Structural Changes of PCL/Organoclay Nanocomposites as Investigatied by Dynamic Mechanical Relaxation and Motion

오광세, 곽승엽

서울대학교 재료공학부

1. Introduction

The field of polymer-clay nanocomposites has recently attracted considerable attention due to the possible technological applications as well as scientific issues concerning them. In particular a better understanding of the formation and the properties of the nanocomposites has been obtained using melt-intercalation of polymers into organoclay (organically modified silicate layers) by mechanical mixing above the softening or melting temperature of the polymer. Depending on the interaction between the organoclay and the polymeric species as well as the preparation conditions, nanocomposites with phase structures ranging from the intercalated to the exfoliated are possible [1-3].

The objective of this study is to report on phenomenological changes of the phase structure of the melt-intercalated poly(ε -caprolactone)/organoclay nanocomposites as additional heat is imposed on them. By monitoring the corresponding changes in the molecular mobility as characterized by dynamic mechanical analysis, the effect of heat history on the phase structure of the nanocomposites has been investigated from viewpoint of the molecular motion.

2. Experimental Section

2.1 Materials

Poly(ε -caprolactone) (PCL) with M_n=80,000 was purchased from Aldrich. It's melting point is about 60℃ and glass transition temperature is about -60℃. Organoclays supplied by Southern Clay Products, Inc. were C25A and C30A. According to the supplier, they were prepared from dimethyl hydrogenated tallow 2-ethylhexyl ammonium (2MHTL8) and methyl tallow bis(2-hydroxyethyl) ammonium (MT2EtOH) and their cation exchange capacity (CEC) was 95 and 90 meq/100g, respectively.

2.2 Preparation of Nanocomposites

Nanocomposites based on PCL were mechanically mixed with Internal Haake Mixer under 100 rpm at 180°C for 450 seconds. The composition of PCL/organoclays is as follows.

Table 1. The composition of PCL/organoclay samples

	PCL wt%	IA[a] wt%	MON[b]
PCLC25A	92.4	2.6[1]	5
PCLC30A	92.6	2.4[2]	5

[a,1,2] intercalating agent, 2MHTL8 (nonpolar), MT2EtOH (polar)

[b] Na⁻-montmorillonite

2.3 Dynamic Mechanical Analysis

Rheometrics RMS 800, was used in dynamic shear oscillatory mode, with 25 mm-diameter parallel plate geometry. All measurements were carried out under nitrogen environment. Isothermal frequency sweeps were taken at different temperatures ranging from 60°C to 260°C and the range of angular frequency was from $\omega = 10^{-1}$ to 10^2 rad/s.

3. Results and Discussion

Figure 1 shows the dynamic mechanical shear moduli, G' and G'', if the melt-intercalated PCL/organoclay nanocomposites as a function of temperature with the corresponding stepwise increase.


(a)   (b)
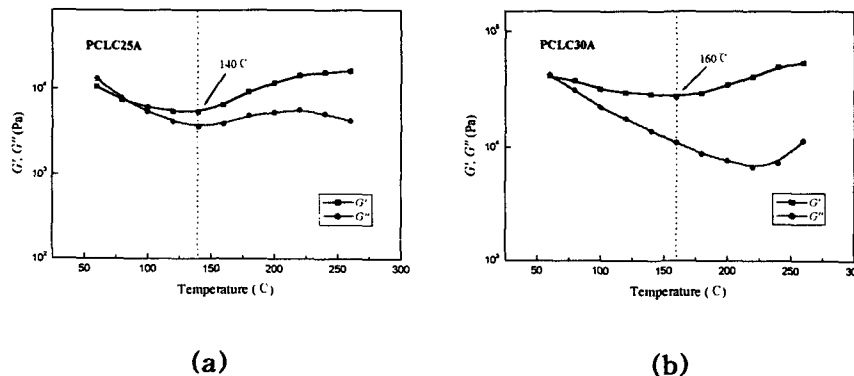
Figure 1. Dynamic mechanical moduli of (a) PCLC25A and (b) PCLC30A measured at $\omega = 1$ rad/s in nitrogen environment.

As the temperature is increased stepwisely, the storage moduli, G' of

PCLC25A and PCLC30A, reach a minimum at 140℃ and 160℃, respectively, and then increases upon continuous heating to 260℃. The former decrease of G' results from the time-temperature correspondence while the latter increase must be accompanied by any structural change in the respective temperature range. Recognizing that the thermal degradation temperature of PCL is higher than 300℃ and also considering other known facts about the PCL polymer, the only possible structural change in the system is further penetration of PCL chains inside the silicate interlayers. This structural change can be indicated from time-temperature superposition master curve of G', which represents the dynamic mechanical behavior over an extended frequency scale at the given reference temperature.

As seen in Figure 2, the $G'(\omega)$ data of PCLC25A at the temperature range from 60℃ to 140℃ and PCLC30A at 60 ~ 160℃ were superposable through the horizontal shift neglecting the vertical shift. However, those at higher temperatures must be corrected by considering the vertical shift factor, b_T. The vertical shift correction is associated with the inherent change of phase structure toward the exfoliated hybrid as a result of additional heat imposition. Further insight into the structural change is made by determining the molecular mobility for the PCLC25A and PCLC30A nanocomposites.


(a)   (b)
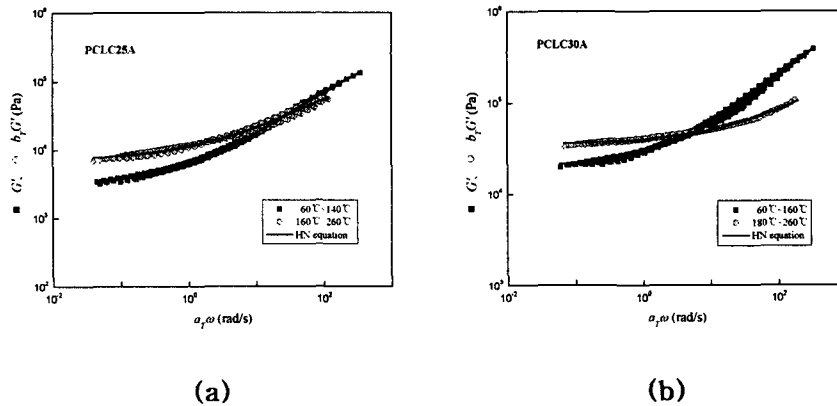
Figure 2. Master curves of G' **of (a) PCLC25A and (b) PCLC30A at the corresponding separated temperature range. The solids lines are fits of** $G'(\omega)$ **to HN equation.**

It has been well known the dynamic mechanical relaxation behavior of polymer systems follows an exponential relaxing process with a distribution of the relaxation times. thus, in order to express the relaxation behavior and determine the single average relaxation time, the dynamic mechanical data must be treated with empirical fitting functions. One of the most effectively used empirical fitting functions is the Havriliak-Negami (HN) distribution function of the relaxation

times. Although this is not so common for dynamic mechanical studies, it has been shown that the HN equation fits the dynamic mechanical relaxation spectrum as well as the dielectric one. Subsequently, the model equation for the modulus may be written as : $G^* = G' + iG'' = G_u - (G_u - G_r)/[1 + (i \tau_{HN}\omega)^\beta]^\alpha$

where G_u and G_r are the unrelaxed and the relaxed modulus, τ_{HN} is the characteristic relaxation time and the exponents α and β, ranging between 0 and 1, are parameters describing the shape of the loss curve [4-6]. From above equation, nonlinear curve fitting is performed on $G'(\omega)$ data to determine τ_{HN} and fitting parameters. The τ_{HN}'s of the two nanocomposites as a function of inverse temperature are shown in Figure 3.
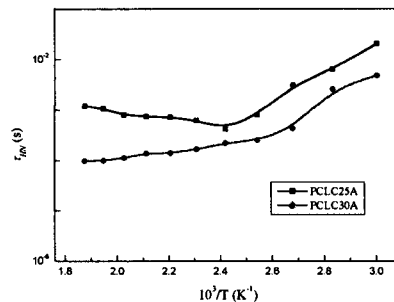
Figure 3. τ_{HN} versus inverse temperature for PCLC25A and PCLC30A.

The τ_{HN}'s at the temperature range of 60℃ to 140℃ or 160℃ decrease with increasing temperature and thus the molecular mobility increases at the corresponding temperature range. However, the slope of decreasing τ_{HN} is reversed for PCLC25A or reduced significantly for PCLC30A. Therefore, the overall trend of τ_{HN}'s further confirms the phase structural changes of PCL based nanocomposites as affected by the heating history.

5. References

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