

Room Temperature Resistance Relaxation Behavior for Carbon Black Filled Conductive Polymer Composites

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ABSTRACT: Room temperature resistance relaxation was studied with respect to carbon black (CB) volume fraction, the type of polymer matrix, and the environment. It was found that resistance of CB filled poly(methylvinylsiloxane) and polypropylene (PP) conductive composites changed at room temperature with different directions and amplitudes, depending on the filler volume fraction and the environment. The room temperature resistance relaxation was ascribed to the local Joule heat at the tunneling

junction or the swelling effect of the solvents. On the other hand, CB filled immiscible PP/Nylon 1212 blends exhibited a stable electrical conduction due to the selective distribution of CB aggregates along the interface between polymer matrices. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3083–3089, 2008

Key words: conductive polymer composites; resistance relaxation; Joule heat; carbon black

INTRODUCTION

Because of the sensitive resistance responses to many external stimuli such as mechanical force,^{1–3} solvent,^{4,5} electrical field,^{6,7} magnetic field,⁸ and ultrasonic field,⁹ conductive polymer composites (CPCs) fabricated by incorporation of conducting fillers into the insulating polymer matrix have found wide applications or great prospects in self-regulating heaters, overcurrent protectors, stress/strain sensors, mechanical damage self-monitoring materials, gas sensors, and so on.^{2,4,10,11} It is widely accepted that the electrical conduction of CPCs is due to the formation of a continuous three-dimensional percolation network throughout the matrix,^{12–14} which contributes to the conduction via direct contact of filler aggregates¹⁵ or electron tunneling across adjacent aggregates.¹⁶ Accordingly, obvious resistance changes under external stimuli are generally ascribed to one or more of the following mechanisms: (1) the destroying–rebuilding competition of the percolation network or the conducting chains,³ (2) the changes in tunneling current due to the varying gap distances and potential bar-

riers,^{14,17} (3) the changes in contact resistance between the closely contacting filler aggregates,¹⁸ and (4) the adsorption of matrix molecules on the filler surfaces.^{4,5} As most of these mechanisms are actually involved with kinetic processes, CPCs often exhibit time-dependent resistance changes at constant temperatures, stresses, or strains.^{19–30}

Many CPCs exhibit a drastic increase in electric resistivity over a temperature range around the melting point (T_m) of the semicrystalline matrix as is termed as positive temperature coefficient (PTC) effect of resistivity, which is usually followed by a rapid resistivity decrease named negative temperature coefficient (NTC) effect. The PTC effect strongly depends on the time related thermal history,^{19,20} so that thermal aging is becoming a common method to eliminate the thermal history and to stabilize the conduction behavior.^{21,22} Tao et al.²³ and Park et al.²⁴ found that annealing at temperatures below and above T_m has different influences on the redistribution of filler aggregates in the matrix and also on the PTC/NTC behavior of CPCs. Their observations were confirmed by Song and Zheng,²⁰ and were explained with respect to the breakdown and reformation of the percolation network at lower temperatures, as well as the agglomeration of carbon black (CB) aggregates and formation of percolation network in the melts. Wu et al.²⁵ further investigated the resistance decay in the melt and ascribed it to the dynamic process of CB network formation. For CB filled amorphous polymers, the effect of thermal aging was generally attributed to the movement of

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CB aggregates²⁶ or the bound rubber related bridging flocculation of the polymer chains.²⁷

Some CPCs exhibit time-dependent resistance changes under constant stresses or strains,^{28,29} which could be well related to the mechanical relaxations of the polymer matrix and the filler distribution in only the amorphous phase.³ Li et al.³⁰ reported that when exposed to solvent vapors CB filled polymer composites also show characteristic resistance increases because of structural relaxation due to matrix swelling. In this article we attempt to ascertain a new kind of resistance relaxation different from previous published results. We found that some kinds of CPCs exhibited obvious but regular resistance changes even at room temperatures without any external stresses or strains, depending on different components and environments. Such resistance changes had seldom been observed or used to be ignored if not too intensive. They were easily misunderstood for unstable contact resistance or normal resistance fluctuation, and brushed aside by simply mentioning "conditioned overnight before testing".^{6,31} It is expected that investigations on such a resistance relaxation could not only provide useful information on the conducting mechanisms of CPCs, but also help to design devices with reproducible and much stabler electrical conduction.

EXPERIMENTAL

Materials and sample preparation

Materials

Poly(methylvinylsiloxane) (PMVS, $\bar{M}_n = 580,000$, $\bar{M}_w = 675,000$, vinyl group concentration 0.08–0.10%) was provided by Hangzhou Jinshi Chemical, China. Nano-silica (SiO_2) (average particle diameter = 20 nm, specific surface area = 280 m^2/g) was supplied by Hangzhou Yadong New Material Factory, China. The main purpose of adding SiO_2 into PMVS was to adjust the operating range for a potential application in stress sensors, and results of comparative experiments showed no appreciable effect of added SiO_2 on the principle of resistance relaxation. CB (Vulcan Xc-605, density 1.85 g/cm^3 , average diameter of primary particles 25 nm) was a product of Cabot, USA. Structural control agent (diphenyl silanediol, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$) was obtained from Hangzhou Jinshi Chemical, China. Dicumyl peroxide (DCP) used as a vulcanizing agent was a commercial product. The formulations of the conductive PMVS vulcanites are listed in Table I.

Polypropylene (PP, T300, $\bar{M}_n = 80,643$, melting flow index 3.0 $\text{g}/10 \text{ min}$) was supplied by Shanghai Petrochemical, China. Nylon 1212 (melting flow index 22.43 $\text{g}/10 \text{ min}$) was obtained from Shandong

TABLE I
Formulations of CB Filled PMVS Conductive Composites

Ingredient	Parts by weight
PMVS	100
SiO_2	20
CB	Varying
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$	10
DCP	2

Dongchen Engineering Plastic, China. To eliminate the oxidation during processing,³² antioxidant B215 ($\bar{M}_n = 647$, $T_m = 180\text{--}185^\circ\text{C}$) provided by Ciba-Geigy, Switzerland was adopted.

Preparation of samples

PMVS, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, SiO_2 , and CB were added into a torque rheometer (Rheomixer 600 from Thermo-Haake) and mixed at room temperature under 30 rpm for 30 min. The mixes were heat treated at 160°C for 2 h and then put into the torque rheometer again after cooled down to room temperature, where DCP was incorporated and mixed for 10 min. The mixes were cured at 165°C and 10 MPa for 15 min to form disc samples of 20 mm in diameter and 3 mm in thickness. Two pieces of copper nets were mounted on the opposite wide surfaces of the sheet during molding to ensure good electrical contacts. After put into a muffle and postcured at $200^\circ\text{C} \pm 2^\circ\text{C}$ for 4 h, the samples were conditioned at room temperature for more than 24 h before testing to minimize the effects of residual thermal stress or filler flocculation.

PP, Nylon 1212, and CB, corresponding to a composition of 47.5/47.5/5 (PP/Nylon/CB) in weight, were mixed with a small amount of antioxidant in the torque rheometer at 195°C and 50 rpm for 15 min, followed by a compression molding at $195^\circ\text{C} \pm 5^\circ\text{C}$ and 10 MPa for 10 min to form samples with a diameter of 20 mm and a thickness of 3 mm. Two pieces of copper nets were mounted on the opposite wide surfaces of the sheet during molding to ensure good electrical contacts. PP/CB composites were prepared in the same way at 180°C . All the composites were conditioned for more than 24 h before testing.

Measurements

The resistance change with time was automatically recorded by a computer controlled system based on a digital multimeter (Escort-3146A, Schmidt Scientific Taiwan, China). Two-probe method was adopted with a measuring voltage of 1 V. Resistance R above $10^8 \Omega$ was measured using a high resistance meter (ZC36, Shanghai Precise Science Instrument, China). For studying the solvent dependence of the resist-

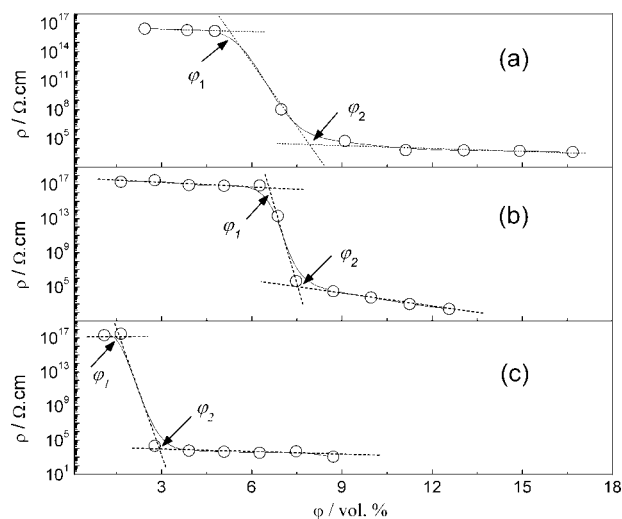


Figure 1 Room temperature resistivity (ρ) as a function of CB volume fraction (ϕ) for CB filled composites with different polymer matrices.

ance relaxation, a sample was simply immersed in the solvent filled in a beaker equipped with a cover. All electrical measurements were carried out in the thickness direction.

RESULTS AND DISCUSSION

Percolation transition

Considering that the filler content dependence of electrical conduction for CPCs could be the source of many contradictory analyses and conclusions about experimental data,²⁷ it is necessary to distinguish the location of the filler volume fraction (ϕ) with reference to the percolation threshold. Figure 1 shows the dependence of volume resistivity (ρ) versus ϕ for PMVS/CB, PP/CB and PP/Nylon/CB composites. It can be seen that these composites exhibit typical percolation phenomena in their respective transition regions, where ρ drops by several orders of magnitude. On the basis of statistical percolation theory,¹² the percolation network comes into appearance in the transition region. Table II lists the estimated lower limit ϕ_1 and upper limit ϕ_2 of the transition region for each kind of composites. The extremely

TABLE II
The Lower (ϕ_1) and Upper (ϕ_2) Limits of the Filler Volume Fraction of the Percolation Transition for Various Conductive Polymer Composites Filled with CB

Composition	ϕ_1 /vol %	ϕ_2 /vol %
PMVS/CB	5.3	8.0
PP/CB	6.5	7.5
PP/Nylon/CB	1.5	2.9

low transition region for CB filled immiscible polymer blends were generally ascribed to the selective distribution of CB aggregates along the interface of the immiscible polymer blends.^{5,33,34}

Resistance relaxation in air

Figure 2 shows the changes in relative resistance R/R_0 with time for PMVS/CB, PP/CB, and PP/Nylon/CB composites, where R_0 is the initial value at the beginning of the measurement and R is instantaneous resistance. Considering that the macroscopic Joule heat and the volume change are negligible under a minor measuring voltage of 1 V, R/R_0 basically reflects the structural evolution of the percolation network at room temperature. R/R_0 changes along different directions depending on the composition. A decrease in R/R_0 is observed in PMVS/CB

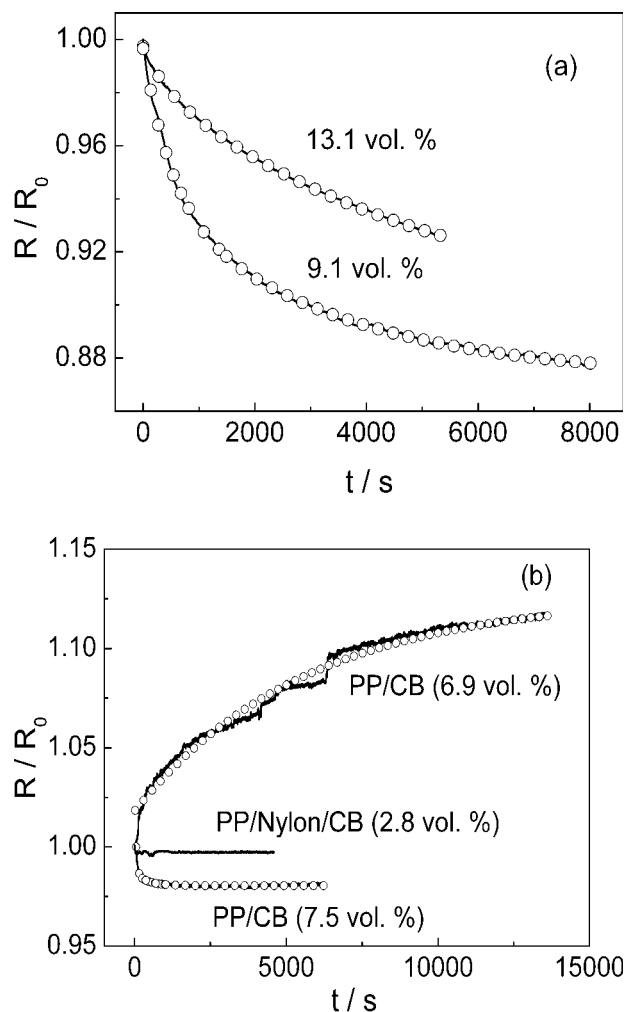


Figure 2 Relative resistance (R/R_0) as a function of time (t) in air for (a) PMVS/CB composites, and (b) PP/CB and PP/Nylon/CB composites. Curve: experimental data; Circle: fitted data.

and PP/CB composites with $\phi \geq \phi_2$. The situation is different for the composites at $\phi_1 < \phi < \phi_2$, where a decrease and an increase is observed in PMVS/CB and PP/CB composites, respectively. Investigations on CB filled high-density polyethylene or nylon resembled the observations in PP/CB composites.

These pronounced time-dependent resistance changes at room temperature differ from those generally called "resistance relaxation" at constant strains.^{3,28} Measurements on standard resistors excluded the possibility of system error induced by the measuring method and instrument. It could neither be caused by the electrical contacts, because (1) corruptions of the copper contacts by absorbed oxygen³⁵ should only result in an increase in R , (2) resistance fluctuation due to poor quality of electrical contact is hardly reversible, and (3) the dependence of resistance relaxation on matrix and also filler content could not be simply interpreted in terms of the electrical contact. In fact, copper nets have already been proved to be a reliable electrical contact at room temperature with very low values of contact resistance.^{36,37}

Figure 3 shows the resistance relaxation for PP/CB composites containing 6.9 vol % and 7.5 vol % CB, respectively, under discontinuous measuring electrical current. The arrows indicate the time at which measuring current was switched on. For the composite containing 7.5 vol % CB equal to ϕ_2 , R/R_0 decreased very slightly with time during continuous measurement while a resistance recovery occurred after the current was switched off. On the other hand, the measuring current caused a resistance increment for the composite containing 6.9 vol % CB, which could hardly recover to the original value after switching off the current. Experimental results also showed that no appreciable resistance changes could be observed even after a much longer time in absence of measuring current. Therefore, the resistance relaxation at room temperature is due to some structural changes under continuous DC measuring current, which might be attributed to the local Joule heat effect.^{6,38} Even through the global self-heating effect is not observed under a measuring voltage as low as 1 V, a local Joule heat inside the sample would occur at the close contacting area between neighboring CB aggregates where the inner tunnel field across the insulating polymer layer is high enough. The local Joule heat could either favor or hinder the electrical conduction, resulting in different resistance relaxations for different systems. On the one hand, the local Joule heat facilitates the electron hopping by thermal activation over the potential barrier,^{17,39} favoring the decrease in the local resistance. Especially, when the inner tunnel field is higher than 10^5 V/cm, the internal field emission appears so as to produce additional pathways.⁴⁰⁻⁴³ This is more pronounced for the composites with

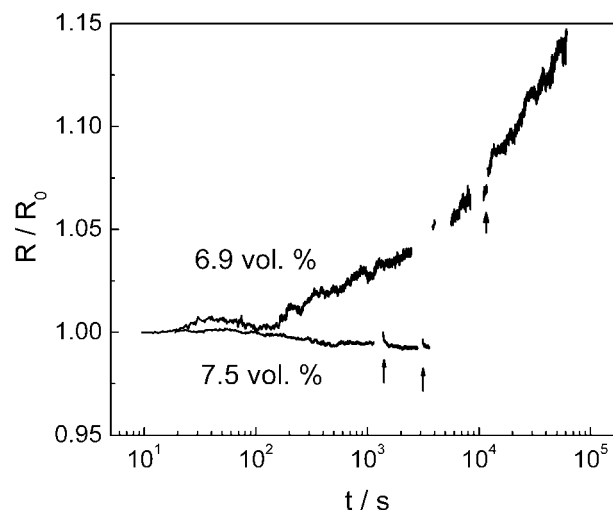


Figure 3 Relative resistance (R/R_0) as a function of time (t) in air for PP/CB composites under discontinuous electrical current at 1 V.

$\phi \geq \phi_2$. The additional pathways due to internal field emission disappear after switching off the measurement current, so that resistance could almost recover to its original value, as shown in Figure 3. On the other hand, the local Joule heat could enlarge the distance between neighboring CB aggregates,⁴⁴ thus leading to a local breakdown of the conducting pathways or a widened potential gap¹⁷ for tunneling, which should be responsible for the resistance increment for the composites with $\phi_1 < \phi < \phi_2$.

The effect of local Joule heat depends on many factors such as gap distance between conductive aggregates, crosslinking density, hardness, thermoelectric power, thermal conductivity, and the thermal expansion coefficient.²² Particularly, since the gap distance between filler aggregates critically depends on ϕ , it is expected that the amplitude of Joule heat induced resistance relaxation also exhibits marked concentration dependence. As shown in Figure 2(a), PMVS/CB composite containing 9.1 vol % CB shows more obvious resistance decrease than that containing 13.1 vol % CB because the closer to the percolation threshold the farther away from perfect is the percolation network and therefore more fragile. On the other hand, it appears that R/R_0 of CB filled semicrystalline polymer at $\phi \geq \phi_2$ behaves more steadily than conductive rubbers with comparable CB contents referring to the percolation threshold. As shown in Figure 2(b), R/R_0 of PP/CB composite containing CB of 7.5 vol % rapidly reaches a plateau after a short time of decrease.

Although many CPCs exhibit an obvious resistance relaxation at room temperature, composites containing immiscible polymer components exhibit highly stable electrical conduction. As shown in

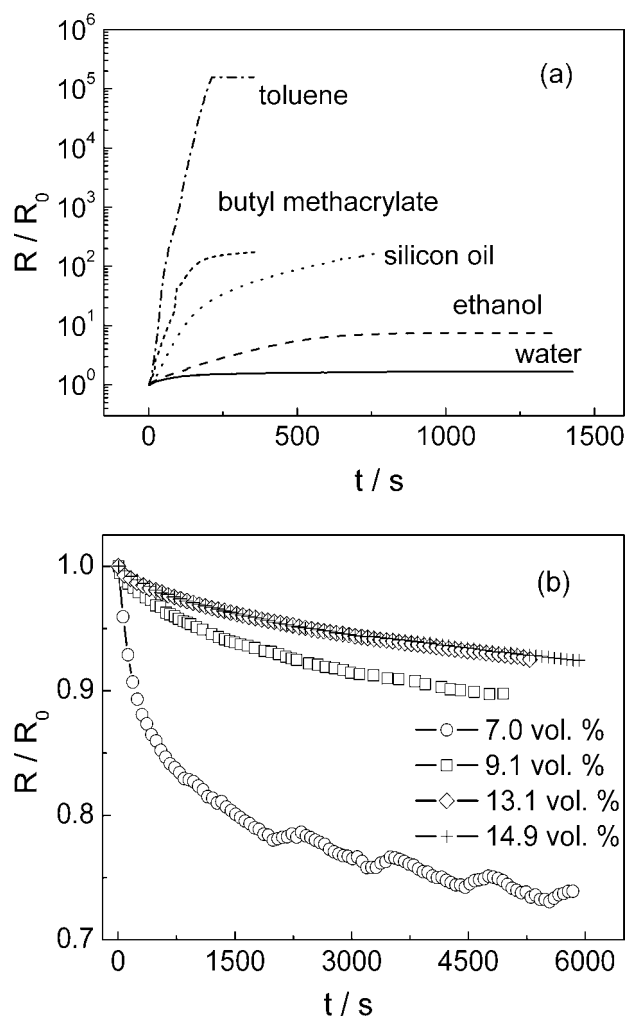


Figure 4 Relative resistance (R/R_0) as a function of time (t) in (a) different kinds of media (toluene, butyl methacrylate, methylphenyl silicon oil, ethanol, and water) for PMVS/CB composite containing CB of 9.1 vol % and (b) castor oil for PMVS/CB composites with different CB volume fractions.

Figure 2(b), R/R_0 for PP/Nylon/CB composite with ϕ located in the percolation transition region only fluctuates in very small amplitude. The stable electrical conduction might result from the selective distribution of CB aggregates along the interface of the immiscible polymer blends^{5,33,34} due to entropy penalty-induced self-assembly.⁴⁵ Our further investigations show that CB filled polymer blends of polystyrene and Nylon 6 also exhibit a fairly favorable stability of R at room temperature. It is therefore expected that the Joule heat induced resistance relaxation could be largely eliminated by applying discontinuous measuring current or choosing proper polymer blends as matrices.

Because the effect of resistance relaxation must be excluded when examining the dependence of the electrical conduction on external stimuli, it is neces-

sary to give a quantitative description on the resistance relaxation. As shown in Figure 2, the relative resistance change could be generally described with a second-order exponential function given as

$$R/R_0 = a + b \exp(-t/\tau_1) + c \exp(-t/\tau_2) \quad (1)$$

where a , b , and c are constants and τ_1 and τ_2 are the mean relaxation times, respectively. Equation 1 confirms that the effect of Joule heat could be associated with multiple relaxation processes.

Resistance relaxation in solvents

As mentioned in the introduction, CPCs often demonstrate characteristic resistance changes when exposed to different solvents. However, the intrinsic resistance relaxation due to Joule heat has not yet been taken into account when studying the effect of solvents. Figure 4(a) shows changes of R/R_0 for PMVS/CB composite containing 9.1 vol % CB and immersed in various solvents while Figure 4(b) shows resistance relaxations in castor oil for PMVS/CB composites with different CB concentrations. In most of the solvents, as seen in Figure 4(a), R/R_0 increases with time in various amplitudes. The plateau for the sample immersed in toluene is due to the limitation of the measurement range. However, the resistance change in castor oil [see Fig. 4(b)] resembles that in air, and data fitting by eq. (1) gives no appreciable distinction in the variation amplitude between these two environments.

TABLE III
Solubility Parameter (Hildebrand Parameter, δ), Polarity Parameter (Fractional Polarity, P), and the Viscosity (η) at Room Temperature (20°C) for Each Solvent Studied

Solvents/polymer	$\delta/(\text{MPa})^{1/2a}$	P^b	$\eta/\text{mPa s}^c$
PMVS	15.3	0	–
Butyl methacrylate	16.8	0.096	–
Methylphenyl silicon oil	17.0	~ 0	~ 250
Toluene	18.2	0.001	~ 0.586
Castor oil	18.2	0.32 ± 0.05^d	986
Ethanol	26.5	0.268	1.19
Water	47.8	0.819	1.0019

The parameters of the polymer matrix are also listed for reference.

^a Data from: Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; Wiley: New York, 1999.

^b Data from: Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, 1991.

^c Data from: Kaye, G. W. C.; Laby, T. H. *Tables of Physical and Chemical Constants*; Longman: Essex, New York, 1995. And: <http://www.chemfinder.com>.

^d Deduced from its complete miscibility with methanol, ethanol, and acetic acid.

According to Li et al.³⁰ resistance changes in solvents could be the result of the structural relaxation due to matrix swelling. It is expected that the intrinsic resistance relaxation due to Joule heat could be shielded if the swelling effect is strong enough, which interprets the resistance increases in Figure 4(a). The swelling effect was generally associated with the solubility parameters δ of the solvent,⁴ but our experiments show that the polarity parameter P of the solvent is another controlling parameter of the swelling effect. Table III lists δ and P as well as the viscosity at room temperature for each solvent. The closer between the solubility parameters and polarity parameters of the solvent and the polymer matrix, the more pronounced is the swelling effect. This accounts for the fact that the amplitude of resistance variation decreases in the following sequence: toluene, butyl methacrylate, methylphenyl silicon oil, ethanol, water. The marked resistance increase in toluene is just due to the similar polarities between toluene and the PMVS matrix, which improves the miscibility between the polymer and the solvent.

The resistance relaxation in castor oil largely differs from that in other solvents, but rather reproduces the change in air, which coincides with previous studies that no obvious changes occur in the volume and several other physical properties of vulcanized silicone rubber after immersed in castor oil for 7 days.⁴⁶ This could be possibly ascribed to the viscosity of the castor oil which is much higher than many other solvents (as shown in Table III) and therefore greatly hinders the diffusion of solvent molecules into polymer matrix. As a result, castor oil does not bring measurable effect on the resistance relaxation and local Joule heat is still the dominant mechanism for the characteristic resistance change of PVMS composites in castor oil.

Filler volume fraction ϕ significantly influences the Joule heat induced resistance relaxation in castor oil. As shown in Figure 4(b), the amplitude of resistance relaxation decreases with increasing ϕ and gradually approaches each other. This could be interpreted in terms of the connectivity of the percolation network.⁴⁷ For CPCs near or during the percolation transition, the conducting network is far from perfection and the electrical current must get through much longer and more tortuous carbon chains, therefore any increase in the additional conducting paths could markedly improve the electrical conduction by some crosslinks or shortcuts added to the persistent CB chains, and vice versa. For composites with high CB volume fractions, the percolation network is already perfect enough so that some changes in additional paths would not bring an appreciable alteration in the connectivity, and therefore the resistance relaxation is much less obvious.

CONCLUSIONS

The measuring voltage as low as 1 V could bring a considerable resistance change with various directions and amplitudes in CPCs at room temperature, depending on the type of the matrix, the filler content, and the environment. The local Joule heat at the tunneling junction dominates the room temperature resistance relaxation in air, while the solubility parameter, polarity, and viscosity of a specific solvent are together responsible for resistance changes in the solvent. The stabler electrical conduction at room temperature for CB filled immiscible polymer blends is due to the selective distribution of CB aggregates along the interface between polymer matrices.

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