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# The Effect of Crystallinity on the Rheological Behavior of Poly(lactide)\*

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The rheological behavior of poly(lactide) samples, with different levels of crystallinity, was investigated. The dynamic shear storage and loss modulus were obtained as a function of temperature at 1 rad/s. From the glassy to the rubbery region, the dynamic shear modulus decreased more than two decades for the initially amorphous poly(lactide) (containing 1% of D-lactide) and about one decade for the annealed (semicrystalline) sample. The dynamic shear modulus data showed that the crystallization rate increased with a decrease of D-lactide in poly(lactide) and an increase of talc (a nucleating agent) in the sample. The steady-state and dynamic shear viscosity were measured at 210°C. The results indicated that the Cox–Merz rule can be used to relate the dynamic shear viscosity to the steady-state shear viscosity. A master curve for the amorphous poly(lactide) was obtained, using the time–temperature superposition principle. The result showed that the temperature dependence of the shift factor can be described by the Arrhenius equation below the glass-transition region, and the WLF (Williams–Landel–Ferry) equation above the glass-transition region.

**Keywords:** Rheology; Poly(lactide); Crystallinity; Tacticity; Thermal degradation

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## INTRODUCTION

Poly(lactide) (PLA) is a biodegradable polymer which has found use in biomedical applications.<sup>[1-3]</sup> A new PLA polymerization process has lowered the cost<sup>[4]</sup> and PLA is being developed for applications in commodity areas such as films and fibers. Lactic acid has two stereoisomeric forms; L-lactic acid and D-lactic acid. PLA is made by ring-opening polymerization of lactides (cyclic dimers of lactic acid). Lactide has three stereoisomeric forms: L-lactide (L,L configuration), D-lactide (D,D configuration), and meso-lactide (D,L configuration). The stereosequence of PLA influences its physical properties and crystallization behavior. Pure poly(L-lactide) and poly(D-lactide) are crystallizable, while poly(meso-lactide) is amorphous.

The neat PLA has a glass-transition temperature from about 50°C to 60°C. The amorphous form of PLA has a relative low modulus above the glass-transition temperature. In order to extend the end use temperature, the mechanical properties above the glass-transition need to be improved. One way to increase the mechanical properties is to crystallize PLA. For broad use of PLA as a load bearing material, it is crucial to develop methods for rapid crystallization. This would allow for short cycle times in processes such as injection-molding.

For PLA derived from L-lactide with a small percentage of D-lactide or meso-lactide, the crystallinity decreases with an increase of the percentage of D in PLA. Above about 15% D-lactide, or meso-lactide, PLA will not crystallize at all. Consequently, the rate of crystallization decreases and crystallization time increases with the increase of the percentage of D in PLA. The increase of annealing temperature (below the melting point) and the presence of nucleating agent can increase the rate of crystallization. The amorphous PLA, with high percentage of D, has a lower glass-transition temperature than that of the crystalline PLA. From the DSC study,<sup>[5]</sup> it was found the melting point decreases with an increase of the percentage of D in PLA. The lower melting point allows for a lower processing temperature. The effect of temperature and molecular weight on the rheological properties of amorphous PLA melts has been studied.<sup>[6]</sup> The objectives of this work are to study the effect of annealing, tacticity, and nucleating agent on the rheological properties of PLA solids and the effect of thermal degradation, tacticity, and nucleating agent on the flow behavior of PLA melts.

## EXPERIMENTAL

The materials used in this study were obtained from the Cargill EcoPLA division. The Ultratalc™ 609 from Pfizer (New York, NY, USA) was compounded, using a twin-screw extruder. The molecular weight of the samples was measured using gel permeation chromatography (Waters Corp., Milford, MA, USA) equipped with a Waters Model 510 pump, Model 410 differential refractometer, and a Model 717 Plus autosampler with  $10^5$ ,  $10^4$ , and  $10^3$  Å Styragel HR columns attached in series. The analysis was performed at 35°C using tetrahydrofuran (THF) as eluent at a flow rate of 1 mL/min. The concentration of PLA was 0.5% and the amount injected was 50 µL. Polystyrene standard were used to generate a calibration curve. A 1 N NaOH solution with 75% methanol and 25% water was used to hydrolyze PLA to form L-lactic acid and D-lactic acid. The fraction of D-lactic acid was subsequently determined on a chiral HPLC system. The HPLC system was a Waters LCM 1 HPLC with a Waters 486 UV detector and a Sumichiral OA 6100 column. A 2.0 mM  $\text{CuSO}_4/\text{H}_2\text{O}$  mobile phase was used as eluent at a flow rate of 1 mL/min. The injection volume was 20 µL, and the concentration of sample was from 200 to 400 ppm. The peak value of the UV spectra was measured at a wavelength of 254 nm and the area of the peak was determined by a computer. The molecular weight and composition of the samples are listed in Table I.

For the solid rheology experiments, the samples were pretreated in a vacuum oven for 24 h at room temperature to remove moisture. The samples were cut from injection-molded tensile bars. The measurement geometry was torsional rectangular bar. The experiments were performed, using a RMS-800 strain controlled rheometer (Rheometrics Scientific, Inc., Piscataway, NJ, USA). The samples were heated from

TABLE I List of PLA samples used in rheology experiments

% D	% talc	$M_n$	$M_w$	PDI
1.1	0	88,150	190,700	2.2
1.2	30	77,070	169,100	2.2
4.1	0	92,970	194,300	2.1
27.3	0	94,190	228,700	2.4
27	30	79,570	194,500	2.4

room temperature to about 120°C at 5°C/min heating rate and 1 rad/s frequency. For the annealed samples, the samples were annealed at 95°C for 20 min and kept in a vacuum oven at room temperature until used for the rheology tests.

For the melt rheology experiments, the samples were cut into squares from injection-molded tensile bars. The samples were dried in a vacuum oven over 24 h to remove the moisture prior to the rheology test. A Rheometrics RS-200 stress controlled rheometer was used for the experiments. The measurement geometry was parallel plates, 25 mm in diameter with a gap of about 1.0 mm. The samples cut from tensile bars were about 3.25 mm in thickness and had a volume equivalent to the volume for a 1.0 mm gap between 25 mm diameter parallel plates. The sample was loaded on the center of the bottom plate. The top plate was then lowered and rotated slowly when it began to touch the sample (to let the sample fill the gap). The steady-state shear viscosity was obtained from the stress sweep experiment and dynamic viscosity was obtained from the dynamic frequency sweep experiment.

The master curve for the amorphous PLA was obtained using the time-temperature superposition principle. The frequency dependence of shear modulus for the amorphous PLA was obtained using a Rheometrics RMS-800 rheometer. The sample was annealed prior to the experiment. The test frequency ranged from 0.05 to 500 rad/s and temperature from -2°C to 100°C.

## RESULTS AND DISCUSSION

The dynamic storage modulus for PLA with different percentages of D is shown in Figure 1. The moduli in the glassy region for the three samples, with different percentages of D, are quite similar. As shown in the glass-transition region, the glass-transition temperature decreases with an increase of percentage of D in PLA. The storage modulus drops about three orders of magnitude from the glassy to the glass-transition region. The storage modulus starts to increase at about 80°C for the 1% and 4% D PLA due to crystallization. The storage modulus for the 1% D PLA increases with a faster rate than that of the 4% D PLA. The 27% D PLA shows no increase in storage

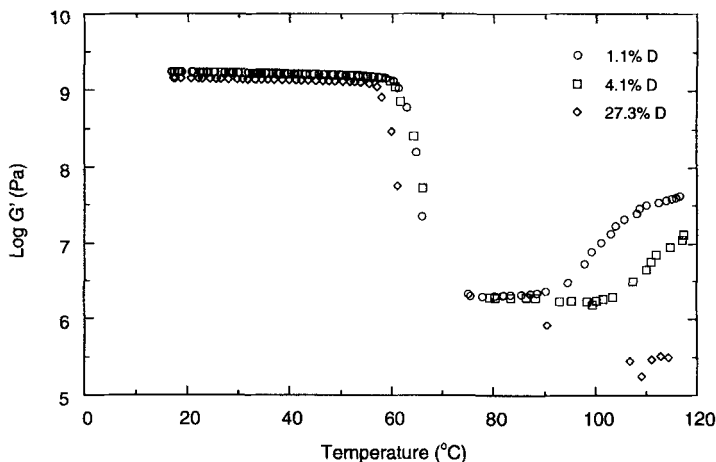


FIGURE 1 The temperature dependence of shear storage modulus for PLA, with different percentage of D at 5°C/m and 1 rad/s.

modulus above the glass-transition region. The storage moduli for the annealed samples are shown in Figure 2. The storage moduli, in the glassy region, are quite similar for the samples with different percentage of D. However, the crystallization has a significant effect on the modulus in the glass-transition region. The storage modulus increases in the glass-transition region with the decrease of the percentage of D. The storage modulus of unannealed and annealed 1% D PLA is shown in Figure 3. The annealing process has a significant effect on the modulus of the 1% D PLA as shown in the figure. Upon crystallization, as expected, the modulus of the unannealed sample approaches that of the annealed sample. The effect of the annealing process on  $\tan \delta$  of the talc-filled 1% D PLA is shown in Figure 4. The peak for the unannealed PLA has a much higher value (1.87) than that (0.2) of the annealed PLA. The ratio of the peak value between unannealed and annealed samples is about 9.4. The peak areas for the unannealed and annealed samples are 18.01 and 2.31, respectively. The effect of talc on the storage modulus of the 1% D PLA is shown in Figure 5. Compared with neat 1% D PLA, the talc-filled PLA has a higher storage modulus in the glassy region and the crystallization process is faster above the glass-transition region.

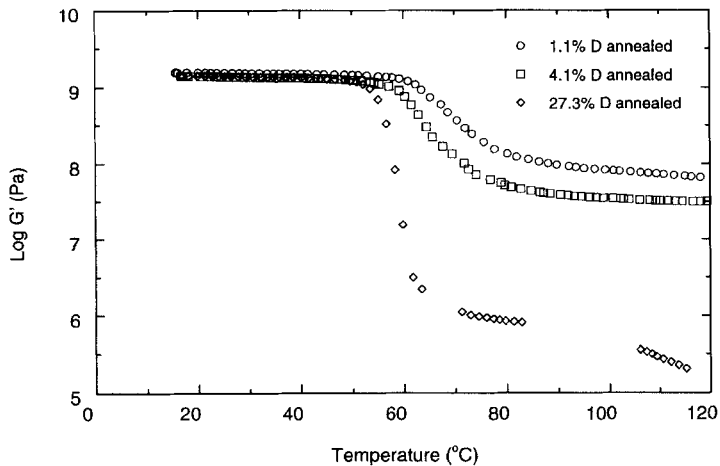


FIGURE 2 The temperature dependence of storage modulus for annealed PLA, with different percentage of D at 5°C/m and 1 rad/s.

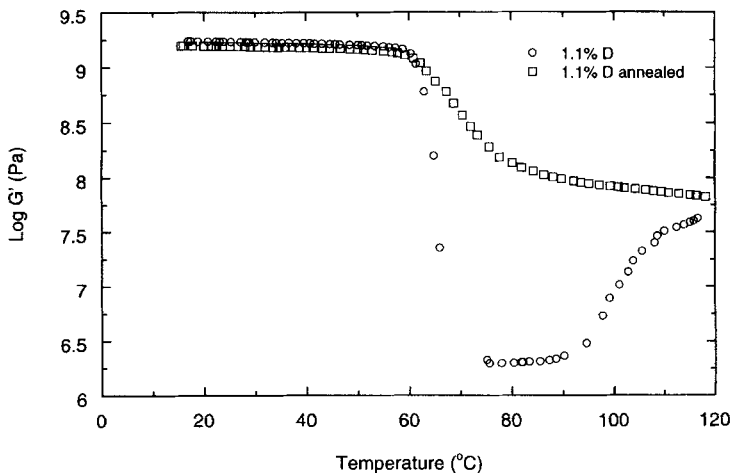


FIGURE 3 The temperature dependence of storage modulus for annealed and unannealed 1% D PLA at 5°C/m and 1 rad/s.

In polymer melt rheology, the dynamic viscosity is often related to the steady-state shear viscosity by employing the Cox–Merz rule<sup>[7]</sup>

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|, \quad (1)$$

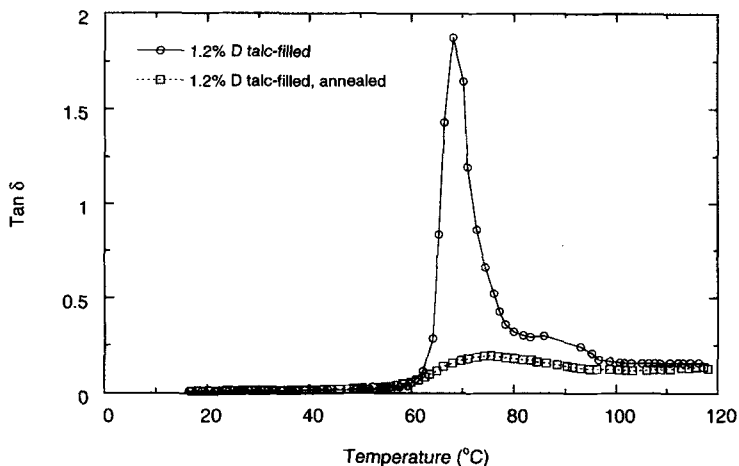


FIGURE 4 The temperature dependence of  $\tan \delta$  for annealed and unannealed 1% D PLA at  $5^{\circ}\text{C}/\text{m}$  and  $1 \text{ rad}/\text{s}$ .

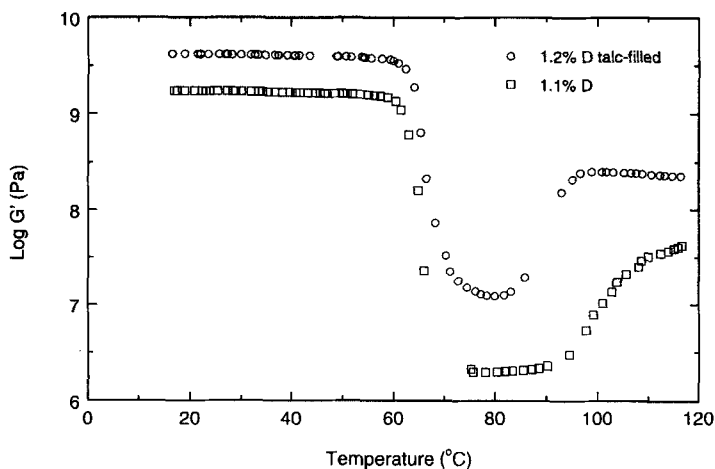


FIGURE 5 The temperature dependence of storage modulus for neat and 30% talc-filled 1% D PLA at  $5^{\circ}\text{C}/\text{m}$  and  $1 \text{ rad}/\text{s}$ .

where  $\dot{\gamma}$  is the shear rate,  $\eta^*$  is the dynamic viscosity, and  $\omega$  is the frequency. The steady-state shear viscosity and dynamic shear viscosity of the 27% D PLA at  $210^{\circ}\text{C}$  are shown in Figure 6. The same sample was used in the three tests shown in the figure and the



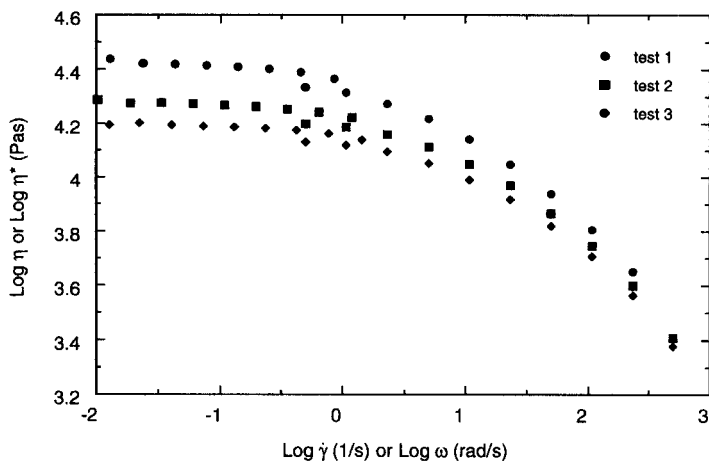


FIGURE 6 The steady-state shear viscosity and dynamic viscosity, as a function of shear rate or frequency, for the 27% D PLA at 210°C.

steady-state shear viscosity was obtained first for each test. The shear rate ranged between 0.01 and 1.0 s<sup>-1</sup> for the steady-state shear testing and the frequency ranged between 0.5 and 500 rad/s for the dynamic shear testing. The viscosity decreases with time due to the thermal degradation as shown in the figure. The thermal degradation affects the viscosity at low shear rate more than the viscosity at high shear rate. The step change in viscosity between steady-state viscosity and dynamic viscosity at about 0.5 rad/s is due to the thermal degradation. It is also shown from the figure that the Cox–Merz rule is satisfied for the 27% D PLA. The effect of talc on the viscosity of 1% D PLA is shown in Figure 7. The viscosity value at small stress is higher for the talc-filled sample than the unfilled sample and there is scatter in the data.

The viscosity of polymer melts can be described by a four-parameter Carreau–Yasuda model<sup>[8,9]</sup>

$$\eta = \eta_0 [1 + (\lambda \dot{\gamma})^a]^{(n-1)/a}, \quad (2)$$

where  $\eta_0$  is the zero shear rate viscosity,  $\lambda$  is a time constant,  $n$  is the power law exponent, and  $a$  is a dimensionless parameter. With

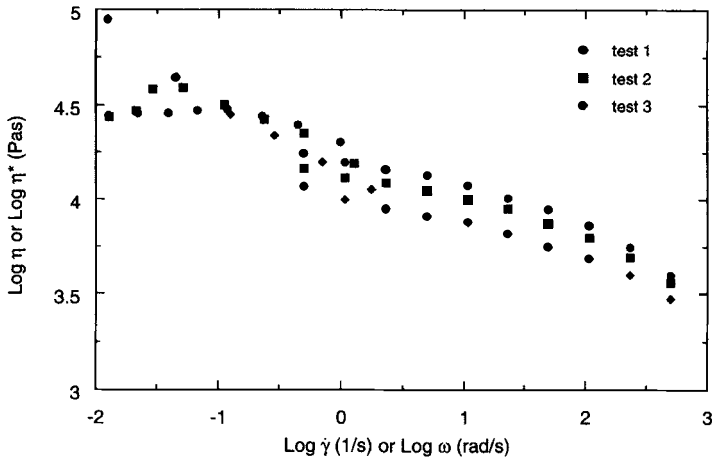


FIGURE 7 The steady-state shear viscosity and dynamic viscosity, as a function of shear rate or frequency, for the talc-filled 1% D PLA at 210°C.

$\eta_0 = 27356$ ,  $\lambda = 0.005703$ ,  $a = 0.43717$ , and  $n = 0.081222$ , the Carreau–Yasuda model provides an excellent fit to the viscosity of the 4% D PLA at 210°C as shown in Figure 8.

The master curve for the 27% D PLA at a reference temperature of 23°C is shown in Figure 9. The 27% D PLA shows a high modulus in the glassy state. The modulus drops about three orders of magnitude in the glass-transition region. The plateau after the glass-transition region shows the entanglement of molecular chains for a linear polymer. The shift factor for 27% D PLA from solid rheology experiment is shown in Figure 10.

The shift factor function can be described by the WLF (Williams–Landel–Ferry) equation<sup>[10]</sup> at temperatures above the glass-transition temperature. The WLF equation is

$$\log(a_T) = \frac{-C_1(T - T_0)}{C_2 + T - T_0}, \quad (3)$$

where  $C_1$  and  $C_2$  are constants,  $T$  is temperature, and  $T_0$  is the reference temperature. Above the glass-transition temperature, the WLF equation provides an adequate fit to the shift factor function of the

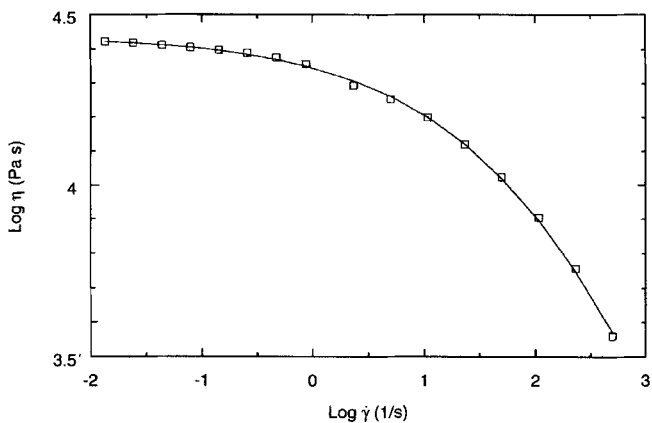


FIGURE 8 The viscosity of 4.1% D PLA at 210°C as fitted by the Carreau–Yasuda model.

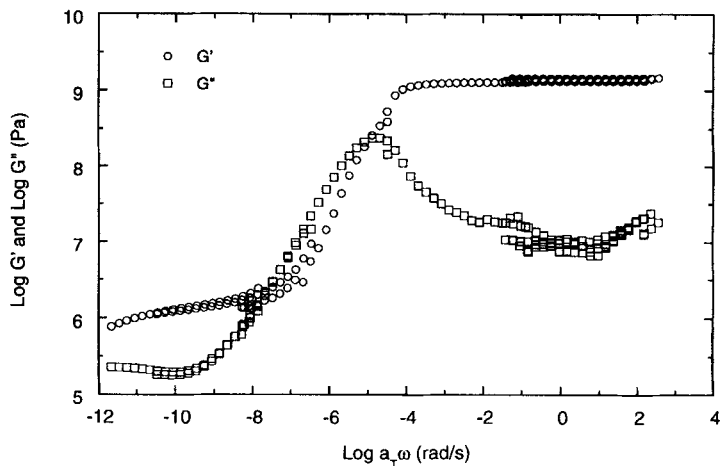


FIGURE 9 The master curve for the 27% D PLA at a reference temperature of 23°C (from the solid rheology experiment).

27% D PLA, with  $C_1 = 6.146$ ,  $C_2 = 20.42$ , and  $T_0 = 57.88^\circ\text{C}$ , as shown in Figure 11.

At the temperature below the glass-transition temperature, the temperature dependence of the shift function follows the Arrhenius

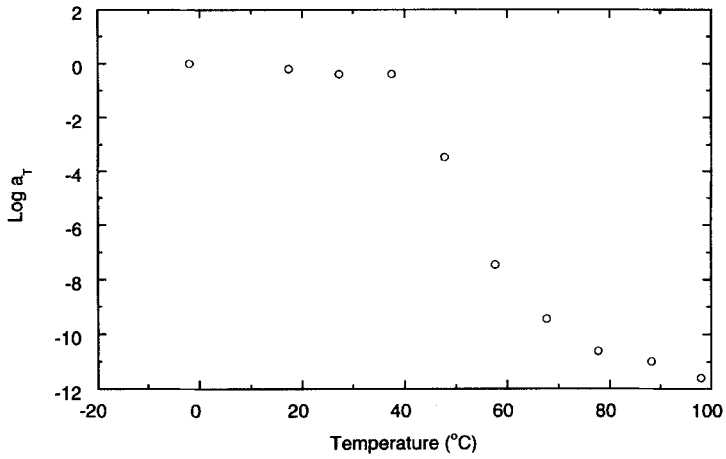


FIGURE 10 The shift factor for the 27.3% D PLA at a reference temperature of  $-2^{\circ}\text{C}$ .

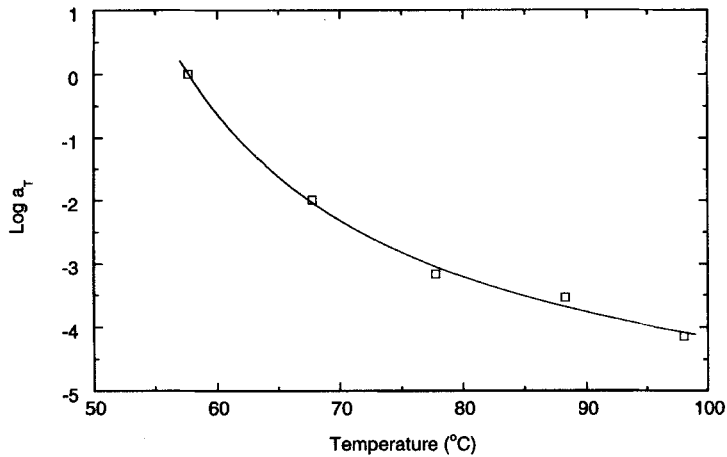


FIGURE 11 WLF plot of the shift factor for the 27% D PLA at a reference temperature of  $58^{\circ}\text{C}$ .

relationship

$$\ln(a_T) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right), \quad (4)$$

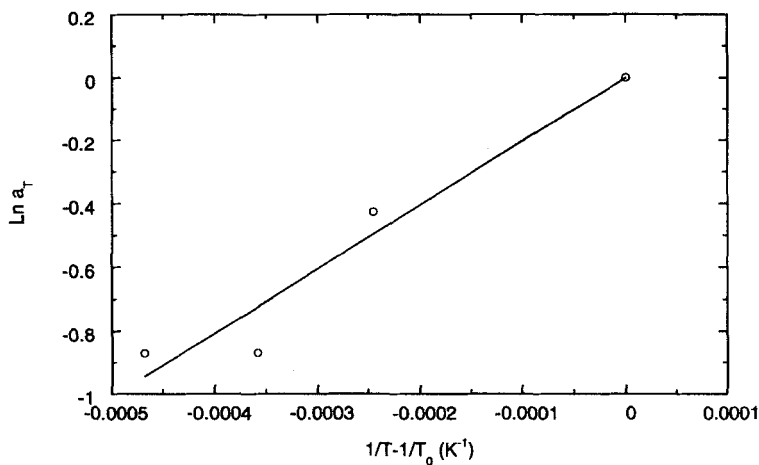


FIGURE 12 Arrhenius plot of the shift factor for the 27% D PLA at a reference temperature of  $-2^\circ\text{C}$ .

where  $E_a$  is the activation energy and  $R$  is the universal gas constant. The shift factor as a function of  $1/T - 1/T_0$  is shown in Figure 12. The slope of the straight line which gives the value of  $E_a/R$  is equal to 2019 K, which gives an activation energy of 16.79 KJ/mol.

## CONCLUSIONS

The storage modulus increased about two orders of magnitude for the annealed, low D PLA at temperatures above the glass-transition temperature. Talc affects both solid and melt rheological properties of PLA. Talc increased the modulus of the PLA in both glassy and glass-transition region. The interaction among the talc particles and resin caused the unstable and high value of the steady-state shear viscosity at the 30% talc loading. The master curve for the 27% D PLA showed the typical relaxation behavior for a linear high-molecular-weight polymer. It had a high elastic modulus in the glassy state, with a shift factor that is flat below the glass-transition temperature. This behavior of the shift factor indicates that the mobility of the PLA molecules is low, and there are few local motions of the molecular chains, below the glass-transition temperature. Above the glass-transition region, the

entanglement of polymer chains caused a plateau in the relaxation modulus.

The thermal degradation is severe at 210°C, which causes a problem in measuring the viscosity of PLA melts accurately. A lower temperature could reduce the thermal degradation effect on the viscosity measurement. A smaller peak in  $\tan \delta$  for the annealed PLA indicates less damping in energy as compared with the unannealed sample. The unannealed sample can absorb more energy than the annealed sample which is more packed in structure. The temperature dependence of the shift factor can be described by the Arrhenius equation below the glass-transition region and the WLF (Williams–Landel–Ferry) equation above the glass-transition region. The Carreau–Yasuda model gives an accurate analytical expression for the melt viscosity data.

### Acknowledgment

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