적분형 구성방정식을 이용한 폴리프로필렌/층상 실리케이트 나노복합재료의 유변학적 특성 분석

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Rheological Characterization of Polypropylene/Layered Silicate Nanocomposites Using Integral Constitutive Equations

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Abstract

Exfoliated nanocomposites of polypropylene/layered silicate were prepared by a melt compounding process using maleic anhydride modified polypropylene (PP-g-MAH) and organoclay. It was found that polypropylene/layered silicate nanocomposites exhibited remarkable reinforcement compared with the pure polypropylene or conventional composite filled with agglomerated organoclay. The polypropylene /layered silicate nanocomposites showed stronger and earlier shear thinning behaviors and outstanding strain hardening behavior than pure polypropylene or other conventional composites in shear and uniaxial elongational flows, respectively. We simulated rheological modeling for the pure polymer matrix and polypropylene/layered silicate nanocomposite in shear and elongational flows using K-BKZ integral constitutive equation. The two types of K-BKZequations have been examined to describe experimental results of shear and uniaxial elongational viscosities of pure polypropylene and polypropylene/layered silicate nanocomposite.

Key Words: nanocomposites, viscoelastic behavior, rheological modeling, K-BKZmodel

1. Introduction

Organic-inorganic noncomposite have attracted great interest from researcher since they frequently exhibit unexpected hybrid properties synergistically derived from two components. One of the most promising composite systems would be hybrids based on organic polymer and inorganic clay minerals consisting of layered silicate. These greatly improved properties depend on the dispersion and orientation of the highly anisotropic clay tactoids in the polymer matrix. However, the exfoliated and homogeneous dispersion of the silicate layers could be achieved only in a few cases, such as polymers containing polar functional groups. This is mostly due to the fact that the silicate layers of the clay have polar hydroxy groups and are compatible only with polymers containing polar functional groups. Since polypropylene does not include any polar groups in its backbone, it has been thought that the homogeneous dispersion of the silicate layers in the polypropylene would not realized. According to the recent literature reports, however, it showed that the exfoliated PP/layered silicate nanocomposites were prepared with the particular combination of polypropylene, organoclay and coupling agent[1-2].

Practical constitutive equation for polymer melts should describe non-linear rheological behaviors

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such as time-dependent memory effects, extrudate swelling, corner vortex in the contraction flow, Weissenberg effect and so on. The constitutive equations are applied to computer simulation of polymer flows and polymer processing. Especially, recent progress in numerical techniques makes it possible to apply integral type constitutive equations to polymer flow and processing problems. The K-BKZ model has been used to analyse many polymer flows and to carry out computer simulation of polymer processing. Nowadays, it is well established that the flow response of complex fluids represents a special case of their non-linear viscoelastic behaviors. However, very little work has been done on non-linear rheological properties of polymer/layered silicate nanocomposites[3-4].

In this study, we attempt to examine the linear and non-linear viscoelastic behaviors of the exfoliated PP/layered silicate nanocomposites in shear and uniaxial elongational flow and simulate the steady shear and transient uniaxial elongational flow properties using the K-BKZ integral constitutive equation.

2. Theoretical background

When the time-strain separability can be assumed, a general form of the K-BKZ integral constitutive equation is given by,

$$\sigma(t) = \int_{-\infty}^{t} m(t-t')[h_1(I,II)C_t^{-1}(t') + h_2(I,II)C_t(t')]dt' \quad \text{---- (1)}$$

where $\sigma(t)$ is the stress tensor at the current time t, and $C_t^{-1}(t')$ and $C_t(t')$ are the Finger and Cauchy strain tensors. Assuming a discrete relaxation spectrum, the time-dependent linear memory function $m(t-t')$ which can be approximately by the generalized Maxwell model

$$m(t-t') = \sum_{i=1}^{n} \frac{G_i}{\lambda_i} exp\left(\frac{-(t-t')}{\lambda_i}\right) \quad \text{------- (2)}$$

with the relaxation time constants λ_i and the relaxation modulus G_i.

The damping function $h_1(I,II)$ and $h_2(I,II)$ are function of the first I and the second II invariants of the Finger strain tensor. To simplify the forms of $h_1(I,II)$ and $h_2(I,II)$, we assume that the normal stress ratio N_2/N_1 in shear flow is constant. Here N_1 and N_2 are the first and second normal stress differences, respectively. The we can define the parameter b as,

$$b = \frac{N_2}{N_1} = \frac{h_2}{h_1 - h_2} \quad \text{------------- (3)}$$

Combination of Equation (1) and (3) yields

$$\sigma(t) = \int_{-\infty}^{t} m(t-t')h_1(I,II)[(1+b)C_t^{-1}(t') + bC_t(t')]dt' \quad \text{---- (4)}$$

There are two representative forms for the damping function in the K-BKZmodel[3-5]. One is proposed by Papanastasiou, Scriven, and Macosko (PSM) as modified by Luo and Tanner (PSM-LT, Equation (5)). Another form is suggested by Wagner and Demarmels (WD) as modified by Fegel and Ottinger (WDFO, Equation (6)),

$$h(I,II) = \frac{\alpha}{(\alpha-3) + \beta I + (1-\beta)II} \quad \text{-------- (5)}$$

$$h(I,II) = \frac{1}{1 + \alpha(I-3)^{0.5}(II-3)^{0.5}} \quad \text{----------- (6)}$$

3. Experimental

The isotactic polypropylene homopolymers of extrusion sheet (HP 550K, MFI 3.5 g/10min, Polymirae Co.) was used as the base polymer resins in this study. The organoclay was a natural montmorillonite modified with a quaternary ammonium salt (Closite®15A, Southern Clay Co.,) via ion-exchange reaction. Maleic-anhydride grafted polypropylene (MA-PP) Polybond-3150, Crompton Co.) having the g-MAH content of 0.50 wt% was used as compatibilizer.

All samples were prepared by melt compounding in a count-rotating Brabender twin-screw extruder. Melt compounding was done at 190℃ and at screw speed of 100 rpm. The compounded melt was water quenched and palletized. For shear rheological measurements the pellets were compression molded into 25mm dia. x 1.5mm thick disks. Also for the elongational rheological measurements, the pellets were compression molded into 57.0mm x 7.0mm x 1.5mm rectangular shape.

The steady and dynamic shear rheological measurements were performed in a parallel-plate rheometer(AR-2000, TA instument) at 190℃. Frequencies of 0.1~200 rad/s were used at a strain amplitude of 10% in order to be within the linear viscoelastic region of the materials. Shear stress relaxation measurement were conducted using the ARES rheometer(Rheometric Scientific). The parallel plate geometry with a 25mm diameter and a gap size of 1mm was chosen and seven strain levels(0.5, 1, 10, 50, 100, 200, 300, and 500%) were used. The viscosity growth during uniaxial elongational flow at a constant extension rate was measured using a Meissner-type elongational rheometer(RME® Rheometric Scientific). The constant extension rates were applied 0.05, 0.1, 0.3, 0.5 and 1.0 s-1, respectively.

4. Rheological Modeling

The relaxation spectrum was calculated from shear measurements by fitting the experimental dynamic moduli $G'(\omega)$ and $G''(\omega)$ to a generalized Maxwell model in terms of the relaxation spectrum coefficients (G_i, λ_i). The evaluation of the discrete relaxation spectrum $H(\tau)$ was carried out by the Rheometric software. Non-linear relaxation modulus, $G(t,\gamma)$, is plotted as a function of time at various strain amplitudes and at 190℃. The shear stress relaxation at various strain amplitudes was studied to obtain experimentally the shear damping function, $h(\gamma)$.

$$h(\gamma) = \frac{G(t,\gamma)}{G(t)} \quad \text{------------} \ (7)$$

where $G(t)$ and $G(t,\gamma)$ are the linear and nonlinear stress relaxation modulus.

Table I. damping function and fitting parameters

	Fitting parameters		
	Pure PP	PP/OLS composites	PP/PP-g-MAH /OLS nanocomposites
WD-FO	n=0.143	a=0.153	a=1.22
PSM-LT	α=0.1	α=0.2	α=2.5
Soskey-Winter	a=0.2, b=1.2	a=0.2, b=1.2	a=2.0, b=1.2

5. Result and Discussion

5.1. Non-linear viscoelastic behaviors

Shown in Figure 1 is the steady-state viscosities taken from start-up of steady shear experiment as a function of shear rate. The stronger and earlier shear thinning behaviors were observed in the PP/PP-g-MAH/OLS nanocomposite at low frequency region. It is an obvious evidence that the polypropylene/layered silicate nanocomposite have a stronger viscoelastic property than pure PP matrix polymer or PP/OLS conventional composite.

Figure 2 shows the transient uniaxial elogantional viscosity growth curve of PP/layered silicate nanocomposite modified by organoclay and coupling agent (PP-g-MAH). This nanocomposite measured at different extension rates shows the strong strain hardening behavior. It is estimated that strain hardening behavior occurred over a wide range of extension rates will be related to the processability such as higher melt strength or lower melt flow index of nanocomposites.

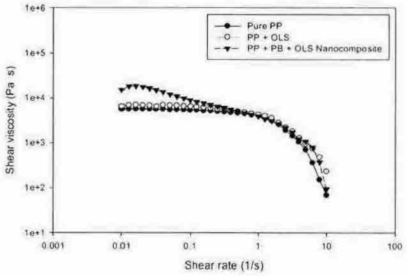

Figure 1. Steady-state viscosity curves for pure PP matrix and composite materials

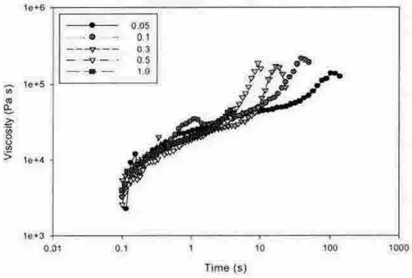

Figure 2. Elongational viscosity of PP/layered silicate nanocomposite at different strain rates

5.2 Modeling

The model predictions for the shear viscosity of pure PP are given in Figure 3, together with the experimental data available. The constitutive equation has been used to predict the Trouton ratio for the pure PP and two composites materials. The model predictions are plotted in Figure 4.

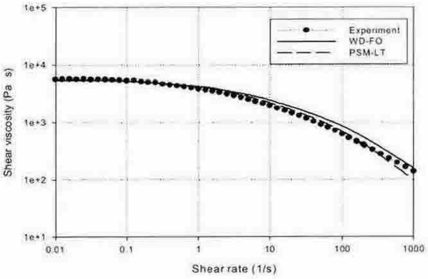

Figure 3. K-BKZmodel prediction for steady-state shear viscosity of pure PP matrix

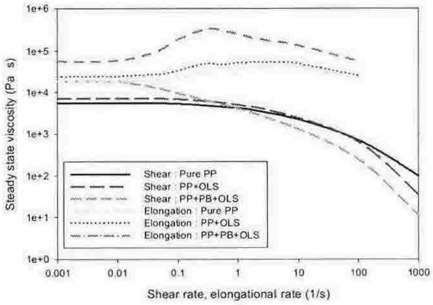

Figure 4. The model prediction for shear and uniaxial elongational viscosity at different strain rates.

6. Conclusion

We prepared the exfoliated polypropylene/ layered silicate nanocomposites using melt compounding process and characterized the rheological properties in shear and uniaxial elongational flows. We modeled the viscoelastic behaviors for the pure PP and polypropylene/ layered silicate nanocomposite by using two kinds of K-BKZ integral constitutive equations. Although WD-FO model does not show the steady state value and diverge to infinite at higher strain rates in uniaxial elongational flow, PSM-LT model agreed well with the experimental results of shear and uniaxial elongational viscosities.

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