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Unsaturated polyester resin/graphite nanosheet conducting composites with a low percolation threshold

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Abstract

In this study, the unsaturated polyester resin/graphite nanosheet conducting composites with a low percolation threshold of 0.64 vol% have been prepared via in situ polymerization under the application of ultrasonic irradiation. Two theoretical approaches (mean-field theory and excluded volume theory) are applied to interpret this low critical volume fraction and the latter can explain the low value better. The microstructures reveal that low value of percolation threshold may be mainly attributed to better conductive network consisting of graphite nanosheet with special morphology and there exists contact resistance in the percolating network formed within unsaturated polyester resin/graphite nanosheet composites. Furthermore, preliminary studies on the influence of graphite nanosheet on the thermal stability of the host unsaturated polyester resin have been performed.

Keywords: Unsaturated polyester resin; Graphite nanosheet; Conducting composite

1. Introduction

Conducting composites have been extensively studied because of their practical applications in light emitting devices, batteries, electromagnetic shielding, electrostatic dissipation, adhesives and other functional applications [1–6]. The electrical conductivity of these composites can be varied in a very broad range between the conductivity of the matrix and the conductive fillers. The transition of the bulk composites from insulator to conductor occurs as the concentration (volume fraction of conducting phase) of the conductive component is increased above a threshold value (the percolation threshold) [7,8]. This critical value is greatly affected by the properties of the fillers and the polymer matrices, processing methods, temperature, and other related factors [9]. Generally, relative large quantities of conductive filler are needed to reach the insulator–conductor transition. However, high filler concentration could always lead to materials redundancy and detrimental mechanical properties [3]. Therefore, main objective in this field is to fabricate conductive composites with minimizing critical volume fraction in filler concentration. Incorporation of conductive fillers with microsize or nanosize may effectively mitigate the detriment and still maintain the conductivity of the composites. Graphite nanosheet, one kind of such fillers, has served as conductive filler in polymer–matrix composites. Celzard et al. [10] first investigated the conductive behavior of 100 μm-thick composite films composed of epoxy resin and expanded graphite flakes with an average diameter of 10 μm and an average thickness of 100 nm. It was only 1.3 vol% graphite sheet that was needed to reach the percolation threshold. Several groups reported that a remarkably low volume fraction of expanded graphite (EG) was needed to satisfy the percolation transition in nylon 6/EG [11], poly(styrene-methylmethaerylate)/EG [12], PS/EG [13–15], PMMA/EG [16] and poly(vinyl chloride)/EG composites [17] via in situ polymerization approach. Inspired by these previous reports, we proposed fragmentation of expanded graphite by ultrasonic irradiation without grinding [18,19]. On the basis of transmission analysis, the thickness of foliated graphite filler varied from 10 to 100 nm, and the aspect ratio (diameter to thickness) is as high as 100–300. The as-produced graphite nanosheet was successfully incorporated into PMMA [20] and PS [21] to fabricate nanocomposites with very low values of percolation threshold, about 1.5 and 1.6 vol%, respectively.

In this paper, we fabricated unsaturated polyester/graphite nanosheet composites under the application of ultrasonic irradiation. The electrical properties of nanocomposites in

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present case are examined using the percolation theory. And experimental results show that the low percolation threshold is mainly ascribed to high aspect ratio and homogeneous dispersion of graphite nanosheet in polymer matrix. The fitted value of the conductivity critical exponent and microstructures confirm that there exists contact resistance in percolating networks. Moreover, preliminary studies on the thermal properties of the resulting composites were also preformed.

2. Experimental

2.1. Materials

The unsaturated resin was supplied by Quanzhou Unsaturated Polyester Resins Factory (Quanzhou, China). The conductive filler used here consists of graphite nanosheet, the average diameter of which is 12.5 μm and the average thickness of which is 51.5 nm. SEM analysis reveals that graphite nanosheets are roughly disk-shaped sheets with thickness less than 100 nm [18]. Moreover, the size and size distribution of the as-produced graphite nanosheet depend on the ultrasonic irradiation time. Detailed procedures and characterization of graphite nanosheet were described in our pervious paper [18].

2.2. Fabrication of unsaturated polyester resin/graphite nanosheet composites

The unsaturated polyester resin/graphite nanosheet composites were prepared according to the following steps. Preweighed unsaturated polyester resin and graphite nanosheet were loaded into a reaction tube. The tube was placed into an ultrasonic bath with water as the coupling fluid. Ultrasonic irradiation was then applied and maintained for several minutes to obtain homogeneous dispersion of graphite nanosheet within the matrix. After a certain time of irradiation, the initiator (methyl ethyl ketone peroxide) and the promoter (cobalt octoate) were added into the mixture. Upon the completion of curing, the cylinder-like products were removed from the tube. Incorporation of graphite nanosheet retarded the curing rate of unsaturated polyester resin. The maximum volume fraction will be the critical concentration at which the mixture cannot be cured. Composites with various graphite nanosheet contents were prepared via this procedure.

2.3. Characterization and measurements

Scanning electron microscopy (SEM, LEO-1530) was used to examine the morphology of graphite nanosheet in the composites. To prevent charging of the samples, a thin coating of gold was deposited. The DC resistivity of unsaturated polyester resin/graphite nanosheet composites was measured along the axial direction and the data were collected by a DT 9205A meter (Haidi, Shenzhen, China). To ensure good electrical contact, the surfaces of the specimens were polished with 1500 grit sandpaper and conductive paint was coated between the electrodes and the specimens. All measurements were made in the linear range of the resistance versus voltage characteristics. Cylinder-like samples with 12 mm in diameter and 10 mm in height were cut for measurements.

Thermogravimetric analysis (TGA) was performed on a TA 5200 differential thermal balance under flowing nitrogen. Samples with weight close to 10 mg were positioned in open vitreous silica pans. Scanning was performed over the temperature ranging from room temperature to 700 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Theoretical interpretation of the conducting properties

3.1.1. Percolation theory

Percolation theory gives a phenomenological description of the conductivity of a disordered system near the insulator–conductor transition. According to this theory, the percolation threshold, p_c, is the critical volume fraction at which the infinite conducting network is first formed. Due to formation of initial percolating path through the composites, the transition from insulator to semiconductor occurs. Above the percolation threshold, the resistivity of the composite is found to decrease as [22]

$$\rho = \rho_0 \left[\frac{p-p_c}{1-p_c}\right]^{-t} \quad (1)$$

where ρ_0 is the resistivity scale factor, p is the concentration of conductive filler (volume fraction), p_c is the percolation threshold, and t is the conductivity critical exponent.

The data for DC resistivity versus graphite particles content are shown in Fig. 1 and fitted to the Eq. (1).

The fitted parameters are 2.01 for the conductivity critical exponent, 0.64% for the percolation threshold, and 0.01 for the resistivity scale factor. The fitted value for the conductivity critical exponent is in excellent agreement with the theoretical universal value $t=2.0$ established by various numerical calculations of random resistor network models [23–25].

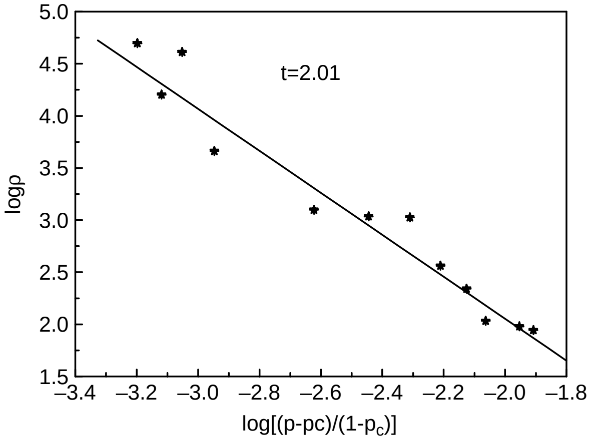

Fig. 1. The DC resistivity versus concentration of graphite for 12 different samples.

The exciting result is the low value of the critical volume fraction p_c, 0.64 vol% (1.2 wt%). In unsaturated polyester resin/expanded milled-graphite and epoxy resin/expanded milled-graphite composites prepared by ultrasonic irradiation [26], the percolation threshold values are about 2 and 5 wt%, respectively. Hence, it is evident that the graphite nanosheet with high aspect ratio is more effective in forming conducting network and lowering the percolation threshold, when the composites are prepared by the same processing method. In the following sections, theoretical interpretations of low percolation threshold will be discussed.

3.1.2. Mean-field theory

Helsing and Helte [27] proposed an approach to determine the critical concentration of a percolating system. This simple approach is based on calculating the average effects of the random resistor network by approximating the binary heterogeneous mixture of insulator and conductor as a homogeneous effective medium. The overall conductivity equation applicable over the full range of concentration can be obtained. Consequently, for thin and flat ellipsoids with major and minor axis length γ and $\eta\gamma$ (γ is the reciprocal of aspect ratio) the percolation threshold is found to be:

$$p_c = 1.18\eta \tag{2}$$

If graphite nanosheet can be approximately described as this type of subject with an aspect ratio (diameter to thickness, 12.1 μm/51.5 nm) of 235, the percolation threshold for unsaturated polyester resin/graphite nanosheet composites will be

$$p_c = 0.502\% \tag{3}$$

Obviously, this prediction is not in good agreement with the value 0.64% in our case. This may be attributed to the following reason. Helsing and Helte's calculations were based on medium of randomly oriented grains, while slight orientation of the graphite nanosheet may exist in the present system [19].

The above approach can also be calculated more empirically, assuming that the critical volume fraction of a conductive powder is related to the empty volume between the particles [28]. And this is directly linked with the concept of excluded volume, which will be introduced in the following section. A conductive composite can be regarded as a conductive backbone with a certain packing density, which is different from the conducting powder according to the particle morphologies. In other words, the aspect ratio greatly affects the critical volume fraction. For the composites with the percolation threshold between 20 and 55%, empirical relationship between the quantities p_c and the filling factor p_c has been given

$$p_c \approx p_p - 5\% \tag{4}$$

where p_p = density of unpacked powder/density of material constituting this powder. In fact, if the critical value diminishes below 20%, the p_c and p_p will approach each other closely, leading to $p_c \approx p_p$. Now, we would like to apply this empirical equation to unsaturated polyester resin/graphite nanosheet composites, although the accurate density of the unpacked powder is not easy to obtain. The apparent density of the graphite nanosheet is about 0.015 g/cm^3 [29]. Taking the graphite with a mass density of 2.25 g/cm^3, a percolation threshold of about 0.67 vol% could then be obtained. This value is close to the fitted value obtained in the above section.

In conclusion, this approach indicates the correlation between the aspect ratio of the fillers and the percolation threshold. Consequently, we will further interpret this point below according to the excluded volume theory.

3.1.3. Excluded volume theory

It has been shown that using filler particles with elongated geometry can achieve a very low critical volume fraction in fabricating conductive composites. Based on the relationship between the low p_c and the special geometry of the fillers, the concept of excluded volume V_e, the volume around an object to the center of the another similar object is not allowed to enter if overlapping of the two objects is to be avoided, was proposed [30,31]. If the excluded volumes of the two objects are able to overlap, the conducting link between them will be formed with certain probability. Therefore, the percolation threshold is directly related to excluded volume of the object rather than the real volume of them.

On the basis of the assumptions mentioned above, the total excluded volume $\langle V_{ex}\rangle$ is defined by

$$\langle V_{ex}\rangle = N_c\langle V_e\rangle \approx \text{const} \tag{5}$$

where $\langle V_{ex}\rangle$ is the excluded volume of an object averaged over the oriental distribution characterizing the system objects, N_c is the critical number density of objects in the system, and V_e is the associated excluded volume. Actually, $\langle V_{ex}\rangle$ is not an invariant but situated for each type of object within a range of values corresponding to the system characterized by a random orientation (low limit) and a system of strictly parallel objects (upper limit). Hence, the critical volume concentration in three dimensions is linked to $\langle V_{ex}\rangle$ by [30,31]

$$p_c = 1 - \exp\left(-\frac{\langle V_{ex}\rangle V}{\langle V_e\rangle}\right) = 1 - \exp(-N_c V) \tag{6}$$

where V is the volume of a pore.

If the filler is disk-shaped, the percolation threshold can be related to the radius and thickness of the disks by

$$p_c = 1 - \exp\left(-\frac{\langle V_{ex}\rangle d}{\pi r}\right) \tag{7}$$

where d is the thickness of the disks and r is the radius of the disks. Because the value of $\langle V_{ex}\rangle$ is expected to lie between 1.8 and 2.8, following double inequality will be given [32]:

$$1 - \exp\left(-\frac{1.8d}{\pi r}\right) \le p_c \le 1 - \exp\left(-\frac{2.8d}{\pi r}\right) \tag{8}$$

With radius $r = 6.05$ μm and thickness $d = 51.5$ nm for the graphite nanosheet [18], the critical volume fraction of unsaturated polyester/graphite nanosheet composites is found to be:

$$0.487\% \leq p_c \leq 0.756\% \quad (9)$$

The fitted value of p_c, 0.64%, indeed falls into this range. This result further supports that morphologies of the graphite nanosheet play an active role in minimizing the percolation threshold. Therefore, we will restrict our attention to the influence of particles morphologies and the microstructures of the composites in the following section.

3.2. Microstructures

Fig. 2(a) and (b) shows the SEM micrographs of unsaturated polyester resin/graphite nanosheet composites with filler content of 1.13 and 1.87 vol%, respectively. With increase in content, graphite nanosheet within the polymer matrix tends to close with others in the surrounding regions and form continuous conductive network, leading to low percolation threshold, although the graphite nanosheet is separated by the polyester resin. We estimate that conduction behavior of composites in present case may be controlled by the contact resistance in percolating network because graphite nanosheet does not directly contact with others surrounding them. According to contact resistance in percolating network proposed by Keblinski and Cleri [33], contact resistance does not need to be related to actually weak or bad contacts between conductive objects, but may be simply due to a geometrically small area of the contacts. It is quite possible that in the systems, in which the conductivity critical exponent $t \approx 2$ is always observed, there always exists a dominance of the contact-resistance term to the network resistivity. This may be the actual reason why the exponent $t \approx 2$ is typically measured up to large values of graphite particle concentration, rather than the applicability of the percolation scaling over a limited content range. The scaling law $\rho \sim (p-p_c)^{-t}$ holds from the percolation threshold, $p_c = 0.64\%$ by volume, up to 1.87%, while in the system controlled by bulk resistivity the percolation threshold scaling law with $t=2$ should be applicable only up to about $2p_c$. Moreover, microstructure revealed by SEM also confirms the fact that the percolation threshold depends very much on the geometry of conductive filler. Filler with elongated can be applied to achieve a very low critical volume fraction because the fiber or sheet with high aspect ratio has great advantage over spherical or elliptical filler in forming conducting networks in matrices.

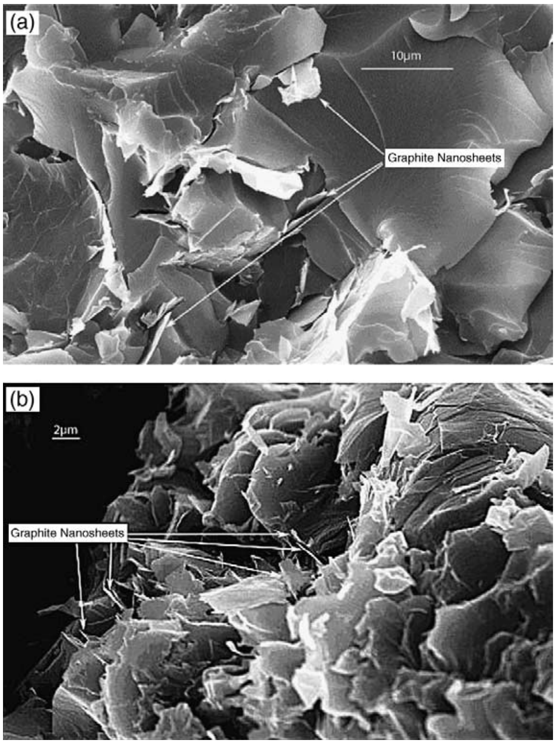

Fig. 2. SEM micrographs of unsaturated polyester resin/graphite nanosheet composites with graphite content of (a) 1.13 and (b) 1.87 vol%.

3.3. Thermal properties

The TGA curves for the unsaturated polyester resin/graphite nanosheet composites with various graphite contents are shown in Fig. 3 (the data are not normalized with respect to the impurity in unsaturated polyester resin for each blend).

Obviously, the TGA curves shift toward lower temperature with increasing graphite content in the composites. This could be attributed to the following reason. Phenolic or alcoholic functional groups generated during acid treatment [18] may effectively retard the copolymerization between the styrene monomer and the polyester double bonds [34] and then decrease the degree of crosslinking of these styrenated polyester resins. Therefore, the thermal stability of unsaturated polyester resins was weakened. For the aforementioned reason, it is meaningless to normalize the TGA data with impurity in the unsaturated polyester resin for each blend. However, it should be pointed out that no dramatic decrease of thermal stability was observed for composites with the graphite nanosheet content up to 3.38 wt%.

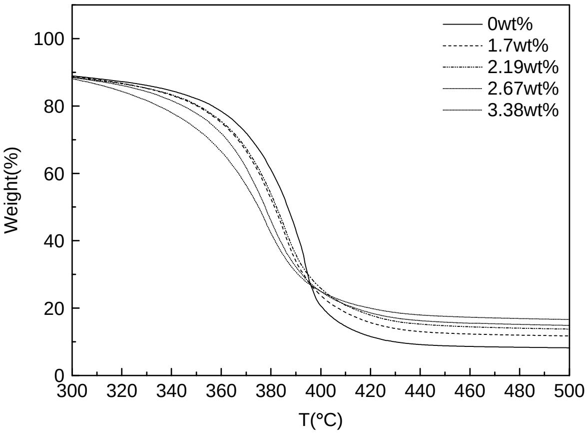

Fig. 3. TGA curves of unsaturated polyester resin/graphite nanosheet composites with graphite weight contents as indicated (for clarity, curves corresponding to some concentrations have been omitted).

4. Conclusions

In this paper, unsaturated polyester resin/graphite nanosheet composite and its electrical properties have been investigated. Experimental results reveal that graphite nanosheet can effectively form better conductive network in the resin and thus improves the electrical conductivity of as-prepared composites by exhibiting a typical percolation transition of conductivity at a very low critical volume fraction, 0.64%. To interpret this low fitted value caused by special morphology of graphite nanosheet, mean-field theory and excluded volume theory are applied. And we have found out that the obtained critical volume fraction falls into the range predicted by the latter. Based on theoretical interpretations and microstructures of composites, we estimate that the reduction of the percolation threshold may be directly related to high aspect ratio and homogeneous dispersion of graphite nanosheet in the polymer matrix resulting from ultrasonic irradiation. SEM micrographs and applicability of the percolation scaling over a large content range indicate that the conductivity of the composites in present case may be controlled by contact resistance in the percolating system. Furthermore, TGA curves show that thermal stability of unsaturated polyester resin/graphite nanosheet composites is slightly weakened because the degree of crosslinking of unsaturated resin may be decreased due to the retardation effect from the functional groups present on the surface of the graphite nanosheet.

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