

***Morphology and Ordering Behavior of Block Copolymer in Block Copolymer/Clay Nanocomposite***

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***1. Introduction***

Polymer/clay nanocomposite has been widely studied because it can give dramatic increase of modulus, strength, permeability and mechanical properties. In order to obtain the improved properties, the distribution of the clay and the inter-domain spacing of the clay layers are the important factors. Because polymer chain must diffuse in layers of clays, a few nm thickness, surfactant on the clay surface is essential to achieve the intercalation or exfoliation of the composite.<sup>1)-3)</sup>

The microstructures and the transition behaviors of block copolymers have been investigated in past several decades due to their self assembling nature.<sup>4)-6)</sup> Recently, the interaction with inorganic has been spotlighted in thin films and composites for application to new materials. The intercalation into the clay layer is affected by the structure. The thin layer of clay can induce changes in morphology and order-to-disorder transition kinetics in the block copolymer/clay nanocomposites. Furthermore, the orientation of the nano-structure of block copolymers along the clay layer can result in the delay of the order-to-order transition.

The viscoelastic properties of SI block copolymer/clay hybrid were studied by Krishnamoorti et al.<sup>7)</sup> However, the effect of the structure and the molecular weight of selectively intercalated block, on the rheological behavior of the composite and the orientation and the ordering kinetics of the block copolymers have not yet reported. In this study we used styrene-isoprene diblock copolymer and styrene-isoprene-styrene triblock copolymers, especially it is well known that polystyrene intercalated in clay layers. We rheologically investigated morphology and ordering kinetics of clay/block copolymer nanocomposite.

## **2. Experiment**

### **2.1 Material**

#### *2.1.1 Clay and Block copolymers*

We used the clay of *Southern clay product Inc.*, the surface of which is modified with Dimethyl dihydrogenated tallow ammonium. (cloisite 20A) SIS block copolymer (Vector 4111) provided by *Dexcopolymers Co.* and SI diblock copolymers and homopolymers synthesized by anionic polymerization were also used. Properties of the block copolymers are shown in table 1.

#### *2.1.2 Sample preparation*

Block copolymer/clay nanocomposite was very simply made by solution casting. Sample were prepared by firstly dissolving a predetermined amount of block copolymer and clay in toluene in the presence of an antioxidant (Irganox 1010) and then slowly evaporating the solvent for 2-weeks. After completely removing solvent under vacuum, the sample was finally annealed at 140°C for about 2 days.

#### *2.2 Rheological Properties*

With using an Advanced Rheometric Expansion System (ARES) with parallel plates of 25mm diameter, dynamic temperature sweep experiment and temperature jumping tests were performed. Dynamic temperature sweep experiment was done under the isochronal conditions with increasing temperature from 160°C to 230°C

## **3. Result and Discussion**

PS is well known to intercalate into clay sheets, while PI rarely does. And Krishnamoorti et al.<sup>7)</sup> reported that SI diblock copolymer can intercalate into the clay sheets more than homo polymers. We obtained the same results in this study. And we further changed the PS portion in diblock and triblock copolymers with similar molecular weight. The results are shown in Fig. 1. As shown in Fig. 1, the domain spacing was independent on the PS portion in the block copolymers in both diblock and triblock copolymers. This indicates that the degree of intercalation is not affected by the PS portion of the block copolymer. In addition, the domain spacings have almost the same values although block copolymers with different molecular weight were used.

The similar result that the effect of molecular weight on intercalation is negligible was reported by other group<sup>8)</sup>. But, the triblock showed more d-spacing of the clay than that diblock copolymers. The reason is thought in this stage that two ends of PS segments in triblock copolymers help the diffuse and intercalating into the clay sheets than diblock copolymers do.

Also ODT(order-disorder transition) and OOT(order-order transition) of block copolymer and clay/block copolymer hybrid were studied with rheological properties. The results are shown in Figure 2. In all cases, the composites and near block copolymers underwent the OOT near 180°C and ODT near 205°C, as shown in Figure 2. Although the modulus shows considerable difference according to the clay content, clay doesn't seem to affect the ODT and OOT of the block copolymer. When the sample were cooled, the G' didn't follow the path of that of heating. This is due to the reduced mobility of polymer chains with decreasing temperature

#### **4. Reference**

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#### **5. Acknowledgment**

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Sample	Mw	Ps %	$M_{wPS}-M_{wPI}-M_{wPS}$	Microdomain
SIS051	59.2K	32.4%	9.6-40-9.6	cylinder
SIS019	68.2K	12.9%	4.4-59.4-4.4	sphere
SI013	24.4K	48.4%	11.8-12.6	lamella
SI012	20.3K	30%	6.1-14.2	cylinder
V4111	143K	18.3%	12.9-117.2-12.9	cylinder
Homopolymer	PI	100K		
	PS	100K		

table 1 Various Properties of Block copolymer sample

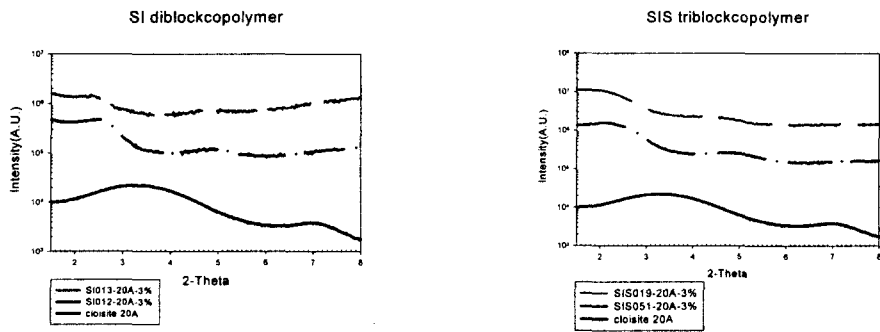


figure 1 XRD graph(D-spacing of SI013 : 3.8nm, SI012 : 3.6nm SIS019 : 4.3nm SIS051: 4.1nm)

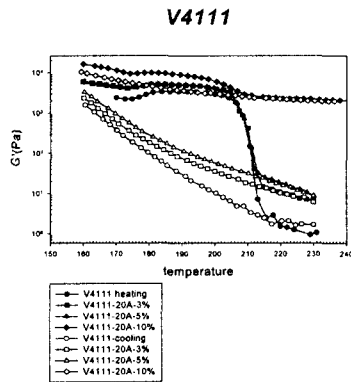


figure 2 temperature sweep of  $G'(Pa)$  at  $\gamma_0=0.03$ ,  $\omega=0.03rad/s$  during heating and cooling between 160C and 230C (left)