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Liquid sensing behaviors of conductive polypropylene composites containing hybrid fillers of carbon fiber and carbon black

Zhuoyan Xu [a], Ning Wang [a], Ning Li [b,*], Guoqiang Zheng [a], Kun Dai [a,*], Chuntai Liu [a], Changyu Shen [a]

[a] College of Materials Science and Engineering, The Key Laboratory of Advanced Materials Processing & Mold of Ministry of Education, Zhengzhou University, Zhengzhou, 450001, People's Republic of China

[b] Henan Energy Chemical Group Co., LTD. Research Institute, Zhengzhou 450046, People's Republic of China

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ABSTRACT

In this paper, carbon black (CB), carbon fiber (CF), and hybrid CF/CB were introduced into polypropylene (PP) to fabricate different conductive composites by melt mixing, respectively. The combined effects of CF and CB on the electrical and liquid sensing properties of PP-based composites were investigated in detail. In virtue of the co-supporting conductive network, percolation threshold of the CF/CB/PP composite was reduced apparently upon the addition of 8 wt.% CF. For liquid sensing measurements, CF/CB/PP conductive polymer composites (CPCs) exhibited a superior liquid sensing behavior with higher responsivity, rapider response and better stability in contrast to the counterpart CB/PP. In addition, the response curves are found to be remarkably characteristic for discriminating different kinds of organic solvents. The present paper provides a new route to tailor the liquid sensing properties of CPCs.

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1. Introduction

Conductive polymer composites (CPCs) are receiving considerable attention from both industry and academia since they could be readily fabricated to address growing demand in many fields [1–5]. Recently, based on the variation in electrical signal, CPCs are desired as sensors for diverse external stimuli, such as liquids [6–8], organic vapors [9], strain [10], heat [11], light [12], etc. In terms of liquid or vapor sensing, CPCs have been regarded as candidates for chemical sensor, solvent leakage detector, and environmental monitor in chemical and petrochemical industry [13–16].

So far, liquid sensing behaviors of CPCs filled with single conductive filler have been studied comprehensively, which are addressed at three main aspects: selective distribution of conductive filler, modification or change of conductive fillers and sensing mechanism. For the first aspect, Narkis et al. [17,18] systematically investigated the liquid sensing of immiscible polymer systems with conductive fillers that were selectively distributed in the interfaces or one polymer phase, such as carbon black (CB)/polypropylene (PP)/nylon 6 (Ny6) [17], CB/PP/thermoplastic polyurethane (TPU) [18], etc. These results indicated that the interfaces are a vital influencing factor on the solvent penetration. On this basis, Pang et al. [19] and Dai et al. [20] promoted the response intensity and response rate of carbon nanotubes (CNTs)/polymethyl methacrylate/ultrahigh molecular weight polyethylene and CB/PP by the unique design of a segregated conductive network. As to the second aspect, Tsubokawa et al. [21,22] harvested a series of liquid sensors with a nice reproducibility and high response intensity by grafting polymers on surfaces of CB particles. On the other hand, Pötschke et al. [7,8,23] turned their eyes to CNTs/polymer composites. They found that a lower CNTs content gave rise to a stronger liquid sensing intensity, indicating a more vulnerable conductive network. Through systematic researches, they proposed that liquid sensing behaviors of CPCs were affected by both the Hansen solubility parameters and the molar volume of the organic solvents, and this result is just related to the last aspect.

Recently, in pursuit of a satisfactory electrical property and the improvement in sensing performances, researchers have enthusiastically resorted to the combination of two conductive fillers [24–27]. For example, Dang et al. [28] reported that the positive temperature coefficient (PTC) intensity can be promoted by introducing carbon fiber (CF) into CB/PP or CB/high-density

* Corresponding authors. Tel.: +86 371 63887969, +86 371 69337626.
E-mail addresses: ncmlining@hotmail.com (N. Li), kundai@zzu.edu.cn (K. Dai).

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polyethylene (HDPE) composites; the negative temperature coefficient (NTC) intensity can be weakened meanwhile. Lin et al. [29] successfully tuned the sensitivity of TPU-based strain sensors by changing hybrid filler ratio of CB to CNTs.

However, there have been few studies on response to organic liquid stimuli with hybrid fillers. In our previous work [30], CB/PP and CNTs/PP were fabricated by melting mixing and the comparison of liquid sensing behaviors between the two composites was studied. Herein, CF as a second filler was introduced into the CB/PP composite. The effects of CF on morphology, electrical and liquid sensing properties of the composites were examined in detail. Furthermore, the underlying mechanism about the conductive properties and sensing behaviors was discussed.

2. Experimental

2.1. Materials

The materials used in this study are isotactic PP, conductive CB and CF. PP (T30S), a product from Dushanzi Petrochemical Co., China, has the following properties: M_w is 3.99×10^5 g/mol, molecular weight distribution is *ca.* 4.6 and the melt flow index (MFI) is 3.0 g/10 min (230 °C, 2.16 kg). CB (VXC-605) was supplied by Cabot. The CF (T300-3K) with an aspect ratio of *ca.* 657 was purchased from Toray Inc., Japan. Both CB and CF were dried at 80 °C for 8 h to remove the water before use. Organic solvents (AR grade) were supplied by Damao Chemical Reagent (Tianjin, China), and used as received.

Fig. 1 displays the typical morphology of the CB and CF. It is noted that CF and CB exhibit an evidently different geometry: in Fig. 1a, it can be seen that most of CB particles exist as grape-like aggregates. This characteristic leans to construct conductive network over short distance, leading to high percolation threshold; in comparison to CB, stick-like CF possesses a large aspect ratio (Fig. 1b), which facilitates the charge transport over long distances but causes damping effect in filler dispersion.

2.2. Sample fabrication

CB/PP, CF/PP and CF/CB/PP composites with different filler concentration were fabricated by a Haake internal mixer (Haake polylab system-Rhemex 252p series, RC9000) at a rotating speed of 50 rpm. The mixing temperature and time were set at 190 °C and 5 min, respectively. The mixture was subsequently pelletized and compressed-molded into sheets at 200 °C for 5 min under a pressure of 15 MPa. Dimensions of samples for liquid sensing test and electrical properties test were both $120 \times 10 \times 0.8$ mm^3. The concentration of CF was fixed at 8 wt.% for CF/CB/PP, which is below the percolation threshold of CF/PP.

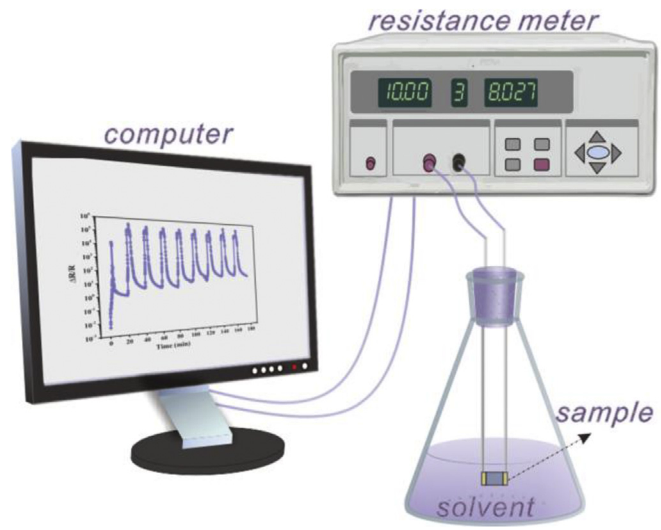

Fig. 2. Schematic diagram of a sample for liquid sensing behavior test.

2.3. Morphology observation

Scanning electron microscopy (SEM) were carried out using a JEOL 7500F SEM. Prior to that, samples were quickly impact fractured after frozen in liquid nitrogen for 30 min and then sputter coated with gold.

2.4. Testing conditions

For electrical resistivity measurement, when the volume resistivity of specimen was lower than 10^6 Ω cm, four probe method was applied, otherwise a high-resistance meter was needed.

As to the test of liquid sensing, the samples were connected at their ends with copper electrodes to minimize the contact resistance. In our previous work [30], liquid sensing behaviors of CB/PP were studied towards xylene, cyclohexane and tetrachloromethane. To identify the combined effect of CF and CB, the same solvents were employed to evaluate the liquid sensing behaviors of CF/CB/PP in this paper. Nine immersion-drying runs (IDR, 5 min in solvent and 15 min in air) test was performed for each analyte. The resistance was simultaneously measured using a resistance meter equipped with a computer. The schematic diagram of the test system is illustrated in Fig. 2. All tests were conducted at *ca.* 25 °C.

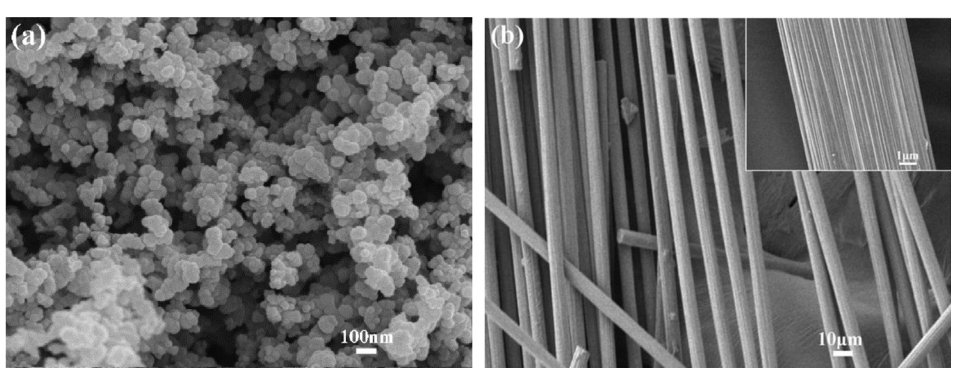

Fig. 1. SEM images of CB (a) and CF (b). The inset in (b) is the morphology of CF at a high magnification.

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