

Electrical conductivity of carbon fibres/polyester resin composites in the percolation threshold region

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Abstract

The electrical conductivity of composites of a polyester resin filled with short carbon fibres has been investigated with a special attention to the properties in the percolation threshold region. A very low percolation threshold (0.7–0.8 vol% of the filler) was confirmed. In contrast to S-shaped curves calculated according to the percolation theory of composites of globular particles, the experimental conductivity vs. fibre content dependence, after a steep increase in the percolation region, increased almost linearly. This atypical behaviour was explained by a different mechanism of formation of fibrous and globular conducting structures above the percolation threshold. An increase in scatter of conductivity values observed at percolation threshold as a consequence of great fluctuation of fibre arrangement manifested itself also in the conductivity–temperature dependences.

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1. Introduction

Conducting polymeric composites based on conductive particles in a polymer matrix are widely used owing to their unique electrical and mechanical properties [1–9]. Most polymers are typical insulators and conductivity of the composite materials predominantly depends on the content and properties of the filler as well as on composite structure. The most general approach to description of charge transport in conducting polymeric composites in relation to the content of conducting particles is provided by the percolation theory. Simple models of the ordering of globular particles in the resistor network in the non-conducting matrix [10,11] revealed that conductivity σ of the percolating system

depends on the concentration of conducting elements v as a power law

$$\sigma = \sigma_0(v - v_c)^t \quad (1)$$

where v_c is the critical volume fraction (percolation threshold) meaning a minimal volume fraction of conducting filler at which a continuous conducting chain of macroscopic length appears in the system. When the concentration of the filler is large (above percolation threshold), the material exhibits graphitic conductivity, indicating that the conduction network is continuous. The critical exponent t expresses the rate of conductivity change depending on the conducting component concentration and σ_0 is conductivity of the conducting phase. It is clear that under these conditions an increase in conductivity of several orders of magnitude at the percolation threshold results in an extremely high sensitivity of this quantity to the particle content.

This study is focused on the electrical behaviour of composites of short carbon fibres (SCF) in the matrix of polyester resin, where a very low percolation limit has

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been reported [3,12]. Special attention is paid to elucidation of the conductivity–temperature dependence in the percolation region.

2. Experimental

2.1. Polymer matrix

A polyester resin (ChS Polyester 109) prepared by mixing the monomer with 1 wt.% of ChS accelerator IV and 3 wt.% of A-initiator XXII was used as a matrix. All components are products of Sindat Plzeň Co. Ltd., Czech Republic.

2.2. Carbon fibres

As a conductive filler, SCF of average diameter 7 μm and length 3 mm, density 1.76 g cm^{-3} , DC conductivity 21 S cm^{-1} (Bestfight, HTA-7-12.000, Toho Rayon Japan) were used. The fibres as received were mixed with 95 wt.% of NaCl crystals (average size 135 μm) and crushed in a mixer at room temperature. Then NaCl was dissolved at 90 $^{\circ}\text{C}$ in water and fibres were separated. Distribution of their length, was evaluated statistically using an image analyser software, corresponding to the logarithmic–normal function with the highest number fraction of fibre lengths in the range 100–150 μm , as was described in a previous paper [12].

2.3. Sample preparation

The polyester resin, accelerator, initiator and carbon fibres were mixed and 10 sets of five composite samples with dimensions 10 \times 10 \times 5 mm with the fibre content ranging from 0 to 6.3 vol% were prepared by cast moulding between two parallel copper electrodes 30 \times 10 \times 1 mm. Then the polyester resin was cured at room temperature for 24 h.

2.4. Conductivity measurement

A Keithley 617 programmable electrometer was used as a source of stabilized DC power. DC conductivity σ was calculated from the current passing through the samples at the field strength $E = 20 \text{ V cm}^{-1}$.

3. Results and discussion

3.1. Conductivity–fibre content dependence

The average values of conductivity σ of five composite samples with an equal filler content at laboratory temperature (26 $^{\circ}\text{C}$) are given in Table 1. A steep conductivity increase at a relatively low concentration of SCF

Table 1
Conductivity of composite materials

v (vol%)	$\sigma = (\bar{\sigma} \pm \delta\bar{\sigma})$ (S cm^{-1})
0	$(4.09 \pm 0.00) \times 10^{-12}$
0.70	$(1.38 \pm 0.34) \times 10^{-11}$
0.77	$(1.41 \pm 1.51) \times 10^{-7}$
0.84	$(1.26 \pm 1.43) \times 10^{-6}$
0.91	$(2.38 \pm 1.15) \times 10^{-6}$
0.98	$(4.43 \pm 1.67) \times 10^{-6}$
1.05	$(3.70 \pm 1.03) \times 10^{-6}$
1.75	$(3.73 \pm 0.88) \times 10^{-6}$
2.10	$(1.11 \pm 0.24) \times 10^{-5}$
2.80	$(4.19 \pm 0.47) \times 10^{-5}$
3.85	$(2.42 \pm 0.05) \times 10^{-4}$
4.20	$(1.24 \pm 0.03) \times 10^{-4}$
4.55	$(1.71 \pm 0.02) \times 10^{-3}$
4.90	$(8.75 \pm 0.02) \times 10^{-3}$
5.25	$(2.64 \pm 0.03) \times 10^{-2}$
5.60	$(7.58 \pm 0.02) \times 10^{-2}$
6.00	$(1.32 \pm 0.00) \times 10^{-1}$
6.30	$(2.13 \pm 0.00) \times 10^{-1}$

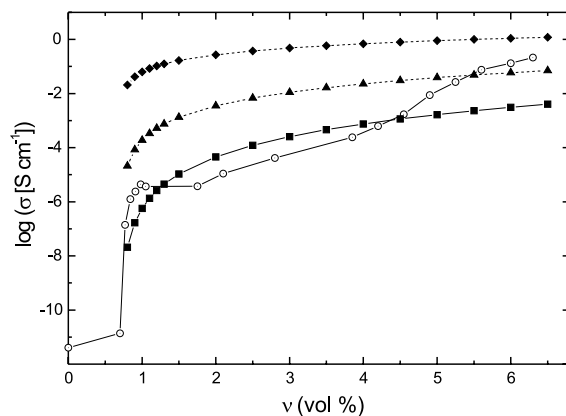


Fig. 1. The dependence of electrical conductivity σ of the composite on the SCF volume fraction, v . Experimental results (\odot), theoretical dependencies calculated according to the Eq. (1) for $\sigma_0 = 21 \text{ S cm}^{-1}$, $v_c = 0.7 \times 10^{-2}$ and $t = 1$ (\blacklozenge), 2 (\blacktriangle) and 3 (\blacksquare).

(≈ 0.7 vol%) appeared (Fig. 1). Only a little higher value of critical concentration (0.9 vol%) has been reported for a composite of carbon fibres (length 1 mm, diameter 8 μm) in epoxy resin [3]. This behaviour is caused by a special mechanism in the formation of intrinsic fibrous structure of the composite. Already at small fibre contents, first contacts arise and the conductivity mechanism changes from tunnelling or hopping of charges between separated fibres to graphitic conductivity of continuous conducting network consisting of fibre chains of macroscopic length.

A great scatter of the results at the percolation threshold (Fig. 2) can be explained by a great fluctuation

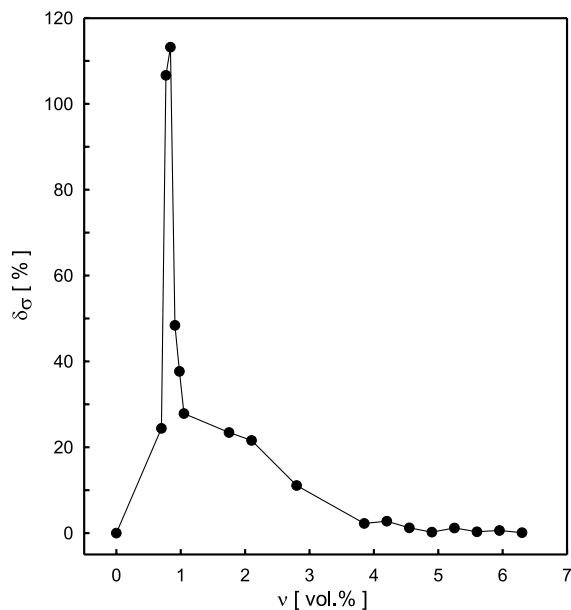


Fig. 2. Dependence of the relative deviation of electrical conductivity $\delta\sigma$ on the SCF content v in the composite.

in the composite structure due to various possible arrangements of SCF in this region. In addition, due to a steep conductivity dependence on the fibre content, a small error in the weighed amount of the filler in composite preparation may cause a great error in composite conductivity.

Theoretical values of critical exponent t calculated for systems of conductive spherical particles in non-conducting polymer matrix lie between 1 and 2 [10,11, 13–18]. The highest experimental value found for composites of a fibrous filler was about 3 [3]. Fig. 1 demonstrates that the shape of our experimental conductivity–fibre content dependence above the percolation threshold distinctly differs from the theoretical S-shaped curves calculated according to Eq. (1) for the critical concentration $v_c = 0.7 \times 10^{-2}$ and three selected critical exponents $t = 1, 2$ and 3. While the theoretical conductivities with increasing fibre content continuously tend to the limit value 21×0.993^t , the experimental dependence after a sudden turn at SCF concentration about 1.75 vol% only irregularly increases. This discrepancy may be explained by different building mechanisms of a conducting network with short fibres or globular particles in the region above percolation threshold.

3.2. Temperature dependence of conductivity and switching effect

Fig. 3 shows that the temperature dependence of conductivity of composite samples in the percolation

region is also significantly influenced by fluctuations in composite structure. In the case of 0.7 vol% of carbon fibres (the lower boundary of the percolation region), the conductivity–temperature dependences for a set of all the five samples with the same fibre content increase nearly linearly (Fig. 3a), which suggests the semiconducting character of the composites, whose conductivity is controlled by tunnelling or hopping of charges between fibres through interlayer of a non-conducting polyester resin.

At 0.77 and 0.84 vol% of carbon fibres (Fig. 3b and c), in the five studied samples with the same filler concentration, the semiconducting character of the composite remained in two of them, while in the three samples a switching effect [12,19] appeared. In this case the initial conductivity (at 26 °C) was much higher than in the previous case, with increasing temperature it slowly decreased at first, between 40 and 60 °C it fell down more than six orders of magnitude and then increased up to the maximum temperature used.

Clearly, this behaviour is due to thermal expansion of the matrix, which causes an increase in the distances between carbon fibres and their disconnection. Starting from the laboratory temperature, the number of fibre contacts only gradually diminished and, as a result, a slight decrease in conductivity occurred. In contrast, however, at a certain critical temperature, interruption of the last conductive paths through a sample caused a sudden drop in conductivity (switching effect). Then, as the particles in the composite are fully separated, the semiconducting character of the composite prevailed and a slight increase in conductivity with temperature is controlled by a charge transport between fibres through non-conducting polymer barriers.

For composites with 0.91 vol% of SCF (Fig. 3d), the switching behaviour was not observed just for one of five samples and at 0.98 and 1.05 vol% of the filler (Fig. 3e and f), the switching effect in all five composite samples occurred. With increasing fibre content in the composites (Fig. 3g), the scatter of results decreased, the critical temperature shifted to higher values and the drop in conductivity diminished.

4. Conclusion

Our results demonstrate that in the polyester resin composites filled with SCF strong fluctuations in structure in the percolation area arise. This leads to a rather atypical course of the conductivity–fibre content dependence above the percolation threshold, which cannot be described by theoretical equation for composites of globular particles. A great scatter of results in the percolation area also significantly influences the occurrence of switching effect during heating of

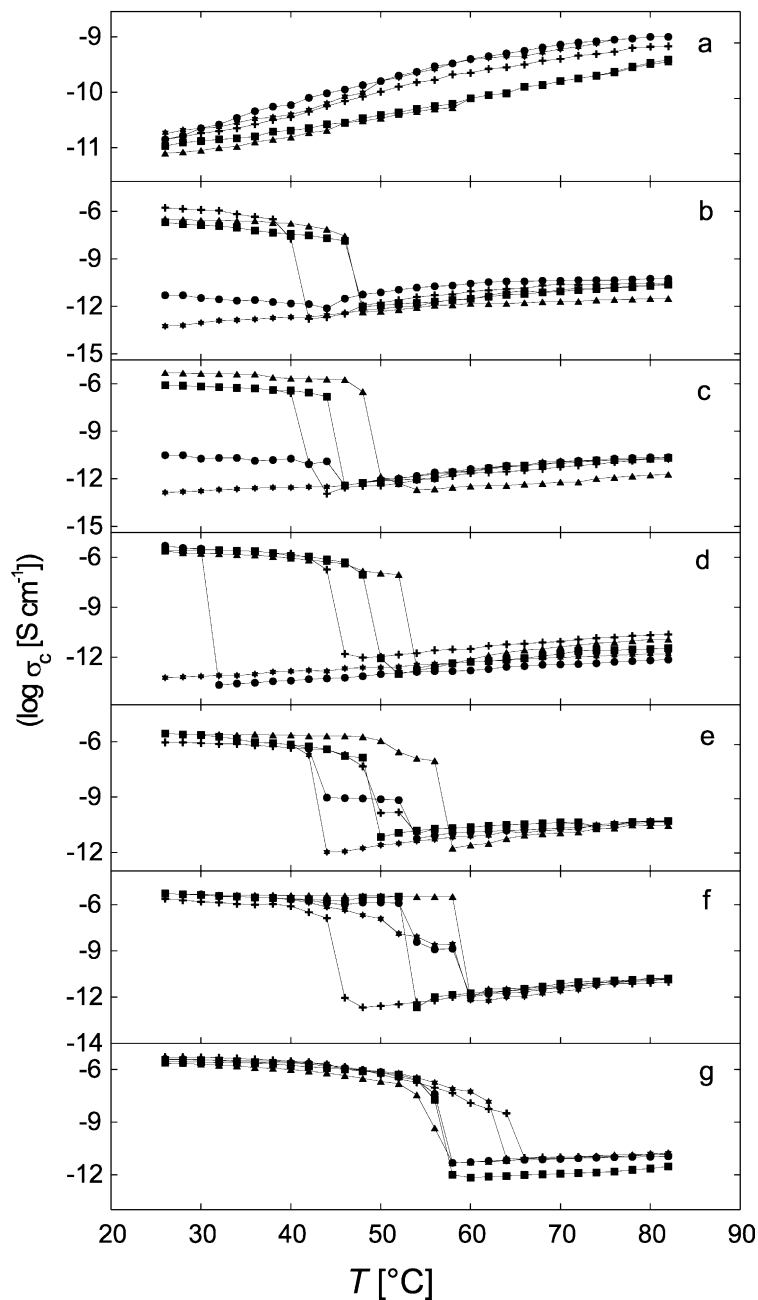


Fig. 3. Dependence of the electrical conductivity σ on temperature T . The content of SCF in the composites (vol%): (a) 0.7, (b) 0.77, (c) 0.84, (d) 0.91, (e) 0.98, (f) 1.05, (g) 2.1.

composite samples. It is clear that to prepare a sample of polymer composites with definite conductivity properties under these conditions is especially difficult and from the point of view of technology the percolation region should be considered as a forbidden area.

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