

Evaluation of the Degree of Exfoliation in Poly(ϵ -caprolactone) Nanocomposites Using by the Dynamic Mechanical Analysis

Jae Woo Chung^{*}, Jae-Deok Jeon^{**} and Seung-Yeop Kwak^{***}

School of Materials Science and Engineering, Seoul National University, San 56-1,

Sillim-dong, Gwanak-gu, Seoul 151-744, Korea

^{*}cwfrank5@snu.ac.kr, ^{**}jdjun74@snu.ac.kr, ^{***}sykwak@snu.ac.kr

ABSTRACT

Poly(ϵ -caprolactone) (PCL) nanocomposites, were prepared using layered silicates with the nonpolar and polar organic modifiers by melt mixing with an internal mixer, PCLOC25A and PCLOC30B, respectively. Additional heat treatment was imposed on the PCL nanocomposites for the complete exfoliation. WXR patterns showed that d_{001} peaks of both nanocomposites were disappeared after the additional heat treatment. This means that the nanocomposites are exfoliated. However it was impossible to evaluate the degree of the exfoliation of both nanocomposites by WXR because d_{001} peaks are undetectable. Thus, linear viscoelastic and relaxation behaviors were measured by DMA. DMA results showed that PCL nanocomposites were completely exfoliated and PCLOC30B is more exfoliated than PCLOC25A because of the specific interaction between PCL and polar organic modifier. Finally, DMA was confirmed as a reliable mean to understand the degree of exfoliation of nanocomposites.

Keywords: nanocomposite, poly(ϵ -caprolactone), degree of exfoliation, dynamic mechanical measurement, polar interaction

1 INTRODUCTION

In the past decades, layered silicate-based polymer nanocomposites have attracted considerable attention because of the dramatic enhancement in strength, modulus, thermal resistance, and gas permeability barrier properties with far less amount of silicate content than that used in conventional filled polymer composites [1]. Layered silicates have layer thickness on the order of 1 nm and very high aspect ratios, e.g., 10-1000, and the interlayer spacing between stacked layers is also about 1 nm [2]. As such features of layered silicates, structures of nanocomposites of two different types such as the intercalation or exfoliation are achievable. The intercalated nanocomposites show regularly alternating layered silicates and polymer with a repeat distance of a few nanometers while the individual layers in exfoliated nanocomposites are irregularly delaminated and dispersed in a continuous polymer matrix [3]. This structural difference in nanocomposites plays a key role in the enhancement of

properties. For the exfoliated nanocomposites, higher mechanical properties are expected because of the larger surface area between reinforcement phase and polymer matrix relative to intercalation nanocomposites [4]. Giannelis et al. reported that thermodynamically stable equilibrium states of the nanocomposites such as intercalated and exfoliated systems depend on various entropic and enthalpic factors [5]. However, since the total entropy change in the system is small, the change of enthalpic factors such as intermolecular interaction determines the structure of nanocomposite [5]. Thus, layered silicate structure depends on the establishment of very favorable polymer-surface interactions to overcome the penalty of confinement condition [6], and the specific interactions driven by polar interaction or hydrogen bonding play a significant role for enhancing dispersion of layered silicate [7]. The structure of nanocomposites has been usually investigated by means of wide angle X-ray diffraction (WXR) and transmission electron microscopy (TEM). WXR and TEM are the powerful tools to prove the direct information on the structure of nanocomposite, but do not provide information about properties caused by the silicate structure [8]. Besides, it is impossible to analyze the overall three-dimensional structure of the silicate layers in nanocomposites. Recently, the interest about the dynamic mechanical analysis for property evaluation of nanocomposite are increasing because it provides information about the particle size, the shape, and the surface characteristics of the dispersed phase as well as enabling the facile characterization of the silicate structure [2,9]. Therefore, the aim of this study is to investigate dynamic mechanical properties such as linear viscoelastic and relaxation behavior occurred by silicate structures and to evaluate the degree of the exfoliation of nanocomposites using by dynamic mechanical analysis (DMA).

2 EXPERIMENTAL

2.1 Materials

Poly(ϵ -caprolactone) (PCL), with a number average molecular weight, M_n , of 80,000 g/mol was purchased from Aldrich. Organically modified montmorillonites (MMT) were supplied from Southern Clay Products, Inc., USA, under the trade name of Cloisite[®]25A (OC25A) and

Cloisite®30B (OC30B). Organic modifiers in OC25A and OC30B were dimethyl hydrogenated tallow 2-ethylhexyl, 2MHTL8, and methyl tallow bis(2-hydroxyethyl), MT2EtOH, quaternary ammonium cations.

2.2 Preparation of nanocomposites

The PCL and organoclay were mechanically mixed with an internal mixer with roller rotors at a rate of 100 rpm at 180 °C for 450 s. The compositions of the PCL/organoclay nanocomposites are given in Table 1. After mechanical mixing, additional heat was imposed to PCL/organoclay nanocomposites until the acquirement of the subsequently exfoliated nanocomposite. The PCL nanocomposite with OC25A is named PCLOC25A, whereas that with OC30B is denoted PCLOC30B.

Samples	Composition (wt%)		
	Poly(ϵ -caprolactone)	Organoclay	
		Modifier	MMT
PCLOC25A	92.4	2.6	5
PCLOC30B	92.6	2.4	5

Table 1: Composition of PCL/Organoclay Nanocomposites

2.3 Measurements

X-ray diffraction measurements were performed using a MAC Science MXP 18A-HF X-ray diffractometer with CuK_α radiation, $\lambda = 1.5405 \text{ \AA}$, generated at 40 kV and 100 mA in order to verify the gallery height and the structure of layered silicate in nanocomposites. Diffraction spectra were obtained in a 2θ range of $1.5\text{--}10^\circ$, and the diffraction angle was scanned at a rate of $3^\circ/\text{min}$. Dynamic mechanical measurements were performed on a rheometrics mechanical spectrometer model 800 (RMS 800). Dynamic isothermal frequency sweeps were performed using a parallel geometry plates 25 mm in diameter at different temperatures ranging between $60 \text{ }^\circ\text{C}$ to $180 \text{ }^\circ\text{C}$, with nitrogen gas purging and an angular frequency ranging from 10^{-1} to 10^2 rad/s . The strain regime which can be regarded as the linear viscoelastic data was determined from strain sweep experiments at strain amplitudes at selected temperatures.

3 RESULTS AND DISCUSSION

3.1 Wide angle X-ray diffraction (WXR)

The exfoliated structure of PCLOC25A and PCLOC30B caused by the additional heat imposition is provided by WXR analysis, as shown in figure. 1 and 2. The d_{001} silicate peaks in both nanocomposites without additional heat treatments after compounding are still detectable, which suggests that these structures remain intercalated.

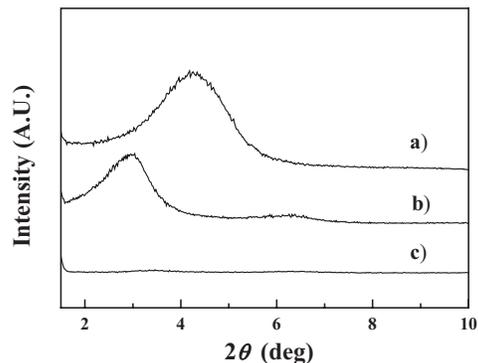


Figure 1: WXR intensity profiles: a) OC25A, b) PCLOC25A before heat treatment, and c) PCLOC25A after heat treatment.

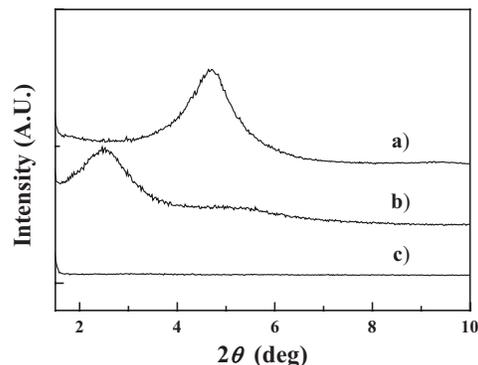


Figure 2: WXR intensity profiles: a) OC30B, b) PCLOC30B before heat treatment, and c) PCLOC30B after heat treatment.

However, the d_{001} peaks of both nanocomposites with the additional heat imposition perfectly are disappeared. This indicates that PCL chains have penetrated further into the silicate interlayers and the both nanocomposites have completely the exfoliated structure due to the additional heat treatment.

3.2 Dynamic mechanical analysis (DMA)

From WXR results, it was proved that both nanocomposites had fully exfoliated structure. However, the degree of exfoliation between the nanocomposites was not compared by WXR data because the d_{001} silicate peaks in both nanocomposites with additional heat treatment were disappeared. Thus, dynamic mechanical measurement was performed. Figure 3 shows the dynamic mechanical behavior of the PCL and the PCL/organoclay nanocomposites. We observed that $\log G''(\omega)$ versus \log

$G''(\omega)$ plots for PCL and both nanocomposites were independent of temperature. This implies that PCLOC25A and PCLOC30B have no structural change from intercalation to exfoliation over the temperature range because both nanocomposites already are completely exfoliated by the additional heat treatment. In addition, figure 3 shows that PCLOC30B has a higher elastic property than PCLOC25A. Since the content of the organic modifiers contained in the nanocomposites is small, the improvement of the mechanical properties caused by organic modifiers could be ignored.

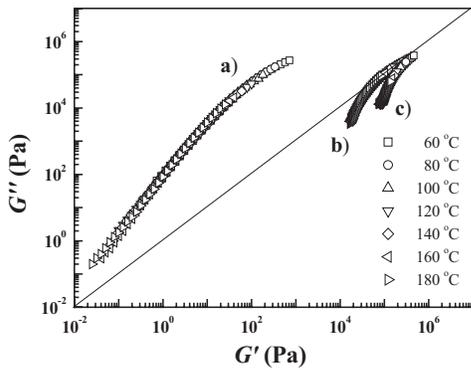


Figure 3: Plots of $\log G''(\omega)$ versus $\log G'(\omega)$ in the temperatures range of 60 to 180°C: a) pure PCL, b) PCLOC25A, and c) PCLOC30B.

This implied that the increase of mechanical properties depends on the degree of exfoliation and more exfoliated silicate structure provides higher elastic properties. Actually, layered silicate structure depends on the establishment of very favorable polymer-surface interactions [6]. PCLOC30B exists the polar interaction between the carbonyl groups in PCL and the hydroxyl groups in organic modifier at the surface of the OC30B. Polar interaction may facilitate the penetration of PCL into the interlayer. Therefore, PCLOC30B is more exfoliated than PCLOC25A. These results show that the degree of exfoliation depends on specific interactions between PCL and organic modifiers. The dynamic viscoelastic master curves were formed by the application of time-temperature superposition (TTS). We observed that the pure PCL exhibited the terminal behavior. On the other hand, for the PCLOC25A and PCLOC30B displayed the non-terminal behavior at low frequency. Then, these low-frequency responses might be indicative of a solid-like behavior [3]. The dynamic complex viscosity master curves, η^* , for the pure PCL and PCL/organoclay nanocomposites are presented in figure 4. Krishnamoorti et al. reported that the rheological properties were unaffected by the choice of the chemical nature of the polymer in nanocomposites [10]. However, relationship between chemical nature of the polymer and organoclay influences on the degree of exfoliation. Thus, the high viscosity of

PCLOC30B is due to the higher degree of exfoliation in PCLOC30B than PCLOC25A

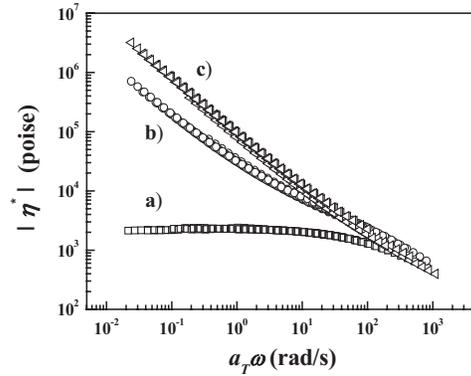


Figure 4: Reduced complex shear viscosities: a) pure PCL, b) PCLOC25A, and c) PCLOC30B.

Krishnamoorti et al. found that a_T values were unaffected by the presence of the silicate [6,10]. However, we found that PCLOC30B shows the different a_T values with pure PCL while PCLOC25A has the similar a_T values with pure PCL. This result is different from so far previously reported study by Krishnamoorti and co-workers. The behavior may be due to formation of highly exfoliated structure in PCLOC30B occurred by the strong interaction between PCL and OC30B. Furthermore, we suggest that the strong interaction between PCL molecules and the modifier in PCLOC30B may form the pseudo-network-like interaction as shown in figure 5.

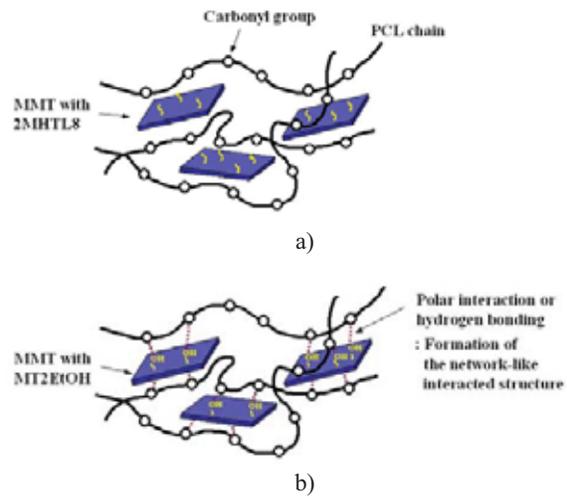


Figure 5: Comparison of the relationship between organoclay and PCL molecules depending on the interaction present in each nanocomposite: a) PCLOC25A and b) PCLOC30B.

Relaxation behaviors of both nanocomposites were evaluated by the activation energy, E_a . C_1 and C_2 were calculated by the nonlinear curve fitting of the WLF equation as follows:[11]

$$\log a_T = \frac{-C_1(T-T_0)}{C_2 + T - T_0} \quad (1)$$

Both C_1 and C_2 are constants, and T_0 is the reference temperature, in this case 120 °C. Subsequently, E_a of flow can be determined using Equation (2), where the WLF equation is substituted into the horizontal shift factor in the Arrhenius equation, which links the activation energy with the horizontal shift factor:

$$\Delta E_a = R \left(\frac{d \ln a_T}{d(1/T)} \right) = 2.303R \left[\frac{C_1 C_2 T^2}{(C_2 + T - T_0)^2} \right] \quad (2)$$

The activation energies become thus dependent on the temperature. Their values are shown in figure 6.

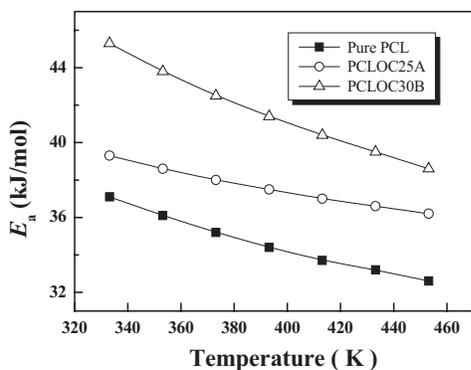


Figure 6. Activation energies for pure PCL, PCLOC25A, and PCLOC30B

The activation energy is a measure of molecular mobility and the energy barrier that must be overcome. It was confirmed from the plots of the activation energies as a function of the temperature that PCLOC30B had remarkably higher activation energies than PCLOC25A and pure PCL. It is attributed to the formation of the *pseudo*-network-like interacted structure caused by the polar interaction in PCLOC30B.

4 CONCLUSIONS

Poly(ϵ -caprolactone), PCL, compounds containing two different types of organically modified silicates, OC25A with nonpolar and OC30B with polar, namely PCLOC25A and PCLOC30B, were prepared by the additional heat imposition as well as the melt mixing using an internal

mixer at 180 °C for 450 seconds. It was verified by WXR D that PCL/organoclay nanocomposites was completely exfoliated through the heat treatment. The $\log G''(\omega)$ versus $\log G'(\omega)$ plots acquired from dynamic mechanical measurement showed that both nanocomposites were independent of the temperature. These mean that both nanocomposites were exfoliated. Then, it showed that PCLOC30B was the more elastic than PCLOC25A. From master curves of the storage moduli and the complex shear viscosity, it was also found that the PCLOC30B with the polar interaction showed a better elasticity than PCLOC25A. These are considered as the fact that PCLOC30B has more exfoliated structure than PCLOC25A due to the polar interaction. In the plots of the temperature versus a_T values, PCLOC30B showed the different a_T values with pure PCL. Furthermore, the activation energy was revealed that the PCLOC30B had remarkably higher activation energies than PCLOC25A and pure PCL. It is attributed to the formation of the *pseudo*-network-like interacted structure by the polar interaction. Consequently, these results suggest that the polar interaction between the polymer and the organic modifier is important factor depending on the silicate structure. Moreover, dynamic mechanical analysis is confirmed as a reliable mean to understand not only the silicate structure but also the relationship between the structure and properties of the nanocomposites.

REFERENCES

- [1] C. Wan, X. Quiao, Y. Zhang and Y. Zhang, Polym. Test 22, 453, 2003.
- [2] S. S. Ray, K. Okamoto and M. Okamoto, Macromolecules 36, 2355, 2003.
- [3] R. Krishnamoorti and E. P. Giannelis, Macromolecules 30, 4097, 1997.
- [4] V. Krikorian and D. J. Pochan, Chem. Mater. 15, 4317, 2003.
- [5] R. A. Vaia and E. P. Giannelis, Macromolecules 30, 7990, 1997.
- [6] E. P. Giannelis, R. Krishnamoorti and E. Manias, Adv. Polym. Sci. 138, 107, 1999.
- [7] S. W. Lim, J. W. Kim, I. Chin, Y. K. Kwon and H. J. Choi, Chem. Mater. 14, 1989, 2002.
- [8] T. J. Pinnavaia and G. W. Beall "Polymer-Clay Nanocomposites," John Wiley & Sons Ltd, 238-249, 2000.
- [9] M. J. Solomon, A. S. Almusallam, K. F. Seefeldt, A. Somwangthanaroj and P. Varadan, Macromolecules 34, 1864, 2001.
- [10] J. Ren, A. S. Silva and R. Krishnamoorti, Macromolecules 33, 3739, 2000.
- [11] J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons Ltd, 274-280, 1980.