

Agglomeration and Electrical Percolation Behavior of Carbon Black Dispersed in Epoxy Resin

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ABSTRACT: In conductive polymer compounds, the filler volume fraction at which a network of touching particles is formed is not a constant but depends on the manufacturing process. By applying three main features—particle–particle interaction, dynamics of agglomeration, and structure of agglomerates—which are well known in colloid science to filled polymers, the electrical percolation behavior can be understood. Thus, it is possible to explain the hitherto found low percolation thresholds of less than 0.5 vol% in carbon-black-filled resins and, hence, further reduce the threshold to 0.06 vol%.

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INTRODUCTION

It is widely accepted that the conductivity of insulating polymers with conductive fillers is a result of the development of a network of touching filler particles. Theoretically, many percolation models have been developed to define the conditions, especially the critical filler volume fraction, at which a network is formed in conductive polymer compounds. The most prominent one was created by Kirkpatrick¹ and Zallen.² In their geometrical models, a regular array on which spherical shaped particles are distributed statistically is examined. In this model, the required minimum filler volume fraction to form a continuous network of touching particles is 16 vol%. This number corresponds with most experimentally found measures since for most polymers and powdery fillers, the experimentally found

critical volume fraction for percolation is 5 to 20 vol%. This, however, is not true for carbon-black-filled resins that conduct with as little as 0.5 vol%.^{3,4}

A different branch of science evaluates under which conditions particles dispersed in liquids agglomerate. This theory of colloids sufficiently describes the interaction among dispersed particles as well as the structure and dynamics of agglomerate formation. Although the analogy to filled polymers is obvious, its application on filled polymers is not established.

In the following, it is shown that by applying the theory of colloids, the results of the experimentally found electrical percolation behavior of carbon-black-filled resins can be explained.

THEORY

Particle–Particle Interaction

Among particles dispersed in liquids or in polymers, respectively, two competitive forces have to

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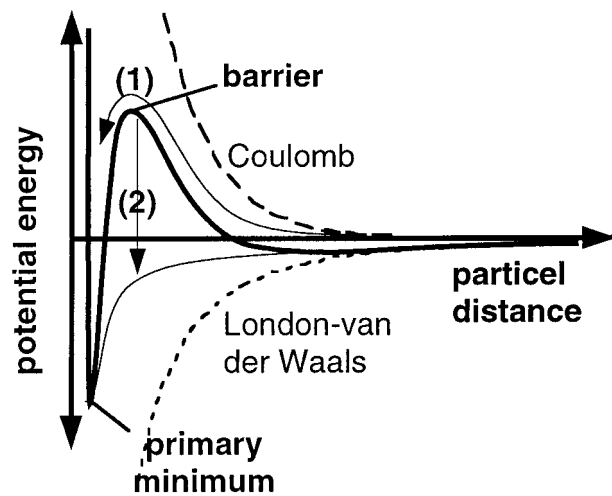


Figure 1 Potential energy curve of two colloidal particles.

be considered.⁵ First, touching particles stick together due to the London–van der Waals force of attraction. Second, surfaces of particles dispersed in a medium become charged, which causes a repulsive coulombic force. Figure 1 shows the total potential energy as a function of particle distance. Depending on the amount of charging, the coulombic force can cause a potential energy barrier. This barrier may be able to hinder the particles from coming into close enough contact with each other to be conductive; i.e., conducting agglomerates cannot form. In order to achieve a permanent contact in the primary minimum and thus to induce the agglomeration process, the potential energy barrier must be surmounted.

It is very unlikely that thermal energy alone is sufficient to surmount an existing potential energy barrier within a reasonable time, but there are two possibilities to accelerate this process. The barrier can be surmounted either by external shear forces, which can be produced by stirring the dispersion [see (1) in Fig. 1] or by reduction of the repulsive coulombic force by increasing the ionic concentration [see (2) in Fig. 1]. Above a critical salt concentration, the barrier is lowered to such an extent that thermal jostling or convection can drive particles into the primary minimum.

Dynamics

Particles dispersed in liquid media, like in polymers above their melting temperature, are influenced by the above mentioned forces but also by

thermal and shear forces. Therefore, they migrate through the medium. Without a potential barrier or with the support of external shear forces, colliding particles may stick together. Thus, even initially homogeneously distributed particles agglomerate gradually.

Usually the model of Kirkpatrick and Zallen is referred to when the insulator-conductor-transition in conductive filled polymers is described. It requires that after dispersion, the filler particles are distributed statistically and remain in their places. If a medium of high viscosity is used and when the production process is very short, it is very likely that these prerequisites are met. However, if a carbon black thermoplast dispersion is being tempered above its melting point, a percolation-like transition in its conductivity is found.⁶ Using the theory of colloids, this transition can be explained by agglomeration, i.e., the movement of filler particles, and with the gradual development of a carbon black network.

In contrast to thermoplastics, resins are liquids of lower viscosity. The process of agglomeration should therefore be much faster and must be considered even if the production process is relatively short.

Structure

When the prerequisite conditions are met, agglomerates start to form in many parts within the polymer and finally combine to a continuous network. Within an agglomerate, the number of particles N is proportional to its radius R to the power of its fractal dimension D . Since D is below 3, the particle density n of an agglomerate decreases with its size, as follows:

$$n = \frac{N}{\frac{4}{3}\pi R^3} \propto \frac{1}{R^{3-D}}$$

A low percolation threshold can thus be obtained when the fractal dimension is low and the network is made up of large agglomerates.

The fractal dimension is influenced by the conditions during and after the agglomeration process. Generally it is between 1.8 and 2.5.^{7,8} After a longer stirring of the dispersion, D increases.⁸ To achieve a percolation threshold as low as possible, this should therefore be avoided.

EXPERIMENTAL

In this study, an epoxy resin based on bisphenol-A (ARALDITE LY556, CIBA GEIGY) with an aro-

matic amine hardener (ARALDITE HY932) were used. The filler was an extra conductive carbon black (PRINTEX XE2, DEGUSSA AG, Germany) with a DBP-absorption of $3.8 \text{ cm}^3/\text{g}$ and a pH of 8.

Three differently treated charges with varying carbon black content were prepared. At first, the resin was mixed with a given amount of carbon black using a dissolver disc at 5500 rpm for one hour. After the hardener was added, the first charge was cured immediately after dispersing the mixture again. In contrast, the second charge was stirred slightly in the mold before curing. For the third charge, a hardener with an increased ionic concentration was used. Herefore a copper chloride-methanol solution (CuCl_2 , anhydrous, FLUKA) was added, and the hardener was desolvitized in vacuum. A change in color of the hardener from red to dark brown indicated a complex formation of the copper chloride with the hardener as found for many aromatic amines.⁹ The salt concentration in the resin was adjusted to $3 \cdot 10^{-6} \text{ mol/g}$. All samples were cured at 80°C for 3 h and at 140°C for 8 h.

The samples were sawcut to squares of 40 mm and covered with conductive silver paint on two opposing sides and a voltage of $2.0 \text{ V}_{\text{DC}}$ was applied to measure the conductivity. A KEITHLEY 485 PICOAMMETER was used to determine currents in the range of $100 \mu\text{A}$ to 1 pA.

To gain an insight into the agglomeration process during the production cycle, a separately produced dispersion containing 0.3 vol% carbon black was used to determine the course of conductivity. Two electrodes were dipped into the dispersion, to which the hardener already had been added, and the conductivity was measured with an alternating voltage of 100 mV (15 Hz). The limit of measurement was 10^{-8} S/cm . To lower the viscosity, the resin was heated to 65°C .

RESULTS AND DISCUSSION

Dynamics and Morphology

If agglomeration of carbon particles occurs in the resin, an increase in conductivity of both dispersion and cured resin should result. Right after stopping the dispersion process, no increase of the conductivity in the 0.3 vol% carbon black-resin-dispersion was observed within the five minutes of examination. Hence, it can be assumed that no agglomerates have developed. This assumption

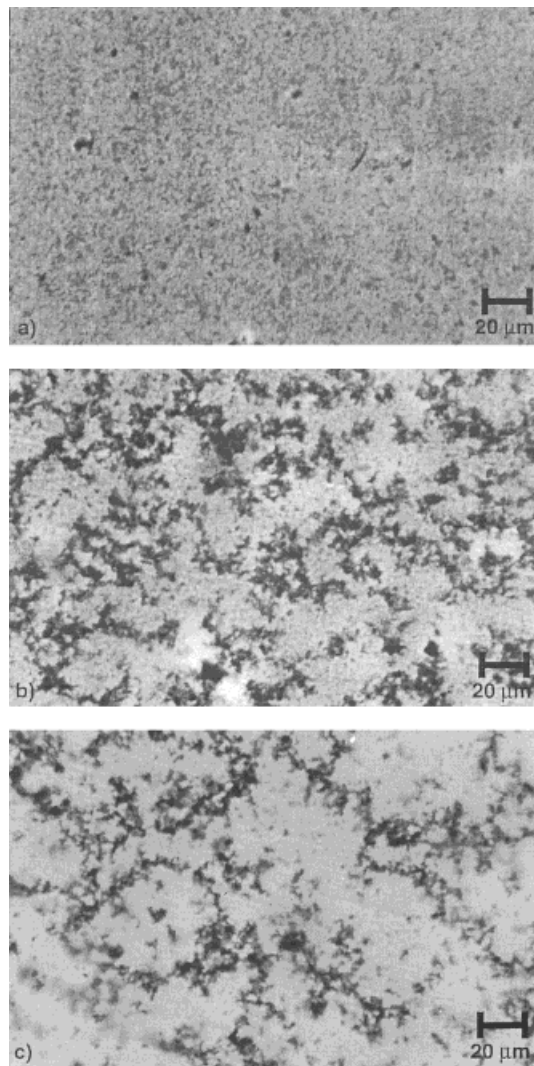


Figure 2 (a) Epoxy resin with 0.6 vol% carbon black, cured after dispersion. (b) Epoxy resin with 0.3 vol% carbon black, cured after shearing. (c) Epoxy resin with 0.06 vol% carbon black, copper chloride concentration of $3 \cdot 10^{-6} \text{ mol/g}$.

can be confirmed by a micrograph (Fig. 2), which shows a thin polished section of a sample of the first charge with a carbon black content of 0.6 vol%. Any stirring or shearing of this sample between the redispersion and the curing had been avoided. As can be seen, the carbon particles are distributed in the resin homogeneously. This manifests that during the curing cycle agglomerates have not formed, and, accordingly, no conducting network has developed. This can be proved by the high resistance of the cured sample too. Its resistivity is above the limit of measurement of $10^{12} \Omega\text{cm}$.

The reason for this is that the carbon black

particles are charged electrostatically in the epoxy resin. This causes the development of a potential barrier that hinders the particles to come into close enough contact to agglomerate and thus to build a conductive network. If the theory of colloids can be applied for carbon black filled resins, this barrier should be exceeded by shear forces or by increasing the ionic concentration of the epoxy resin.

To prove this, moderate shear forces were applied to the dispersion by stirring with a dissolver disc at 45 rpm. The conductivity increases and reaches a stationary value after about one minute. After stopping the shearing, a steep increase in conductivity can be noticed that flattened out after a few seconds. Figure 3 shows this course of conductivity. Due to this, it can be assumed that light shearing causes the formation of agglomerates. Another clue to back up this hypothesis can be seen in Figure 2(b), which shows a thin polished section of a sample of the second charge after curing. It contains a filler volume fraction of 0.3%, and it can be seen that some agglomerates have formed. They appear as dark zones in the micrograph. As dispersed carbon particles can

still be found in the bright zones, the particles are only partly flocculated. But this is sufficient to form a conductive network and to reduce the resistivity of this sample to $10^5 \Omega\text{cm}$.

As can be seen, shearing induces the agglomeration process, which verifies the hypotheses that a potential barrier exists that can be surmounted by shear forces.

The second way to improve the forming of agglomerates is to increase the ionic concentration of the epoxy resin and thereby lower the potential barrier. After adding copper chloride into the dispersion, a slow increase in conductivity can be observed (Fig. 4). It can be expected to find agglomerates, which would support the hypothesis that a potential barrier exists. Figure 2(c) shows a sample containing 0.06 vol% carbon black to which copper chloride was added before curing. The carbon particles now form a voluminous floc structure. Large carbon-depleted areas reaching sizes up to $100 \mu\text{m}$ are generated, while carbon particles are not larger than $0.5 \mu\text{m}$. In contrast to the sheared sample, hardly any dispersed carbon particle can be found. This much finer structure in comparison to the sheared sample can also be

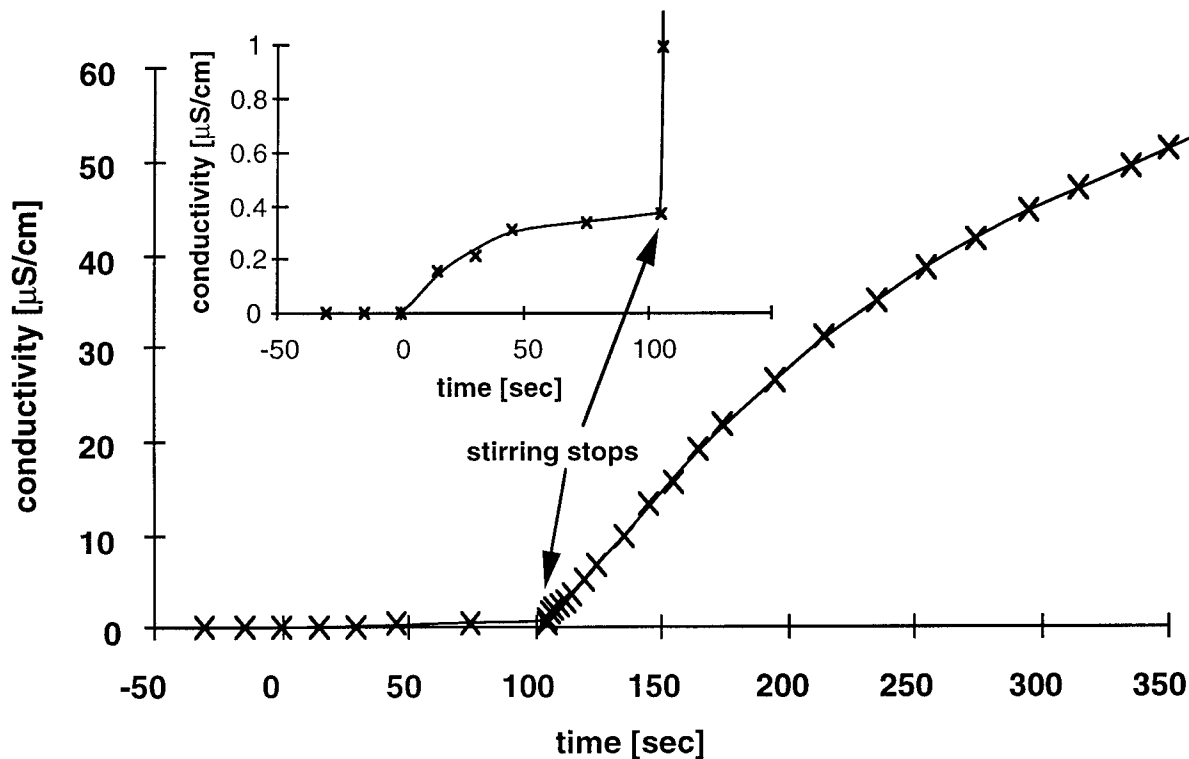


Figure 3 Conductivity course of liquid epoxy resin filled with 0.3 vol% carbon black after dispersion. Between $t = 0$ s and $t = 105$ s, the resin is stirred with a dissolver disc at 300 rpm.

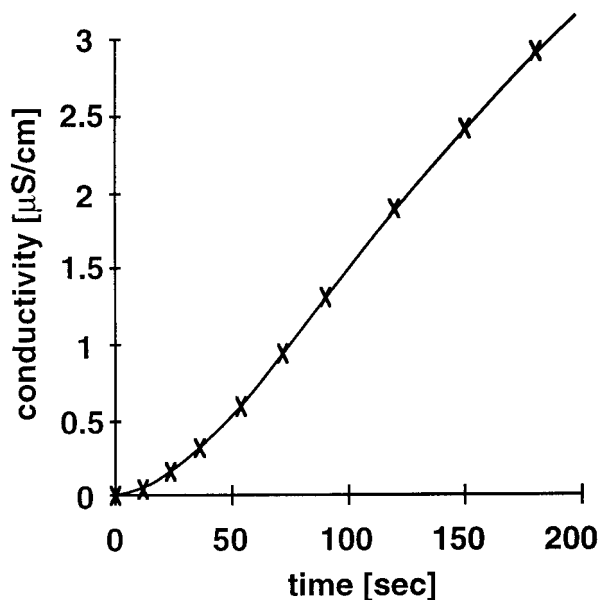


Figure 4 Conductivity course of liquid epoxy resin to which $3 \cdot 10^{-6}$ mol/g copper chloride is added, filled with 0.3 vol% carbon black after dispersion.

based on the fact that shear forces cause agglomerates to become compacted. Though the carbon black content is 10 times lower than in the first nonconductive sample, it is conductive with a resistivity of $10^5 \Omega\text{cm}$.

Increasing the ionic concentration of the resin provides agglomeration of carbon particles. In this way, no external forces are necessary to drive particles into the primary minimum. That way, an increase in conductivity can be measured within the dispersion without stirring it.

As can be seen from these experiments, a potential barrier exists that can be exceeded by stirring or adding salt. This barrier is formed by electrostatic charging of carbon particles in epoxy resin and hinders the agglomeration of the carbon black by thermal jostling. The theoretical possibility to surmount this barrier by external shear forces or by increasing the ionic concentration was found to operate also experimentally. This proves the existence of a potential barrier since the dispersion is nonconductive before or after curing, while it is conductive after stirring it or increasing the ionic concentration by adding salt, as theoretically explained before.

Percolation Threshold

The formation of a network can be influenced by shearing or by increasing the ionic concentration

as demonstrated above. Both treatments have an effect on the morphology of the filler network and also on the percolation threshold.

The resistivity of differently treated samples is shown as a function of the carbon black content in Figure 5. The percolation threshold is 0.9 vol% when the resin is cured immediately after redispersion. After stirring the dispersion and thus inducing the agglomeration process, the threshold is reduced to 0.3 vol%. Increasing the ionic concentration provides the agglomeration much better than shearing the resin to get an open, voluminous network structure. A percolation threshold as low as 0.06 vol% is achieved this way, a value even lower than values found elsewhere in literature.

CONCLUSION

Percolation of particles in viscous liquids is a geometrical problem as one of the interactions between the filler particles as well. Therefore, polymer compounds such as carbon-black-filled epoxies have to be seen as colloids to which attractive and repulsive forces between the carbon particles are important.

When conductive polymers are initially produced, carbon particles are homogeneously distributed. Due to the potential energy, the development of agglomerates is energetically more favorable than the dispersed state. The attainment of this potential minimum can be hindered kinetically, however, by a potential barrier. Their tendency though to stick together, possibly aided by external shear forces, enables them to build agglomerates that combine and finally build one conductive network.

The experimental investigation proves that the dispersion of carbon black in epoxy resin is electrostatically stabilized; i.e., the particles are hindered to reach the potential minimum by a potential energy barrier. This interpretation of the results is proven since the theory that agglomeration can be induced by shear forces or by increasing the ionic concentration concurs with the experimentally found results.

Furthermore, it is important to notice that the percolation threshold depends upon the morphology of the conductive network, which again is influenced by the processing route. The highest efficiency can be reached by increasing the ionic concentration. This way, nearly the whole amount of carbon black forms large and voluminous ag-

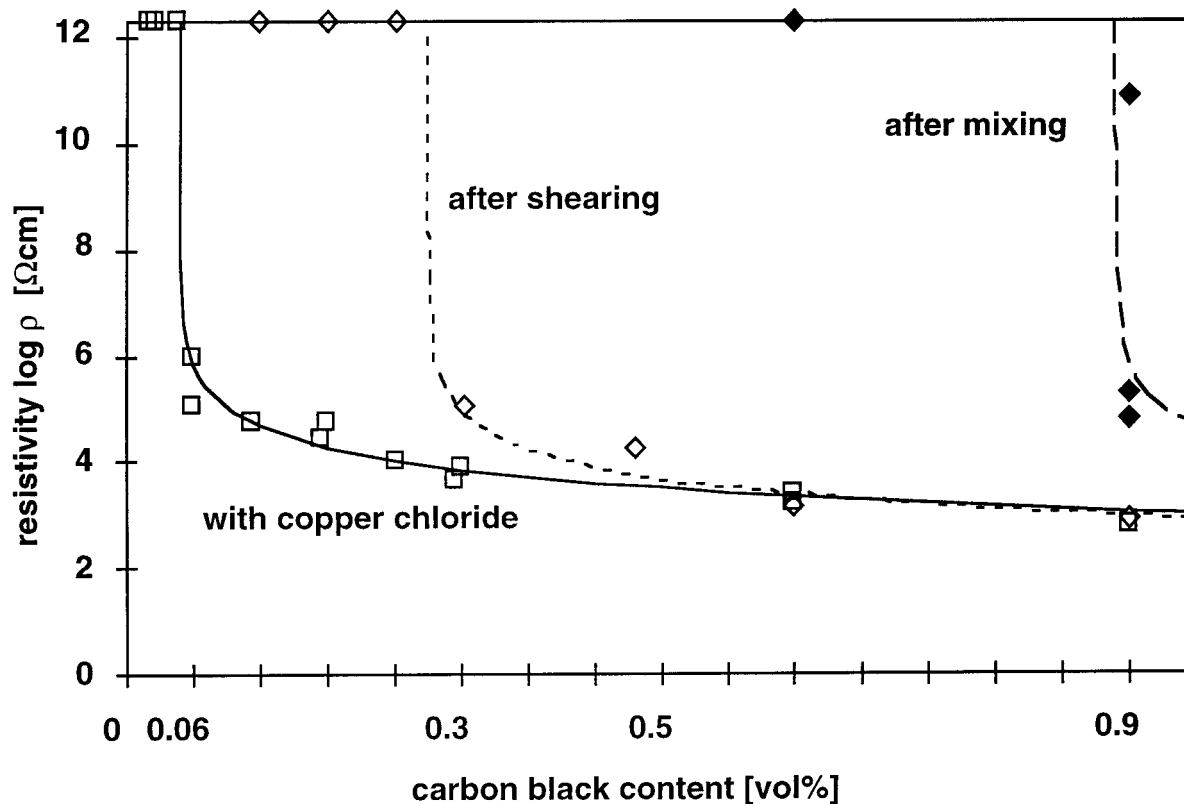


Figure 5 Resistivity of differently treated charges of carbon-black-filled epoxy resin versus carbon black content.

glomerates with a fine structure only using relatively little amount of filler particles. As a result, a percolation threshold as low as 0.06 vol% was achieved. Theoretically, this low percolation threshold can be explained only by considering the fractal structure of the agglomerates and the extension of the carbon-free areas.

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