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A novel sensor for organic solvent vapors based on conductive amorphous polymer composites: carbon black/poly(butyl methacrylate)

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Summary

Conductive composites from carbon black/poly(butyl methacrylate) (CB/PBMA) are synthesized through polymerization filling. The experimental results indicate that relatively low percolation threshold (~6wt%) is associated with the composites. When the composites are exposed to good solvent vapors of the matrix polymer, the electric resistance of the composites drastically increases by over 10^4 times. In the case of poor solvent vapor, however, the electrical response of the composites is rather weak, demonstrating selective gas sensibility. In addition, environment temperature exerts great influence on the responsivity of the composites against organic vapors. The higher the temperature, the faster and the stronger the electrical response. It was also found that the response of electric resistance of the composites against good solvent vapors is provided with sufficient reproducibility and stability. It can thus be concluded that the CB/PBMA composites can be used as promising gas sensing materials in practice.

Introduction

Electrical resistivity of intrinsically insulating polymers can be lowered by dispersing conductive fillers, e.g., carbon black (CB), in the polymer matrices. As the filler content exceeds a certain critical value (called percolation threshold), which is generally attributed to percolation phenomenon, at least one conducting path is established throughout the matrix resulting in an insulator-conductor transition accordingly [1, 2]. These conductive polymer composites have broadened the traditional applications of polymers in modern industry. For example, one of their desirable properties lies in the positive temperature coefficient (PTC) behavior characterized by a drastic rise in volume resistivity as temperature approaches the melting point of the matrix resin [3, 4]. The mechanism is generally attributed to the difference in thermal expansibility between the components. Especially in the case of polymer melting, polymers possess much greater thermal expansion coefficients than conventional inorganic conducting fillers [5].

In recent years, new classes of polymeric materials fabricated from conductive carbon black/polymer composites have been developed and studied for applications as sensors in chemical and biomedical fields, like solvent leak detector and "electronic noses" capable of monitoring and determining the constituents of a sample gas [6~11]. The working principle of these polymer composites sensors has been described on the basis of percolation theory in analogy to the above-stated PTC type composites. Being exposed to various gases, the polymer matrix of the composites would swell up [11] or experience damage of its crystalline structure [12]. As a result, sorption of a vapor into such a composite matrix causes a change in the electrical resistance by influencing the length of percolation paths between the conducting particles within the composites. It is found that the effect of swelling or variation in crystalline structure on the composites conducting capacity depends notably on the solvent nature, namely, at least one polymer in the composites is capable of absorbing organic solvent vapors by a dissolution process.

So far, the composites made from semicrystalline polymers-grafted carbon black/semicrystalline polymers have showed large electric resistance responses and good reproducibility toward certain organic vapors [12~18]. Semicrystalline polymers were grafted onto carbon black surface by chemical methods [17] or radiation process [18]. The modification of carbon black can make its dispersion in composite materials more uniform and stable. Tsubokawa and co-workers demonstrated that a slight change in the crystalline structure of the polymer matrices due to the absorption of good solvent vapors results in remarkable increase of electric resistance of the composites prepared according to the aforesaid technical route [12~18].

Carbon black filled polymer composites are usually manufactured by melt-mixing or solution-mixing method. Because of the presence of some polar groups such as hydroxyl, carboxyl, etc., on the surface of carbon black, interaction between carbon black particulates is hard to be overcome by the limited shear force during compounding, resulting in uneven dispersion of the filler particles in the composites. That is, the carbon black has to present itself as larger agglomerates, reducing the probability of the formation of conduction networks as compared with smaller particles for the same filler content and arrangement [2]. A high percolation threshold is thus observed, which might be disadvantageous to the gas sensing ability and mechanical properties of the composites as well. Therefore, the dispersion status of carbon black particles in a polymer matrix is a key factor that influences the composites conductivity.

To breakdown the large carbon black agglomerates into smaller aggregates and to decrease the percolation threshold of the composites, polymerization filling was conducted in our laboratory. It is expected that the tiny monomer molecules might be able to penetrate into the carbon black agglomerates, so that the subsequent polymerization would produce composites with extensive small carbon black aggregates and hence lower the percolation threshold [19]. The packing density of the composites would also be increased accordingly. The authors of the present paper synthesized poly(butyl methacrylate) based composites by polymerizing butyl methacrylate monomers at the presence of carbon black. The conductive properties and electrical response of the composites in various organic solvent vapors are measured and discussed hereinafter with the objective of showing the feasibility of the composites serving as gas sensors.

Experimental

Materials

Conductive carbon black (XC-72) supplied by Cabot Inc., with a N_2 specific surface area of about $254m^2/g$ and diameter of 50-70nm, was dried in vacuum at 110°C for 48h before use. Besides, the monomer, butyl methacrylate, was distilled for two times and the initiator, benzoyl peroxide (BPO), was purified by recrystallization from chloroform and methanol prior to the polymerization filling process.

Composites preparation and characterization

The carbon black/poly(butyl methacrylate) (CB/PBMA) composites were prepared as follows. Typically, CB (3.2g), butyl methacrylate (16.8g) and a small quantity of BPO were added into a 100ml flask with a reflux condenser. Having been treated by ultrasonic agitation for 1h, the reaction mixture was stirred with a magnetic stirrer at 100~110°C under nitrogen for 5~6h. Afterwards, the product was added into 20ml CCl_4 and stirred for 1~2h at room temperature to produce paste composites. Then, the product which had been dried in vacuum at room temperature for 48h was dispersed in tetrahydrofuran (THF) and centrifuged at $1.6x10^4$rpm for 30min. The supernatant solution was removed by decantation. The procedures were repeated until no more polymer could be detected in the supernatant layer.

The molecular weight of the polymer was analyzed by gel permeation chromatography (Waters Breaze GPC system). Depending upon the content of carbon black, number average molecular weight, M_n, of the synthesized PBMA ranges from $1.9x10^4$ to $5.3x10^4$. A JSM-6330F scanning electronic microscope (SEM) was employed for observing freeze-fractured surfaces of the composites. All the SEM samples were gold sputtered prior to observation.

Performance measurement

The measurement of electric resistance of the PMMA/CB composites was carried out as follows. Conventional $7.5\times2.5cm^2$ glass slides were cut into $1.0\times2.5cm^2$ strips. Then two parallel copper wires (0.1mm in diameter, at intervals of 1mm) were coiled onto a piece of the glass strip serving as electrodes. The above composite paste was uniformly coated onto the glass strip to form composite film 30-40μm thick.

The electric resistance variation of the composites against the organic solvent vapor was measured through a digital multimeter by hanging the composite resistor in a glass container saturated with the organic solvent vapor. When the electric resistance reached the maximum, the composite resistor was immediately moved out of the container. The corresponding responsivity is described by the ratio of the transient resistance to the initial resistance in air.

Results and discussion

Figure 1 shows the relationship between electrical resistivity of the PBMA based composites and the content of CB. As an electrical percolation threshold corresponds to the lowest concentration of conducting particles at which continuous conducting chains or conducting networks are formed, it can be roughly determined from the peak position of the first derivative of the curve shown in Figure 1, that the percolation threshold of the composites lies in about 6wt%. In comparison with conventional single polymer based composites made by dispersing mixing [20], evidently the present composites percolate at a relatively low filler loading. Such a low critical value might result from the above-mentioned effect of reduced sizes of CB aggregates caused by polymerization filling. To evidence this consideration, the composites' morphologies were examined by SEM. As seen in Figure 2, the CB aggregates dispersed in the matrix are generally smaller than 100nm. With a rise in CB concentration, the amount of CB aggregates increases but no large agglomerates appear. This ensures the formation of conduction pathway at low CB content.

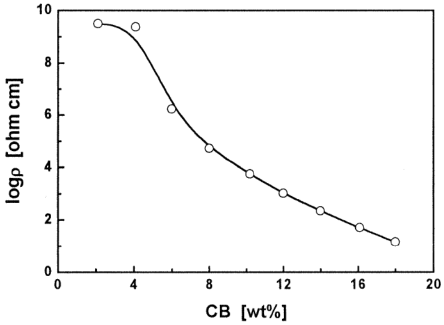

Figure 1 Electrical resistivity of the CB/PBMA composites as a function of CB content

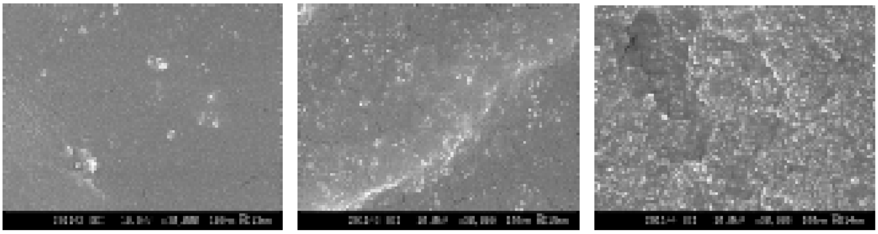
(a) (b) (c)

Figure 2 SEM micrographs of the CB/PBMA composites. CB content: (a) 2wt%; (b) 6wt%; (c) 14wt%.

Prior to the discussion of the gas sensibility of the composites in detail, the optimum CB content should be determined first. In general, the performance of conductive composites at percolation region is quite unstable and fluctuates easily due to a slight change in environmental conditions, such as temperature [21]. It is thus expected that when the composites are exposed to organic vapors the maximum increase in composites resistivity might also be perceived within this region. Accordingly, the dependence of maximum responsivity of the composites on CB content is measured in saturated THF and ethyl acetate vapors, respectively. Both of them are good solvents of PBMA. As shown in Figure 3, however, the results are far from the above estimation. The curves peak up at around 16wt% of CB. It means the mechanism is different from that of PTC phenomenon. Provided that conductive paths have formed throughout the matrix polymer, lower CB concentration would enhance the partial discontinuance of the contact CB driven by the swollen matrix while less amount of the matrix facilitates a fast transportation of the solvent vapor. The competition between the two opposite factors leads to the appearance of the peak-like dependence of responsivity on CB content as well as the optimum CB contents higher than the percolation threshold (Figure 3). Therefore, CB loading of a reproducible vapor sensible conductive polymer composite with acceptable responsivity should exceed the previously described percolation region (Figure 1). Accordingly, the composites with 16wt% of CB are employed in the subsequent analyses of the current paper.

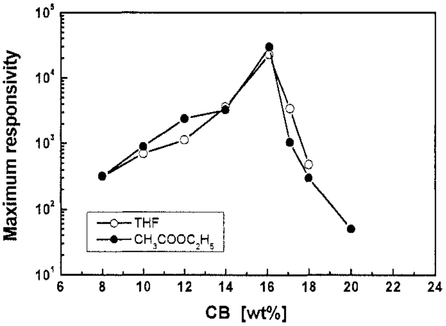

Figure 3 Maximum electrical responsivity of the CB/PBMA composites as a function of CB content at 35°C.

Since PBMA belongs to amorphous polymers, separation of the conductive fillers resulting from its swelling or dissolving should account for the drastic rise in the resistivity of the composites. It is seen from Figures 4(a)~(d) that the composites' resistances increase by $1\sim3\times10^4$ times in the good solvent vapors for PBMA (i.e., chloroform, THF, ethyl acetate and benzene), and immediately return to their initial values when the composites are transferred into air. The response times, within which the resistances of the composites reach the maxima from the initial values, are quite short (~20s). These mean that the present composites represent potential candidates for organic vapor sensors. On the other hand, the electric response of the composites in poor solvent vapor (i.e. methanol) is marginal (Figure 4(e)). It further demonstrates the importance of the solubility of polymer matrix in solvent.

On the basis of above results, it can be deduced that the electrical response of the composites consists of two processes. At first, both the matrix and the fillers absorb solvent vapors as the composites encounter with solvent vapor. The absorption rate and quantity are controlled by the factors such as surface morphological structure of the composites, affinity of polymer matrix and filler particles to solvent vapor, concentration or partial pressure of solvent vapor, etc. Secondly, swelling or dissolving of partial matrix polymer happens. During this stage, the nature of the matrix polymer, including molecular weight and solubility, plays the leading role. Careful analyses of these items might help to improve the sensing function and to reveal the ultimate mechanisms.

Returning to Figures 4(a) and (b), it is worth noting that when the electric resistances of the composites in $CHCl_3$ and THF vapors get to the maxima, there are slight drops in the curves instead of leveling off. This is referred to as the negative vapor coefficient (NVC) effect [22]. Similar to negative temperature coefficient (NTC) phenomenon, NVC results from the newly formed conducting networks. Since the mobility of CB particles is greatly increased in the swollen matrix, some damaged conducting paths due to volume expansion of the matrix can be re-constructed.

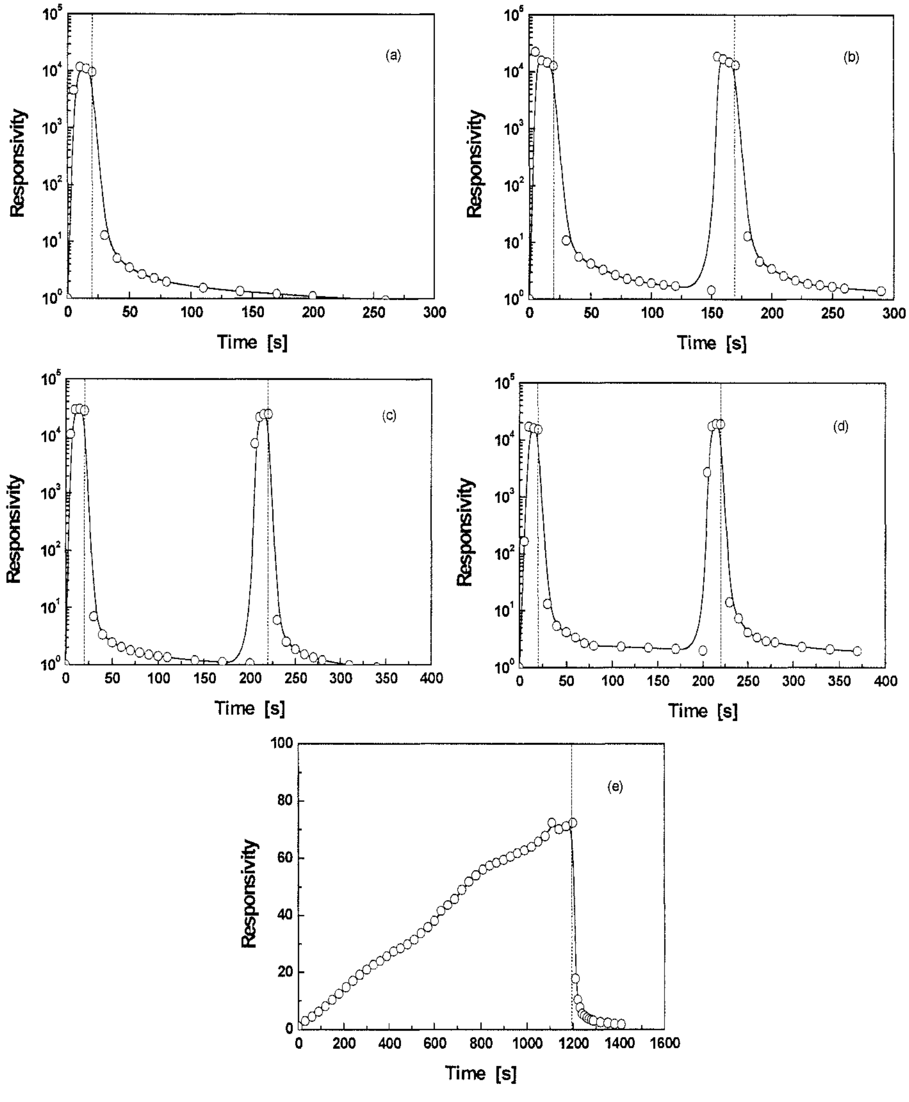

Figure 4 Electrical response of the CB/PBMA composites (CB content: 16wt%) against various organic solvent vapors at 35°C. The dash lines define the vapor absorption and desorption zones. Organic solvent vapor: (a) $CHCl_3$; (b) THF; (c) ethyl acetate; (d) benzene; (e) methanol.

The effect of temperature on the responsivity of the composites is evaluated in chloroform and THF vapors (Figure 5). The higher the temperature, the faster the electrical responses of the composites to the organic vapors. This can be attributed to that the partial pressure or concentration of an organic solvent vapor increases with increasing temperature. As a result, the vapor absorption of the composites is accelerated with a rise in temperature. In addition, an elevated temperature promotes the dissolution of the matrix polymer and the decrease of matrix viscosity, which renders vapor absorption easier. Owing to the same reasons, the rise of working temperature also results in an increase in the responsivity.

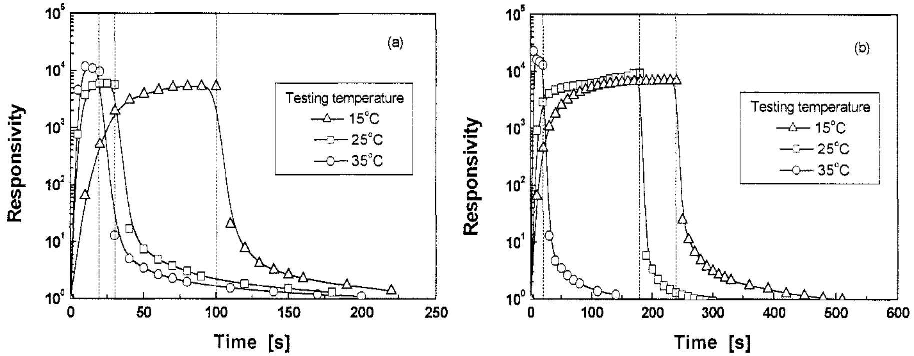

Figure 5 Effect of temperature on the responsivity of the CB/PBMA composites (CB content: 16wt%) against (a) $CHCl_3$ and (b) THF vapors. The dash lines define the vapor absorption and desorption zones

By examining the curves shown in Figure 5, the effect of glass temperature T_g of the matrix can be found. Below and above T_g of PBMA (~27°C), the response behaviors are quite different. The profiles of the curves measured at 35°C greatly differ from those at 15°C. The latter is characterized by a gradual increase in responsivity and takes longer time to reach the maximum responsivity. It is believed that the lower viscosity of PBMA below its T_g should take the responsibility. That is, acceleration of electrical response to organic vapors by means of increasing temperature would be more prominent in the glass state of the matrix polymer than in the rubbery state. The irregularity of the response behaviors at 25°C towards $CHCl_3$ and THF vapors (cf. Figures 5(a) and (b)) might originate from (i) the meta-stability of PBMA at a temperature close to its T_g, and/or (ii) the difference in activity of the solvents.

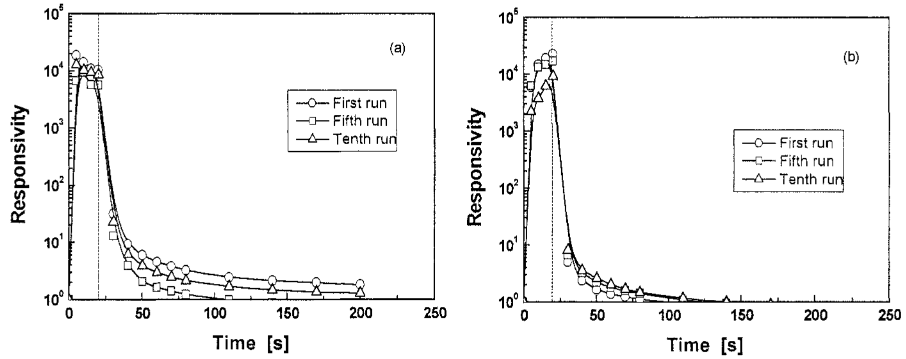

Figure 6 Electrical response of the CB/PBMA composites (CB content: 16wt%) against (a) THF and (b) ethyl acetate vapors at 35°C. The dash lines define the vapor absorption and desorption zones

As viewed from engineering angle, performance reproducibility is critical. Figure 6 exhibits the responses of the composites against THF and ethyl acetate vapors, respectively. Obviously, the electrical responses of the composites are excellently reproducible in repeated cycles of exposure to the organic solvent vapors and to the air, as reflected by the overlapped curves except for a slight decrease in responsivity.

This again indicates that the CB/PBMA composites are promising materials as gas sensors.

Conclusions

1. Carbon black/poly(butyl methacrylate) conductive composites prepared by polymerization filling are characterized by relatively low percolation threshold (~6wt%) and even dispersion of carbon black particles. When the composites are exposed to organic good solvent vapors for the matrix polymer, their electrical resistances increase drastically by over 10^4 times, and then recover immediately if the composites are transferred to the air.
2. Effect of temperature on the responsivity of the composites against organic vapors is notable. A rise in temperature from a value lower than T_g of the matrix to the one higher than the T_g can remarkably improve the electrical response performance. During repeated cycling tests, the composites exhibit good reproducibility of gas sensing, demonstrating the promising application potential. More detailed work will be done to find out the mechanisms involved.

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