



Short communication

Structuring tri-continuous structure multiphase composites with ultralow conductive percolation threshold and excellent electromagnetic shielding effectiveness using simple melt mixing



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ABSTRACT

Tri-continuous structure poly(vinylidene fluoride)/polystyrene/high density polyethylene (PVDF/PS/HDPE) ternary blends was fabricated as a candidate for structuring high electrical performance composites. By adding MWCNTs and tuning the thermodynamic and kinetics conditions, the selective distribution of MWCNTs in interfacial PS phase were formed after melt mixing. These composites displayed ultralow conductive percolation threshold and excellent electromagnetic shielding effectiveness by this structuring process.

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1. Introduction

Conductive polymer composites (CPCs) containing electrical nanofillers are new alternative candidates for integrated circuits, high charge-storage capacitors, electrostatic dissipation, electrostatic painting and electromagnetic interference shielding applications based on their own superiorities, such as their lightweight, low cost, good processability, and tunable conductivities over a wide range [1–7].

Firstly, in order to achieve the percolation threshold and satisfactory electrical conductivity, high nanofiller loading is often essential [8]. However, a high nanofiller concentration always results in poor mechanical properties, complex processing, and high cost. Therefore, decreasing the value of the percolation threshold of the nanofiller as much as possible is a very significant factor in preparing conductive polymers, whether in reducing the cost of material or in simplifying processing procedure.

The most effective way to decrease the percolation threshold of composites is controlling selective distribution of conductive filler at the phase interface to achieve “segregated network structure” [9–16]. Nevertheless, the formation of such segregated structures

almost allows all of the conductive fillers stay at the interfaces of the polymer domains, which prevents molecular diffusion between the polymer granules leading to poor mechanical performance [13,15,16] and the segregated structure is easily destroyed during post melt processing, also complicated chemical modification and toxic reagents [13,16] are often involved.

In addition, a major precondition for CPC with satisfactory electromagnetic interference shielding effectiveness (EMI SE) is that the electrical conductivity is at least 1 S/m, which can only be achieved at a relatively high content of electrical nanofillers. An EMI SE value of at least 20 dB is typically required for conductive polymer composite (CPC) materials to be commercially applicable in EMI shielding devices [17–19]. Yang etc [18] previously reported on MWCNTs loading composites with accounting for good EMI shielding effectiveness (20 dB). However a high nanotube content (7 wt% of MWCNTs) was needed. Recently, Maiti etc [19] had demonstrated a unique and novel method for the preparation of highly EMI shielding (~20.2 dB) polystyrene/multiwalled carbon nanotubes/graphite nanoplate (PS/MWCNT/GNP) nanocomposites at extremely low loading of MWCNTs (~2 wt %) and GNP (~1.5 wt %). Nevertheless, complicated procedures and toxic reagents were still unavoidable. It is therefore that integrating low percolation threshold, high effective EMI SE and easy processability to fabricate a desirable CPCs material is still a severe challenge.

In recent years, through a combination of composite droplet [20–26] and co-continuous blend morphology preparation

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methodologies, a hierarchical structure, composed of a tri-continuous structure [27–29], has been realized by melt mixing in ternary blends which can be as a candidate to prepare high electrical performance CPCs material. Therefore, in the current study, we developed an effective way to achieve an ultralow percolation threshold and excellent electromagnetic shielding effectiveness in immiscible ternary blends containing MWCNTs. Through tuning the thermodynamic and kinetics conditions, a tri-continuous structure in PVDF/PS/HDPE ternary blends and the selective distribution of MWCNTs in interfacial PS phase were synchronously formed after melt mixing. The composite shows an ultralow percolation threshold of 0.022 vol% and good reproducibility after several times of processing. This value obtained here is the smallest percolation threshold reported in the open literature for melt mixing multiphase composites. More important, these composites displays excellent shielding effectiveness of 31 dB with only 1.6 vol% MWCNTs loading.

2. Experimental

The experimental details about the materials, preparation and characterizations were described in the [Supplementary Material](#).

3. Results and discussion

The loss modulus thermograms for different pure phase and the blends are shown in Fig. 1. It indicates that the T_g for PVDF, HDPE and PS is -38.76°C , -120.47°C and 116.5°C , respectively. All loss modulus thermograms for the blends reveal the almost same T_g peaks as that observed for each pure phase, which indicates immiscibility of all the phases.

The phase morphology of ternary blends is shown in Fig. 2. Fig. 2a shows schematic of tri-continuous structure in ABC ternary blends. SEM photos of PVDF/PS/HDPE blends in Fig. 1b shows a total continuous structure of different phase. In order to distinguish the phases, the PS is etched by xylene, uniform cracks pervaded entirely throughout the sample (shown in Fig. 2c) can be clearly seen, in contrast to Fig. 2b. Then the EDS data of the other two areas in this sample are given. According to Fig. 2d, C and F atoms can be seen in one of the phases while the other phase only shows C atom. This demonstrates that the PVDF phase and HDPE phase can be accurately distinguished. The spreading coefficient value for $\lambda_{\text{PS/HDPE}}$ shows a positive value of 3.8 mN/m while the other two is negative, indicating a complete wetting case, where the PS phase is

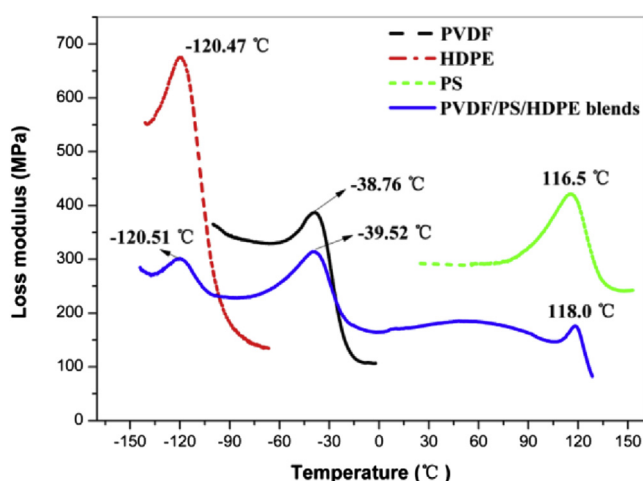


Fig. 1. DMA curves of loss modulus as a function of temperature for different samples.

expected to situate between PVDF and HDPE interface, as observed experimentally in Fig. 2c. Fig. 2e shows the polarized optical microscope (POM) image obtained at room temperature. The PVDF (bright white domains, corresponding to the crystalline structure) and HDPE phases (in dark yellow) appear as the main components and are separated by a thin PS layer (notice the black domains corresponding amorphous). Tri-continuous structure with the PS located at the interface between PVDF and HDPE is verified again.

The presence of a PS layer at the interface of the cocontinuous PVDF/HDPE blends significantly reduces the PS volume fraction required for its percolation and continuity development as compared to classical binary HDPE/PS and PVDF/PS blends. Continuity data based on gravimetric solvent extraction clearly demonstrate this effect and are shown in Fig. 3. It can be seen that in this complete wetting triple phase system, a PS volume composition as low as 11 vol% results in a PS phase continuity of about 80%, a very high level of continuity for such a small volume fraction of PS. Moreover, the PS layer continuity increases with increasing PS volume content, reaching an apparent maximum value of approximately 95%. This high continuity is beneficial for the construction of electrical conduction pathways when MWCNTs was confined into the PS layer.

In order to investigate the effect of MWCNTs loading on the evolution of tri-continuous structure in PVDF/PS/HDPE blends and confirm the construction of MWCNTs network and its selective distribution in PS layer. Firstly, PS layer continuity as a function of MWCNTs content is illustrated in Fig. 4a. It can be noted that with MWCNTs loading increasing, PS continuity display a downtrend, about declines 10% with MWCNTs content increase to 0.5 vol%. However, a still high continuity (>85%) can be maintained even with high MWCNTs loading which is beneficial to the formation of MWCNTs network. Fig. 4b and c shows the SEM micrographs of PVDF/PS/HDPE blends with 0.05 vol% and 0.3 vol% MWCNTs loading. Tri-continuous structure is observed for both of the samples according with the PS continuity results in Fig. 4a. From Table S3, the wetting coefficient data predict that the thermodynamic interaction is the strongest between CNTs and PS, and a stable distribution of CNTs at the PS layer between the PVDF and HDPE phases can be achieved. From the TEM observation of Fig. 4d and e, it manifests that MWCNTs forms a perfect continuous layer locating at the interface of PVDF/HDPE. Based on the above results, it can be concluded that most MWCNTs were embedded in PS phase which is consistent with our predication. Then the selective solvent extraction is further employed to observe the localization of MWNTs (shown in Fig. 4f). When the PVDF is dissolved first, the obtained solution is clear, concluding that MWCNTs are not in the PVDF phase. After immersing the samples in xylene for 24 h, the solution becomes dark caused by the MWCNTs dispersion which indicates that MWCNTs is located at PS layer in composites. This observation agrees well with the result obtained from previous theoretical predication. Additionally, the optical micrographs of the samples are used to further verify the location of MWCNTs. Because of the difference of light transmittance, phase region is easily distinguished in Fig. 4g and h. The dark interface between PVDF and HDPE can be apparently observed which is attributed to the inferior light transmittance of MWCNTs. Obviously, this morphology is most favorable for the formation of a conductive pathway in the sample, thus indicating the greater potential for reducing the electrical resistivity.

The MWCNTs content dependence of electrical conductivity for the different composites is presented in Fig. 5. The typical percolation behaviour is seen for all the three composites. With the increase of MWCNTs content in the samples, the electrical conductivity of all the samples increases. The electrical conductivity of samples with high MWCNTs content increases by about ten

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