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ORIGINAL CONTRIBUTION

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Dispersion of carbon black in a continuous phase: Electrical, rheological, and morphological studies

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Abstract This work investigates the dispersion of carbon black (CB) aggregates into various polymeric matrices to increase electric conductivity. The effect of matrix viscosity on CB morphology and, consequently, on the blend conductivity was thoroughly addressed. The electric conductivity increases from 10^{-9} to 10^{-4} when less than 3% CB aggregates were dispersed into the PDMS liquid of various viscosities. The CB threshold loading was found to increase from 1% to 3% as the viscosity rose from 10 cp to 60 000 cp. This finding shows that an ideal loading with CB aggregates is far below that (generally 15%) of a typical pelletized CB loading. Moreover, the microscope and RV tests reveal that CB aggregates diffuse and form an agglomerate-network when the conductivity threshold is reached in a low-viscosity matrix. However, a CB aggregate-network was observed when the threshold value was attained in a high-viscosity matrix. These two mechanisms can be distinguished at approximately 1000 cp. Finally, experimental observation shows that the increase of viscosity during curing does not influence the conductivity of the composite while the CB aggregates dispersed in a thermoset matrix. The minimum viscosity during curing, however, was found to be critical to CB dispersion morphology and, consequently, to ultimate electric conductivity.

Keywords Electric conductivity · Matrix viscosity · Aggregate-network · Agglomerate-network · Conductivity threshold

Introduction

The electric conductivity of an insulating polymer can be increased when it is compounded with conductive fillers such as copper powders, silver powders, and carbon black powders. The improvement obtained with metal powders is insignificant because the metal particles are too large to create sufficient contacts. Among all the available fillers, carbon black (CB) is the most effective one [1, 2, 3, 4, 5, 6, 7, 8, 9].

Carbon black is formed by combusting heavy oils in a furnace. The carbon condenses in droplets, called prime particles. The prime particles coalesce into aggregates. Aggregates composed of few prime particles compactly fuse to form low-structure blacks; those of many prime particles can generate high-structure blacks with considerable branches. For a given mass of CB aggregates, a high-structure black usually presents a greater surface area for electron conduction than does a low-structure black. However, once the structure is built, typical hydrodynamic shear forces cannot deform it. This paper uses the term "fluffy" to denote high-structure CB aggregates that exhibit good conductivity. In certain situations, aggregates can cluster into large groups, bound by Van der Waals forces, called agglomerates. Agglomerates are typically

10–100 μm in size and can be broken by hydrodynamic forces.

Compounding plastic with conductive fluffy CB can increase the conductivity by five to six orders of magnitude. Such an application was commercialized over twenty years ago and has been widely employed in antistatic or filtration fields. Conductive blends can be prepared in several ways. The most popular method is to compound CB pellets (about 1–2 mm in size) into a polymeric matrix, using a banbury mixer or twin-screw extruder [10, 11, 12, 13, 14, 15, 16, 17, 18]. However, most related studies have focused on improving bulk properties, such as electric conductivity or mechanical properties of the blends, as the CB agglomerates were dispersed into the polymeric matrix by intensive shearing. Scientists generally agree that for a given weight of carbon black, finer agglomerates enable more particles to be evenly distributed in a fixed volume of plastic. Thus, smaller interparticular distances can be achieved and, consequently, electrons can be transferred from particle to particle throughout the matrix. Accordingly, a system that includes all its CB particles in fluffy form, with the size of aggregate, may be in its optimal condition for electron conductivity. However, the impact of matrix properties, such as viscosity and the degree of crosslinking, on the aggregate dispersion and, consequently, on the blend's conductivity have not been extensively examined.

This work focuses on the dispersion of conductive fluffy CB in PDMS (poly-dimethyl siloxane) liquid of various viscosities. The dispersion morphology was related to the electric conductivity of the blend. The effects of crosslinking of the polymeric matrix on the CB dispersion and on the conductivity of the thermoset composite were also examined. This study aims to yield further insight into the relationship between CB dispersion and the resulting conductivity in a fixed, thermoplastic system over a range of viscosities and a thermoset system. Results in this study can be applied to assess the ideal compounding ratio of CB aggregates in a given polymeric system. Moreover, the discrepancy between the feeding ratio of an ideal and that of a real system, into which CB is compounded, is reasonably explained.

Experimental procedures

Fluffy carbon black (CB) was used as a conductive filler: Vulcan XC72, supplied by Cabot, had aggregate density of 1.8 g/cm^3, a surface area of 254 m^2/g (N_2), and a plasticizer absorption value, DBP (dibutyl phthalate), of 188 ml/100 g. Various grades of poly(dimethyl siloxane) (PDMS, 99.6% purity) from Dow Cornig, with viscosities from 10 cp to 60 000 cp were used as suspending media for the fluffy CB powders. Uncrosslinked silicon rubber (RTV-573, Rhodorsil) with a crosslinking agent (60R, Rhodorsil) was used as another CB suspension medium with a structure similar to that of PDMS but that was curable at room temperature.

In the experiment with PDMS as the medium, fluffy CB was poured into a PDMS matrix in a high-shear ball miller. The volume fraction of the CB aggregates in the suspension ranged from 1% to 4.5% and each sample was sheared within 36 h for perfect dispersion. An optical microscope (Nikon AFX-DX) was employed to observe particle distribution following dispersion. Transmission micrographs were obtained using a mounted camera. A tiny amount of suspension (4–5 μl) was dropped onto a glass slide and phoyographs of random locations were taken. The viscosity was measured in a DV-III cone and plate rheometer (Brookfield) for low viscosity blends (1–10^5 cp), and in a SR-5 parallel plate rheometer for high viscosity blends ($>10^4$ cp). The electric conductivity was measured using a RT-1000 multimeter (Marlborough), on a cell with two inserted, 1×1×0.05 cm^3 metal electrodes, separated by 3 cm.

In the experiments with CB epoxy composite, DER-331 (Diglycidyl ether of bisphenol A; Dow Chemical) combined with curing agent HN-2200 (cycloaliphatic anhydride, Hitachi) were used as a suspending medium. The fluffy CB was separately dispersed into DER-331 and HN-2200 matrices, following the milling procedure mentioned above. The well-dispersed samples were mixed in the ratio 5:4 (DER-331: HN-2200) and the rheology test to monitor curing and the conductivity test following post-cure were then performed. The morphology of the CB-filled composites was examined by optical microscopy mentioned above. Thin sections (1 μm) were prepared using a MT 990 microtome (RMC).

Results and discussion

Figure 1 illustrates the dependence of the electric conductivity, in (Ω-cm)$^{-1}$, on the volume fraction of CB powders for various PDMS viscosities. Figure 1 reveals that, for a low viscosity PDMS (10 cp), the conductivity increases sharply with CB loading. The conductivity then becomes saturated at conductivity around 10^{-4} and changes insignificantly when the CB loading is further increased. Figure 1 reveals two notable phenomena. First, the saturation points increase with the viscosity of PDMS, contradicting the prediction of percolation

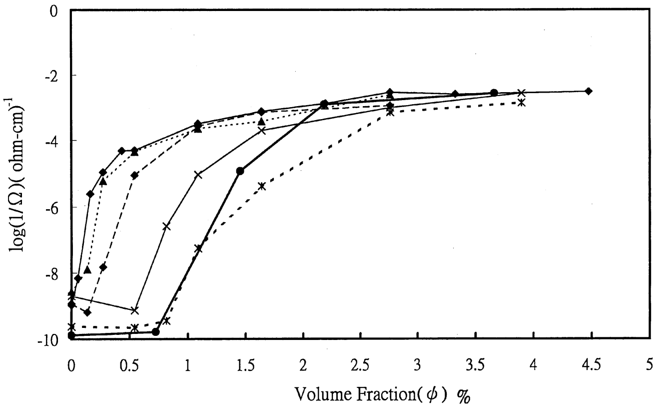

Fig. 1 Dependence of the electrical conductivity on the volume fraction of carbon black dispersed in PDMS liquids with various viscosities. *Diamonds on solid line* 10 cp, *triangles* 100 cp, *diamonds on dotted line* 500 cp, *crosses* 1000 cp, *asterix* 60 000 cp, *circles* silicon rubber

theory in which a fixed 3-D array is assumed and conductivity is thus independent of the viscosity. Secondly, although a high viscosity liquid was applied- 60 000 cp PDMS, similar to a real polymeric molten stage, the saturation point only increased to approximately 3%, which is far below that of a typical pelletized CB loading (generally 15%). The discrepancy is discussed in detail later.

Close observation of the CB aggregate distribution reveals an interesting phenomenon. Figures 2a and b are a series of photographs to illustrate the CB aggregate distribution. Figure 2a shows that, at low PDMS viscosity (500 cp), the CB aggregates diffuse and form loosely structured agglomerates. The increase in CB loading enlarges the agglomerates and, eventually, a conducting network is constructed. The conductivity increases abruptly once this network is formed (from Fig. 2a.2 to a.3); the CB threshold loading can thus be determined. However, for a highly viscous PDMS (60 000 cp), the aggregate diffusion slows down significantly and the structured agglomerates are no longer formed. The conducting network depends on the connection of each individual aggregate. Figure 2b displays a sequence of pictures that demonstrate evenly distributed fluffy CB. The light transmission decreases as the CB loading increases. The aggregate-network can hardly be recognized since the CB aggregate is too tiny to be distinguished individually under the optical microscope. However, the threshold value can still be determined from the abrupt increase in conductivity (Fig. 2b.2 to b.3). Notably, the definition of threshold loading herein is the CB loading that increases the conductivity up to 10^{-4} $(\Omega\text{-cm})^{-1}$ magnitude.

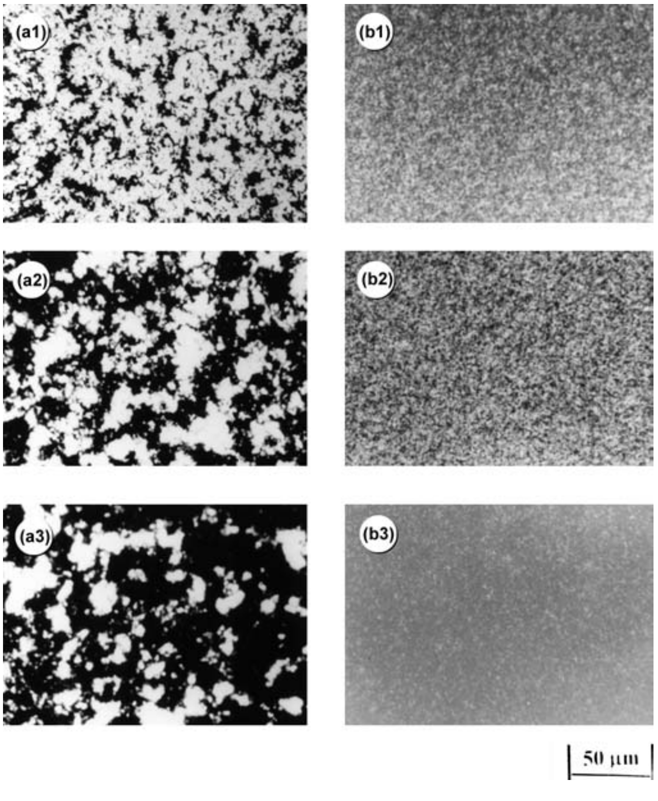

Fig. 2a, b Optical micrographs for carbon black aggregates dispersed in PDMS liquids. Dispersion of 0.13%, 0.27%, and 0.54% carbon black by volume into 500 cp PDMS are shown in **a**.1 to **a**.3. The correspondent conductivities are 6.36×10^{-10}, 1.50×10^{-8}, and 9.04×10^{-6} $(\Omega\text{-cm})^{-1}$, respectively. In contrast, dispersion of 0.81%, 1.09%, and 1.64% carbon black by volume into 60 000 cp PDMS are shown in **b**.1 to **b**.3. The correspondent conductivities are 3.56×10^{-10}, 5.63×10^{-8}, and 4.21×10^{-6} $(\Omega\text{-cm})^{-1}$, respectively

Percolation was developed in 1970 to describe the lattice distribution in a matrix. The percolation threshold is the concentration at which an infinite network appears in an infinite lattice. The observations presented here can be interestingly compared to the theoretical results. For a simple cubic lattice, the percolation threshold is around 31%. However, for a hypercubic lattice for which d equals 7, the threshold value is only 8.3% [19]. This result indicates that a more complex lattice geometry supports a smaller percolation threshold. Our experimental work gives a CB threshold of about or below 3%. This result is close to the empirical percolation threshold, 6%, provided by Rejon et al. [20]. Since the CB dispersion lattice consists of either structured aggregates or complex agglomerates, both are believed to form a network much easily and result in a smaller threshold than does any simple geometry lattice. In short, although the geometry of the CB particles is too complex to be predicted by percolation theory, the trend predicted by that theory fits the observation presented here.

Figure 3 shows the dependence of relative viscosity (RV) on CB loading. Adding rigid particles to a liquid alters the flow field. This hydrodynamic disturbance, first theoretically described by Einstein, leads to an

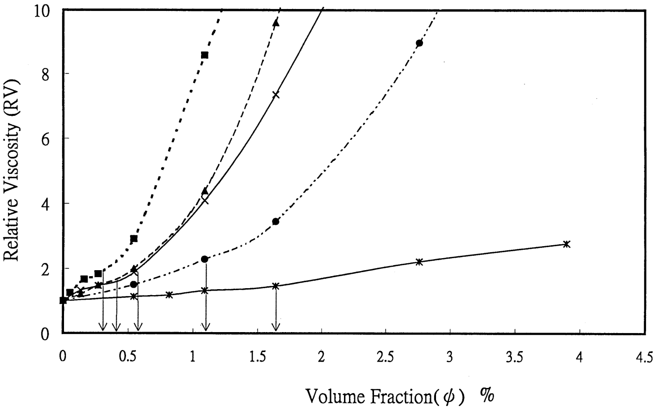

Fig. 3 Dependence of relative viscosity (RV) on the volume fraction of carbon black dispersed in PDMS liquids with various viscosities. *Squares* 10 cp, *triangles* 100 cp, *crosses* 500 cp, *circles* 1000 cp, *asterix* 60 000 cp

increase in viscosity because of the cutting of the flow pattern and the rotation of particle. At very low concentrations, the relative viscosity is linearly proportional to the particle loading. The coefficient of proportionality depends on the shape of the particle. For example, Einstein predicted that the coefficient should be 2.5 for spherical particles. R. Simha and others have generalized Einstein's work for particles with other shapes [21]. Some experimental work has also been performed to examine the viscosity behaviors due to the dispersion of tobacco virus particles or other asymmetric particles. All studies show that the asymmetry of the particle markedly increases the coefficient of proportionality. Restated, the coefficient greatly exceeds 2.5 for a dilute dispersion of asymmetric particles. Figure 3 reveals that for suspensions of CB aggregates, each curve in its dilute region is linear and its slope increases as the viscosity decreases. Figure 4 explains this finding. The figure clearly shows that huge agglomerates composed of CB aggregates can be easily formed at viscosity below 1000 cp. The probability of "collision followed by agglomeration" is increased by the fast diffusion of fluffy CB induced by a low viscosity liquid. In contrast, CB diffusion is suppressed as the viscosity of matrix increases and the CB agglomerates shrink to yield eventually the aggregate dispersion shown in Fig. 4f. A larger CB agglomerate is more complex and asymmetric, therefore, increasing the coefficient of the RV proportionality in the dilute region (see Fig. 3).

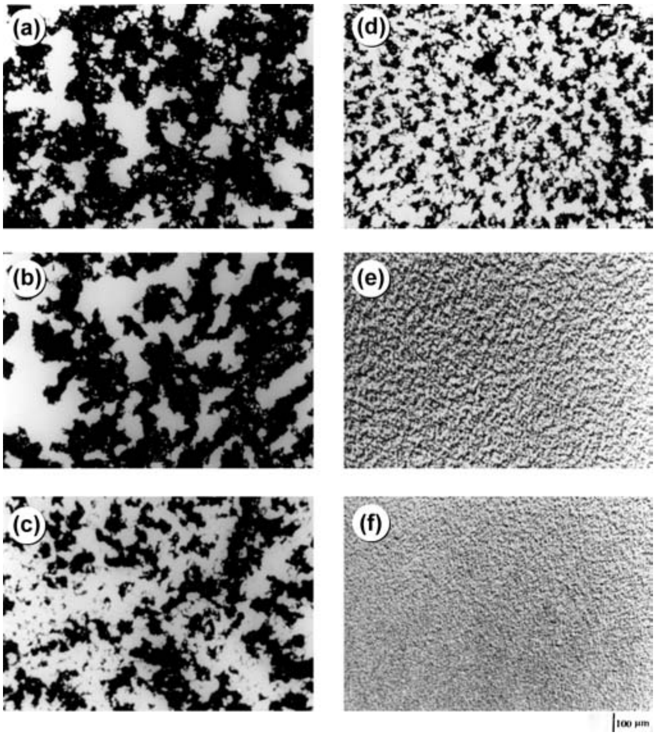

Fig. 4a–f Optical micrographs for 0.43% volume fraction of carbon black dispersed in PDMS liquids with various viscosities: (**a**) 10 cp (**b**) 100 cp (**c**) 500 cp (**d**) 1000 cp (**e**) 10 000 cp (**f**) 60 000 cp

Neither the Einstein nor the Simha theory can effectively describe high-concentration dispersion. At high concentrations, viscosity can be increased by more than an order of magnitude when the particle interaction becomes extreme. Unfortunately, theories for such materials are less developed and can be extremely complex. The sharp increase of RV is generally considered to follow from the interaction between particles. However, the average distance between two CB agglomerates, which begin to interact with each other, is similar to the average distance between which an electron can be easily transferred. Both distances are believed to be in the order of a nanometer. Accordingly, the deviation point of RV under CB loading must be similar to the threshold value of electric conductivity under CB loading. Figure 5 shows the dependence of the RV deviation point and the threshold conductivity on PDMS viscosity. As expected, these two curves match very closely. This result verified the above hypothesis that an agglomerate-network or an aggregate-network is formed; that is, the interaction among particles starts to become important when the threshold value of CB loading is reached.

Notably, the two mechanisms, previously discussed in relation to Figs. 2a and b- the agglomerate-network and aggregate-network-can be clearly distinguished at the threshold value of 1000 cp, as shown in Fig. 5. The structured agglomerate-network caused by particle diffusion dominates conductivity in liquids with a viscosity under 1000 cp. The aggregate-network, however, dominates conductivity in liquids with a viscosity over 1000 cp. This result is consistent with Fig. 4. In practice, a typical compounding process from 10^4 cp to 10^6 cp is far above 1000 cp. Therefore, the conductivity mechanism for a real polymer compounding is highly

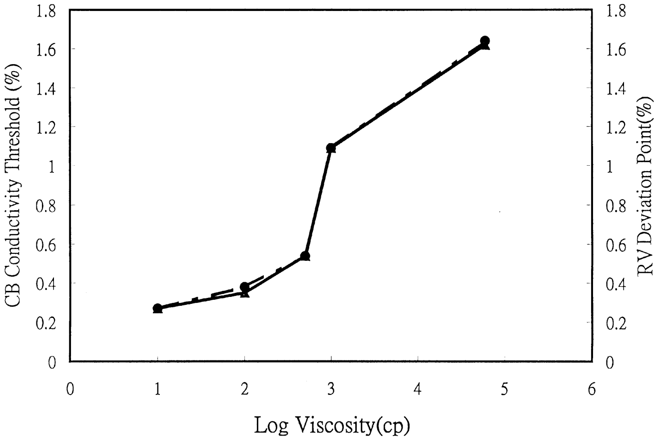

Fig. 5 Dependence of the RV deviation point and threshold conductivity on PDMS viscosity. *Triangles* CB conductivity threshold, *circles* RV deviation point

associated with the "aggregate-network" model. Ensuring a perfect "aggregate dispersion" in a polymer matrix thus becomes very important. However, the bulk density of CB aggregate is known to be one twelfth of that of a typical polymer pellet. This extremely low ratio makes the direct compounding of CB aggregate impossible. Compounding with pelletized CB, which has much higher bulk density than CB aggregate, has thus become very popular. Consequently, today's polymer industry is focussed on shearing the pelletized CB into CB aggregates by extensive mixing. In practice, a realistic loading of CB powders is about 15% [22, 23, 24], far beyond the saturation point of 3% seen in Fig. 1. This result implies that most of the pelletized CB dispersed in a polymer matrix is not in the aggregate form. Either the pelletizing formulation or the compounding process must be improved to achieve an effective dispersion of CB aggregate [25, 26, 27].

An experiment involving silicon rubber, which has a structure similar to that of PDMS but a viscosity that varied in time, was performed to further investigate the impact of viscosity on electric conductivity. The conductivity was monitored as the curing progressed (see Fig. 6). The conductivity remained at the initial value independently of the increase of viscosity. This result suggests that once the agglomerate network is established in the low-viscosity suspension, the increase of the viscosity due to curing only functioned to embed the structure. Accordingly, the lowest viscosity in the curing process governs the conductivity of a CB thermoset system.

Fluffy CB was dispersed in an epoxy system following two curing processes- high temperature and room temperature- to further confirm the thermoset effect [28, 29]. In high-temperature curing, the viscosity dropped first because of the temperature effect [30]. It then rose dramatically due to fast crosslinking. In contrast, in room-temperature curing, the viscosity slowly increased because of light crosslinking. The viscosity then rose sharply as the temperature finally rose to 50 °C (see Fig. 7). Notably, the drop in viscosity was not observed for the sample precured at room temperature. Figure 8 shows that curing at high temperature yields higher conductivity than does curing at room temperature. Figure 9 displays the microtone of both systems and clearly shows that the high temperature sample possesses a superior structured agglomerate-network. Figures 8 and 9 show that better conductivity follows the fall in viscosity that induces the formation of superior network. Again, the epoxy results confirm the above claim that the minimum viscosity in the curing process governs the conductivity of a CB thermoset system.

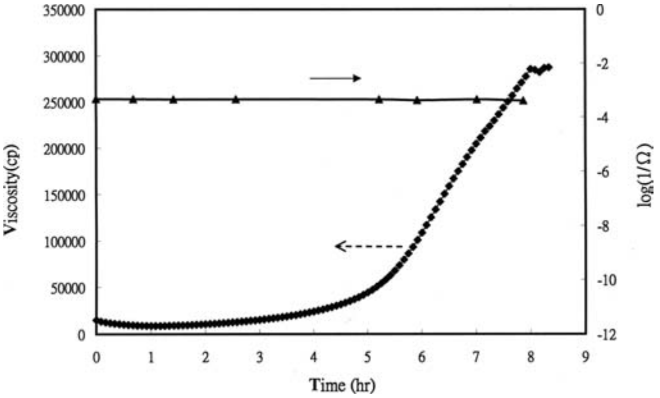

Fig. 6 Conductivity was monitored as the curing of silicon rubber progressed

Conclusion

In this study, carbon black (CB) aggregates were dispersed into various polymeric matrices. The effect of matrix viscosity on CB morphology, and thus on the

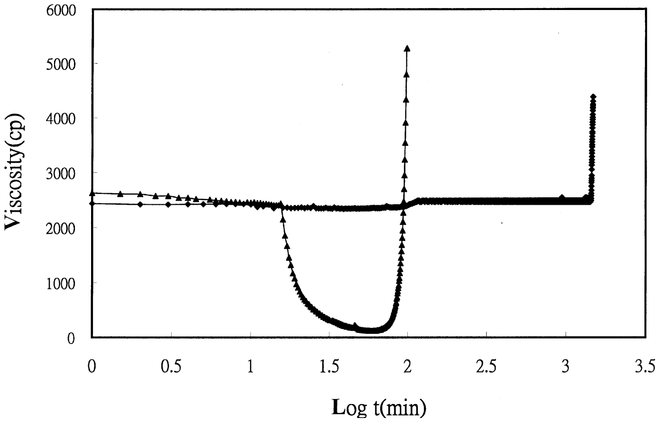

Fig. 7 Fluffy carbon black dispersed in an epoxy system following two curing processes. *Triangles* high temperature (90 °C cure); *circles* low temperature (25 °C precure, then 50 °C cure)

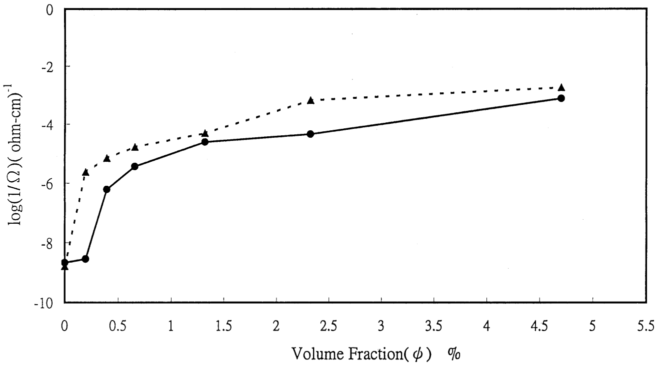

Fig. 8 Dependence of electrical conductivity on the volume fraction of carbon black dispersed in epoxy matrices via different curing processes. *Triangles* high-temperature curing; *diamonds* low-temperature curing

composite conductivity, was comprehensively examined. The results yield the following conclusions:

1. Electric conductivity increases from 10^{-9} to 10^{-4} when less than 3% CB aggregates were dispersed into the PDMS liquids of various viscosities. The CB threshold loading was found to rise from 1% to 3% as the viscosity increased from10 cp to 60 000 cp. This finding shows that an ideal loading with CB aggregates is far below that (generally 15%) of a typical pelletized CB loading.
2. The microscope and the RV tests reveal that CB aggregates diffuse and form an agglomerate-network when the conductivity threshold is reached in a low-viscosity matrix. However, a CB aggregate-network was observed when the threshold value was reached in a high-viscosity matrix. These two mechanisms could be distinguished at about 1000 cp.
3. When the CB aggregates have dispersed in a thermoset matrix, the increase in viscosity during curing does not influence the conductivity of the composite. The lowest viscosity in the curing process, however, was critical for CB dispersion morphology and, consequently, for ultimate electric conductivity.

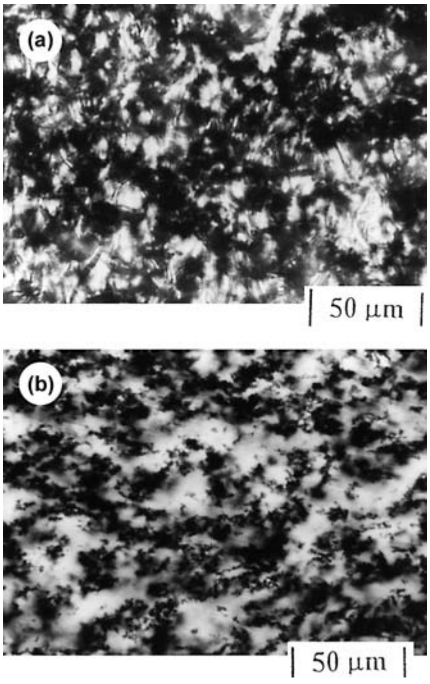

Fig. 9a, b Optical microscopy micrographs of 0.66% volume fraction of carbon black dispersed in epoxy matrices via (**a**) high temperature curing (**b**) low temperature curing as described in Fig. 7. The yielding conductivities for (**a**) and (**b**) are 1.67×10^{-5} and 3.65×10^{-6} $(\Omega\text{-cm})^{-1}$, respectively

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