Conducting Property of Carbon Black Filled Poly(ethylene glycol)/Poly(methyl methacrylate) Composites as Gas-Sensing Materials

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ABSTRACT: To reveal the role of crystalline polymers in carbon black (CB) filled amorphous polymer composites and improve the mechanical properties of composite films, CB/poly(ethylene glycol) (PEG)/poly(methyl methacrylate) (PMMA) composites were synthesized by polymerization filling in this work. The electrical conductive property and response to organic solvent vapors of the composites were investigated. The composites, characterized by a relatively low percolation threshold ($\sim$ 2.1 wt %), had lower resistivity than CB/PMMA composites prepared with the same method because of the different dispersion status of CB particles in the matrix polymer. The concentration and mo-lecular weight of PEG notably influenced the electrical response of the composites against organic vapors. The drastic increase in the electrical resistance of the composites in various organic vapors could be attributed mainly to the swelling of the amorphous polymer matrix in the solvent but not to that of the crystalline polymer. These findings could help us to understand the conductive mechanism and electrical response mechanism of the composites as promising gas-sensing materials. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2322–2328, 2008

Key words: composites; sensors; swelling

INTRODUCTION

Electrically conductive polymeric composites consisting of carbon black (CB) and intrinsically insulating polymer matrices have been found to be applicable to vapor sensors and electronic noses in chemical, biomedical, and environmental fields to detect solvent leakage and to monitor and determine sample gases.[1–3] These conductive polymer composites function as sensors on the basis of the change in their electrical properties upon exposure to the sensing environment. Being exposed to an organic vapor, the polymer matrix of the composites swells, and this decreases the connectivity between the conductive particles within the composite films and causes a change in the electrical resistance.[4] It has been found that the effect of swelling on a composite's conducting capacity notably depends on the nature of the organic solvent; that is, at least one polymer in the composite is capable of absorbing the organic solvent vapor by a swelling or dissolution process.[5]

Because the addition of CB would degrade the processability and mechanical performance of composites, the reduction of its dosage without a loss of the conductive properties of composites is highly desired. Narkis and colleagues[6,7] found that CB-filled immiscible polymer blends, such as polypropylene/nylon 6 and high-impact polystyrene (PS)/linear low-density polyethylene, have very low percolation thresholds because of the effect of double percolation in comparison with composites using a single polymer as the matrix. The systems are rather sensitive to swelling, temperature, and pressure because of the heterogeneous distribution of CB particles.

Recently, polymerization filling has been employed to fabricate CB-filled, amorphous-polymer-based composites.[8–11] Because of the intimate interfacial contacts between the conductive filler particulates and the polymer matrix, the composites exhibit low percolation thresholds, sufficient vapor sensitivity, and reproducibility against organic vapors. The factors that can influence the response of the electrical resistance of the composite sensors against organic solvent vapors include the content and dispersity of CB in the composites, the molecular weight and molecular weight distribution of the polymer matrix, and the composite preparation method. In addition, changes in environmental conditions (e.g., temperature, species, and concentration of organic vapors) also affect the sensing performance of the composites.

Because case II diffusion of the solvent molecules in CB/poly(methyl methacrylate) (PMMA) composites plays the leading role in the swelling process,[12] CB/PMMA composite films break easily when absorbing organic vapors. The addition of poly(ethylene glycol) (PEG) would improve the mechanical properties of the composites as gas-sensing film materials. On the other hand, it is important to reveal the effect of the addition of a crystalline polymer to CB-filled amorphous polymer composites on their conductivity and gas sensibility. Therefore, CB-filled PEG/PMMA (CB/PEG/PMMA) composites with different CB and PEG contents were fabricated through *in situ* polymerization of methyl methacrylate (MMA) in the presence of CB and PEG in this work. The effects of the mass ratio of PEG to PMMA, the molecular weight of PEG, and the nature of the organic solvent on the electrical response behavior of CB/PEG/PMMA composites in organic solvent vapors were investigated.

EXPERIMENTAL

Conductive CB, supplied by Alfa Aesar Co., Ltd. (Tianjin, China) with a surface area of 80 m^2/g and an average diameter of 42 nm, was dried *in vacuo* at 110°C for 48 h before use. The monomer, MMA, was distilled two times, and the initiator, benzoyl peroxide (BPO), was purified by recrystallization from chloroform and methanol before the polymerization filling. PEG (number-average molecular weight = 400, 600, or 1450) was dried at 30°C *in vacuo* for 48 h before use.

CB/PEG/PMMA composites were prepared as follows. Typically, 1.6 g of CB, 16.0 g of MMA, 2.0 g of PEG, and 0.4 g of BPO were added to a 100-mL flask with a reflux condenser. After being treated by ultrasonic agitation for 0.5 h, the mixture was stirred at 90–95°C under nitrogen for 20–30 min. After being dried *in vacuo* at room temperature for 48 h, the product was weighed, and the monomer conversion rate and CB content were calculated. Afterwards, the product was added to 40 mL of CHCl$_3$ and stirred for 2–3 h at room temperature to produce pasty composites.

The subsequent preparation of the specimens for measuring electrical resistance and electrical responses to saturated organic solvent vapors is described in our previous article in detail.[8] The parameter that quantifies the variation of composites' resistance in saturated solvent vapor is named the maximum responsivity or R_{max}/R_0, where R_{max} is the maximum resistance of the composites in organic vapor and R_0 is the initial resistance of the composites in air before they meet the testing vapor. The response time, Δt_{max}, is defined as the time needed to reach the maximum responsivity. The response

rate, V_{max}, is defined as the ratio of the maximum responsivity over the response time.

To observe the dispersion status of the conductive fillers in the matrix polymer, an XL-30 scanning electronic microscope (Philips, Eindhoven, Holland) was employed. The samples were obtained through freeze fracturing and then gold sputtering before the observation.

RESULTS AND DISCUSSION

Inherently insulating polymers can be made conductive with the incorporation of electrically conducting fillers, and this is usually attributed to a percolation effect. The composites change from an insulator to a semiconductor and/or conductor with a rise in the filler content. The dependence of the electrical resistivity of CB/PEG/PMMA composites prepared by polymerization filling on the CB content is shown in Figure 1. The percolation range evidently lies within CB concentrations of approximately 1.0–6.0 wt %. According to the peak position of the first derivative of electrical resistivity with respect to the CB fraction, it can be roughly estimated that the percolation threshold for the composites lies at about 2.1 wt %. To demonstrate the effect of the addition of PEG on the electrical resistivity of the composites, CB/PMMA composites were also prepared by polymerization filling under the same reaction condition. As shown in Figure 1, the electrical resistivity of CB/PEG/PMMA composites is about 1 order of magnitude lower than that of CB/PMMA composites at the same CB concentration in the percolation region. This means that the electrical conductive pathways can be established more easily in CB/PEG/PMMA composites than CB/PMMA composites. Figure 2 presents scanning electronic microscopy (SEM) micrographs of CB/PEG/PMMA composites with
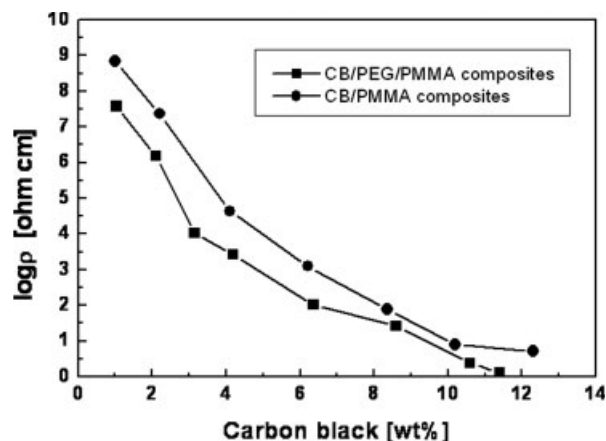

Figure 1 Electrical resistivity (ρ) of CB/PEG/PMMA (10/80) and CB/PMMA composites prepared by polymerization filling as a function of the CB content. The number-average molecular weight of PEG was 1450.
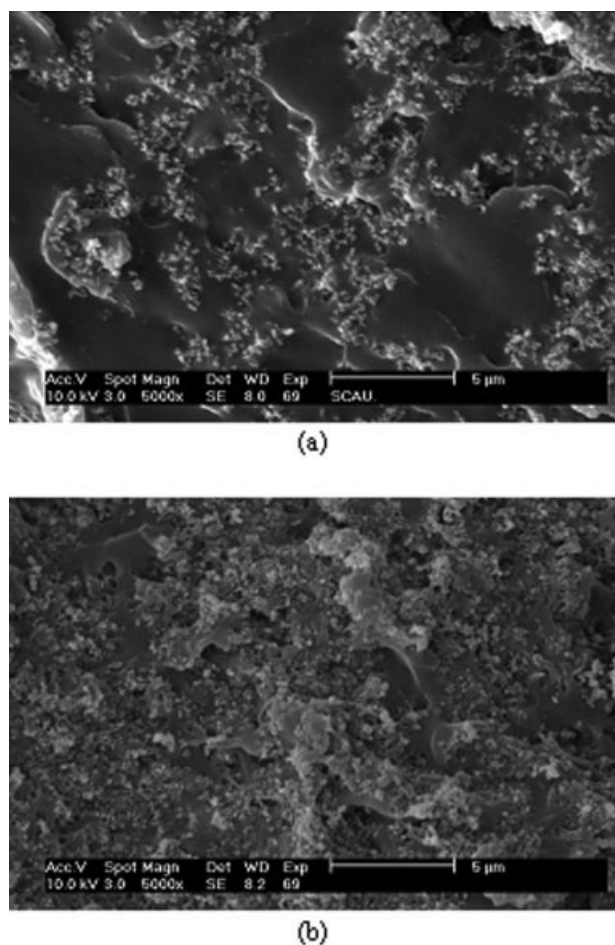
(a)

(b)

Figure 2 SEM micrographs of CB/PEG/PMMA (10/80) composites prepared by polymerization filling. The CB contents were (a) 2.1 and (b) 8.5 wt %.

different CB contents. Unlike the even distribution of CB particles in the polymer matrix for CB/PMMA composites,[13] the small CB aggregates in CB/PEG/PMMA composites can be clearly seen in Figure 2(a,b) because of the influence of PEG. The addition of the crystalline phase leads to an increase in effective contacts among CB particles; this ensures the formation of conductive networks at a lower CB concentration. In addition, clear lines of demarcation between PEG and PMMA cannot be observed when the PEG/PMMA mass ratio is 10/80. This indicates that PEG molecules might be soluble in the PMMA matrix, and a miscible polymer blend might be obtained because of the good affinity of PEG.

Figure 3 gives the maximum responsivity of CB/PEG/PMMA composites against acetone, CHCl$_3$, and benzene vapors as a function of the content of CB, which is a good solvent of PMMA. The strongest response is observed at a CB concentration (8.5 wt %) much higher than the percolation threshold of the composites. This coincides with the results for other CB/polymer composites.[8–11] The effects of the nature of the
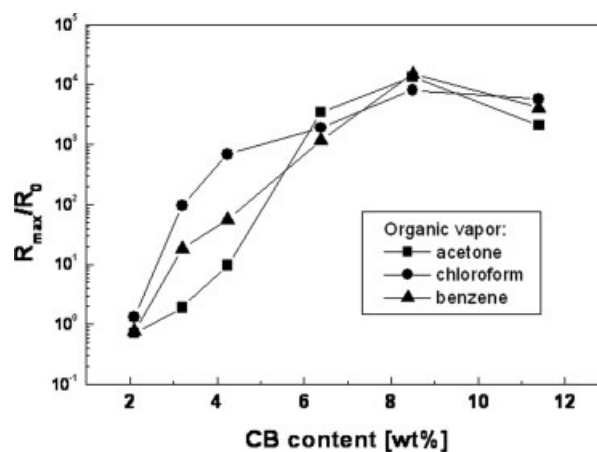
Figure 3 Dependence of the maximum electrical responsivity (R_{max}/R_0) of CB/PEG/PMMA (10/80) composites on the CB content in various organic vapors at 30°C.

polymer matrix, the filler particulates, and the filler/matrix interaction should be considered.

With respect to CB-filled polymer blends, the influence of the polymer matrix concentration should be discussed. Figure 4 shows the effect of the PEG concentration on the electrical resistivity of CB/PEG/PMMA composites with a CB content of about 8.4 wt %. Obviously, the lowest electrical resistivity of CB/PEG/PMMA composites is observed at a 10 wt % PEG concentration. Interestingly, the electrical resistivity of the composites notably increases from 91.4 to 1.99 × 10^3 Ω cm when the PEG concentration rises from 10 to 20 wt %. Besides, the electrical resistivity of the composites further increases with the PEG concentration. To clearly understand the drastic variation in the composites' resistivity, the morphologies of the composites were examined with SEM
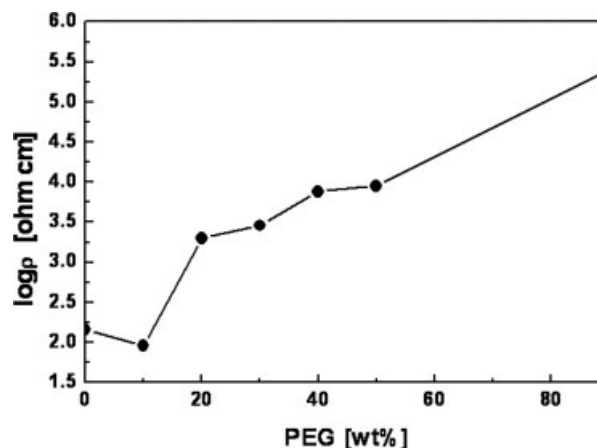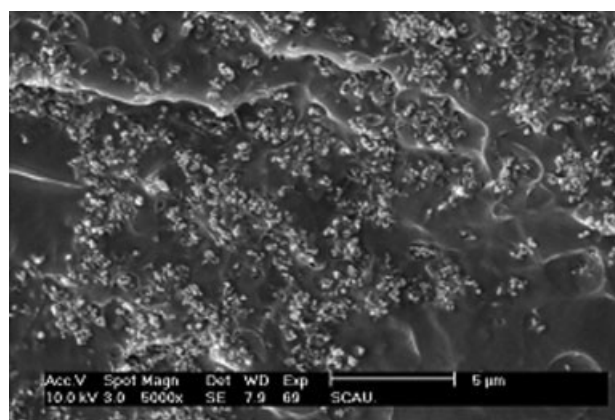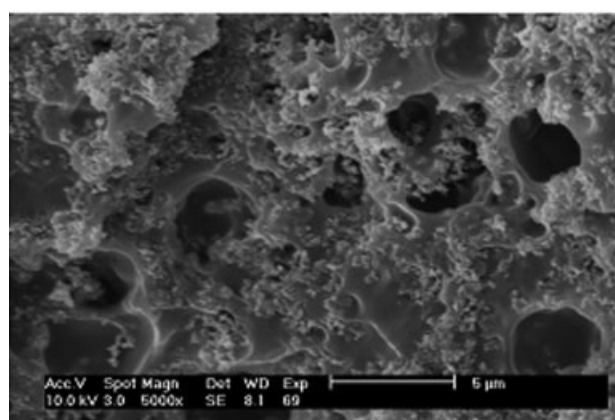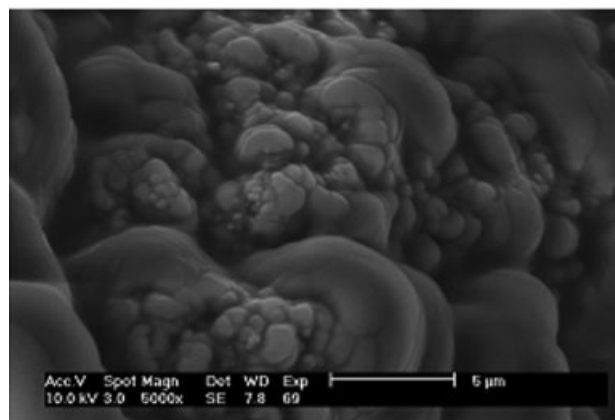

Figure 4 Dependence of the electrical resistivity (ρ) of CB/PEG/PMMA composites with a CB content of about 8.4 wt % on the PEG concentration. The number-average molecular weight of PEG was 600.

(a)

(b)

(c)

Figure 5 SEM micrographs of CB/PEG/PMMA composites with a CB content of about 8.4 wt % prepared by polymerization filling. The PEG/PMMA ratios were (a) 0/90, (b) 20/70, and (c) 50/40.

with PEG concentrations of 0, 20, and 50 wt %. As shown in Figures 5(a) and 2(b), a relatively even distribution of small CB aggregates in the polymer matrix and closer filler/matrix contacts can be obtained at a 0 or 10 wt % PEG concentration. Comparatively, larger CB agglomerates can be seen with increasing

PEG concentration, as shown in Figure 5(b,c). When the PEG concentration reaches 50 wt %, CB aggregates, nearly surrounded by the polymer matrix, cannot come together to form three-dimensional conductive networks. Obviously, the conductive mechanism involved in the composites is related to the dispersion status of CB particles in polymer blends.

To explain more clearly the distribution state of CB particles, the CB/PEG/PMMA composites were extracted in a Soxhlet apparatus with water for 72 h. Figure 6 shows the morphologies of CB/PEG/ PMMA composites (8.4 wt % CB with a PEG concentration of 20 or 30 wt %) when the PEG phase was removed. Many huge hollows or holes can be clearly seen. Furthermore, few CB particles were removed from the polymer matrix in the extraction process. These results demonstrate that CB particles are mainly distributed in the PMMA phase.

The effect of the PEG concentration on the maximum responsivity and response time of CB/PEG/ PMMA composites against saturated $CHCl_3$ vapor at
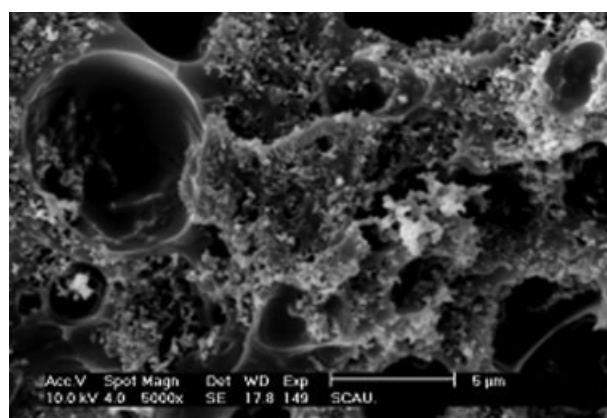
(a)
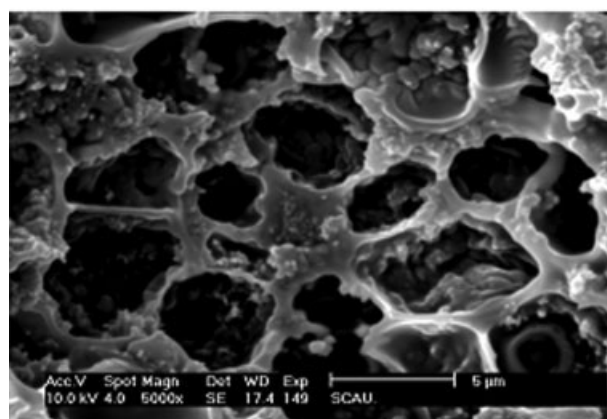
(b)

Figure 6 SEM micrographs of CB/PEG/PMMA composites (CB content = 8.4 wt %) when the PEG phase was removed by water. The PEG/PMMA ratios were (a) 20/70 and (b) 30/60.
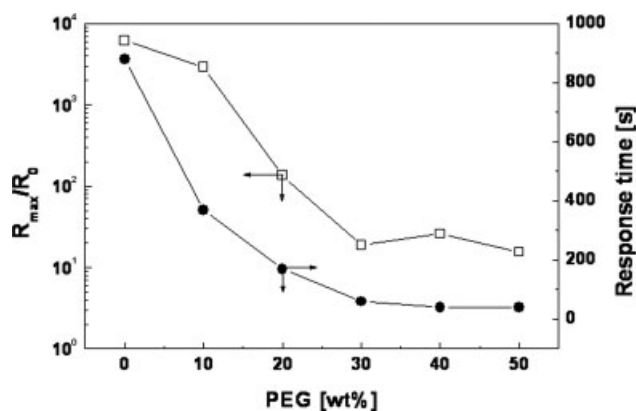
Figure 7 Effect of the PEG content on the maximum responsivity (R_{max}/R_0) and response time of CB/PEG/PMMA composites in CHCl₃ vapor at 30°C.

30°C are shown in Figure 7. The maximum responsivity of the composites sharply decreases from 2.9×10^3 to 19 times with the PEG concentration increasing from 10 to 30 wt %. That is, the higher the PEG concentration is in the composites, the lower the maximum responsivity is of the composites in organic vapor. This result indicates that the drastic variation of electrical resistance of the composites in organic solvent vapors mainly results from the volume expansion of the amorphous phases in the matrix polymer. Li et al.[14] found that the contribution of the crystalline polymer phase in CB-filled triblock copolymer PS–PEG–PS composites to electrical resistance changes of the composites in organic solvent vapors was negligible. With respect to CB/PEG/PMMA composites, the swelling or partial dissolution of the amorphous PMMA should be the most important factor for the electrical response behavior of the composites in organic vapor. On the other hand, the authors believe that high electrical resistivity of the composites with a high PEG concentration also results in low responsivity of the composites in organic vapor.

In addition, as shown in Figure 7, the response time of the composites against saturated CHCl₃ vapor also appears to rapidly decrease with the increase in the PEG concentration. Such a phenomenon should be attributed to the addition of PEG with a low molecular weight (number-average molecular weight = 600). Because PEG as a plasticizer can reduce the glass-transition temperatures and viscosity of the composites, this makes organic vapor sorption and permeability in the composites easier. Lewis et al.[15] demonstrated that plasticized polymer composites with a lower glass-transition temperature showed more rapid responses to the test analyte vapors. When they were exposed to saturated solvent vapors, the absorption induced amorphous matrix swelling, and CB particle disconnection

was faster in the composites with a higher PEG concentration.

The molecular weight of the polymer matrix is another important factor influencing the electrical resistivity and responsivity of CB-filled polymer-based composites. As shown in Table I, the electrical resistivity of CB/PEG/PMMA composites (CB content = 8.4 wt %) decreases with the increase in the molecular weight of PEG. This is because CB particles in a lower molecular weight polymer matrix aggregate more easily to produce larger CB agglomerates on account of the flowability of the matrix polymer or the mobility of the macromolecular chains of the matrix. Therefore, the three-dimensional conduction networks will be built more difficultly. Table I also shows the effect of the molecular weight of PEG on the maximum responsivity and response rate of the composites in saturated CHCl₃ vapor. It is clear that the higher the molecular weight is of PEG, the more sensitive the composites are to organic vapors, and the quicker the composites' response is.

Table II shows the electrical resistance response data of CB/PEG/PMMA composites against various organic vapors at 30°C. The electric resistance of the composites drastically increases to 7.8×10^3 to 1.7×10^4 times in benzene, chloroform, ethyl acetate, and acetone vapors, which are good solvents for PMMA. This result supports the potential of the composites serving as gas sensors. On the contrary, methanol is not a good solvent of PMMA. The maximum responsivity of the composites in methanol vapor is only about 260 times. Obviously, the maximum responsivity of the composites in organic vapors should be related to the difference of the solubility parameters ($|\Delta\delta|$) between the organic solvent and PMMA, as shown in Table II. Besides, V_{max} follows the order as a function of the vapor species: chloroform > acetone > ethyl acetate > benzene ≫ methanol. It should be related to the saturated vapor pressure of the organic solvent (see the p^0 values in Table II). The higher saturated vapor pressure of the organic solvent usually corresponds to a higher response rate. The difference between the responses of the

TABLE I
Effect of the Molecular Weight of PEG on the Electrical Resistivity (ρ) and Responsivity of CB/PEG/PMMA Composites[a]

M_n[b]	CB content (wt %)	ρ (Ω cm)	R_{max}/R_0[c]	Δt_{max} (s)	V_{max} (s⁻¹)
400	8.39	95.2	1343	260	5.2
600	8.35	91.4	2935	270	10.9
1450	8.5	26.4	8069	290	27.8

[a] The PEG/PMMA mass ratio was set at 10/80.
[b] Number-average molecular weight of PEG.
[c] Organic vapor = CHCl₃; testing temperature = 30°C.

TABLE II
Electrical Response Data of CB/PEG/PMMA Composites (8.5 wt % CB and 10/80 PEG/PMMA) in Various Vapors at 30°C

Vapor	R_{max}/R_0	Δt_{max} (s)	V_{max} (s^{-1})	p^0 (10^4 Pa)[a]	$|\Delta\delta|$ (J$^{1/2}$/m$^{3/2}$)
Chloroform	8,070	290	27.8	3.23	2.0
Acetone	17,770	780	22.8	3.79	0.9
Ethyl acetate	11,910	950	12.5	1.61	2.8
Benzene	7,880	790	10.0	1.59	2.4
Methanol	260	1,200	0.22	2.16	8.7

[a] Saturated vapor pressure of the solvent at 30°C.[16]

composites to different good solvent vapors shows that the vapor-induced variation in the electrical resistance is controlled by both thermodynamic and kinetic factors. In other words, the drastic rise of the electrical resistance of the composites can be attributed mainly to the sufficient swelling of the polymer matrix, which results in the disconnection of conducting networks in the composites. To observe more clearly the electrical responses of the composites against different organic vapors, the time dependence of the electrical response of CB/PEG/PMMA composites (8.5 wt % CB content) versus various organic vapors is shown in Figure 8. Obviously, it is similar to the electrical responses of CB/PMMA composites against organic vapors.[13] It is further demonstrated that the electrical response of CB/PEG/PMMA composites in organic vapors is mainly due to the swelling of PMMA phases.

Because the swelling of the polymer matrix is an important factor for the electrical response of CB/polymer composites against organic vapors, the morphologies of CB/PEG/PMMA (10/80) composites (CB content = 8.4 wt %) swelling in CHCl$_3$ vapor were observed by SEM. As shown in Figure 9, the

swelling of the polymer matrix is very obvious in comparison with Figure 2(b). The result is different from that reported by Tsubokawa et al.,[17] who supposed that CB-filled crystalline or semicrystalline polymer composites after absorbing a solvent vapor would form honeycomb-like pores.

CONCLUSIONS

CB/PEG/PMMA conductive composites are characterized by a relatively low percolation threshold ($\sim$ 2.1 wt %). The electrical resistivity of the composites is lower than that of CB/PMMA composites with the same CB content in the percolation region. The concentration and molecular weight of PEG notably influence the electrical resistivity of the composites because they may affect the distribution of CB particles in the polymer matrix. It has been demonstrated that CB particles are mainly distributed in the PMMA phase.

The PEG concentration and molecular weight are also important factors influencing the electrical responses of CB/PEG/PMMA conductive composites against organic vapors. The drastic variation of the electrical resistance of the composites in organic solvent vapors mainly results from the volume expansion of the amorphous phases in the matrix
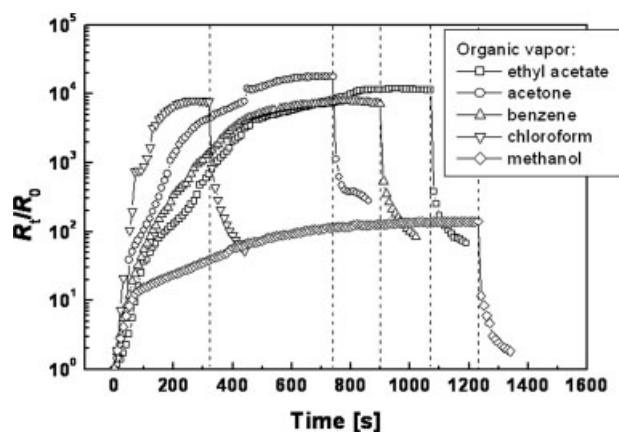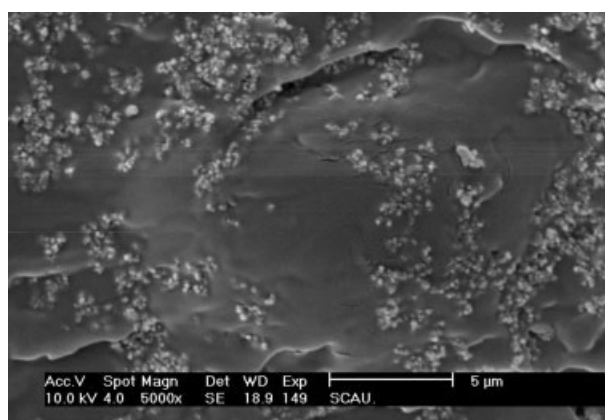

Figure 8 Electrical response curves of CB/PEG/PMMA composites (CB content = 8.5 wt %) to various organic vapors. The dashed lines define the vapor absorption and desorption zones. R_t/R_0 is defined as the time dependence of composites resistance variation, where R_t is the transient resistance and R_0 is the original resistance.

Figure 9 SEM micrograph of the swelling of CB/PEG/PMMA (10/80) composites (CB content = 8.4 wt %) in CHCl$_3$ vapor.

polymer. Compared with CB-filled crystalline or semicrystalline polymer composites, these composites have different swelling behavior. These findings should help to reveal the role of crystalline polymers in CB-filled amorphous polymer composites.

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