Viscoelastic properties of exfoliated polyamide-6/layered silicate nanocomposite

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Polymer-layered silicate nanocomposites have drawn a great deal of attention due to the significant improvement in mechanical, thermal, and barrier properties caused by a small amount of inorganic layered silicate, where the clay phase is dispersed in the second polymer matrix phase at a nanometer level, as compared to pure polymers or conventional composites [1–6]. However, various improved properties of nanocomposites as expected could be achieved only in a few cases, such as polymers containing polar functional groups because nanolayers are extremely difficult to disperse in polymer matrices due to their tendency for face-to-face stacking and inherent hydrophilic properties. This is mostly due to the fact that the silicate layers of the clay has polar hydroxyl groups and are compatible only with polymers containing polar functional groups. Thus, to improve properties in the nanocomposites, the clay surfaces should be modified by the insertion of an organic cationic surfactant, such as an ammonium or phosphonium cation with long alkyl chains, into the silicate interlayer by cation exchange reactions [7]. The nanocomposite obtained from modified clay realizes superior properties of which conventional polymer composites hardly accomplish. Such properties may originate from the microstructure and the polar interaction, as well as the excellent mechanical properties of clay itself such as high strength and high modulus.

In this letter, polyamide-6 (PA6) (Danamid E grade polycaprolactame, Zoltek Rt., Hungary) was melt-processed in a Rheomex S 3/4″ single screw extruder with Nanofil 784 (Süd-Chemie AG, Germany) silicate modified with an ω-amino acid for improved interaction. Set temperatures of the three zones of the extruder were 220–240–250 °C, while screw speed was fixed at 50 rpm. The extrudate was injection molded into dog-bone type specimens using a Battenfeld BA 250 CD machine at 220–230–250–260 °C set temperatures. Using the prepared samples, we investigated the effect of interfacial interaction on the characteristic structures formed and on the viscoelastic properties of polyamide-6/organoclay nanocomposites.

The samples prepared were designated as N78405 and N78420. The first four letters stand for the silicate type used here; N784 (Nanofil 784). The last two digits mean the volume percent of the silicate in the nanocomposite; 05 (0.5 v%), and 20 (2.0 v%). These samples were then compression molded into either disc and film types for rheological measurement and structure analyses, respectively, using a HP-200L apparatus (Kee-Pae, Seoul, Korea) at 250 °C under the pressure of 1000 psi.

To confirm exfoliation and structure of the prepared nanocomposites, X-ray diffraction (XRD) measurements were performed using a Phillips PW-1847 diffractometer with CuKα characteristic radiation (wavelength: 0.154 nm). Exfoliation and structure of the nanocomposites in the nanoscale were also qualitatively verified through direct visualization using transmission electron microscopy (TEM, CM200, EDS DX-4, Phillips). In addition, we measured their rheological properties using a rotational rheometer with a parallel-plate geometry (Physica, MCR300, Germany) on samples of 1-mm thickness and 25 mm diameter at 240 °C. Using oscillatory shear mode loading conditions, we examined the durability of the samples against vibration or periodic external stress. Dynamic viscoelastic properties such as storage modulus (G′), and loss modulus (G″) were then measured as a function of frequency within the linear viscoelastic region.

Fig. 1 shows XRD patterns of PA6 and its nanocomposites containing Nanofil 784 having an original gallery distance (d_{001} spacing) of 1.71 nm. The maximum diffraction peak of the nanocomposites almost disappears regardless of clay content, implying the exfoliation of the layered silicate in the polymer matrix. Based on this XRD result, it is expected that the individual silicate layers are well dispersed in the polymer matrix, though a small diffraction peak is observed around 4.7° with increasing clay

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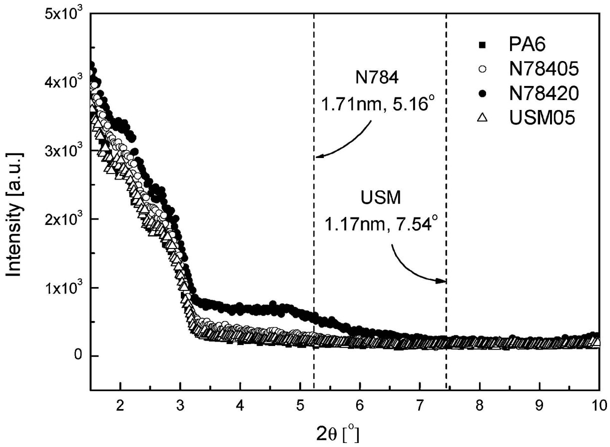

Figure 1 XRD patterns for nanocomposites (N78405, N78420, and USM05). The dashed line indicates the location of the silicate (001) reflection of Nanofil 784 and USM05, repectively.

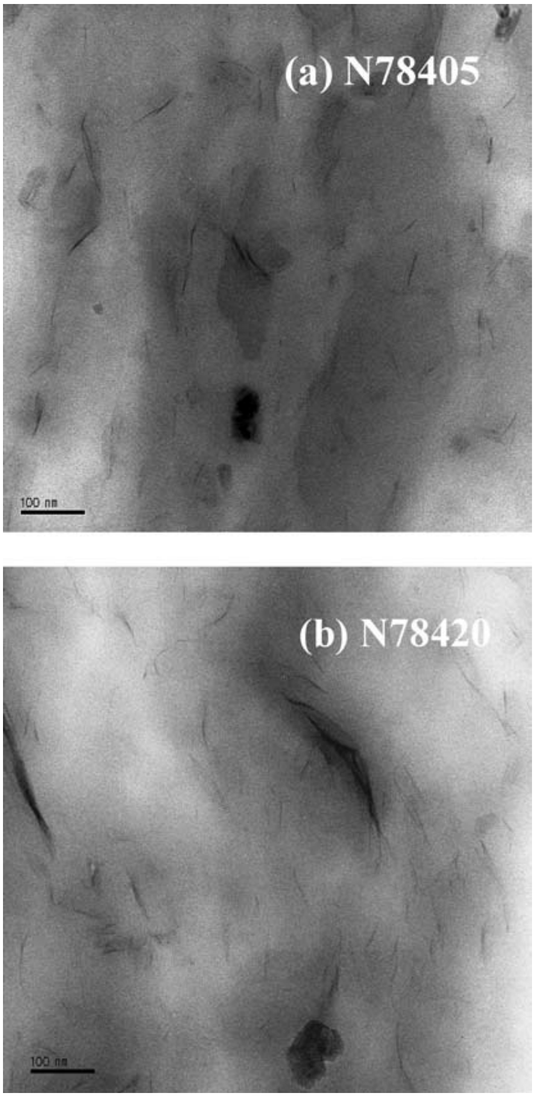

Figure 2 TEM images of nanocomposites: (a) N78405 and (b) N78420.

content. This means the transition of morphology from complete to partial exfoliation. Furthermore, XRD pattern of PA6 nanoocomposite with unmodified clay (USM05) also shows an exfoliated state, possibly due to polar characteristics of unmodified clay itself. This morphological characteristics can be also clearly observed in the TEM micrographs shown in Fig. 2. This partial or complete exfoliation morphology developed may be attributed to a strong interfacial adhesion between PA6 and Nanofil 784. Pozsgay *et al.* [8] reported that exfoliation occurs only above a critical gallery distance corresponding to the thickness of two aliphatic chains, which indicates that delamination is determined by organophilization and gallery structure. In order to investigate how interfacial interactions affect the rheological properties of the nanocomposites, their viscoelastic characteristics were measured and analyzed using a rotational rheometer. It is known that the rheological properties of polymer/clay nanocomposites are determined by a combination of the mesoscopic structure and the strength of the interaction between the polymer and the clay. The mesoscopic structure does not depend only on the strength of polymer/clay interaction but also on the inherent viscoelastic properties of the matrix in which the clay layers are dispersed [9].

The viscoelastic properties of particulate suspensions depend on structure, particle size, and shape. Thus, rheology can be used to provide a tool to examine the structural evolution and the dispersion quality of polymer/clay nanocomposites in the melt. The rheological properties measured at 240 °C for PA6 and its nanocomposite containing Nanofil 784 are plotted as a function of angular frequency in Fig. 3. With oscillatory measurement, we can investigate the viscoelastic response of materials without any destruction of the internal structure of the samples if the experiment is performed within the linear viscoelastic region [10, 11]. In order to assure this conditions, a test was performed to verify the linear correlation between amplitude and material function such as storage or loss modulus prior to the angular frequency sweep test. In the case of PA6, the amplitude of deformation was fixed at 10% in the dynamic measurement. However, the amplitude pre-set for the oscillatory measurement to give a linear viscoelastic response abruptly decreased (0.1∼1%) upon the addition of Nanofil 784, which means the solid-like characteristic of nanocomposites caused by strong interfacial adhesion between PA6 and Nanofil 784 [12, 13]. This solid-like properties may orginate from the expoliation morphology and the polar interaction, as well as the excellent mechanical properties of clay itself such as high strength and high modulus as mentioned above. Thus, with solid-like properties and expoliation morphology, we can conjecture that a specific structure of strong interaction between PA6 and clay is formed in nanocomposite.

A distinct increase in storage modulus (G′) and a continuous decrease of the slope of frequency dependence are also observed at low frequencies, which can be considered as an indication of the formation of a specific solid-like structure of well-dispersed layered silicates. On the

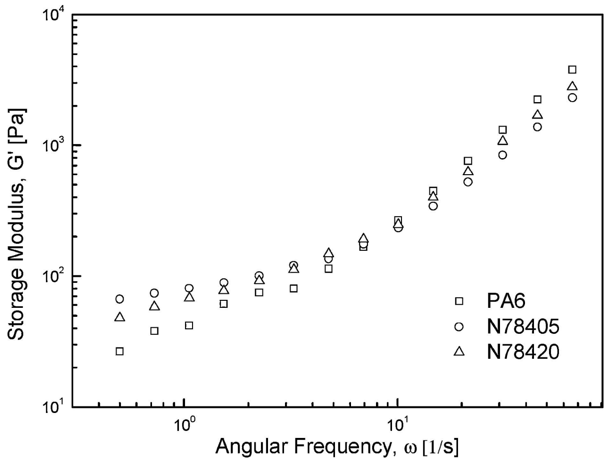

Figure 3 Storage modulus (G′) of PA6 and its nanocomposites (N78405 and N78420).

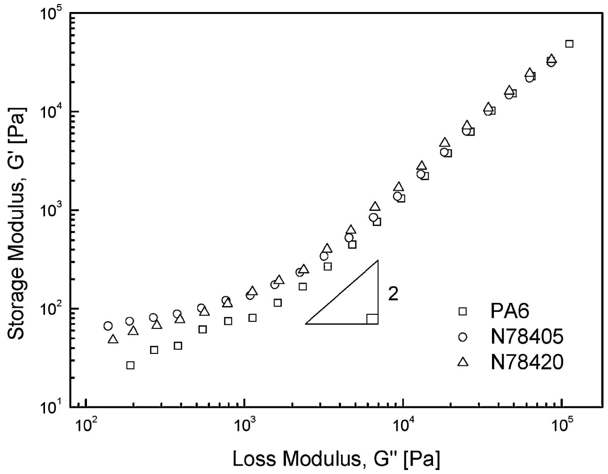

Figure 4 Modified Cole–Cole plot (G′ vs. G″) of PA6 and its nanocomposites (N78405 and N78420).

other hand, the storage modulus of N78405 was found to be higher than that of N78420. This result could be explained by the partial exfoliation of the silicate at large concentration. As shown in Fig. 1, N78420 exhibits a weak scattering peak around 4.7°, which is absent from the XRD trace of N78405. This indicates the transition of morphology from complete to partial exfoliation with the increase of silicate content. The change in the extent of exfoliation reduced the interfacial area, resulting in the decrease of storage modulus. The conclusion drawn above is obviously strongly supported by the morphological characteristic which was observed in the TEM images of Fig. 2.

Furthermore, a modified Cole–Cole plot, a logarithmic plot of G′ against G″ can be used as an effective method to explain structural changes occurring as a result of loading a filler into a polymer matrix at a fixed temperature [14–17]. Here one may consider the frequency to be an input variable, whereas both G′ (energy stored) and G″ (energy dissipated) are output variables of the fluid under oscillatory shear. Providing that the filled polymer has a homogeneous structure with no structural changes due to the addition of the filler, the modified Cole–Cole plot of the composite superimposes on the plot of the polymer matrix creating a master curve. However, in the case of our nanocomposites, their Cole–Cole plots deviate from that of the PA6 matrix regardless of silicate content, which indicates again a structural change on the addition of Nanofil 784. These structural changes are more prominent at low silicate content, showing a larger degree of deviation. These results agree well with the reverse trend of storage modulus (G′) as the Nanofil 784 content of the composite increases. In the case of polymer blends, a modified Cole–Cole plot depends only slightly on the molecular weight distribution of the components. Han and Jhon [18] found that such a plot is virtually independent of temperature and molecular weight for high molecular weight homopolymers.

In conclusion, we investigated the effect of interfacial interaction on the extent of exfoliation and structure as well as on the rheological properties of polyamide-6 (PA6) processed with Nanofil 784 layered silicate. XRD diffractograms indicated a large extent of exfoliation of the silicate caused by strong interfacial interaction between PA6 and Nanofil 784. The formation of such a morphology was further supported by TEM images. In addition, the rheological properties like storage modulus (G′) and a modified Cole–Cole plot (G′ vs. G″) of the composites indicated the formation of a specific structure of well dispersed exfoliated layered silicates, which was also induced by the strong interfacial interaction between PA6 and Nanofil 784.

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