

poly(ϵ -caprolactone)/organoclay 나노복합체에 있어 용융 박리에 수지 점도가 미치는 영향

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Effect of matrix viscosity on the melt exfoliation of clay in preparation of poly(ϵ -caprolactone)/organoclay nanocomposites

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1. Introduction

Polymer/layered silicate nanocomposites have recently received considerable attention from both academia and industry as an effective way to overcome the shortcomings of conventional polymer. When the silicate layers are exfoliated and randomly distributed in polymer matrix, the nanocomposites exhibit improved mechanical, thermal and barrier properties. However, there are many factors to be considered for preparing nanocomposites with exfoliated silicate layers. First of all, the interaction between polymer and silicate layer should be controlled for polymer chains to diffuse into silicate layers by reducing strong attractive force between silicate layers. This may be achieved by modifying hydrophilic silicate with an organic modifier, which can favorably interact with hydrophobic polymer. Secondly, the shear stress applied during melt mixing may affect the exfoliation of silicate layers. It has been observed that exfoliated nanocomposites can be prepared only when the shear stress enough to overcome the van der Waals force between silicate layers is applied. On the other hand, it was found in our previous study¹ that the exfoliation of organoclay becomes faster as the molecular weight decreases and the mixing temperature increases. This indicates that

exfoliation of silicate layers is closely related to the diffusion of matrix polymers through the inter-crystalline region of silicate layers, and therefore the viscosity of matrix polymers.

In this study we choose poly(ϵ -caprolactone)(PCL)/organoclay nanocomposites as a model system. The viscosity effect of matrix polymer on the melt exfoliation behavior of an organoclay in PCL is investigated systematically by changing the molecular weight of PCL, processing temperature and the shear stress.

2. Experimental Section

Three PCLs with different molecular weight, $M_n = 10000$ (PCL10K), 42500 (PCL43K) and 80000 (PCL80K) g/mol, were supplied from Sigma-Aldrich Chem. Co. Cloisite[®] 30A (C30A) as an organoclay was obtained from Southern Clay Products Inc. The PCL/organoclay nanocomposites were prepared under shear using Mini-Max Molder. The shear rate was varied from 9.7 to 32.8 rad/s. The mixing ratio of PCL/organoclay was kept constant at 93/7 by weight for all cases. The mixing time was varied from 6 min to 60 min, and the temperature was varied from 100 to 200 °C. The change in the degree of exfoliation of silicate layers with mixing conditions was observed using an X-ray diffractometer (MAC Science, MXP 18A-HF). CuK α ($\lambda = 1.5405$ Å), generated at a voltage of 40 kV and current of 30 mA, was used as a source. Diffraction angle was scanned from 1.5° to 10° at a rate of 2 °/min. After subtracting background intensity from raw diffraction profiles, the crystallinity of organoclay is calculated to be proportional to the area of (001) plane peak. The melt viscosity of PCL was measured using a Rheometrics rheometer (RMS 800) under the oscillatory mode with a parallel-plate fixture. Dynamic frequency sweep experiments were performed in linear viscoelastic region at the temperatures of 100, 120, 140, 160, 180 and 200 °C, under nitrogen atmosphere to minimize thermal degradation of polymer. The frequency sweep employed was ranged from 0.1 to 100 rad/s.

3. Results & Discussion

Three PCL/organoclay hybrids prepared using PCLs with different molecular weight, which contain the same amount of organoclay (7 wt%), were observed with the polarized optical microscope. However, it is noteworthy that some association of agglomerates in mm-order can be found in a part of the hybrid

prepared with PCL10K (*see* the inset of Figure 1(a)). Poor breaking-up of clay agglomerate into primary particle can be due to the lower viscosity of PCL10K. It is observed from Figure 1(b) and (c) that the content of primary particles for PCL80K decreases as compared to the case for PCL43K. This indicates that the greater breaking efficiency of primary particles into nanosclae building block, .i.e. crystallites or low-angle intergrowth of silicate crystallites in sub-micron size can be achieved in PCL80K rather than in PCL43K.

The effects of mixing time on the structure of hybrid can be seen in figure 2. As the mixing time becomes longer than 6 min, the peak of (001) plane is observed at around 2.5. This indicates that the intercalation takes place for longer mixing time than 6 min. The diffusion of PCL into the gallery of silicate layers becomes more difficult as the molecular weight of PCL increases and as a result, the intensity of (001) reflection for PCL80K decreases more slowly with increasing the annealing time as observed in Figure 2. Furthermore, the XRD peak for the hybrid of PCL43K disappears completely when the mixing time is longer than 60 min, which indicates the exfoliation of silicate layers by the diffusion of polymer chains into the gallery of organoclay.

The results for two PCL-hybrids (PCL43K-hybrid and PCL80K-hybrid) prepared at various temperatures for 20 min are shown in Figure 3, where the crystallinity of organoclay is plotted as a function of $1/\eta^*$, assuming the diffusion constant of polymer chains through inter-crystalline region is proportional to $1/\eta^*$ of matrix polymer. The average value of crystallinity decreases as $1/\eta^*$ of matrix polymer increase, in other words, the viscosity of matrix decreases. This indicates that the exfoliation of silicate layers is closely related to the diffusion rate of matrix polymer through the inter-crystalline region of silicate layers because the diffusion becomes faster as the viscosity of matrix decrease. Also, it is noteworthy that the crystallinity for PCL80K-hybrid is larger than that for PCL43K-hybrid. A large entropy loss takes place when a polymer chain in melt with a radius of gyration about a few tens of nanometer diffuses through inter-crystalline region and/or is intercalated into a narrow gallery of silicate layers. Thus it is expected that larger chain is more difficult to penetrate through inter-crystalline region, and finally through the gallery of silicate layers rather than smaller one. It can be concluded that the degree of exfoliation is not only a function of viscosity, but strongly dependent on the molecular weight of polymer.

4. Reference

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- 2) M. B. Ko, *Polymer Bulletin*, 45, 183 (2000).

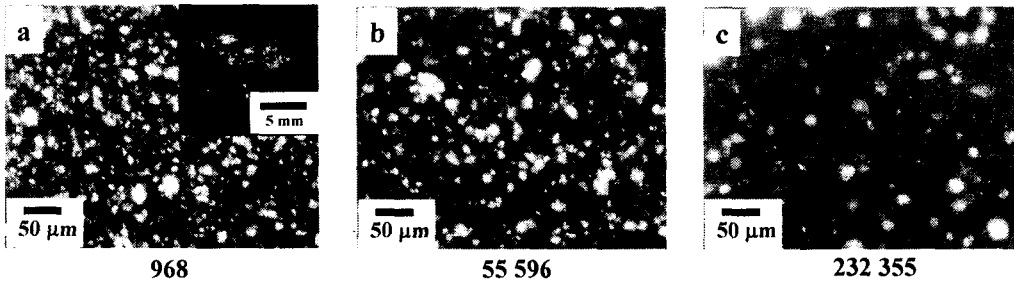


Figure 1. Polarized Optical Microscope Observation of Cloisite[®] 30A Clay in the Hybrids prepared at 100°C and 32.8 rad/sec: (a) 10K, (b) 43K, (c) 80K. The number below each micrograph indicates the maximum shear stress.

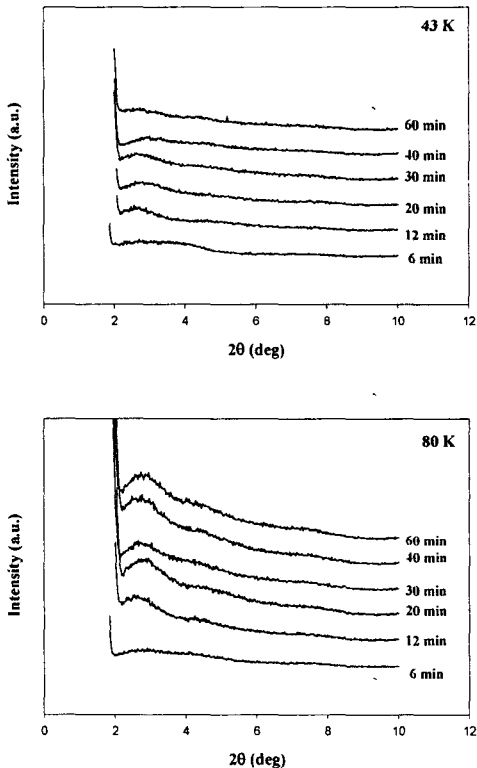


Figure 2. XRD patterns for the hybrids prepared under the shear rate of 32.8 rad/sec for various mixing time

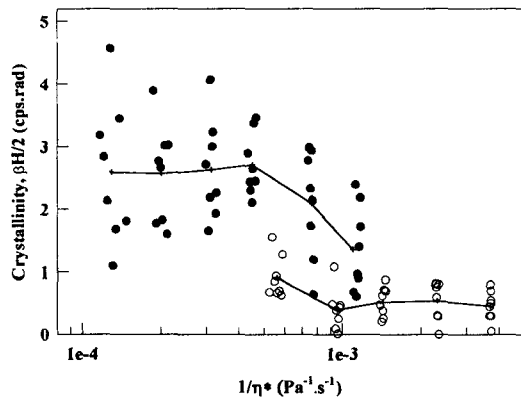


Figure 3. Crystallinity as a function of reciprocal viscosity, showing that clay-exfoliation is governed strongly by the diffusion of polymer chains in the inter-crystalline region. Mixing was performed for 20 minutes.