SIS 블락공중합체/클레이 나노복합재에서의 블록 공중합체의 질서-질서 및 질서-무질서 전이에 관한 연구

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Order-to-Order and Order-to-Disorder Transition of SIS block copolymer with Clay

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Abstract

We investigate the effect of an anisotropic silicate layer on the order to order(OOT) and order to disorder(ODT) transitions of a block copolymer in block copolymer/clay nanocomposites by using synchrotron small angle X-ray scattering(SAXS), and rheology. The block copolymer employed in this study was polystyrene-block-polyisoprene-block-polystyrene copolymer(SIS). The degree of intercalation of the clay in the presence of SIS was examined by wide angle X-ray diffraction(WAXD). The gallery spacing of the clay depended upon total molecular weights of block SIS rather than the volume fraction of PS block in SIS. The dispersion of the tactoids in a specimen prepared by melt blending where strong shear and elongational force are present is much finer then that in another specimen prepared by solution blending. At given clay content, the shear modulus at disordered state and mechanical properties of the former specimen are better than those of the latter. Interestingly, we found that the T_{ODT} of SIS in a specimen with 1% of the clay, which was prepared by melt blending, was decreased 10℃ from that of neat SIS. On the other hand, the T_{ODT} for another specimen prepared by solution mixing did not change even if the clay was added as large as 5%. However, the OOT for both specimens was not changed.

1. Introduction

Polymer/clay nanocomposites have been studied extensively due to their excellent thermal and mechanical properties compared with inorganic filler-based polymer composites.[1] Krishnamoorti and coworkers studied about the block copolymer-based nanocomposite.[2] For polystyrene-block-polyisoprene (SI) copolymer based nanocomposites, the increase in the clay galley layer (or intercalation degree) was larger than compared with PS-based nanocomposite. Very recently, they also investigate the order-to-disorder transition (ODT) and the order-to-order transition (OOT) between hexagonally packed cylinder micro-domains (HEX) and body-centered

cubic micro-domains (BCC) using a polystyrene-block-poly (ethylene-co-butylene) -block-polystyrene (SEBS).[3)-4)] In this study, we studied order to order transition and order to disorder transition of blockcopolymer in SIS blockcopolymer/clay nanocomposites, using SAXS, and rheology. Also, the intercalation degree of the clay in the presence of SIS was investigated with the aid of wide-angle X-ray diffraction(WAXD).

2. Experimental

Cloisite 20A (Southern Clay Product Inc.) is a montmorillonite modified with dimethyl dihydrogenatedtallow ammonium to increase the domain (d) spacing of Na+-montmorillonite. The block copolymer employed in this study was a polystyrene-block-polyisoprene-block-polystyrene (SIS) (V4111; Dexco Inc.).

Nanocomposites consisting of V4111 with various amounts of the clay were prepared by dissolving the mixtures in toluene (about 10 wt % of solid) at room temperature for 2 days in the presence of an antioxidant (Irganox 1010, Giba-Giegy Group), then slowly evaporating the solvent for 2 weeks. After any trace of the solvent was completely removed, the specimens were annealed at 140℃ for 48h in vacuum. Another specimens were also prepared by melt mixing of the mixtures at 170℃ using by Brabender internal mixer with 70 rpm under nitrogen environment, and are further annealed at 140℃ for 48h in vacuum to compared with solution-blended specimens.

Using an Advanced Rheometrics Expansion System (ARES) with parallel plates of 25 mm diameter, a dynamic temperature sweep experiment and a frequency sweep experiment was done. A dynamic temperature sweep experiment was done under isochronal conditions with increasing temperature from 160 to 230℃. The heating rate was 0.5 ℃/min, and the strain amplitude and the angular frequency (w) were 0.03 and 0.05rad/s, respectively. Sample's thickness was about 1mm.

Small angle x-ray scattering experiments were done as synchrotron source at 4C1 beam line, Pohang Light SOURCE using the wavelength, 0.1618 nm equipped a monochromatic device.

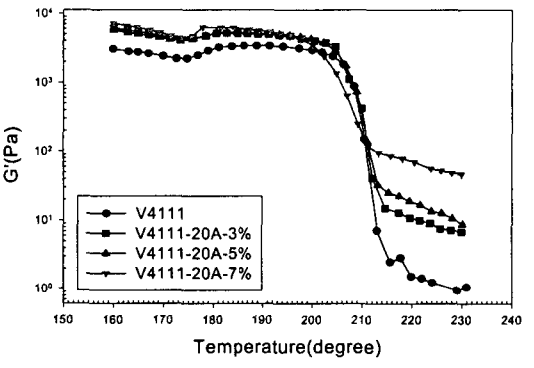
3. Results and Discussion

Figure 1 gives temperature sweep of G' at a heating rate of 0.5℃/min for neat SIS, SIS/clay with different amount of clay prepared by two different methods: (a) solution casting and (b) melt blending. The T_{OOT} and T_{ODT} of neat V4111 are determined as 174±1℃ and 210±1℃, respectively. When a specimen was prepared by solution casting, T_{OOT} and T_{ODT} are not changed even if the clay is added as larger as 7 wt %. The reason is due to poor dispersion of silicate tactoids.

However, when a specimen was prepared by melt mixing, it was seen that the T_{ODT} decreased with increasing amount of the clay. The reason of decrease in T_{ODT} might be due to the fact that SIS near the clay was severely affected by clay; thus SIS chains in these regions play as a role of defect; thus disordering could occur easily. But for a specimen prepared by solution casting, effective areas of

clay, which make the ordering of PS chains difficult, are quite small due to the agglomeration. Thus, even if a large amount (~ 7 wt %) of clay is added, the T_{ODT} was not changed for specimens prepared by solution casting. However, melt blending samples showed very finer clay (some clay layers are exfoliated although most clays are intercalated). The effective clay areas increased, which results in decreased T_{ODT}. It is of interest to note that once SIS/clay nanocomposites has lower T_{ODT}, nanocomposites at 200℃ should have disordered micelles, whereas SIS neat block copolymer exhibited BCC microdomains.

a)



b)

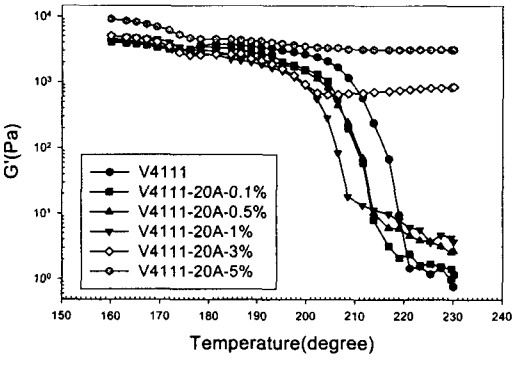


Fig 1. a) Temperature sweep of G' at a heating rate of 0.5℃/min for neat SIS, SIS/clay with different amount of clay prepared by solution casting.
b) Temperature sweep of G' at a heating rate of 0.5℃/min for neat SIS, SIS/clay with different amount of clay prepared by melt blending.

4. Conclusions

In this study, we have shown that the TLDT of SIS in SIS/clay nanocomposites prepared by melt mixing decreased up to 10℃. This is because the clay was dispersed very well in the SIS matrix; thus the effective contact areas between SIS and the clay were significantly increased. On the other hand, when nanocomposites were prepared by solution blending and annealing, the TLDT did not decrease even though the amount of clay is as large as 7 wt %. However, the TOOT was not changed for both specimens, and the d-spacing of the clay for specimens prepared by melt mixing was essentially the same as that for another specimens prepared by solution casting and annealing.

References

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