Poly(lactic acid) Stereocomplex Formation: Application to PLA Rheological Property Modification

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ABSTRACT: Poly(lactic acid) (PLA) stereocomplex formation in isothermal conditions in the absence and presence of a nucleating agent was studied from a rheological point of view due to sensitivity of viscoelastic properties to structural changes during this process. PDLA was melt blended in low concentrations with PLLA to produce a stereocomplex. Amorphous samples were prepared and crystallization was carried out in a rheometer at high temperatures to simulate melt processing conditions. Stereocomplexation was explored over time by measuring rheological parameters in small deformation oscillatory shear mode at a low frequency using parallel plate geometry. Kinetic data obtained by this means was compared to data from calorimetric studies, showing a different trend depending on the characterization method. Moreover, after the completion of crystallization, final crystalline structure was probed over a wide range of frequencies to investigate the rheological modification role of PDLA on PLLA major component. Differences in rheological characteristics of asymmetric PLLA/PDLA blends as compared to neat PLLA were associated to the structural changes happening because of the formation of the stereocomplex. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 41073.

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INTRODUCTION

Poly(lactic acid) (PLA) is a fast growing bio-based and compostable polymer that has raised lots of interest recently. Because of the presence of a chiral carbon atom, lactic acid has two enantiomeric forms called L-lactic acid and D-lactic acid. This can lead to an interesting phenomenon where L- and D-rich PLA chains called PLLA and PDLA respectively, cocrystallize and form a crystal structure known as a stereocomplex.[1] PLA stereocomplex is distinguished from PLLA or PDLA homocrystals by a 50°C higher melting point. In the last decade, PLA has become widely available commercially as a cost-competitive bio-based polymer with applications in packaging, textile, and molded parts.[2–4] This has augmented the need to overcome PLA deficiencies such as low heat resistance, slow crystallization, and low melt strength. Currently available PLA are mainly made from L-Lactic acid as this is the preferred form naturally obtained through fermentation routes. Progress has been made however to produce D-lactic acid and therefore could open the way to the use of PLA stereocomplex to solve the aforementioned obstacles.[5–8] Up to now, investigations have mainly focused on gaining an understanding of the stereocomplexation phenomenon with the emphasis on the crystallization mechanism and on the effect of different parameters such as molecular weight, optical purity as well as the blend preparation method and crystallization conditions.[9–27] In terms of applications, PLA stereocomplex has been investigated as a nucleation site for PLA homocrystallization,[21,28–34] as a thermo-mechanical properties modifier[35,36] as well as in PLA nanocomposites.[37–40] However, very few reports exist on the improvement of PLA rheological properties with the use of a stereocomplex.[41] Despite good mechanical, optical, and barrier properties, rheological properties of PLA are relatively inadequate for some processing techniques that require melt elasticity, i.e., the so-called melt strength. This is particularly limiting for processes such as film blowing and extrusion foaming where melt elasticity is required to retain film or foam structure prior to solidification. Thus, the first objective of this work was to explore the influence of stereocomplex on PLA melt rheology.

On the other hand it is also interesting to study the PLLA/PDLA cocrystallization by rheological measurements. Many reports exists on PLA crystallization mostly based on calorimetric studies, reviewed elsewhere.[42] Rheological monitoring of PLA homocrystallization as well has been done by a number of researchers[43–45]; however, there is no study on rheological
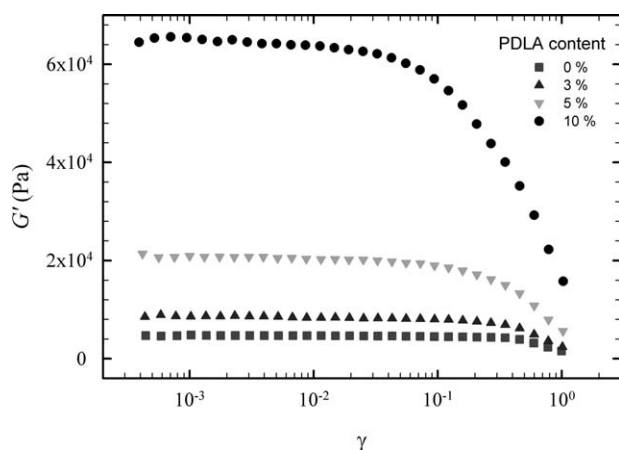
Figure 1. Elastic modulus as a function of strain for annealed samples with PDLA concentration between 0 and 10%.

monitoring of PLA stereocomplex formation. It is known that nucleation and plasticization have a significant effect on PLA homocrystallization.[46] In a previous study on the stereocomplex formation for melt mixed PLLA/PDLA blends it was shown that these modification techniques are also helpful for acceleration of stereocomplex formation even at elevated temperatures, with nucleation having a major contribution.[47] Therefore, the second objective of this work was to probe the effect of a nucleating agent on stereocomplex formation through rheological measurements. Results have been compared to kinetic data obtained via calorimetry and the difference in the response of material is explained taking into account the evolution of PLA microstructure by stereocomplex formation from the melt.

EXPERIMENTAL

Materials
PLLA and PDLA were semicrystalline commercial grades provided by NatureWorks LLC and Hycail, respectively. According to the producers they contained 2% D-units and 0.5% L-units, respectively. Molecular weights of the polylactides were measured via a ViscotekTDAmax GPC apparatus (Malvern Instruments Ltd) equipped with a triple detection system. The measured weight-averaged molecular weight (M_w) and polydispersity index (M_w/M_n) were 109 kg/mol and 1.57 for PLLA and 61 kg/mol and 2.1 for PDLA. An aromatic phosphonate (Eco-promote-NP) from Nissan Chemical Industries, Ltd with a particle size of 0.1–0.2 μm was used as nucleating agent.

Blend Preparation
Different formulations were prepared via a melt-blending technique using a LabTech twin-screw extruder. Mixing was carried out at 180°C at a rotation speed of 200 rpm and a feeding rate of 4 kg/h. Neat PLLA was processed at the same operating conditions and was used as a reference. The extruded blends were vacuum dried at 55°C for 2 days prior to characterization.

Rheological Measurements
Extruded samples were compression molded to disk-shaped specimens using a Carver laboratory press. The molding temperature was set to 240°C and the mold assembly was removed and quenched in liquid nitrogen to obtain amorphous samples.

Previously through X-ray diffraction analysis it has been shown that this procedure results in completely amorphous samples, thus stereocomplex formation takes place only during the rheological characterization process.[21] Also tests were performed at 180°C, which is above the melting and crystallization temperature of PLA homocrystals; therefore results were not affected by PLA homocrystallization. Dynamic melt rheological measurements were performed using an MCR 502 rheometer (Anton Paar) with parallel plate geometry. Plates diameter was 25 mm and gap size was set to 1.2 mm. Initially, dynamic strain sweep tests were performed on annealed samples to determine the linear viscoelastic region. For the crystallization monitoring, time sweep characterization was done at a frequency of 1 Hz for 30 min. Then, to investigate the effect of the crystalline structure formed during the time sweep test on the rheological properties of the blend, frequency sweep tests were performed in the frequency range of 0.1–300 rad/s. All tests were conducted under a blanket of dry nitrogen to minimize hydrolytic degradation.

RESULTS AND DISCUSSION

Effect of Stereocomplex on Linear Viscoelastic Region
Figure 1 shows the variation of elastic modulus (G') as a function of applied strain (γ) obtained at a frequency of 1 Hz for annealed samples with different concentrations of PDLA. It is clear that increasing the PDLA content results in an increase in G' as more stereocomplex is formed. Moreover, the linear viscoelastic region is significantly reduced as the PDLA concentration is increased. For neat PLLA the higher limit is 45% whereas for a blend with 10% PDLA it is decreased to about 2%. Similar behavior is observed for the well dispersed carbon nanotubes (up to 7%) in PLA matrix.[48] On the basis of these results a low strain of 0.5% was chosen for the rheological measurements.

Rheological Monitoring of Stereocomplex Formation
Time sweep tests were performed on amorphous samples at 180°C and a frequency of 1 Hz to monitor the variation of rheological properties with time that is an indication of stereocomplex formation at the test temperature. In Figure 2, G' is plotted versus time for blends with different amounts of PDLA.
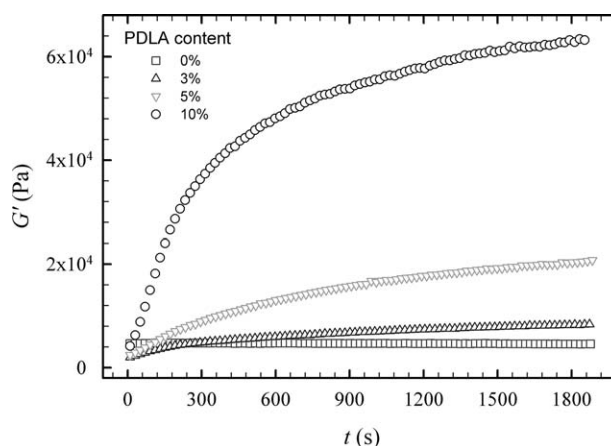

Figure 2. Elastic modulus as a function of time for initially amorphous samples with different PDLA concentrations.

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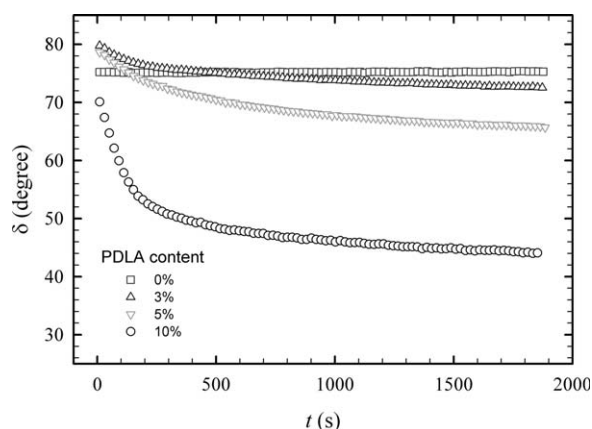
Figure 3. Variation of phase angle with time as an indication of stereocomplex formation.

First of all, for neat PLLA variation of G' in the time frame of the test was small. Therefore, the material was thermally stable at these conditions. By adding PDLA to PLLA, the initial value of G' decreased below that of neat PLLA. This was expected since PDLA had a lower molecular weight as compared to PLLA and its initial G' was equal to 113.5 Pa, which was much smaller than that of PLLA and decreased due to thermal degradation. Therefore, in the absence of any other mechanism, elastic modulus of the blends should have followed a decreasing trend. However, for PLLA/PDLA blends as time went by, G' gradually increased until it reached a plateau where variations of elastic modulus were small enough to assume that the stereocomplex formation was completed. The final value of the elastic modulus, $G'(\infty)$ depended on PDLA concentration and was in agreement with the values obtained for annealed samples in strain sweep tests.

To demonstrate the effect of stereocomplex formation in the test conditions on melt elasticity, phase angle (δ) as a function of time is presented in Figure 3 for the investigated blends. Neat PLLA showed a constant phase angle of 75° in the absence of any PDLA to cocrystallize with. Meanwhile, PLLA/PDLA blends revealed a decrease in phase angle, indicating that stereocomplex structure formed and contributed to an increase in melt elasticity. Higher PDLA concentration resulted in a lower phase angle, reaching a value of 44° for 10% PDLA.

It should be noted that G''/G' is equal to tan(δ). Therefore, a decrease in δ is equal to a decline in G''/G'. Because of the blends' viscosity build-up with time, both G' and G'' increased. However, a higher rate of increase for G' resulted in a total decrease in G''/G', which means a higher elasticity with time.

In prior work, It has been assumed that the amount of crystalline phase scales with G' based on the following equation[49]:

$$\chi(t) = \frac{G'(t) - G'(0)}{G'(\infty) - G'(0)} \quad (1)$$

where χ is the relative crystallinity, $G'(t)$ is the elastic modulus at time t, $G'(0)$ is the initial elastic modulus, and $G'(\infty)$ is its final value. Therefore, to investigate the kinetics of stereocomplex formation based on rheological data, χ is plotted versus crystallization time in Figure 4.

From this figure it can be seen that crystallization rate depends on PDLA concentration and as the PDLA amount in the blend is increased, the stereocomplex formation rate is increased. Stereocomplex formation half-time ($t_{1/2}$) was between 3.8 and 8.3 min depending on PDLA concentration.

Comparing Rheology with DSC. It is interesting to compare the kinetic data obtained from rheological measurements with those from calorimetry.[47] In Figure 5, kinetic curves corresponding to stereocomplex formation at 180°C for the blend with 5% PDLA are compared. It is noteworthy that presented data are only related to the presence of stereocomplex in the system since the test temperature was above the PLLA homocrystal melting point and the absence of PLLA homocrystal was shown previously through XRD and DSC characterizations.[21]

Figure 5(a) shows the variation of relative crystallinity obtained with rheological (χ_{Rheo}) and calorimetric (χ_{DSC}) measurements as a function of time. χ_{Rheo} was higher as compared to χ_{DSC} until 60% stereocomplex formation, after which it falls below the DSC curve. This difference in kinetic data is better illustrated in Figure 5(b), which shows χ_{Rheo} as a function of χ_{DSC}. The diagonal line represents a situation if exact kinetic data was obtained from rheometry and DSC. At low relative crystallinity values, a big difference between the experimental data and the diagonal line is observed, which is diminished as crystallization proceeds. This discrepancy may be explained by considering the specific case of stereocomplex formation and of the complex crystalline structure formed in isothermal conditions. It was shown that a dual network/spherulitic crystalline morphology is formed by cocrystallization of PLLA and PDLA chains.[21,47] Spherulites are higher order structures, which takes longer time to produce and grow. On the other hand, network structure is composed of smaller crystallites formed at a shorter time scale at different spots where PLLA and PDLA chains are in the vicinity of each other. Therefore, the effect of enantiomeric chains connection to each other is more significant on melt rheology at the initial stages of stereocomplexation. Physical connection of two chains results in an apparent increase in molecular weight. Also the chain structure evolves from a linear to a branched structure. Furthermore, if more than two chains
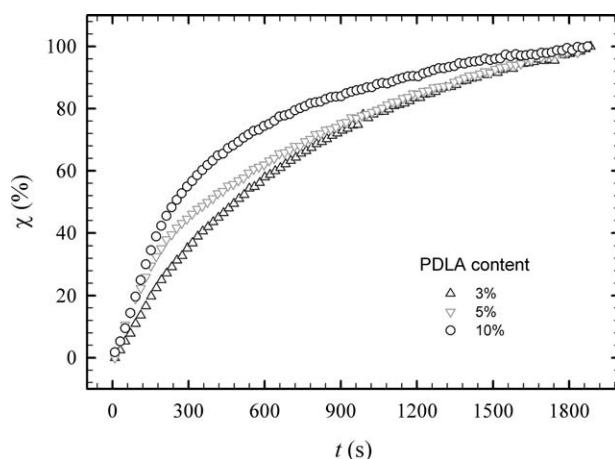

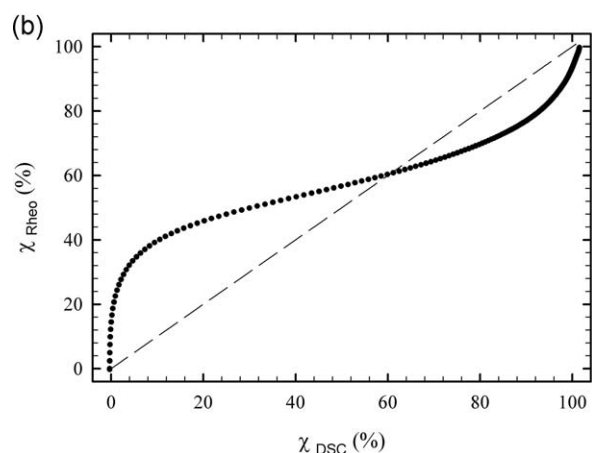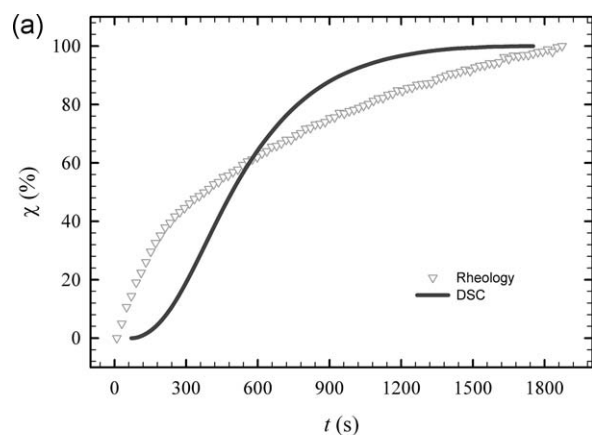**Figure 4.** Relative crystallinity as a function of time for blends with 3, 5, and 10% PDLA.

Figure 5. Comparison of relative crystallinity for 5% PDLA blend obtained by rheological and calorimetric measurements at $T_c = 180°C$: (a) χ_{DSC} and χ_{Rheo} as a function of time, (b) χ_{Rheo} as a function of χ_{DSC}.

are involved in stereocomplexation, physical cross-linking may occur. All these reasons result in an increase in elasticity and PLA viscosity, thus a higher rheological response in the earlier stages of crystallization.
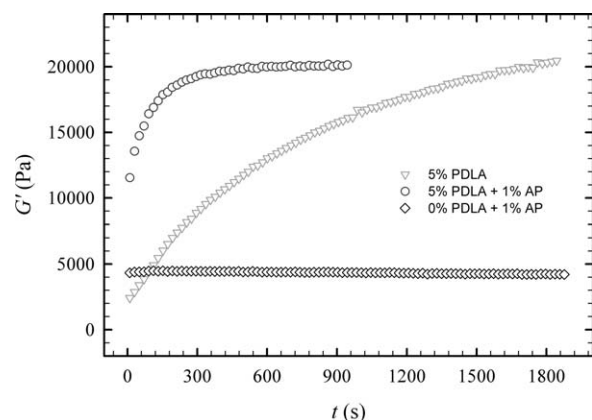

Figure 7. Comparison of relative crystallinity as a function of time for 5% PDLA blends without and with nucleating agent obtained by rheological and calorimetric measurements at 180°C.

Effect of Nucleating Agent. It has been shown through calorimetric studies that an aromatic phosphonate has a significant nucleating effect on PLA stereocomplex formation.[47] This was further investigated by tracing the variation of elastic modulus with time in the presence of this material. Figure 6 shows G' as a function of time for three samples. The straight line corresponds to the sample without PDLA having 1% nucleating agent. Thus, the material is thermally stable in the presence of nucleating agent with no significant decrease in G' after about 30 min. The curve presented with downward triangle symbol is related to the blend with 5% PDLA as illustrated in Figure 2 and is shown for the sake of comparison. Finally, the blend with 5% PDLA and 1% nucleating agent is presented with open circles. The initial point for the sample with PDLA and nucleating agent was higher as compared to the other two blends, suggesting that the stereocomplex formation had already progressed to some extend from the time that sample was placed in the rheometer until time sweep test was started. In addition, the plateau was reached much faster compared to the unmodified blend.

Figure 6. Elastic modulus as a function of time for amorphous samples: 1% nucleating agent without and with 5% PDLA and 5% PDLA blend without nucleating agent.
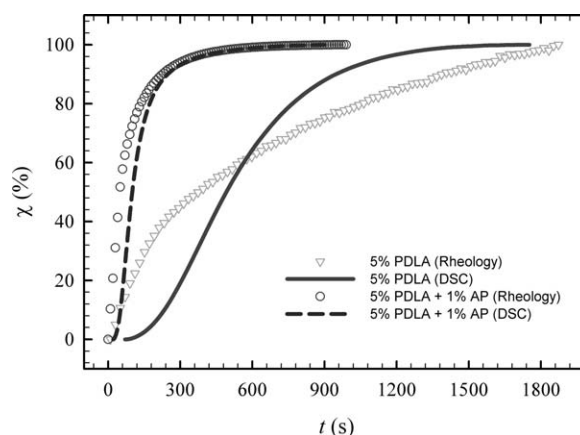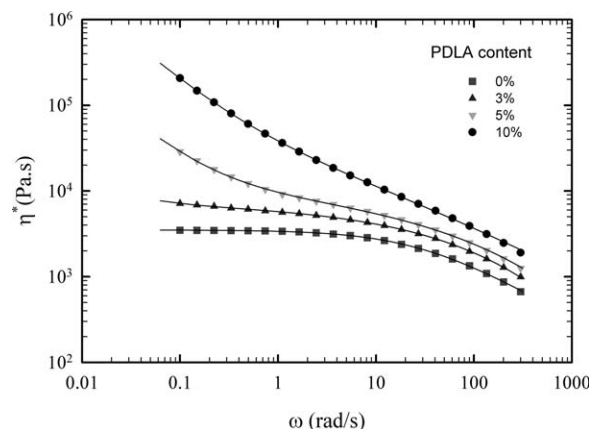

Figure 8. Complex viscosity versus frequency at 180°C for neat PLLA and blends with 3, 5, and 10% PDLA after completion of stereocomplex formation.
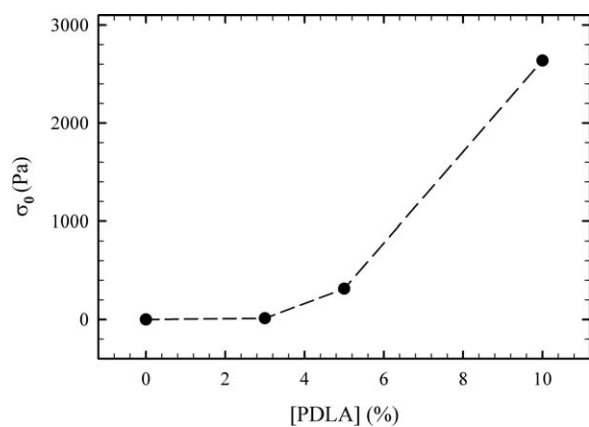
Figure 9. Yield stress as a function of PDLA concentration.

G' values for the nucleated sample are transformed to relative crystallinity according to eq. (1) and compared in Figure 7 to unmodified blend's relative crystallinity obtained from rheology and DSC characterization. To find the initial point for the nucleated sample, data were extrapolated to the initial value of elastic modulus for the unmodified blend. Similar to the unmodified blend, the kinetic curve for the blend containing 1% aromatic phosphonate and 5% PDLA obtained from DSC characterization is illustrated. On the basis of Figure 7, it can be concluded that heterogeneous nucleation was highly effective to

enhance the stereocomplex formation at high temperatures. Stereocomplex formation half-time was reduced from 375 s for unmodified blend to 50 s in the presence of aromatic phosphonate. For the nucleated sample as well, the rheological data showed an earlier increase in relative crystallinity compared to DSC curve. However, since the stereocomplex formation was much faster in this case as compared to the unmodified blend, this difference is not as notable.

Effect of Stereocomplex on PLA Rheological Properties

To investigate the effect of stereocomplex on the rheological properties of PLA, frequency sweep tests were performed on samples, which had already completed stereocomplexation in isothermal time sweep tests. In Figure 8, complex viscosity is plotted as a function of oscillation frequency for neat PLLA as well as blends with 3, 5, and 10% PDLA.

PLLA showed a η^*-ω relationship typical of linear polymers with a Newtonian plateau at low frequencies. However, as soon as PDLA was introduced to PLLA, the complex viscosity data was shifted upward, especially at lower frequency region. This behavior was more evident for 5 and 10% PDLA blends where complex viscosity does not stabilize to a viscosity plateau value at low frequency, thus showing a significant frequency dependent behavior.

To further analyze the crystalline morphology present in our blend, the viscosity increase ratio of the investigated blends was
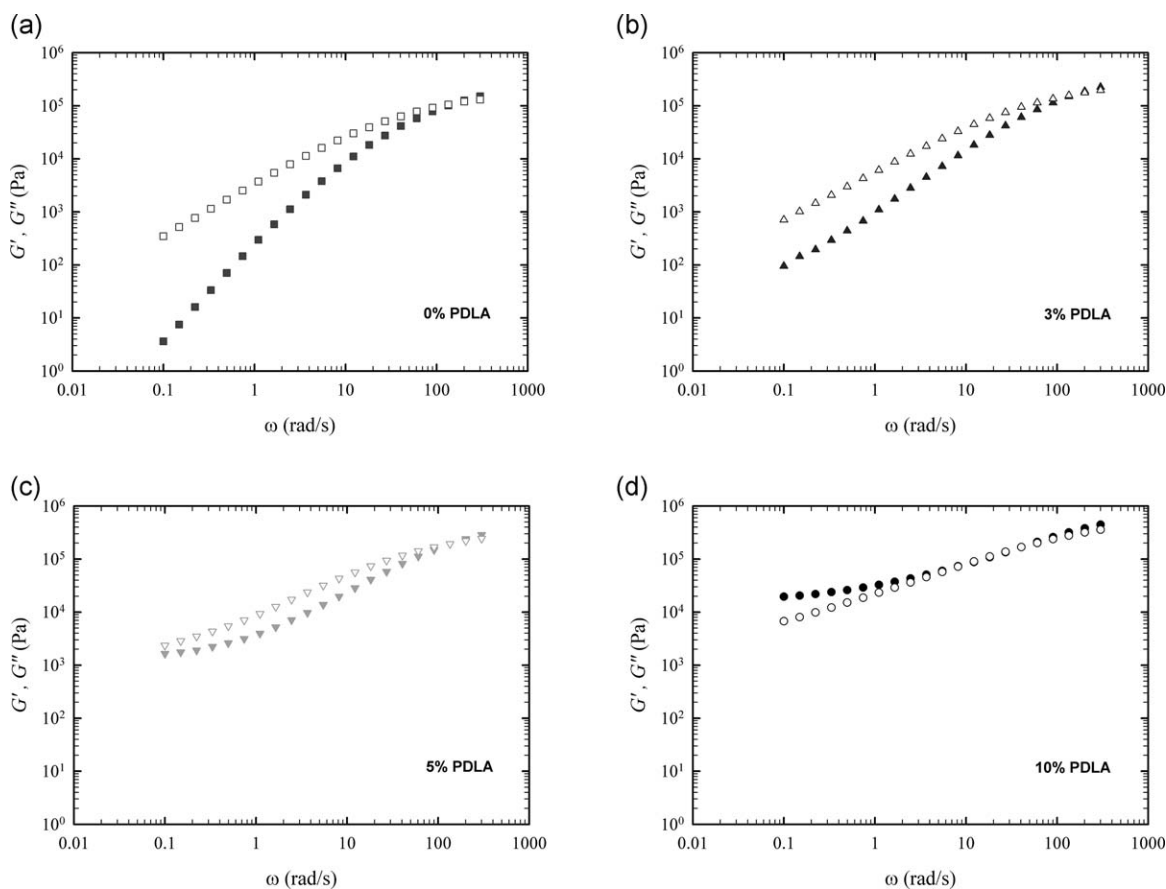

Figure 10. Elastic (filled symbols) and loss (open symbols) moduli as a function of frequency for neat PLLA and blends with 3, 5, and 10% PDLA.
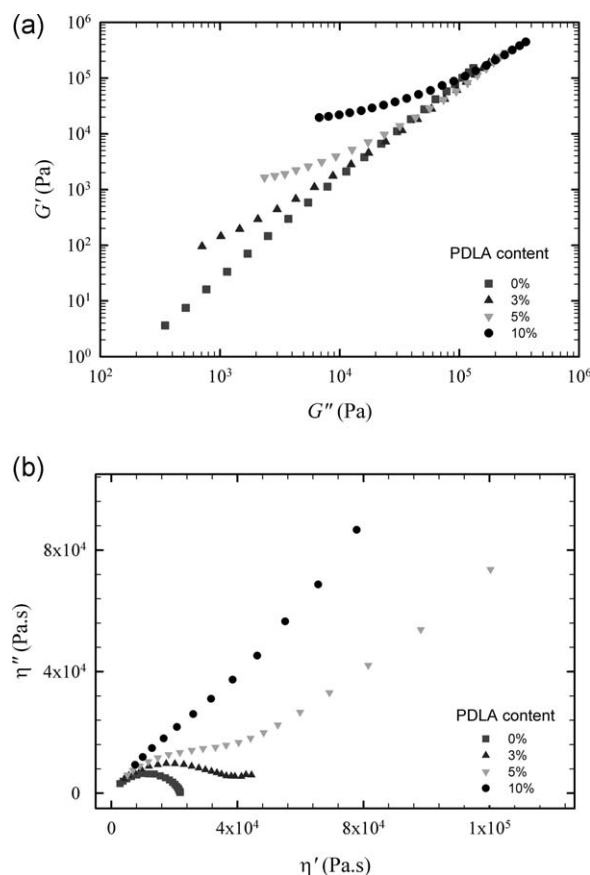
Figure 11. Cole–Cole plots for neat PLLA and blends with 3, 5, and 10% PDLA: (a) G' versus G'' and (b) η'' versus η'.

compared with predictions from a solution viscosity model. If the stereocomplex is present in the form of isolated and noninteracting "solid particulates" in an amorphous matrix of PLA, the effect of crystallinity should be similar to the effect of adding a solid filler. The experimental viscosity increase ratio was compared to prediction from Krieger-Dougherty model at the frequency of 0.1 rad/s. This model is used to predict the viscosity of concentrated suspensions:

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\varphi}{\varphi_{max}}\right)^{-A\varphi_{max}} \quad (2)$$

where η is the viscosity of the suspension, η_0 is the matrix phase viscosity, φ is the volume fraction of solid particles, φ_{max} is the maximum packing equal to 0.61, and A is a constant equal to 3.28. The first question arising with the use of a solution model is how to calculate the volumetric solid fraction. Since one PDLA chain crystallizes with one PLLA chain, in an ideal situation for 100% stereocomplex yield, the stereocomplex content can be assumed as two times the PDLA concentration. However, it was shown previously that stereocomplexation efficiency is around 50%. Therefore, we can assume that the "solid fraction" to be used in the Krigher–Dougherty model corresponds roughly to the PDLA (weight) fraction. One obvious simplification is made in this process. It is to neglect the density difference between the crystalline and amorphous phases since the volume fraction of denser crystalline matter should be slightly

smaller than the weight fraction. Comparing the Krieger–Dougherty prediction with experimental data shows that the effect of PDLA addition on the blend viscosity is substantially higher than that obtained from a suspension model. For example, at a PDLA content of 10%, the model predicted a 1.5 times increase in viscosity while experimental data showed a value of 60 times increase. This clearly confirms that the huge viscosity increase observed in presence of the stereocomplex cannot be simply explained by the presence of noninteracting solid spherulites dispersed in a matrix of amorphous PLA. It must therefore be concluded that the solid crystalline fraction present in the PLLA matrix are not isolated crystallites or spherulites and must have some level of interaction, possibly through a network tying PLA chains at a much finer level and that can explain the dramatic viscosity increase.

Accordingly, it was assumed that the PLA melt containing stereocomplex structure had a yield stress to describe the significant viscosity increase at low frequencies. Equation (3), which is the Carreau–Yasuda model with an extra term accounting for the yield stress was employed to fit the complex viscosity data.

$$|\eta*(\omega)| = \frac{\sigma_0}{\omega} + \eta_0 [1 + (\lambda\omega)^a]^{\frac{(n-1)}{a}} \quad (3)$$

where η^* is the complex viscosity, σ_0 is the yield stress, ω is the frequency, η_0 is the zero-shear viscosity, λ is the characteristic relaxation time, a is the Yasuda parameter, and n is the shear thinning index. Solid lines presented in Figure 8 represent the predictions of eq. (3). As it is clear from the figure, eq. (3) predicts very well the complex viscosity data. Predicted yield stress is plotted as a function of PDLA concentration in Figure 9. The blend with 3% PDLA had a yield stress of 12 Pa and by increasing the PDLA content to 5%, an upward trend was observed in yield stress value. On the basis of the presented data points, a rheological percolation was assumed at 4.5% PDLA content where the horizontal line connecting the first two points crosses the diagonal line connecting the last two points.

Comparison of the material functions such as storage and loss moduli in relation to material composition is a proper approach to understand the role of the stereocomplex structure and its concentration on PLA viscoelastic behavior. Therefore, in Figure 10 the variation of elastic and loss moduli as a function of frequency is compared for neat PLLA and PLLA/PDLA blends with different PDLA contents after being crystallized in time sweep tests.

For neat PLLA a G'-G'' relationship typical of linear polymers is observed where at low frequencies G' is proportional to ω^2 and G'' is proportional to ω. When 3% of PLLA is replaced by PDLA, both dynamic moduli shift up and G' becomes closer to G''. Further addition of PDLA (5 and 10%) results in higher G' and G'' values and G' becomes more independent of the frequency. At 5% PDLA concentration G' and G'' get too much close to each other at 0.1 rad/s, it seems they cross at a lower frequency. In the case of 10% PDLA, the elastic nature of the material becomes more significant. G' is above G'' at frequencies below 5 and above 60 rad/s and between these frequencies G' and G'' overlay. The high increase in G' at low frequencies

suggest that there is a structure forming in the presence of PDLA and the microstructure is changing progressively.

Cole–Cole plots are commonly used in the literature to describe the viscoelastic properties of heterogeneous polymeric systems and the transformation in their microstructure as a result of temperature variation, branching, or structure formation. Therefore, these plots are presented in Figure 11 for better illustration of this change in microstructure. Figure 11(a) is the plot of G' versus G'' and Figure 11(b) η'' versus η' for the four studied blends. For the neat PLLA G' versus G'' and η'' versus η' show linear and semicircular behavior, respectively, which is expected from the linear chain structure of the PLA. On the other hand, by increasing the PDLA content in the blends, G' versus G'' shifts upwards and deviates from neat PLA showing that the microstructure is evolving. The same conclusion can be drawn from η'' versus η' plot where addition of PDLA results in a tale in semicircular behavior, which shifts upward as the PDLA content is increased from 3 to 10%. This deviating behavior is also observed in the composites of PLA with structuring materials such as silica and carbon nanotubes.[48,50]

CONCLUSIONS

Rheological monitoring of PLA stereocomplex formation kinetics at high temperatures was performed for the first time for asymmetric PLLA/PDLA blends. Crystallization half-time was in the range of 4–8 min showing a dependency on PDLA concentration. It was shown that the elastic modulus was more sensitive to crystallization in the early stages of the crystallization process. This was associated to interaction or network formation between the crystallites resulting in apparent molecular weight increase and branching. In addition, it was shown that crystallization kinetics can be significantly increased in the presence of an aromatic phosphonate, which was employed as a nucleating agent. Frequency sweep tests performed on crystallized specimens showed a remarkable increase in viscosity and elasticity of the blend as PDLA content was increased above 3%. Complex viscosity versus frequency data could be predicted quite well with the Carreau–Yasuda model with an extra term accounting for a yield stress. On the basis of the plot of the yield stress as a function of PDLA content, a rheological percolation is achieved at 4.5% PDLA content. Low frequency region data in the complex viscosity and dynamic moduli graphs as well as cole–cole plots also suggest the transformation of chain microstructure from a linear to a branched architecture in the presence of a small concentration of PDLA.

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