

Organic Liquid Stimuli-Response Behaviors of Electrically Conductive Microfibrillar Composite with a Selective Conductive Component Distribution

Kun Dai,^{1,2} Yi-Chuan Zhang,¹ Jian-Hua Tang,³ Xu Ji,³ Zhong-Ming Li¹

¹State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065 Sichuan, People's Republic of China

²The Key Laboratory of Advanced Materials Processing & Mold of Ministry of Education, School of Materials Science and Engineering, Zhengzhou University, 450002 Zhengzhou, People's Republic of China

³College of Chemical Engineering, Sichuan University, Chengdu, 610065 Sichuan, People's Republic of China

Received 20 June 2011; accepted 9 August 2011

DOI 10.1002/app.35455

Published online 2 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This article reports the organic liquid stimuli-response behaviors of carbon black (CB)-filled electrically conductive microfibrillar poly(ethylene terephthalate) (PET)/polyethylene (PE) composite (FCMC) with CB particles selectively localized at PET microfibrils' surfaces. It was found that FCMC's thickness and CB concentration affected its responsivity significantly, a thinner FCMC film with a high CB content exhibited higher responsivity and better signals. In immersion-drying tests, FCMC displayed high and stable responsivities after six immersion-drying runs, indicating that the solvent absorption/desorption equilibrium state was achieved. After long-term immer-

sion, FCMC showed obviously different organic liquid stimuli-response behaviors with faster response rate in immersion and higher terminal resistivity platform in drying, compared with samples without immersion treatment. Conductive network's microstructural changes induced by the long-term immersion and evident capillary effect, which resulted in slow evaporation of remaining solvent in FCMC's interfaces, are the reasons for the phenomenon.

© 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4466–4474, 2012

Key words: carbon black; microfibrillar blend; organic liquid stimuli-response behavior; mechanism

INTRODUCTION

Conductive polymer composites (CPCs) have received great attention due to their popular applications such as antistatic materials,¹ electromagnetic interference shielding,² and positive temperature coefficient (PTC) materials.^{3,4} In recent decades, based on resistivity variation of CPCs exposed to vapor or organic solvent stimuli, the so-called vapor sensing and liquid sensing, that is, organic liquid stimuli-response behaviors of CPCs were investigated more and more frequently.^{5–10} On the basis of these studies, CPCs have been exploited for fabrication of chemisensors,^{11,12} vapor detector arrays, and "electronic noses"^{13,14} capable of sensing, quantifying, and discriminating various organic vapors and

solvents in chemical and petrochemical industry, environmental monitoring, and food industry.

As one of the most important CPCs used as liquid and vapor sensors, carbon category materials (such as carbon black (CB), carbon nanotubes (CNTs), etc.)-filled single-polymer composites have been studied by many researchers^{7–9,15–18}; however, they have many limits in service. For example, their sensitivity and selectivity cannot be balanced when they were used to detect various organic vapors and solvents. Many CB-filled single-polymer composites are only sensitive to one solvent or they display similar organic liquid stimuli-response behaviors to different analytes. One of the key reasons is that these CPCs' response manners are restrained due to single-polymer matrix's monotonic nature such as polarity and permeability.

CB or CNTs-filled immiscible binary or hybrid polymer composites offer a good opportunity for this challenge. The sensitivity and selectivity of CPCs can be easily tuned by using immiscible CPCs consisting of two or more polymers with various natures and volume ratios. Furthermore, the microstructure of these CPCs (which determines the organic liquid stimuli-response behaviors of CPCs) can be tailored by controlling the conductive component distribution and topological morphology of the

Additional Supporting Information may be found in the online version of this article.

Correspondence to: Z.-M. Li (zml@scu.edu.cn)

Contract grant sponsor: National Outstanding Youth Foundation of China; contract grant number: 50925311.

Contract grant sponsor: Nature Science Foundation of China; contract grant number: 20876099.

Journal of Applied Polymer Science, Vol. 124, 4466–4474 (2012)
© 2011 Wiley Periodicals, Inc.

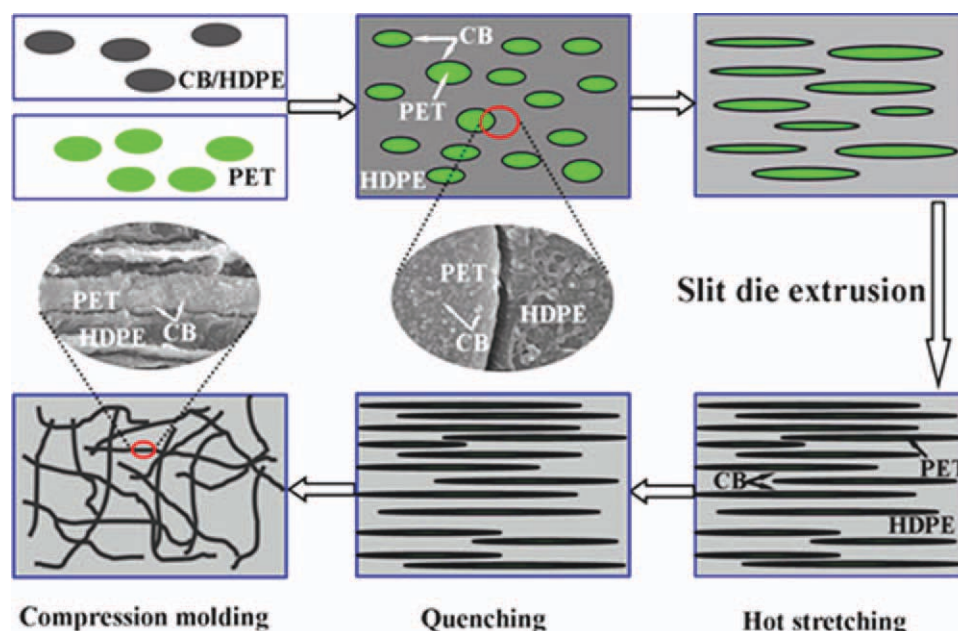


Figure 1 Fabrication procedure and morphology development of FCMC by extrusion-hot stretching-quenching technique. The volume ratio of PET to PE in CB/PET/PE is 1 : 3.2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CPCs through varying polymer matrices and processing techniques.

Nevertheless, up to now, there have been few studies on organic liquid stimuli-response behaviors of CB-filled immiscible binary or multiple polymer composites. Narkis et al.^{19–23} utilized immiscible polymer blends of high-impact polystyrene (HIPS) and ethylene vinyl acetate (EVA) copolymer to produce electrically conductive filaments with CB by a capillary rheometer process.¹⁹ They found that HIPS/EVA interface and selective swelling effect of the polymers influenced the sensing properties obviously, and liquid transport principle was an important basis for interpretation of the sensing behavior of immiscible blend-based filaments in contact with liquids. Through their technique, low cost and good processability liquid sensors can be prepared; nevertheless, the sensitivity of their systems was generally low.^{19–23}

In our previous work,^{24–26} a CB-filled electrically conductive *in situ* microfibrillar poly(ethylene terephthalate) (PET)/polyethylene (PE) composite (FCMC) was successfully fabricated through a slit die extrusion-hot stretch-quenching technique. The schematic illustration of fabrication processing and morphology development of FCMC is shown in Figure 1. A well-defined PET microfibrils were generated *in situ* by stretching and CB particles migrated from PE matrix to the surfaces of PET microfibrils gradually owing to the interfacial tension, viscosity, chemical groups on the surface of CB particles, and the processing order. The selective distribution of CB particles and the morphology were then preserved via quenching. After compression

molding, because of the fine contact between CB-coated PET microfibrils, a percolation threshold as low as about 3.8 vol % was obtained. In a following study,²⁶ it was found that FCMC was quite sensitive to thermal stimulus. As a specially constructed CB-filled immiscible CPC, FCMC is a good candidate to study organic liquid stimuli-response behaviors of immiscible CPCs due to its subtle microstructures.

In this article, the dependence of organic liquid stimuli-response behaviors on FCMC film thickness and CB concentration was investigated. To reveal the influences of microstructural changes, organic liquid stimuli-response behaviors of FCMC during several swelling–deswelling processes, that is, immersion-drying runs (IDRs), were explored. Effects of residual solvent after different immersion process were studied. Organic liquid stimuli-response mechanism, which is determined by the microstructure of conductive network and its evolution, was discussed in particular.

EXPERIMENTAL

Materials

The materials used in this work include electrically conductive CB, high-density PE, and PET. The CB, model VXC-605, from Cabot with a dibutyl phthalate absorption value of $148 \pm 15 \text{ cm}^3/100 \text{ g}$, was dried at 120°C for 10 h to get rid of the water before use. PE (5000S) is a commercial high-density PE of DaQing Petroleum Chemical, Daqing, China, with melt flow rate of 0.9 g/10 min (190°C , 21.6 N), and its number-average molecular weight is $5.3 \times 10^5 \text{ g/mol}$. PET

was donated by LuoYang Petroleum Chemical, LuoYang, China, which is a commercial grade of textile polyester with a number-average molecular weight of about 2.3×10^4 g/mol.

Preparation of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites

FCMCs were prepared by the extrusion-hot stretching-quenching process, the procedures were previously reported in detail.^{25,26} The ribbon with a thickness of about 0.2 mm, in which microfibrils were generated and preserved, was finally prepared. Then, the ribbon was pelletized and compression molded into sheets with different thicknesses (200, 400, 500, and 2000 μm) at 150°C (the processing temperature of PE) for 10 min with a pressure of about 5 MPa. All these sheets were cooled to room temperature by cold compression molding for 5 min. Because of the high melting point of PET (about 257°C),⁴ the *in situ* PET microfibrils can be successfully reserved in the composite.

Morphological observation

The specimens were frozen in liquid nitrogen for 1 h and then quickly impact fractured. The fracture surfaces were coated with a gold layer to make them conductive and then observed with a Leica Cambridge LTD Stereoscan 440 scanning electron microscope (SEM).

Electrical properties and organic liquid stimuli-response behaviors test

Before electrical properties and organic liquid stimuli-response behaviors test, samples were annealed for 8 h at 80°C to remove internal stress' effects developed during processing (mainly compression molding). Two-probe method was applied for resistivity measurement.

In organic liquid stimuli-response behaviors tests, the length and width of samples were 10 and 2 mm, respectively, cut from the compression-molded sheets. Samples with various thicknesses (200, 400, 500, and 2000 μm) and CB concentrations (4.22, 4.93, 5.85, and 7.21 vol %, the dependence of FCMC's resistivity on CB content is available in our previous work^{25,26}) were prepared to study the effect of the thickness and CB loading on organic liquid stimuli-response behaviors. The contact and drying cycles for FCMC were processed as follows, first 5 min immersed in the liquid and then 15 min in air for 10 runs (an IDR is 20 min). To study the effect of immersion on the microstructure change and reproducibility, some samples were immersed in solvent for a longer time, 72 h, and then they were placed in

air for another 7 days for absolute drying, followed by another 10 IDRs tests, with the same conditions as mentioned above. To study the effect of residual solvent, drying processes after 6-, 30-, and 72-h immersion were studied. For these processes, samples were allowed to dry for 80 min in air.

All the tests were performed at 25°C. The real-time data were recorded by a computer. The applied voltage is fixed at 10 V. For immersion-drying measurements, the thicknesses were fixed at 200 μm , and the concentration of FCMC is 4.93 vol %. This CB content is just beyond the percolation threshold (detailed information about the percolation behavior and typical morphology of FCMC with 4.93 vol % CB is available in our previous work²⁵), the conductive network constructed by CB particles-coated PET microfibrils is just formed and thus sensitive to external stimuli.²⁶

In this study, the good solvent for PE matrix, xylene, which will result in significant swelling of PE, thus the evident variation of resistivity of FCMC, was selected to study the relationships between the microstructure change of conductive network and the organic liquid stimuli-response behaviors. The responsivities presented in this article were all defined as R_t/R_0 like many researchers,²¹ where R_0 is the initial resistance of the sensor and R_t is the measured resistance at the time t .

RESULTS AND DISCUSSION

The effects of the thickness and CB concentration

The organic liquid stimuli-response behaviors of CPCs can be understood by polymer-liquid interactions and liquid transport in polymer films.¹⁹ An important factor related to the interaction and the liquid transport is the permeability (P), which is represented by the solubility (S) and diffusivity (D) coefficients of the solvent, that is, $P = S \times D$. Between them, solubility of the solvent in the membrane polymer is a key factor, which is further associated with the solubility parameter. Generally, high solubility can be obtained when the solvent and the membrane polymer have similar solubility parameters. Another important factor is whether the membrane polymer is in the glassy or rubbery state, where evident permeation occurs in an elastomeric membrane.¹⁹ However, for a certain CB-filled two-phase polymer immiscible composite in a given solvent, these parameters do not seriously affect the organic liquid stimuli-response behaviors. Instead, its organic liquid stimuli-response behaviors depend significantly on the thickness of samples, the concentration of CB particles, the CB distribution, the microstructure, etc. Nevertheless, these parameters

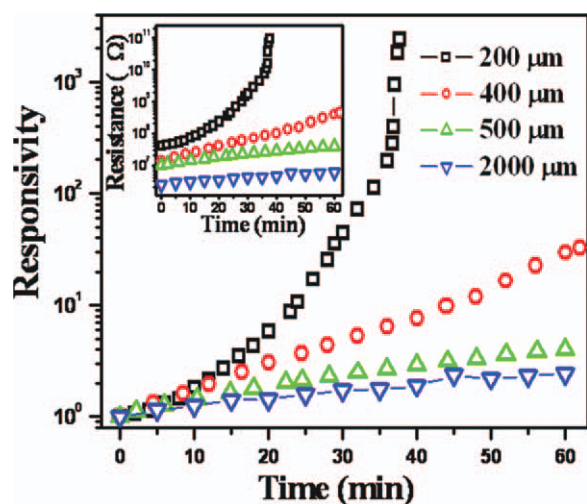


Figure 2 The relationship of responsivity vs. time of CB-filled electrically conductive microfibrillar PET/PE composites with different thicknesses. The volume ratio of PET to PE in CB/PET/PE is 1 : 3.2. The responsivity is defined as R_t/R_0 , where R_0 is the initial resistance of the sample and R_t is the measured resistance at the time t . The inset shows the relationship of resistance vs. time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

have not been paid enough attention so far. In this work, these factors will be focused on first.

Figure 2 shows the relationship of responsivity vs. time for FCMC films with different thickness in xylene. An obvious trend is that the thinner film exhibits faster and stronger responses. For instance, after the sample is immersed in the solvent for 30 min, the 200- μm -thick sample shows a responsivity of 43.7, whereas the 2000- μm -thick sample is only 1.7. Such a large difference has not been reported for CB-filled multiphase immiscible CPCs, suggesting that once the solvent molecules permeate the surface layer of FCMC sample, the overall resistance of the films was affected by the ratio of the surface area to the volume.⁸

Considering the changes of conductive network upon the solvent penetration, the film thickness dependence of the conductivity can be understood. In FCMC films, the conductive network was built by the contact of CB-coated PET microfibrils. Because of the incompatibility between PET and PE, clear interfaces existed between conductive network and PE matrix.²⁵ The interphase region and its continuity play significant roles in the liquid-transport process in immiscible polymer blends.²¹ The liquid preferentially permeates through the weak interfaces, followed by selective sorption from these regions. Consequently, swelling of polymers results in the resistivity increase. Similarly, for the FCMC material, xylene, certainly, preferentially permeated through the interfaces, where most of the CB particles were localized. Because of the strong capillary effect (the

dispersed-phase PET assumed in the form of microfibrils, with cylindrical morphology and large surface areas, resulting in a large amount of interfaces and strong capillary effect), the penetration process would be faster than the CB-filled single-polymer CPC and many CB-filled multipolymer CPC. After that swelling of PE matrix forced the CB-coated PET microfibrils to move more or less, and thereby, destroyed the conductive network, leading to the increased resistivity.

Taking into account the microstructure features of the CPC sheets, the effect of the thickness can be well explained. As shown in Figure 3, the conductive paths in the permeated layer were mostly damaged by swelling, but in "B," the conductive paths can still work well, which determines the resistivity of the FCMC. For thinner samples, the whole sample would be completely and quickly soaked, resulting in serious breakup of the conductive paths and a sharp increase of the resistivity as shown in Figure 2. While for thicker sample, within the same time, B still occupied rather large volume, the slow and gentle resistivity variations were thus displayed.

At a constant sheet thickness, the dependence of the organic liquid stimuli-response behavior on the conductive filler loading is shown in Figure 4. The faster and stronger responsivity was observed in the low CB concentration FCMC sample with a less perfect conductive network. This implies that the poor conductive pathways tend to obviously disconnect when exposed to xylene. However, FCMC

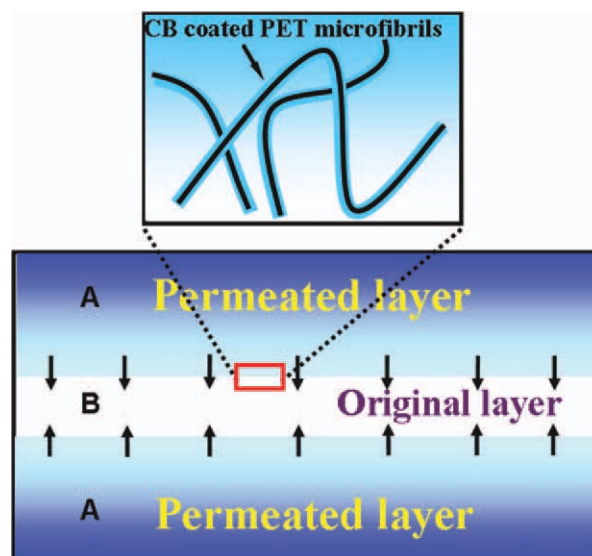


Figure 3 The illustration of permeation route of the xylene in CB-filled electrically conductive microfibrillar PET/PE composites. "A" represents the region that has been permeated by xylene and "B" is the unaffected region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

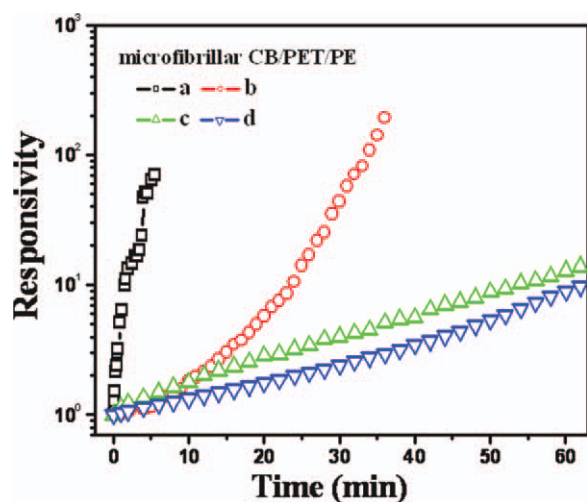


Figure 4 The relationship of resistivity vs. time of CB/PET/PE with different CB concentrations. The volume concentrations are 4.22% (a), 4.93% (b), 5.85% (c), and 7.21% (d), respectively. The thickness is 200 μm . The volume ratio of PET to PE in CB/PET/PE is 1 : 3.2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

containing quite low CB particles shows poor signals with obvious fluctuation.

Based on these results, a high resistivity with a stable response signal can be expected by preparing a thin sample with a relatively high CB loading. For this purpose, the FCMC sample with a CB concentration of 4.93 vol % and a thickness of 200 μm was selected for further investigation.

Organic liquid stimuli-response behaviors during IDRs

To evaluate the reproducibility of liquid sensors, the organic liquid stimuli-response behaviors during several IDRs were studied.^{8,20,21} Figure 5 shows the typical resistivity–time curve of the FCMC sample exposed to xylene in the first IDR. The resistivity increases substantially during the whole immersion process. This phenomenon greatly differs from the classic results,^{15,21,27} in which the time dependence of resistivity is composed of two parts: a very fast increase of resistivity at first, followed by a decelerated variation. This difference can be attributed to the processing technique and microstructure variance of different samples. For instance, in Lewis' work, the samples were prepared by spin coating or dipping, and films with a very small thicknesses (40–60 μm or even less) were thus obtained.^{15,27} The small thickness could only hold a tender network, which would damage fast and seriously once upon exposure to the analyte, leading to the sharp resistivity increase. Later, the equilibrium of the conductive network was gradually approached, and at this

stage, the conductive path changed slightly, resulting in the gentle rise of the resistivity. Similar phenomenon was also reported by Narkis and co-workers, but in their work, the result was related to surface microstructure of the sample prepared by capillary rheometer extrusion. Interfaces in the skin region were larger than the inner region, and the conductive network was damaged more easily.²¹

In this work, FCMC films were prepared by compression molding with a thickness of 200 μm . Their thickness is slightly thicker, and the conductive network is perfectly formed by contact of CB-coated PET microfibrils with a quite large size compared to the usual conductive components like CB particles.²⁶ These factors hinder the broken down process of the conductive network and lead to the delay of the appearance of solvent absorption equilibrium state,²⁸ shown as a gradual resistivity increase in the first run.

Unlike the previous research, in which the resistivity always descends during the subsequent drying process^{15,21,27,28} most interestingly, the FCMC sample shows a continuous increase of resistivity, only after a certain time, the resistivity starts to go down. Because of the capillary effect, the solvent stayed in the cylindric interfaces between PET microfibrils and PE matrix cannot evaporate easily, resulting in the delay of the maximum resistivity (6.3 min, it is 1.3 min late after the drying was preformed) and a higher terminal resistivity platform than the initial resistivity (1.79 times higher than the initial value). This observation indicates that the interfaces of immiscible CPC play an important role in organic liquid stimuli-response behaviors.

To reach the solvent absorption/desorption equilibrium state, which is usually considered as an

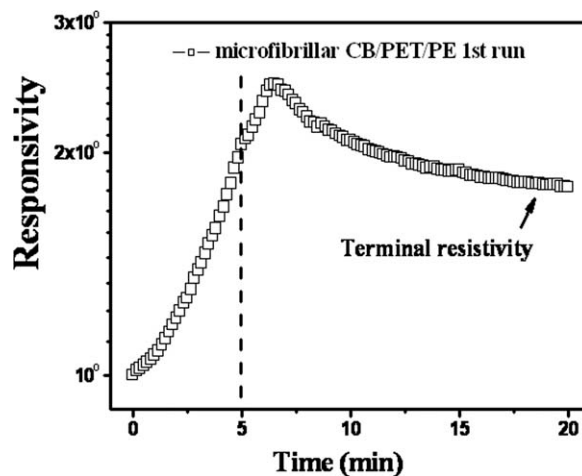


Figure 5 Resistivity–time relationship of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites. The CB concentration is 4.93 vol %. The volume ratio of PET and PE in CB/PET/PE is 1 : 3.2. The thickness of the sample is 200 μm .

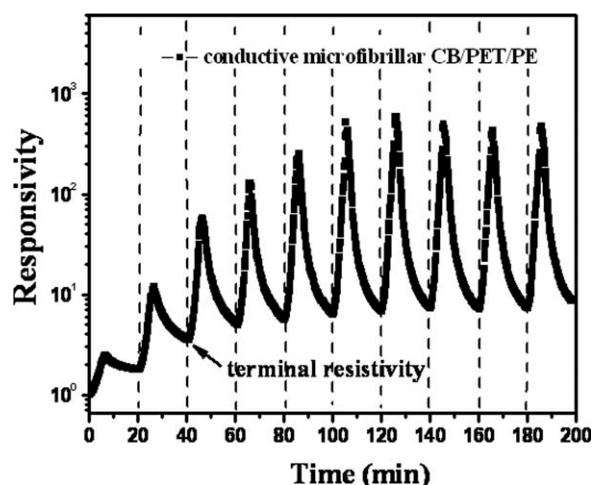


Figure 6 Responsivity–time relationship of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites for 10 immersion-drying runs (for each run, 5-min immersion in xylene and then 15-min drying in air). The CB concentrations is 4.93 vol %. The volume ratio of PET and PE in CB/PET/PE is 1 : 3.2. The thickness is 200 μm .

important factor related to the reliability of responsivity, more IDRs were measured, as shown in Figure 6. The maximum responsivity reached 12.6 in the second run, which is 4.8 times larger than that in the first IDR. This indicates again, after the first IDR, that the solvent absorption/desorption equilibrium was not reached. The remaining solvent together with the new xylene absorbed in the second run caused further damage of the conductive paths, thereby increasing the maximum responsivity. In the third and fourth IDR, the higher maximum responsivities were also obtained. However, after the sixth IDR, the value changed weakly, indicating that the equilibrium was reached.²⁸ An excellent reproducibility appeared from then on. Zhang and coworkers suggested that the arrangement of CB particles in the matrix leads to the equilibrium due to the healing of the defects formed during composite preparation through the repeated swelling/deswelling processes, so that the metastable conduction pathways become stabilized after the annealing-like training.²⁹ Certainly, FCMC underwent the similar process during the IDRs. It is worthwhile to note that the FCMC film exhibits relatively good reproducibility of the resistance once the equilibrium state forms via the annealing-like IDR.

It is noted that in the former five IDRs, the terminal resistivities rose gradually but quite slightly. This phenomenon was caused by the residual xylene. After the sixth IDR, the terminal resistivity keeps invariant due to the equilibrium of the remaining solvent volume.

To observe the influence of long-term repeated swelling–deswelling processes-induced arrangement of conductive network, the organic liquid stimuli-

response curve in the 10th IDR is shown in Figure 7. Compared with the organic liquid stimuli-response behavior in the first IDR (Fig. 5), the maximum responsivity increases to 468.9, which is 180 times larger than the initial maximum responsivity (only 2.6). This result indicates that the conductive network becomes more sensitive after 10 annealing-like IDRs. The microstructural change must be induced by the long-term solvent absorption as well as the effect of the residual solvent.

Organic liquid stimuli-response behaviors during 10 IDRs after a long time immersion

As mentioned above, the FCMC samples only reached the equilibrium state after six IDRs (see Fig. 6), and then the good repeatable responsivity appeared. In other word, the conductive network microstructure of the FCMC material is quasi-stable. Naturally, the next work is dedicated to evaluate the electrical responsivity of the pretreated samples, namely, the samples were first immersed in xylene for 72 h (the total immersion time for 10 IDRs is 50 min, and the time to reach the solvent absorption/desorption equilibrium is 30 min) and then used for organic liquid stimuli-response behaviors measurement as shown in Figure 8.

After a long time of immersion, the curve shape changes significantly in comparison to that of original samples. The maximum responsivity of every run rises greatly. For example, the maximum responsivity is only 257.6 in the fifth IDR of the original sample; however, for the pretreated sample, it increases to 2354 in the same run. In addition, in Figure 8, at the end of the first to fifth IDR, the terminal resistivity increases obviously. After five IDRs,

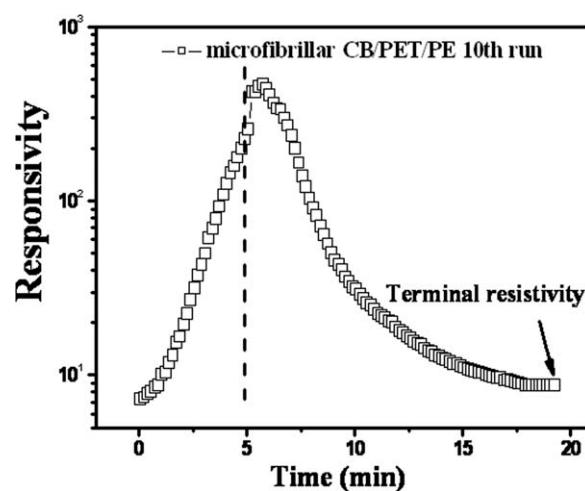


Figure 7 Responsivity–time relationship of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites. The CB concentration is 4.93 vol %. The volume ratio of PET and PE in CB/PET/PE is 1 : 3.2. The thickness is 200 μm .

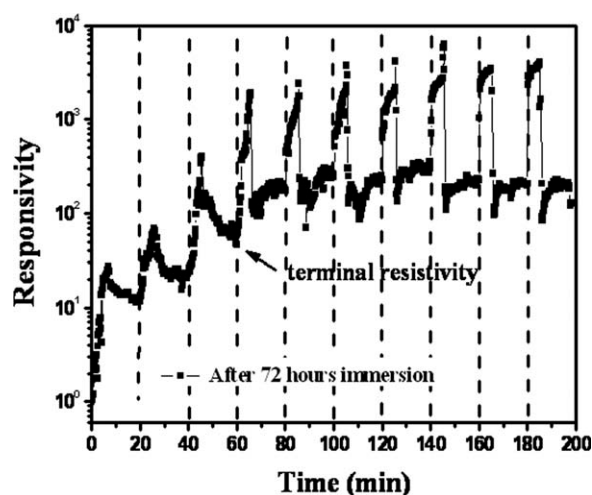


Figure 8 The relationship of responsivity vs. time of CB-filled electrically conductive microfibrillar PET/PE for 10 runs after being permeated in xylene for 72 h. The thickness is 200 μm .

the terminal resistivity of the sample had become about two orders of magnitude higher than the original terminal resistivity. Besides, through the whole 10 IDR, a sharp resistivity increasing at the beginning of immersion and a sharp resistivity decreasing at the beginning of the drying were also observed. For clear observation, the responsivity–time relationship of FCMC for the first and 10th IDR before and after the 72-h immersion is represented in Figure 9(a,b) for comparison.

In the case of the first IDR [Fig. 9(a)], the sample after 72-h immersion shows a rapid response rate and a higher maximum responsivity during immersion, as well as the higher resistivity platform during drying than the original sample in the first IDR. For the 10th IDR of samples after 72-h immersion [Fig. 9(b)], the shape of the responsivity–time curve changes more dramatic both in the immersion and in the drying process. A much sharper response rate was displayed in the start of immersion, followed by a consequent resistivity platform, which changes more weakly; a much sharper decrease of the resistivity in the start of drying was also observed. After that, it is also a platform with higher resistivity than the samples without long-term isothermal treatment.

To study the origin of these interesting phenomena as mentioned above, microstructural change induced by long-term immersion was then studied by SEM. Micrographs of the morphology for FCMC before and after 72-h immersion in xylene are shown in Figure 10. It is found that the interfaces between PET microfibrils and PE matrix were enlarged mildly after the long-term immersion, thus causing a worse conductive network. Understandably, in the succeeding IDR measurement, the rapid penetration of xylene through the enlarged interfaces results in

the larger response rate and higher responsivity than samples without immersion in the first IDR, and more amount of the remaining solvent due to the increasing volume of interface regions leads to the higher resistivity platform in drying as shown in Figure 9(a). With increasing IDR times, higher maximum responsivities of samples after treatment were thus performed due to further damage of the worse conductive network.

The remaining solvent in the interfaces during drying would also be an important reason for the microstructural change. Drying process of samples after immersed in xylene for different times (6, 30, and 72 h) is shown in Figure 11. It is found that the longer immersion time was applied on the sample, the higher terminal resistivity was obtained, and after 72-h immersion, during drying, the terminal

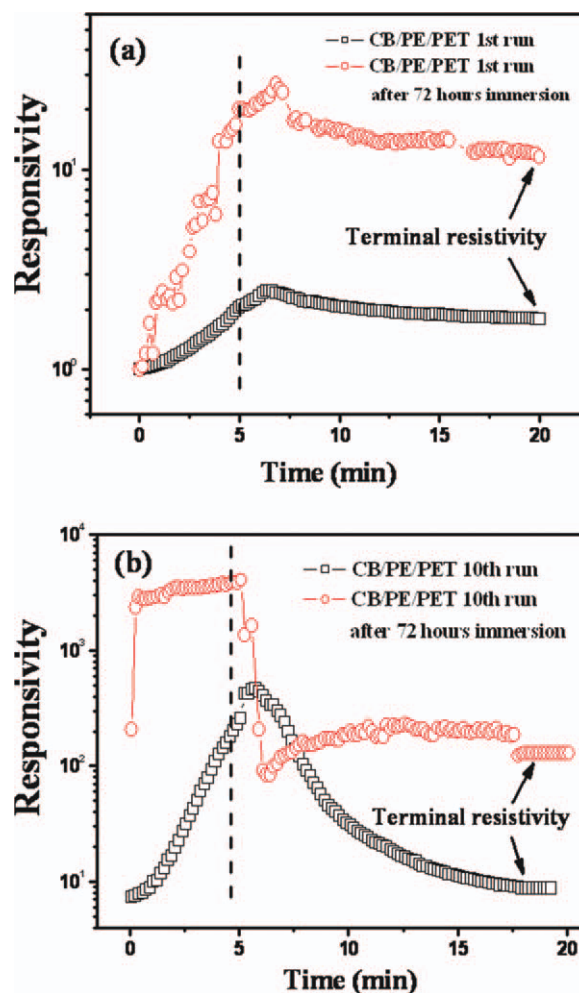


Figure 9 Responsivity–time relationship of CB-filled electrically conductive *in situ* microfibrillar PET/PE composites for the first (a) and 10th (b) immersion-drying runs before and after the 72-h immersion. The CB concentration for CB/PET/PE is 4.93 vol %. The volume ratio of PET and PE in CB/PET/PE is 1 : 3.2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

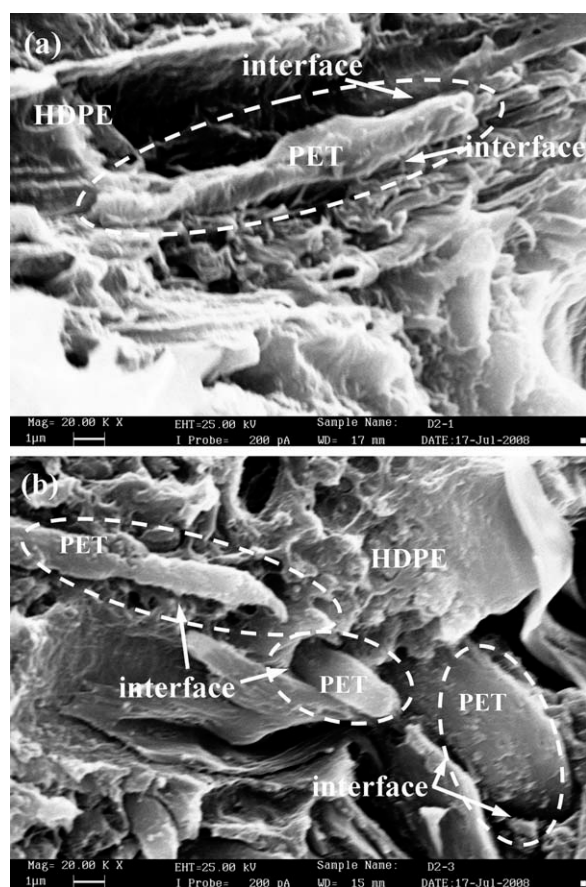


Figure 10 SEM micrographs of the CB-filled electrically conductive microfibrillar PET/PE before (a) and after (b) 72-h immersion in xylene, respectively. The volume ratio of PET to PE in CB/PET/PE is 1 : 3.2.

resistivity is two orders of magnitude higher than the original sample, indicating much remaining solvent was still stored in the interfaces between PET microfibrils and PE matrix. Because of the capillary effect, slow evaporation of the remaining xylene at the interfaces must change the microstructure of the conductive network further.

In Figure 8, higher terminal resistivity platform in drying of every IDR than that of samples without 72-h immersion is also attributed to the increasing amount of remaining solvent, which makes the conductive network impossible to recover to its original state. The equilibrium state was reached at about the fifth IDR, whereafter, the terminal resistivity changes weakly.

In summary, conductive network's microstructure of FCMC and its development induced by swelling/deswelling and effect of remaining solvent affect immiscible CPCs' organic liquid stimuli-response behaviors significantly. Interfaces between PET microfibrils and PE matrix play an important role in organic liquid stimuli-response behaviors. The interfaces enlarged by swelling after long immersion will influence FCMC's organic liquid stimuli-response

behaviors further. This study has important implications for applications of immiscible CPC sensors during long-time use. However, for CB/single-polymer composites, due to the weak interface, some novel response phenomena upon organic liquid stimuli will not be observed. For instance, in this work, if CB/single-polymer composites were used as specimens, the interesting liquid sensing behaviors after several IDRs or long-term immersion with higher responsivity, faster response rate in immersion, and higher terminal resistivity platform in drying would not be found (see Supporting Information).

CONCLUSIONS

CB-filled electrically conductive *in situ* microfibrillar PET/PE composite (FCMC) with a unique dispersed-phase morphology and special CB distribution was tailored and prepared successfully through the slit die extrusion-hot stretch-quenching process. In this composite, the dispersed phase was formed into microfibrils *in situ*, and most CB particles were selectively localized on the surfaces of these PET microfibrils.

Thickness and CB concentration of FCMC films influence their organic liquid stimuli-response behaviors significantly. High responsivity with stable response signals can be achieved by thin sample with a relatively high CB content. Organic liquid stimuli-response behaviors during 10 IDRs were tested. After six IDRs, the shape of the responsivity–time curve changes weakly, indicating that the solvent absorption/desorption equilibrium state was reached. Interfaces between the PET microfibrils and

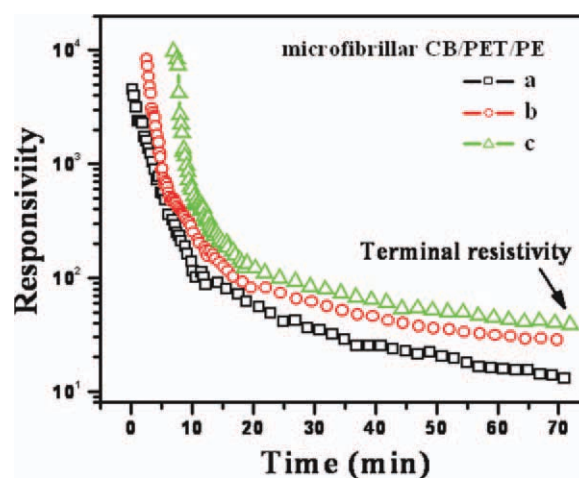


Figure 11 The relationship of responsivity vs. time of CB-filled electrically conductive microfibrillar PET/PE composites after permeation in xylene for different times, 6 (a), 30 (b), and 72 h (c). The thicknesses are both 200 μm . The volume ratio of PET to PE in CB/PET/PE is 1 : 3.2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PE matrix, where most of CB particles were localized, play an important role on these organic liquid stimuli-response behaviors. The interface affects the penetration path of xylene and the swelling of PE obviously, thus the conductive network constructed by CB-coated PET microfibrils. These results illustrate that morphology and CB distribution are key factors for immiscible CPC's organic liquid stimuli-response behaviors.

After 72-h immersion, microstructural change of the interfaces generates different organic liquid stimuli-response behaviors in the succeeding 10 IDR with higher responsivity, faster response rate in immersion, and higher terminal resistivity platform in drying. These phenomena have not been reported in previous work. It indicates that microstructural changes during applications of liquid and gas sensors based on CB-filled immiscible CPCs will influence their following use. Organic liquid stimuli-response behaviors of FCMC to different solvents and temperature stimuli will be discussed in our forthcoming article.

The authors thank Mr. Zhu Li from Analytical & Test Center of Sichuan University for his help in the SEM observation.

References

- Li, C. S.; Liang, T. X.; Lu, W. Z.; Tang, C. H.; Hu, X. Q.; Cao, M. S.; Liang, J. *Compos Sci Technol* 2004, 64, 2089.
- Das, N. C.; Liu, Y. Y.; Yang, K. K.; Peng, W. Q.; Maiti, S.; Wang, H. *Polym Eng Sci* 2009, 49, 1627.
- Xu, H. P.; Dang, Z. M.; Shi, D. H.; Bai, J. B. *J Mater Chem* 2008, 18, 2685.
- Xu, X. B.; Li, Z. M.; Dai, K.; Yang, M. B. *Appl Phys Lett* 2006, 89, 032105.
- Bouvier, A.; Feller, J. F.; Castro, M.; Grohens, Y.; Rinaudo, M. *Sensor Actuat B: Chem* 2009, 138, 138.
- Siegmann, A.; Pavlovsky, S. *J Appl Polym Sci* 2009, 114, 1390.
- Zhang, B.; Dong, X. M.; Song, W.; Wu, D. C.; Fu, R. W.; Zhao, B.; Zhang, M. Q. *Sensor Actuat B: Chem* 2008, 132, 60.
- Kobashi, K.; Villmow, T.; Andres, T.; Pötschke, P. *Sensor Actuat B: Chem* 2008, 134, 787.
- Pötschke, P.; Andres, T.; Villmow, T.; Pegel, S.; Brunig, H.; Kobashi, K.; Fischer, D.; Haussler, L. *Compos Sci Technol* 2010, 70, 343.
- Villmow, T.; Pegel, S.; Pötschke, P.; Heinrich, G. *Polymer* 2011, 52, 2276.
- Li, J. R.; Xu, J. R.; Zhang, M. Q.; Rong, M. Z.; Zheng, Q. *Polymer* 2005, 46, 11051.
- Kobashi, K.; Villmow, T.; Andres, T.; Haubler, L.; Pötschke, P. *Smart Mater Struct* 2009, 18, 035008.
- Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Rong, M. Z. *Carbon* 2004, 42, 2551.
- Severin, E. J.; Sanner, R. D.; Doleman, B. J.; Lewis, N. S. *Anal Chem* 1998, 70, 1440.
- Doleman, B. J.; Lonergan, M. C.; Severin, E. J.; Vaid, T. P.; Lewis, N. S. *Anal Chem* 1998, 70, 4177.
- Li, R. J.; Xu, J. R.; Zhang, M. Q.; Rong, M. Z. *Carbon* 2003, 41, 2353.
- Sisk, B. C.; Lewis, N. S. *Langmuir* 2006, 22, 7928.
- Chen, S. G.; Hu, J. W.; Zhang, M. Q.; Rong, M. Z.; Zheng, Q. *Sensor Actuat B: Chem* 2006, 113, 361.
- Narkis, M.; Srivastava, S.; Tchoudakov, R.; Breuer, O. *Synth Met* 2000, 113, 29.
- Srivastava, S.; Tchoudakov, R.; Narkis, M. *Polym Eng Sci* 2000, 40, 1522.
- Segal, E.; Tchoudakov, R.; Narkis, M.; Siegmann, A. *J Polym Sci Part B: Polym Phys* 2003, 41, 1428.
- Segal, E.; Tchoudakov, R.; Mironi-Harpaz, I.; Narkis, M.; Siegmann, A. *Polym Int* 2005, 54, 1065.
- Segal, E.; Tchoudakov, R.; Narkis, M.; Siegmann, A. *J Mater Sci* 2004, 39, 5673.
- Li, Z. M.; Xu, X. B.; Lu, A.; Shen, K. Z.; Huang, R.; Yang, M. B. *Carbon* 2004, 42, 428.
- Dai, K.; Xu, X. B.; Li, Z. M. *Polymer* 2007, 48, 849.
- Dai, K.; Li, Z. M.; Xu, X. B. *Polymer* 2008, 49, 1037.
- Koscho, M. E.; Grubbs, R. H.; Lewis, N. S. *Anal Chem* 2002, 74, 1307.
- Wei, C.; Dai, L. M.; Roy, A.; Tolle, T. B. *J Am Chem Soc* 2006, 128, 1412.
- Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Li, J. R.; Rong, M. Z. *Carbon* 2003, 41, 369.