생분해성 고분자/clay 나노복합체의 유변학적 특성

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Rheological characterization of biodegradable polymer/clay nanocomposite

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Introduction

There have been considerable interests in biodegradable polymers, which are used to reduce pollution caused by plastic wastes. Among the polymers, synthetic biodegradable aliphatic polyesters (BDPs) [1] were considered as the most promising biodegradable plastics because of low production cost and easy processibility in large-scale production. However, these polymers still have limited applications due to their higher cost compared with conventional plastics. To complement these kinds of defects, we adopted polymer-clay nanocomposite system. Polymer-clay nanocomposites are materials that display rather unique properties such as barrier properties, fire resistance and increase of mechanical properties, even at low clay content, when compared to conventional mineral-filled polymers [2]. Nanocomposites have been demonstrated with many polymers of different polarities including poly(ethylene oxide) [3,4], epoxy [5], polyurethane [6], polyimide [7] and polyaniline [8,9]. Recently, biodegradable polymers have been adopted to produce poly(ε-caprolactone) (PCL)-MMT [10] intercalated nanocomposites.

In this study, we prepared biodegradable polymer-clay nanocomposite via solution casting method, and investigated their rheological properties via a rotational rheometer with various test modes. Important rheological informations to enhance an applicability of the biodegradable polymers are thereby obtained.

Experimental

Synthetic BDP (Skygreen 2109, SK Chemical, Korea) was the copolymer obtained from polycondensation of diols and dicarboxlic acids with a weight-averaged molecular weight of

6.0×10^4 g/mole. Cloisite 25A (Southern Clay Products, USA) was the organophilic clay, modified with cationic surfactant. The BDP and its nanocomposites samples were obtained from the solvent casting method. We designated our samples as BDP00, BDP03, BDP06, BDP09 and BDP15. The last two digits represented the weight percent of organophilic clay in polymer (BDP) matrix. Disk type samples of these nanocomposites were prepared using a compression molding at 140℃ to measure the rheological properties.

To measure the rheological properties, we used a parallel-plate geometry (MCR 300, Physica, Germany) at 140 ℃. Shear viscosities were measured as a function of shear rate for each sample. The storage (G′) and loss moduli (G″) were also obtained as a function of frequency with the deformation of 3%.

Results and Discussion

In order to investigate the shear viscosity (η) *vs.* shear rate ($\dot{\gamma}$) relationship, we fit the measured viscosity to the Carreau model [11] in Eq (1) and the results are shown in Figure 1:

$$\eta = \frac{\eta_0}{\left[1+(\lambda\dot{\gamma})^2\right]^{(1-n)/2}} \qquad (1)$$

Here, η_0 is the zero shear viscosity, λ is a characteristic (or relaxation) time, and n is a dimensionless parameter, where the slope of η *vs.* $\dot{\gamma}$ in the power-law region is given by (n-1). Carreau Model [Eq. (1)] parameters obtained from BDP/clay nanocompsoites are given in Table 1.

The universal curves give a Newtonian plateau at low shear rates and power-law behavior at high shear rates, as shown in Figure 2. For BDP/clay nanocomposite in the melt state, a transition from a Newtonian plateau to a shear-thinning region occurs at a critical shear rate, $\dot{\gamma}_c$ [4,12]. Furthermore, $\dot{\gamma}_c$ is approximately equal to the inverse of the characteristic time of polymer/clay nanocomposites, which is the longest relaxation time required to the elastic structures of polymer/clay nanocomposites [12]. We found that there is a strong correlation between λ and $\dot{\gamma}_c$ for BDPX. We postulate that $\lambda\dot{\gamma}_c$ is a universal constant with a value of 2/3, where λ depends on both clay volume fraction and its nanostructure. The constant value, $\lambda\dot{\gamma}_c \cong 2/3$ is illustrated in Fig. 2.

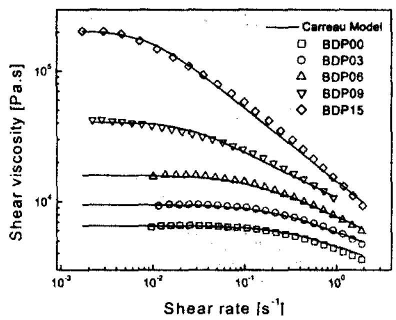


Fig. 1. Shear viscosity of nanocomposites

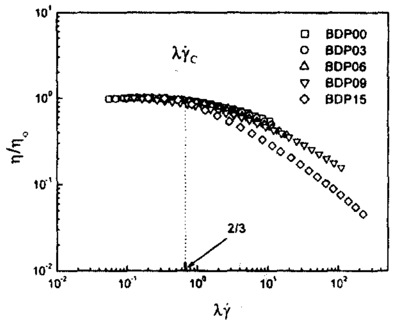


Fig. 2. Scaled plot of η/η_0 *vs.* $\lambda\dot{\gamma}$

Sample Codes	η_0(Pas)×10^{-4}	λ (s)	n	$\dot{\gamma}_c$
BDP00	0.66	5.69	0.76	0.12
BDP03	0.95	5.08	0.69	0.11
BDP06	1.60	9.49	0.67	0.07
BDP09	4.06	44.90	0.65	0.015
BDP15	20.54	115.89	0.44	0.006

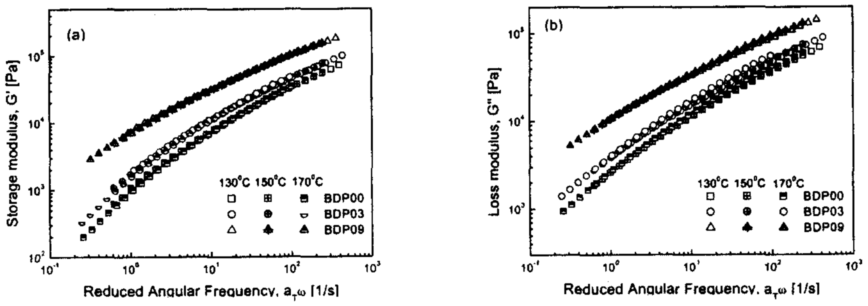
Table 1 Carreau Model [Eq. (1)] parameters and critical shear rate obtained from BDP/clay nanocompsoites

The dependence of viscoelastic behavior on layered clay concentration was investigated using the master curve for different nanocomposites, as shown in Figure 3 (reference temperature, 150 °C). It is clear that the master curves are smooth within the whole frequencies measured. Namely, the time-temperature superposition can be applied to our samples. At all frequencies, both G' and G" for nanocomposites increase monotonically with increasing clay loading. The behavior of G' and G" at low frequency for nanocomposite with high clay content is consistent with the response of a viscoelastic solid. For high frequencies, the overall viscoelastic behaviors are similar for different clay content, with the exception of a monotonic increase [13]. Also, the monotonic increases of shift factors for each system collapse into one line. This result means that the temperature dependent relaxation processes observed in the viscoelastic measurements are unaffected by the presence of clay layers [13,14].

Conclusion

The shear viscosity of BDPX increased with increasing clay content, since the presence of clay particles resists flow. Also, in contrast to BDP00, BDPX with clay loading exhibit more shear-thinning behavior due to the reorientation of dispersed clay particles and deformation of the polymer matrix. Comparison of the linear viscoelastic responses of nanocomposites shows the effect of clay at low frequencies.

Fig. 3. Storage (a) and loss (b) moduli for nanocomposites



References

[1] J. Kim, T. K. Shin, H. J. Choi, and M. S. Jhon, *Polymer* **40**, 6873 (1999).

[2] J. M. Gloaguen, and J. M. Lefebvre, *Polymer* **42**, 5841 (2001).

[3] P. Aranda, and E. Ruiz-Hitzky, *Chem. Mater.* **4**, 1395 (1992).

[4] H. J. Choi, S.G. Kim, Y. H. Hyun, and M. S. Jhon, *Macromol. Rapid Commun.* **22**, 320 (2001)

[5] T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, *Chem. Mater.* **7**, 2144 (1995).

[6] Z. Wang, and T. J. Pinnavaia, *Chem. Mater.* **10**, 1820 (1998).

[7] K. Yano, A. Usuki, and A. Okada, *J. Polym. Sci, Part A: Polym. Chem.* **35**, 2289 (1997).

[8] J. W. Kim, S. G. Kim, H. J. Choi, and M. S. Jhon, *Macromol. Rapid Commun.*, **20**, 450 (1999).

[9] B. H. Kim, J. H. Jung, J. W. Kim, H. J. Choi, and J. Joo, *Synth. Met.* **117**, 115 (2001).

[10] G. Jimenez, N. Ogata, H. Kawai, and T. Ogihara, *J. Appl. Polym. Sci.* **64**, 2211(1997).

[11] P. J. Carreau, D. C. De Kee, and R. P. Chhabra, *Rheology of Polymeric Systems: Principles and Application*, Hanser Publishers, New York, **1997.**

[12] R. G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford University Press, **1999**.

[13] J. Ren, A. S. Silva, and R. Krishnamoorti, *Macromolecules* **33**, 3739 (2000).

[14] M. J. Solomon, A. S. Almusallam, K. F. Seefeldt, A. Somwangthanaroj, and P. Varadan, *Macromolecules* **34**, 1864 (2001).