

Study of polylactide stereocomplex formation with combined Raman spectroscopy and rheology

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Introduction

Poly(lactide) (PLA) plays a prominent role in many biologically based and biodegradable polymers. It already represents about one fifth of global polymer production capacity and there are several companies that plan to invest, or are already investing, in further capacity.¹ PLA can be produced by ring-opening polymerization of L-lactide or D-lactide, yielding polymers PLLA and PDLA, respectively, with a high degree of stereoregularity. Despite this, PLA has a slow crystallization rate. In the amorphous state, the low glass transition temperature (~63°C) also limits PLA's applications, even in the packaging industry. Items such as hot beverage cups and disposable cutlery made with PLA would lack the thermal resistance of fossil-based alternatives like polystyrene.

Nucleation is a conventional strategy for overcoming the limitations of PLA. PDLA, in low amounts, has been found to be a highly effective nucleating agent for PLLA.² This was attributed to the formation of a stereocomplex in which the 103 left-handed PLLA helix intimately combines with the 103 right-handed PDLA helix. The result is a new crystalline phase showing 31 PLA-sc helices.³ The crystalline structure of PLA-sc increases the melting point from ~165-170°C for PLLA and PDLA up to ~230-235°C. This would allow PLA-sc to compete with the thermo-mechanical properties of polypropylene, polyamide-6, and polybutylene terephthalate.

At the laboratory level, PLA-sc can be prepared by mixing the proper ratio of PLLA and PDLA solutions in an appropriate solvent (usually chloroform or tetrahydrofuran). While this procedure is convenient at a small laboratory scale, melt compounding of PLLA and PDLA must be carried out for larger amounts. In this application note, the Thermo Scientific™ HAAKE™ MARS_{XR} Rheo-Raman System is used for the larger-scale production and analysis of PLA-sc. The MARS_{XR} Rheo-Raman System combines a Thermo Scientific DXR3 Flex Raman Spectrometer with a Thermo Scientific HAAKE MARS™ 40 Rotational Rheometer. By exploiting the unique capabilities of this combined instrument, we were able to determine, for the first time, how several parameters impact the kinetics of PLA-sc.

Methods

Four different polylactides were selected for this study, half at a lower melt flow index (MFI) (14-15 g/10 min, 190°C, 2.16 kg) and half at a higher MFI (30-40 g/10 min, 190°C, 2.16 kg). The first set of PLLA/PDLA was designated as the HW series and the latter as the LW series.

To begin, PLLA and PDLA pellets were ground into powders, which were then sieved to ensure an approximate particle size of 1 mm. Equal amounts of PLLA and PDLA powders were then mixed immediately before being poured between the plates of the rheometer (heated at 240°C). After 2 minutes, the melted sample was cooled at a specific temperature (190, 200, or 210°C). At temperature equilibration, a pre-shear was applied to the molten sample at a given shear rate (0, 20, 60, 100, 140, or 220 s⁻¹) for 15 s. After pre-shear was completed, small-amplitude oscillatory shear (SAOS) testing was used (stress controlled at 100 Pa, 6.28 rad/s, 1 mm gap) and G', G'', and η* data were collected over time. Raman spectra were recorded during the rheological experiments on the same samples. The laser beam was focused at the limit of the upper plate radius, where the shear rate has its maximum value.

Results

Raman spectroscopy can differentiate PLLA/PDLA from the stereocomplex due to a change in the polarizability of the polymer chain when PLLA and PDLA are wrapped together. The C=O stretching band was selected as a probe to detect PLA-sc. PLLA and PDLA show a band with a maximum at 1772 cm⁻¹. In PLA-sc, the band is shifted to 1754 cm⁻¹.

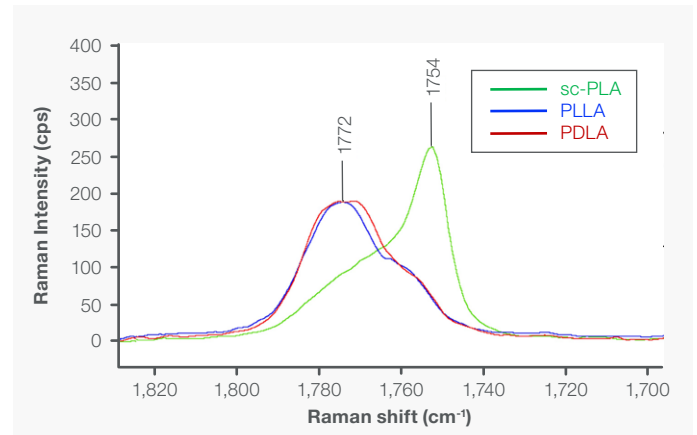


Figure 1. Raman spectra of PLLA, PDLA, and PLA-sc.

Using the following formula, a Raman index for PLA-sc formation was derived by analyzing all spectra collected during the SAOS experiments:

$$I' = \frac{(I_{1754} - I_{1772})}{(I_{1754} + I_{1772})}$$

(A comparable index can be derived from the |η*| vs time curves, but this will not be discussed here.)

A characteristic induction time for PLA-sc formation and crystallization can be determined from rheological data, as shown in Figure 2.

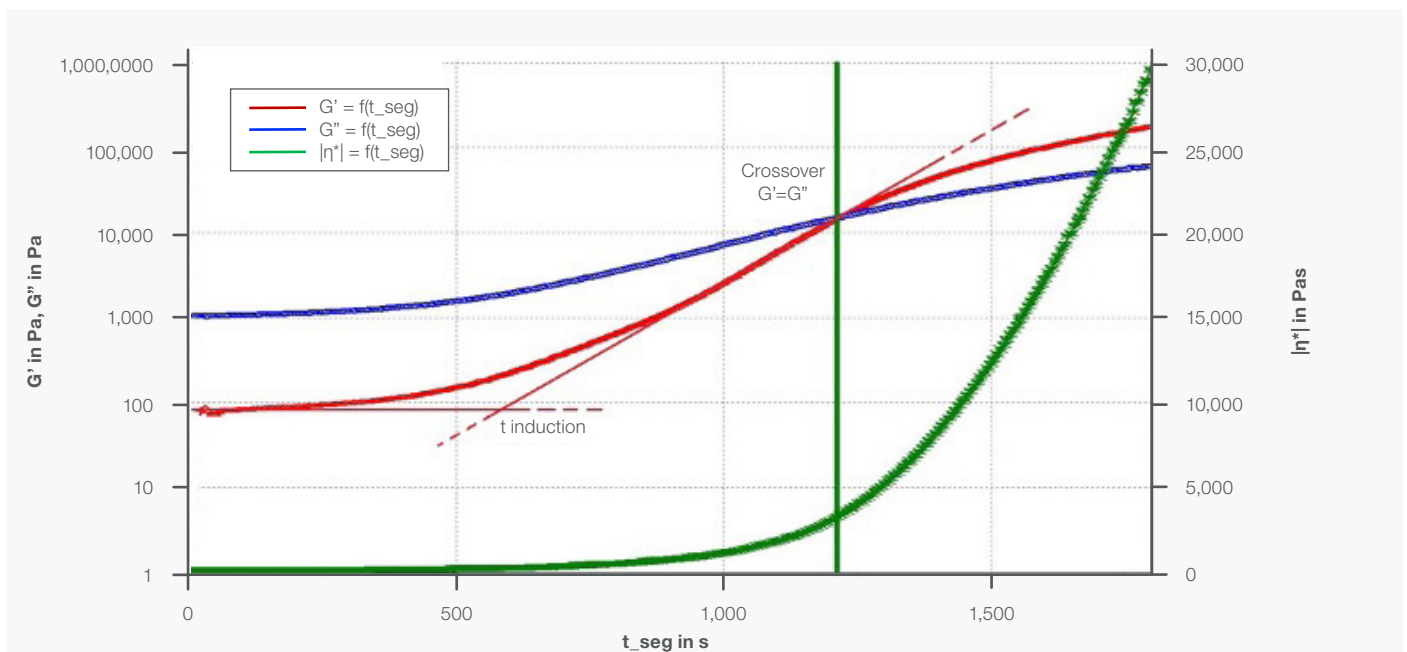


Figure 2. Typical curves showing the change in G', G'', and |η*| over time.

The effect of an increased shear rate during the pre-shear step is marked by a reduction in the induction time. Without pre-shear, PLA-sc formation was significantly slowed, as the mixing rate of PLLA and PDLA chains by thermal motion is very low. PLA-sc was not detected within the timeframe of the experiment (1,800 seconds). (Note: This value was selected

after time sweep testing was used to assess the limit of PLA's thermal stability under experimental conditions.) For other shear rate values, G' and spectroscopic index I' scaled similarly with respect to time. For example, Figures 3 and 4 show two indices for shear rates of 20 and 100 s^{-1} (at 190°C for the LW series).

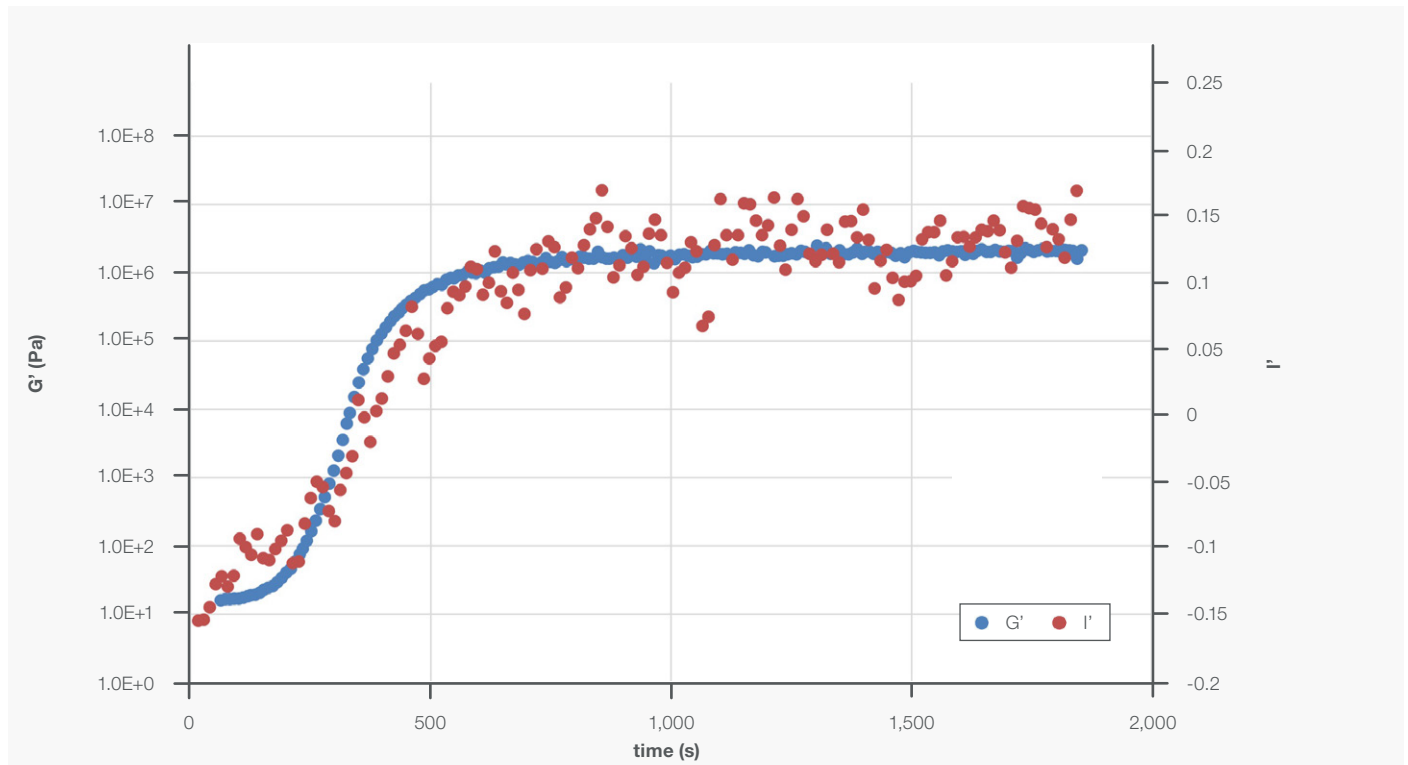


Figure 3. Change of G' and I' over time with an applied shear rate of 20 s^{-1} .

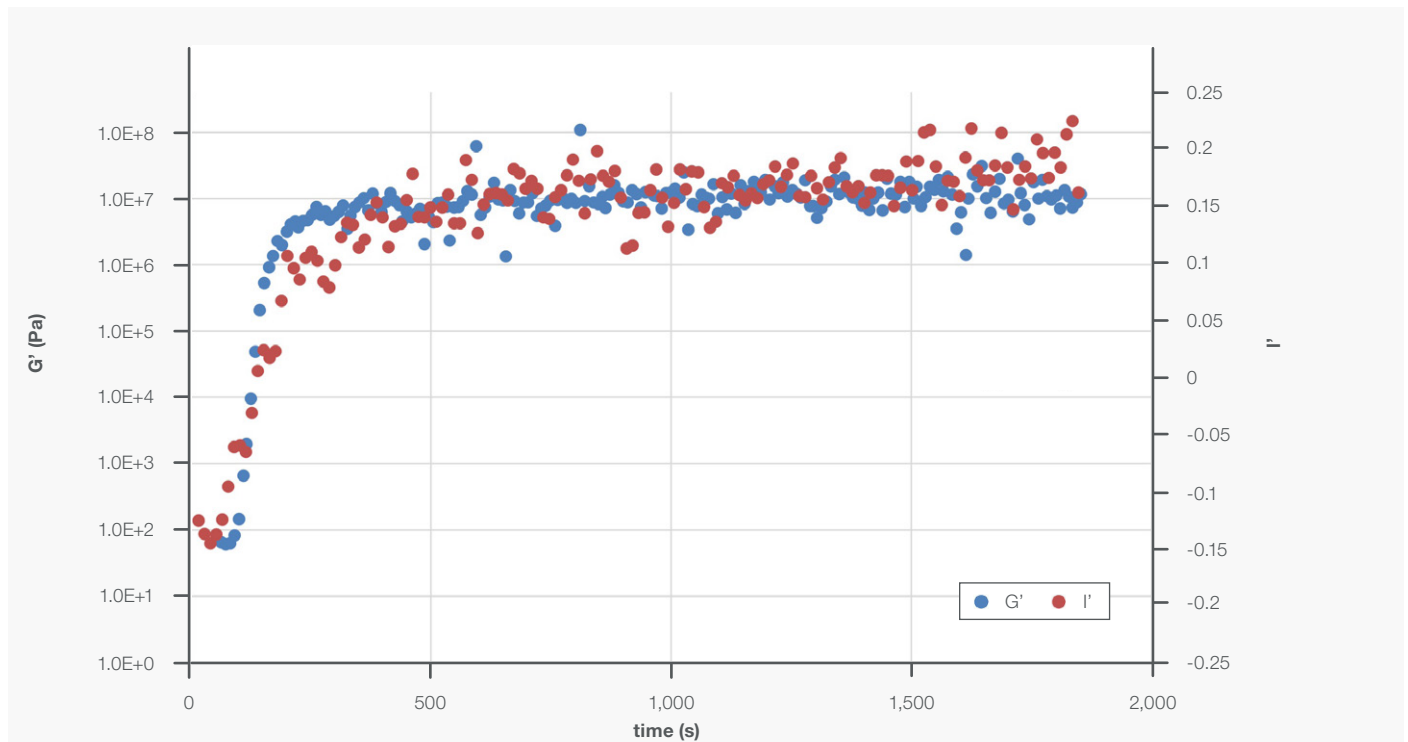


Figure 4. Change of G' and I' over time with an applied shear rate of 100 s^{-1} .

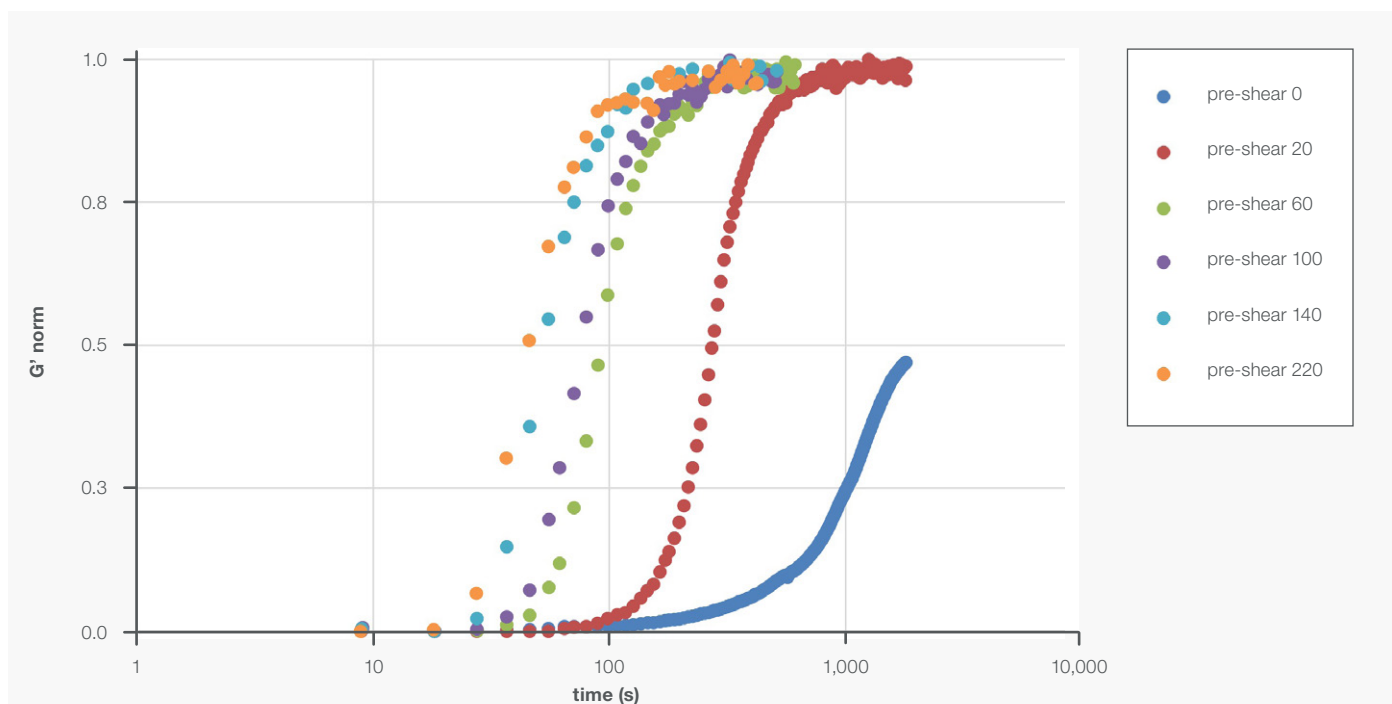


Figure 5. Normalized G' values vs time at 190°C for the LW series.

For both the HW and LW series, the effect of initial modulus difference was removed with the normalized modulus G'_{norm} , which was calculated by logarithmic normalization of G' values according to the following formula:

$$G'_{norm} = \frac{\log \left(\frac{G'(t)}{G'_{min}} \right)}{\log \left(\frac{G'_{max}}{G'_{min}} \right)}$$

The effect of shear rate on induction time is clear when comparing G'_{norm} vs time for different shear rates (Figure 5).

Conclusions

Formation of a polylactide stereocomplex (PLA-sc) was investigated for the first time using a unique combination of Raman spectroscopy and rheology. The effect of shear rate on PLA-sc formation and crystallization was measured with a rheometer and unambiguously corroborated with Raman spectroscopy.

Acknowledgments

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