

POLY(LACTIC ACID) PROPERTIES AND PROSPECTS OF AN ENVIRONMENTALLY BENIGN PLASTIC: MELT RHEOLOGY OF LINEAR AND BRANCHED BLENDS¹

Hans J. Lehermeier and John R. Dorgan²

Department of Chemical Engineering
Colorado School of Mines
Golden, CO 80401

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2) Author to whom correspondence should be addressed; electronic mail: jdorgan@mines.edu

ABSTRACT

Six blends of poly(lactic acid) (PLA) with an L:D ratio of 96:4 and varying branched to linear content were studied. These blends quickly degrade when in the presence of moisture and/or elevated temperatures and thus the material properties change. Two methods of obtaining stable properties are analyzed. First, it is demonstrated that tris(nonylphenyl) phosphite effectively stabilizes the viscosity of PLA. Second, this study utilizes the fact that the kinetics of thermal degradation leads to a pseudo steady state in which material properties change slowly. The zero shear viscosities of thermally conditioned PLAs show a positive deviation from ideality. An enthalpy of mixing perspective cannot adequately explain this deviation. It is therefore suggested that the free volume in these blends is responsible for the observed deviation.

KEY WORDS: blends, poly(lactic acid), polylactide(s), polymer architecture, rheology, thermal properties.

1. INTRODUCTION

1.1. Green Aspects

Plastic packaging materials are everywhere in our daily lives. From food wrappings and containers to detergent and soft drink bottles to foam packaging for shipping delicate goods, many products are surrounded by or contained in polymeric materials. Currently, most polymeric packaging materials are based on non-renewable fossil resources. Incineration of these materials makes a net contribution to atmospheric CO₂ and plastics currently account for in excess of 20% of the nation's landfills. In addition, many widely used materials, notably polystyrene and poly(vinyl chloride), are made from noxious or toxic monomers. Clearly, there exists a need for the development of "green" packaging materials that would be based on renewable resources, would not involve the use of toxic or noxious components in their manufacture, and could allow composting to naturally occurring degradation products or could be recycled easily. However, for acceptance in the marketplace these materials must be competitive on a cost-performance basis.

Such a biodegradable family of polymers made from monomers obtained from renewable sources can be produced and will soon become competitive in the marketplace. This material is poly(lactic acid) (PLA), the polymer of lactic acid which can be made by the fermentation of corn.

1.2. PLA Chemistry

Due to the chiral nature of lactic acid, the stereochemistry of PLA is complex. Figure 1 shows the L and D enantiomers of lactic acid along with its possible dimer rings and the polymer chain structure. The lactide rings were used as the monomer for the polymers used in

this study. Control of the ratio of L to D monomer content is an important molecular feature of PLAs which has a large effect on material properties.

1.3. Property Comparison

As mentioned above, acceptance of PLA will be based on performance. Fortunately, PLA does possess good physical properties that are in fact, very similar to polystyrene. A comparison of physical properties of PLA having an L:D ratio of 94:6 to other commodity plastics is given in Figure 2 [1].

2. MATERIALS AND METHODS

2.1. Materials

All polymers in this study were synthesized by Cargill-Dow Polymers via melt polymerization with stannous octoate as catalyst and subsequently blended in a twin screw extruder. Polymers with an L:D ratio of 96:4 were used. A common method of imparting different melt flow properties into plastics is to alter the chain architecture through the introduction of branching. Chain branching was produced through peroxide initiated crosslinking of linear material by reactive extrusion [2]. Six different blends varying in the ratio of branched to linear content were studied; increments of 20% by weight were employed. All blends experienced the same experimental thermal history before analysis. TNPP was obtained from Aldrich and used as received.

2.2. Methods

As previously discussed, PLA quickly degrades into its constituents when in the presence of moisture and/or elevated temperatures. This makes it difficult to measure fundamental properties. For this reason tris(nonylphenyl) phosphite (TNPP) was used as a

stabilizer during testing. In effect, TNPP reconnects polymer chains that have broken due to moisture and elevated testing temperatures. Too low of a TNPP concentration results in the polymer chains breaking down and too high a concentration results in the polymer increasing in molecular weight. It was determined that 0.35 wt.% TNPP yielded the optimum stabilization level [3]. The TNPP stabilized material was compared with unstabilized PLA.

The glass transition and melting temperatures of the six blends without TNPP stabilizer were measured on a Perkin Elmer DSC 7 differential scanning calorimeter. The samples were conditioned prior to testing by 1) heating from 0 °C to 200 °C at 10 °C/min, 2) holding at 200 °C for 5 minutes, and 3) cooling from 200 °C to 0 °C at 5 °C/min [1]. The samples were then tested by ramping the temperature from 0 °C to 200 °C at 10 °C/min. The glass transition temperature was determined at the inflection point in a heat flow versus temperature plot. The melting temperature was determined as the point where the endotherm reached a maximum.

Molecular weight was measured via GPC by Cargill-Dow Polymers.

The TNPP stabilized samples were mixed to 0.35 wt.% TNPP in a Haake Rheodrive 5000 mixing bowl at 180 °C. Both before and after running in the Haake, all samples were dried overnight in a vacuum oven at 40 °C and 2500 Pa vacuum. Disks for the rheometer were compression molded at 180 °C into 25 mm diameter discs approximately 3.2 mm thick and were again dried in the vacuum oven overnight at 180 °C prior to testing.

Dynamic moduli and viscosity were measured in a Rheometrics RMS-605 rheometer using parallel plates. A special pressure canister containing molecular sieves was installed in the inlet air line to the oven to exclude moisture and hydrolytic degradation during testing.

Measurements were made from high frequencies to low. For the TNPP stabilized samples the 25 mm sample disks were pressed in the rheometer at 220 °C to uniformly fill the 50 mm plates to a final gap spacing of approximately 0.75 mm. The temperature was allowed to stabilize for 10 minutes before testing was started. The unstabilized samples were tested with 25 mm plates with a gap spacing of approximately 2 mm. Because the properties of unstabilized PLA continually change over time when at elevated temperatures, the unstabilized samples were conditioned at 200 °C for 7800 seconds to allow the sample sufficient time to reach a quasi-steady state after which the properties change very slowly.

3. RESULTS AND DISCUSSION

3.1. DSC

Measured glass transition and melting temperatures obtained from five duplicate runs for each blend along with the associated standard deviation values are reported in Table I. The glass transition temperature is approximately 57.7 °C and ΔC_p is approximately 0.50 J/g °C. The melting temperature decreases as the linear content of the blend increases.

3.2. Molecular Weight

The weight average molecular weight (M_w) results for the unstabilized PLA samples are shown in Table II. The post test results are for samples which underwent a 7800 second conditioning at 200 °C followed by testing in the rheometer at 180 °C. The four intermediate blends of the linear and branched polymers have M_w 's between the pure linear and branched polymers. The molecular weight does decrease during testing, indicating that the polymer chains degrade into smaller chains.

3.3. Stability

Figure 3 shows the effects of TNPP stabilization on the complex viscosity for the 40% linear blend. Addition of 0.35 wt.% TNPP dramatically improves the stabilization of the viscosity. It should be noted that the unstabilized sample was tested at 200 °C while the TNPP stabilized sample was tested at 220 °C. As the temperature is increased, the rate of change in the viscosity as a function of time also increases. Therefore, since the TNPP sample was tested at a higher temperature and the viscosity changed at a slower rate than the unstabilized sample, the TNPP effectively stabilizes the viscosity. The typical testing times in the rheometer are less than 1800 seconds, which suggests that TNPP is a suitable stabilizer for testing PLA at elevated temperatures.

3.4. Typical Viscoelastic Spectra

A typical viscoelastic spectra for the unstabilized samples is shown in Figure 4 for a 100% linear sample. The master curve was obtained from data collected at 160, 180, and 200 °C and referenced to 200 °C. Slopes of 2 for G' and 1 for G'' indicated that the terminal regime was reached and the zero shear viscosity was attained. Data for the TNPP stabilized samples will be reported in a future publication.

3.5 Comparison of Viscosity for Blends

A summary of the zero shear viscosity for the six unstabilized blends is shown in Figure 5. The line for the log additivity rule was calculated from:[4]

$$\ln(\eta_{app})_{blend} = \sum_i w_i \ln(\eta_{app})_i \quad (1)$$

where η_{app} is the apparent viscosity and w_i is the weight fraction of the i th component of the blend. A positive deviation from the log additivity rule is observed in blends that are miscible

with one another. A similar result for linear and branched blends of polyethylene has been previously reported [4]. There are two possible explanations for the positive deviation from the log additivity rule.

The first explanation of the positive deviation involves favorable energetics of mixing (i.e., $\Delta H_m < 0$). In the presence of highly specific and favorable molecular interactions, polymer chains resist deformation. Since the blends are composed of a mixture of two nearly identical polymers, differing only by branched content, the enthalpy of mixing is assumed to be approximately zero. Accordingly this mechanism does not appear plausible for the present system.

The second explanation is related to the free volume of the polymer chains. The Doolittle equation relates free volume to the viscosity: [5]

$$\eta = A \exp \left(B \left[\frac{V - V_f}{V_f} \right] \right) \quad (2)$$

where V is the total system volume and V_f is the free volume. Therefore, as the free volume increases, the viscosity decreases and vice versa. This suggests that the viscosity of the blends is higher than the log additivity rule predicts, because the free volume has decreased. This decrease in free volume within the blends may appear aphysical. However, it must be remembered that degradation of the material during the conditioning period produces low molecular weight species capable of affecting the free volume.

4. CONCLUSIONS

The present study explores the effects of varying branched content in PLA blends. DSC measurements reveal that while the glass transition temperature is not affected by

blending, the melting temperature is steadily depressed with increasing linear content. It is demonstrated that TNPP may be used to effectively stabilize the viscosity of these thermally degradable materials. Alternatively, the kinetics of thermal degradation leads to a pseudo steady state in which the material properties change slowly. This effect was exploited to study rheological properties of PLA.

The zero shear viscosities of thermally conditioned PLAs show a positive deviation from ideality. Such a deviation is difficult to explain from an enthalpy of mixing perspective. Accordingly it is suggested that the free volume in such blends is responsible for the observed effects.

REFERENCES

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Table I. DSC results for unstabilized PLA blends.

Blend (% Linear)	T_g (°C)	T_m (°C)	$\bullet C_p$ at T_g (J/g °C)
0	57.9 ± 0.2	152.6 ± 0.3	0.53 ± 0.03
20	57.4 ± 0.2	152.2 ± 0.3	0.51 ± 0.03
40	57.6 ± 0.1	152.0 ± 0.2	0.49 ± 0.01
60	57.7 ± 0.5	151.5 ± 0.3	0.48 ± 0.03
80	57.6 ± 0.4	151.1 ± 0.2	0.47 ± 0.04
100	57.5 ± 0.4	151.0 ± 0.3	0.52 ± 0.03

Table II. Weight average molecular weight results for unstabilized PLA blends.

Blend (% Linear)	Prior to Testing	After Testing
0	150k	120k
20	130k	105k
40	120k	150k
60	120k	120k
80	120k	110k
100	110k	90k

FIGURE CAPTIONS

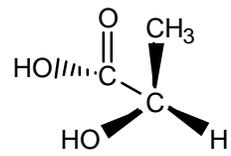
Fig. 1. Stereochemistry of lactic acid, lactide rings, and PLA chain.

Fig. 2. Physical properties of PLA compared to other common plastics.

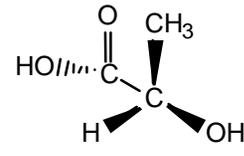
Fig. 3. Use of 0.35 wt.% added TNPP results in a nearly constant viscosity.

Fig. 4. Master curve of conditioned PLA sample constructed using time temperature superposition of data collected at 160, 180, and 200 °C, and referenced to 200 °C.

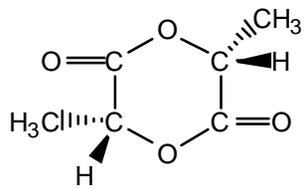
Fig.5. Zero shear viscosity of unstabilized PLA blends compared to the log additivity rule.



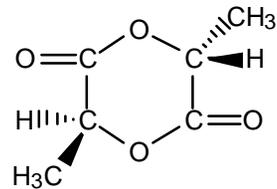
D-lactic acid



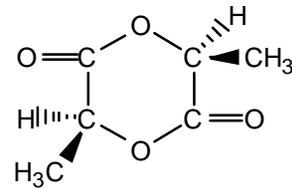
L-lactic acid



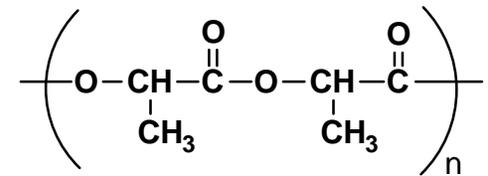
DD-lactide



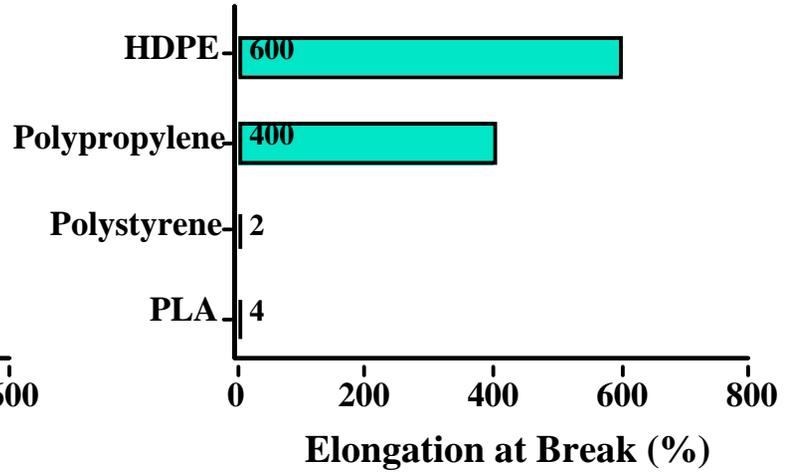
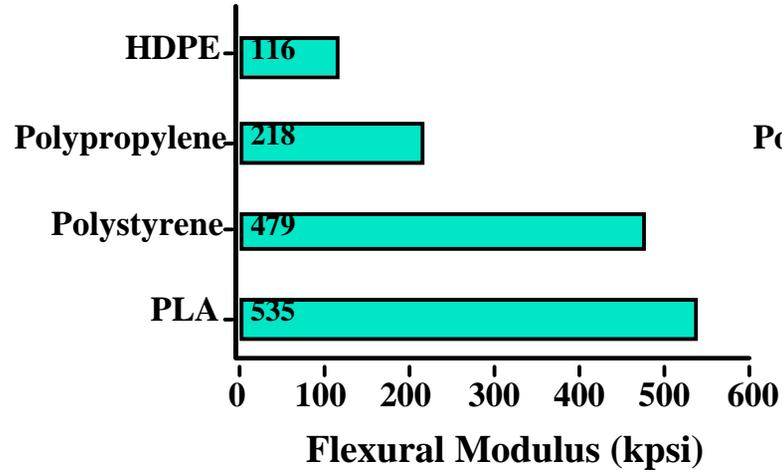
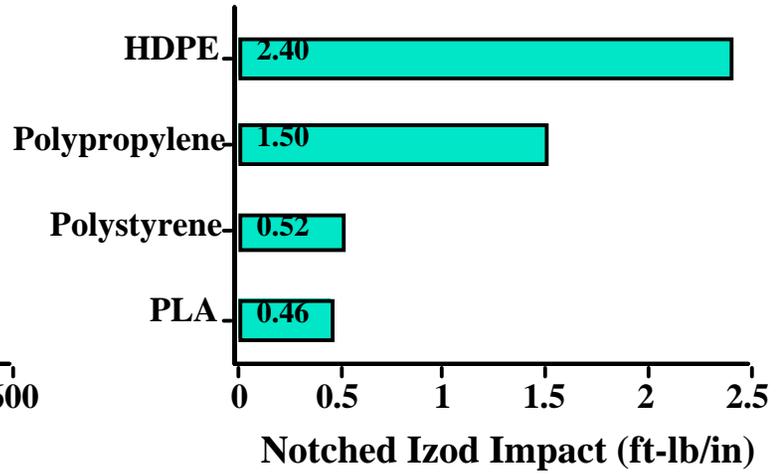
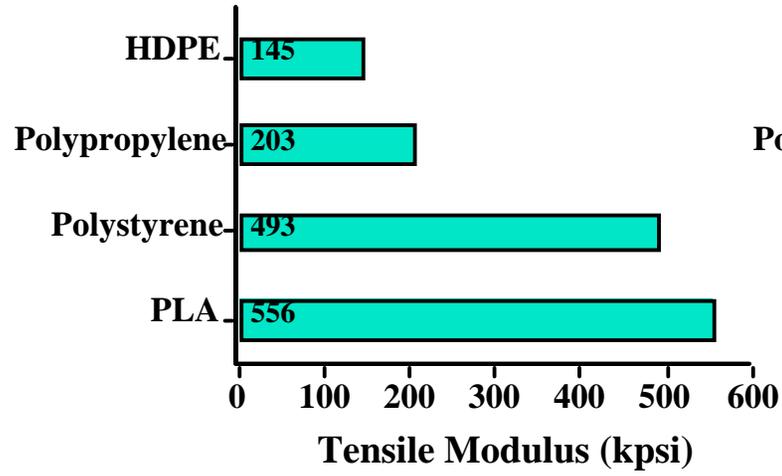
LD-lactide



LL-lactide

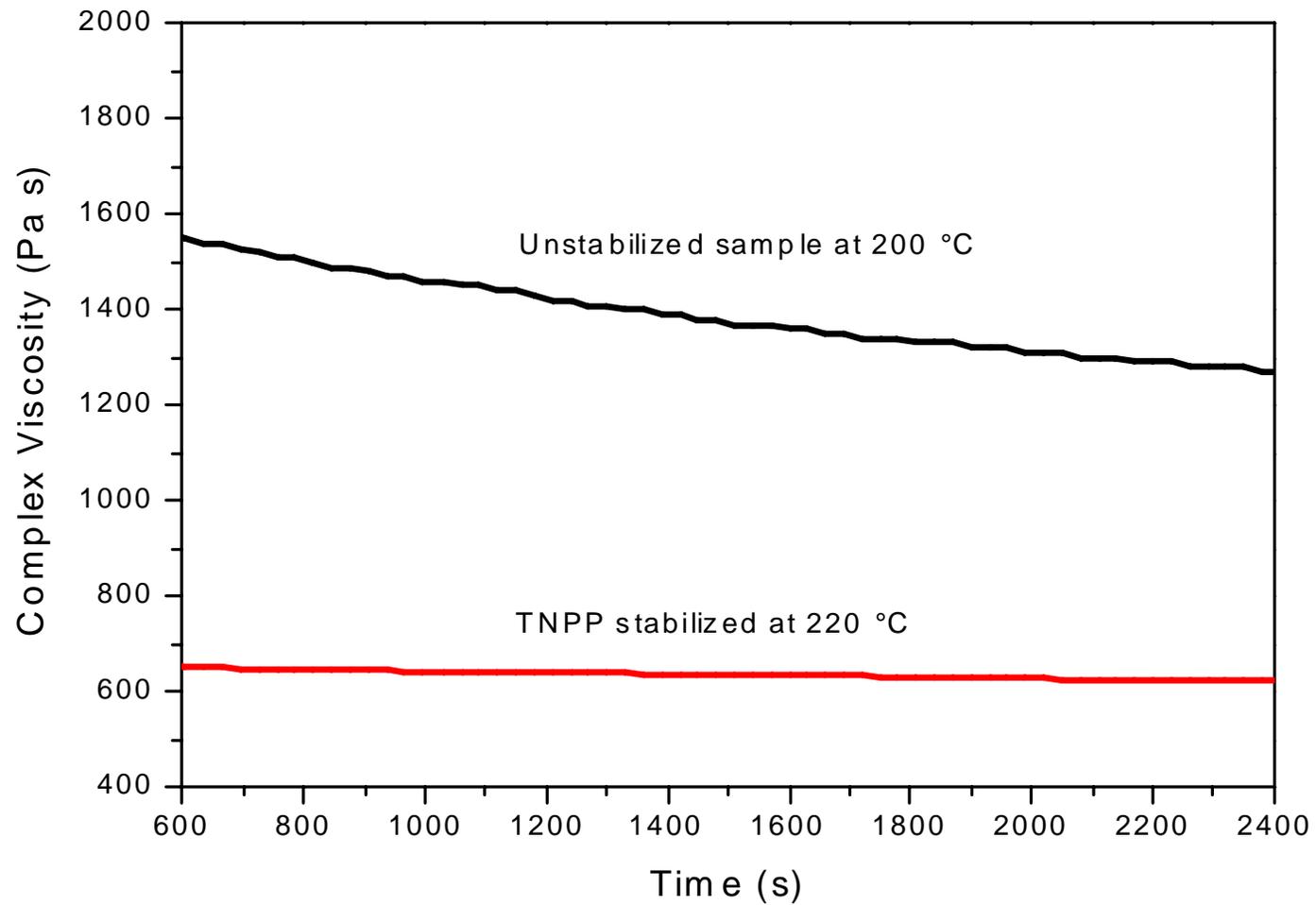


poly(lactic acid) (PLA)



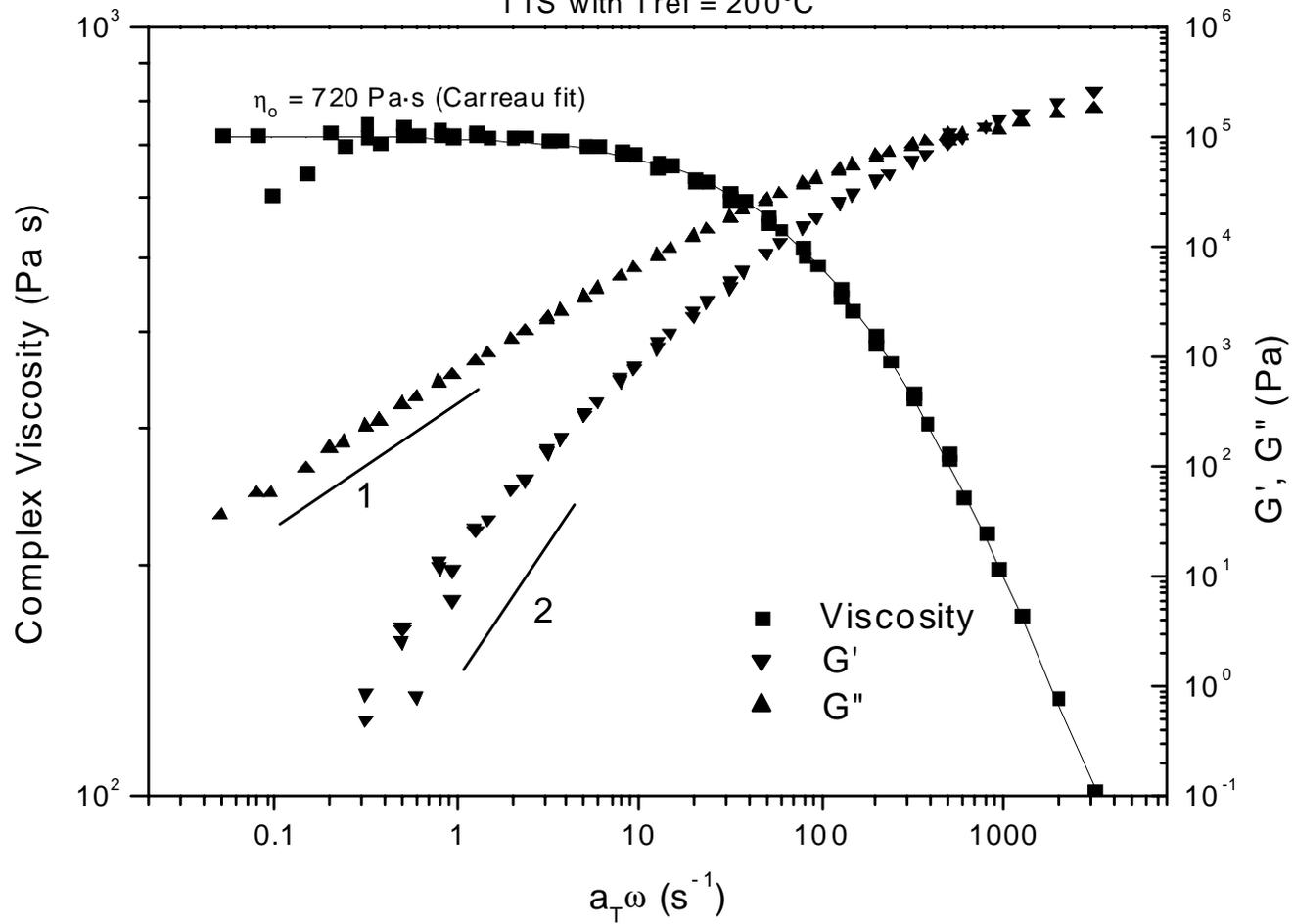
Effect of TNPP Stabilization on Viscosity

40% Linear PLA



100% Linear PLA Dynamic Spectrum

TTS with Tref = 200°C



Zero Shear Viscosity of PLA Blends

TTS with $T_{ref} = 200^{\circ}C$

