CREEP AND RECOVERY OF POLYLACTIC ACID AND ITS CLAY NANO-COMPOSITE

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Abstract

This work focusses on exploring the long-term rheological behavior of polylactic acid and its nano-composites containing 3% clay. Creep and recovery experiments were performed at 160 °C for the neat PLA and its composite. Zero-shear rate viscosity was determined and used to determine the terminal relaxation time. Also, the continuous retardation spectra were calculated from the creep data and found to be consistent with those from the oscillatory data.

Introduction

Polylactic acid (PLA)/montmorillonite layered silicate (clay) composites have received tremendous attention in recent years due to their unique and environment-friendly nature. As an aliphatic polyesters, PLA has exhibited excellent biocompatibility and biodegradability [1]. Taken 40% of the biodegradable plastics market, the material has found increasing applications in biomedical implants, automotive interior components, and flexible to rigid packaging. To overcome some drawbacks of the material including low mechanical integrity and poor thermal stability [2,3], clay (montmorillonite layered silicate) has been incorporated and proven to be an effective in many cases [4,5,6]. Although PLA/clay composites have been extensively studied, the system is still not well understood especially regarding how the clay affects the melt rheology of the matrix.

Previously, we have conducted oscillatory shear tests to evaluate the short-term rheological properties of PLA and its nano-composites with 1%, 3% and 6% montmorillonite (clay). [6] It is found that the clay filler increases the storage modulus (G’) and the dynamic viscosity especially at lower frequencies. Such reinforcement is presumably coming from the interaction between the clay and the surrounding polymer chains, as supported from the presence of long chain modes in the discrete relaxation spectra. However, the data generated were primarily in the short-term region and it is of particular interest of this work to explore the long-term behavior and study how clay affect the system. It is expected that such rheological results would provide valuable information to the simulation and optimization of the blown film process that is being studied in the group. Recently, we have prepared blown filmed PLA/clay composite film and found that clay accelerates the crystallization process, exhibits reinforcement effects on the glassy modulus of the composites and decreases the oxygen permeation. [7] To further improve the quality of the films, melt rheological data are needed to evaluate and optimize the processing.

Creep and recovery experiment is the most important tool to bring insights into the melt behavior of polymers. In a typical creep test, a constant shear stress \( \sigma_0 \) is applied to the sample at time \( t = 0 \) s and the time dependent deformation \( \gamma(t) \) is measured. The creep compliance \( J(t) \) is defined as

\[
J(t) = \frac{\gamma(t)}{\sigma_0} = J_g + J_d \varphi(t) + \frac{\zeta}{\eta}
\]

where \( J_g \) is the glassy recoverable compliance, \( J_d \) is the retarded steady-state recoverable compliance which is often more than 104 \( J_g \). \( \varphi(t) \) is the recoverable creep compliance function which ranges from 0 to 1 as time goes from 0 to infinity. \( \eta \) is the limiting low rate shear viscosity often taken to be the zero shear viscosity. [8] When time = \( t_0 \), the stress \( \sigma_0 \) is set to zero and then the sample is allowed to recover. During the recovery stage, the recoverable compliance \( J_r \) can be related to the recoverable strain \( \gamma_r \) and the shear stress applied in the previous creep step,

\[
J_r(t_r) = \frac{\gamma_r(t_r)}{\sigma_0} = \frac{\gamma(t_0) - \gamma(t_r)}{\sigma_0}
\]

where \( t_r \) is the recovery time.

In this work, we aim to examine the effect of clay on the long-term behavior of PLA. For this, creep and recovery experiments are conducted on neat PLA and its composite with 3% clay. Zero-shear viscosity and the terminal relaxation time are determined and compared. Additionally, continuous retardation spectrum is calculated from the creep compliance and the previously obtained oscillatory shear data [6], respectively. The implications of the results are also discussed.

Methodology

Materials

The material studied is a polylactic acid, Ingeo™ Biopolymer 403D3, purchased from NatureWorks LLC. The polymer contains 4.4% D-lactide. Organically treated montmorillonite Cloisite 30B was purchased from Southern Clay Products (Gonzales, TX). The PLA/clay composites (3% clay by weight) were melt blended under a nitrogen atmosphere using a Barbandar mixer. For easy comparison, neat PLA was also blended with itself under
the same blending condition. All of the materials were stored under desiccant before use.

**Rheological measurements**

Creep and recovery measurements were performed using a TA Instruments (TA AR2000ex) rheometer. Disk-shaped samples of 25 mm diameter and 2.0 mm thickness were used for parallel plate rheometry. Nitrogen gas was used during the tests to minimize sample degradation. Creep measurements were conducted at 160 °C with a shear stress of 5 Pa for 20 minutes. Note that the other shear stresses such as 10 and 20 Pa were also tried and found to be all in the linear viscoelastic region. However, in order to ensure a final strain at the end of the creep to be within 100%, 5 Pa was chosen. Also, the torque applied during the creep phase was 100 times higher than the residual torque of the rheometer determined. After 20 min creep, the stress is removed and the sample is allowed to recover at the same temperature for 3 h.

Time sweep measurements were also performed using the same equipment and sample geometry as the creep/recovery measurements to check the thermal stability of the samples. Nitrogen gas was used during the tests to minimize sample degradation. Such scans were conducted at 160 °C for 5 h, with 1 rad/s testing frequency and 3% shear strain, within the linear viscoelastic region.

**Results and discussion**

Before running the creep and recovery experiments, oscillatory measurements were performed to check the thermal stability of the sample which is prone to be thermally degraded when exposed to elevated temperature for a long time. For this, the dynamic viscosity is measured at 160 °C and shown in Figure 1 as a function of time. In the 5 h test, the complex dynamic viscosity varies within 2.5%, presumably due to experiment fluctuation, indicating that the material is stable during the 5 h time window.

The strain evolution during the creep and recovery is shown in Figure 2 for both neat PLA and the composite. The neat PLA undergoes larger strain deformation during the creep phase and less strain is recovered afterwards. In fact, during the 3 h recovery, 47% of strain is recovered for the 3% PLA/clay sample whereas only 20% is recovered for the neat PLA.

Based on the strain data, creep compliance and the recoverable compliance are generated and shown in Figure 3 for the neat PLA and 3% PLA/clay composite. The slope of logarithmic compliance vs logarithmic time is 1 in the terminal zone for both samples, indicating the materials have reached steady state at the end of the creep. As expected, the creep compliance of the composite is lower than the neat PLA, due to the reinforcement effects as observed previously in the oscillatory experiments [6]. After 3 h recovery, the recovery compliance seems to have reached the plateau. The steady-state recoverable compliance is 0.0258 and 0.0357 Pa⁻¹ for the neat and 3% PLA/clay samples, respectively. The higher steady state recoverable compliance indicates the increased melt elasticity upon adding 3% clay.
function of creep time \( t \) and recovery time \( t_r \), respectively.

Previously [6], we found that clay strongly increases the dynamic viscosity especially at the lower frequency (shear rate), as shown in Figure 4. It is of interest to measure the zero-shear viscosity and study the effect of the clay in the low shear region. For this, we determine the zero-shear viscosity and the steady-state compliance following method recommended by Ninomiya [9]. The Creep compliance in steady state shear, \( J(t)_s \), can be written as

\[
J(t)_s = J_e + \frac{(t)}{\eta}
\]

where \( t \) represents the time and \( J_e \) is the steady-state compliance. Division of both sides by \( t \) gives

\[
\frac{J(t)_s}{t} = \left( \frac{J_e}{t} \right) + \left( \frac{1}{\eta} \right)
\]

Then, in a \( J(t)/t \) vs. \( 1/t \) plot, the interception at the ordinate gives \( 1/\eta \) and the limiting slope is \( J_e \). In reality, sometime, the steady state cannot be surely have been reached for some thermal stability reasons, and an extrapolating method has been proposed by Ninomiya. This method suggests plotting \( mJ(t)/t \) against \( 1/t \), where

\[
m \equiv \frac{d \log J(t)}{d \log t}
\]

The extrapolated interception at the ordinate is \( 1/\eta \). In this work, we use equation (4) to determined \( J_e \) and equation (5) for the zero-shear viscosity (for safety).

As shown in Figure 5, the \( J(t)/t \) and \( mJ(t)/t \) are plotted against \( 1/t \). For the sake of clarity, only data taken at creep time from 5 to 20 min are shown. The zero-shear viscosity \( \eta_0 \), determined to be 9792 and 24435 Pas for the neat PLA and the composite, respectively. The values are higher than those determined at higher shear rates, indicated as the dash lines in Figure 4. The \( J_e \) turns out to be 5.6 x 10\(^{-3}\) and 1.94 x 10\(^{-3}\) Pa\(^{-1}\) for the neat PLA and the composites, giving to a terminal relaxation time \( \lambda \) of 54 and 474 s respectively, through a relation, \( \lambda \approx \eta_0 \times J_e \). The results clearly shows stronger clay effect at low shear (terminal) region.

Finally, we are interested in determining the continuous retardation spectrum from the creep data and compare the results found from the dynamic data. According to Schwarzl and Staverman [10], retardation spectrum \( L(\tau) \) can be deferred from

\[
L(\tau) = \frac{d J(t)}{d \ln t} - \frac{d^2 J(t)}{d (\ln t)^2} \bigg|_{t=\tau}
\]

where \( t \) is the creep time and \( \tau \) is the retardation time. For the dynamic data obtained previously [6], we first determine the relaxation spectrum \( H(\tau) \) from the storage modulus \( G' \) and also from the loss modulus \( G'' \). The obtained two sets of relaxation spectra are averaged and used to calculate the retardation spectrum. Details follow:

**Relaxation Spectrum \( H(\tau) \) from \( G' \)**

\[
H(\tau) = AG'd \log G'/d \log \omega \bigg|_{1/\omega=\tau}
\]

\[
A = (2 - m)/2\Gamma \left( 2 - \frac{m}{2} \right) \Gamma \left( 1 + \frac{m}{2} \right) = \frac{\sin(m\pi/2)}{m\pi/2}
\]

**Relaxation Spectrum \( H(\tau) \) from \( G'' \)**

\[
H(\tau) = BG'' \left[ 1 - \frac{d \log G''/d \log \omega}{|1/\omega=\tau|} \right]_{1/\omega=\tau}
\]

\[
B = (1 + |m|)/2\Gamma \left( 3/2 - \frac{|m|}{2} \right) = \frac{\sin(m(1+|m|)/2)}{\pi(1+|m|)/2}
\]

After averaging the two sets of \( H(\tau) \), the data are used to determine \( L(\tau) \), along with the dynamic data of \( G' \) and \( G'' \) through

\[
L(\tau) = \frac{H(\tau)}{[G'(1/\tau) - G''(1/\tau) + 37H(\tau)]^2 + \pi^2 H^2(\tau)}
\]
The retardation spectrum determined directly from the creep compliance and those from the dynamic data are shown in Figures 6 and 7 for the neat PLA and the composite, respectively. The data generated from creep compliance seem to be a little larger than those from the dynamic data. However, both spectra show similar curvature as to the retardation time dependence. The results supports the use of continuous spectrum to predict the melt rheology data in a broader time (frequency) range.

References

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Conclusions
This work focuses on exploring the long-term rheological behavior of polylactic acid and its nanocomposites containing 3% clay. Creep and recovery experiments were performed at 160 °C for the neat PLA and its composite. Zero-shear rate viscosity as well as the terminal relaxation time are found to be higher upon adding the clay filler. The continuous retardation spectra calculated from the creep data are consistent with those from the oscillatory data. The results supports the use of continuous spectrum to predict the melt rheology data in a broader time (frequency) range.