

# THERMAL STABILIZATION OF HIGH MOLECULAR WEIGHT L-POLYLACTIDE

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## Abstract

Poly(lactide) (PLA) polymers are among the most promising plastic made from renewable resources. Thermal stabilization of these polymers remains a challenging issue of their industrial processing. We have studied the effect of TNPP in the scope of preventing the molecular weight reduction of PLA at its processing temperature. The stabilizing effect of TNPP was found to strongly depend on the concentration used.

## Introduction

In the prospect of the decrease of the world resources in oil and in a concern to limit the contribution of plastics to the greenhouse effect and waste disposal, the use of polymers such as poly(lactides) that are produced from renewable resources consists of a very interesting alternative. Poly(lactide) is mainly produced from corn but other crops such as wheat and sugar beet and renewable agricultural waste are also considered. PLA is a thermoplastic and biodegradable polyester with the following structural unit:



It can be synthesized following two processes: 1) an ester condensation of 2-hydroxy lactate (lactic acid), and 2) a ring opening polymerization (ROP) of lactide, a cyclic dimer produced from the dehydration of lactic acid, in the presence of metal alkoxide catalysts. However, only ROP results in PLA with high molecular weight.

One main problem with PLA is its lack of thermal stability at elevated temperatures such as those encountered in polymer processing. In the presence of moisture and at high temperature, PLA degrades considerably. Different mechanisms of degradation can be active, such as reformation of the monomer, hydrolysis, and/or thermolysis, depending of the environmental conditions [1]. For example it has been shown that above 250°C, degradation due to free radicals is likely to occur [2], but up to 215°C hydrolysis is the main mechanism of degradation [1].

Several authors have shown the interest of using TNPP (tris(nonylphenyl)phosphite) as a stabilizer for PLA [3-6]. However, TNPP will stabilize PLA only if it is used in the right amount. It has been shown that if TNPP is added at a too low concentration, it results in the breakdown of polymer chains, while if the concentration is too high there is a risk of increasing the molecular weight, since TNPP can reconnect cleaved chains [4]. Either case is detrimental to PLA, furthermore if one is interested in characterizing the

polymer rheology, which requires long measurement times at high temperature. In this work, we use time sweeps under small amplitude oscillatory shear to examine the effect of different amounts of TNPP on the linear viscoelastic properties of a high molecular weight L-isomer poly(lactide).

## Material and Structure Characterization

### Materials

The L-poly(lactide) (PLLA) used in these experiments is a high molecular weight ( $\approx 200\,000$  g/mol) material with an L-isomer:D-isomer ratio of approximately 98:02 (Biomer L9000®, Biomer Biopolyesters, Germany). This material contains no additive or thermal stabilizer. The added heat stabilizer, tris(nonylphenyl)phosphate (TNPP), a liquid at room temperature, was supplied by Aldrich Chemicals (Sigma-Aldrich, USA). Data provided by the suppliers for these two materials are listed in Table 1.

### Mixing and pressing procedures

Before mixing, PLLA pellets were pre-dried in a vacuum oven at a temperature of  $40 \pm 1^\circ\text{C}$ , as suggested by the manufacturer. Three different TNPP concentrations in PLLA were characterized in this study: 0.25, 0.35 and 0.50 wt%, along with the pure PLLA sample. Mixing of TNPP and PLLA was performed in an internal mixer (C.W. Brabender Instruments, USA) at  $180^\circ\text{C}$  under nitrogen atmosphere (60 kPa). PLLA pellets (25 g) and different amounts of TNPP were introduced in the mixer's chamber. In order to avoid the pellets from being ejected out of the chamber during introduction, the rotation speed of the rotors was adjusted to 5 RPM. After the material was added, the chamber was closed, the rotors speed was increased to 30 RPM and the nitrogen inlet was connected. Sufficient blending was achieved when constant torque and temperature was observed (7-8 minutes). The pure PLLA sample also underwent mixing in order to go through a similar thermo-mechanical history as the blends.

After mixing, the materials were compression molded at  $180^\circ\text{C}$  (Carver Presses, USA). One press was used to mould the blend at  $180^\circ\text{C}$  and the second to cool the sample down to ambient temperature. Details of the pressing conditions are summarized in Table 2. After pressing, 12 disks of 25 mm diameter with a thickness of about 1.25 mm were obtained. These disks were subsequently dried in a vacuum oven for 24 hours before rheological measurements at  $40 \pm 1^\circ\text{C}$ .

### DSC and rheological measurements

Differential scanning calorimetry measurements were performed (DSC 1, Perkin Elmer, USA) on TNPP, pure PLLA and PLLA+0.25% wt TNPP. The samples, weighed with an analytical balance, were between 5 and 10 mg. The temperature was increased from 50 to 220°C at a constant rate of 10°C/min.

Rheological measurements were performed using a controlled-stress rheometer (CSM Bohlin Rheometer, Malvern Instruments, UK) with a 25 mm parallel plates geometry. Thermal stability measurements were carried out under nitrogen atmosphere at 180°C. For all experiments the imposed strain was 0.05 and the frequency 0.628 rad/s.

## Results and Discussion

Results from the DSC measurements of PLLA samples are presented in Figure 1. An endothermic peak was observed at approximately 68°C for the PLLA sample containing TNPP, but was absent in the pure PLLA sample curve. This peak was associated to enthalpy relaxation after the glass transition. The exothermic peak observed at 111°C for the PLLA+TNPP sample is most probably due to crystallization, since that sample was quenched from the molten state (see pressing procedures), while the pure PLLA sample used came from a resin pellet.

Figures 2 to 5 present the rheological investigation of the thermal stability of the pure PLLA sample, and of PLLA containing 0.25, 0.35 and 0.50%wt TNPP, respectively. The different curves represent different replicates with fresh samples at each condition. A small variation in the initial values of the complex viscosity and loss modulus was observed, however the trend as a function of time was similar from sample to sample. For the pure PLLA (Figure 2), a large decrease in complex viscosity and loss modulus was noted. After 5000 s, both had gone down by 35%. In Figure 3, the rheological data are shown for a concentration of 0.25% wt of TNPP. The decrease of the complex viscosity was again continuous but slightly lower than for the pure sample, i.e. 22% after 5000 s.

The behaviour was very different for a concentration of 0.35% wt TNPP (Figure 4). The complex viscosity (and loss modulus) initially decreased but started to increase after approximately 1500 s. After about 6000 s, the complex viscosity was stabilized to a value just slightly lower than the initial one (~6% lower). The complex viscosity remained constant after this increase for another 6000 s, after which it started to decrease again. Finally, for PLLA+0.50% wt TNPP (Figure 5), a similar initial decrease in complex viscosity and loss modulus was again followed by an increase, but after a shorter time than in the case of the 0.35% wt, i.e. 600s. Furthermore, the complex viscosity and loss modulus grew beyond the initial values. The rheological properties started to decrease again at longer times (~10<sup>4</sup> s).

The loss in rheological properties can be related to a loss in molecular weight. A possible estimation can be made using two assumptions: 1) the complex viscosity at a frequency of 0.628 rad/s is representative of the zero-shear viscosity  $\eta_0$ , which is a reasonable assumption considering the value of  $G'$  compared to  $G''$  (Figures 2 to 5), and 2)

using a proportionality scaling law between  $\eta^*$  and weight average molecular weight, i.e.  $\eta^* \sim M_w^{3.7}$  [7]. Using these approximations, we could relate a decrease in complex viscosity of 35% (pure PLLA sample) to a variation of 10% in molecular weight. For the case with 0.25% wt TNPP, the decrease in  $M_w$  is of 9%, which is still quite important. In terms of material processing, considering that the residence time in equipments is relatively short (of the order of a few minutes), this loss does not seem so detrimental. However, Cicero et al. have shown that it can nevertheless impact the properties of PLA melt-spun fibers [3]. Furthermore, if fundamental studies on the rheology of these materials need to be carried out, thermal stability on a long enough time range is an essential condition. It should be mentioned that an equation proposed to relate zero-shear viscosity with molecular weight [7]:

$$\eta_0 \text{ (Pa.s)} = (2.3 \times 10^{-15}) M_w^{3.7}$$

results in an estimation of a molecular weight of 85 000 g/mol, which is much lower than the value provided by the manufacturer (200 000 g/mol). Two reasons might explain this large discrepancy: 1) the molecular weight provided by the manufacturer is over-estimated, and/or 2) the samples have gone considerable degradation during mixing and pressing. These two aspects will be investigated in a near future.

The best of four TNPP concentration for the PLLA under investigation has shown to be 0.35% wt. Complex viscosity reached a constant value after 6000 s, similar to the initial value, therefore further rheological measurements may be achieved past that time and carried out for another 100 minutes. This may be sufficient for a reasonable rheological characterization of the material.

The strange behaviour (properties decrease followed by increase) observed with the 0.35 and 0.50% wt stabilizer has been attributed to the particular action of TNPP. Cicero et al. [3] have considered many different mechanisms for the action of TNPP in its stabilizer role with PLA. NMR studies have revealed that the most probable mechanism for molecular weight stabilization is chain extension [3], though the possibility that phosphorus may or may not be incorporated into the chain backbone is still an open question. Therefore, the rheological properties variations observed in our work may be related to competing mechanisms, i.e. chain scission through hydrolysis, and chain extension by the action of TNPP. It seems that at short times, the hydrolysis was more important than the “repair” of chains, while chain extension became dominant later on. Obviously, the 0.50% wt TNPP consisted of a too high concentration since chain extension became so important that the molecular weight rose above the original one. The final decrease of the complex viscosity and loss modulus was most probably due to the fact that TNPP has been used up [3]. Another possible explanation for the strange behaviour is the recrystallization of a higher melting crystal at 180°C. In our future work we will investigate this possibility, along with the hypothesis of competing effects (hydrolysis and chain extension) at higher temperatures in order to obtain information about the kinetics of the two competing reactions.

## Conclusions

Tris(nonylphenyl)phosphite (TNPP) has been used in order to stabilize the molecular weight of a commercial L-poly lactide, close to its processing temperature, i.e. 180°C. It has been found that a too small or too large concentration of stabilizer is detrimental to the material because of competing effects such as chain scission and chain extension that results in molecular weight decrease and increase, respectively. In our study, the best of four concentrations was found to be 0.35% wt for this high molecular weight PLLA.

## References

[1] D. R. Witzke, PhD thesis, Michigan State University (1997)

[2] F.-D Kopinke, M. Remmler, K. Mackenzie, M. Möder, O. Wachsen, Polymer Degradation and Stability 53 (1996) 329-342

[3] John A. Cicero, John R. Dorgan, Steven F. Dec, Daniel M. Knauss, Polymer Degradation and Stability 78 (2002) 95-105

[4] Hans J. Lehermeier, John R. Dorgan, Polymer Engineering and Science, (December 2001), Vol.41, No.12

[5] John R. Dorgan, Hans J. Lehermeier, Liviu-Iulian Palade and John Cicero, Macromol. Symp. 175 (2001) 55-66

[6] Liviu-Iulian Palade, Hans J. Lehermeier, John R. Dorgan, Macromolecules 34 (2001) 1384-1390

[7] Dorgan, J. R., Lehermeier, H., Mang, M., J. Poly. Env. 8(1) (2000) 1-9

Table 1. Materials properties

Characteristics of PLLA (from supplier)	
Molecular Weight (Mw):	> 200 000 g.mol <sup>-1</sup>
Melting point:	169°C
Glass transition temperature:	56°C
Melt flow index:	3-6 g/10 min
D-lactide:	2%
Residual lactide:	0.2%
Characteristics of TNPP ( from supplier)	
Density:	0.99 g/ml
Flash point:	113°C
Boiling point:	360°C/760 mmHg
Molecular Weight:	689 g/mol

Table 2. Time and pressure during compression moulding

On the first press (180°C):	-5 min without pressure -2 min at 1 ton -4 min at 4 tons
On the second press (25°C):	-4 min at 4 tons

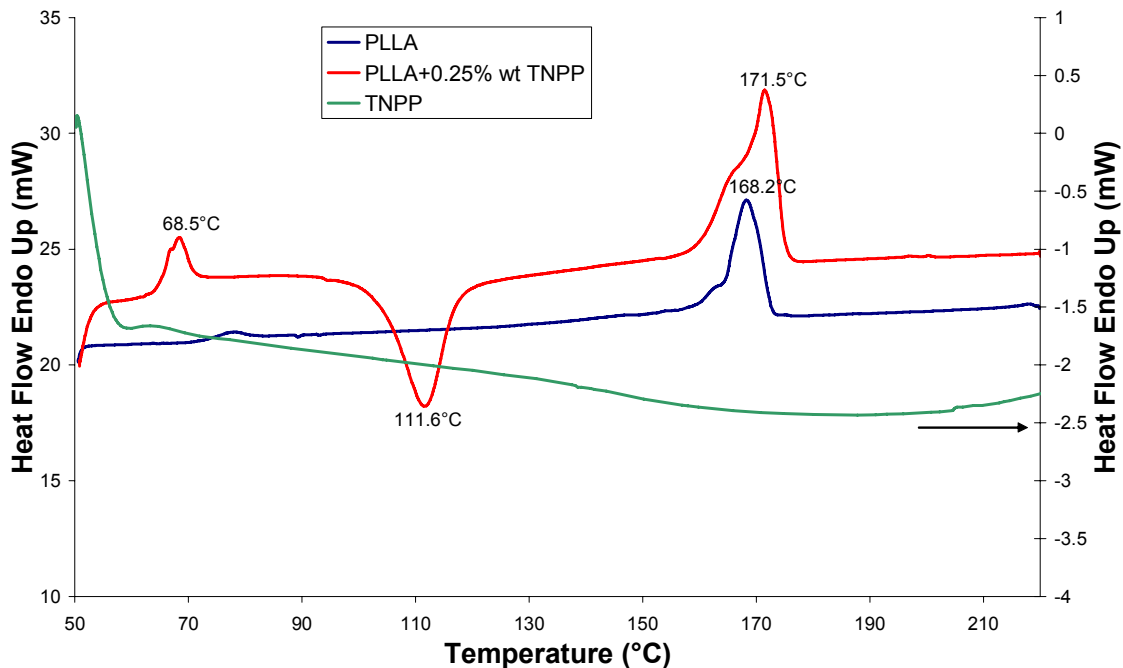


Figure 1. Results from DSC measurements for TNPP, pure PLLA and PLLA+0.25% wt TNPP.

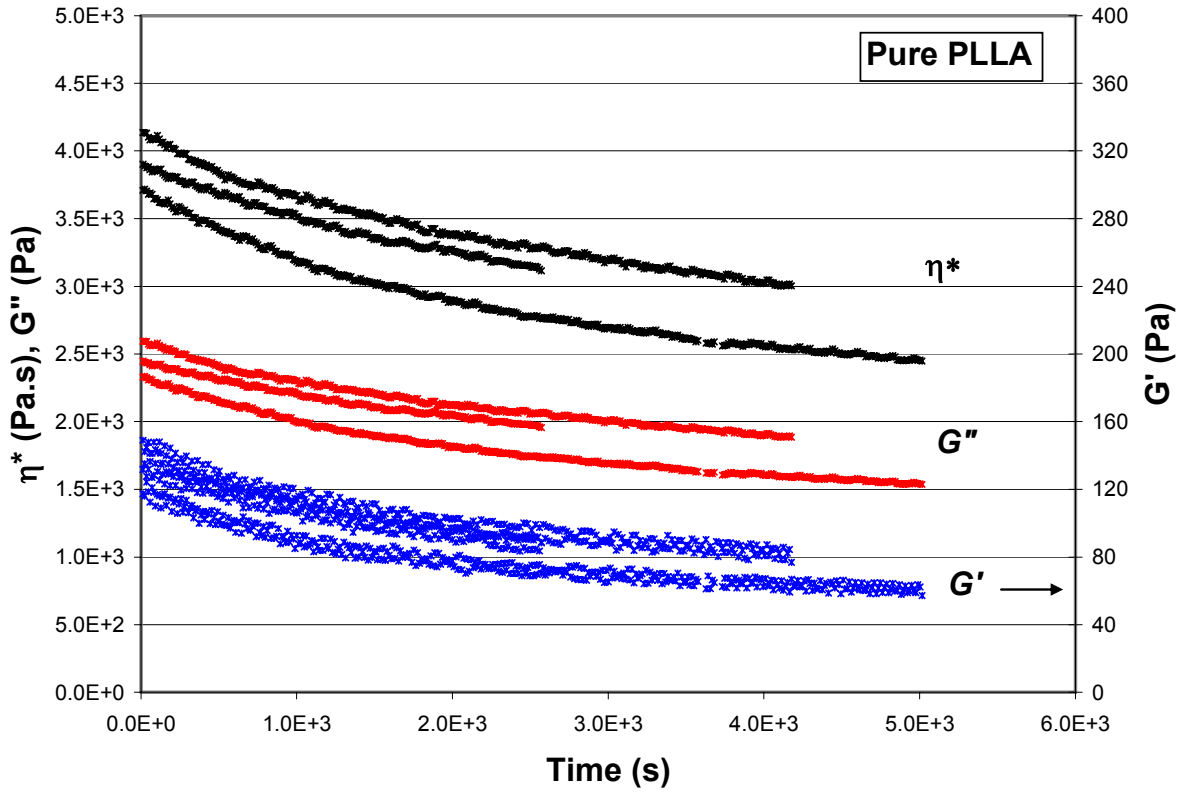


Figure 2. Complex viscosity and complex moduli as functions of time for pure PLLA (strain 0.05 and 0.628 rad/s).

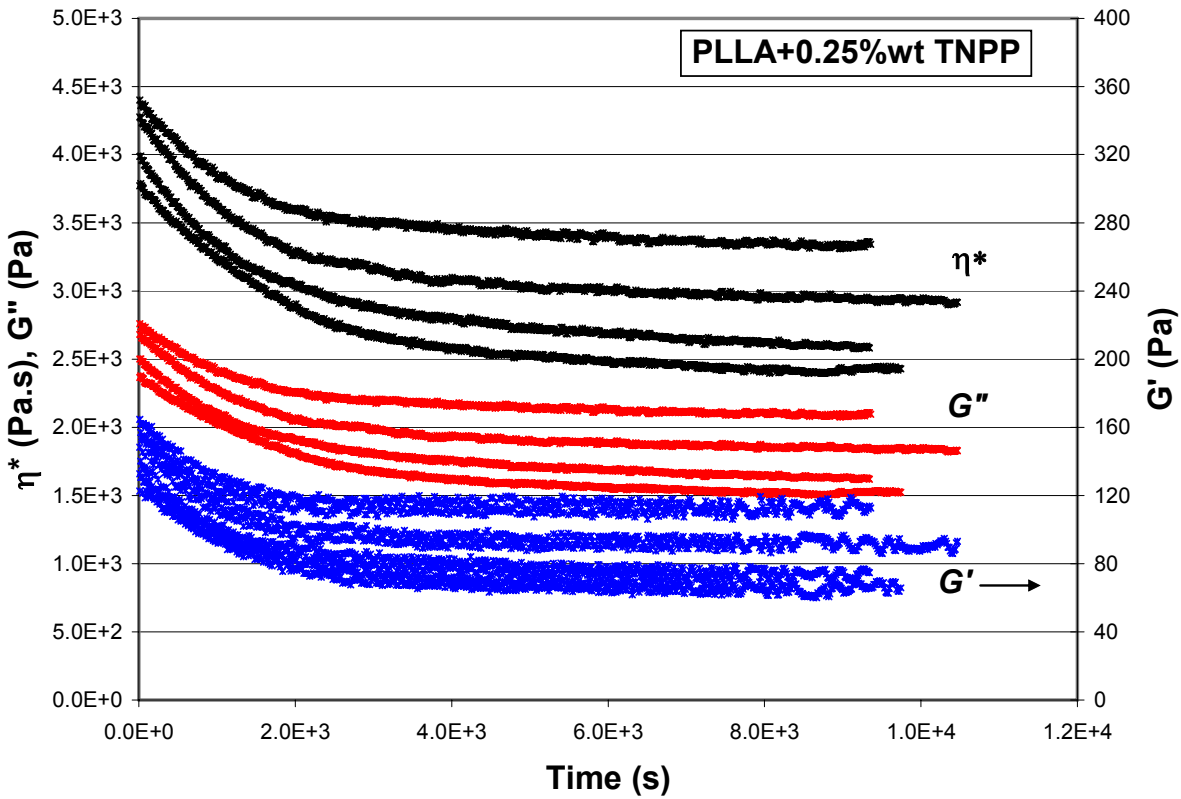


Figure 3. Complex viscosity and complex moduli as functions of time for PLLA+0.25%wt TNPP (strain 0.05 and 0.628 rad/s).

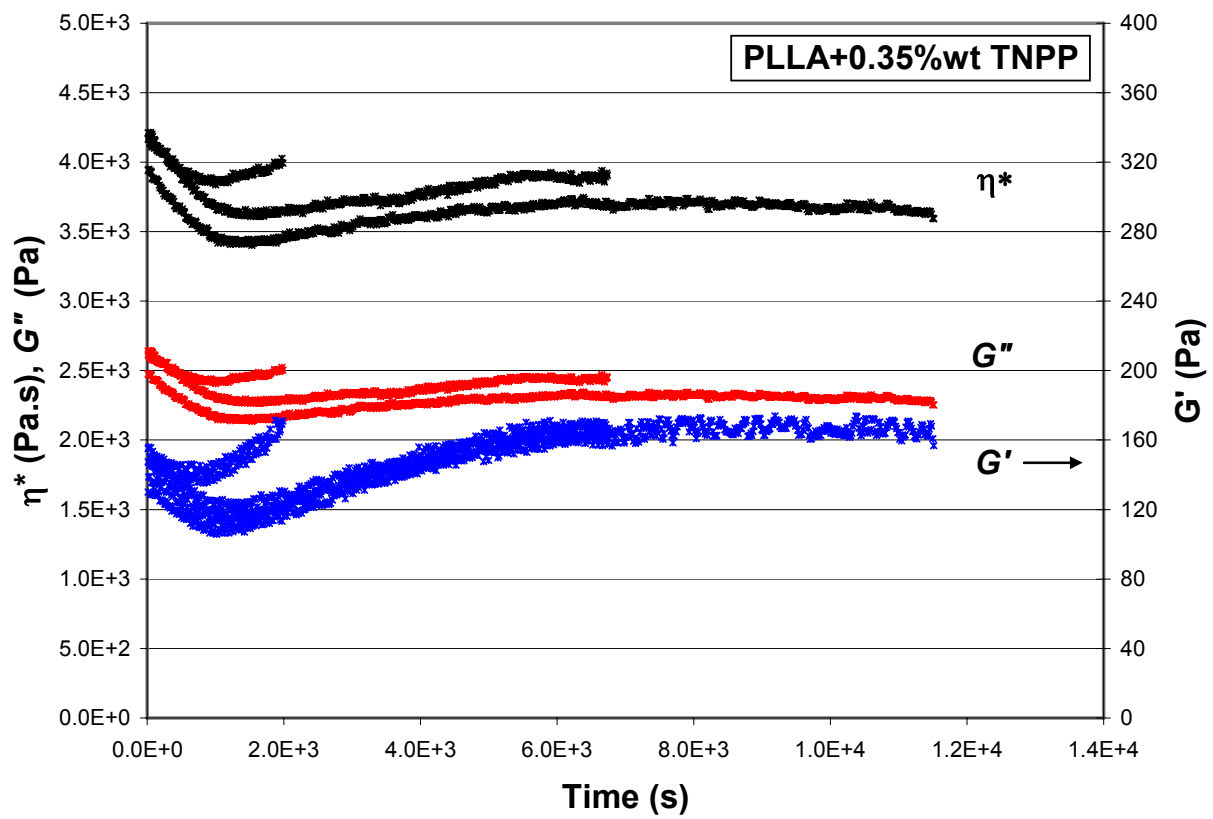


Figure 4. Complex viscosity and complex moduli as functions of time for PLLA+0.35%wt TNPP (strain 0.05 and 0.628 rad/s).

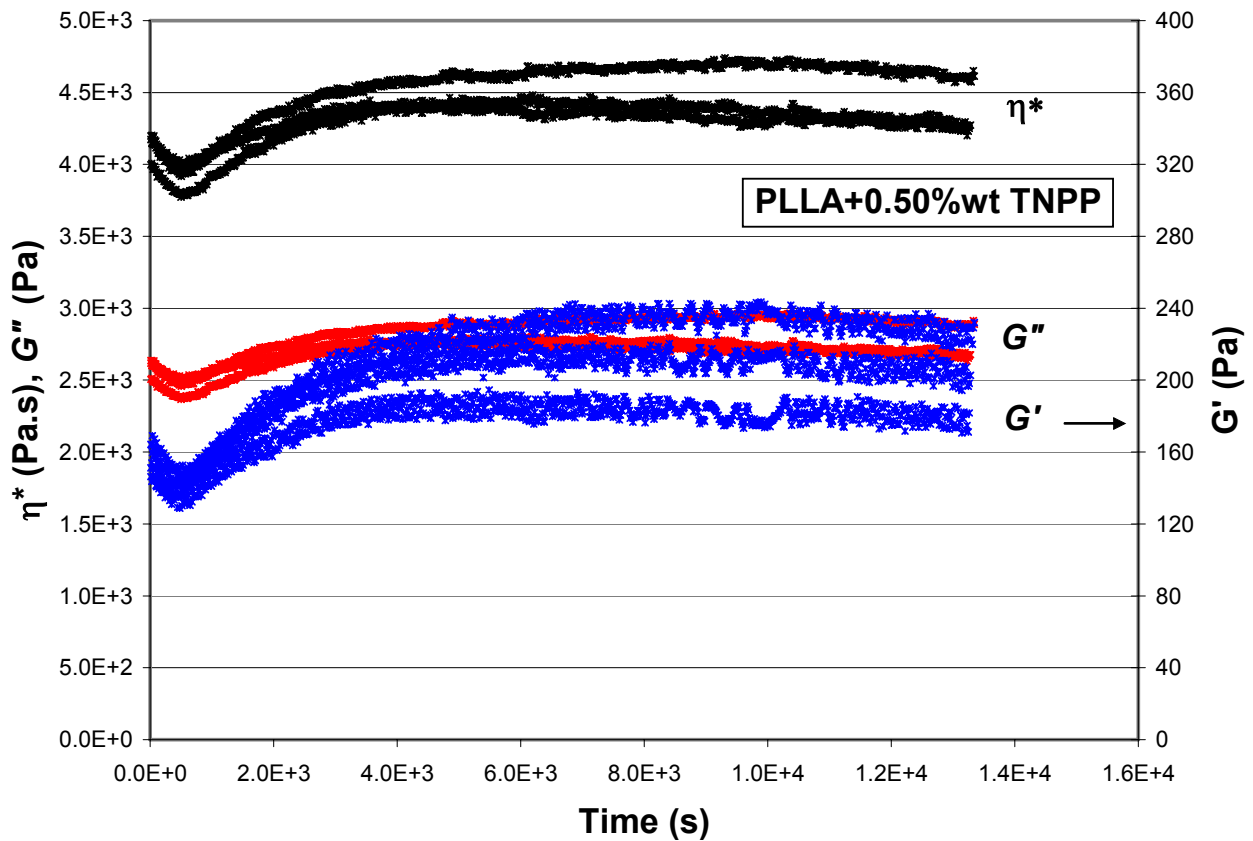


Figure 5. Complex viscosity and complex moduli as functions of time for PLLA+0.50%wt TNPP (strain 0.05 and 0.628 rad/s).