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Curing and percolation for carbon black-epoxy-amine nanocomposites

T.H. Wu^a, A. Foyet^{a,1}, A. Kodentsov^a, L.G.J. van der Ven^b, R.A.T.M. van Benthem^{b,c},
G. de With^{a,b,*}

^a Laboratory of Materials and Interface Chemistry, Dept. of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600, MB, Eindhoven, the Netherlands

^b Laboratory of Physical Chemistry, Dept. of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600, MB, Eindhoven, the Netherlands

^c DSM Materials Science Center BV, PO Box 18, 6160, MD, Geleen, the Netherlands

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ABSTRACT

Particle agglomeration in carbon black (CB) filled epoxy (CB-E) and carbon black filled epoxy-amine (CB-EA) nanocomposites with CB concentrations ranging from 0.25 to 1.25 vol% was investigated by performing conductivity measurements as a function of time at 20 °C. For the thermoplastic CB-E samples the change in conductivity was not pronounced, while for the thermosetting CB-EA samples a percolation transition was observed appearing at ≈ 0.2 vol%. The concentration 1.25 vol% was selected for both CB-E and CB-EA samples to perform *in situ* isothermal electrical conductivity measurements at 20, 50, 70, and 100 °C, respectively. At higher temperature, the agglomeration process was faster, resulting in an initially sharp increase of conductivity. Despite the conductivity development of CB-EA samples being faster than that of CB-E samples, they are reaching lower final conductivity values, indicating that cluster aggregation for the CB-EA samples is restricted by polymer gelation, as confirmed by scanning and isothermal differential scanning calorimetry (DSC). Furthermore, thermodynamic DSC studies showed that no particle-particle and particle-polymer chemical reactions occurred during the epoxy-amine curing. However, physical adsorption of the epoxy and amine components on the CB particles is the likely cause for the observed slightly higher amine-epoxy reaction rates in the presence of CB. Particle agglomeration is thereby attributed to be controlled by diffusion-limited cluster aggregation (DLCA). Finally, the microstructures of CB-EA samples after curing were investigated by using TEM. The fractal dimension d_f was determined and showed a smaller value as compared to the universal DLCA value, illustrating the influence of gelation on fractal formation in this system.

1. Introduction

Generally, polymers are electrically insulating materials, having typically a volume resistivity from 10^{12} to $10^{15} \Omega \text{ cm}$ [1]. However, by incorporating conductive particles, polymers can be converted from insulators to (semi)conductors, which can be used in a number of advanced applications such as electromagnetic interference shielding [2,3], sensors [4,5], electrostatic dissipation [6], electrically conductive adhesives [7,8] and, possibly, as an anticorrosive coating material [9].

The insulating-to-conductive transition of these conductive composites is not a gradual one, but characterized by an abrupt increase with several orders of magnitude at a certain particle loading [10–13], where a conductive particle network is formed throughout the

polymeric matrix. This critical concentration is called the percolation threshold. For example, a recent paper describing CB composites for piezo-resistive sensing reports a threshold range of about 8–18% [14]. For proper control of the properties, thermal annealing appeared to be important. In fact, several other papers emphasize the role of thermal annealing [15–17].

Percolation theory has been extensively developed since the early 1970s. The work done, as reviewed by Kirkpatrick and Zallen [18,19], showed that a minimum of 16 vol% particle concentration is required for random percolation. However, for carbon-black (CB) thermosetting systems, many experiments showed a much lower percolation threshold [10,13,20–23]. A basic kinetic theory was developed for non-random dynamic percolation, in which particle-particle interaction is described

* Corresponding author. Laboratory of Materials and Interface Chemistry, Dept. of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600, MB, Eindhoven, the Netherlands.

E-mail address: G.deWith@tue.nl (G. de With).

¹ Present address: Dupont, Grossmatte 4, CH-6014, Luzern, Switzerland.

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by two competitive forces: attractive London-van der Waals forces and repulsive Coulomb forces due to the surface charge of the dispersed particles. Once the repulsive forces are overcome by thermal energy, mechanical stirring or modification of the surface charge, particle agglomeration occurs during which a percolating structure is formed irreversibly [22,24]. Strain applied during processing can break the targeted structure.

Also fractal structures have been taken into account [12,13,23,25]. A fractal is a structure showing self-similarity at various length scales [10,26]. Two models have been well-accepted when referring to the kinetics of fractal aggregation. One is Diffusion-Limited Cluster Aggregation (DLCA), which was first proposed by Witten and Sander [27], and applied by, e.g., Chen et al. for crosslinked epoxy composites filled with intrinsically conductive Phthalocyanine nanocrystals [24]. In this model, fractal clusters attach to each other at the first collision, as Brownian motion easily overcomes any weakly repulsive interactions, building up the percolating network irreversibly. The other model is Reaction-Limited Cluster Aggregation (RLCA) [28], for which it is assumed that the possibility of irreversible aggregation due to first contact of clusters is small: multiple collisions are needed, as the repulsive interactions are more substantial and form an energy barrier which is less easily overcome. Fractal structures are characterized by their fractal dimension d_f which has been used extensively to determine the mechanism of fractal aggregation. For DLCA, the d_f -value has been found to be universally 1.85 ± 0.05 [20,29], while for RLCA $d_f = 2.1 \pm 0.05$ [20,30].

These theories offered a clear picture of dynamic percolation, including the effect of thermal annealing [15–17]. However, the influence of (chemical) reactions in the matrix, that is cross-linking effects, was hardly taken into account. In particular for conductive coatings, using almost inevitably cured systems, the effect of curing is important, as it directly influences filler particle mobility. The present work is aiming to fill this gap, at least partially, by measuring *in situ* the conductivity for non-crosslinking (thermoplastic) CB-epoxy dispersions (CB-E) and crosslinking (thermosetting) CB-epoxy-amine systems (CB-EA), and monitoring the kinetics of the curing reaction for CB-EA samples by differential scanning calorimetry (DSC). Since the epoxy matrix is insulating, particle aggregation can be detected by measuring the electrical conductivity. Hence, conductivity measurements were performed isothermally at various temperatures in order to understand the mechanism of particle agglomeration as well as the influence of cross-linking. To reinforce these results, the fractal structure of a CB-EA sample with a CB concentration above the percolation threshold was investigated by using TEM, and the fractal dimension d_f determined.

2. Experimental

2.1. Preparation of CB-epoxy composite

Carbon black (KEC-600J, AkzoNobel) was ground into a fine powder in a mortar and dried at 50 °C for 5 days under vacuum. Thereafter, a master batch with 2 vol% of CB was prepared by dispersing this powder in a bisphenol A based epoxy resin (Epikote 828, Resolution Nederland BV, Fig. 1a, equivalent weight (eqw) per epoxide group 187 g mol^{-1}) for 8 h at 6000–15000 rpm by using a disk agitator (Dispermat CA40-C1, VMA) until a homogeneous dispersion was obtained. During this process the temperature remained below about 80 °C. No additives were used in the whole process. In order to prepare CB-E samples with CB concentrations ranging from 0.25 to 1.25 vol% with similar CB dispersion characteristics, we diluted aliquots of the CB master batch with the required amounts of the same epoxy resin as used for making the master batch. For each sample, mechanical stirring was performed for 1 min, and thereafter immediately applied on polycarbonate substrates by using a quadruple applicator (Erichsen GmbH & Co. KG). Subsequently, the samples were placed into a temperature-controlled cell (time required about 30 s) to cure them at the various

temperatures, meanwhile performing conductivity measurements (Section 2.2). For the curing samples (CB-EA), a crosslinker (Jeffamine D230, Huntsman, Fig. 1a, average aminohydrogen eqw of 60 g mol^{-1}), was added by keeping the desired CB concentrations (0.25–1.25 vol%) and the epoxy/NH molar ratio at 1.2/1. All these preparation processes were kept in exactly the same order to establish a fair comparison between the CB-E and CB-EA samples.

2.2. *In situ* conductivity measurements

For conductivity measurements the composites casted on polycarbonate substrates were introduced in a curing cell (Fig. 1b) consisting of a brass box for thermal control and equilibration. The cell was set to a fixed temperature, allowed to equilibrate before sample introduction, and kept at constant temperature during curing. Four-point measurements were done using a stage having four gold electrodes with a distance of 0.5 cm mounted on a device that could control the depth in the micrometer range. For bulk measurements the electrodes were placed into the samples until reaching the substrate (sample thickness about 100 μm). Currents ranging from 1 to 7 μA were applied to the sample using a Keithley electrometer 273, the voltage was recorded using a Keithley electrometer model 6517A and the conductivity was calculated from the slope of the current-voltage graph. Measurements were repeated after several time intervals during the curing process. No current was applied to the sample during the delay time. The surface conductivity was measured similarly probing only on the very top surface of the coating. Each measurement was repeated twice and the corresponding error bar is indicated in Fig. 2.

2.3. Image analysis

After curing, the coating/polycarbonate composites were microtomed in order to observe the cross-sectional morphology by transmission electron microscopy (Tecnai, FEI). For the calculation of the fractal dimensions d_f , three images with identical magnification were taken from different locations for each sample.

2.4. Curing kinetics by DSC measurements

2.4.1. Dynamic heating scans

Dynamic runs with constant heating rates were carried out using a DSC (Perkin-Elmer Pyris 1). After sample preparation (Section 2.1), 5–8 mg of each mixture was put in an aluminum DSC pan which was hermetically sealed thereafter. After being put in the DSC chamber and equilibrated for 1 min at 0 °C, the temperature scans started with scanning rates ranging from 2.5 to 25 °C/min, respectively.

2.4.2. Isothermal runs

The sample preparation for the isothermal DSC studies was the same as for the dynamic heating scans. The DSC chamber was preheated to the desired temperature before putting the Al pans in the chamber. Data were recorded after thermal equilibrium was reached. At the end of each run, samples were cooled down to 0 °C rapidly in the DSC chamber. After equilibration at 0 °C for 1 min, a temperate heating scan was performed on the same sample aiming to obtain the residual reaction heat ΔH_R .

3. Results and discussion

3.1. *In situ* conductivity measurements

3.1.1. Variation with CB concentration

The bulk conductivity for CB-E samples, in which no curing occurs, was measured as a function of CB concentration at room temperature for six days, the results of which are shown in Fig. 2a. Immediately after the dispersions were applied on the substrates, the electrical

Fig. 1. (a) Structure of Epikote 828 (Poly(Bisphenol A-diglycidylether)) and Jeffamine D230 (polyoxypropylenediamine) and (b) schematic diagram of the *in situ* conductivity measurement set-up during curing.

conductivity of the CB-E samples showed a clear correlation with the CB concentration. However, the difference between conductivities is rather small and no clear percolation transition is observed. After 4 h, the conductivity value for each sample increased by about 2 orders of magnitude, except for the sample with 1.25 vol% which only showed an increase by about a factor of 5. After 6 days the conductivities did not change anymore and the dispersions reached their equilibrium state. In order to elucidate the mechanism of the conductivity increase, the surface conductivity of the dispersions equilibrated for 6 days was measured. Apart from a slight variation that was observed in the sample with CB 0.25 vol%, the samples displayed surface conductivities identical to their bulk ones, indicating that particle segregation to the surface did not occur. The increase in conductivity can thus be attributed to particle agglomeration that forms long-range conductive pathways in the resin. The agglomeration took place spontaneously after the applied shear force (of the mixing process) was removed, revealing that the CB is thermodynamically prone to aggregation in this epoxy resin, thereby reducing the interfacial energy. However, particle-particle interaction in CB-E samples is quite weak, and any tiny movement can modify the

agglomeration state, thereby reducing the conductivity. Hence, during the whole measuring period the samples were not moved and each individual measurement was done within 3 s in order to avoid external influences on the particle agglomeration process as far as possible [31].

The conductivity behavior for CB-EA samples, in which curing does occur, was rather different. As displayed in Fig. 2b, immediately after application, the conductivities increased with increasing CB content, similarly as for the CB-E samples. However, already after 1.5 h, as curing was proceeding, the conductivity curves for samples containing 0.50 vol% CB and above displayed a conductivity jump of about two orders of magnitude. After 3 days the conductivity appeared to be approximately the same as after 1.5 h. These experiments were done just to make sure that some aftercure does not influence the results. For the 0.25 vol% samples hardly any conductivity change was measured. This indicates, firstly, that this low CB concentration is at or below the percolation threshold, and that at this concentration agglomeration is not thermodynamically preferred in the epoxy-amine matrix. Either by adsorption on, or by reaction with the CB particles, the amine stabilized the CB dispersion. Secondly, it indicates that the percolation behavior

Fig. 2. DC conductivity as a function of CB concentration; (a) CB-E samples; (b) CB-EA samples; (c) $\ln \sigma_{DC} - \log(p - p_c)$ plot with fit curve for obtaining the parameters p_c and t using Eq. (1) and data from the CB-EA samples cured for 3 days. For clarity, a typical error bar is given only once in (a) and (b). The different time points used are purely due to the difference in response time of the two systems.

at or above the 0.50 vol% level is driven by the crosslinking reaction.

According to percolation theory, when the particle concentration p is close to the percolation threshold p_c , i.e., $|p - p_c| \ll 1$, the conductivity follows a universal law [15]:

$$\sigma_{DC} \propto (p - p_c)^t \quad (1)$$

where σ_{DC} (S/cm) is the DC conductivity of the sample and t a characteristic exponent. Above p_c , percolation pathways exist [30] through which the electrons can be transported through 'infinite' clusters, contributing to the DC conductivity value. The p_c and t values were obtained by non-linear fitting of $\ln \sigma_{DC}$ versus $\ln(p - p_c)$ for the 3 day data resulting in $p_c = 0.24$ vol% and $t = 2.9$ (the same fit for the 1.5 h data gave $p_c = 0.21$ vol% and $t = 3.2$). Alternatively, linear fits value with a fixed p_c were made increasing the value of p_c with step $\Delta p_c = 0.05$ vol% in the range of $p_c = 0.25$ to 0.5 vol%. The best fit obtained for the 3 day data (Fig. 2c) also shows that the $p_c = 0.24$ vol%, which is dramatically smaller than the theoretical value 16 vol%. Hence, we conclude that $p_c \cong 0.2$ vol%. The corresponding t -value is 2.9 ± 0.14 . A (simplified) Monte Carlo simulation for 3-dimensional random percolation yielded 2.0 ± 0.2 . However, such a simulation does not take in to account specific interactions and reactions. In particular the large difference, similarly as the difference between experimental percolation thresholds in the order of 0.2% versus the theoretical threshold of about 16%, suggests that non-random, fractal-like networks may be formed in the system [10,32–38].

The final conductivities for the CB-E composites are higher than those of the CB-EA composites, as the carbon black particles in these materials are relatively free to move, also after prolonged time. For the CB-EA composites the network is fixated early in the curing process, also for low temperature, so that all composites obtain about the same final conductivity.

3.1.2. Variation with temperature

Fig. 3a displays the *in situ* conductivities measured isothermally at different temperatures for CB-E 1.25 vol% samples. At all temperatures, the samples showed sharply increasing conductivity values initially, followed by a gradual transition into a plateau. The rate of conductivity increase and level of conductivity are strongly related with temperature. For samples measured at 70 and 100 °C, the conductivity jumped about 2–3 orders of magnitude and turned stable fast within about 200 min. Such a phenomenon has been correlated in colloidal systems [24] with the mobility of particles controlled by their Brownian motion and the viscosity of the matrix, as both are temperature-dependent. In our system, elevating temperature also enhances the diffusion rate of CB, and eases to overcome the repulsive force between particles, leading to a higher conductivity level for samples measured at a higher temperature.

Fig. 3. *In situ* conductivity as a function of time at various temperatures; (a) CB-E samples; (b) CB-EA samples. The different time points used are purely due to the difference in response time of the two systems.

The results obtained from the CB-EA 1.25 vol% samples (Fig. 3b) showed a different profile. After a sharp increase of conductivity at 70 °C and 100 °C within about 30 min, all samples reached the same conductivity level regardless of temperature and time. Moreover, the increasing-to-plateau transition is faster as compared with the corresponding CB-E samples. This indicates that the presence of the amine and/or curing reaction on the one hand speeds up the initial aggregation of the network formation, while on the other hand it also fixates the final agglomeration state to a certain common level, so that the final conductivity (about 10^{-3} S/cm) for CB-EA samples is less than that for CB-E samples. In order to further understand the interaction between curing and agglomeration for the CB-EA samples, DSC studies were performed on CB-EA samples with 1.25 vol% CB, labeled from now with just CB-EA.

Temperature can affect curing but the fact that the levels are all the same indicates that, when curing occurs, the network is so quickly fixed that, irrespective of the temperature, the same conductivity results. It is already relevant to note here that the times needed to reach the plateau conductivity values are all in agreement with the kinetics of the curing reaction having achieved a noticeable degree of conversion ($\alpha > 0.4$, Fig. 5) but below the gelation point (achieved at t_g , Table 3).

3.2. Thermodynamics

3.2.1. Dynamic studies

Dynamic DSC scans were carried out with increasing rates ranging from 2.5 to 25 °C/min on epoxy-amine samples containing no CB (EA) and 1.25 vol% CB (CB-EA). The total reaction enthalpy for each run, ΔH_T , was calculated by integrating the area under the peaks in the thermograms (Table 1). The average ΔH_T -values show that the reaction enthalpy of the EA samples is slightly higher than that of the CB-EA samples. The ΔH_T -value of the CB-EA samples corrected for their CB weight content (using 1.25 vol% $\cong$ 2.5 wt%) is almost the same for both systems, namely 334 J/g for the EA samples and 315 J/g for the CB-EA samples.

The reaction activation energy E_a was calculated according to Kissinger's method [39],

$$E_a = -Rd \ln(q/T_p^2)/d(1/T_p) \quad (2)$$

where R is the gas constant, q is the heating rate in a dynamic scan and T_p is the peak temperature in the thermograms (Table 1). A linear fit of a plot of $\ln(q/T_p^2)$ versus $1/T_p$ (Fig. 4a) resulted in an E_a value of 53.1 ± 1.5 kJ/mol for the EA samples and 52.7 ± 4.0 kJ/mol for the CB-EA samples, where $\pm$ denotes the standard deviation. These values can be regarded as identical.

Another method to analyze the value for E_a was reported by Ozawa [40–42]. The method uses dynamic DSC results considering a

Table 1

The peak temperature T_p (°C) and total reaction enthalpy ΔH_T (J/g) as obtained by DSC dynamic heating scans for samples without particles (EA) and with 1.25 vol% CB (CB-EA) for several heating rates. The average values for ΔH_T are given as well ($\pm$ denotes the sample standard deviation).

Heating rate (°C/min)		2.5	5	10	15	20	25	Average ΔH_T (J/g)
EA	T_p	95.6	108.8	125.1	133.8	-	-	
CB-EA	T_p	90.1	107.0	122.0	127.4	133.2	-	
EA	ΔH_T (J/g)	345	347	329	339	-	311	334 ± 15
CB-EA	ΔH_T (J/g)	338	302	315	-	304	-	315 ± 17

temperature gradient in the chamber and gives the relationship between E_a , q , and T_p as:

$$E_a = -R \ln q / d(1/T_p) \quad (3)$$

A linear fit of $\ln q$ versus $1/T_p$ (Fig. 4b) results in $E_a = 59.6 \pm 1.5$ kJ/mol for the EA samples and 59.0 ± 4.0 kJ/mol for the CB-EA samples. These two values can also be considered the same.

The results of the Kissinger and Ozawa analysis are apparently different. However, since $d(\ln q/T^2)/d(1/T) = d(\ln q)/d(1/T) - 2T$ and noting that the maximum peak temperature range is not very large, we may approximate $d(\ln q/T_p^2)/d(1/T_p)$ by $d(\ln q)/d(1/T_p) - 2\langle T_p \rangle$ where $\langle T_p \rangle$ represents the average peak temperature. Doing so results in a correction of $2R\langle T_p \rangle$ and from the Kissinger analysis we have $53.1 + 6.6 = 59.7$ kJ/mol and $52.7 + 6.5 = 59.2$ kJ/mol for the EA and CB-EA samples, respectively, in very good agreement with the values from the Ozawa analysis (fitting directly $d(\ln q)/d(1/T_p) - 2T_p$ versus $1/T_p$ yields, of course, exactly the same results as the Ozawa fit). The difference in values is thus due to different approximations made; however, the remaining question what should be considered as the most reliable expression is outside the scope of this paper.

In a more general context, the above is a formal description of the reaction kinetics with an overall activation energy common to the curing field but opposed to a more fundamentally correct rate equation based on elementary reactions [43]. It is clear, though, that the (empirical) activation energies are only slightly different. As also the reaction enthalpies are slightly different, the presence of CB does have a slight diluting effect on the curing reaction, which can be related to the initial conditions and molar ratios employed. Because it is highly unlikely that CB reacts with itself, [44], the percolation transition in a CB-EA sample is considered to be mainly due to the diffusion process of CB, corresponding to diffusion-limited cluster aggregation (DLCA), accelerated by increasing temperature.

3.2.2. Isothermal studies

The epoxy-amine curing reaction has been identified as an autocatalytic reaction [20,41,42,44,45]. The conversion rate $d\alpha/dt$ at constant temperature is controlled by two rate constants, k_1 and k_2 , and can be formulated as:

Fig. 5. The degree of conversion α as a function of curing time for CB-EA composites (with 1.25 vol% CB) cured isothermally at 100, 70, and 50 °C, respectively. Inset: estimate for t_c in the conductivity curves.

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(\alpha_{\max} - \alpha)^n \quad (4)$$

in which $\alpha_{\max}$ denotes the maximum conversion and m and n represent kinetic exponents. The reaction rate is large at the beginning and decreases with increasing conversion.

Isothermal DSC studies for CB-EA samples (with 1.25 vol% CB) and EA samples were carried out at 100, 70, and 50 °C, respectively. The degree of conversion α [44] can be obtained from

$$\alpha = \int_0^t (dH/dt) dt / \Delta H_T \quad (5)$$

where dH/dt is the measured heat flow rate and ΔH_T is the total reaction enthalpy obtained by dynamic scans. For α_{end} , the degree of conversion at the end of the reaction [44], we have

$$\alpha_{\text{end}} = (\Delta H_T - \Delta H_R) / \Delta H_T \quad (6)$$

Fig. 4. Plots of $\ln(q/T_p^2)$ versus $1/T_p$ according to (a) Kissinger's model, and (b) plots of $\ln q$ versus $1/T_p$ based on Ozawa's model. In both plots, the fitted lines are displayed.

Table 2

The degree of conversion at the end of the reaction α_{end} and the reaction rate constants k_1 and k_2 (obtained via fitting) for CB-EA and EA samples cured isothermally at 100, 70, and 50 °C, respectively.

	CB-EA			EA		
T (°C)	100	70	50	100	70	50
α_{end}	0.99	0.94	0.89	0.98	0.96	0.93
k_1 (s ⁻¹)	0.031	0.0107	0.0021	0.023	0.0074	0.002
k_2 (s ⁻¹)	0.164	0.0355	0.0103	0.144	0.033	0.0081

where ΔH_R is the residual heat measured by a subsequent temperature scan immediately after the isothermal curing reaction [42,45]. The results of α_{end} for both the CB-EA and EA samples cured at different temperatures are displayed in Table 2. For both systems curing at a lower temperature resulted in a lower α_{end} value. Fits according to eq. (4) were made, an example of which is shown in Fig. 5 where α is plotted as a function of curing time for CB-EA samples cured at 100, 70, and 50 °C, respectively. A nice match between the experimental data and the fitted lines can be observed. The reaction rate parameters k_1 and k_2 obtained are given in Table 2, together with the ones obtained from the EA samples via the same fitting procedure.

At the same curing temperature, the k_1 and k_2 values obtained from the CB-EA samples are slightly higher than those of the EA samples, revealing that an additional acceleration of the epoxy-amine reaction was caused by the presence of CB. Since the activation energies for both systems are the same, this difference appears in their Arrhenius frequency factor [44], i.e., their entropy. Rather than joining in the chemical reaction, the surface groups on the CB particles, e.g., carboxylic acid salts, carbonyl- and OH-groups [46], provide a template, locally adsorbing both reactants and thus increasing their reaction probabilities, while selective adsorption of one of the reactants would have had the opposite effect. Detailed surface analysis of the carbon black is lacking but a study using FTIR, XPS and LEIS [46] indicates that carboxylic acids and phenolic hydroxyl groups are present at the CB surfaces. An adsorption effect of the reactants stabilizes the initial particle dispersion. When the reactants are taken away by the chemical reaction, on the one hand the particle dispersion stability is reduced, while on the other hand fixation of the particle dispersion occurs due to the polymer network formation, overall leading to a fractal CB network (see section 3.3). Sumita et al. [47] proposed a model considering the percolation phenomenon as a phase-separation process. Another model was reported by Welling and co-workers [48,49] in which it is assumed that the flocculation of CB particles at a certain critical concentration results from a phase-transition. In these two well-accepted models, the changes in CB-polymer interfacial energy were considered as the trigger for the formation of a percolating structure. As can be noted from the aforementioned results, the presence of amine, either directly interacting with the surface groups of CB, or indirectly changing the interfacial energy between the CB and the polymer, evidently enhanced the percolation network formation process if sufficient CB is present to establish a long-range network.

3.2.3. Influence of polymer gelation

As a result of the on-going reaction of the epoxy resin with the amine crosslinker, the viscosity will increase with concomitant accelerated hindrance of cluster diffusion. However, it is not experimentally possible to measure viscosity *in situ* by means of imposed shear, since that would destroy the fractal structure build up. We therefore chose to take the gelation point of the epoxy/amine system as a measure for the time to hindered cluster diffusion. Theoretically gelation occurs when the reaction achieves a certain degree of conversion α_c , which is predicted to be [50]:

$$\alpha_c = [r(f_a - 1)(f_e - 1)]^{-1/2} \quad (7)$$

where r is the off-stoichiometric ratio between amine and epoxy and f_a

Table 3

The gelation time t_g obtained by DSC and the time t_c when the *in situ* conductivity stopped developing for CB-EA samples (with 1.25 vol% CB) measured, respectively, at 100, 70, and 50 °C.

	100 °C	70 °C	50 °C
t_g (min)	9	30	128
t_c (min)	12–26	35–60	130–160

and f_e denote the functionalities of amine and epoxy, respectively. Accordingly, for our system, α_c was calculated from eq. (7) as 0.634. By correlating this value to our experimental result, the time for each sample to reach their gel points t_g can be obtained (Table 3). The corresponding times t_c at which the conductivity stops developing and reaches the final plateau, as shown in the inset in Fig. 5, are also given.

A good correlation is obtained between the t_g - and t_c -values (Table 3). It was reported [51] that the vitrification point of thermosetting polymers is reached soon after the gelation point. In this sense, the vitrification time estimated by conductivity measurements (i.e., t_c) is in good agreement with the vitrification time of the polymer matrix as estimated from the degree of conversion (i.e., t_g). This clearly confirms that the cluster aggregation process, especially at a later stage, is strongly influenced by the polymer crosslinking, which restricts the mobility of CB clusters and fixates them through forming permanent polymer networks.

3.3. Fractal dimension

Fig. 6 displays TEM images of a CB-EA sample (containing 1.25 vol % CB). The particles are distributed homogeneously in the polymeric matrix, and the aggregates show self-similarity under different magnifications, a characteristic of fractal structures.

Lin et al. [29,30,52] proved that both the DLCA and RLCA models display universal behavior. The process features, fractal dimensions and aggregation kinetics, under either regime are identical regardless of the type of particle. In this study, the fractal dimensions for CB-EA samples were estimated for two samples with extreme reaction rates: one cured at 100 °C (CB-EA-H) and the other at 20 °C (CB-EA-L). The calculations were performed by using the software Frac_Lac [53] based on the box counting method, in which the linear dimension was changed by a factor 2. Three different images taken from different locations of each sample with the same magnification were used.

The calculations showed that the d_f -values for the CB-EA-H and CB-EA-L samples are 1.56 ± 0.04 and 1.66 ± 0.03 , respectively. For the CB-EA-H samples, although the clusters obtained more energy to diffuse due to the higher curing temperature, the curing reaction also proceeded much faster than for the CB-EA-L samples. Consequently, gelation was achieved earlier, arresting the fractal development and resulting in a smaller d_f -value. In contrast, clusters within a CB-EA-L sample were less mobile, but have longer time to aggregate before reaching the gelation point. Under such conditions the influence of the curing reaction is smaller, contributing to a d_f -value that is closer to the theoretical value for DLCA. However, the d_f -values for both the CB-EA-H and CB-EA-L samples are in all cases smaller than the DLCA value 1.85, indicating that as long as a curing process is present, the fractals formed in this system cannot reach their ideal d_f -value.

4. Conclusions

CB epoxy composites without (CB-E) and with amine cross-linker (CB-EA) were studied. The CB-E materials with CB concentration ranging from 0 to 1.25 vol% showed no typical percolation characteristics. Agglomeration of CB in this system is thermodynamically favored, taking place spontaneously regardless of concentrations, contributing to the increase of conductivities until reaching the equilibrium state. In

Fig. 6. TEM images at different magnifications of a CB-EA sample (with 1.25 vol% CB).

contrast, when amine was added to this system (CB-EA), a clear percolation transition was observed. Below the percolation threshold ($\cong 0.2$ vol%), the CB particles remained well dispersed, while above the threshold the particles agglomerated, resulting in a conductivity increase of about 3 orders of magnitude. The agglomeration process for both the non-crosslinking CB-E and the crosslinking CB-EA systems was temperature dependent. Increased temperature reduces the matrix viscosity and enhances the Brownian motion. Both effects increase the mobility of the CB particles, leading to an acceleration of agglomeration. For the CB-E samples, the repulsive interactions between the particles are limited, thus an increasing conductivity level was obtained for samples measured isothermally with increasing temperature. However, for the corresponding CB-EA samples, in which particle agglomeration was fixated in later stages, identical and lower final conductivity levels for all CB-EA samples were obtained, clearly showing the influence of the matrix crosslinking process.

DSC studies confirmed that the fixation of particle aggregation could be attributed to the matrix crosslinking. The gelation time t_g of the curing reaction shows a good correlation with the time t_c for the arrest of the conductivity development. Moreover, no chemical reaction between particles or between particle and polymer could be detected. The conversion profile could be fitted well with the auto-catalytic model, indicating that the only chemical reaction taking place is the epoxy-amine curing. Agglomeration is confirmed to be merely a diffusion process, corresponding to diffusion-limited cluster aggregation (DLCA). Microstructure studies revealed the fractal nature of the CB clusters. The fractal dimensions d_f for CB-EA samples with 1.25 vol% are found to be in all cases lower than the universal DLCA value, 1.85 ± 0.05 , indicating that the presence of amine is critical for the percolation transition to occur, but that the inevitable crosslinking arrested particle aggregation. Clusters have less time to grow into the expected dimension of the standard DLCA process, resulting in a d_f -value of 1.55 for CB-EA samples cured at 100 °C and 1.65 for the ones cured at 20 °C.

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