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Effect of coating of graphite particles with polyaniline base on charge transport in epoxy-resin composites

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Abstract Investigations of charge transport, in epoxy resin composites of graphite particles coated with a non-conducting polyaniline-base layer, showed that particle shape and surface structure may crucially affect the percolation behaviour of the systems. In contrast to the gradual increase in the DC conductivity of composites in the range 20–52 vol.% for pure graphite particles, due to their fragmentary nature, a steep rise of several orders of magnitude in conductivity, appeared in composites of graphite particles coated with 10 wt.% of polyaniline base at a particle concentration 50 vol.%. The frequency and temperature dependences indicate that, in both cases, at the maximum loading used (52 vol.%), the obtained material had ohmic conductivity. In contrast, the conductivity of epoxy composites of graphite particles, coated with 20 wt.% of polyaniline base, only slightly increased over the whole range of particle concentrations. These findings suggest that, in the case of 10 wt.% polyaniline coating, due to the irregular surface structure, a certain amount of uncoated material is present, which enables the formation of conducting contacts with ohmic conductivity in the percolation area. The 20 wt.% polyaniline coating forms a compact non-conducting layer on the surface of the graphite particles, thus preventing electrical contact.

Introduction

In the last few years, polymer composites of conducting particles dispersed in a non-conducting polymer matrix have been receiving increasing interest, providing new materials with tailored properties, suitable for various electrical and electromagnetic applications. Charge transport in such materials has been the object of many researchers in the past. It is generally accepted that the conducting mechanism in composites of conducting particles can be described by percolation theory [1–9]. At low filler concentration, the conductivity of the material is controlled by the non-conducting matrix. When the filler concentration increases, and the gap between the particles is less about 10 nm, slight charge transport due to a hopping [10, 11] or tunnelling [12–16] mechanism may be expected. At a critical volume fraction (percolation threshold) at which a continuous chain of particles with macroscopic length and ohmic conductivity in the system appears, a rise in composite conductivity of several orders of magnitude occurs, followed by a slower increase in conductivity with the particle concentration approaching the value of the conducting filler.

Analysis of the dielectric properties of composites filled with electrically conducting particles showed that frequency dependence of conductivity is closely related to the character of the charge transport in the material.

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At low frequencies, the real part of the complex conductivity:

$$\sigma'(f) = f\varepsilon_0\varepsilon''(f) \qquad (1)$$

has a constant value (low frequency plateau) equal to the DC conductivity σ_{DC}. Here, ε_o is the dielectric constant of free space, and $\varepsilon''(f)$ is the dielectric loss factor. At higher frequencies (relaxation region), the conductivity increase can be described by the power law [3, 4]:

$$\sigma'(f) \approx f^x \qquad (2)$$

The exponent x is a sensitive criterion of the character of the conductivity of the composite, with the limit $x = 1$ for a non-conducting matrix and $x = 0$ for a material with ohmic conductivity, where a space-conducting network of particles is present.

The present experiments show that not only the electrical properties, but also the particle structure and character of their interactions, may significantly influence both the percolation threshold and the width of the percolation region. Understandably, the conducting properties of the particle surface play a crucial role in the formation of conducting chains in the material. For a model system of conducting spheres, randomly distributed in a non-conducting matrix, percolation at 16–17 vol.% was calculated [19]. In contrast, only 1–2 vol.% was found in composites of short carbon fibres [4, 20, 21] as a consequence of the easy formation of a conducting network by fibres already at low concentration.

In our preceding paper [22], the strong influence of the coating on carbon fibres in polymer composites, by a non-conducting layer of polyaniline base, on percolation behaviour was demonstrated. The electrical properties of composites of graphite particles coated with the same polymer are the object of this study.

Experimental

Materials

The epoxy resin (ChS Epoxy 531, Spolchemie, Czech Republic) was cured with diethylamine. The matrix had a density of 1.2 g cm^{-3} and DC conductivity <10^{-14} S cm^{-1}. Graphite (MEGA, Czech Republic; density 2.1 g cm^{-3}, DC conductivity 300 S cm^{-1}) was used as received. Morphology of particles (Fig. 1) was assessed with JSM 6400 JEOL microscope.

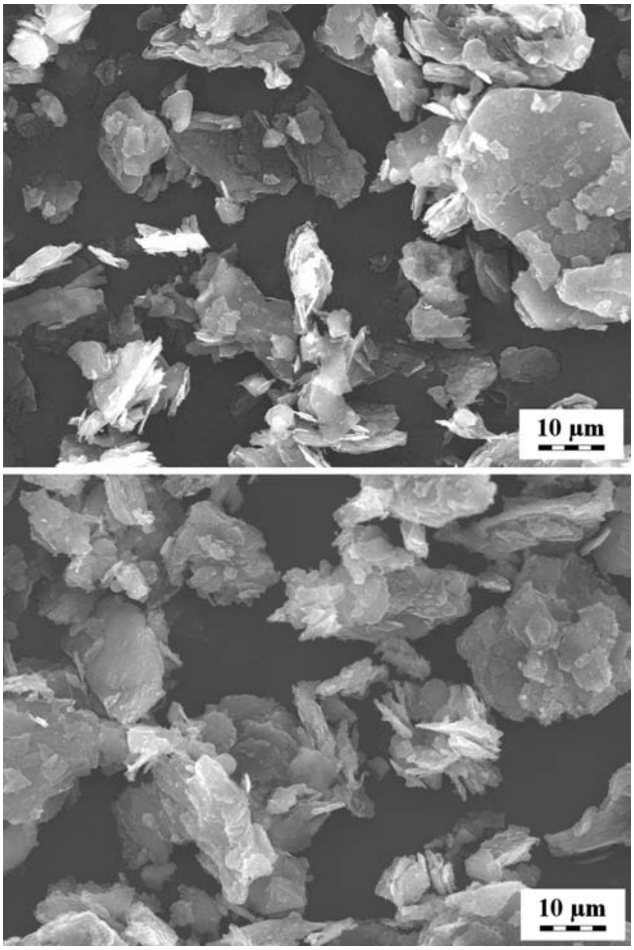

Fig. 1 SEM micrographs of uncoated graphite particles (top) and coated particles with 20 wt.% polyaniline base (bottom)

The coating of graphite with polyaniline

Graphite particles were coated with PANI in ethanol (50 vol.%)–water mixture containing 0.2 M aniline hydrochloride and 0.25 M ammonium peroxydisulfate at room temperature. Graphite (18 g or 8 g) was suspended in 50 mL of aniline hydrochloride solution in ethanol, and the polymerization of aniline was started by adding an equal volume of an aqueous oxidant solution. The mixture was stirred with a magnetic bar. The polymerization was completed within 15 min. The PANI-coated particles were separated on a filter, and rinsed with 0.2 M hydrochloric acid and acetone, and dried. Conducting protonated PANI was converted to a non-conducting PANI base by immersion of PANI-coated particles in 1 M ammonium hydroxide. The 100 mL of reaction mixture generates after polymerization and deprotonation ~2 g PANI base. The PANI-base-coated graphite particles thus contained 10 and 20 wt.% of PANI base, respectively.

Composite preparation

Three series of composites (Table 1) with uncoated graphite particles and particles coated with 10 and 20 wt.% of polyaniline base were prepared. The maximum concentration, at which a homogeneous material could be obtained, was 52 vol.% of the filler.

Conductivity measurement

Disc-shaped samples, 15 mm in diameter and 2.8 mm thick, were produced by cast moulding. The fronts of the samples were sputtered with a gold layer to ensure good contact between the composite and electrodes. A Keithley 6517 programmable electrometer was used as a source of stabilized power. The DC conductivity was calculated from the current–voltage dependence in the range of 1–20 V. The AC conductivity was measured in the range of 10^2 to 10^5 Hz by Hioky 3522 LCR Hi Tester (Japan).

Results and discussion

The dependence of the DC composite conductivity on the pure graphite particle volume concentration Φ showed that, at low graphite content up to about 20 vol.%, the conductivity corresponded to that of a non-conducting or semi-insulating matrix ($\sigma_{DC} \approx 10^{-12}$–$10^{-13}$ S cm^{-1}). Then the conductivity gradually increased and at maximum loading (52 vol.%) it reached the value 2×10^{-3} S cm^{-1} (Fig. 2). The decreasing slope of $\sigma(f)$ versus f plots in double logarithmic coordinates in the dispersion region (Fig. 3), indicating a decrease in the exponent x with increasing particle concentration from $x = 1.0$ at 19.5 vol.% of the filler (virtually non-conducting material) to 0 at maximum loading (Table 1), suggests a gradual building up of a conducting structure of particle chains with ohmic conductivity.

Table 1 The critical exponents, x, for composites with various particle concentration Φ of neat and PANI-base-coated graphite particles embedded in epoxy resin

Φ (vol.%)	Neat	Graphite +10 wt.% PANI base	Graphite +20 wt.% PANI base
20	1.0	–	–
25	0.76	1.0	0.94
34	0.66	1.0	0.94
44	0.05	–	–
49	0	1.0	0.94
52	0	0.6	0.94

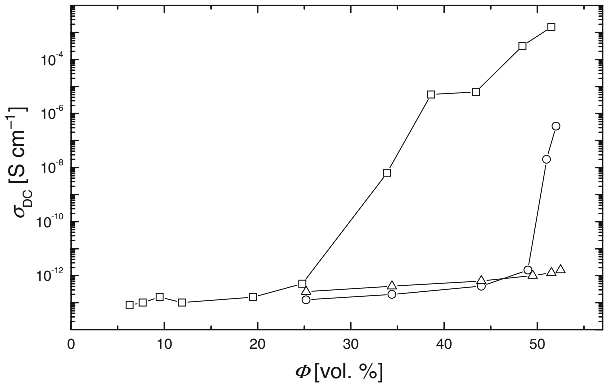

Fig. 2 The dependence of the DC conductivity σ_{DC} of composites on the volume fraction Φ of uncoated (□) and coated particles with 10 wt.% (○) and 20 wt.% (△) of PANI base at 20 °C

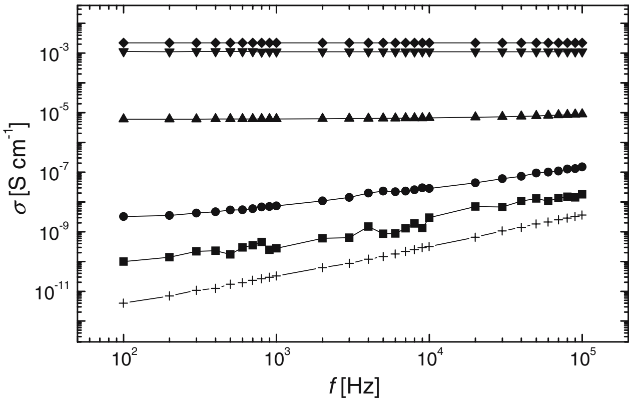

Fig. 3 The dependence of the conductivity σ' on the frequency f for composites of graphite particles. Particle concentration (vol.%): (+) 1.95, (■) 25.2, (●) 34.4, (▲) 44, (▼) 49, (◆) 52

The conductivity of composites with coated particles at both the above-mentioned PANI concentrations increased up to about 50 vol.% of the filler only slightly, and then stayed virtually close to the conductivity of the matrix (Fig. 2). Then, in the case of the coating with 10% PANI, it steeply rose and at 52 vol.% of particles it reached a value of about five orders of magnitude higher. For particles with 20 wt.% of PANI coating, only a slight increase in conductivity continued.

Unlike for a pure graphite composite, the frequency dependences of conductivity of the samples with PANI-base-coated particles (Figs. 4 and 5) up to 50 vol.% of particles provided an x-value of about 1, which corresponds to a non-conducting material. At a higher content of particles with 10 wt.% of coating the exponent decreased to 0.6, i.e. a value characteristic for a semi-conducting transport mechanism. For a composite of particles with 20 wt.% of

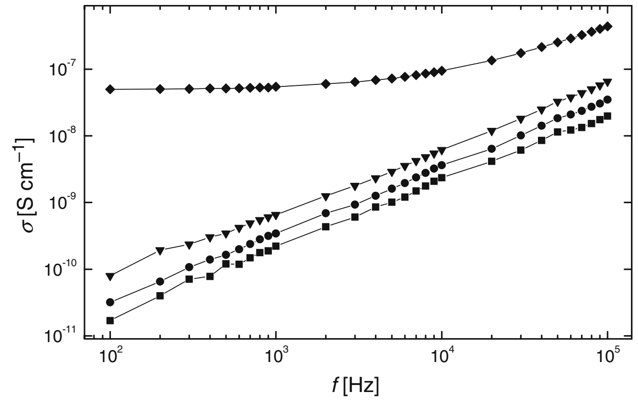

Fig. 4 The dependence of the conductivity σ on the frequency f for composites of coated graphite particles with 10 wt.% of PANI base. Points denoted as in Fig. 3

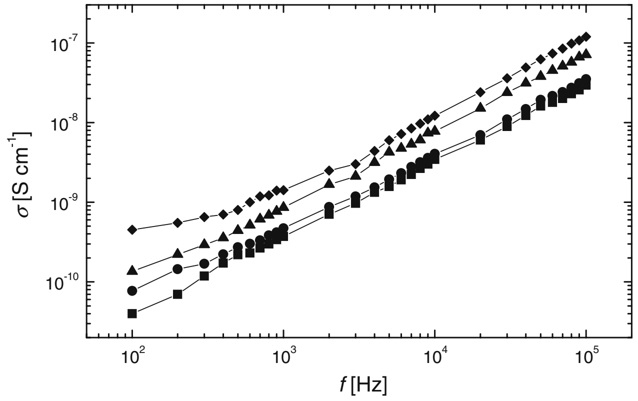

Fig. 5 The dependence of the conductivity σ on the frequency f for composites of coated graphite particles with 20 wt.% of PANI base. Points denoted as in Fig. 3

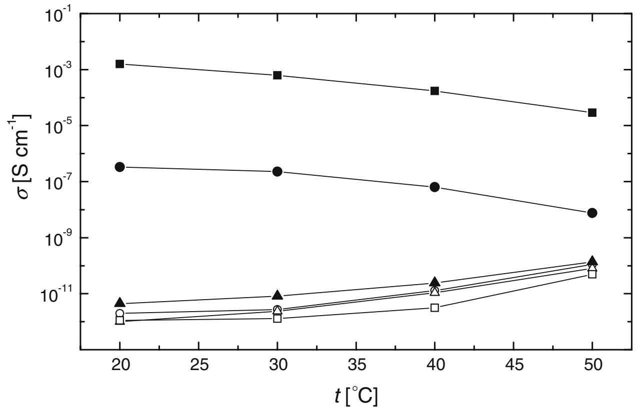

Fig. 6 The dependence of the conductivity σ on the temperature t. Particle/vol.%: (■) pure graphite/52, (□) pure graphite/25, (●) 10% coating/52, (○) 10% coating/50, (▲) 20% coating/52, (△) 20% coating/50

PANI base, the exponent $x = 0.94$ indicates that the non-conducting or semi-insulating character of the composite remained unchanged up to the highest filler content.

Elucidation of the charge transport character in the studied material provided dependences of conductivity on the temperature (Fig. 6). Increasing conductivity with temperature for composites at the start of the conductivity rise (at 25 vol.% of pure graphite and 50 vol.% of coated particles as well as at 52 vol.% of the filler coated with 20 wt.% of PANI) suggests non-conducting or semi-conducting behaviour. In composites with pure graphite and particles with 10 wt.% of PANI at maximum loading, the conductivity decreased with increasing temperature, which demonstrates that paths with ohmic conductivity in the material are present.

In contrast to a steep conductivity increase at the percolation threshold, in composites with aggregated carbon black particles or short carbon fibres [22–24], the slow formation of conducting paths of intimate contacts between uncoated graphite particles in the percolation region from about 20 to 50 vol.% may result from the fragmentary structure of the used product. A similar cause of continuous increase in composite conductivity, over several decades of volume percents, has been considered with polypropylene composites with shungite filler [25] and composites of hard metal particles in paraffin wax [26]. This phenomenon suggests the possibility of reproducibly preparing a semi-conducting sample with the required conductivity in the critical range 10^{-12} to 10^{-3} S cm^{-1} as a material suitable for construction of various electronic devices.

The ohmic conductivity in a composite with 52 vol.% of the filler coated with 10 wt.% of PANI base shows that a certain small amount of uncoated parts of graphite particles, due to the fragmentary structure, must be present. Under these circumstances, the formation of conducting contacts between particles perists up to a relatively high particle concentration (50 vol.%), when the particles are sufficiently close to each other. A similar effect has been found in epoxy resin composites of short carbon fibres coated by PANI base [22]. On the other hand, particles with 20 wt.% of PANI base are obviously perfectly coated with a non-conducting layer, and the composite conductivity with filler concentration increases only slightly due to tunnelling and a hopping charge-transport mechanism.

Conclusion

It has been demonstrated that the percolation behaviour of polymer composites based on electrically conducting graphite particles is significantly affected by the particle structure. Especially for particles coated with a non-conducting layer of PANI base, the irregularity of the surface coating at low PANI content may make a perfect coating impossible. In this case, due to the presence of uncoated conducting regions on the particle surface, the formation of conducting pathways can set in only at higher particle concentrations, when a sufficiently close particle structure in the copolymer arises. If the coating of the graphite particles with PANI base is complete, the charge transport at any particle content may occur only by a tunnelling and hopping mechanism and not by percolation.

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