

Electrically Conductive Thermosetting Resins Containing Low Concentrations of Carbon Black

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ABSTRACT: A cured vinyl ester resin containing electrically conductive carbon black (CB) particles shows electrical percolation at very low CB concentration (<0.5 phr). CB particles have a strong tendency to agglomerate in a low-viscosity resin, such as vinyl ester, unsaturated polyester resin, and epoxy resins. The agglomeration process in the low-viscosity vinyl ester resin generates electrically conductive paths already in the resin's liquid state, which undergo partial fixation by room temperature curing and full fixation by hot postcuring. The fully cured castings containing CB concentrations above percolation are characterized by a constant, temperature-independent conductivity, over a wide temperature range. The current-voltage relationships of the cured vinyl ester/CB castings obey a power-law dependency. The presence of the continuous CB paths in the vinyl ester casting is clearly observed in fracture surfaces formed at 100°C.
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Key words: conductive plastics; vinyl ester; carbon black

INTRODUCTION

Thermosetting polyester/carbon black (CB) castings exhibit an unusual phenomenon of insulator-conductor transition at extremely low CB concentrations.¹ Interestingly, a similar phenomenon is found in thermosetting epoxy/CB castings.² In both cases, the insulator-conductor transition occurs at CB concentrations well below 1% v/v, actually even < 0.5% v/v. In both cases, the CB is added to relatively low-viscosity resins, compared with the addition to highly viscous thermoplastic melts. The structuring of the CB particles is more likely to occur in such low-viscosity-crosslinkable resins if a sufficient clustering time is provided. Moreover, the epoxy and polyester resins are reactive; therefore, the crosslinking reactions take place in the presence of the CB particles. Thus,

chemical linking between carbon particles to the network of the thermosetting matrix is much more likely to occur, compared to thermoplastic matrices where mainly physical bonding is expected. According to Jachym,¹ the conductivity of pure polyester decreases with the reaction progression, whereas the same polyester with CB shows an opposite effect. The electric conductivity of pure CB, pure polyester, and polyester/CB mixtures below the percolation concentration all rise with temperature, whereas polyester/CB castings (above the percolation concentration) show conductivity decrease with a rising temperature.³ The same source excludes the possibility of forming conducting paths resulting from the directly touching CB particles and emphasizes the importance of bond formation between the carbon particles and the polyester resin. The latter, described as conducting bonds between the particles and polyester molecules, is further studied by showing a correlation between ESR spectrum and electrical conductivity of the resin as a function of

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Table I Gelation and Heat Release in the Vinyl Ester/Carbon Black Castings

Initiator (phr)	Accelerator (phr)	Carbon Black Type/Conc.	Gelation Time (min)	Remarks
0.5	0.2	EC/0.3phr	—	No gelation
1.0	0.1	EC/0.3phr	155	—
1.2	0	EC/0.3phr	—	No gelation
1.2	0.2	EC/0.3phr	80	—
1.25	0.22	EC/0.3phr	75	—
2.0	0.3	EC/0.3phr	73	—
3.0	0.48	EC/0.3phr	13	Sample warms up

polymerization temperature and accelerator concentration.⁴ Polyester/silver powder castings showed a percolation concentration of 2% v/v and were described as systems where current is conducted via discrete paths.⁵ Polyester/CB castings percolated at 0.2% w/w and the conductivity was found to decrease linearly with temperature.⁶ These authors modeled their systems as nonhomogeneous dispersions of CB particles surrounding large insulator regions. The application of alternating electric field during gelation of liquid polyester/CB systems results in much higher conductivities and lower percolation concentrations.⁷ Microgelation in cured polyester resins was studied as a function of the resin composition. Microgel formation has a great effect on the reaction kinetics.⁸ Low percolation thresholds, < 0.5% v/v CB, were found in epoxy/CB castings. The threshold was further reduced to 0.06% v/v by applying

concepts based on colloid science, where conductive networks were formed via agglomeration.² The present article describes the electrical behavior of vinyl ester resins containing low CB concentrations.

EXPERIMENTAL

Vinyl ester containing 45% styrene (Derakane 411-45, Dow Chemicals, Midland, MI) was cured with 2 phr methyl ethyl ketone peroxide (MEKP) and 0.3 phr cobalt naphthenate. CB EC-300 (1000 m²/g) was supplied by Akzo, Netherlands. Details on the curing and postcuring conditions are given in the discussion. The cured samples were coated with nickel paint to eliminate the contact resistance effect. Fracture surfaces for SEM analysis prepared at liquid nitrogen temperature were gold-sputtered. Some samples were fractured at 100°C.

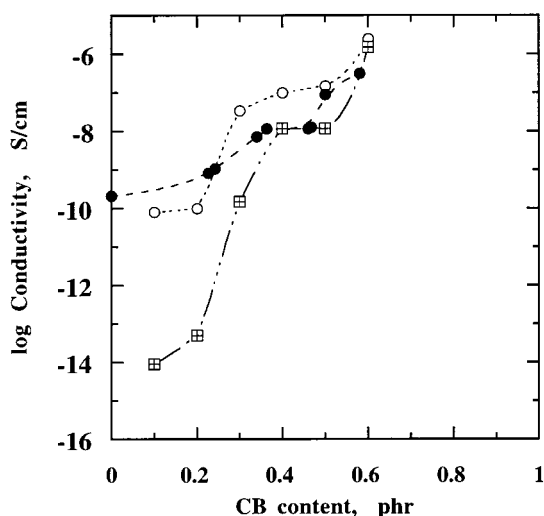


Figure 1 Conductivity versus EC black content: ●, liquid resin, ○, 24 h room-temperature curing, ◻, 30 days room-temperature curing.

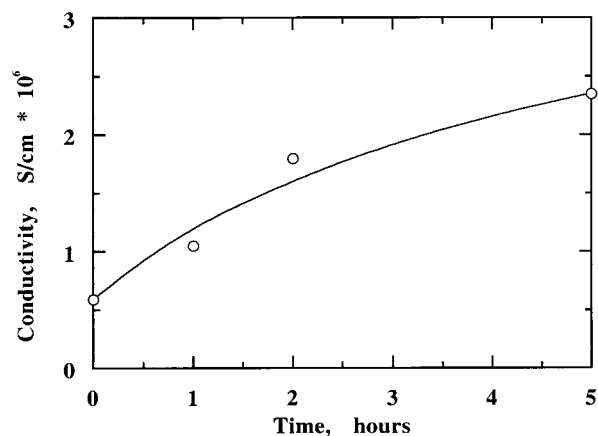


Figure 2 Effect of postcuring at 60°C on conductivity as a function of the postcuring time. Vinyl ester/EC black, 0.6 phr.

Table II The Effect of Gelation Time on the Conductivity of the Cured Castings

Gelation Time (min)	Conductivity (ohm cm) ⁻¹
15	2.7×10^{-9}
70	5.9×10^{-6}
100	2.8×10^{-6}

Vinyl ester/EC black, 0.6 phr.

RESULTS AND DISCUSSION

Preliminary studies focused on the gelation behavior of vinyl ester resin containing EC black, as shown in Table I. It will be shown later that the

gelation time has a significant effect on the conductivity of the resulting castings. Figure 1 shows the dependence of conductivity on EC black concentration in the liquid state before curing, 24 h after room temperature curing and also 1 month after room temperature curing. Below percolation (ca. ~ 0.3 phr EC black), the 24 h cured specimens show somewhat lower conductivities than their liquid vinyl ester/CB counterparts. Agglomeration structuring (clustering) already took place in the liquid resin. Moreover, the 24 h cured samples, with CB concentrations above percolation, exhibit conductivities higher than the liquid vinyl ester/CB uncured samples, resulting from further structuring in the system undergoing curing presumably associated with the microgelation pro-

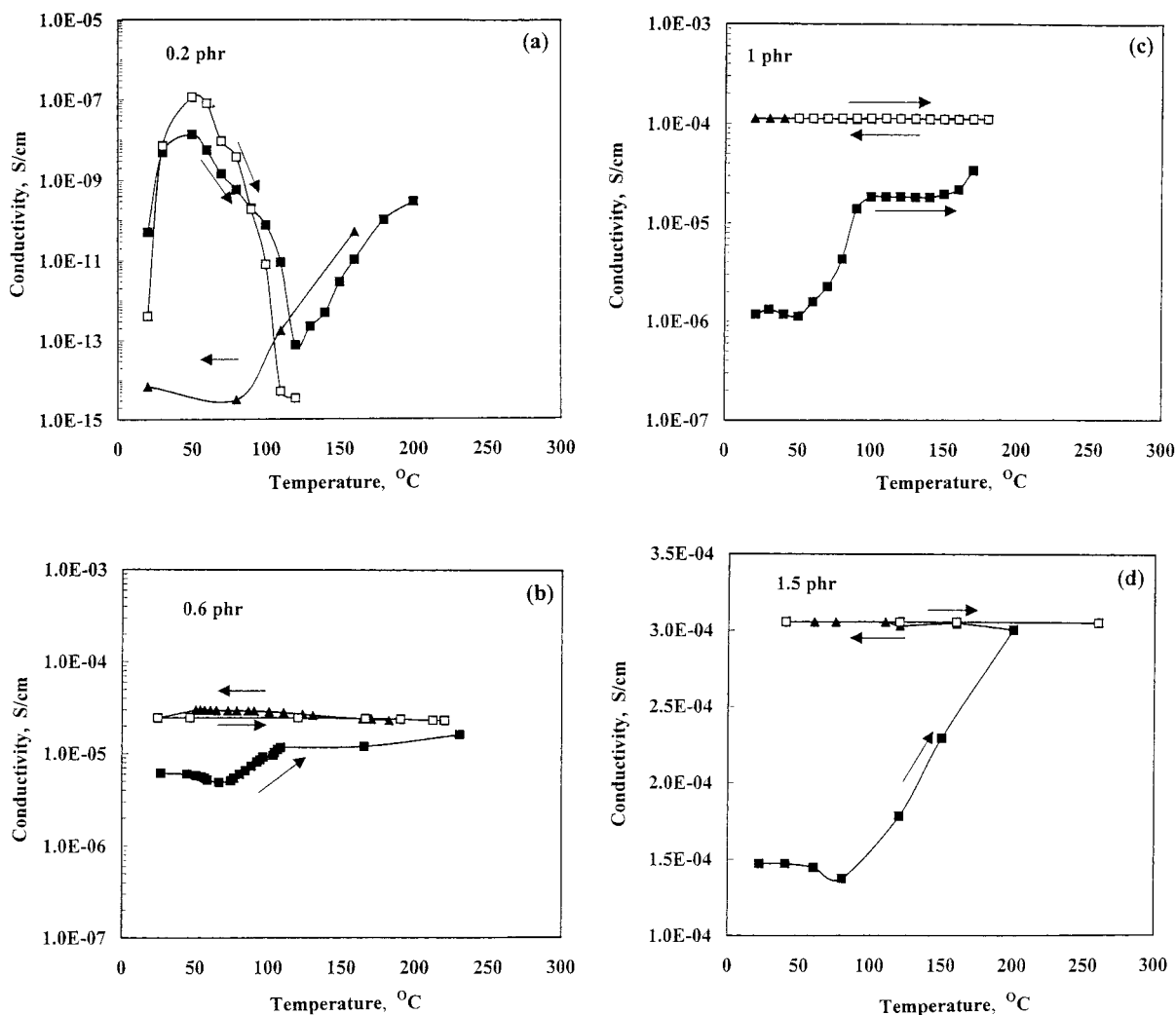


Figure 3 Conductivity-temperature cycles of vinyl ester containing: (a) 0.2, (b) 0.6, (c) 1.0, (d) 1.5 phr EC black. ■, Heating, 1st run; ▲, cooling; □, heating, 2nd run.

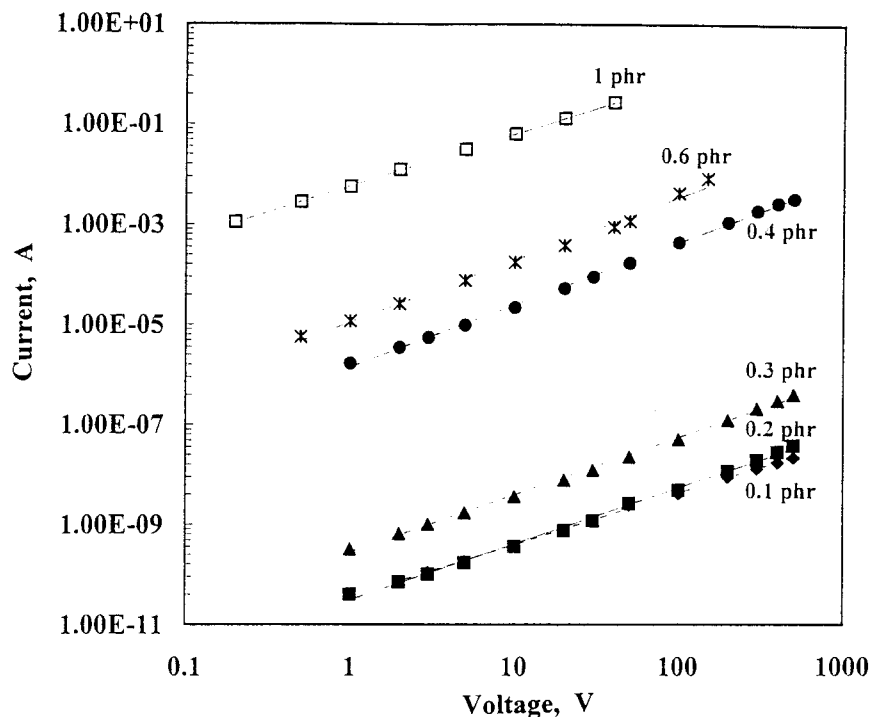


Figure 4 Current–voltage behavior of vinyl ester castings containing various EC black contents.

cess. This conductivity increase is large since the pure resin undergoes a significant conductivity reduction on crosslinking¹ (i.e., the net conductivity increase is significant). Figure 1 also shows that the 1-month cured castings, especially below percolation, have lower conductivities than the liquid uncured vinyl ester/CB samples. It is assumed that the resin in contact with the CB particles is still not fully cured (longer gel times are noted at the higher EC black concentrations) after 24 h; however, after 1 month, curing is practically completed leading to the further measured conductivity decrease. Postcuring at 60°C of a sample with 0.6 phr CB, well above percolation, has an opposite effect (i.e., conductivity increase with the curing time, as shown in Fig. 2). This behavior may be attributed to the net result of the combination of curing completion and further agglomeration at the elevated postcuring temperature, where the latter dominates. To conclude, at 0.6 phr CB, well above percolation, the conductivities of the three samples (Fig. 1 at 0.6 phr CB) (i.e., the uncured, 24 h, and 1-month room-temperature-cured) are similar; thus, the CB concentration is the dominant parameter. Table II shows the effect of gelation time at room temperature on the resulting conductivity of vinyl ester

castings containing 0.6 phr EC black. It is clearly seen that a short gelation time, 15 min, results in an insulating sample, whereas at the longer gelation times the same compositions are conductive. Recalling that the liquid system (0.6 phr EC) prior to gelation is conductive (Fig. 1) and heats up on curing (Table I), it is likely that on fast gelation and temperature rise some disruption of the conductive networks, existing in the liquid resin, is taking place. Therefore, the curing kinetics has a profound effect on the resulting conductivities of the cured castings.

Figure 3 demonstrates conductivity–temperature diagrams for vinyl ester castings (24 h cured) containing 0.2–1.5 phr CB. The CB percolation concentration, estimated from Figure 1, is about 0.3 phr and, therefore, whereas Figure 3(a) depicts a sample slightly below, or within the beginning of the percolation region, Figure 3(b–d) depicts samples with CB concentrations (0.6–1.5 phr) beyond the percolation zone. Interestingly, these three samples, after the first heating run to about 200°C, become very stable resistors each showing a constant conductivity independent of temperature (room temperature to ca. 200°C) and heating direction (i.e., cooling or heating). The glass transition temperature of the cured resin is

$\sim 100^\circ\text{C}$, manifesting itself only during the first heating run. It has no effect on the conductivity of the fully cured (after the first heating run) samples containing EC black above the percolation concentration. The conductive paths in these samples are thus structurally permanent, insensitive to the volume changes accompanying a temperature change from room temperature to 200°C , which includes the glass transition temperature. The potential practical application of such stable resistors within the resistivity range shown should be further explored. This description does not apply to the sample with 0.2 phr CB [Fig. 3(a)], which is slightly below percolation. After the first heating run, this sample undergoes a dramatic conductivity change from 10^{-7} to 10^{-13} S/cm, corresponding to a temperature rise from 50 to 120°C . This behavior is typical to positive temperature coefficient (PTC) materials,^{10–12} where polymer/CB samples, roughly within the percolation region, show a significant resistivity increase associated with a first or even a second-order transition (i.e., melting or glass transition temperature of the matrix polymer). The quality of conductive paths in samples containing CB concentrations close to percolation is such that they undergo gradual, but significant, structural changes on thermal cycling. The interesting behavior shown in Figure 3(a) will be fully explored in a future study focusing on vinyl ester/CB and polyester/CB systems close to and within the percolation transition. The initial conductivity rise accompanying the first heating run (Fig. 3) is found also by postcuring at 60°C with increasing time, as in Figure 2. The current–voltage relationships shown in Figure 4 depict a roughly similar behavior: $[I] = 0.3 \times 10^{-11} [V]^{1.15}$, for all the samples shown, below and above percolation.

SEM micrographs of freeze-fractured surfaces of a neat vinyl ester casting and of vinyl ester/CB castings (0.3 and 0.6 phr CB) are shown in Figure 5. The neat sample [Fig. 5(a)] depicts a developed freeze-fractured surface, which complicates observation of the CB clusters in the low CB concentration containing sample (0.3 phr CB). Nevertheless, the formation of a segregated nonuniform distribution of CB particles, which actually undergoes agglomeration/clustering during the room temperature curing, can be seen in Figure 5(c) (0.6 phr CB). Further studies aiming at developing different fracturing conditions, which may lead to a better observation of the CB particles' distribution, were done. It was found that the fracturing of neat vinyl ester castings at $\sim 100^\circ\text{C}$

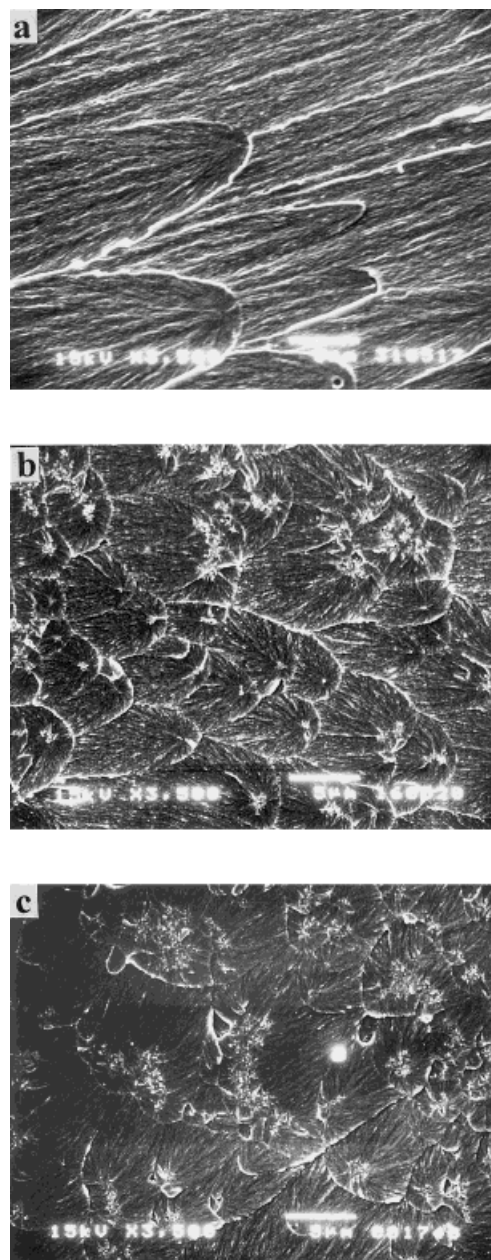


Figure 5 SEM micrographs of freeze-fractured surfaces of vinyl ester cured castings: (a) neat, (b) 0.3, and (c) 0.6 phr EC black.

produced fracture surfaces much smoother than at the liquid nitrogen temperature and thus provided a better background for observation of the CB clusters in the vinyl ester/CB castings. This is shown in Figure 6(a) for a sample containing 0.6 phr CB, where the conductive CB paths are clearly seen. The freeze-fractured surface of the same casting [Fig. 6(b)] is much less informative. Figure 6(a) thus depicts the very significant ag-

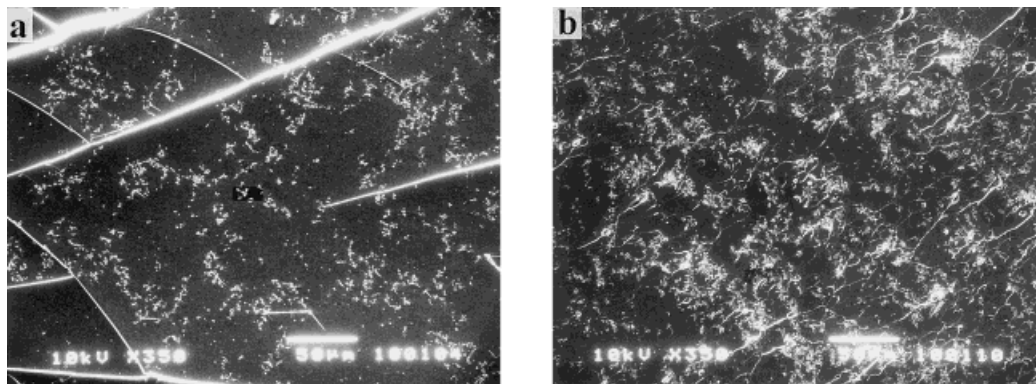


Figure 6 Vinyl ester castings containing 0.6 phr EC black. Fracture surfaces at (a) 100°C, (b) freeze-fractured surface.

glomeration tendency of CB particles distributed within a liquid vinyl ester resin undergoing curing. The process of formation of the conductive networks may be interfered by a too fast curing, a too exothermic curing reaction, too high initial viscosity of the resin, and by the tendency of the specific CB particles used to agglomerate. The different tendency level of CB particles to cluster in various thermoplastic melts undergoing dynamic compounding/processing operations was recently described.¹³ Whereas clustering in such highly viscous molten matrices occurs only under dynamic processing conditions, in the liquid resins, such as vinyl ester, static conditions following a vigorous mixing step are preferred to allow the CB particles to move freely and cluster in the low viscosity resin, without the interference of an external dynamic field. Once the conductive paths have formed in a liquid resin and the recommended curing cycle has elapsed, fixation of the CB conductive network can be performed by a postcuring step, similar to the one used in the present work. The same applies to the other thermosetting/CB systems, such as the ones based on unsaturated polyester, epoxy, and other resins.

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