Organic vapor sensibility of carbon black/polyethylene wax composites

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Composites from carbon black filled intrinsically insulating polymers are typical electric conductive materials having the advantages of easy regulation of resistivity over a wide range [1]. Depending upon the variations in external excitations, like temperature, pressure, etc. [2, 3], the composites resistances would change greatly, which provides possibilities for the materials functioning as sensors and switches.

Recently, several groups reported the feasibility of the composites employed as chemisensing materials [4–8]. The basic working principle lies again in the electrical switching induced by absorption of chemicals (in the form of vapors or liquids), i.e. reversible breakdown of the conduction paths throughout the composites as a result of volume expansion. The group of Tsubokawa achieved the grafting of crystalline polymers (polyethyleneimine (PEI) [5] and polyethylene glycol (PEG) [6]), for example, onto carbon black by direct condensation of surface carboxyl groups with terminal amino and hydroxyl groups of the grafting polymers using N,N'-dicyclohexylcarbodiimide (DCC) as a condensing agent. When the modified carbon black was incorporated into the same species of polymer as the grafting polymer, high sensibility of the composites to some organic vapors was observed as characterized by the drastic increase in electric resistance. In contrast, Narkis and coworkers focused their interests on carbon black filled immiscible polymer blends, like polypropylene (PP)/nylon 6 [7] and polypropylene/thermoplastic polyurethane (PP/TPU) [8]. The extruded filaments from the composites displayed increasing resistance upon exposure to various organic liquids. The interphase region, its quantity, and continuity played a significant role in the liquid-transport process.

For practical applications, carbon black/polymer composite films were deposited on substrates to construct chemical gas sensor array [9, 10]. Since each sensor contains a different polymer composite film, gases and gas mixtures can be identified by the pattern response of the array, which allows a much more general-purpose chemical gas sensor capable of broadly detecting and recognizing different constituents. Results indicated that a reduction in sensor area by an order of magnitude does not reduce sensor response [10]. Miniaturization of the composites sensor arrays might thus be available.

With respect to the characteristics of the matrix materials employed in chemisensor composites, it was believed that dissolve of crystalline phase of a composite matrix in solvents facilitates polymer swelling and conductive networks disruption [6]. The gas sensitivity decreases with increasing molecular weight of the matrix polymer [6]. According to these findings, it seems that a crystalline polymer with lower molecular weight should be qualified. Therefore, polyethylene wax is selected as the matrix of the carbon black filled composites in the present paper. By studying the electric responsivity of the composites against organic vapors, the feasibility of carbon black/polyethylene wax composite serving as a sensing material can be examined. It might also broaden the spectrum of the matrix polymer candidates for the functional composites. Polyethylene wax is a low molecular weight polymer with very low viscosity that helps to wet out and disperse many plastic additives and colorants. It has been used as pigment (including carbon black) dispersion media for long. Taking the advantage of these features, it is expected that the microstructural homogeneity and the gas sensitivity of the composites can be improved.

Polyethylene wax (PE wax, XH200), supplied by Chengdu Xianghe Special Wax Co., China, was used as the matrix polymer. Its viscometric average molecular weight, M_η, is 2100. Conductive carbon black (XC-72) purchased from Cabot Co. (specific surface area: 254 m^2/g, DPB value: 174 ml/100 g, average particle size: 50–70 nm), was dried at 110 °C in vacuum for 48 hr before use. To improve the dispersion of carbon black in the composites, the conductive particles were pretreated by grafting polymerization of butyl acrylate onto their surfaces. The monomer butyl acrylate, supplied by Guanghua Chemical Plant in Shantou, China, was used without further purification. The typical grafting procedures proceeded as follows. First, the emulsion consisting of lauryl sodium sulfate, octyl phenol ethoxylate, and deionized water was stirred thoroughly and heated to 80 °C. Then, the dried carbon black was added into the system. After sonication for 30 min, the initiator $K_2S_2O_8$ and the monomer were gradually incorporated under continuous stirring. Having reacted for 2 hr, the system was heated to 85 °C within 30 min. Eventually, the products were cooled down and mixed with the demulsifier (dilute chlorhydric acid). The percentage grafting of poly(butyl acrylate) (PBA) attached to the carbon black particles is 2.9, as determined by a Shimadzu TGA-50 thermogravimetric analyzer. To observe the morphological variation of carbon black

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before and after grafting treatment, the particles were thoroughly dispersed in ethanol with sonication and then characterized with a JEM-2010H transmission electron microscope (TEM).

The composites of PE wax and carbon black were prepared by solution mixing. That is, the untreated carbon black (CB) or grafted carbon black (denoted by CB-g-PBA, in which the homopolymerized PBA had been extracted in advance) was put into toluene and well dispersed in the solvent by ultrasonic. After that, the toluene solution containing dissolved PE wax was added into the system. Having been continuously stirred at 100 °C for 1 hr, the mixture was coated onto a glass electrode, prepared by winding fine copper wire onto a glass plate [11], to form composites film with an area of about 10 × 20 mm^2 and thickness of about 0.08–0.12 mm.

Electrical response of the composites to solvent vapors was measured by hanging the electrode coated with the composites film in a glass conical flask containing pure solvent (tetrahydrofuran, cyclohexane, *n*-hexane, CCl_4, CH_2Cl_2, $CHCl_3$, C_2H_5OH, benzene, toluene, and xylene) at the bottom. The distance between the composites and the solvent surface was 3–4 cm. DC electric resistance was recorded by a digital ohmmeter (Victor VC9808). When the resistance approached to an equilibrium value (absorption stage), the sample was removed to dry air (desorption stage). The corresponding responsivity is characterized by the ratio of the transient resistance to the initial resistance in air.

As a conductive composite, its switching from high to low resistance should be known first. The percolation curve of untreated CB/PE wax composites is shown in Fig. 1. With the addition of CB, the electrical resistivity of the composites is significantly reduced as expected. Accordingly, the percolation threshold can be estimated at about 4.5 wt%. Compared with the value of CB/low density polyethylene (LDPE) composites prepared by melt compounding [2], that lies in about 14 wt%, it is evident that the conductive paths are constructed at rather low filler concentration in the current PE wax based composites. This difference should result from the characteristics of the matrices and the ways of mixing. Conventional commercial LDPE has a much higher molecular weight than PE wax, and solution blending is able to bring about a good molecular level of mixing, so that smaller amount of CB is sufficient to cause insulator–conductor transition in the PE wax based composites. In general, a composite with good conductivity and low CB content is highly desired because processability of the composites is always deteriorated in the presence of particulate fillers. The CB/PE wax composites reported here have met the requirement, indicating that the matrix and compounding technique are properly selected.

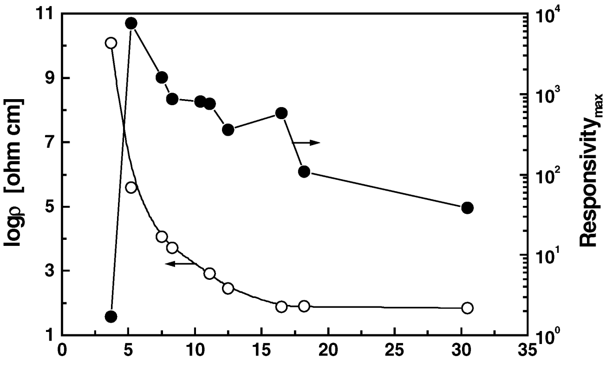

Figure 1 Electrical resistivity, ρ, and maximum responsivity to THF vapor at 35 °C of untreated CB/PE wax composites as a function of CB content.

When the composites are exposed to THF vapor, the resistance increases greatly within short time and then gradually recovers in air. This is essentially necessary for a sensing material. To have a comprehensive picture of the response behavior of the composites, the maximum responsivity of the composites is also plotted in Fig. 1 as a function of CB content. It is seen that the electrical responses are different in the case of different CB loadings. The higher CB fraction corresponds to lower responsivity. Considering that the operation mechanism is closely related to matrix swelling and interparticulate expansion, an increased CB content might certainly decrease the mobility of the particles and the damage probability of the conductive nets as well. In addition to the aforesaid phenomenon that the composites with higher CB content have reduced responsivity, it is found that the composites with CB content lower than the electrical percolation threshold also exhibit poor sensitivity. It means that the composites with rather high resistivity fail to act as chemisensors because only a few CB particles are involved in the conduction paths and the breakdown of these paths cannot induce large-scale variation in the composite resistivity. Therefore, a qualified composite candidate must have CB content higher than the percolation threshold.

Fig. 2 further examines the response behaviors of the composites against different solvent vapors. Clearly, the present composites exhibit different maximum responsivity to different organic vapors. It proves that the PE wax based composites are feasible candidates for gas sensors accompanied by certain selective sensitivity. By calculating the differences between solubility parameters of the matrix polymer and the solvents, on the other hand, it can be seen that all the $\Delta\delta$ values are quite small. It again evidences the criterion that the matrix polymer with solubility parameter close to that of a solvent is a prerequisite for an acceptable responsivity of the composites against the solvent gas [11].

When comparing the maximum responsivity of the composites to different solvent vapors (Fig. 2), it is somewhat difficult to find out the regularity. However, some useful information can be acquired in case the solvents are classified according to their structural similarity. For the group of $CHCl_3$, CH_2Cl_2, and CCl_4, for example, higher saturated vapor pressure of the solvent corresponds to higher maximum responsivity of the composites. This principle also works in the case of other two groups, the one of cyclohexane and *n*-hexane, and the other of toluene, xylene, and benzene. It means that the response process is a thermodynamic one, in which the solvent vapor concentration plays a leading role.

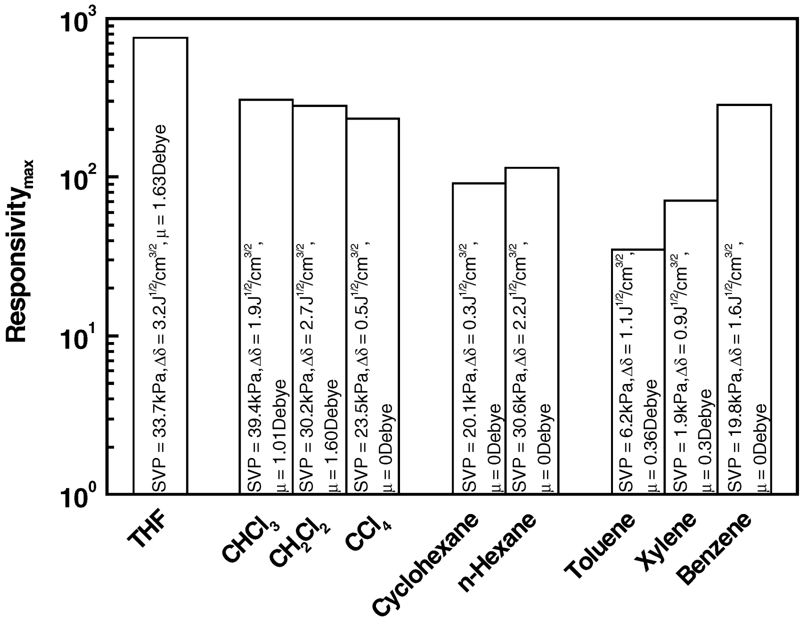

Figure 2 Maximum responsivity of untreated CB/PE wax composites (CB content: 11.1 wt%) to diverse organic vapors at 35 °C. SVP and μ denote saturated vapor pressure and dipole moment of the solvent, respectively. The value of $\Delta\delta$ represents the absolute difference between the solubility parameters of PE wax and the given solvent.

We should be aware of that some polar substances were inevitably introduced into PE wax during its manufacturing. As a result, polarity of the solvents should be taken into consideration owing to the interaction between PE wax and the polar portions of the solvents. This might account for the complexity of the dependence of the maximum responsivity on solvent species. Otherwise, exposure to $CHCl_3$ vapor should have resulted in the highest responsivity over all the other solvents appearing in Fig. 2 as it has the highest saturated vapor pressure.

Although the above discussion reveals the potential of the PE wax composites incorporated with untreated carbon black as vapor sensing materials, it still remains open whether the responsivity can be further improved. Considering that Tsubokawa and coworkers have shown the effectiveness of grafted carbon black in increasing the dispersibility of the fillers and gas responsiveness [5, 6], the authors of the present work also follow similar technical route and briefly look into the results hereinafter.

The untreated CB particles appear in the form of agglomerates, in which the primary particles connect with each other having branched chain-like structure (Fig. 3a). These agglomerates are very resistant to disintegration. The limited shear force applied during

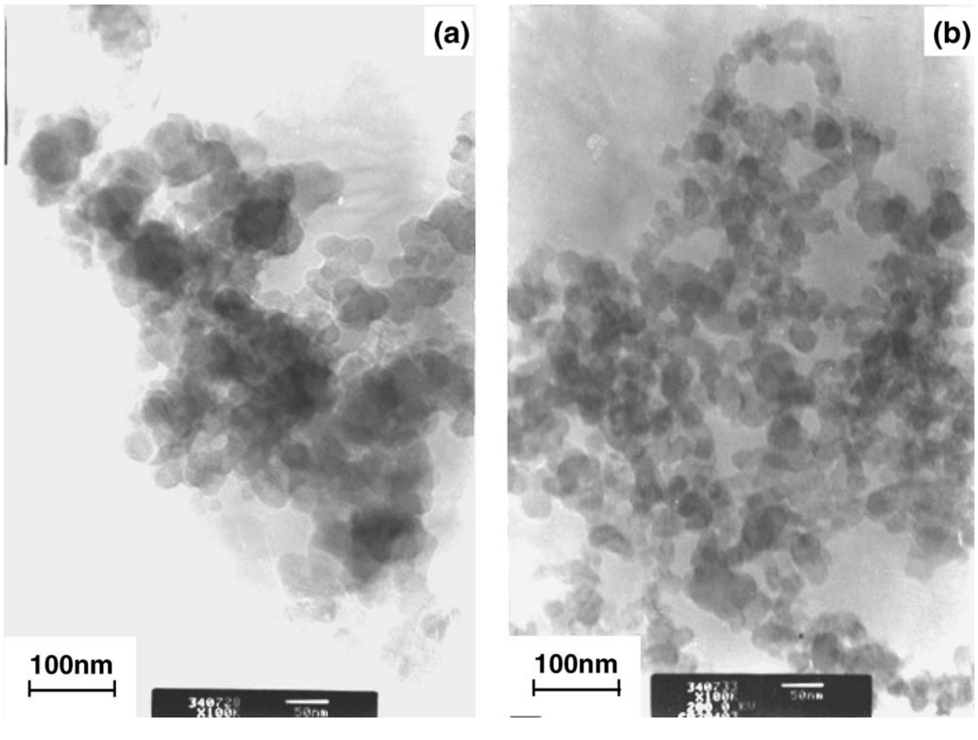

Figure 3 TEM photographs of: (a) CB as-received and (b) CB-g-PBA dispersed in ethanol.

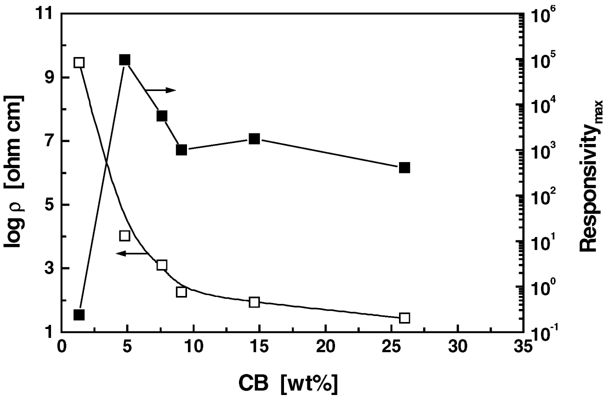

Figure 4 Filler content dependences of electrical resistivity, ρ, and maximum responsivity to THF vapor at 35 °C of CB-g-PBA/PE wax composites.

solution mixing with PE wax could not well separate the agglomerates and the resultant composites have to contain substantial large clusters of the agglomerated CB particles. The efficiency of either conduction network establishment or breakdown driven by matrix swelling has to be relatively low consequently. After graft polymerization, however, the smallest perceivable units of the CB agglomerates become smaller and their edges are no longer clearly discernible (Fig. 3b). Such a change demonstrates the role of the grafting polymer, i.e. separating and connecting the CB nanoparticles. It is believed that the compatibility between the hydrophilic CB particles and hydrophobic matrix would be increased as a result of the introduction of the hydrophobic grafting polymers onto the filler surfaces.

Fig. 4 gives the filler content dependence of resistivity of the composites with the grafted CB. In comparison with Fig. 1, the percolation curve in Fig. 4 is shifted to lower filler regime. It means that under the same CB loading the composites filled with the grafted CB have lower resistivity. Evidently, it can be attributed to the improved dispersion of the conductive fillers in the matrix, which increases the number of the effective conductive paths.

The electrical responses to THF vapors of the composites with grafted CB are shown as a function of CB content in Fig. 4. On the whole, the maximum responsivity is about 10 times higher than that of the composites with untreated CB in the case of identical CB concentration (refer to Fig. 1). This should again result from the improved dispersion of the CB particles. In the case of the same CB content, the filler particles with graft pretreatment are well spread over the matrix than the untreated ones. Smaller amount of the grafted CB particles is enough to build up conduction networks. When the composites are exposed to certain organic solvent vapor, swelling of the matrix would easily broaden the distances between the grafted CB particulates because their agglomerates are much smaller than those formed by the untreated CB. In other words, under the same driving force generated by matrix swelling, much more conduction paths are cut in the composites with grafted CB than in those with untreated CB.

On the basis of above study, it can be concluded that carbon black filled polyethylene wax proves to be able to act as organic vapor sensing material, accompanied by satisfied processability. Filler content and solvent species are important influencing factors related to the electrical responsivity. When carbon black surfaces are pregrafted with polymers, the composites conductivity and gas sensitivity can be further increased significantly, as a result of improved dispersion status of the fillers. These findings provide knowledge basis for optimizing the composites for specific sensor application.

Acknowledgments

The financial support by the National Natural Science Foundation of China (Grant 50133020), the Team Project of the Natural Science Foundation of Guangdong, (Grant 20003038), and the Talent Training Program Foundation of the Higher Education Department of Guangdong Province are gratefully acknowledged.

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Received 11 March
and accepted 31 March 2004