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Morphological Characterization of Tri-Continuous Conductive PP/PMMA/EAA Carbon Black Composites.

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The conductivity of multiphase polymer blends containing conductive fillers can be strongly influenced by the phase morphology and any preferential partitioning of the filler between phases. One such example is carbon black (CB) filler in a ternary blend of polypropylene (PP), poly(methyl methacrylate) (PMMA), and ethylene-acrylic acid (EAA). [1,2] In this study, we investigated the morphological features of a ternary blend of polypropylene (PP), poly(methyl methacrylate) (PMMA), and ethylene-acrylic acid (EAA) with carbon black (CB) to provide a fundamental understanding of the changes in electrical conductivity as a function of compounding sequence and annealing time.

Four blends were prepared, each with the same overall composition, 42.0 PP / 42.0 PMMA / 15.5% EA / 0.5% CB by volume, but with the CB added either as a separate component or pre blended into one of the polymers (Table 1). The resistivity as a function of annealing time (Table 1) was independent of which phase the CB was added initially but strongly dependent on the annealing, reaching much lower resistivities than would be expected for a single phase polymer with only 0.5% CB.

The CB distribution was determined by Transmission Electron Microscopy (TEM) (Figure 1). Samples were stained with a 0.5% RuO_4 solution for 16 hours. Ultrathin (70-100 nm) sections were cut at room temperature using a Leica UC7 microtome and Daitome Sonic knife. Images were collected on a Hitachi 7000 TEM at 125 keV. All three polymer phases and the CB could be distinguished in this way. The CB was found in all samples to be partitioned preferentially in the EAA phase, independent of how it was added in the compounding stage.

The phase morphology was determined by Scanning Electron Microscopy (SEM) (Figure 2). Block face samples were stained with a 0.5% RuO_4 solution for 16 hours and then faced at room temperature removing roughly 1 micron of material. Samples for demonstrating the 3d morphology were prepared by solvent etching for 4 hrs in THF. A Hitachi 3400 VP-SEM was used to image the block face samples in BSI mode and the etched samples in SEI mode. Block face samples showed that the EAA phase was dispersed in the PP phase initially, but partitioned to the PP/PMMA interface with annealing. In addition, the characteristic dimensions of the PP/PMMA domains coarsened with annealing. The solvent etched samples demonstrated that the PP/PMMA was bi-continuous

The combination of TEM and SEM demonstrated that, independent of which phase the CB is added to prior to compounding, the CB partitions to the EAA phase, increasing the local concentration above the percolation threshold. Upon annealing the EAA phase partitions to the PP/PMMA interface resulting in a tri-continuous structure which results in the high conductivities observed.

References:

[1] Shen, L *et al*, Polymers International, **61** (2012) p. 163.
[2] Paul J. Brigandi *et al*, Journal of Applied Polymer Science, **132** (2015), p. 42134.

	Sample Composition (Volume %)							**Resistivity** log ρ (Ω cm)		
	Single Components:				Pre-Blended Batches					
Component ID:	PMMA	PP	EAA	CB	PMMA-CB	PP-CB	EAA-CB	Anneal Time (min) at 190 °C		
CB	0	0	0	100	1.2	1.2	3.2			
Sample ID:								6	30	150
PP/PMMA/(EAA-CB)	42.0	42.0					16.0	>8	4.3	3.6
PP/(PMMA-CB)/EAA		42.0	15.5		42.5			>8	4.6	3.6
(PP-CB)/PMMA/EAA	42.0		15.5			42.5		>8	4.4	3.7
PP/PMMA/EAA/CB	42.0	42.0	15.5	0.5				>8	4.8	3.8

Table 1. Sample Composition and Resistivity vs. Annealing Time.

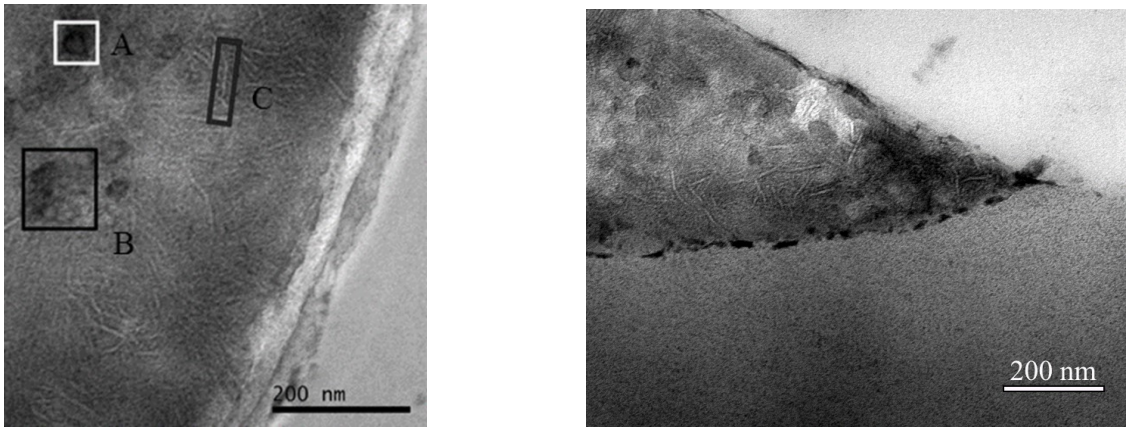

Figure 1. TEM images of PP/PMMA/(EAA-CB) annealed for 150 minutes. LEFT: A) A CB particle, B) Several agglomerated CB particles. C) EAA crystalline lamellae. RIGHT: Area showing PMMA (light phase), PP (dark uniform phase) and EAA (dark phase in between PMMA and PP).

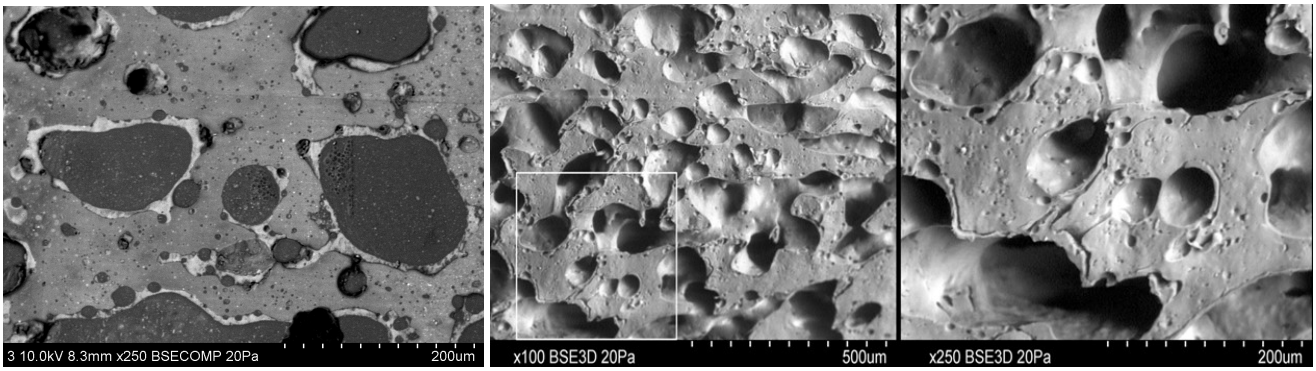

Figure 2. SEM images of PP/PMMA/(EAA-CB) annealed for 150 minutes. LEFT: Stained block face where compared to the PP phase, the PMMA is dark and the EAA is light. CENTER/RIGHT: Etches sample showing percolation of the void structures produced by dissolving the PMMA.

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