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Vapor sensing performance as a diagnosis probe to estimate the distribution of multi-walled carbon nanotubes in poly(lactic acid)/polypropylene conductive composites

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT)/poly (lactic acid) (PLA)/polypropylene (PP) with different polymer blend ratios were fabricated by melt processing method. When fixed the MWCNT content at 1.0 wt.%, A6P4 (PLA/PP 60w/40w) showed the lowest resistivity, which is attributed to the formation of a co-continuous structure. According to the thermodynamics prediction, MWCNT is estimated to be selectively distributed in PLA phase. To further investigate the MWCNT localization behavior in polymer blend, a two-step compounding sequence approach was utilized to fabricate Pre-PLA (*i.e.*, MWCNT were firstly mixed with PLA) and Pre-PP composites. Morphology observation and rheology tests were then carried out to demonstrate the MWCNT distribution in the composites. Vapor sensing behaviors of CPCs towards organic vapors with different polarity were investigated in detail. CPCs with higher PLA content showed a higher responsivity to dichloromethane, a 'good solvent' to PLA. CPCs containing higher PP content exhibited a higher responsivity towards xylene due to the strong interaction between PP and the xylene vapor. While for cyclohexane, a 'poor solvent' to PLA and PP, all the CPCs demonstrate a low responsivity. Interestingly, the vapor sensing feature can be used to testify the MWCNT localization in the polymer blend as a diagnosis probe.

1. Introduction

Conductive polymer composites (CPCs) have attracted much attention in the past several decades for their excellent mechanical, electrical and thermal properties. Normally, they are prepared by incorporating carbonaceous nanofillers such as carbon black (CB) [1–3], carbon nanotubes (CNTs) [4–6] or graphene [7–10] into the insulating polymer to make them electrically conductive. Based on construction of the conductive networks by contact between neighboring fillers, many potential applications of CPC such as thermal sensor [11], strain sensor [12], chemical sensor [2,13–16] and electromagnetic shielding materials [17–19] have been widely investigated. When the nanofillers loading reaches a certain value in polymer, a conductivity transition of composites from insulator to conductor always occurs, which is called the percolation phenomenon, corresponding to the conductive network formation in polymer matrix. However, too much filler content may impair the mechanical property and processability of composites. Thus how to achieve a lower percolation threshold (P_c) without sacrificing the overall property of composites is still an interesting work to be explored.

In the past several decades, much work has been done to reduce the P_c by designing conductive network architectures. CNTs are widely used as a kind of filler in polymer composites for their large aspect ratio, excellent mechanical and electrical properties [20–22]. However, the high van der Waals forces of CNTs make them a poor dispersion in polymer matrix, thus preparing CNTs

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filled CPCs with excellent filler dispersion state is still a challenging work. CNTs filled polymer blend has become a topic aiming to improve the dispersion and distribution of CNTs to some extent. Pang et al. [23–25] fabricated carbon nanotubes (CNTs) filled polymer composites with segregated structures, the CNTs were firstly mixed with high-density polyethylene (HDPE), then a thin layer around the ultrahigh molecular weight polyethylene (UHMWPE) granules was formed through hot compression molding. Double percolation occurred when the segregated structure was achieved, it generally lead to a much lower percolation threshold (the P_c of CNT/HDPE/UHMWPE composites is 0.049 vol.%). The concept of double percolation was firstly proposed by Sumita et al. [26]. Generally, using immiscible polymer blend pair is regarded as an effective way to lower the P_c of composites. Gödel et al. [27,28] investigated the multi-walled carbon nanotubes (MWCNT) filled poly(styrene acrylonitrile) (SAN)/polycarbonate (PC) composite with different compounding sequences, the kinetics factors of MWCNT selective localization were discussed in detail and results indicated that MWCNT would transfer to the PC phase finally, and the composites with co-continuous structure showed a lower P_c. Xu et al. [29] prepared poly(lactic acid) (PLA)/poly(ε-caprolactone) (PCL) composites containing acid-oxide MWCNT (A-MWCNT). They discussed the relationship between polymer blend ratio and electrical resistivity of composites, a co-continuous structure with excellent conductivity can be achieved when the PLA/PCL ratio was 60w/40 w with A-MWCNT content of 1 wt.%. Chen et al. [30] utilized graphene oxide (GO) to trap MWCNT at the interface of PLA/ethylene-co-vinyl acetate (EVA) blend, interestingly, the P_c is only 0.06 wt.%, which is much lower than PLA/EVA/MWCNT composite (*ca.* 0.24 wt.%). They also selected organoclay [31] to control MWCNT selective localization in PC/poly(vinylidene fluoride) (PVDF) blend, and the composite showed an apparent morphological change from sea-island structure to the co-continuous structure, where the MWCNT were mostly trapped at the interface of polymer blends by organoclay.

When it comes to the percolation behavior of CPCs, chemiresistors may be the most embodied CPCs as 'smart material' owing to their abundant responses to external chemical stimuli, especially for the CPCs whose filler content is a little higher than the P_c. In our previous work, we investigated the vapor sensing behavior of CB or CNTs filled PLA composites towards different organic vapors [2]. Results indicated that the CPCs with different carbon fillers exhibited different sensing performance, which is ascribed to the nanostructure of filler and the solubility parameter between PLA and organic solvents. Feller et al. [32–34] fabricated chitosan/MWCNT and PLA/MWCNT composites *via* spray layer by layer (sLbL) technique. They discussed the vapor sensing mechanism and proposed the modified Langmuir-Henry-Clustering (LHC) model to predict the sensing process of CPCs when upon exposure to different organic vapors. Chatterjee et al. [35] fabricated MWCNT filled polymer composites as e-nose in detecting the volatile organic compound of exhaled lung cancer breath, which indicates a potential application in biomarker and medical fields. In other words, the vapor sensor has been regarded as a potential device in identifying toxic vapors and health monitoring.

In this study, polypropylene (PP)/PLA blends filled with MWCNT were prepared *via* melt processing. Composites with different blend ratios were fabricated and the MWCNT distribution in polymer blend was investigated by thermodynamic prediction. Compounding sequence approach was also used to discuss the kinetics migration of carbon filler during melt processing. Finally, the vapor sensing tests were utilized to examine filler localization by comparing the responsivity of composites towards different organic vapors.

2. Experimental

2.1. Materials

Poly(lactic acid) (4032D NatureWorks, USA) used in this study is commercial product containing 98% L-isomeric content, density of 1.24 g cm^{-3}, its M_W and M_N are 2.23×10^5 g mol^{-1} and 1.06×10^5 g mol^{-1}, respectively. Polypropylene (T30S) was supplied by Dushanzi Petroleum Co., China. Its density is 0.91 g/cm^3 and the M_W is 39.9×10^4 g mol^{-1}. Carboxylic multi-walled carbon nanotubes (MWCNT) with diameters of 20–40 nm, average length of about 50 μm were supplied by Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Sciences. Their special surface area (SSA) is higher than 110 m^2 g^{-1} and purity is higher than 95 wt.% Analytical grade solvents dichloromethane, xylene and cyclohexane were purchased from Damao Chemical Reagent Co. Ltd. (Tianjin, China).

2.2. Composites preparation

Prior to compounding, PLA, PP and MWCNT were all dried in a vacuum oven at 60 °C for 24 h. The PLA/PP/MWCNT ternary composites were fabricated by melt compounding using a Haake internal mixer (Haake polylab system-Rhemex 252p series, RC9000, Germany) at 190 °C with a rotation speed of 60 rpm for 8 min. To study the effect of compounding sequence on the localization of MWCNT, two compounding strategies were employed:

a The three components were added into the mixer chamber simultaneously and compounded at 190 °C for 8 min;
b The MWCNT was premixed with PLA or PP for 3 min at 190 °C first, then another polymer was added into the chamber for further mixing for another 5 min.

The obtained mixtures were pelletized and hot compression molded into thin film at 190 °C for 5 min under the vacuum condition with a pressure of *ca.* 10 MPa by using a vacuum hot-press machine (FM450, Beijing Future Material Sci-tech Co., Ltd., China). The sample dimension for electrical property test is $100 \times 10 \times 0.6$ mm^3. To simplify the expression, the samples with different component ratio are noted as AxPy, where x and y represent the composition of PLA and PP in composites, respectively. The composite premixed with PLA or PP is referred as Pre-PLA and Pre-PP, respectively.

2.3. Characterization

2.3.1. Electrical resistivity measurement

The dimension of the samples for electrical resistivity measurement was $100 \times 10 \times 0.6$ mm^3. Copper mesh was embedded into two ends of the sample to ensure good contact between the sample and resistivity meter (TH2683, Changzhou Tonghui Electronics Co., Ltd., China). The resistivity ρ is calculated by using the equation of $\rho = RS/L$, where R is the volume resistance, S is the cross-section area of the strip, and L is the length between the electrodes. For each sample, at least five specimens were tested to ensure the measurement accuracy.

2.3.2. Scanning electron microscope (SEM)

The surface morphology of the MWCNT filled CPCs was investigated using a field emission scanning electron microscope (FESEM) (JEOL JSM-7500F, Japan) with an accelerating voltage of 5 kV. Before observation, the specimens were all cryofractured in liquid nitrogen for at least 30 min, after that the fractured surfaces were then sputtered with a layer of platinum to avoid the electrical charging.

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