S1-1) was supplied by Shanghai Kajet chemical Co., Ltd; All other chemicals (flake graphite, concentrated sulfuric acid, phosphoric acid, potassium permanganate, hydrogen peroxide, absolute ethyl alcohol, hydrochloric acid, hydroiodic acid, stearamide) were obtained from Sinopharm Chemical Reagent Co. Ltd and used as-received without further purification.

2.2 Synthesis of GNS

The graphene oxide (GO) was synthesized with an improved Hummers' method^[10]. A 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO_4 (18.0 g), producing a slight exotherm to 35-40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (~400 mL) with 30% H_2O_2 (3 mL). After 12 h of static time, the mixture was centrifuged (4000 rpm for 4 h), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. Finally, GO solid was obtained after drying in vacuum oven at 60 °C for 12h.

GNS was prepared by reducing GO at hydriodic acid with acetic acid (HI-AcOH) system [11]. Firstly, 1 g of GO was dispersed in 0.5 L AcOH. Following, 20 ml HI was added. After that, the mixture was kept reacting at 50°C for 24h with constant stirring. Then the mixture was treated by centrifugation isolation followed with 120 ml EtOH, 120 ml 30% HCl and 120 ml deionized water washes respectively. Finally, GNS solid was obtained by vacuum-dried at 60 °C for 12h.

2.3 Synthesis of EVA/CB-GNS composites

The total mass of the EVA/CB-GNS composite was 40g, of which the content of CB and stearamide was 18% and 3% respectively, and the content of EVA was determined by controlling the percentage of GNS. In turn, EVA, stearamide, GNS and CB were added to the torque rheometer (Shanghai Kechuang XSS-300). The materials were kept mixing at 110°C for 10 min, and the rotate speed was 65 n/min.

Finally, the EVA/CB-GNS composites were compression molded into sheets by press vulcanizer at 120 °C for 5 min, under 5 MPa.

2.4 Characterization of the as-prepared samples

The diffraction behavior of samples were studied by X-ray diffractometer (XRD, Bruker D8 Advance), using $\text{Cu K}\alpha$ radiation ($\lambda=0.154\text{nm}$) at a scanning rate of 2°/min. The morphologies of graphene samples were characterized by transmission electron micrograph (TEM, JEOL

JEM-2100F). Fracture surfaces of the composite samples were characterized by scanning electron microscope (SEM, JEOL JSM-6360LV). The volume resistivity was tested by digital four-probes method (Suzhou Jingge ST2258C) at room temperature, relative humidity 50%, based on National Standard of China GB/T 3048.3-2007. The mechanical property of samples was tested by tension tester (SANS, CMT4304) based on National Standard of China GB/T 1040.2-2006. The melting and crystallization behavior were investigated by differential scanning calorimeter (DSC, TA Q20). Samples were heated from $-30\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$ to eliminate thermal history, then cooled to $-30\text{ }^{\circ}\text{C}$ at the same rate to analyze their crystallization property and heated again to analyze their melting property.

3. Results and discussion

3.1 XRD analysis

The XRD patterns of GO and GNS are shown in Fig. 1. There is a diffraction peak (001) of GO at 10.39° , and it indicates that graphite has been oxidized to graphene oxide. The two new broad peaks which appear at 24.19° and 42.99° on the XRD spectra of GNS, are an indication of the reduction of GO [12].

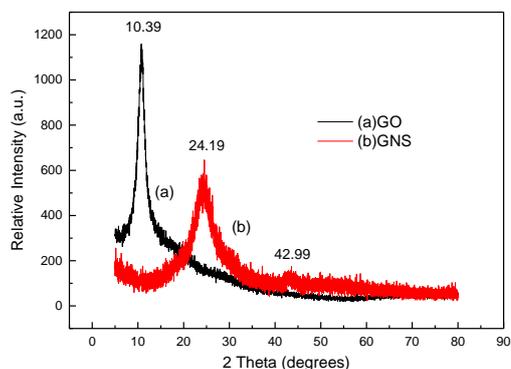


Fig. 1. XRD patterns of GO and GNS.

3.2 TEM analysis

The TEM image of GNS is shown in Fig. 2. The surface of the GNS presents many folds, because graphene is a two-dimensional flat with a large surface energy, and the surface wrinkling can maintain its thermodynamic stability. It can be seen in Fig. 2 that the GNS consists of about three graphite layers.

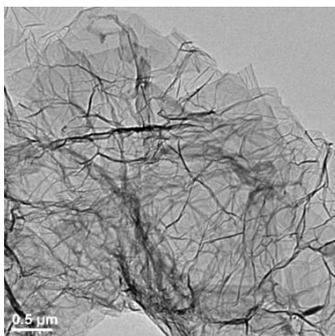


Fig. 2. TEM image of GNS.

3.3 Electrical property of EVA/CB-GNS composites

According to the Standard JB/T-10738-2007, the volume resistivity of shielding material must be lower than $100 \Omega \cdot \text{cm}$. Fig. 3 shows the volume resistivity of EVA/CB with different content of CB. It can be seen that the electrical property of the composites increased significantly in the CB content range of 18wt% to 25wt%. The volume resistivity of EVA/CB was decreased to $36.4 \Omega \cdot \text{cm}$ when the CB content was 28wt%. However, the high content of CB is harm to the smoothness and extrusion procession performance of shielding layer.

In order to reduce the addition content of conductive filler, the content of CB was determined as 18wt%, so that the effect of graphene content on electrical property of EVA/CB-GNS was studied. As can be seen from Fig. 4, the volume resistivity of EVA/18%CB-GNS decreases rapidly with the increase of graphene content. The volume resistivity of EVA/18%CB-GNS is decreased to $32.6 \Omega \cdot \text{cm}$ only by adding 1.5wt% of graphene. Due to the excellent conductivity of graphene, adding a small amount of graphene can greatly increase the electrical property of the composites.

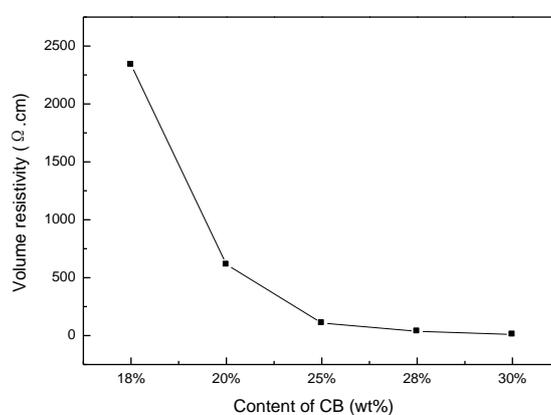


Fig. 3. Effect of the content of CB on volume resistivity of EVA/CB

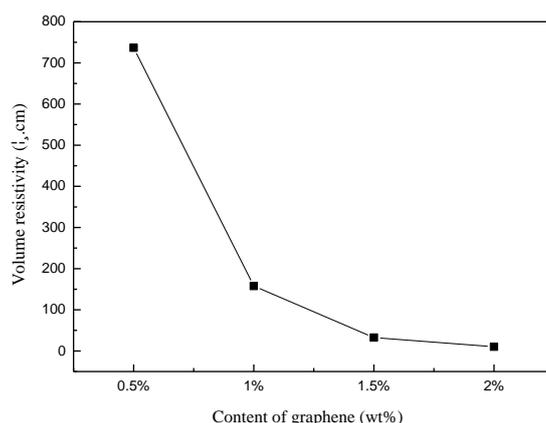


Fig. 4. Volume resistivity of EVA/18%CB-GNS with different content of graphene

The SEM micrograph images of EVA/18%CB and EVA/18%CB-1.5%GNS are shown in Fig. 5. CB shows a poor dispersability in Fig. 5(a), but it's better in Fig. 5(b). It may be because CB particles were loaded on the surface of GNS uniformly rather than distributed randomly inside the EVA matrix. Another advantage is a three-dimensional conductive network can be formed due to the synergistic effect between CB and GNS^[13].

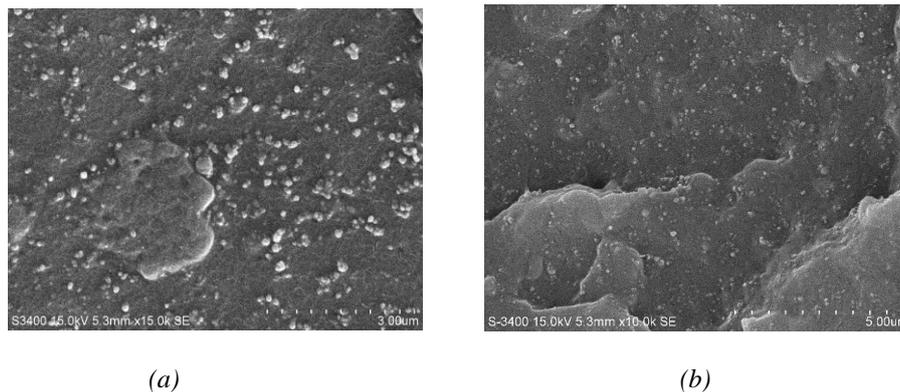


Fig. 5. SEM micrograph images of (a) EVA/18%CB and (b) EVA/18%CB-1.5%GNS.

3.4 Mechanical property of EVA/CB-GNS composites

Table 1 shows the mechanical property variation of the composites. It can be seen that when the content of CB was confirmed as 18%, the elongation at break and tensile strength decreased with the increasing content of GNS. It proves the bad compatibility between graphene and EVA. However, the elastic modulus of EVA/CB-RGO is better than that of EVA/CB because of the excellent elasticity modulus of graphene.

According to JB/T 10738-2007, the elongation at break and tensile strength of semiconductive shielding material used in XLPE cable must be higher than 200% and 10MPa respectively. Considering the mechanical and electrical properties of the composites, EVA/18%CB-1.5%GNS has the best performance.

Table 1. Mechanical property of EVA/18%CB-GNS with different content of graphene.

	EVA/18%CB	EVA/18%CB-1%GNS	EVA/18%CB-1.5%GNS	EVA/18%CB-2%GNS
Tensile strength /MPa	15.9	14.6	12.1	8.9
Elasticity modulus /MPa	23.7	34.6	31.3	30
Elongation at break /%	568.9	483.2	238.6	103.5

3.5 Thermal property of EVA/CB-GNS composites

Fig. 6 shows the melting behavior of the composites. It can be seen that the location of melting peak increased from 72.1°C to 75.1°C after adding only 1.5 % of GNS. This indicates that small amount of graphene increases the size and perfection of the crystal^[14]. Comparing the Fig. 6(c) and Fig. 6 (d), it can be found that CB also can enhance the thermal performance of the composite, but the effect is not as obvious as GNS.

Fig. 7 shows the cooling curves of the composites. It can be seen that the location of crystallization peak increased from 52.4°C to 55.8°C after adding only 1.5% of GNS. GNS has played a heterogeneous nucleus role in EVA that enhanced the crystallization rate of composite^[15]. However, with the increase of GNS, the movement of polymer molecular chains are blocked, and there is more contact probability between EVA and GNS, which might reduce the effect of crystal lattice^[16]. In general, the crystallization behavior depends on the GNS impact on both heterogeneous nucleation and crystal growth.

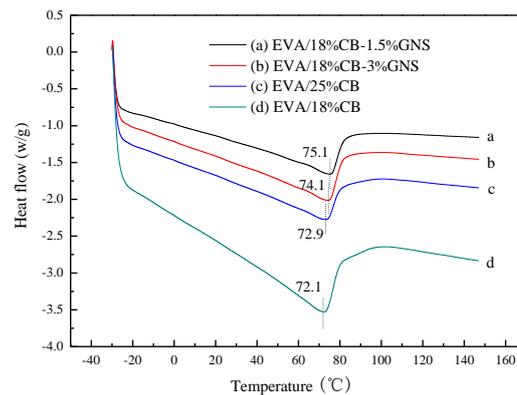


Fig. 6. Heating thermograms of EVA/CB and EVA/CB-GNS.

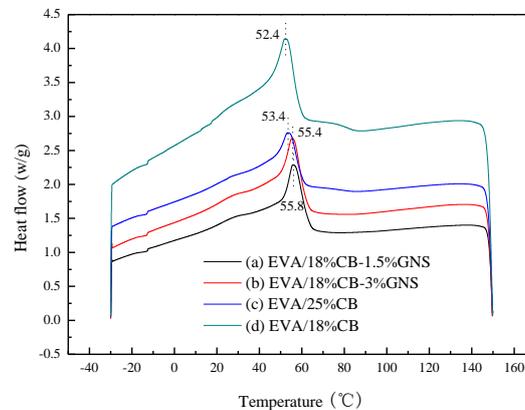


Fig. 7. Cooling thermograms of EVA/CB and EVA/CB-GNS.

4. Conclusions

In summary, a semiconductive shielding material used in XLPE cable has been prepared by adding GNS, CB and stearamide into EVA. At low GNS loading, a three-dimensional conductive network can be formed due to the synergistic effect between CB and GNS, so the electrical property of the composites was greatly increased. Meantime, the CB improved the dispersability of GNS in EVA to a certain extent. EVA/18%CB-1.5%GNS, by contrast, has the best electrical and mechanical performance. In addition, 1.5% of the GNS also enhanced the thermal performance of the composite.

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