

폴리에틸렌/실리케이트 나노복합체의 모폴로지 변화와 이방상 형성에 관한 연구

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Morphology Evolution and Anisotropic Phase Formation of the Maleated Polyethylene-Layered Silicate Nanocomposites

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Introduction

Polymer-layered silicate (PLS) nanocomposites have attracted a great attention due to their academic and industrial importance. They have shown dramatic improvements in mechanical, thermal and barrier properties with a small amount of inorganic layered silicate. Moreover, they can provide good model system for the studies of the phase behavior of polymer-nanoparticle mixture as well as the polymer chain dynamics in the confined geometry. From the structural point of view, PLS nanocomposites can be classified into *Intercalated* and *Exfoliated*. *Intercalated* state is termed for the nanocomposite structure where the extended polymer chains are inserted into the gallery space between the individual silicate layers preserving the well-ordered multi-layer structures of silicate. *Exfoliated* state implies the structure where the interaction between the individual silicate layers no longer exists. An ideal exfoliated state, where the silicate plates are homogeneously dispersed in polymer matrix, is one of the ultimate aims in the fabrication of PLS nanocomposite. However, it is well known that because it is hard to exfoliate the tightly stacked silicate plates with van der Waals gap, the favorable interaction between silicate and matrix polymer is necessary for the exfoliation.

Recently, Balazs and coworkers conducted simulation based on analytical self-consistent theory (SCF), considering the interactions among polymer, silicate and organic modifier. They predicted that the nanocomposite with monodisperse silicate plates would form various mesophases depending on the interactions and the concentration of silicate. To the best of our knowledge, however, there is no experimental research dealing with the structural change with the content of silicate filler, which is mainly due to the difficulty of preparing highly loaded nanocomposites with homogeneous dispersion of silicate plates. Because the natural silicate plates have the broad distribution of size and shape, it can be expected that the structural evolution of the real nanocomposite system should be quite different from the

ideal monodisperse case.

In this work, maleated polyethylene (MAPE)/organically modified montmorillonite (20A) nanocomposite is used as a model system to investigate the structural evolution of nanocomposite with the content of natural silicate filler. To overcome the limitation in processing, the extremely slow relaxation and high elasticity of highly loaded nanocomposites, the maleated polyethylene with a low molecular weight is used. With this approach homogeneous nanocomposites are successfully prepared up to the highest silicate content of 36 vol %.

Experimental

Materials

Maleated polyethylene (MAPE) was obtained by Aldrich Co. The basic characteristics of MAPE used in this study, are summarized in Table 1. Organophilic montmorillonite (Cloisite 20A, abbreviation: 20A) used in this study were purchased from Southern Clay. 20A is known to be ion-exchanged with dimethyl dehydrogenated tallow ammonium ions. It was found that 20A contains organic modifier of about 30wt% by the measurement of TGA. Specific gravity of 20A measured by pycnometer was 1.8g/ml. Nanocomposites were prepared by melt intercalation method. MAPE was mechanically mixed with 20A for 20min in brabender mixer at 160 °C. For all the content of silicate extruded fiber samples were prepared to verify the effect of the preparation history on the structure formation. The extrusion was conducted with a capillary viscometer (Rosand RH5) at a high shear rate of $1,000\text{s}^{-1}$.

Characterization

The periodic structure of silicate layers in the MAPE/20A nanocomposite was evaluated by the synchrotron SAXS with point focusing ($0.2 \times 0.2\text{mm}$) at the 4C2 beamline in the Pohang Accelerator Laboratory (PAL), Korea, consisted of 2GeV LINAC accelerator, storage ring, Si (111) double crystal monochromator, ion chambers. The measured intensity was corrected for background scattering, a detector noise and absorption by the sample. The morphology of MAPE/20A nanocomposite was observed by TEM (Philips CM-20 transmission electron microscope) after cryogenic ultra-microtoming (RMC MT7000). The birefringence was studied by a polarized optical microscopy (POM, A Leitz, Model Laborlux 12 Pols) coupled with a Mettler FP-2 hot stage at 160°C.

Result and Discussion

Morphology evolution of the nanocomposites

Figure 1 show the SAXS patterns of extruded nanocomposites. The scattered intensities of the extruded nanocomposite were recorded in the vertical direction to the shear direction. Although the extrusion process enhances intensity and sharpness of the (001) reflection peak slightly, the SAXS patterns of both samples are intrinsically same except for a nanocomposite with 9vol% silicate.

The measured d-spacings are plotted as a function of the content of silicate in Figure 2. The solid line is the d-spacing evaluated with the Vincent and coworkers' equation, which is established according to the Brown's description, where disc-shaped particles have an alternative parallel arrangement.

$$(2R + b)^2 (H + a) = \frac{\pi R^2 H}{\phi} \quad (1)$$

ϕ is the volume fraction of the 20A particles, R and H are the radius and the thickness of the disc, respectively. a and b are the separation gap between adjacent discs (face to face

distance) and a lateral separation (edge to edge distance), respectively. Thus, the d-spacing of the silicate layers corresponds to the sum of H and a . The parameters $2R$ and b are 140 and 30nm, respectively, which are evaluated from the investigation of TEM images. Since 20A is the montmorillonite coated with organic modifier, we considered H as the effective thickness of 2.3nm (basal spacing of 20A) instead of the thickness of the pure clay platelet 0.95nm, in order to simplify tertiary systems consisting of MAPE, modifier and pure clay into secondary system consisting of MAPE and 20A. The predicted solid line agrees quite well with the measured d-spacings of nanocomposites up to the silicate content of 18vol%. The good consistency between experimental data and the fitted line indicates that the silicate layers are quite homogeneously distributed over the whole range of silicate concentration. The deviation above 21vol% is due to the structural change of nanocomposite, which is discussed below.

The d-spacing of silicate layers in MAPE/20A nanocomposites varies via four stages (I ~ IV) as a function of content of silicate. In the lowest content range up to 9vol% (stage I), the periodicity of the silicate layers is not observed without extrusion process, which implies that the silicate plates have the disordered and exfoliated structure in polymer matrix. In the content range between 12 and 18vol% (stage II), each nanocomposite shows a single plane peak, corresponding to the (001) reflection of basal spacing. The layer spacing gradually decreases following the prediction by eq. (1), which implies that the nanocomposites have the ideally exfoliated morphology with homogeneous dispersion of silicate plates. These results support that the periodicity of the silicate layers is originated from the steric interaction between silicate layers having anisotropic shape, as predicted by Balazs and coworkers. In the content range of 21 to 24vol% silicate (stage III), nanocomposite shows distinct dual structure indicating the coexistence of exfoliation and intercalation. The d-spacing of the higher angle peak is below 3.5nm approximately, which corresponds to the layer spacing between silicate plates with two or three polyethylene chain inside the gallery. The peak corresponding to the exfoliated silicate plates persists but its d-spacing deviates from the prediction of Eq. (1). The relative intensity of the peak corresponding to the intercalated portion is higher at the higher content of silicate of 24vol%, which is a typical behavior at a transition region. The present result clearly demonstrates that the attractive interaction between silicate plates becomes dominant at a critical content of silicate even with the quite favorable interaction between silicate plates and polymer chain. In this particular nanocomposite system, the critical length for this transition is 9 nm approximately. Above 27vol% of silicate (stage IV), only one plane peak is observed. It indicates the intercalated structure of silicate layers. The layer spacing also gradually decreases with the concentration of silicate.

Anisotropic phase formation of the nanocomposite

Figure 3a-c show the polarized optical micrographs of the as-mixed nanocomposites. Figure 3d shows the polarized optical micrograph of the extruded nanocomposite fiber with 18vol% silicate. The samples on the slide glass were squeezed very slowly with a cover glass to minimize the history of sample preparation at 160°C. The unextruded nanocomposites show the optical anisotropy not from 9vol% but from 12vol%. The nanocomposite containing 9vol% silicate shows clear birefringence in extruded state, not in the unextruded state. It indicates that the nanocomposites show a shear-induced optical anisotropy. Also the extruded nanocomposite fiber with 18vol% silicate shows a more brightened and colorful texture than the unextruded one.

Figure 1. SAXS patterns of nanocomposites.

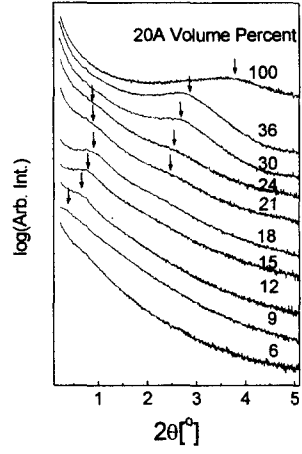


Figure 2. The measured d-spacings from Figure 1.

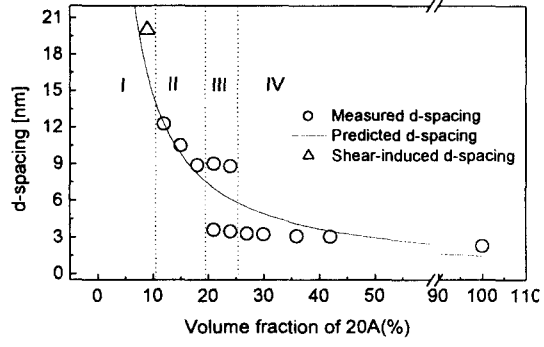


Figure 3. The polarized optical micrographs of the nanocomposites.

