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Synthesis and Properties of Graphene/Carbon Nanotube/Epoxy Resin Composites

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Carbon nanotubes with multi-layer graphene sheets (excellent mechanical properties, chemical stability, electrical properties, and thermal properties) are excellent modifiers and ideal functional enhancement materials for composite materials. It has strong adhesion and good overall mechanical properties, but epoxy resin cross-linked and cured after brittle, impact resistance and resistance, stress cracking ability is poor. Therefore, the introduction of nanoparticles in epoxy resin for modification is proved to be a very effective method. This article proposes the modification of carbon nanotubes and graphene sheets, and adds epoxy resin with the help of solution mixing and melt, mixed methods to prepare composite materials. The characterization methods and the modification effects are characterized. Through the mechanical properties, thermal conductivity, and conductivity and electrical properties of the composites, the modification enhancement effect was evaluated, and the mechanism of modification of the impurities is enhanced.

1. Introduction

In 1991, Japanese scientists unexpectedly discovered molecular images similar to tubular structures when using high-resolution electron microscopy to study the structure of C60 and charcoal. It was assumed that the model was multi-layered, hollow, carbon, and the wall was composed of six rings and ends of carbon. The seal consists of a five-membered ring or a six-membered ring (Wu et al., 2016). These carbon tubes are found to have a length of several tens of nanometers, several millimeters to several millimeters, and a layer-to-layer distance of about two, both ends, closed by hemispherical end caps, and each cylinder surface under an electron microscope. It is a symmetrical parallel stripe with a hollow center and a concentric circle in cross section (Sharma et al., 2018). Carbon nanotubes high resolution structure is given in Figure 1.

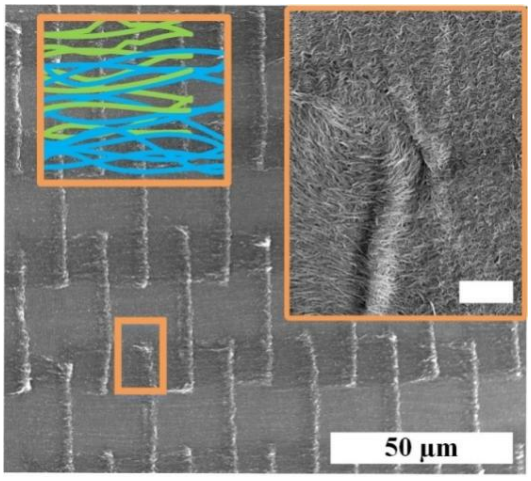

Figure 1: Carbon nanotubes high resolution structure

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Polymeric carbon nanotube composites have good mechanical, electrical and thermal conductivity, but the use of polymer carbon nanotube composites is limited due to the difficulty of carbon nanotubes, dispersion, and the high cost of carbon nanotubes. Graphite thin material, as a promising nanofiller, not only has a high aspect ratio, high conductivity and a unique graphitized planar junction, but also has a low manufacturing cost. This topic is a new attempt to prepare epoxy carbon nanotubes graphene composites by using one-dimensional carbon nanotubes and two-dimensional graphenes (Chen et al., 2016; Du and Chao, 2018). The one-dimensional carbon nanotubes and graphene are bridged in the matrix, which inhibits the agglomeration of the carbon nanotubes and also prevents the graphite from being deposited in a dilute manner (Du et al., 2018). The fillers can perform well in the matrix. The research idea of this paper is to prepare epoxy resin composites with multi-layered graphene material, modified multi-walls with concentrated nitric acid and concentrated sulfuric acid, and carbon nanotubes as fillers. This article will use the laboratory solution mixing method to prepare composite materials, improve the dispersion of the filler in the matrix, and compare the effect of nano-filler dispersion.

2. Preparation of composite materials by solution mixing

2.1 Preparation of Carbon Nanotubes Composites by Solution Method

The mechanical dispersion of carbon nanotubes in epoxy resins is more difficult to disperse than in thermoplastic materials, because relatively low shear stress is difficult to achieve effective dispersion in epoxy-based materials. It is difficult to effectively disperse the carbon nanotubes in the epoxy resin by conventional mechanical or electromagnetic impact mixing (Wang et al., 2017). Increasing the temperature or adding a solvent can reduce the viscosity and degree, and reduce the shear force required for dispersion, so that good dispersion can be achieved under the condition of conventional mechanical stirring, and the partial agglomeration of carbon nanotubes can be uniformly dispersed. Schematics of CNT/epoxy nanocomposites fabricated in solvent mixing method are given in Figure 2.

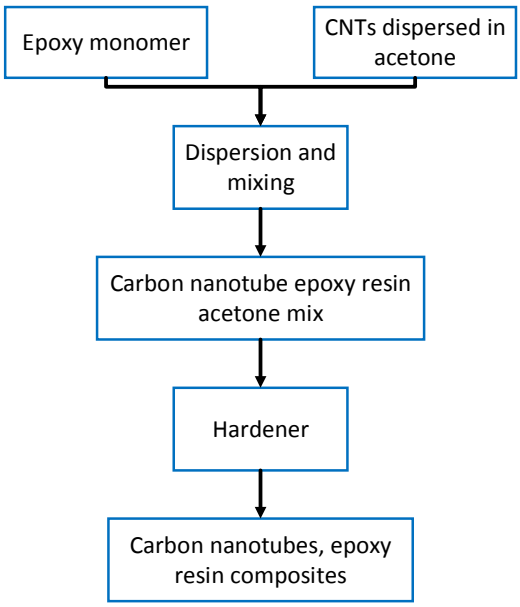

Figure 2: Schematics of CNT/epoxy nanocomposites fabricated in solvent mixing method

2.1 Preparation of composite materials by solution mixing

2.2.1 Experimental raw materials

Acetone, Shanghai Lingfeng Chemical Reagent Co., Ltd., Purity
Epoxy resin, Shanghai Resin Factory Co., Ltd.
Curing agent, Shanghai Resin Factory Co., Ltd.
According to the second chapter homemade expanded graphene;
According to Chapter 2 Concentrated Sulfuric Acid, Concentrated Acid Modified Carbon Nanotubes

2.2.2 Experimental Instruments

Agitator, model for precision power electric mixer, Changzhou Guohua Electric Co., Ltd.;
Digital thermostat water bath, model for the Shanghai Jiangxing Instrument Co., Ltd.;
Three-necked flask, volume is 500ml.
Rotary chip vacuum millet, model type, origin for Shanghai Shengke Instrument Equipment Co., Ltd.;
Electric heating temperature blast dry box, model for type, Shanghai Xin Miao Medical Device Manufacturing Co., Ltd.;
Ultrasonic cleaning machine, model number is Ningbo Haishu Kesheng Ultrasonic Equipment Co., Ltd.;
Vacuum drying box, model, Shanghai Shenxian constant temperature equipment factory.

2.2.3 Experiment process

Solution preparation method of composite materials:
1)Weigh the modified multi-walled carbon nanotubes and expanded graphene, and place them in a three-necked flask. The amount of acetone is poured into a three-necked flask, and the temperature of the three-necked flask is lowered and placed in an ultrasonic cleaner. Ultrasonic dispersion in the hours.
2) After the completion of the ultrasound, 120g of epoxy resin 6002 is weighed, poured into a three-necked flask, and the three-necked flask is placed in a constant-temperature water bath at 80 degrees and continuously stirred for one hour.
3) Remove the three-necked flask from the water bath and put it into the tank for 1 hour to completely volatilize the solvent acetone.
4) After cooling, add the curing agent epoxy curing agent and stir the stirrer for 10 minutes. Stir the mixture and inject it into a mold for drawing, conducting, and heat-conducting.
5) Place the mold in a vacuum drying oven, set the temperature at 0°C, hold for 1 hour, raise the temperature to 80°C, and incubate for 6 hours to prepare a composite material. Curing time period of epoxy resin is given in Figure 3.

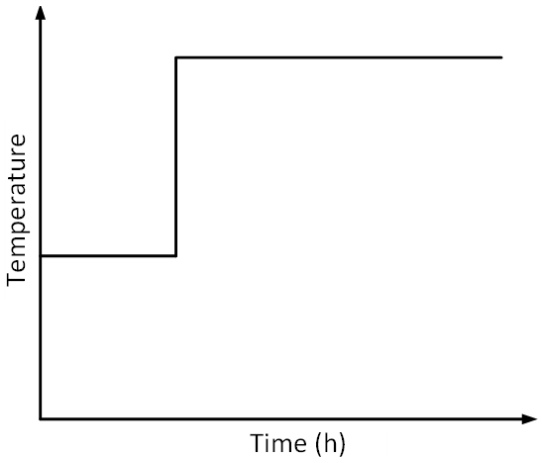

Figure 3: Curing time period of epoxy resin

2.2 Characterization and testing

2.3.1 Mechanical Analysis

According to the standard injection of the composite material around a plastic tensile test specimen, as shown in Figure 4, the standard size of the GB/T 1040-92 tensile test specimen (Park et al., 2017). Tensile test uses Shenzhen Rigger Tensile Testing Machine Co., Ltd. tensile tester RSM-4050, test speed is 4mm/min (Chen et al., 2017). The size of the standard sample in GB/T1040-92 is given in Table 1.
The graph shows that the filler content is the tensile curve of the composite material. It can be seen from the figure that the epoxy resin and its epoxy carbon nanotube composite materials are brittle materials and all show brittle fracture at the time of fracture (Li et al.,2016). Table 2 shows the tensile strength and elongation at break of different nano-fillers and their composites. It can be seen from the figure that both the tensile strength and the elongation at break of the composites have been improved with the increase of filler content and the addition of multi-layered graphite flakes.

Table 1: The size of the standard sample in GB/T1040-92

Symbol	Name	size	Tolerance
L	Total length (min)	150	-
H	Distance between clamps	115	±5.0
C	Intermediate parallel section length	60	±0.5
G	parallel section width	50	±0.5
W	Gauge (or valid portion)	20	±0.2
D	thickness	4	±0.2
B	Middle parallel width	10	±0.2
R	Radius (minimum)	50	±0.2

Table 2: Properties of epoxy composites containing various carbon nanofillers

Material	Tensile strength	(%)a	Elongation at break	(%)b
EP	45	0	3.4	0
1.0wt%P-CNTs/EP	56	24.4	3.5	2.9
1.0wt%M-CNTs/EP	60	33.3	5.7	47.1
1.0wt%(4:1)M-CNT/MGPs/EP	62	37.8	5	67.6

2.3.2 Heat Loss Test

Thermogravimetric analysis is a commonly used method for studying the thermal stability of materials. It is a technique for obtaining the relationship between temperature and mass changes of materials by using thermostables under the program temperature control (Watanabe et al., 2018). The Figure 4 shows the thermogravimetric curves are obtained from pure epoxy, and from the room temperature up to 900 degrees at the heating rate. The addition of fillers has little effect on the thermal stability of epoxy resin composites (Kwonet al., 2016), and the thermal weight loss curves of composites and pure materials almost coincide with each other, and there is no decrease in stability caused by the addition of fillers.

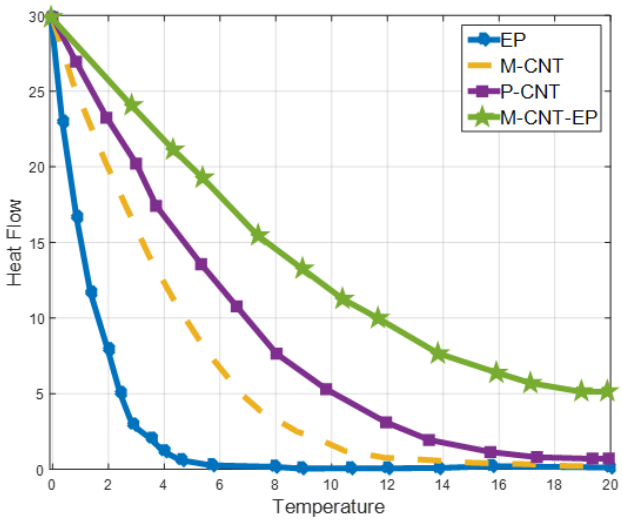

Figure 4: TGA curves of EP and epoxy nanocomposites-Temperature-Heat Flow curve

2.3.3 Conductivity test

The volume resistivity of the sample is measured using a digital high-impedance meter manufactured by Shanghai No. 6 Meter Factory Co., Ltd. The operating frequency of the working voltage is 25%-80% for the test relative humidity (Lee et al., 2017).

$$\rho_v = R_v \times \frac{Ae}{t} \tag{1}$$

$$Ae = \frac{\pi}{4} \times (d_1 + g)^2 \quad (2)$$

The graph shows the relationship between filler content and volume resistivity in epoxy resin composites (Ghaleb et al., 2017). As can be seen from the Figure 5, with the increase of filler content, the volume resistivity of composites decreases the most, which is followed by composite materials, and the composite material has the largest resistance (Khan et al., 2018).

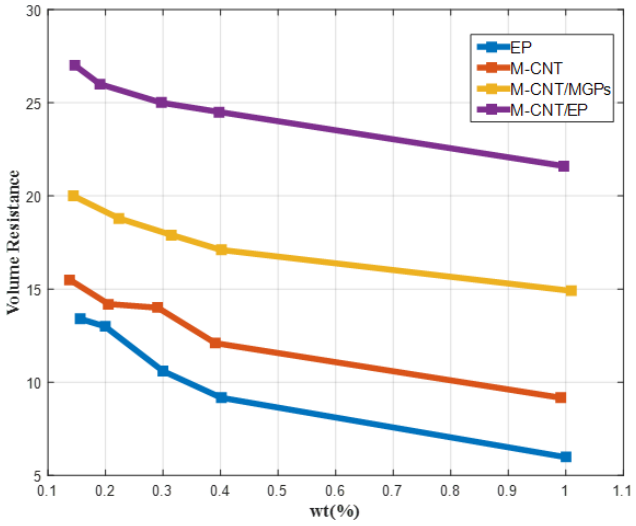

Figure 5: The relationship between filler content and volume resistance of epoxy resin composite materials

3. Conclusion

In this chapter, acetone is used as a solvent. The carbon nanotubes are first dispersed in a solution of acetone, and then the epoxy resin is dissolved in an acetone solution and the filler is uniformly dispersed in the epoxy resin. The mechanical properties, thermal properties and conductive properties of the composites prepared by this method have been greatly improved. The strength of the composite material in which the modified carbon nanotubes is better than that of the unmodified carbon nanotubes, and the maximum tensile strength is obtained in the simultaneous addition of the unmodified carbon nanotubes. This is due to the simultaneous addition and the dispersion in the matrix is the best. With the addition of carbon nanotubes and graphene materials, the high thermal conductivity of the carbon nanotubes and graphite thin materials is brought into the composites, and the trend increases linearly with the weight percentage increase. The thermal conductivity of the modified carbon nanotubes added in the content is slightly higher than the thermal conductivity of the unmodified carbon nanotubes, because the modified carbon nanotubes have higher dispersion performance than the modified carbon nanotubes. The penetration in the matrix, while adding at the same time, the thermal conductivity increase most, because at the same time when the filler and the best dispersion, the carbon nanotubes do not entanglement, uniform dispersion, and graphene does not stack.

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