Characterization of Specific Interactions in Organoclay Nanocomposites

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Introduction

Polymer/layered silicate nanocomposites have attracted great interest over the past decade because of their remarkably improved physical properties compared with pristine polymers or conventional micro- and macrocomposites.[1,2]

In this study a new method for the preparation of the polymer/organoclay nanocomposite is proposed in order to improve the dispersion of clay in the polymer matrix. A two-step process of the solution blending and the subsequent melt mixing in a Brabender mixer was found to be effective in obtaining well-dispersed nanocomposites of poly(stryrene-*co*-acrylonitrile)/poly(vinyl chloride) blends, and of poly(acrylonitrile-*co*-butadiene-*co*-styrene). The values of both interaction parameter (χ_{ab}) and interaction energy density (B) were calculated by using molar attraction constants of the specific functional groups derived from the Hoy's Table.[3] In case of the nanocomposites based on the miscible polymer blend, the glass transition behavior of the nanocomposites was analyzed by using the well-known Kwei equation[4] and the Gordon-Taylor equation.[5] Also, XRD, TEM, thermal and mechanical tests of the nanocomposites were used to provide additional information of the interaction between polymer and clay particles.

Experimental

Materials. Poly(styrene-*co*-acrylonitrile) (SAN) (the mass ratio of styrene/acrylonitrile is 75/25), poly(vinyl chloride) (PVC) and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) were purchased from the Aldrich Chemical Co. Three different organoclays with different functionalities from Southern Clay Products were used: Cloisite 10A(C10A), Cloisite 25A (C25A) and Cloisite 30B (C30B).

Nanocomposite Preparation. The ternary mixture of SAN, PVC and C25A in the form of exfoliated polymer/clay nanocomposites was prepared by a solvent casting method using THF as a cosolvent, and subsequent melt mixing in a Brabender mixer (Haake Rheometer 90). The preparation method was termed 'SOAM'. The binary mixtures of ABS/C10A, ABS/C25A and ABS/C30B nanocomposites were also prepared by the SOAM method.

Results and discussion

Characterization of Organoclays in the Nanocomposites. The formation of a nanocomposite of polymer and organoclays was observed by XRD and then confirmed with TEM images. In case of the miscible polymer blend system, XRD curve of the nanocomposite prepared by the SOAM method exhibited no peaks, implying a fully exfoliated morphology. Figure 1 shows TEM micrographs of SAN/PVC/C25A nanocomposites prepared by the SOAM method. The dark silicate particles are clearly seen. The clay layers were exfoliated in the SAN/PVC matrix and the large silicate particles were absent. These results corresponded with XRD results.

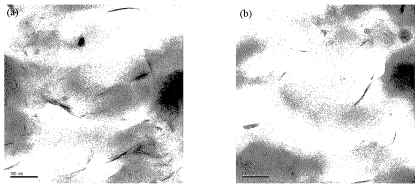

Figure 1. TEM images of (a) SAN/PVC(80/20)/C25A and (b) SAN/PVC(20/80)/C25A nanocomposites.

The XRD patterns of the ABS nanocomposites prepared by the SOAM method exhibited a well-developed exfoliated morphology. In Figure 2, TEM images of ABS nanocomposites containing various types of organoclays are shown.

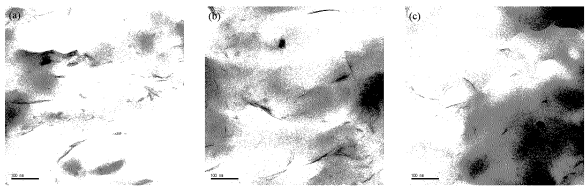

Figure 2. TEM images of (a) ABS/C10A, (b) ABS/C25A and (c) ABS/C30B nanocomposites.

Flory-Huggins Interaction Parameter. The layer thickness for the PVC/C25A nanocomposite was greater than that for the SAN/C25A mixture, indicating that PVC molecules have better affinity with the hydrophobic surfaces of C25A than SAN molecules do. In case of the ABS nanocomposites, XRD and TEM results show that the layer thickness of the ABS/C30B nanocomposite is greater than that of the ABS/C10A or the ABS/C25A system, suggesting that ABS molecules have better affinity with the hydrophobic surface of C30B than C10A or C25A. Based on the solubility parameters, the value of the Flory-Huggins interaction parameter between PVC and C25A (1.60 J/cm^3) is smaller than that for the SAN/C25A system (3.68 J/cm^3). Hence, the calculated interaction parameters of pairs could be interpreted by the fact that the interaction between PVC and C25A was thermodynamically favorable. Also, in case of the ABS nanocomposite, the interaction parameter of the ABS/C30B (2.16 J/cm^3) is smaller than that of the ABS/C10A (2.94 J/cm^3) and the ABS/C25A (2.67 J/cm^3). Thus, it can be deduced that the interaction between ABS and C30B was thermodynamically favorable.

Thermodynamic Models. Several equations have been proposed to describe the composition dependence of the T_g of the miscible polymer blends. For the systems with specific interaction such as hydrogen bonds, the most suitable relation is the Kwei equation. The data of the SAN/PVC/C25A nanocomposite prepared by solution blending only are compared with the values calculated according to the Kwei equation in Figure 3-(a). Here, the value obtained for the adjustable parameter, q was 14.3, suggesting that the specific interaction responsible for miscibility is strong. Glass transition temperatures of the SAN/PVC/C25A nanocomposite prepared by the SOAM method were plotted against the weight fraction of SAN. In the nanocomposites prepared by the SOAM method, the extent of the breaking of the self-association interactions and the forming of the inter-association interactions through hydrogen bonding was much smaller than in the nanocomposites prepared by solution blending only. Thus, the Gordon-Taylor equation was used in this case. The fit of the experimental data to the Gordon-Taylor equation is also shown in Figure 3-(b). The fitting constant, K was 0.37, indicating that the interaction between the polymer matrix and C25A is strong.

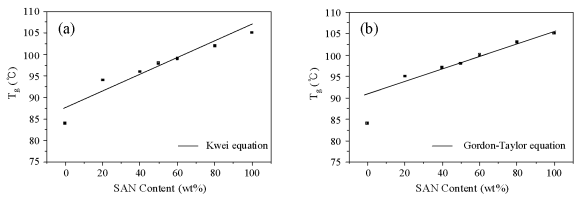

Figure 3. T_g vs composition for SAN/PVC/C25A nanocomposite.

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