Rheological, Electrical, and Microwave Properties of Polymers with Nanosized Carbon Particles

R. Kotsilkova,¹ D. Nesheva,² I. Nedkov,³ E. Krusteva,¹ S. Stavrev⁴

¹Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria ²Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

³Institute of Electronics, Bulgarian Academy of Sciences, Sofia, Bulgaria

⁴Space Research Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received 7 July 2003; accepted 27 October 2003

ABSTRACT: The rheology, dc-conductivity, and microwave properties of acrylic, polyurethane, and epoxy composites containing 0–15 vol % of nanosized carbon particles have been investigated. Carbon nanoparticles (1–3 nm) are produced by a shock wave technology. Steady-state shear and oscillatory flow tests are applied to investigate the rheological properties of dispersions; dc-conductivity and MW absorption/reflection are investigated for solid composite films. Rheological characteristics are used for the evaluation of agglomeration processes of nanoparticles in dispersions, as controlled by volume fraction and processing technology. The percolation threshold is interpreted as a structural transition from a dispersed to an agglomerated state and it is found to depend significantly on the type of the matrix polymer. Above the percolation threshold, the presence of carbon nanoparticles produces a strong increase in the viscosity of dispersions as well as of the electrical conductivity and microwave properties of solid composites. A good correlation between the three characteristics is found for the systems in a wide range of carbon volume fractions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2220-2227, 2004

Key words: conducting nanocomposites; rheology; microwave properties

INTRODUCTION

The application of composites made of insulating polymers and highly conductive fillers is becoming very important due to their electromagnetic shielding, wave absorption, conductivity, and prevention of electric charging.^{1–5} Among all the available fillers, carbon black, carbon fibers, and, recently, carbon nanotubes are the most effective for thermoplastics and thermosets. The electrical properties of carbon black-filled polymer composites have been extensively studied with both fundamental and applied purposes.⁶⁻¹³ Only a few studies correlate the electrical conductivity of carbon-filled polymers with the ability to absorb electromagnetic waves.⁵ However, the relationships between rheology, electrical conductivity, and microwave properties are not well studied for polymer composites.

The conductivity of polymer composites filled with carbon black strongly depends on the filler content. At some critical filler content, called the percolation threshold, a sharp increase of the conductivity by several orders of magnitude occurs. This phenomenon is mostly explained in terms of the percolation theory, and it is related to the agglomeration of particles and

formation of an infinite cluster.^{11–16} For most polymers the critical volume fraction for percolation is determined between 5 and 20 vol %, which is in agreement with the geometrical models.^{14,15}

Recently, a lower percolation threshold has been observed for carbon black-filled epoxy resins⁶⁻⁸ not obeying the predictions of the standard percolation model, which is suitable for randomly dispersed but not interacting fillers. Colloid theory is applied to describe interactions among particles and agglomeration processes in relation to composite conductivity.^{1,17} Scientists generally agree that, for a given weight of carbon black, finer agglomerates enable the achievement of smaller interparticular distances and, therefore, electrons can be transferred from particle to particle throughout the matrix.18-23 Several authors¹⁸⁻²⁰ have noticed that the electrical and structural properties must be affected by the preparation conditions of the material, namely by the occurrence of a colloidal phase. The preparation of well-defined systems for such specific applications requires the control to be on dispersion processes and structure.^{1,24–27} In the recent reviews on electrical conductivity of binary mixtures,^{18,19} it is assumed that the mixing process may induce electrical charging of carbon particles and thus might stimulate interactions between particles and polymeric host. Such effects are not well investigated with respect to rheological and microwave properties.

Correspondence to: R. Kotsilkova (kotsil@clphchm.bas.bg).

Journal of Applied Polymer Science, Vol. 92, 2220-2227 (2004) © 2004 Wiley Periodicals, Inc.



Figure 1 X-ray diffraction spectra of nanosized carbon particles (NCP).

For these reasons, the present work is focused on the relationships between rheology, conductivity, and microwave properties. We investigate composites of various resins: acrylic, polyurethane and epoxy, which incorporate nanosized carbon particles synthesized by a shock wave technology. The factors varied for manipulation of interactions among particles and agglomeration processes are volume content and processing technology. The rheological characteristics are correlated with conductivity and microwave properties in a wide concentration range of the filler. The results of this study can be applied to assess the optimal compounding conditions of carbon nanoparticles in a given polymeric system to maintain certain physical properties.

EXPERIMENTAL

The filler component used in this study consisted of nanosized carbon particles (NCP) synthesized by a shock wave propagation method from the free carbon of the explosive.²⁸ By using optimal synthesis conditions (pressure, time, and temperature), it was possible to obtain carbon nanoparticles with a controlled size and content. The NCP consist of disordered graphite (67 wt %) and diamond (33 wt %), and the particles have a mean diameter of 1–3 nm, a specific surface of 590 m²/g (BET), and a specific gravity of 1.86 g/cm³. Figure 1 presents the results of the X-ray diffraction analysis of the NCP filler. The peaks at *d* = 3.36 Å and *d* = 2.08 Å demonstrate reflections of the graphite and the diamond, respectively.

Acrylic resin (polymethyl-acrylate, BASF), polyurethane (polyol–isocyanate, BASF), and epoxy resin (Araldit, CIBA) were used as matrix polymers. Dispersions of carbon nanoparticles (0–15 vol % NCP) in the matrix resins were prepared by two steps of processing: (1) 15 min of high-speed mixing at 7000 rpm followed by (2) 1 h of stirring in magnetic field at room temperature. The processing technology ensured good dispersion of NCP within the matrix resin. Solid nanocomposite films of acrylic resin and polyurethane were prepared from dispersions by solvent evaporation and polymerization at room temperature followed by 4 h of postcuring at 60°C. Epoxy systems with amine hardener (EH-629, Vianova) in the ratio of 100 : 30 were cured in the course of 1 h at room temperature, followed by postcuring for 3 h at 140°C.

The rheological measurements of the dispersions were performed by a Rheotron Brabender viscometer using cone-plate geometry. Steady-state shear measurements were carried out in the shear rate region from 0.1 to 100 s^{-1} . Oscillatory shear mode with frequency sweeps between 0.1 and 75 s⁻¹ at low strain amplitude was used to measure the dynamic moduli within the linear elastic range.

The volume dc-conductivity of the solid composites was measured at room temperature with a Keithley 610C electrometer. Thin sections were cut from the films having dimensions of approximately 10 mm length, 1 mm width, and a thickness of 0.01 mm. Planar electrical contacts (\sim 1 mm spaced and 1 cm long) were made of silver paint on both length sides of the samples. Different applied voltages were used on different samples, depending on the level of conductivity of the specimens, thus a voltage of 100 V was applied for the matrix polymer and the composites below 5 vol % of carbon and a volatage of 1 V was applied for the composites above 5 vol % of carbon. A minimum of three samples has been used to determine the electrical properties of each composition.

A method in a fixed frequency domain at 9.4 GHz has been provided for determination of microwave absorption (a, %), reflection (r, %), and transmission (t, %). The measuring device used in this method consists of a reflectometer circuit in the free space with two opposite directed horns: transmitter and receiver. A deposition of metal sheet ("short circuit") at a definite distance from the horns was used to avoid the problems connected with the position of samples in the near-zone to the horns. The samples were films with a thickness of about 0.01–0.02 mm, which were subsequently positioned at the place of the short circuit.

RESULTS AND DISCUSSION

Rheological characterizations of dispersions

Our study has been focused on two factors, the filler content and the shearing during processing. Thus, we expect to control the agglomeration process that can change the rheological properties of nanoparticle dispersions and probably can improve the physical properties of composites.

Figures 2(a) and (b) show the low amplitude dynamic moduli, G' and G'' versus angular frequency, ω ,

Figure 2 Low amplitude storage G' (a) and loss G'' (b) moduli vs. angular frequency, ω , of NCP/acrylic dispersions at volume concentrations of 0, 1, 2, 5, 8, and 10%; $T = 20^{\circ}$ C is the experimental temperature. The arrows show the theoretical slopes of 2 and 1 for $G'(\omega)$ and $G''(\omega)$, respectively. The inset in (a) with a slope of $m \approx 5$ presents the linear dependence of the storage modulus G' vs. the filler content

of sample NCP/acrylic dispersions with various volume contents of the filler. In the concentration range of 0-10% of NCP, a significant increase in the storage modulus *G*' is found, while the corresponding increase in the loss modulus *G*" is much lower. However, the values of *G*" keep higher than these of *G* in all samples, so the fluidity dominates the elasticity in the concentration range studied.

at a low frequency of $\omega = 0.2 \text{ s}^{-1}$.

An additional relaxation process is observed in the terminal flow region, presented in Figures 2(a) and (b). If the volume fraction of NCP increases from 1 to 10%, the terminal slopes of G' and G'' decrease from the theoretical values, $G' = \omega^2$ and $G'' = \omega$, and reach an equilibrium plateau at low frequencies. The inset in Figure 2(a) shows a log–log plot of the storage modulus G' versus the filler content at a small frequency of $\omega = 0.2 \text{ s}^{-1}$. The high slope $m \approx 5$ of the straight line

through the data demonstrates clearly the additional relaxation. We interpret these observations with agglomeration of NCP in the dispersion, starting at relatively low filler content (1–2%), and consequently, with increasing the size and number of the agglomerates at a filler content above 2%, the particle network is being formed.

As pointed out in a few studies,^{27,29,30} dispersions of nanoparticles are characterized by very strong interparticle interactions and a variation of the degree of dispersion can change the particle order. In our study NCP dispersions were prepared by two steps of intensive shearing: step 1, 15 min of high-speed mixing, followed by step 2, 1 h of stirring in a magnetic field. Figure 3 compares the viscosity curves of carbon/ acrylic dispersions after steps 1 and 2 of shearing for various NCP volume concentrations (1-10%). The viscosity of dispersions after step 2 is much lower than that measured after step 1 of shearing. The effects become significant at high filler concentrations and at low shear rates, wherein the dispersions after stirring in a magnetic field show about five times lower viscosity than the samples sheared only by high-speed mixing. We interpret this observation in terms of decrease of plasticity. Step 2 of shearing in a magnetic field induces an extensive dispersion of nanoparticles within the polymer matrix. It is expected that finer particles enable the achievement of smaller interparticle distances and, consequently, the network formation could be controlled. Therefore, we could control the dispersion state and the agglomeration process of nanoparticles in the systems studied, if the rheological properties are optimized by shearing.

Dispersions of NCP in polyurethane and epoxy resin show qualitatively similar rheological behavior. The rheological characteristics are further correlated

Figure 3 Viscosity vs. shear rate of 1, 2, 8, and 10 vol % NCP/acrylic dispersions, as influenced by the shearing during processing: step 1, high-speed mixing; step 2, additional stirring in a magnetic field, $T = 20^{\circ}$ C.







Figure 4 Conductivity vs. NCP volume fraction of nanoparticles for composites of acrylic, polyurethane, and epoxy matrices at $T = 25^{\circ}$ C, cured after step 2 of magnetic mixing.

with conductivity and microwave properties to evaluate the role of the structure of nanodispersions on the physical properties of solid nanocomposites.

Conductivity of solid composites

One of the main features of composites filled with conductive particles is that the agglomerates of particles in the infinite cluster (particle network) are still separated by thin gaps of a polymer layer, which results in a variety of conduction mechanisms in such composites.^{22,23} Because of this, factors that influence agglomeration processes will play an important role for control on the conduction mechanisms.^{31,32} The variables used for controlling the agglomeration processes and the rheological properties of NCP dispersions, such as volume content [Figs. 2(a) and (b)] and shearing (Fig. 3) have been studied with respect to the conductivity of composites. Figure 4 compares the dc-conductivity versus volume fraction of nanoparticles of composite films of acrylic, polyurethane, and epoxy matrix, cured after the step 2 of mixing. As seen in Figure 4, the electrical conductivity of composites slightly increases with increases in the filler content below the percolation threshold ($\Phi < \Phi_{pt}$), if com-

pared with that of the pure matrix resin. This is associated with the formation of single agglomerates of carbon nanoparticles separated by thin polymer barriers, so that charge hopping²⁷ may occur with increases in the filler content. Our further studies on the carrier transport mechanism of those composites around the percolation concentration are in progress. Above the percolation threshold ($\Phi > \Phi_{pt}$), the conductivity increases by 10 orders of magnitude and it is attributed to formation of carrier paths of particle agglomerates. The percolation threshold strongly depends on the type of the matrix polymer and increases in the order $\Phi_{\rm pt} \approx 3\%$ (polyurethane), 4% (acrylic resin), and 6% (epoxy resin). Further on, the conductivity saturation is associated with the formation of an infinite cluster (particle network), wherein the values of conductivity change insignificantly when the carbon loading is increased in the range $\Phi > \Phi_{st}$. The saturation point, $\Phi_{\rm st}$, changes in the order of 7% for polyurethane, 8% for acrylic, and 10% for epoxy resin, respectively. The values of conductivity in the saturation region are similar for the three types of composites (1-9 S/cm).

As seen in Figure 4, the polyurethane, acrylic, and epoxy nanocomposites differ in conductivity with varying the carbon volume fraction. This can be attributed to both the viscosity and the nature of the matrix polymers. Table I compares the viscosity and the conductivity of the pure polymers and of their 10% NCP composites. The results confirm findings by Rwei et al.⁸ that a low matrix viscosity assists in the formation of conductive paths in the systems. So, particle diffusion is much easier within the low viscosity polyurethane ($\eta = 1.3$ Pa.s) and acrylic resin ($\eta = 2.1$ Pa.s) matrices. The conductive pathways and the infinite cluster are formed at lower NCP content than within the epoxy resin of the highest viscosity ($\eta = 25$ Pa.s). If the nature of the matrix polymer is presented by its conductivity, it is found that the pure epoxy resin shows higher ionic conductivity (10^{-8} S/cm) than the other polymers (10^{-10} S/cm) . However, it does not improve the conducting properties of epoxy/NCP composites, which are significantly lower than these of other composites in the filler concentration range studied.

TABLE IViscosity (at $\dot{\gamma} = 100 \text{ s}^{-1}$), Conductivity, and MW Absorption Characteristics of the Matrix Polymersand the 10 vol % Carbon Compositions

Matrix polymer	$\frac{\text{Viscosity (Pa.s)}}{\Phi = 0 \%}$	Conductivity (S/cm)		MW absorption (%)	
		$\Phi = 0 \%$	$\Phi = 10 \%$	$\Phi = 0 \%$	$\Phi = 10 \%$
Polyurethane	1.3	1.79×10^{-10}	1.60	0	37.1
Acrylic resin	2.1	$7.24 imes 10^{-10}$	8.55	0	30.3
Epoxy resin	25.0	$4.20 imes 10^{-8}$	0.014	0	11.2

Figure 5 Conductivity vs. volume fraction of filler for NCP/acrylic resin composites, as influenced by the shearing during processing: step 1, high-speed mixing; step 2, additional stirring in a magnetic field, $T = 25^{\circ}$ C. Arrows show the shift in the percolation threshold toward lower values by intensive shearing.

Figure 5 demonstrates to what extent shearing by the two mixing techniques used allows changing the conductivity of the NCP/acrylic composites. Higher overall conductivity and slight decreases in the percolation threshold ($\Phi_{pt} \approx 3\%$) are observed for samples prepared after step 2 (magnetic stirring), in comparison with samples prepared after step 1 (high-speed mixing), where $\Phi_{pt} \approx 4\%$. The comparison of the rheological results (Fig. 3) with the conductivity results (Fig. 5) leads to the suggestion that the reduction of the size of particle agglomerates and the possible charging of NCP during the more intensive shearing are the main reasons for the slight overall improvement of the electric conductivity of composites.

Microwave characteristics of composites

Figure 6 shows the microwave absorption, *a*, and reflection, r, versus volume content of nanoparticles for NCP/acrylic composite films cured after high-speed mixing. Above the percolation threshold of $\Phi_{vt} \approx 4\%$, the microwave characteristics sharply increase. Thus, at the saturation point $\Phi_{st} \approx 8\%$, the absorption and the reflection reach values of about 35 and 8%, respectively. Comparing Figure 5 with Figure 6, one can see that a strong correlation exists in the concentration dependence of conductivity and microwave absorption/reflection. In general, the microwave characteristics at 9.4 GHz and the conductivity are significantly improved by increasing the carbon volume fraction. The percolation threshold and the saturation point appear at the same volume concentrations of carbon for both conductivity and wave absorption. Obviously, both characteristics depend in a similar way on

the formation of carrier paths and infinite cluster of particle agglomerates.

Similar to conductivity, the microwave characteristics of nanocomposites depend significantly on the type of the polymer matrix. Table I compares the microwave absorption, *a*, of the samples containing 10% of nanosized carbon particles. Thus, the MW absorption of the composites decreases significantly if the basic polymer changes in the order polyurethane, acrylic, and epoxy resins. The results clearly show that the low viscosity and the low conductivity of the matrix polymer improve significantly the microwave properties of the composites.

Rheological determination of the percolation concentration and the saturation point

Our study has shown that factors influencing agglomeration processes play an important role in conductivity and microwave properties. These results allow us to propose the rheological characterization of dispersions as a very useful way for controlling both physical characteristics of the solid composites.

The dependence of viscosity versus volume fraction of the filler is discussed to predict the percolation threshold and the saturation point. Figure 7 presents the experimental data of the viscosity at a high shear rate η ($\dot{\gamma} = 100 \text{ s}^{-1}$) versus volume fraction, Φ , for NCP/acrylic dispersions. The viscosity increases nonlinearly with increases in the nanoparticle content. At very low concentrations the viscosity is linearly proportional to the particle loading and this hydrodynamic disturbance is theoretically described by Einstein, Simha, etc., for particles with different shapes.^{33,34} Further on, the concentration dependence of viscosity becomes nonlinear and increases sharply with increases in the filler content, which is associated with the agglomeration processes of nanoparticles









Figure 7 Viscosity vs. volume fraction of filler of NCP/ acrylic dispersions—experimental and models: experimental data of the viscosity at $\gamma = 100 \text{ s}^{-1}$ (open symbols); viscosity calculated by the Einstein [eq. (1)] and Frankel— Acrivos model [eq. (2)]. Arrows indicate the calculated values of the percolation threshold, Φ_{pt} , and the saturation point, Φ_{st} .

within the matrix polymer and the infinite cluster formation. A number of empirical and semiempirical models are proposed to describe the nonlinear dependence of viscosity. Only the Frankel–Acrivos model³⁴ has been shown to be applicable for colloidal dispersions to predict the rapid rise of viscosity at high concentrations, accounted for by the hydrodynamic interactions of neighboring spheres.

The Einstein [eq. (1)] and Frankel–Acrivos [eq. (2)] models have been proved to describe the viscosity data in our study, as well as to determine both critical concentrations wherein the agglomeration processes occur and the infinite cluster is formed. These critical concentrations are interpreted as the percolation threshold and the saturation point. Figure 7 plots the experimental data of viscosity versus volume content of the filler and the theoretical predictions by the two models. For the dispersions studied, the Einstein equation is applicable only at very low filler concentrations below 1%, wherein interactions between nanoparticles are negligible. Obviously, at volume fractions higher than 1%, nanoparticle interactions in the dispersions become significant and this produces nonlinear viscosity. However, as seen in Figure 7, the Frankel-Acrivos equation fits well the experimental data at a much higher concentration range (4–12%). It allows for the suggestion that, in the region of 1-4%, the interactions between particles are in progress, but particle agglomerates are formed and start to contact each other at 4%, which produces a rapid rise of viscosity. For the calculations in eq. (2), to determine $\varphi_{\rm m}$ (maximum packaging density), we adopt a suggestion of Thomas³⁵ for plotting experimental rheological data $[(\eta/\eta_0) - 1]^{-1}$ versus φ and extrapolating to the

zero ordinate. A value of $\varphi_m = 0.16$ was determined as maximal packaging density of the nanoparticles studied.

Einstein model:

$$\frac{\eta}{\eta_0} \approx 1 + 2.5\varphi \tag{1}$$

Frankel-Acrivos model:

$$\frac{\eta}{\eta_0} \approx \frac{9}{8} \left\{ \frac{(\varphi/\varphi_m)^{1/3}}{1 - (\varphi/\varphi_m)^{1/3}} \right\}$$
(2)

where η is the effective viscosity of suspension; η_0 is the viscosity of pure liquid; φ is the volumetric filling factor; φ_m is the maximal packaging density of 0.16 (vol. part). We designate the volumetric concentration, Φ , as described above.

Based on the discussions above, we used the Frankel–Acrivos model to determine the percolation threshold and saturation point from the viscosity data (see Fig. 7, arrows). The volume concentration wherein the Frankel-Acrivos model begins to fit the experimental viscosity data is accepted as the percolation threshold (e.g., $\Phi_{pt} \approx 4\%$). Logically, the percolation threshold is associated with the concentration wherein the viscosity starts to increase rapidly because of intensive agglomeration of nanoparticles (and hence leading to conductive pathway formation). Further increases in the volume filler concentration results in contacting of agglomerates, so a particle network is formed; this is reflected in the sharp increase of viscosity. We examine the curvature, K, for the Frankel–Akrivos equation $[K = y'' / (1 + y'^2)^{3/2}]$ by finding its first and second derivative. We then examine in more detail the concentration interval between 3 and 12%. An inflection point exists at $\Phi \approx 8\%$ (7.6% for the example dispersion studied). The first derivative of the curvature function exhibits a minimum at this point. We assume the concentration value of 8% as the approximate limiting value (the saturation point), after which the rate of viscosity rise becomes higher. We relate the qualitative changes in the dispersions due to the particle network formation throughout the concentration range (and at $\Phi_{pt}\approx$ 4% and $\Phi_{st}\approx$ 8% in particular) with the alteration of other physical properties, such as conductivity (Figs. 4 and 5) and microwave absorption (Fig. 6), but only to such an extent to which the solid film properties depend on the microstructure, and hence on the initial structure formation, determining the viscosity as well.

Correlation between viscosity, conductivity, and microwave characteristics

The relationship between rheological properties, conductivity, and microwave characteristics is the main



Figure 8 Correlation between viscosity and conductivity. The points present data for the filler concentrations: 0, 1, 3, 5, 6, 8, 10, and 12 vol % NCP in acrylic resin. Correlation coefficient of 0.966 and a relative mean square error of 6.5% are determined in the concentration range of 0–8 vol %. Arrows indicate the calculated values of the percolation threshold, $\Phi_{pt'}$ and the saturation point, Φ_{st} .

objective of this study. The experimental data of the concentration dependence of the dc-conductivity, microwave characteristics, and viscosity have been discussed in Figures 4–7, and the same critical concentrations $\Phi_{\rm pt}$ and $\Phi_{\rm st}$ have been determined for the three functions studied for a definite matrix polymer. We explain this relation by the effect of interparticle spacing, wherein interactions between nanoparticles cannot be neglected.

We calculate the interparticle distance (IPD) considering a hexagonal lattice of particles with a diameter d = 3 nm using the Pelster–Simon eq. (27), for the description of the volume filler factor $\Phi = \Phi_m [d / (d$ + IPD)].³ The IPD of about 5 and 3.3 nm was calculated at the critical concentrations of 4 and 8%, respectively. At $\Phi_{\rm pt} \approx 4\%$, the three characteristics–conductivity, MW absorption, and viscosity-began to increase (as seen in Figs. 5–7). Obviously, Φ_{pt} (IPD = 5 nm) could be attributed to the electrostatic interactions between nanoparticles, which appear if the mean distance between them is in the range of 2d.^{1,27} Such a small spacing induces both the nanoparticle agglomeration and the charge hopping. Further on, at Φ_{st} = 8%, the IPD reaches the value of 3.3 nm, which allows formation of an infinite particle network and is associated with saturation of both conductivity and microwave absorption.

Based on the above discussion of the effects of interparticle spacing, Figure 8 presents the correlation between the viscosity and conductivity at filler concentrations of 0, 1, 3, 5, 6, 8, 10, and 12%. The correlation coefficient was calculated by linear regression analysis. As seen in Figure 8, the correlation between viscosity and conductivity is very good for the filler concentration region below $\Phi_{st} = 8\%$ (the saturation point). A correlation coefficient of 0.966 and a relative mean square error of 6.3% were determined for the viscosity versus conductivity function. Further increase of the filler concentrations at $\Phi > \Phi_{st}$ leads to a different effect on both characteristics. The good correlation between the viscosity and the conductivity up to the saturation region confirms the effectiveness of using the viscosity function as a tool for predictable determination of both the percolation threshold and the saturation point.

Figure 9 shows the correlation between the microwave absorption and the conductivity of the same systems shown in Figure 8. The correlation coefficient of 0.985 is determined and the error is 7.8%, which seems to be very good in the full concentration range of 1–15% of NCP. The present results lead to a suggestion that the electrical conductivity and the microwave properties of composites have a similar behavior with increasing the volume content of carbon nanoparticles. It is associated with a nanoscale hopping mechanism, which could appear at very small IPD $\approx 2d$, due to the electrostatic interactions between nanoparticles through a very thin polymer layer.

The correlations presented in Figures 8 and 9 have a structural origin, showing that the agglomeration processes affect in a similar way the viscosity of the dispersion and both physical characteristics of the solid composite. Therefore, rheological characteristics could be used as a practical tool for preliminary prediction of the agglomerated state of dispersions in the region between the percolation threshold and the saturation point of the systems.



Figure 9 Correlation between microwave absorption and conductivity. The points present data of the filler concentrations: 1, 3, 5, 6, 8, 10, 12, and 15 vol % NCP acrylic resin. Correlation coefficient of 0.985 and a mean square error of 7.8% are determined in the full concentration range.

CONCLUSION

Nanosized carbon particles containing disordered graphite and diamond were studied as a conductive filler in acrylic, polyurethane, and epoxy resins. The rheological response of the systems is compared and discussed in relation with the resulting electrical conductivity and microwave absorption properties of the composite films. Rheology is used for characterizing the dispersed state and the agglomeration processes of nanoparticles in the matrix polymer. It is shown that the control on the rheological properties by increasing the carbon volume content and shearing during processing allows the improvement of overall conducting properties of solid composites.

Good correlations were found between the three characteristics-viscosity, conductivity, and microwave absorption-if the volume fraction of filler is below the saturation. The correlations have a structural origin, showing that the agglomeration processes affect in a similar way the characteristics of systems in the liquid and solid state. The viscosity function is proposed as a practical tool for determination of the percolation threshold and saturation point.

The samples produced in this study are examples of macroscopic nanoparticle composites. Nanosized carbon particles produced by shock wave technology may offer new opportunities to modify both the electrical and microwave properties of insulating polymer matrices. The relationship between rheology and physical properties can be applied to assess the optimal compounding conditions of carbon nanoparticles in a given polymeric system. Further work will include investigations on the conducting mechanism at low filler concentrations as well as evaluation of the effect of carbon nanoparticles on the mechanical properties of the conductive films.

R.K. thanks the Alexander von Humboldt Foundation for the support by a postfellowship program. The cooperation of S. Kolev for the microwave measurements is gratefully acknowledged.

References

- 1. Schmid, G. Clusters and Colloids; VCH: Weinheim, 1994.
- 2. Andrade, J. S.; Ito, N.; Shibusa, Y. Phys Rev B 1996, 54, 3910.

- Ponomarenco, A.; Schevchenko, G.; Enikolopyan, N. S. Adv Polym Sci 1990, 96, 125.
- 4. Pötschke, P.; Fornes, T. D.; Paul, D. R. Polymer 2002, 43, 3247.
- 5. Dishovsky, N.; Grigorova, M. Mater Res Bull 2000, 35, 403.
- Flandin, L.; Prasse, T.; Schueler, R.; Dchulte, K.; Bauhofer, W.; Cavaille, Y. J. Phys Rev B 1999, 59, 14349.
- Prasse, T.; Flandin, L.; Schulte, K.; Bauhofer, W. Appl Phys Lett 1998, 72, 2903.
- Rwei, S. P.; Ku, F. H.; Cheng, K. C. Colloid Polym Sci 2002, 280, 1110.
- 9. Feng, J.; Chan, C. M. Polym Eng Sci 1998, 38, 1649.
- 10. Luo, Y.; Wang, G.; Zhang, B.; Zhang, Z. Eur Polym Mater 1998, 34,1221.
- Mallette, J. G.; Marquez, A.; Manero, O.; Castro-Rodriguez, R. Polym Eng Sci 2000, 240, 2272.
- 12. Mucha, M.; Marszal, J. Polymer 2000, 41, 4137.
- 13. Ghosh, P.; Chakrabarti, A. Eur Polym Mater 2000, 36, 1043.
- 14. Kirkpatrick, S. Rev Mod Phys 1973, 45, 574.
- Zallen, R. The Physics of Amorphous Solids; Wiley: New York, 1983.
- Stauffer, D.; Aharony, A. Introduction to Percolation Theory; Taylor & Francis: Washington, DC, 1992.
- 17. Hiemenz, P. C. Principles of Colloid and Surface Chemistry; Dekker: New York, 1986; Chap. 4.
- 18. Carmona, F. Physica A 1989, 157, 461.
- 19. Lux, F. J Mater Sci 1993, 28, 285.
- Schueler, R.; Petermann, J.; Schuelte, K.; Wentzel, H. P. J Appl Polym Sci 1997, 63, 1741.
- Sandler, J.; Shaffer, M. S. P.; Prasse, T.; Bauhofer, W.; Schulte, K.; Windle, A. H. Polymer 1999, 40, 5967.
- 22. Chekanov, Y.; Ohnogi, R.; Asai, S.; Sumita, M. J Mater Sci 1999, 34, 5589.
- 23. Medalia, A. I. ubber Chem Technol 1986, 59, 432.
- Kotsilkova, R.; Krusteva, E. In Proceedings of the 6th European Conference on Rheology, Eurheo'2002; Münstedt, H.; Kashta, H.; Merten, J., Eds.; Erlangen: Germany, 2002, p. 99.
- Kotsilkova, R.; Krusteva, E.; Nesheva, D.; Djunova, T.; Stavrev, S. In Nanosciences & Nanotechnology IV; Balabanova, E.; Dragieva, I. 2003, 3, 169.
- Kanapitsas, A.; Pissis, P.; Kotsilkova, R. J Non-Cryst Solids 2002, 305, 204.
- 27. Pelster, R.; Simon, U. Colloid Polym Sci 1999, 277, 2.
- 28. Stavrev, S. U.S. Patent 5353708, 1994.
- 29. Bradley, J. S. In Clusters and Colloids; Schmid, G., Ed.; VCH: Weinheim, 1994; p. 549.
- 30. Schön, G.; Simon, U. Colloid Polym Sci 1995, 273, 101 and 202.
- Wong, Y. W.; Lok, K. L.; Shin, F. G. J Appl Polym Sci 2001, 82, 1549.
- Pomagailo, A. D.; Rosenberg, A. C.; Ufljand, I. E. Metal Nanoparticles in Polymers; Chemistry: Moscow, 2000.
- 33. Simha, R. J Appl Phys 1952, 23,1020.
- 34. Frankel, N. A.; Acrivos, A. D. Chem Eng Sci 1967, 22, 847.
- 35. Thomas, D. G. J Colloid Sci 1965, 20, 267.