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Effect of carbon black concentration on electrical conductivity of epoxy resin–carbon black–silica nanocomposites

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Abstract This work presents an insight into the conductivity-carbon black (CB) concentration relationship of nanocomposites. High conductivity is observed above 14% CB loading (% on mass of epoxy resin), indicating the generation of conductive networks throughout the nanocomposites. Observation of the relationship between the natural logarithm of conductivity values versus CB loading shows a remarkable increase in conductivity when the CB loading increases from 19 to 24%. In this region (percolation) a relatively small increase in CB loading produces a large increase in conductivity. When the quantity of CB is low (<14%), the resistivity of the nanocomposite is only slightly different from that of the base polymer; further increase in CB loading beyond the critical concentration region (>24%) causes marginal change in conductivity. The uniformity of the nanocomposites is evidenced by both microstructure (Si-mapping) and macro-property (resistance versus distance relationship) analyses.

Introduction

Carbon black (CB) is virtually pure elemental carbon that is produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons. Current worldwide production is about 6.8 million tonnes per year; approximately 90% of CB is used in rubber applications, 9% as a pigment, and the remaining 1% as an essential ingredient in diverse applications [1]. CB is widely used as a reinforcing agent in rubber products to improve the physical and mechanical properties of systems; addition of CB can increase hardness, modulus, tensile and tear strength, and fatigue and wear resistance of unfilled rubber [2, 3]. Carbon black is used in plastics to provide ultraviolet (UV) resistance because CB can absorb the UV radiation and act as a free-radical acceptor to inactivate the active intermediate species formed in the degradation process [4–7]. Introduction of CB causes modification to the rheology of suspensions, which is influenced by the affinity between CB, the liquid vehicle, and other fillers [8–11]. Due to its excellent pigment properties, CB is employed in the manufacture of printing inks, coloured plastics, fibres, lacquers, nanocomposites and papers [12]. In addition, CB has been adopted as an additive in batteries to improve the service properties [13, 14].

More recently, by incorporating CB into insulating polymers, various ranges of conductive composites have been obtained. Conductive polymer composites are used in different applications such as electronic equipment [15, 16], important strategic materials such as electromagnetic interference shielding [17], and in dissipation of static electricity [18]. Conductive composites have also been used for the manufacture of stress and bending sensors [19, 20]. The level of conductivity depends upon loading level and dispersion degree of CB apart from polymer-CB interactions, and physicochemical characteristics of the CB. However, the situation is so complicated that it can only be determined experimentally [21, 22]. Moreover, most of these publications are limited to the CB filled individual polymer or polymer blends. Very few efforts

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have been made to investigate the electrical properties of a system with other solid additives.

Although silica is an insulator in nature, it does impose significant effect on electrical behaviour of nanocomposites [23]. In other work [24], when varying the concentration of silica in epoxy resin–CB–silica nanocomposites, we have established that the electrical properties of these materials are determined by the conductive paths of CB influenced by ‘networks’ of silica. With increasing content of silica, CB particles are optimally dispersed, contributing to the generation of a conductive network between CB particles via direct particle contact and tunnelling effect. Resistivity of the nanocomposite decreases abruptly with increasing ratio of silica to CB, then decreases gradually and reaches a plateau around a ratio of 0.6:1.0 (SiO_2:CB). Further increase in silica content results in an increase in resistivity. The work described herein explores the effect of varying the CB concentration on conductivity for epoxy resin–CB–silica nanocomposites systems.

Experimental

Materials

Carbon black (Vulcan-P Fluffy) and Silica (EH5) were kindly supplied by Cabot Corporation. Transparency films (CG3460) were obtained from Hewlett Packard. Ethyleneglycol-*n*-butylether acetate, glycidyl end-capped poly (bisphenol A-co-epichlorohydrin), isophoron diisocyanate, and all general purpose chemicals were obtained from Sigma-Aldrich.

Measurement of particle size

Particle size and distribution of CB and silica powder were measured by Coulter N4 MD sub-micron particle analyzer; results are shown in Fig. 1.

Preparation of nanocomposites

About 5.5 g epoxy resin was mixed with CB (33% w/w) and silica in 10–40 cm^3 (depending upon solids content) 2-butoxyethylacetate, 5.56 cm^3 isophorone diisocyanate was added and the mixture stirred for 2 h and then rolled in a bead mill for 10 h. The resulting dispersion was applied as a 60-µm layer onto transparency film using a No. 6 K-bar control coater. The nanocomposites were cured for 3 min at 100 °C, then for 3 min at 150 °C. All the nanocomposites were aged for 24 h in ambient conditions before testing, in order to release residual thermal stress.

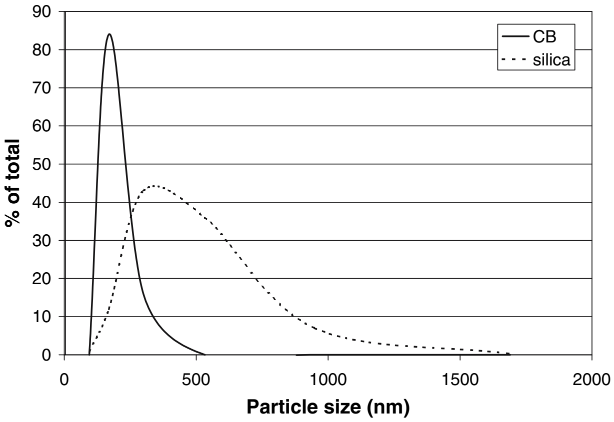

Fig. 1 Particle size distribution of CB and silica as supplied

Electrical measurements

100 × 12 mm (approx.) strips of the cured nanocomposite were cut; exact width and thickness of strips was measured using a Mitutoyo micrometer (0.001 mm), while the length was measured using slip gauges (Coventry Gauge & Tool Co. Ltd., M-88). Resistance (*R*) was measured using a digital multimeter (Robin, AR 6002) at ambient temperature and resistivity (ρ) calculated according to Eq. (1) [18]; *L* is length, *A* is cross-sectional area:

$$R = \frac{\rho L}{A} \tag{1}$$

Conductivity is the reciprocal of resistivity and is arithmetically equal to $1/\rho$.

Morphological properties

Morphology of nanocomposite was examined using a scanning electron microscope (SEM, LEO 1530 FEGSEM, LEO Electron Microscope Ltd., England).

Si-mapping technology

The distribution of elemental Si in the nanocomposites was measured by Scanning Electron Microscopy (SEM, JEOL JSM820, Japan) and Energy Microanalysis Dispersive X-ray mapping (EDX, Rontec GmbH, Edwin System, K German).

Results and discussion

Effect of CB content on conductivity

It was observed that electrical conductivity of the nanocomposites is highly dependent on CB concentration. Plots of resistivity (Fig. 2) and the natural logarithm of conductivity values (Fig. 3) versus % CB content (% on mass of epoxy resin) clearly show the effect of conductive CB loading on the volume resistivity and conductivity of the nanocomposites, respectively. The electrical resistivity of the same nanocomposites with 4 and 9% CB was investigated, the resistance of these nanocomposites (with dimensions of about 90 × 12 × 0.02 mm) was over 2,000 MΩ, which was over the measurement scale of multimeter used and consequently no accurate data are included. However, there appears to be little evidence of conductivity for nanocomposites containing 4–9% CB in comparison with the insulating polymer alone when no CB is present. There is a definite transition in the conductivity of the nanocomposites from an insulating matrix below 14% CB to a conducting one above 14% CB. Observation of the ln plot shows a steep increase in conductivity within the range 19–24% CB and within this concentration range the nanocomposites have semiconducting properties, shifting to highly conducting materials above 24% CB. When the CB content is increased from 24% to 33% the conductivity of nanocomposite only increases slightly.

At low levels of CB loading the conductive particles are insulated by the polymer and silica particles and are isolated from each other; the nanocomposite conductivity is nearly equal to that of the epoxy resin polymer alone. As can be seen in SEM images (Fig. 4) there are many 'islands' of CB particles that exist in the nanocomposite surrounded by insulating polymer matrix and silica particles. Incorporation of conductive CB in the insulating polymer matrix increases the conductivity of the system; as the CB loading increases, mutual contact between CB aggregates occurs to an increasing extent and a sharp increase in conductivity is observed at a certain critical concentration defined as the percolation limit [25, 26]. Here this can be seen to be in the region 19–24% CB (as indicated on Fig. 3), where a relatively small increase in CB loading produces a large increase in conductivity. SEM images in this region (Fig. 4c) show that there are more 'islands' in the nanocomposites and consequently the relative distances between CB particles and aggregates are reduced dramatically, some even have direct contact, which facilitates electron transfer, giving rise to high conduction. When the distances between particles are within several nanometres the effect, with respect to conduction, it is equivalent to direct particle contact as the electrons can easily jump over such small distances according to the electrical field radiation theory; this is known as electron tunnelling. When conductive paths are formed throughout the nanocomposite it affects a sharp increase in conductivity.

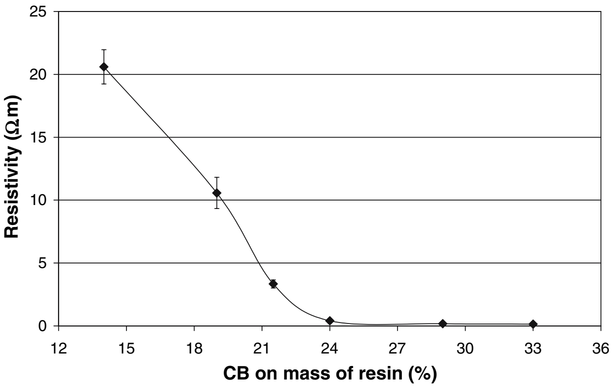

Fig. 2 Effect of %CB content on resistivity of epoxy resin–CB–silica nanocomposites. Error bars calculated ± standard deviation of 10 repetitions

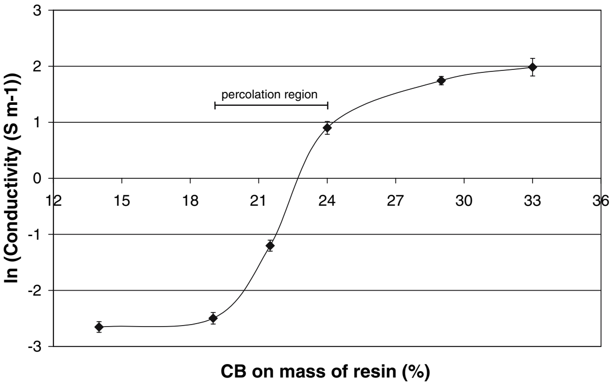

Fig. 3 Effect of %CB content on conductivity of epoxy resin–CB–silica nanocomposites. Percolation region indicated. Error bars calculated ± standard deviation of 10 repetitions

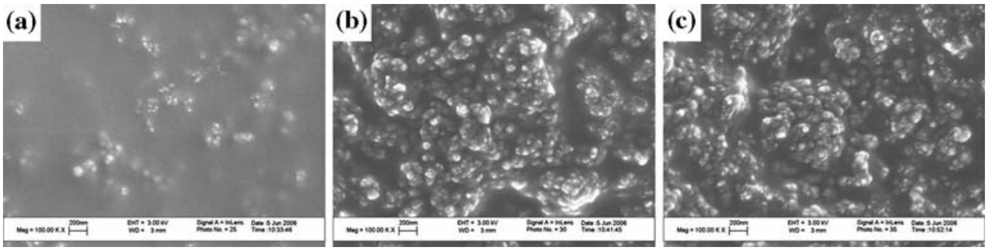

Fig. 4 SEM images of nanocomposites: (**a**) 9% CB; (**b**) 14% CB; (**c**) 21.5% CB. Scale bar = 200 nm

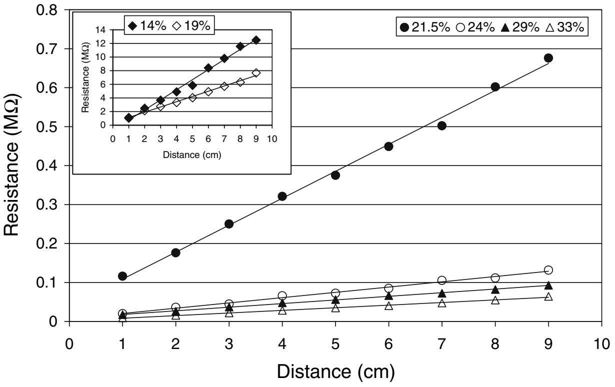

Fig. 5 Effect of distance of contact separation on resistance for different %CB concentrations

Beyond the critical concentration, the rate of increase in conductivity with increasing CB concentration occurs at a much slower rate, because in this region the increase in CB concentration simply signifies an increase in the number of networks formed. The phenomenon is analogous to a continuous conducting wire (constituting an interconnecting chain) which is formed throughout the insulating matrix at the critical concentration, and further increase in concentration of the conducting species simply increases the diameter of that conducting wire. Obviously the nanocomposites exhibit CB content dependence on conduction, though the change in volume conductivity with composition does not exhibit a simple linear additive characteristic. The percolation threshold and drastic increase in volume conductivity exists where the concentration of the CB becomes sufficient to provide continuous electrical networks through the polymer matrix.

Uniformity of the film

One key issue in the manufacture of nanocomposites is ensuring homogeneity. Herein, the uniformity of the nanocomposites was addressed from both a macroscopic and microscopic standpoint. Uniformity was first assessed by investigation into variation of macro electrical resistance with varying distance between contact points. The relationship between resistance and distance for different CB concentrations is shown in Fig. 5 and correlation data for straight-line linear regression shown in Table 1. It is observed that all correlation coefficients and R^2 values are over 0.99, which indicates the resistance of nanocomposites is linearly dependent on distance and consequently implies a very high reliability of homogeneity in the nanocomposites.

Macroscopic determination of homogeneity was achieved through analysis of the distribution of silica in the nanocomposites by Si-mapping, as shown in Fig. 6. It is observed that the silicon dioxide was homogeneously distributed in the nanocomposites for all the samples analysed. Based on the experimental findings stated above, we believe the nanocomposites prepared are homogenous in the distribution of CB and silica throughout the host epoxy resin polymer matrix.

Table 1 Linear regression trend line equations for Fig. 5

CB content (%)	Equations of trend line[a]	R^2	Correlation coefficient
14.0	$R = 1.4808d – 0.7197$	0.9908	0.9954
19.0	$R = 0.7695d + 0.3725$	0.9918	0.9959
21.5	$R = 0.0692d + 0.0394$	0.9966	0.9983
24.0	$R = 0.0136d + 0.0069$	0.9919	0.9960
29.0	$R = 0.0093d + 0.0087$	0.9974	0.9987
33.0	$R = 0.0067d + 0.0017$	0.9963	0.9981

[a] R = resistance (MΩ); d = distance (cm)

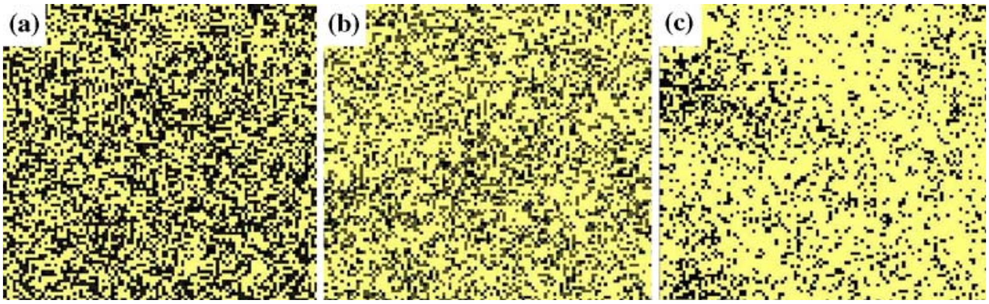

Fig. 6 Si-mapping of epoxy resin–CB–silica nanocomposites: (**a**) 9% CB; (**b**) 14% CB; (**c**) 21.5% CB. Magnified 1000×. Light areas show presence of Si

Conclusions

Conductivity of the epoxy resin–CB–silica nanocomposites arises from electron transfer between CB particles and aggregates incorporated in the host polymer matrix and separated by silica particles. At low concentrations of CB, when a continuous conductive network is not formed, the conductivity of the system depends mainly on the conductivity of the base polymer but, at higher concentrations conductive networks are formed and the conductivity of the nanocomposite mainly depends on the conductivity of CB particles. Conductivity as a function of CB content shows an S-shaped dependency with three regions: non-conducting; semiconducting; and conducting. Nanocomposites with low CB content are almost nonconductive, however, at a critical concentration of CB (>14%), conductivity is observed. The conducting elements of these paths either make physical contact or are separated by very small distances across which electrons can transfer by the tunnelling effect. A percolation threshold is seen between 19 and 24% CB, wherein a slight increase in CB concentration affects a large increase in conductivity. Increasing the CB content above the percolation threshold (>24%) allows the composites to refine their conducting paths and establish network redundancies that raise the conductive cross-section of the material and lower the volume resistivity gradually, but no sharp increase in conductivity is observed.

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