

Cross-WLF parameters to predict rheological properties of polylactic acid

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ABSTRACT

The prediction of poly(lactic)acid rheological properties is complicated by thermal degradation. A series of PLA samples has been investigated to calculate Cross-WLF parameters to predict the MWD, temperature and shear rate dependence of the viscosity. A free volume model was also used to predict the viscosity of PLA/L-lactide concentrated solutions.

INTRODUCTION

Poly(lactic)acid is one of the most important biodegradable polymers developed on a large scale and produced using renewable feedstock and by means of bacterial bio-activity.

Predicting its rheological properties starting from the molecular weight distribution (MWD) has not been possible up to now mainly because degradation processes seriously affect the reliability of many attempts to measure its LVE. In addition ring opening polymerization (ROP) does not allow to span a sufficient range of polydispersity index values to validate molecular models. Therefore the parameters governing the dynamics of the polymer chains in the melt are not yet available. Only in the last few years, for instance, it was recognized that reptation correctly applies to this biopolymer with the usual power law molecular weight dependence of the viscosity of the entangled melt with the expected exponent 3.4¹. In this work a

series of PLA samples synthesized by ROP and with different molecular weight M_w has been investigated with the aim to calculate the correct Cross-WLF parameters able to predict the MWD, temperature, pressure and shear rate dependence of the shear viscosity in the melt and the viscosity of PLA/L-lactide concentrated solutions.

MATERIALS AND METHODS

For this study two grades of linear PLA (named in the following “PLA 1” and “PLA 2”) were taken into account (amount of D-lactic acid less than 1%).

Table 1. MWD and transition temperatures data of the PLAs investigated.

	M_n (kDa)	M_w (kDa)	M_w/M_n	T_g (°C)	T_m (°C)
PLA 1	72.1	128.1	1.78	60.4	174.5
PLA 2	97.2	170.2	1.75	60.5	175.3

Concentrated PLA/L-lactide solutions were prepared by means of a Haake Banbury mixer at 180°C (much lower than the L-lactide boiling point 255°C)².

To investigate the thermal stability oscillatory measurements were performed with a rotational rheometer (Ares LS II, TA Instruments) equipped with the parallel plate geometry ($R=12.5$ mm, gap ranging from 1 to 2 mm). Isochronal ($\omega=6.28$ rad/s) and isothermal ($T=200^\circ\text{C}$) time sweep tests were performed on dried and as-received samples

(named in the following “wet”). The former were obtained by drying pellets under nitrogen flow at 60°C for 4 days to remove moisture. The flow curve has been determined by means of a capillary rheometer (Göttfert, model Rheograph 2002) using a round-hole capillary with $L/D=30$.

THERMAL STABILITY

Isochronal and isothermal time sweep tests were used to test the thermal stability. Figure 1 shows a typical example of the obtained results for the loss tangent $\tan\delta$ of two PLAs with different M_w and different moisture content.

In all cases the loss tangent increases with time. This suggests that degradation phenomena produce a M_w decrease. The difference between the initial loss tangent values reflects the different molecular weight of the two PLAs. The loss tangent increment is lower for dried samples, as expected. Data in Figure 1 were fitted to the following equation:

$$\tan\delta(t) = \tan\delta_0 + (\tan\delta_{inf} - \tan\delta_0)(1 - e^{-t/\tau}) \quad (1)$$

where $\tan\delta_0$ is the loss tangent value at the beginning of the test, $\tan\delta_{inf}$ is the limit value for long time while τ represents the characteristic time constant of the degradation process.

In Table 2 are reported the best fit values obtained.

On the one side, it is possible to observe that the τ values of wet samples are comparable and seem to be independent on M_w . On the other side, the τ values of dried samples are more than doubled. This indicates a minor molecular weight reduction in absence of moisture.

Due to the presence of gas bubbles developed during the degradation processes, the LVE functions could not be correctly measured. For this reason, only the loss tangent has been reported here, being the

property less influenced by the geometry used. For this reason only measurements with the capillary rheometer were taken into account.

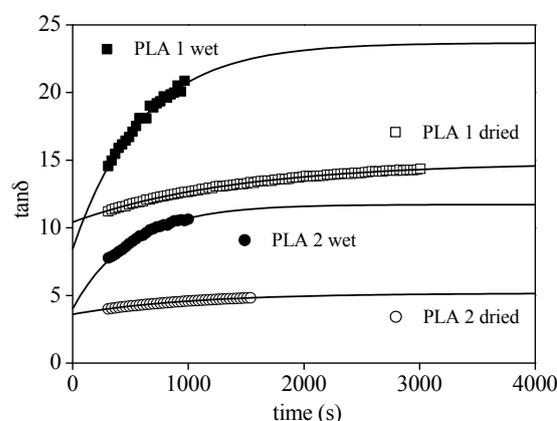


Figure 1. Time dependence of the loss tangent at 200°C for wet and dried PLA 1 and PLA 2 samples. Best fit with Equation 1.

Table 2. Best fit values for the time evolution of $\tan\delta$ according to Equation 1.

	$\tan\delta_0$	$\tan\delta_{inf}$	τ (s)
PLA 1 wet	8.4 ± 0.8	23.7 ± 0.8	601 ± 90
PLA 1 dried	10.4 ± 0.1	14.8 ± 0.1	1408 ± 22
PLA 2 wet	4.0 ± 0.4	11.7 ± 0.2	490 ± 45
PLA 2 dried	3.6 ± 0.1	5.1 ± 0.1	1019 ± 13

MODELING THE VISCOSITY OF PLA MELTS

The prediction of the rheological behavior of PLA melts is limited to the dependence of its Newtonian viscosity η_0 on molecular weight M_w :

$$\eta_0 = KM_w^\alpha \quad (2)$$

even if controversial results are found in the literature mainly due to the previously cited thermal and hydrolytic degradation^{3,4}. Only in 2005 Dorgan et al.¹ definitively stated that a value for the exponent $\alpha=3.4$ correctly describes the viscosity of linear PLA according to the predictions of the reptation theory.

Proposed predictive model

The aim of this study is to work out correct Cross-WLF parameters for PLA melts with polydispersity index between 1.7 and 2. To do this, it is fundamental to dry the samples carefully, in order to prevent hydrolysis and to check possible molecular weight changes during the tests.

The semi-empirical model adopted is that based on the Cross equation:

$$\eta(\dot{\gamma}, T, P) = \frac{\eta_0(T, P)}{\left[1 + \frac{\eta_0(T, P)}{\tau^*} \dot{\gamma}\right]^n} \quad (3)$$

where η is the viscosity, n the power law index and τ^* is a characteristic stress value.

The parameters n and τ^* , often claimed to be dependent only on the chemistry, are also slightly MWD dependent. We will consider them as constant, because our aim is to predict the flow curve of PLA melts with polydispersity index around 2 as typical of PLA samples obtained by ROP.

Once n and τ^* are chosen one has to correctly assess the temperature and pressure dependence of the Newtonian viscosity η_0 . The Williams-Landel-Ferry (WLF) equation is suited for the case and has been used in its form referred to the glass transition temperature T_g of the polymer:

$$\text{Log}[\eta_0(T, P)] = \text{Log}D_1 - \frac{C_{1,g}(T - T_g)}{C_{2,g} + (T - T_g)} \quad (4)$$

where $C_{1,g}$ and $C_{2,g}$ are constants. D_1 is the Newtonian viscosity at $T=T_g$ and $P=0$. The pressure dependence of the viscosity is taken into account assuming a linear pressure dependence of the glass transition temperature:

$$T_g(P) = D_2 + D_3P \quad (5)$$

where D_2 is the value of T_g at atmospheric pressure while D_3 is related to the polymer compressibility.

Cross-WLF model parameters determination for PLA melts

At the beginning the Cross equation was tested to ensure a satisfactory matching with the experimental data for the two PLAs.

Furthermore it was found that the n values for different samples varies only in a small range ($0.83 < n < 0.89$). Slight differences are probably due to minor details of the MWD. This parameter was then assumed to be constant and set as $n=0.84$. The τ^* values were all in the range between 204 and 263 kPa and a value equal to 204.8 kPa was chosen as reported in a technical report of the Moldflow software about the characterization of PLA⁵.

Thermo-rheological simplicity of PLA was also checked by means of master curves construction.

Once the Cross parameters were chosen, the M_w dependence of η_0 was investigated to correctly determine K and α . Due to the many controversial results present in the literature, carefully dried samples were taken into account to clear up this point.

The molecular weights of the two samples cover a range that is too small to lead to reliable best fit parameters. For this reason a set of samples with different M_w values was created by degradation of PLA 2 thermally treated directly in the barrel of the capillary rheometer.

The flow curves obtained are reported in Figure 2 where the viscosity decrease with increasing residence time at 200°C can be appreciated.

In Figure 3 a master curve has been built shifting these curves. This was done with the aim to check a kind of time-molecular weight superposition principle. The good quality of the master curve obtained reveals a decrease in M_w without appreciable changes of the polydispersity. To further

support this argument one can observe that the n and τ^* values are practically constant.

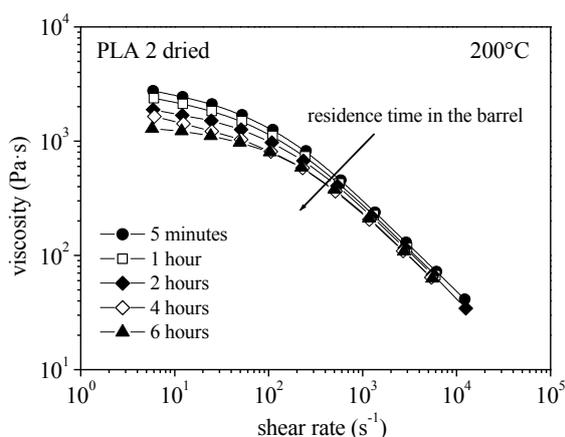


Figure 2. Flow curves of PLA 2 dried samples kept at 200°C for different times within the barrel of the rheometer.

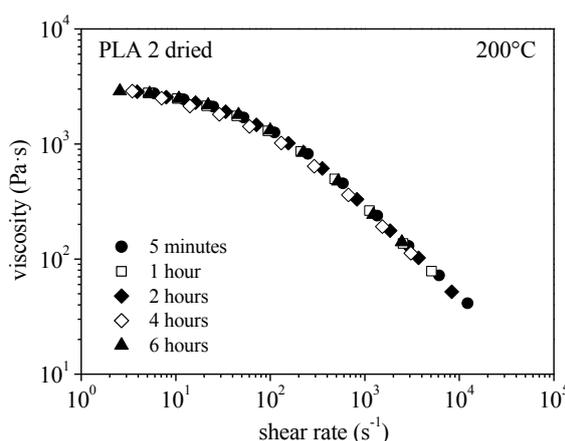


Figure 3. Master curve obtained for PLA 2 using the data in Figure 2.

To check both the M_w decrease with increasing residence time $t_{200^\circ\text{C}}$ and to check its constant value during a test (around 10 min) GPC measurements were performed at the beginning and at the end of each test. The results are reported in Table 3 together with the Newtonian viscosity values obtained by fitting the data.

In Figure 4 the Newtonian viscosity data calculated at 200°C together with those found in the literature are reported^{1,3}. The best fit value of the power law exponent of Equation 2 ($\alpha=3.56$) is in good agreement

with that reported in the literature ($\alpha=3.4$). The slight difference could be due to minor polydispersity effects.

Table 3. Molecular weights and Cross parameters at the beginning and at the end of the test for PLA 2 dried samples and kept at 200°C in the barrel of the rheometer.

$t_{200^\circ\text{C}}$ (h)	$M_{w,\text{start}}$ (kDa)	$M_{w,\text{end}}$ (kDa)	η_0 (Pa·s)	n	τ^* (Pa)
0	157.0	159.4	3003	0.84	223900
1	156.9	146.6	2566	0.84	207900
2	138.7	135.4	1985	0.84	206800
4	132.9	132.1	1711	0.80	163900
6	129.9	131.8	1339	0.86	221700

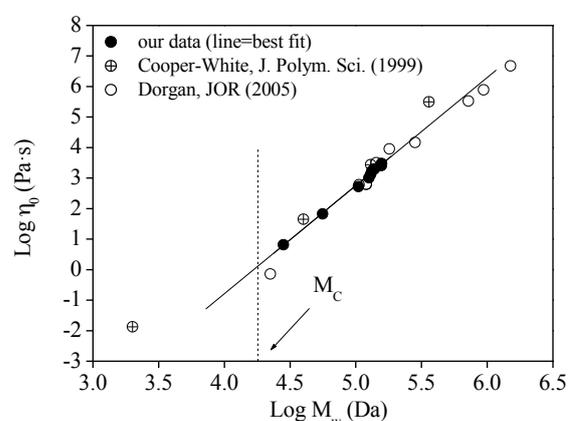


Figure 4. Molecular weight dependence of the Newtonian viscosity for PLAs at 200°C.

Concerning the temperature dependence of the viscosity an attempt was made to build a master curve using flow curves measured with the capillary rheometer. A lower bound of the temperature range explored was dictated by the crystallization temperature of PLA while an upper limit was dictated by degradation processes.

In the literature a high quality set of data on this topic can be found¹. WLF parameters by Dorgan et al. were thus chosen after a check of the agreement of our shift factors, even if covering a small temperature range, with those presented by these authors ($C_1=3.24$ and $C_2=164.9^\circ\text{C}$, $T_{\text{ref}}=180^\circ\text{C}$). The WLF coefficients referred at

T_g (61°C) were then calculated and were respectively $C_{1,g}=11.64$ and $C_{2,g}=45.9^\circ\text{C}$. The value of K in equation 2 and already calculated at 200°C could then be translated at $T=T_g$, giving $K=4.9510^{-7}$ Pa·s.

In Figure 5 a final comparison is made between all of the measured flow curves for PLA 1 and PLA 2 and the predicted ones. The agreement is excellent in all the range of molecular weight and shear rate explored.

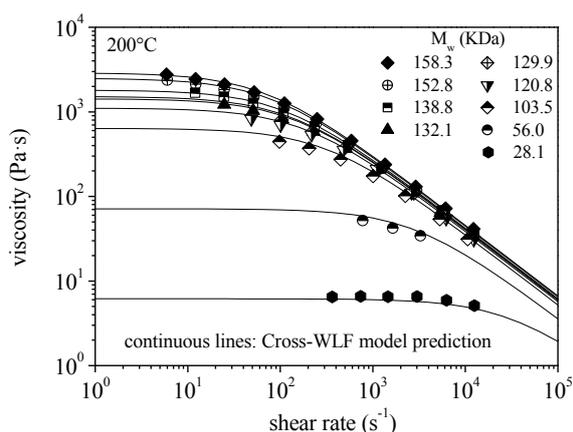


Figure 5. Flow curves of PLA 1 and PLA 2 samples compared to the Cross-WLF model predictions.

The pressure dependence of the viscosity was not yet included in the model. The pressure values involved are not so high to force one to consider also this aspect.

For the sake of completeness, to face also this topic, the parameters in equation 5 have to be chosen. Concerning D_2 our calorimetric data indicated a T_g value equal to 61°C while for D_3 , after a careful assessment of the literature, a value equal to $9.547 \cdot 10^{-8}$ (K/Pa) was identified⁵.

In other words a linear dependence of the glass transition temperature was chosen of the form:

$$T_g(P) = 61 + 0.0095 \cdot P \quad (6)$$

where P must be expressed in bar and T_g in °C.

MODELING THE VISCOSITY OF PLA/L-LACTIDE SOLUTIONS

In industrial polymerization processes, one generally observes the transition from an initial low viscosity phase to a very viscous final one. It is thus fundamental to assess the concentration dependence of the viscosity for a correct plant design. In the following a model to predict the viscosity of PLA/L-lactide concentrated solutions is proposed.

The model

The Newtonian viscosity η_0 of a concentrated solution can be expressed using the following scaling law:

$$\eta_0 \propto \varphi^\gamma M_w^{3.4} \zeta(T, \varphi) \quad (7)$$

where ϕ is the polymer volume fraction, γ is a parameter governing the dependence of η_0 on concentration and ζ is a friction coefficient representing the resistance to flow of a chain segment as it moves within the solution. It is clear from Equation 7 that ζ depends on both T and ϕ . To determine the value of γ it is not possible to make use of isothermal η_0 values of solutions with different ϕ values, because the monomeric friction coefficient in turn depends on T . In principle, measurements should be done in a state of iso- ζ . To ensure iso- ζ conditions the following scaling law may be useful in which the friction coefficient is related to the fractional free volume of the polymeric solution:

$$\zeta(T, \varphi) \propto \exp[1/f(T, \varphi)] \quad (8)$$

This states that iso- f conditions are equivalent to iso- ζ conditions, and consequently this situation is desirable to correctly evaluate γ . In the literature the parameter γ is generally found between 3.4 and 4.

On the one hand, when $T \leq T_g$ polymers exhibit a substantially constant fractional free volume whose value is $f(T_g) = f_g$. On the other hand, when $T > T_g$ one finds that f linearly increases with T with an expansion coefficient α_f :

$$f = f_g + \alpha_f(T - T_g) \quad (9)$$

As a consequence, knowing both T_g and α_f , it is possible to calculate the free volume at each temperature. It is reasonable to assume that solutions at different concentration levels have the same f_g , because the addition of solvent small molecules within the polymer chains increases the free volume f and diminishes, at the same time, $T_{g,sol}$. To determine the glass transition temperature of a solution the following well known equation can be used:

$$T_{g,sol} = \frac{\alpha_{f,p} \phi T_{g,p} + \alpha_{f,s} (1 - \phi) T_{g,s}}{\alpha_{f,p} \phi + \alpha_{f,s} (1 - \phi)} \quad (10)$$

in which $\alpha_{f,p}$ and $\alpha_{f,s}$ are the free volume expansion coefficients of the pure polymer and pure solvent. The respective glass transitions, $T_{g,p}$ and $T_{g,s}$ are given in Kelvin. For a solvent, if an experimental measure of T_g is not possible, one can assume with a good approximation degree the value obtained by the rule $T_{g,s} = 1/2 T_{m,s}$ for solvents whose molecules are symmetric and $T_{g,s} = 2/3 T_{m,s}$ for solvents whose molecules are asymmetric. Here $T_{m,s}$ is the melting temperature of the solvent. Concerning $\alpha_{f,s}$ a practically universal value equal to 10^{-3} K^{-1} can be chosen as typical of simple liquids like low molecular weight organic solvents ($M_{w-lactide} = 144.13 \text{ g/mol}$). The value of $\alpha_{f,p}$ can be determined by means of rheological measurements on the molten polymer. It has been pointed out that the free volume expansion coefficient of a concentrated solution $\alpha_{f,sol}$ practically coincides with that of the pure polymer $\alpha_{f,p}$ ⁶.

For concentrated solutions a fraction above 40÷50 wt% is intended. The $\alpha_{f,p}$ value can be inferred by the temperature dependence of a_T previously described in the WLF equation. Once chosen the $C_{1,g}$ and $C_{2,g}$ values previously determined one can obtain $\alpha_{f,p}$ using the following equations:

$$C_{1,g} = \frac{B}{2.303 \cdot f_g} \quad (11)$$

$$C_{2,g} = \frac{f_g}{\alpha_{f,p}} \quad (12)$$

where B is a constant $\cong 1$.

If, as mentioned, $\alpha_{f,sol} \cong \alpha_{f,p}$, at a certain temperature T the difference of fractional free volume f between a polymer and its solutions is essentially driven by T_g . As a consequence, one can consider that solutions with different concentration values of a polymer at the same $(T - T_g)$ value are also in the same fractional free volume state. This is the desirable condition to be able to express the concentration dependence of the viscosity through ϕ^γ .

Assessment of the parameters of the predictive model for the viscosity of concentrated PLA/L-lactide solutions

Newtonian viscosity prediction curves of PLA 2/L-lactide concentrated solution were estimated using the procedure and the data previously exposed.

Capillary rheometer tests were done on solutions having different concentrations (PLA 2 \geq 80 wt%) with the aim to check the predictions of the model. The real concentrations of polymer in the solutions were determined by TGA analysis. Concentrated solutions with PLA contents lower than 80 wt% were prepared but not taken into account due to inhomogeneities. In Figure 6 the experimental data obtained for four solutions at different concentration values are reported together with the predictions of the model at study.

As a general trend, one observes that the prediction slightly overestimates the viscosity.

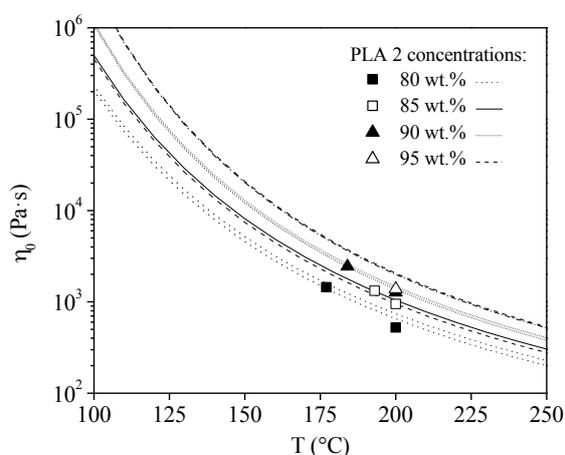


Figure 6. Newtonian viscosity predictions (lines, upper and lower limits) compared to experimental data of PLA 2/L-lactide solutions (points).

This difference could be ascribed to the mixing process employed to prepare the solutions, during which thermolysis, hydrolysis and shear stress may play a role lowering a bit the molecular weight of PLA. It must be noticed that the expansion coefficients of the polymer and its concentrated solution are supposed to be the same ($\alpha_{f,sol} \approx \alpha_{f,p}$). The literature suggests that this is reasonable but small differences cannot be excluded⁶. In addition the same fractional free volume at T_g for the polymer and its solutions is conjectured. To end with the list of approximations, the glass transition temperature of lactide was inferred using the empirical rule $T_{g,s} = 2/3 T_{m,s}$. This led to a T_g value of -27°C for the lactide.

CONCLUSIONS

In this work the results of the rheological characterization of PLA grades with different molecular weights and similar polydispersity have been illustrated and discussed.

Using capillary rheometry, dried and thermally degraded samples were investigated to determine Cross-WLF parameters. All of the model parameters were carefully assessed and the predictions of the semi-empirical Cross-WLF equation were found to be in excellent agreement with a set of experimental data covering a significantly broad range of molecular weight, shear rate and temperatures.

Finally data on PLA/L-lactide concentrated solutions were used to test the validity of a free volume model to predict their Newtonian viscosity.

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