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Nanostructured carbon black filled polypropylene/polystyrene blends containing styrene–butadiene–styrene copolymer: Influence of morphology on electrical resistivity

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ABSTRACT

This paper is part of a comprehensive study on using selective localization of carbon black (CB) at the interface of immiscible polymer blends in order to reduce the percolation threshold concentration and enhance the conductivity of the blends. CB was successfully localized at the interface of polypropylene/polystyrene (PP/PS) blend by introducing styrene-butadiene-styrene (SBS) tri-block copolymer to the blend. In CB-PP/PS/SBS blends, CB has higher affinity for the polybutadiene (PBD) section of the SBS copolymer, whereas in CB-PP/PS blends, CB prefers the PS phase. PP/PS interface is one of the preferred locations for the SBS copolymer in the (PP/PS) blend; at which the PBD section of the SBS copolymer forms a few nanometers thick layer able to accommodate the CB nano-particles. The influence of SBS addition on the morphology and electrical properties of various PP/PS blends filled with 1 vol% CB were studied. SBS influence on the conductivity of PP/PS blends was found to be a function of the PP/PS volume ratio and SBS loading. The most dramatic increase in conductivity was found in the (60/40) and (70/30) PP/PS blends upon the addition of 5 vol% SBS. 5 vol% SBS was found to be the optimum loading for most blends. Using 10 vol% of SBS was reported to deteriorate electrical conductivity of the conductive co-continuous PP/PS blends. For all blends studied, SBS addition was found to compatibilize the blends. Finer morphologies were obtained by increasing SBS loading.

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1. Introduction

Conductive polymer composites (CPCs) are produced by incorporating a critical amount of a conductive filler, which is referred to as the percolation threshold, in an insulating polymer matrix [1,2]. These composites have many applications, including antistatic materials, electrostatic discharge (ESD) dissipation and electromagnetic interference (EMI) shielding [3,4]. CPCs have many advantages over traditionally used conductive materials, like metals, in terms of corrosion resistivity, adaptability to application needs, weight, processability and cost [5,6]. Among all available conductive fillers, carbon black (CB) has been extensively

used in production of packaging composites for (ESD) protection applications [3,7]. CB has a significant cost advantage over the highly conductive carbon materials like carbon nanotubes, and chemical stability and weight advantage over metallic fibers, flakes and powders.

According to the CB aggregate structure, CBs are categorized into a high structure and a low structure [3]. High structure CB is characterized by more branching and chaining per primary aggregate compared to the low structure CB. The main disadvantage of the low structure CB-filled polymer composites is the high concentration of CB (~15–20 wt%) required to achieve the percolation threshold. Such high filler loading affects the composite mechanical properties, processability and increases the cost of the final composite [8,9]. Moreover, the sloughing of the CB powders is an environmental concern [10,11]. Technical

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problems associated with using low structure CB can be solved by using the high structure CB. Percolation threshold of polymer composites filled with high structure CB is typically between 2.5 and 6 wt% depending on the polymer and CB types [8,12]. But this grade of CB is very expensive compared to the low structure grade CB; therefore reducing CB loading is of technical and economic importance.

Among all of the processes investigated to reduce the percolation threshold in CB composites, the double percolation technique is the most promising method [3,8]. In a blend of two polymers and CB, CB was found to have different affinity for each polymer in the blend; thus it will selectively disperse in one of the two phases or accumulate at the interface. The percolation in such blends is governed by the percolation of the CB rich phase and the continuity of this phase in the blend [3,13]. The selective localization of the filler at the interface provides a composite with the lowest filler loading if the interfacial region was continuous. Unfortunately, for most polymer blends studied, CB did not show affinity for the interface [14–22].

Very few successful methods to selectively localize CB at the interface have been proposed. Gubbels and coworkers [23] investigated a kinetic strategy and a thermodynamic strategy to selectively localize CB at the interface of a binary immiscible polymer blend. In the kinetic method CB was first mixed with the polymer for which it has the lowest affinity, and then the polymer for which CB has the higher affinity was added. CB is expected to move from the less favorable phase to the more favorable one through the interface. The main drawback of this strategy is the difficulty in choosing the correct mixing time to accumulate most of CB at the interface. In the thermodynamic method, CB particles were oxidized to modify their surface properties so that localization of CB at the interface was favored. However, those particles are not readily available. Feng and coworkers [24] suggested varying the viscosity of one of the immiscible polymer blend components to control the CB dispersion. This method worked in PP/PMMA blends but it may not be a universal method.

In our previous work [25], we showed that we could reduce the percolation threshold of CB-filled (70/30) polypropylene/polystyrene (PP/PS) blend by introducing styrene-butadiene-styrene (SBS) copolymer. We have successfully localized CB at the interface of PP/PS blend by adding SBS copolymer to the blend. 40% reduction in percolation threshold was found upon the addition of 5 vol% SBS due to the selective localization of CB at the interface of PP/PS blend; and due to the change of dispersed PS phase morphology into a rod-like structure. In CB–PP/PS/SBS blends, CB showed higher affinity to the polybutadiene (PBD) section of the SBS copolymer, which was selectively localized at the PP/PS interface, within the PP phase and within the PS main particles coating the PS sub-particles and connecting them together. However, for CB–PP/PS blends, CB has higher affinity to the PS phase; thus the conductivity of the blend is governed by the percolation of the PS phase and the continuity of this phase within the blend matrix.

In this work, in order to have a better understanding for the CB/PP/PS/SBS blends, the effect of SBS addition on the electrical and morphological properties of 1 vol% CB filled

PP/PS blends as a function of PP/PS volume ratio and SBS loading were studied. In our previous work [25], we concentrated on the (70/30) PP/PS blend in which PS was the dispersed phase. In this work, the influence of SBS addition on five different 1 vol% CB filled PP/PS blends representing three distinct morphologies are studied. The morphologies studied in this work are PP dispersed in PS phase with PP/PS volume ratio equal to 30/70, co-continuous PP/PS blends in the PP/PS volume ratio range of (40/60) – (60/40) and PS dispersed in PP with PP/PS volume ratio of (80/20). This is a more complete study of compositional effects and different types of morphology.

2. Experimental

Carbon black used in the study was high structure Black Pearls (BP 2000, Cabot) (pH 7, surface area 1487 m²/g, particle size 12 nm [26]). The main characteristics of interest of the polymers used are listed in Table 1. All materials used in this study were kindly provided by the manufacturers, Cabot, Huntsman, Nova Chemicals and Kraton.

2.1. Composites preparation

All composites were prepared by melt mixing in a Haake Rheomix series 600 batch mixer. The mixer is connected to a Rheocord90 control panel. Prior to compounding, PS and PP pellets were dried under vacuum at 70 °C for about 16 h, and the mixer was preheated to 200 °C. Mixing was conducted at 50 rpm for 13 min. The polymers were thoroughly dry-mixed before feeding to the mixing chamber. The polymers were melt mixed for 3 min before CB was added and then mixed for an additional 10 min. At the end of mixing, molten composite was collected from the chamber and immediately quenched in liquid nitrogen. For electrical resistivity measurements, a Carver compression molder was used to prepare 76 × 76 × 2 mm plates. The plates were annealed in the molder at 200 °C for 15 min under 30 MPa pressure.

2.2. Characterization

2.2.1. Transmission electron microscopy (TEM)

TEM micrographs were taken using Philips Morgagni 268 microscope at an acceleration voltage of 70 kV.

Table 1
Properties of polymers used in the study

Polymer	MFI (g/10 min) ^a	Density at 25 °C ^a	Density at 200 °C ^d
PP (Huntsman HO-500)	5 ^b	0.9	0.77
PS (Nova PS-1500)	6 ^c	1.04	0.97
SBS ^e (Kraton D-1102K)	14 ^c	0.94	

^a Provided by the manufacturer.

^b ASTM D 1238 (230 °C/2.16 kg).

^c ASTM D 1238 (200 °C/5 kg).

^d Calculated according to data and procedure in chapter four of Ref. [27].

^e PS content 28.5 wt%.

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