



Enhancing the conductivity of carbon nanotube filled blends by tuning their phase separated morphology with a copolymer



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ABSTRACT

We describe an approach to engineer bi-continuous conductive blends of polymers and multiwall carbon nanotubes (MWNTs) by formation of a percolating network of MWNTs in one phase of the blend. Thereto, spinodal decomposition combined with compatibilization by an interfacially segregated random copolymer (rcp) is proposed. A systematic study of the effect of the concentration of the random copolymer poly(styrene-random-methyl methacrylate) (PS-r-PMMA) on the electrical conductivity of a phase separating poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) blend with MWNTs was performed above the spinodal temperature (at 220 °C) and at room temperature. Compatibilization results in a huge conductivity increase, whereby blends with 0.5 wt% MWNTs and 0.25 wt% copolymer exhibit the same conductivity as percolating bi-phasic blends with 2 wt% MWNTs. In addition, the linear viscoelastic moduli show a power law increase with the concentration of copolymer. It was deduced that the observed increase in conductivity was caused by a substantial morphology refinement and increased degree of cocontinuity after copolymer addition leading to the formation of double percolated networks in the blends. These findings were corroborated with optical micrographs and scanning transmission electron microscopy (STEM) images for blends with 0.5 wt% and 2 wt% carbon nanotubes, respectively. The morphology changes can be explained by an interfacial tension reduction, which alters structure dynamics during annealing. The effectiveness of the long random copolymer in compatibilizing the blend is attributed to multiple interface crossings coupled with the ability of the copolymer blocks to anchor into the homopolymers. This simple approach can provide a pathway to develop low cost and ubiquitous high performance dielectric materials with ultra-low percolation thresholds.

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1. Introduction

Blending of polymers and conductive nanoparticles has opened pathways to engineer materials by synergistically combining the electrical, optical and mechanical properties of the different components [1]. State of the art applications of polymeric carbon nanotube composites with excellent conducting and dielectric properties are sensors and actuators [2], supercapacitors [3], and artificial muscles [4]. However, a high percolation threshold of

nanotubes often results in inferior mechanical properties, adverse processing conditions, and increased production costs. Hence, the challenges of decreasing the percolation threshold of conductive fillers and obtaining a stable fine morphology are regularly addressed in order to fabricate high performance dielectric polymeric composites and blends with tailored dielectric properties.

Owing to the dependence of performance and properties of polymer blends on the morphology, various strategies have been developed for the refinement and stabilization of morphology during processing. In this regard, thermodynamically controlled localization of block copolymers [5] is a classical approach for compatibilization of an immiscible blend. Furthermore, nanoparticle addition has been proven to be a successful strategy to

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refine and stabilize bi-phasic morphologies thermodynamically [6] or kinetically [7]. Coating the nanoparticle surface with a polymer [8] or tuning the surface polarity [9] are commonly employed methods to obtain interfacial segregation of the nanoparticles. However, the latter compatibilization method is often difficult and non-viable due to the required surface modification.

Co-continuous morphologies in polymeric blends have proven to be a successful strategy to develop hierarchical structures containing a three-dimensional percolating particle network [10,11]. To improve the electrical conductivity, various strategies have been applied to widen the co-continuous window in bi-phasic blends. Efforts have been directed to kinetically trap nanoparticles within one phase of the blends, since particles can stabilize the co-continuous microstructure [12]. Furthermore, kinetically driven interfacial jamming of particles provides an alternative means to stabilize co-continuous morphologies [13]. In addition, thermodynamic stabilization of the rapid coarsening of interconnected structures during phase separation in polymer blends has been addressed [14]. The dynamic coupling between polymer–polymer phase separation and polymer-particle phase wetting [15] has been successfully controlled by modifying the interaction of nanoparticles with phase separating polymer systems [16]. However, the compatibilizing efficiency of the nanoparticle depends on the change in the free energy of mixing between the two homopolymers, and the effect is more pronounced for immiscible systems [17].

Due to the sensitivity of the state of morphology to the selectivity of particle localization, processing conditions, state of nanoparticle dispersion and sequence of components addition, the ergodicity of the stability of the co-continuous structures is ill-defined. In addition, added complexity in determining the final morphology is encountered when conductive fillers with large aspect ratio are used. The mechanism of localization of carbon nanotubes and nanorods in polymer blends is a fast and effective transfer process, governed by the subtle balance of the interfacial energy between the fillers and the polymer components [18]. The selective localization of MWNTs is also influenced by the molecular weight of grafted polymer chains on MWNTs as recently shown for SAN/PPE blends, and the localization can effect the blend morphology [19]. In this regard, the chemical affinity caused by functionalization of MWNTs determines the selective localization of MWNTs in a polymer blend of PS/P2VP and even in nanostructured block copolymer materials [20]. In summary, the commonly employed method for developing percolating structures in polymer blends involves surface modification, stringent choice of interfacial energies and kinetic migration of nanoparticles to the interface of polymer blends, which for most polymer systems is difficult, expensive and not applicable [21].

It has been shown that compatibilizers can be used to enhance the formation of a percolated network structure in homopolymers by promoting a more homogeneous particle dispersion [22]. In polymer blends, the combination of a copolymer and nanoparticles is an uncommon strategy to create a percolating network with low particle content. It is noteworthy to mention that a SBS block copolymer has been used in an immiscible PP/PS blend for selective localization of carbon black at the interface to produce a co-continuous morphology with low percolation threshold [23]. Recently, a selective localization of MWNTs in the interfacially localized PMMA shell of ternary PS-PVDF-PMMA blends was realized by a combination of suitable processing conditions and PMMA modification of the nanoparticles [24]. Tailoring the graphene oxide surface in order to promote reactive compatibilization with a copolymer has been used to develop a percolating network in PLA nanocomposite blends [25]. In this perspective, we demonstrate a new and facile route for developing macroscopic and nanoscopic

co-continuous structures by introducing a random copolymer to a phase separating blend system with carbon nanotubes preferentially segregated in one blend phase.

This paper reports for the first time an analysis of the effect of a compatibilizer on the electrical conductivity of a phase separating polymer blend. The rationale behind the present work is to use phase separation via spinodal decomposition to generate a co-continuous morphology with a connected network of MWNTs that is stabilized with a random copolymer. In this contribution, we demonstrate the combined effect of a random copolymer and MWNTs in improving the connectivity and refinement of a phase separated blend to enhance the conductivity. Considerable efforts have been dedicated to designing percolating carbon nanotube polymer composites [26] and conducting polymer blends [27], but the methodology of combining phase separation as a tool to control the localization of nanoparticles and compatibilization with a copolymer to stabilize the phase separated structure has not yet been conceived. As a proof of concept, we have compatibilized a model polymer blend system using an inexpensive and easily available random copolymer. Thereto, a lower critical solution temperature (LCST) type blend consisting of (40/60) poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) has been chosen as a model blend system. The results presented in our work offers a unique approach to tune the phase separated morphology to achieve a significant reduction in the percolation threshold of MWNTs in polymer blends. The findings presented in our work will pave the route to develop ubiquitous phase separated conducting blends.

2. Experimental section

2.1. Materials

Both the components of the LCST blend, poly[(α -methyl styrene)-co-acrylonitrile] (P α MSAN) (Luran KR2556) and poly(methyl methacrylate) (PMMA) (Lucryl G77) were obtained from BASF. The blend P α MSAN-PMMA is miscible at low temperatures and undergoes a transition to a phase separated state by spinodal decomposition at around 165 °C for blends containing 40 wt% P α MSAN [28]. The amine functionalized multiwall carbon nanotubes MWNTs (NH₂-MWNTs, NC3152) were kindly provided by Nanocyl. The surface free energy of functionalised MWNTs is of the order of 45 mN/m [29]. The surface free energy at 220 °C is estimated to be 25.9 mN/m for PMMA and in the range of 27.4–34.5 mN/m for P α MSAN [30]. Hence, we have chosen NH₂-MWNTs for the study, as the polar NH₂-MWNTs has a surface free energy closer to P α MSAN, which would drive their localization in the P α MSAN phase. Bose et al. [31] indeed reported selective localization of these MWNTs in the P α MSAN phase of 40/60 P α MSAN/PMMA blends. Poly(styrene-random-methyl methacrylate) (PS-r-PMMA), a random copolymer was obtained from Polysciences (15783-250). The copolymer has a molar mass of 270,000 g/mol and is composed of 70 wt% styrene and 30 wt% methyl methacrylate. The copolymer has a glass transition temperature (T_g) of 102 °C, whereas the T_g of P α MSAN and PMMA is respectively 124 °C and 109 °C.

2.2. Blend processing

P α MSAN nanocomposites, 40/60 (wt%/wt%) and 85/15 (wt%/wt%) P α MSAN/PMMA blends were prepared with or without NH₂-MWNTs and copolymer by melt mixing, using a 15 cm³ DSM microcompounder at 200 °C with a rotational speed of 60 rpm for 20 min. All components were added simultaneously into the mixer. The melt mixing was conducted under an inert nitrogen

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