Time dependent percolation of carbon black filled polymer composites in response to solvent vapor

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Conductive composites made by mixing insulating polymers and conducting fillers can be used as gas sensors owing to the effect that the composites resistance increases drastically on being exposed to organic solvent vapors and returns to the initial value when the materials are removed to dry air [1]. One might thus quantify and distinguish odors of interests accordingly. It is generally believed that matrix swelling, which enlarges the inter-filler distances, accounts for the sensing ability [2].

From the point of view of percolation, this matrix swelling induced switching from low to high resistance of the composites should have the same nature as filler aggregation induced switching (that describes the abrupt change of composite conductivity with changing filler loading) and temperature-induced ones (PTC, positive temperature coefficient phenomenon) [3]. That is, because the contact status of the fillers (or inter-filler gap) determines the conduction level of the composites, any stimulation that can result in variation in the filler arrangement would provide corresponding excitation-controlled function. It explains that one composite is associated with diverse sensitivities to temperature, pressure and environment [1, 4]. On the other hand, as a result of viscoelastic feature of polymers, the electrical percolation in polymer composites was found to be a function of molding time [5], melt viscosity of matrix [5], annealing time [6, 7], and rate of heating [8]. In short, microstructure relaxation of composites should be closely related to the reversible formation and destruction of the conduction paths.

The present communication reports the time dependence of the percolation habit in response to organic vapor, in hope of providing knowledge that enables a comprehensive understanding of the percolation behavior in polymer composites within a uniform framework. Besides, it is also expected to develop a simple approach to inspect the structure evolution of the composite materials in solid state.

In this work, water-borne polyurethane filled with carbon black via latex blending acts as the model composite. The selection of the matrix is based on the following considerations: (i) synthesis of water-borne polyurethane belongs to environmental friendly process, which would not generate pollution like other polymerisations; (ii) chemical structure of the soft and hard segments of the polymer can be easily changed to satisfy needs of properties and applications; and (iii) the polymer latex possesses good film formability, which facilitats composites manufacturing. Recently, the authors showed that by adjusting the sizes of the polymeric spheres, the percolation threshold of carbon black/water-borne polyurethane system can be as low as 0.2 vol% (∼0.1 wt%), and the tensile strength of the composites is also be increased [9]. These advantages that are seldom observed in conventional particulate composites might ensure the performance of the composites as gas sensors.

Polyoxypropylene glycol (molecular weight = 2000) acting as the soft segments of the water-borne polyurethane in this work, was supplied by Jinling Petrochemical Company of Nanjing, China, and dried at 120 °C in vacuum for 24 hrs before use. Analytically pure ethylenediamine anhydrous (EDA), triethylamine (TEA) and dibutyltin dilaurate were dehydrated via 4 Å molecular sieves for more than 1 week prior to the experiments. Dimethylolpropionic acid (DMPA) was dried in vacuum at 80 °C for 24 hrs. Isophorone diisocyanate (IPDI) was used without further purification. Carbon black (type XC-72, specific surface area = 254 m^2/g, DPB value = 174 ml/100 g, particle size

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= 50–70 nm), purchased from Cabot Co. Ltd., was dried in vacuum at 110 °C for 48 hrs before use.

The carbon black/water-borne polyurethane (CB/WPU) composites were prepared by adding the fillers into urethane prepolymer before emulsification. The latter with the terminal isocyanate (OCN-R-NCO) was prepared by the reaction of slightly superfluous IPDI with polyoxypropylene glycol. A typical procedure is described as follows. 20.0 g of the polyether were heated up to 120 °C for 4 hrs. When the temperature is cooled to 80 °C, 8 droplets of the catalyst dibutyltin dilaurate and 6.2 g of IPDI were added. After 2 hrs of reaction, 1.09 g DMPA (dissolved by small amount of DMF) was added into the mixture. The reaction proceeded for additional 4 hrs and then certain amount of carbon black is incorporated. After 10 h, the mixture was cooled to room temperature and neutralized with TEA. An aqueous dispersion was obtained by adding water and the chain extender EDA.

The CB/WPU conductive composite films were obtained by coating the aforesaid latex onto epoxy plates with comb electrodes, which were dried at ambient temperature for at least 1 week. After that, the composite films 40–60 μm thick were stored in a desiccator for further electrical measurements. Electrical response of the composites to solvent vapor was detected by hanging the electrode coated with the composites film in a glass conical flask containing pure solvent at the bottom. The distance between the composites and solvent surface is about 4 cm. Besides, the resistance variation of the composites with absorbed solvent in dry air was measured by hanging the composites in a glass conical flask containing silica gel at the bottom. DC electric resistance was recorded by a digital multimeter at 30 °C. The corresponding responsivity is characterized by the ratio of the transient resistance to the initial resistance in air.

Fig. 1 illustrates the dependence of composites conductivity on CB content. The percolation threshold is roughly estimated to be 0.95 wt%, much lower than the values of conventional composites (>10 wt%). It is believed that the following factors are responsible for the significantly reduced percolation threshold [9]. (i) When water evaporates, the hydrophobic soft segments of WPU favor inter-diffusion of the macromolecules across the boundary, eventually resulting in compact interlocking of the latex particles and segregated structures with large polymeric domains, and rather thin inter-domain gaps available for CB deposition. (ii) The strong interaction between the ionic hydrophilic groups on WPU and the polar groups on CB ensures more intimate mixing, and lowers the randomness of CB dispersion.

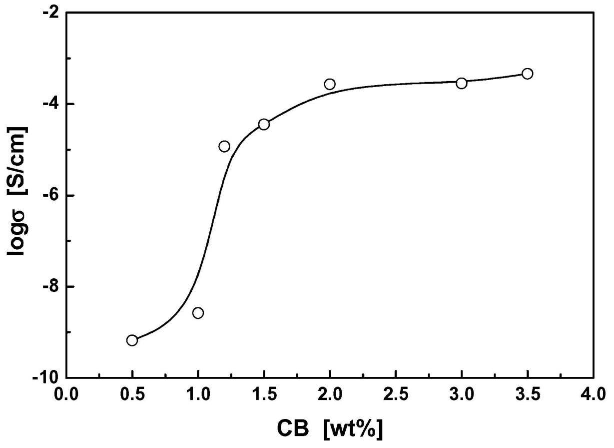

Figure 1 Room temperature electrical conductivity, σ, of CB/WPU composites as a function of carbon black content.

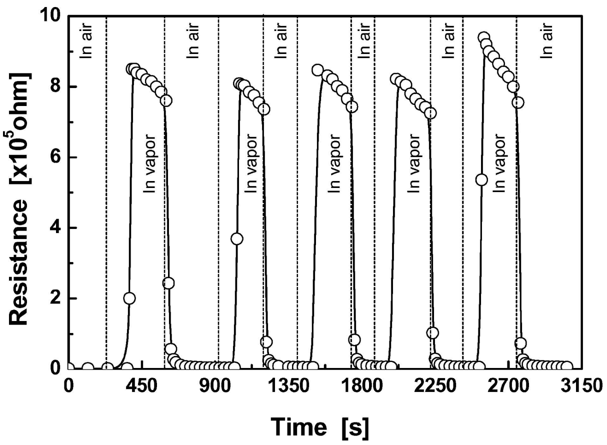

Figure 2 Cyclic responses of electrical resistance of CB/WPU composites against saturated acetone vapor at 30 °C as a function of time. CB content: 5.0 wt%.

When the composites meet an organic vapor (Fig. 2), the resistance increases by several orders of magnitude as stated before. Besides, the original resistance can be recovered when the composites are transferred to air. Obviously, the reversible variation in the resistance can also be attributed to the percolation phenomenon. Owing to solvent sorption and desorption, the matrix polymer is swelled and deswelled accordingly, leading to changes in the contact number of filler particles [10].

From Fig. 2, it is seen that the change in composites resistance does not occur immediately after the surrounding atmosphere is changed. Some time is required. It is reasonable because migration of solvent molecules in CB filled polymer composites belongs to Case II diffusion [11]. The matrix has to relax for responding to the osmotic swelling pressure and to rearrange the macromolecular chains to accommodate the penetrant molecules. Accordingly, the CB redistribution is forced to take place since the mobility of CB is controlled by the bulk mobility of the polymer surrounding the CB particles [6]. If the earlier analysis is correct, the time needed to initiate resistance variation in response to solvent vapor should be a function of CB content. After all, formation of conduction networks depends on the effective number of contacts of CB particles. As illustrated in Fig. 3, the response times of the composites are arranged in the same order as the CB contents: 2.0 wt% < 3.5 wt% < 5.0 wt%. It manifests that the composite with filler content close to the percolation threshold (i.e., 0.95 wt%) exhibits the shortest response time. The results coincide with the earlier deduction. The higher the CB concentration, longer is the time needed to destroy the conduction networks.

Since the response manner is a function of structural relaxation, as manifested earlier, Arrhenius relationship

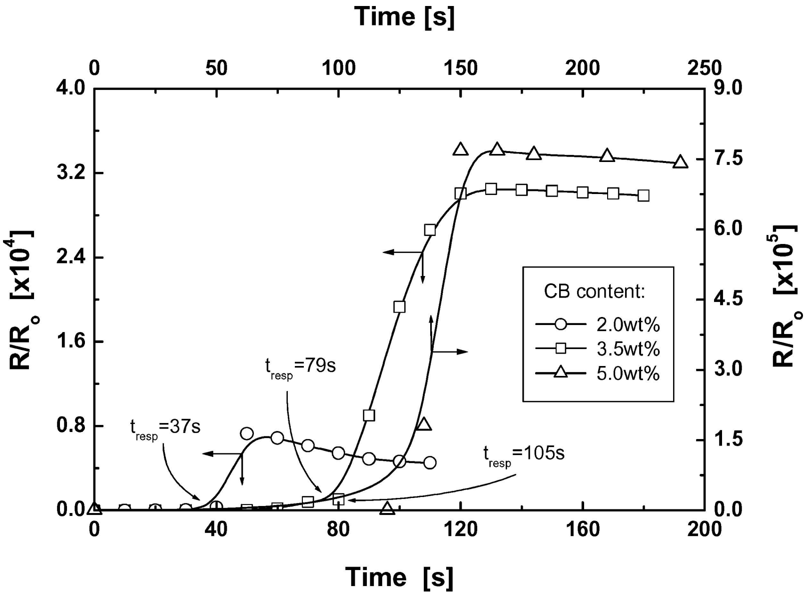

Figure 3 Responses of electrical resistance of CB/WPU composites against saturated acetone vapor. The response time, t_{resp}, is defined as the time when the composites resistance starts to remarkably increase. R: the transient resistance; R_0: the initial resistance; Temperature: 30 °C.

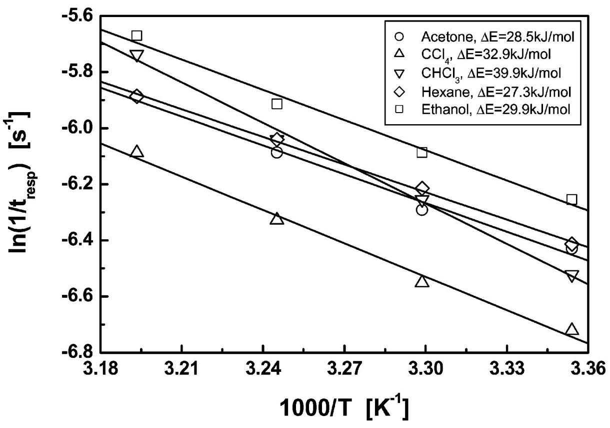

Figure 4 Arrhenius plots of inverse response time measured in different vapors at a constant vapor concentration of 10 ppt (parts per thousand by volume). CB content: 3.5 wt%. ΔE denotes the activation energy calculated from Arrhenius equation.

that describes the processes of thermal activation should be valid for the kinetics of resistance variation of the composites. Fig. 4 shows the Arrhenius plots of the inverse response time measured in different vapors from 25 to 40 °C when the vapor concentration is fixed. Evidently, this is the case as expected. Sumita *et al.* found that for the composite with filler content lower than the percolation threshold, the conductive CB network can be constructed in the matrix as characterized by a drastic decrease in composite resistance when the composite is maintained at a temperature higher than the glass-transition temperature or the melting temperature of the matrix [6, 7]. The critical annealing time at the onset of resistance reduction also changes with CB content and follows Arrhenius equation. According to these findings, they claimed that one can quantify the CB/matrix interfacial interaction. Returning to the current work, it is known that our results coincide with theirs in spite of different stimuli. Therefore, the time needed by the composites to respond to solvent vapor is able to act as a measure of the filler mobility. Because the activation energies determined in vapor-sensing tests (Fig. 4) are much lower than those obtained during the annealing tests [6, 7] due to the different mechanisms involved, monitoring of the development of aggregation structure of CB particles in matrix polymer can be carried out by the two approaches. Besides, cross-checking of the equivalency of the results from the same composites through the vapor-sensing tests and annealing tests might yield more information about the composites' microstructure and interfacial interactions.

On the basis of earlier discussion, it can be concluded that the carbon black/polyurethane composites exhibit percolation-like transition from low to high resistance in organic vapors, which resembles the annealing-induced percolation processes [6, 7] and is strongly dependent on time. The response time varies with CB content and is correlated with temperature by Arrhenius equation. According to the Arrhenius activation energies determined in organic vapors under constant concentration, one might evaluate the effect of filler/matrix interfacial interaction on the relaxation property of the matrix and the structure evolution of the composites in solid state. Further discussion in this aspect will be available in another paper of the authors.

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