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Alternating electric field induced agglomeration of carbon black filled resins

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Abstract

This letter reports on our observation that an alternating electric field is able to induce the formation of an electrically conducting network in carbon black (CB) filled resins well below the zero-field percolation threshold. Compared with the recently presented dc method, the ac agglomeration is more efficient in two respects: it proceeds significantly faster under equivalent conditions and is still effective at higher ionic concentration. In contrast to the ramified form of dc-induced CB networks, ac agglomeration favors the formation of parallel CB chains. The experimental results can be explained taking into account ionic conductivities of the matrices as well as charges and field induced dipoles on the CB particles. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon black; Electrically conducting resin; Electrically induced percolation

Carbon black (CB) is widely used as a filler to modify the mechanical, electrical and optical properties of the medium in which it is dispersed. In particular, electrical conductivity can be achieved in isolating polymers by the incorporation of highly structured CB. The dc conductivity of these composite materials is due to the formation of a network of CB particles within the matrix. The conductivity increases sharply at a characteristic particle concentration ϕ_c known as the percolation threshold [1,2]. In the case of resin/CB systems, percolation thresholds as low as 0.2 wt% were found. In this respect, the recently reported $\phi_c = 1.5\%$ for an epoxy resin with amine hardener (hereafter denoted as amine-system (LY556/HY932)) seems to be an exceptionally high value [3–5]. However, a conclusive explanation of this observation was given using a model based on colloid theory. The model assumes charging of the CB particles during the dispersion process and electrostatic stabilization of the epoxy/CB system below a weight fraction of 1.5% CB [6]. Direct evidence for the negative excess charge on CB particles in the amine-system (LY556/HY932) was obtained from microscopic observation of the dc electric field induced agglomeration process. The dendritic growth of the CB network clearly starts at the positive electrode only [4,7]. Coulomb repulsion between CB particles seems to be too strong as to allow for cluster formation in the bulk of the samples. It has been pointed out that the negative excess charges on the CB particles are probably due to chemical reactions between surface groups on the CB particles and the basic polymeric matrix [8]. The dc agglomeration is not successful whenever the ionic conductivity of the resin is too high as was shown for the case of an epoxy resin with anhydride hardener (hereafter referred to as anhydride-system (LY556/HY917)) [9].

The present work reports on the influence of an ac electric field on the agglomeration process in CB/resin systems. For electro-rheological fluids it is well known that particle chain formation can be achieved by ac as well as by dc fields [10,11]. The four different resins investigated here were chosen to cover a large range of ionic conductivities (2×10^{-9}–1.5×10^{-4} S/m) and to vary from acidic to basic behavior. ac and dc agglomeration are compared with respect to the time-dependent development of the CB networks and the geometric form of these networks.

The following resins have been investigated in this study: (1) epoxy resin based on bisphenol-A resin (Araldite LY556, Ciba Geigy) and an aromatic amine hardener (Araldite HY932) (amine-system (LY556/HY932): ratio 100/30), (2) epoxy resin based on bisphenol-A resin and an anhydride hardener (Araldite HY917) (anhydride-system (LY556/HY917): ratio 100/90), (3) reactive thinner (Araldite LY5052, Ciba Geigy), (4) vinylester resin (Derakane 411-C50, Dow Chemical). Acid or amine numbers of these polymers are given together with the ionic conductivities in Table 1. As CB PRINTEX XE2,

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Table 1
Properties of the investigated polymers: acidity/basicity, ionic conductivity, percolation threshold, particle charge and behavior in the dc and the ac case

Polymer	Amine number (AM), acid number (ac) (mg KOH/g substance)	σ_{ion} (S/m)	ϕ_c (wt%)	Particle charge	dc agglomeration			ac agglomeration		
					Network	Geometric form	Formation in bulk	Network	Geometric form	Formation in bulk
LY556, HY932	AM[a]: 480	2×10^{-9}	1.5	Strongly negative	Yes	Ramified	No	Yes	Ramified	No
LY556, HY917	AC[a]: 350	1×10^{-4}	0.2	Positive	No			Yes	Chain like	Yes
LY5052	AM: 130	3×10^{-6}	0.5	Negative	No			Yes	Chain like	Yes
Vinylester resin	Both negligible	7×10^{-7}	0.25	No	Yes	Chain like	Yes	Yes	Chain like	Yes

[a] Only the values of the hardeners are given since they determine the chemical properties of the polymer.

DEGUSSA AG has been used. The CB–epoxy dispersion was stirred with 2000 rpm for 2 h. Then the hardener was added and the dispersion was homogenized again for 15 min with 1000 rpm.

For the optical microscopy glass slides with sputtered palladium strip electrodes and an electrode spacing of 500 μm were used. The network formation was observed with a high resolution VISITRON SYSTEMS digital B/W camera system mounted on a microscope. The time-dependent conductivity during the electric field-induced agglomeration was observed with two parallel brass electrodes which were dipped into the dispersion during the curing.

Since most of the investigations on dc agglomeration were done using the amine-system (LY556/HY932), we start the presentation of our experimental results with a comparison between ac and dc agglomeration for this case. Fig. 1 shows conductivities versus time for a CB content of 1% at three different temperatures and a dc (open symbols) or an ac (1 kHz, filled symbols) electric field of 125 V/cm. The decrease in matrix viscosity with rising temperature eases the formation of CB networks and leads to higher conductivity values of the hardened composite. These final conductivity values do not differ significantly for dc and ac case. However, the times needed for the CB network formation are significantly shorter for the ac case (factor 3 at 50 °C). Time-dependent evolution of the conductivities and final conductivity values of the cured samples are nearly independent of frequency in the range from 100 Hz up to 10 kHz. However, at 1 MHz, the ac agglomeration has slowed down to the dc case.

The CB network formation was observed by in situ optical microscopy. Fig. 2 shows the ac agglomeration of the amine-system (LY556/HY932) filled with 0.1% CB in an electric field of 400 V/cm at 19 and 180 min after starting the process. Narrow dendrites are growing from both electrodes into the dispersion in contrast to the dc case where the growth starts exclusively at the positive electrode

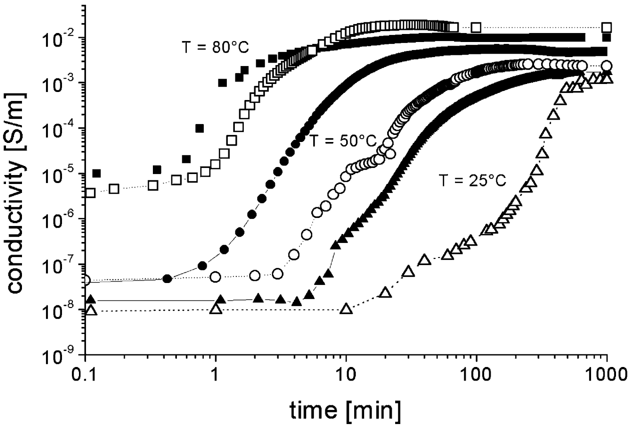

Fig. 1. Time dependence of the dc electrical conductivity of the amine-system (LY556/HY932) filled with 1% CB for an applied electric dc (open symbols) or ac (1 kHz, filled symbols) field strength of 125 V/cm at three curing temperatures (25 °C (△, ▲), 50 °C (○, ●), 80 °C (□, ■)).

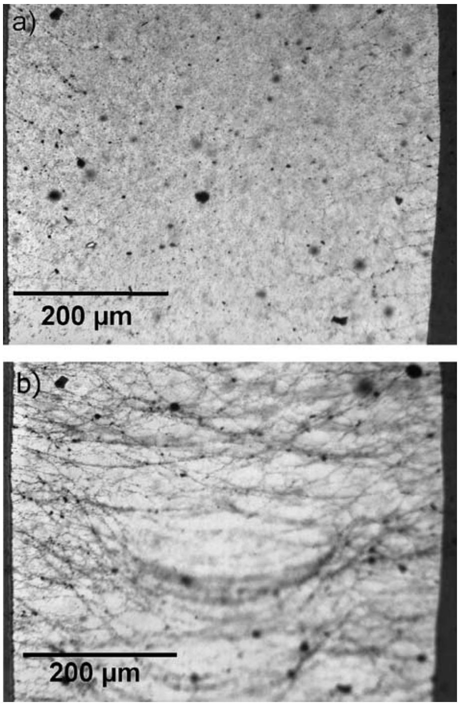

Fig. 2. Transmission optical micrographs of the amine-system (LY556/HY932) taken after 19 and 180 min ($E = 400$ V/cm, $f = 1$ kHz, $T = 25$ °C).

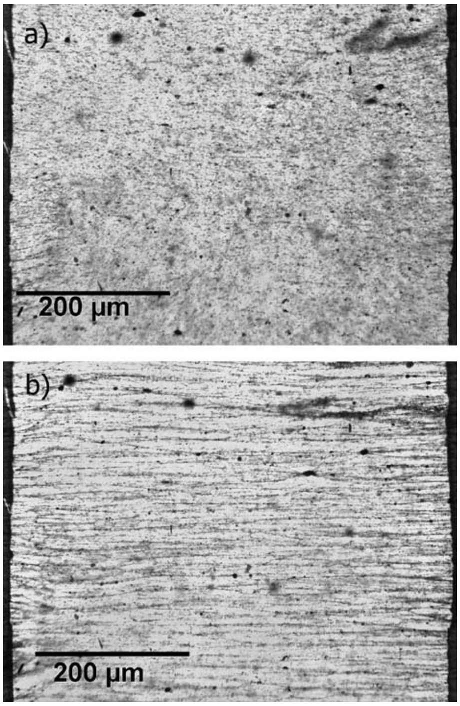

Fig. 3. Transmission optical micrographs taken after 7 and 50 min for the anhydride-system (LY556/HY917) ($E = 400$ V/cm, $f = 1$ kHz, $T = 25$ °C).

[4]. CB cluster growth in the bulk of the sample was not observed. Fig. 2b shows the completed network after 180 min. During the agglomeration, the current increased from 0.2 nA up to 1.2 µA.

In order to observe the influence of acidity/basicity properties and of the ionic conductivity on the electric field induced agglomeration, we alternatively investigated the anhydride-system (LY556/HY917) because of its high acidity and its five decades higher ionic conductivity (see Table 1). For 0.1% CB insulating behavior of the cured specimens indicated that a dc field could not induce a CB agglomeration in this material. At the same time, a small positive excess charge on the CB particles could be proven [8]. On the other hand, ac agglomeration successfully induced a conducting CB network under equivalent conditions. Fig. 3 shows the ac agglomeration of the anhydride-system (LY556/HY917) filled with 0.1% CB by applying an ac electric field of 400 V/cm. After 7 min the appearance of CB clusters and dendrites can be observed not only at both electrodes but also in the bulk of the sample. Fig. 3b shows the network formation after 50 min. This network obviously consists of straight CB chains in strong contrast to the ramified dendrites in the amine-system (LY556/HY932). Although somewhat differing in the chemical behavior (see Table 1) LY5052 behaves similarly to the anhydride-system (LY556/HY917): dc agglomeration is not possible, in the ac case straight chains grow in the bulk of the sample.

The chemically nearly neutral vinylester resin was investigated in dc and ac electric fields of 400 V/cm as an example for a system with uncharged CB particles. In both cases a network formation similar to the anhydride-system (LY556/HY917) was observed for 0.1% CB.

Properties of the matrix materials, zero-field percolation thresholds and experimental results are summarized in Table 1. All observations can be explained satisfactorily by taking into account excess charges and field-induced dipoles on the CB particles as well as the ionic conductivity of the polymer. A central feature of all field-dependent effects is the existence of medium range attractive forces between field-induced dipoles on the CB particles the polarizability of which is based on their conductivity. Additionally, long range Coulomb repulsion between charged CB particles and short range van der Waals attraction have to be considered. In the amine-system (LY556/HY932) the CB particles carry strong negative excess charges and the system has a low ionic conductivity. Thus, in an ac field the dendrites start growing supported by dipole–dipole interaction from the electrodes where the CB particles can discharge. Since both electrodes are involved in the network growth, the agglomeration in an ac field proceeds faster than in the dc case. In the bulk material, no aggregation is visible since the electrostatic repulsion cannot be overcome by the dipole–dipole attraction. If there were no curing restrictions, all particles would be incorporated in the network. On the other hand, the anhydride-system (LY556/HY917) with weakly charged CB particles and a high ionic conductivity shows no dc agglomeration. We suggest that the dc electric field inside the sample is shielded by electric double layers formed by mobile ions at the electrodes. This shielding does not occur in an ac field of sufficient frequency resulting in the observed network formation. Now, the small excess charges cannot prevent cluster formation in the bulk. The behavior of LY5052 can be explained in the same way.

In contrast to the epoxy resins, the chemically neutral vinylester resin produces no excess charge on the CB particles and the ionic conductivity of the matrix is low. Therefore, field-induced agglomeration as well as cluster formation in the bulk occurs in both dc and ac fields.

In conclusion, the application of ac fields allows electrically stimulated agglomeration of CB particles in various polymeric dispersions without special requirements on the ionic concentration or on the amount of excess charges on the particles. Due to its higher effectiveness, the ac field-induced CB agglomeration might also be successful in systems with higher viscosity.

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