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**Polymer / Layered Silicate Nanocomposite and Their Rheology**

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**Introduction**

The blending of polymeric melts with inorganic clays yield polymer nanocomposites which exhibit not only a dramatic increase in tensile strength and heat resistance but also a drastic decrease in gas permeability compared with those of a pure polymer matrix [1-5]. These unique properties render the nanocomposites as ideal materials for products that range from high barrier packaging for food and electronics to strong, heat-resistant automotive components. From the structural point of view, two types of polymer-clay nanocomposites are possible. *Intercalated* nanocomposites are formed when one or a few molecular layers of the polymer are inserted into the clay galleries with fixed interlayer spacings. *Exfoliated* nanocomposites are formed when the silicate nanolayers are individually dispersed in the polymer matrix, the average distance between the segregated layers being dependent on the clay loading. The separation between the exfoliated nanolayers may be uniform (regular) or variable (disordered). Exfoliated nanocomposites show greater phase homogeneity than intercalated nanocomposites. This structural difference is one of the primary reasons that the exfoliated state is so effective in improving the performance properties of clay composite materials. Owing to their unique phase morphology and improved interfacial properties, the nanocomposites exhibit improved performance properties compared to conventional composites. From the processing and application points of view,

the mechanical and rheological properties of these nanocomposites are of vital importance. It is also be important to relate their mechanical and rheological properties to the nature and microstructure of the nanocomposites. Furthermore, these nanocomposites appear to be an ideal system to probe the dynamics and statics of confined polymers[4-5]. Our group have also worked on fabrication and chacterization of the nanocomposites for several polymer systems[6-10].

Recently, we investigated the rheological evidence for the microstructure of intercalated polystyrene/layered silicate nanocomposites [6]. The rheological measurement method monitored the microstructural change which causes non-terminal behaviors. However, there have been no reports which relate the rheological behavior of polymer/layered silicate nanocomposites to their phase morphology (intercalated or exfoliated) and to the interfacial characteristics between the polymer chains and layered silicates. In this study, polystyrene (PS)/clay, polystyrene-co-maleic anhydride (PS-co-ma) /clay and polyethylene-graft-maleic anhydride (PE-g-ma) /clay nanocomposites, which have different interfacial properties and phase morphology, are fabricated. The rheological behavior of polymer/clay nanocomposites is also dependent on their microstructure( *Intercalated* or *Exfoliated* )[8]. The rheological behavior of block copolymer/clay was also investigated[9].

## **Experimental**

### **Preparation of Nanocomposite**

Three different series of PS/clay, PS-co-ma/clay and PE-g-ma/clay nanocomposites are fabricated in a Brabender batch mixer. They are fabricated by introduction the premixed PS/clay, PS-co-ma/clay and PE-g-ma/clay mixtures(simple stirring polymer pellet with organoclay)to heated mixer at 190C. Mixing is continued for 10min at a 45rpm mixing speed. The weight percent of clay is 3 ,5 and 10wt% in each series of composites.

### **Rheometry**

Three different series of composites fabricated in Brabender mixer are compression molded (cylinder form of 25mm diameter, 2mm height) at 190°C to make samples to measure the rheological behaviors. The rheological properties of each nanocomposite series are measured by ARES (Advanced Rheometric Expansion System) in oscillatory mode with a parallel plate geometry using 25mm diameter plates at 220°C. All measurements were performed with 2K FRTN1 transducer with a lower resolution limit of 0.02g/cm.

### **X-ray diffraction(WAXD)**

The degree of swelling and the interlayer distance of the clay in the nanocomposites were studied by means of wide angle X-ray diffraction of Rigaku Inc. - diffractometer equipped with an intrinsic germanium detector system using Cu K radiation. The scanning rate is 20/min from 1.20 to 100 .

### **Result and Discussion**

The rheological behavior of polymer/layered silicate nanocomposites is strongly dependent not only upon their microstructure but also upon the interfacial characteristics [Fig. 1-b,c,d]. Three different types of behavior are identified for polystyrene (PS)/clay, polystyrene-co-maleic anhydride (PS-co-ma)/clay and polyethylene-g-maleic anhydride (PE-g-ma)/clay systems. The PS/clay nanocomposites exhibit a slight enhancement at low frequency because of its simple intercalated structure and little interaction. Both storage and loss moduli increased with silicate loading at all frequencies and showed non-terminal behavior at low frequencies which is a typical behavior of nonhomogeneous system with ordered microstructures. The rheological behaviors in intercalated polystyrene/layered silicate nanocomposite depend not only on the intercalation of polymers, but also on the alignment of silicate layers. Furthermore, the real time intercalation dynamics [Fig.1-a] of polystyrene into the layered silicate, monitored by rheological measurements,

were also consistent with our simple quantitative analysis.

On the other hand, the PS-co-ma/clay nanocomposites have a similar intercalated structure but exhibit a distinct plateau-like behavior at low frequency since the PS-co-ma has a strong attractive interaction with the silicate layers. Finally, PE-g-ma/clay nanocomposites display an exfoliated structure with a strong interaction so that they exhibit both a distinct plateau-like behavior at low frequency and enhanced moduli at high frequency. The percolation structure of the clay particles, which has high aspect ratio, is also responsible for the distinct non-terminal behaviors in exfoliated structure. Block copolymer/clay nanocomposites are also fabricated and their rheological behavior of the nanocomposites is very different from that of SBS.

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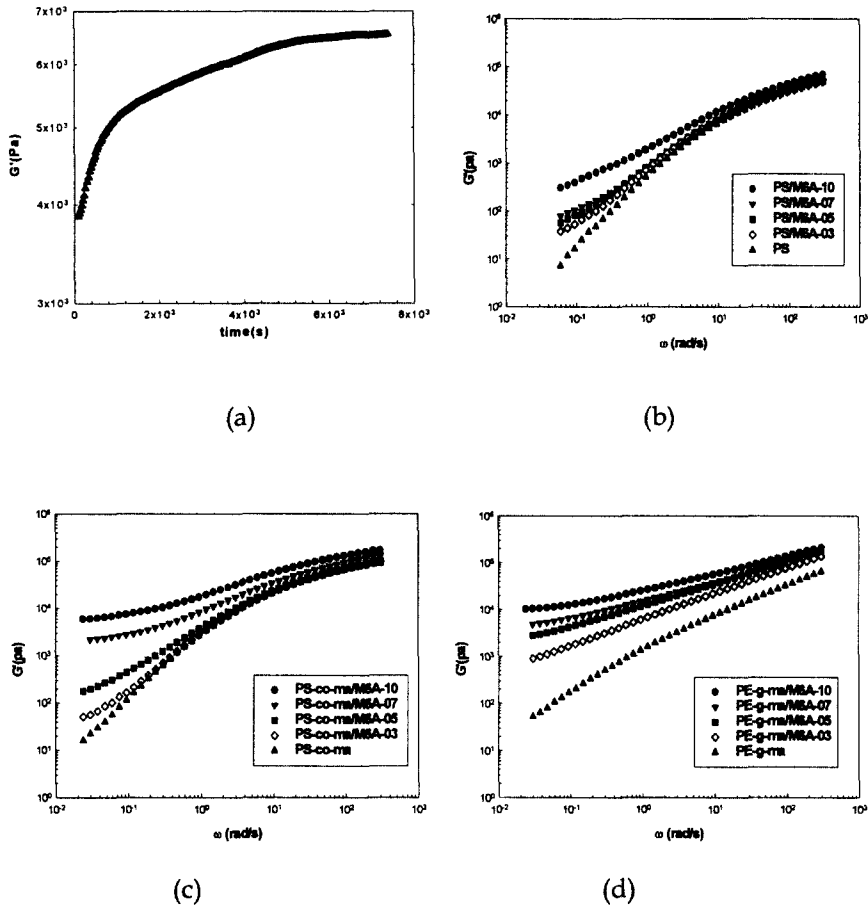


Figure 1. Storage modulus of Polymer /Clay Nanocomposites  
 (a) Real-time intercalation dynamics of PS/clay (b) PS/M6A, (c) PS-co-ma/M6A ,  
 (d) PE-g-ma/M6A