



# Carbon nanotube induced double percolation in polymer blends: Morphology, rheology and broadband dielectric properties



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## ARTICLE INFO

### Article history:

Received 18 October 2016

Received in revised form

22 February 2017

Accepted 26 February 2017

Available online 28 February 2017

### Keywords:

Morphology development

Polymer blends

Dielectric properties

Nanocomposites

## ABSTRACT

In this study, we investigate the effect of multi-walled carbon nanotube (MWCNT) on the rheology, morphology and broadband dielectric properties of polypropylene:polystyrene (PP:PS) blends (PP:PS—10:90, 50:50 and 90:10). Transmission electron microscopy showed that MWCNTs were localized at the interface and inside the PS phase, regardless of the polymer blend ratio. Employing scanning electron microscopy, we observed that addition of MWCNT led to a transition from dispersed to interconnected morphology for the blends with PS as minor phase (PP:PS/50:50 and PP:PS/90:10). We propose that the selective localization of MWCNT in PS and at the interface slowed down the breakup mechanisms, increasing the lifetime of PS/MWCNT elongated domains, thus decreasing the amount of PS/MWCNT needed to percolate in PP phase. In addition, it is proposed that MWCNT located at the interface act as bridges between PS/MWCNT domains, favouring the coarsening of PS/MWCNT domains. The dielectric properties of the polymer blends PP:PS/50:50 and PP:PS/90:10 confirmed that double percolation was achieved with increase in MWCNT content. This transition provided the possibility to tune dielectric properties of the PP:PS/MWCNT blends. The double percolated structure offered high imaginary permittivity, while the dispersed morphology presented low imaginary permittivity. In other words, this study reveals that manipulating blend morphology can lead to blends with capacitive or dissipative characteristics.

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## 1. Introduction

Blending immiscible polymers is one of the most cost-effective methods to develop new materials with enhanced properties and performance than existing polymeric materials. Addition of nanoparticles to polymer blends can lead to versatile materials with advantageous mechanical, charge storage, electrical and magnetic properties [1–3]. When nanoparticles are mixed with polymer blends with two or more phases, they tend to localize in a preferred phase depending on different governing parameters, such as thermodynamic [4–6] and kinetic [7–9] parameters, determining the localization of the nanoparticles to one of the polymer phases or the interface.

It is well known that the electrical conductivity of polymer blends filled with electrically conductive fillers depends on the percolation of the polymer phases and the percolation of the filler particles. That is, if the polymer blend is co-continuous, then both

phases are said to be percolated. If the conductive fillers are selectively localized and percolated through one continuous polymer phase, then this is considered as double percolation. The concept of double percolation was initially described by Sumita et al. [4,10] for carbon black (CB) filled immiscible polymer blends, and it has been applied for other systems with conductive fillers such as carbon nanotubes [11,12], carbon fibers [13], graphene [14], graphite nanosheets [15], etc. The double percolation phenomenon provides advantages over single-phase polymer composites [3,12] since it is possible to achieve improvement in conductivity at very low filler contents via selective localization of the conductive particles in one of the phases, or at the interface. For instance, Gubbels et al. [7,16] showed that the localization of the filler influences the electrical percolation of the blend system polyethylene:polystyrene/carbon black (PE:PS/CB), and the electrical conductivity passes through a maximum when the particles are localized at the interface.

In fact, filler selective localization in the polymer blends may cause morphological changes, affecting the final properties and performance of the material. Stabilization of domain size by

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addition of nanoparticles has been extensively reported [17–24]. The function of the nanoparticles in reducing the coarsening has been explained by decrease in interfacial tension by localization of the filler at the interface [18,24], coalescence suppression due to nanoparticles acting as barriers at the interface [17,19], increase of viscosity, elasticity of the phase containing the nanoparticles or a combination of these parameters [17,19–21,23]. Opposite to the vast research in morphology refinement, results regarding co-continuity improvement in the blends by addition of nanoparticles are scarce [12,16,19,25,26]. The increase of domain size was attributed to several factors such as filler localization [16,19], filler functionalization [12], filler geometry [26] and particle self-networking in the host polymer [25]. In terms of localization, Kontopoulou et al. [19] showed that the morphological changes in a clay-filled polypropylene:maleated ethylene propylene rubber (PP:EPR-g-MAN) blend depended on whether the filler was localized in the dispersed or matrix phases. When the clay was localized in the dispersed phase, coalescence was favoured, while localization of clay particles in the matrix phase suppressed coalescence substantially. On the other hand, Poyekar et al. [12] showed that functionalization of multi-walled carbon nanotube (MWCNT) with sodium salt of 6-amino hexanoic acid (Na-AHA) or 1-pyrene-carboxaldehyde (PyCHO) provided differences in viscosity ratio, leading to structural changes in the blend morphology. Na-AHA MWCNTs functionalization provided co-continuous structures for both polyamide6: (acrylonitrile butadiene styrene copolymer) (PA6:ABS) blend at 40:60 wt% and PA6:ABS/60:40 wt%. The co-continuity enhancement started at earlier stages of mixing than the corresponding blends with unmodified MWCNT. On the other hand, PyCHO modified MWCNTs did not cause any change in the dispersed morphology of PA6:ABS/40:60 wt% blend, while dispersed to co-continuous transition happened for the PA6:ABS/60:40 wt% blend.

In this work, we studied the double percolation induced by MWCNT addition into the polypropylene:polystyrene (PP:PS) blend with PS as the minor phase. The transition from dispersed to co-continuous morphology was explained in terms of the selective localization of MWCNT in PS, and the changes in viscosity and elasticity ratios between the MWCNT filled PS phase and the unfilled PP. It was proposed that the selective localization of MWCNT in PS and at the interface slowed down the breakup mechanisms, and MWCNT at the interface might acted as bridges between PS/MWCNT domains, favouring the coalescence, and shifting the morphology from dispersed to co-continuous. This morphological transition provided the possibility to tune dielectric properties of the PP:PS/MWCNT blends. It was found that the double percolated structure offers high imaginary permittivity, while the dispersed morphology presents low imaginary permittivity.

## 2. Experimental

### 2.1. Materials and composites preparation

Polypropylene (PP) H0500HN ( $M_w = 209,300$  g/mol, MFI = 5 g/10min) was provided by Flint Hills Resources<sup>®</sup>. Polystyrene (PS) Styron<sup>®</sup> 615APR ( $M_w = 193,249$  g/mol, MFI = 14 g/10min) was obtained from Americas Styrenics LLC. Multi-walled carbon nanotube (MWCNT) (Nanocyl<sup>™</sup> NC7000) was purchased from Nanocyl S.A. (Sambreville, Belgium). Per the manufacturer, MWCNTs were produced with the catalytic chemical vapor deposition process, and had an average diameter of 9.5 nm, a length of 1.5  $\mu\text{m}$ , and a surface area of 250–300  $\text{m}^2/\text{g}$ . Fig. S1 in Supplementary Information provides additional data about Nanocyl<sup>™</sup> NC7000 inner and outer diameter size distribution. Polymer nanocomposites were prepared employing a Haake<sup>™</sup> Rheomix series 600 OS (Thermo Scientific Inc,

USA) internal batch mixer connected to a Polylab<sup>™</sup> OS platform. Five systems with different MWCNT concentrations were studied: PS, PP, PP:PS/10:90 vol.%, PP:PS/50:50 vol.% and PP:PS/90:10 vol.%. Prior to mixing, polymer pellets were dried at 60 °C overnight under vacuum. Compounding was performed at 50 rpm and 200 °C for 15 min (this rotation speed corresponded to 40  $\text{s}^{-1}$  average shear rate calculated using the approximation of two adjacent sets of concentric cylinders [27]). The mixing procedure comprised two steps: PP and PS pellets were melt mixed for 3 min, and then MWCNTs were added and melt mixed for an additional 12 min. In addition, the neat systems were processed at the same mixing conditions. After mixing, the samples were molded into a rectangular cavity with 42 × 25  $\text{mm}^2$  dimensions and 0.88 mm thickness using a Carver compression molder (Carver Inc. Wabash, IN) at 200 °C for 15 min under 41 MPa pressure.

### 2.2. Materials characterization

To investigate the selective localization of MWCNT in the molded nanocomposites, transmission electron microscopy (TEM) was carried out on a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA) at a 200 kV acceleration voltage with a standard single-tilt holder. The images were captured by a Gatan UltraScan 4000 CCD Camera (Gatan, Pleasanton, California, USA) at 2048 × 2048 pixels. Samples for the TEM observations were cryo-ultramicrotomed using a Leica EM UC6 microtome setup in nitrogen atmosphere at temperature ranges of –50 °C to –70 °C.

Scanning electron microscopy (SEM) was performed to observe PP:PS blends morphology using a FEI XL30 SEM equipment (FEI Hillsboro OR, USA) at an accelerating voltage of 20 kV. To obtain a better contrast between phases, the molded samples were etched using Tetrahydrofuran (THF) to remove the PS phase. After etching, the samples that kept an integrated structure were cryo-fractured in liquid nitrogen, dried in a vacuum oven at 60 °C for 1 day, and then placed on SEM stubs. The samples that lost their integrated structure were washed with THF until removal of all PS phase. Then, 3  $\mu\text{l}$  of the solution was placed on a cover-glass and mounted on the top of a SEM stub. To prevent scanning problems and image artifacts due to the accumulation of electrostatic charge at the surface of the samples, all samples were coated with gold in an argon atmosphere.

To study the factors affecting the blend morphology upon addition of MWCNT, rheological measurement was done using an Anton-Paar MCR 302 rheometer at 200 °C using 25 mm parallel plate geometry with a gap of 1 mm. Small amplitude oscillatory shear measurements were performed in the linear viscoelastic region under small amplitude oscillatory shear  $\gamma = 1\%$ . Parameters such as relaxation time and elasticity ratio were calculated from the complex viscosity data ( $\eta^*$ ) in the frequency range from 0.025 rad/s to 628 rad/s. The shear viscosity at the average mixing shear rate of 40  $\text{s}^{-1}$  for the neat PP, neat PS, neat blends and the corresponding MWCNT filled systems was measured using a Kayeness (Dynisco) capillary rheometer (Morgantown, PA), model LCR600 D8052M-115 2046 WVS. The melt polymer sample was extruded through a 0.508 mm ( $L/D = 20$ ) die (entrance angle 120°) at 200 °C. Measurements were taken by a load cell. The results were sent to the KARS software, where Weissenberg-Rabinowitsch correction was performed for each data set.

The micro-dispersion state of MWCNT within PP, PS and the blends was evaluated using light transmission microscopy (LM) on 1  $\mu\text{m}$  thick cuts of the compression-molded samples. The cuts were prepared using a Leica<sup>®</sup> EM UC6 (Leica Biosystems, Germany) ultramicrotome at room temperature. An Olympus<sup>®</sup> BX60 optical microscope (Olympus Inc, USA) connected to an Olympus DP80 camera was used to capture the images from different cut sections

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