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Liquid sensing properties of carbon black/polypropylene composite with a segregated conductive network

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ABSTRACT

Conductive carbon black (CB)/polypropylene (PP) composite with a segregated structure has been prepared by localizing CB particles preferentially at the interfaces between PP particles. Liquid sensing properties of the composite were investigated by detecting the variations of the electrical resistance toward different solvents. It is found that the composite has a good sensing selectivity. For the liquid sensing behaviors test during immersion-drying runs, a high sensing responsivity, but a poor reproducibility in 'good solvents' is observed. Higher liquid sensing responsivity and faster response rate have been achieved under a high environmental temperature or utilizing the immersion pretreatment. Based on these results, it is suggested that the segregated structure and the Flory–Huggins interaction parameter χ_{12}, which is related to the solubility parameter, molecular volume and temperature are the key influencing parameters for liquid sensing behaviors of the conductive polymer composite (CPC).

1. Introduction

On the basis of the resistivity variations when exposed to external stimuli, like liquids [1–5], organic gases [6,7], thermal field [8,9], mechanical stress [10–12], etc., conductive polymer composite (CPC) based sensors have interested many researchers. In recent decades, the CPC based liquid sensing material, which is a promising sensor candidate for solvent leakage, environmental and food safety monitoring, etc., has been investigated intensively [1–5]. These sensors can be employed as various security and control devices for containers or pipelines in industrial plants, gas stations, or refineries [3]. For instance, Tsubokawa et al. [13,14] fabricated a series of CPCs based liquid sensors by using crystalline polymer-grafted carbon blacks as the conductive fillers. These sensors were applied to detect the contamination in solution, showing nice sensing selectivity and reproducibility. Villmow et al. [15] studied the liquid sensing behaviors of multiwalled carbon nanotube (MWCNT)/polycarbonate (PC) CPC toward various solvents. They proposed a model allowing the calculation of the time depending relative resistance change. Kobashi et al. [16] found that a high MWCNTs content or a high crystallinity led to a lower liquid sensing responsivity of the MWCNT/poly(lactic acid) (PLA) CPC. They attributed this phenomenon to the denser MWCNTs network in the CPC, which caused a blocking influence on the penetration of the solvent molecules.

Interestingly, Narkis et al. [17] reported that the interfaces played an important role in the liquid sensing behaviors for CB/polypropylene (PP)/nylon 6 (Ny6) CPC. In this CPC, Ny6 served as the dispersed phase and CB particles were preferentially located at the PP/Ny6 interfaces. The CPC was very sensitive to methanol and the origin was accounted for the accumulation of methanol at the PP/Ny6 interfaces. Furthermore, they [18] found that the CB/PP/thermoplastic polyurethane (TPU) CPC exhibited significant interphase debonding after exposure to 1-propanol, which manifested again that the interfaces were a key factor affecting the solvent penetration. Dai et al. [19] studied the solvent stimulus-response behavior of CB/poly (ethylene terephthalate) (PET)/high-density polyethylene (HDPE) CPC film in xylene. They found that the interfaces between PET microfibrils and PE matrix enlarged after long-time immersion, leading to a higher responsivity and a faster response rate during the immersion drying run (IDR) for the immersion-pretreated samples. Pang et al. [20] prepared a high responsive liquid sensing material with carbon nanotubes (CNTs) being selectively distributed at the interfaces between ultrahigh molecular weight polyethylene (UHMWPE) and poly (methyl methacrylate) (PMMA). Based on the reports as mentioned above,

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it is deduced that the interface is of great importance to the responsivity of a CPC based liquid sensor. Segregated CPC, for which, the conductive fillers are localized at the interfaces between polymer particles, no doubt, is a promising candidate for a liquid sensor.

CB, which has a low dimension, possesses the advantages of low price and wide range of sources [13,21,22]. Thus, in our previous work [23], CB was selected as the conductive filler to fabricate CB/PP CPC with a novel segregated structure. The comparison of the liquid sensing behaviors to several solvents between the segregated CB/PP CPC and common CB/PP CPC was studied briefly. It was found that compared with the common CB/PP CPC, segregated CB/PP CPC showed better selectivity, higher response rate and higher response intensity. Nevertheless, in order to apply the segregated CB/PP CPC as a liquid sensor, more detailed research about the selectivity and reproducibility of the CPC toward more solvents is necessary.

In this article, to fully understand the liquid sensing mechanism of the segregated CB/PP CPC, liquid sensing behaviors of the CPC toward more solvents and under different temperatures were studied in detail. The reproducibility of the composite to xylene, chloroform and ethyl acetate was studied during eight consecutive IDRs. In addition, the dependence of the liquid sensing behaviors on long-term use was also estimated. By considering the influence of the microstructural evolution of the conductive network in the CPC and the Hansen solubility parameter, the liquid sensing mechanism was discussed.

2. Experimental

2.1. Materials

The materials used for this study involve isotactic PP (T30S) and conductive CB. The PP is a commercial product of Dushanzi Petroleum Chemical Co. (Xinjiang, China) with the molecular weight distribution ca. 4.6 and the melt flow index (MFI) 3.0 g/10 min (230 °C, 2.16 kg). Its M_w is about 3.99×10^5 g/mol. The CB, model VXC-605, purchased from Cabot with a dibutyl phthalate absorption value of 148 ± 15 cm^3/100 g.

2.2. Sample preparation

The PP particles were prepared as follows: PP pellets were dissolved in xylene at 135 °C for 2 h to get a solution with a concentration of 10 wt%. After the solvent was completely evaporated, the obtained PP bulks were smashed into particles using a high speed mixer. CB and PP particles were then added in ethanol under the mechanical stirring (300 rpm) for 1 h and the sonication treatment at 30 °C for another 1 h. After the complete evaporation of ethanol, the mixed particles were compression molded into films at 190 °C for 5 min with a pressure of 15 MPa. The preparation process schematic of the segregated CB/PP composites is illustrated in detail in Fig. 1.

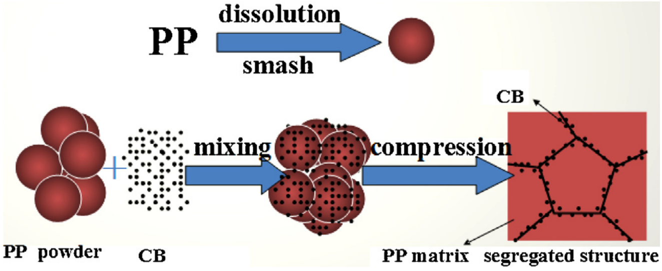

Fig. 1. Schematic diagram of the preparation process of CB/PP CPC with a segregated conductive network.

2.3. Morphology characterization

For morphology observation, the CB/PP CPC was fractured after frozen in liquid nitrogen for 1 h. The PP particles and the fractured surface were covered with a layer of platinum to make them conductive, and then observed with a 7500F JEOL field emission scanning electron microscope (FESEM).

2.4. Liquid sensing behaviors test

In the present paper, the length, width and thickness of the samples used for liquid sensing test are 10 ± 0.2, 2 ± 0.1, and 0.1 ± 0.01 mm, respectively. Copper grids, which were used as the electrodes, were embedded into the ends of the samples to eliminate the effect of the contact resistance. In order to estimate the selective sensitivity of the CPC, the liquid sensing responsivities (defined as R_t/R_0, where R_0 is the initial resistance of the sensor and R_t is the resistance at time t during test) of the CPC in xylene, chloroform, dichloromethane and ethyl acetate for 90 s was compared. In order to study the liquid sensing reproducibility of the CPC, eight IDRs (10 s in solvent and 8 min in air) were performed in xylene, ethyl acetate, and chloroform with different chemical characteristics. The effect of temperature on liquid sensing was also studied. In addition, in order to evaluate the liquid sensing behaviors of the CPC after long-term use, some samples were immersed in xylene and ethyl acetate for 24 h and then dried absolutely in air for 72 h. The influence of the immersion on the microstructure change was investigated by comparing the liquid sensing behaviors of the original samples with that of the pretreated samples. For the measurement, the variation of the resistance was recorded continuously by a computer equipped with a high resistivity meter (model TH2683, supplied by Changzhou Tonghui Electronics Co., Ltd.). For liquid sensing behaviors test, 8 IDRs measurement was performed at 30 °C in a drying oven. The other tests were all started at ca. 10 °C and tested at 30 °C except for the test at different temperatures.

The solvents, xylene, carbon tetrachloride, methylene dichloride, and ethyl acetate were used as received. The characteristics of these solvents and the polymer, PP, were shown in Table 1 [24,25].

Table 1
Characteristics of solvents and PP used in the present paper [24,25].

Material	δ [a]	δ_d [b]	δ_p [c]	δ_h [d]	Boiling point (°C)	Molar volume (cm^3/mol, 25 °C)
Polypropylene	18.0	18.0	0	1	–	–
Dichloromethane	20.2	18.2	6.3	6.1	40	63.9
Xylene	17.9	17.8	1.0	3.1	138.5	123.3
Ethyl acetate	18.2	15.8	5.3	7.2	77	98.5
Chloroform	19.0	17.8	3.1	5.7	61	80.7

[a] δ ($MPa^{0.5}$): Hansen solubility parameter (HSP).
[b] δ_d ($MPa^{0.5}$): HSP for dispersion interactions.
[c] δ_p ($MPa^{0.5}$): HSP for polar interactions.
[d] δ_h ($MPa^{0.5}$): HSP for hydrogen bonding interactions.