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Co-continuity of thermoplastic elastomer rubber-based nanocomposites

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The properties of vulcanizate/clay nanocomposites can be enhanced by optimizing the microstructure of their elastomer/clay precursors.

The composition range where each phase of an immiscible polymer forms a continuous network, or co-continuity, is strongly related to the viscosity ratio, interfacial tension, processing conditions, and whatever else affects the mobility of a material interface.[1–4] Here, we describe the effects of different polypropylene-g-maleic anhydride polymers, as compatibilizers, on the degree of exfoliation and co-continuity of thermoplastic elastomer (TPE) nanocomposites based on polypropylene/ethylene-propylene-diene monomer (PP/EPDM).[5,6] X-ray diffractometry patterns and transmission electron microscopy (TEM) micrographs show that nanocomposites range from an intercalated structure to a coexistence of intercalated tactoids (relatively ordered stacks) and exfoliated layers. The significant increase in crystallization temperature (∼20°C) could be beneficial for molding applications because of the faster solidification and shorter cycle time. The relaxation time obtained by stress relaxation experiments shows that the key parameter that determines the dispersion level in nanocomposites is the mobility of the compatibilizer. This is indicated qualitatively by molecular theories, in which chain movement into the interlayer galleries occurs primarily through the mechanism of reptation (sliding). Solvent extraction and gravimetry measurements of continuity show that the compatibilizer affects the co-continuity composition range through its effect on the dispersion level of nanoclays (see Figure 1).

We found that incorporating clay reduces the continuity index of the EPDM phase. The effect is more pronounced in intercalated nanocomposites than semi-exfoliated ones: see Figure 1(a). On the other hand, an increase in EPDM content reduces the continuity index of the thermoplastic phase. However, the rate of reduction decreases when the dispersion level improves and the continuity index of the samples prepared using the semi-exfoliated PP nanocomposite is about 0.2 higher than that of TPE prepared using pure PP: see Figure 1(b). Since the

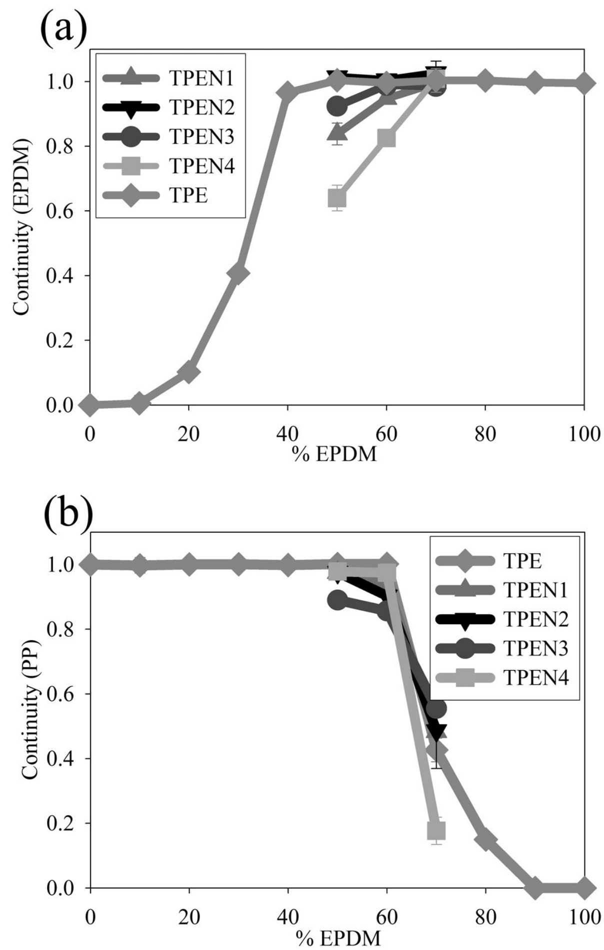

Figure 1. *The continuity indices of polypropylene/ethylene-propylene-diene monomer (PP/EPDM) (a) from non-cross-linked specimens and PP (b) from irradiated samples (corrected for thermoplastic phase solubility in cyclohexane at room temperature and irradiated EPDM solubility in xylene). TPE: Thermoplastic elastomer. N: Sample number.*

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capillary number (Ca) for this system is much larger than 1, the mixing process basically involves distributive mixing that leads to rearrangement and deformation of the phases. The main breakup mechanism is that of highly elongated threads by means of capillary instabilities that produce a line of smaller droplets. Breakup occurs when a thread diameter for which Ca<1 is reached if the residence time during the mixing process is longer than the breakup time.[4] Thus, the higher continuity of PP in semi-exfoliated systems may be attributed to the higher melt strength of the thermoplastic threads of such systems. Larger tactoids act as defects that reduce breakup times. Given that TPE formation is the first step for thermoplastic vulcanizate (TPV) production, and that the thermoplastic phase should have a certain amount of continuity, these results suggest that more EPDM could be incorporated into the semi-exfoliated system before formation of a matrix-dispersed particle structure.

We also investigated the effect of continuity on the rheological (flow) behavior of TPE nanocomposites. We observed a direct relation between the maximum time-dependent viscosity in a stress growth experiment (often referred to as the normalized stress growth viscosity overshoot) and the continuity of prepared TPE nanocomposites. When PP is a continuous phase, a higher EPDM continuity index leads a lower overshoot of normalized stress growth viscosity. It appears that the rubber phase can adapt to the applied stress more readily when the rubber connectivity is more complete. These observations are potentially useful in providing qualitative information about continuity indices, especially in view of the time-consuming solvent extraction and gravimetry measurements otherwise required. At high EPDM composition, we again found that the significant change in morphology could influence the overshoot of normalized stress growth viscosity. Finally, using extraction techniques and scanning electron microscopy, we showed that nanoclay particles remain mainly in the PP phase.

This study suggests that optimization of the microstructure and properties of TPV/clay nanocomposites is enhanced by optimizing the microstructure of their precursor TPE/clay nanocomposites. We are now investigating the effect of procession conditions on the morphology of these materials.

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