

## Nanocomposites Involving Polymer Blends

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### Introduction:

The area of polymer matrix based nanocomposites is a major subject in polymer science with emphasis on exfoliated clay based composites (1). Nanotechnology relevance to polymer blends has been briefly reviewed in a recent polymer blends book (2). Several areas will be discussed in this lecture where polymer blends play a unique role in nanocomposites or where nanoparticle inclusion in phase separated polymer blends can offer novel properties. The first of these subjects involves compatibilization of phase separated polymer blends with nanoparticle incorporation. A large number of examples now exists in the literature where this observation has been reported. The second subject discussed involves the unique percolation path existing at the interface of phase separated polymer blends. Inclusion of nanoparticles at this interface can lead to percolation pathways at considerable lower concentrations than offered by dispersion in a homogeneous polymer matrix. This is, of course, most relevant for electrical conductivity but could be applied to photovoltaic properties, thermal conductivity or ion transport. The third area to be discussed involves polymer blend based nanocomposite utility for emerging technologies where novel properties have been observed or proposed.

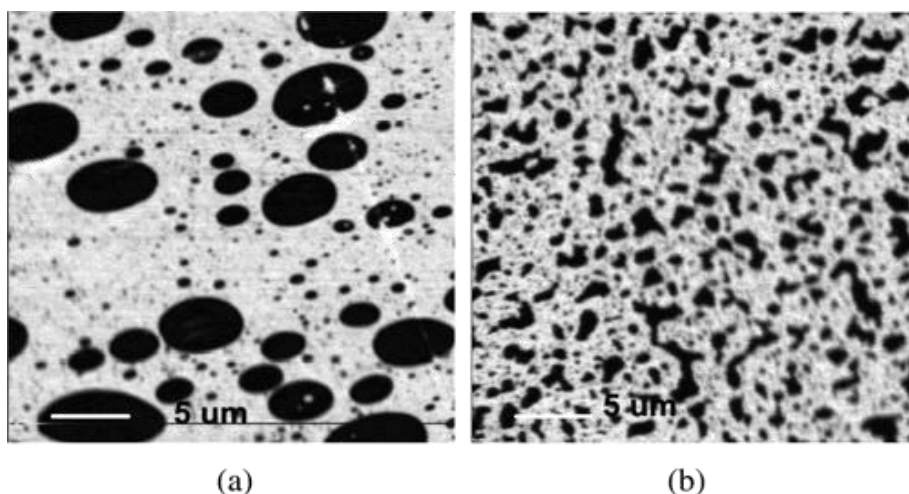
### Nanoparticle Compatibilization of Polymer Blends

While nanoparticles have been incorporated in polymer blends (carbon black for elastomer blends typically employed in tires; silica modification for various applications), the most recent interest has evolved from the observation of compatibilization of phase separated polymers. A number of examples involving diverse polymer blends with various nanoparticles has been noted in the open literature as shown in Table 1. The examples in Table 1 demonstrate the improved dispersion (reduced phase size) of the polymer blends with nanoparticle incorporation similar to that expected with block or graft copolymer (comprised of the blend constituents) addition. An example of the compatibilization effect of addition of nanoclay to a polystyrene/poly(methyl methacrylate) blend is illustrated in Figure 1. In addition to the PS/PMMA noted, large decreases in domain size was observed with organoclay addition to polycarbonate/SAN and PMMA/EVA blends (10). It was hypothesized that in-situ grafts of polymers were formed on the clay surfaces

**Table 1 Examples of Nanoparticle Compatibilization of Polymer Blends**

Polymer 1	Polymer 2	Nanoparticle	Comments	Ref.
Polypropylene	Ethylene-octene copolymer	nanosilica	Reduced phase size, slightly improved impact	3
Polypropylene	Poly(ethylene oxide)	organoclay	Reduced phase size leading to transparency	4
Nylon 6	SAN, ABS	organoclay	Reduced phase size; clay in Nylon 6 phase	5
PVF <sub>2</sub>	EVA	organoclay	Reduced phase size, clay	6

			type and VAc content important	
Polypropylene	Polystyrene	nanosilica	Reduced phase size and more homogeneous particle size distribution	7
Poly(methyl methacrylate)	Polycarbonate	organoclay	PC dispersed phase size decreased with clay addition	8
Poly(phenylene oxide)	Nylon 6	organoclay	PPO particle size decreased from 4.2 $\mu\text{m}$ to 1.1 $\mu\text{m}$ with 2wt% clay	9
Poly(methyl methacrylate)	Polystyrene	WS <sub>2</sub> nanotubes	Reduced domain size and surface roughness	10

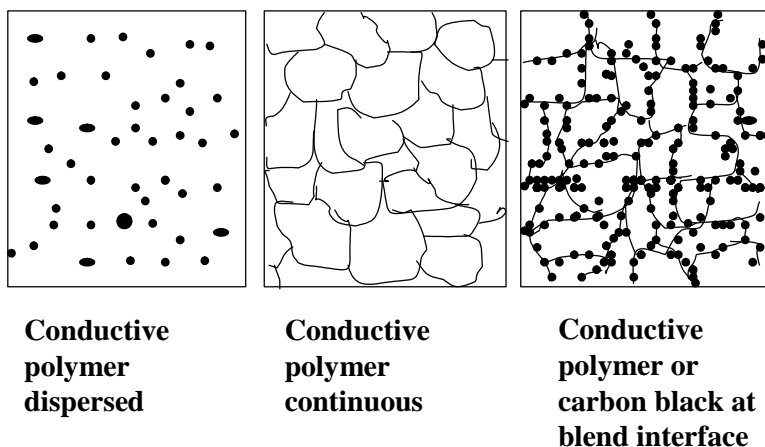


**Figure 1** Scanning transmission X-ray microscopy images (30 $\mu\text{m}$  x 30 $\mu\text{m}$ ) of PS/PMMA blends annealed at 190 °C for 14 hours (taken at 285.2 eV, the adsorption energy of PS, PS is dark): (a) PS/PMMA (30/70) (b) PS/PMMA/clay (27/63/10) (reprinted with permission of reference: Si, M., Araki, T., Ade, H., Kilcoyne, A. L. D., Fisher, R., Sokolov, J. C. and Rafailovich, M. H., *Macromolecules*, (2006) 39, p. 4793, copyright (2006) American Chemical Society)

during processing. The resultant grafted clay thus concentrated at the interface similar to block or graft copolymer addition. An alternative explanation similar to this would be that physical adsorption of the polymers on the surface would yield an analogous situation. Another hypothesis noted in the literature involves concentration at the interface suppressing particle coalescence as well as adjusting the viscosity ratio of the constituents which also affects phase dimensions (12, 13). In many examples, improved mechanical properties are observed (specifically impact strength) along with the improved dispersion that results with nanoparticle addition. An analogous case involving polymer blends and nanocomposites is the addition of a polymeric coupling agent to a polymer nanocomposite of which many examples exist (1, 2).

#### Percolation Pathways in Polymer Blends: Nanocomposites

Phase separated polymer blends with similar volume fraction in the blend exhibit an interface which percolates through the blend. Addition of nanoparticles which concentrate at the blend interface yields a nanoparticle percolating pathway of interest for various transport mechanisms including electrical conductivity. This is illustrated in Figure 2.



**Figure 2** Percolation Network in Polymer Blends (ref. 2)

The addition of conductive particles to phase separated polymers has been well shown to exhibit threshold percolation conductivity at levels much lower than with homogeneous polymeric systems due to the concentration of the conductive particles at the interface. This has been observed with carbon black (14), multiwalled carbon nanotubes in SBR rubber blends with polybutadiene (15), and carbon black in polyethylene/polystyrene blends (16) where the threshold percolation was 0.4 wt% versus the expected 16 wt% in a homogeneous system. Water borne polymer blends (such as immiscible emulsion blends) yield a percolation network upon water removal (17). Addition of conductive nanoparticles to these blends should yield a novel percolation conductive pathway.

### Nanocomposites Involving Polymer Blend Matrices in Emerging Technologies

Various examples exist in the literature where the addition of nanoparticles to polymer blends yield desired properties for emerging applications. The addition of silver nanoparticles (18) or nickel nanoparticles (19) to poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonic acid) blends for improved hole injection properties is one example. In the biomaterials area, the combination of biodegradable polymer blends can be utilized to optimize the properties desired as scaffolding materials including bioadsorbability rate. Poly-2-hydroxyethyl methacrylate/poly( $\epsilon$ -caprolactone)/hydroxyapatite for bone repair nanocomposites (20) and polylactide/ poly( $\epsilon$ -caprolactone)/organoclay (21) offering an improved mechanical property balance are specific examples. Immiscible polymer blends as a matrix for composite and conductive bipolar plates for fuel cells have been proposed (22) where carbon black is one of the constituents. Polymer blends containing conductive particles have been investigated for sensors. A specific example involves impact polystyrene/EVAc blends containing carbon black (23). The carbon black concentrates in the EVAc phase offering higher conductivity than equivalent loadings in either polymer yielding improved sensitivity for solvent sorption (24).

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