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Rheology of Wood Flour Filled Poly(lactic acid)

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Abstract

This work investigates the rheological properties of wood flour filled poly(lactic acid) at typical processing temperatures, i.e. 155°C, 165°C and 175°C, using a parallel plate rheometer run in oscillatory mode. Materials with three different filler loading levels (10, 20 and 30% wt.) are characterized together with the neat matrix. Considering the complex viscosity curves, it is found that a single master curve can be obtained, which allows to predict the viscosity of the material at any filler loading level and any temperature that are included in the interval tested.

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Keywords: Wood Polymer Composites; Poly(lactic acid); Rheology

1. Introduction

The increasing perceived importance of environmental issues has driven a remarkable collective interest towards plastics that are biodegradable [1,2]. The most common of such materials is poly(lactic acid) or PLA. The main drawback of this material is its cost, which is much higher than oil based commodity thermoplastics. The use of natural fibres as fillers offers the possibility of reducing material cost and, in some cases, also to increase mechanical properties, without altering its environmental sustainability character [3].

On the other hand, filling a thermoplastic polymer with natural fibres gives rise to a number of drawbacks. For instance, material viscosity increases and, due to localized viscous heating during processing, material degradation is more likely to occur [4]. This is especially true for PLA that is very sensitive to heat induced hydrolytic

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degradation [5]. Therefore, it is very important to characterize the viscosity of natural fibre filled PLA and optimize processing conditions in order to allow good quality of the final product.

In this work a commercially available PLA has been filled with wood fibers at three filler loading levels. From these compounds, rheometry testing at typical processing temperatures has been performed using a parallel plate rheometer in oscillatory mode to measure complex viscosity. For completeness, pure matrix samples have also been characterized. A single master curve is obtained that can reasonably predict the complex viscosity of molten composites within temperature and filler volume fraction range that has been investigated.

Nomenclature

η^*	complex viscosity	T, T_0	current and reference temperature
G', G''	complex moduli: storage and loss	a_T	thermal shift factor
ω	frequency	ϕ	volumetric concentration
η_0, λ, c, n	Carreau-Yasuda parameters	ϕ_m, m	Krieger Dougherty parameters
C_1, C_2	Williams Landel Ferry parameters	b_ϕ	concentration shift factor

2. Materials and methods

2.1. Materials

The matrix is a commercial poly(lactid acid) named NEVIBIO PLA 0509 purchased from Nevicolor S.p.A, Luzzara (RE), Italy. Its melting temperature is 150°C and has a density of 1.22 g/cm³ at 23°C. The natural filler is wood flour from spruce, with a bulk density of 1.4 g/cm³. It has been purchased from JELU, Rosenberg, Germany under the commercial name of JELUXYL HW 50/100.

All rheometry specimens are in the form of 25 mm diameter discs. Neat PLA samples have been punch cut from a 1.5 mm thick slab obtained by compression molding at 180°C with a pressure of 70 bar. The composites contain 10, 20 and 30 wt.% wood fibers and have been prepared as follows: the filler has been compounded together with PLA using a twin screw co-rotating extruder to obtain the 30 wt.% composite. The fiber concentration has been imposed through a gravimetric feeder. The relevant processing parameters are: flat temperature extrusion profile at 155°C and screw speed of 100 RPM and have been chosen to prevent thermal and hydrolytic degradation inside the extruder. Wood fibers and PLA have been dried at 85°C for 24 hours before compounding. The compound pellets has been further processed by single screw extrusion to obtain 50 mm x 2 mm slabs. During this second extrusion, the 30 wt.% compound has also been diluted with the neat matrix in the hopper, so that composites at 10 wt.% and 20 wt.% wood fiber content have been obtained in addition to the original 30 wt.%. Again a flat 155°C temperature profile has been imposed. The composite specimens have been finally punch cut from the extruded slabs.

After processing, some of the specimens have been dissolved in chloroform to measure wood fibers geometric features. These are reported in Tab. 1: the filler is in the form of short fibers (aspect ratio less than 10). Possibly, the fibers could have been shortened during compounding and extrusion.

Table 1. Wood fibers geometric features. Values in parentheses represent standard deviations

Length (μm)	Diameter (μm)	Length/Diameter
986.1 (102.6)	311.2 (50.42)	3.2 (0.33)

2.2. Rheometry

The specimens have been first dried at 75°C for 24 hours in a vacuum oven, then they have been placed in a strain controlled parallel plate rheometer in nitrogen atmosphere (ARES, Rheometric Scientific) equipped with 25 mm diameter titanium plates. The viscoelastic response of materials has been measured through a frequency sweep test, in which oscillation frequency ω has been varied from 0.1 rad/s to 100 rad/s. The oscillation amplitude has been chosen in such a way that the materials were in the linear viscoelastic domain. In particular, different strain values have been chosen for the various materials, i.e. 0.05% for the 30 wt.% and the 20 wt.%, 0.1% for the 10 wt.%, and 1% for neat PLA. The storage modulus G' and the loss modulus G'' have been measured as a function of frequency. These quantities have been used to calculate the complex viscosity:

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \quad (1)$$

3. Results and discussion

The complex shear moduli of neat PLA and the 10 wt.% and 30 wt.% composites are shown in Fig. 1a at 155°C. The 20wt.% is not shown to avoid making the picture too busy. The complex moduli increase with frequency. In the range 10 – 100 rad/s we can see the intersection of the two moduli: this indicates the transition from fluid-like behavior at low frequency to solid-like behavior at higher frequencies. At higher temperatures (165°C and 175°C), the curves are similar, except that the behavior is only fluid-like in the frequency range that was tested.

The complex viscosity of all materials at 155°C is shown in Fig. 1b, while the complex viscosity at 165°C and 175°C are shown in Fig. 2a and 2b respectively. Complex viscosity decreases with frequency and temperature, while it increases with fiber mass fraction, which is what would be expected.

In order to better comprehend temperature dependence of viscosity results, we will use the time temperature superposition [6]: the complex viscosity curves can be displaced diagonally in a bi-logarithmic plot in order to construct a single master-curve that can be used to predict the complex viscosity of the fluid at any temperature. Let us consider the PLA complex viscosity curves first, and let us move the complex viscosity of PLA at 165°C and 175°C onto the complex viscosity curve of PLA at 155°C. By doing this, we will consider 155°C as the reference temperature T_0 .

The same procedure can be applied also keeping temperature constant, for example at the reference temperature, and varying the natural fiber content, as introduced by Highate and Whorlow [7], see also Barnes [8]. Thus, the viscosity curves of all composites will be translated diagonally until they meet the complex viscosity curve of neat PLA at 155°C, which is the same curve that was obtained previously.

The results of the curve shifting are pictured in Fig. 3: the single master-curve that has been obtained represents a completion of the complex viscosity curve of neat PLA at 155°C. As can be seen comparing Fig. 1b with Fig. 3, the master curve reaches high values of frequency. Curve fitting of the master curve can be achieved with the Carreau-Yasuda equation:

$$\eta_{PLA,155}^* = \frac{\eta_0}{\left(1 + (\lambda\omega)^c\right)^{\frac{1-n}{c}}} \quad (2)$$

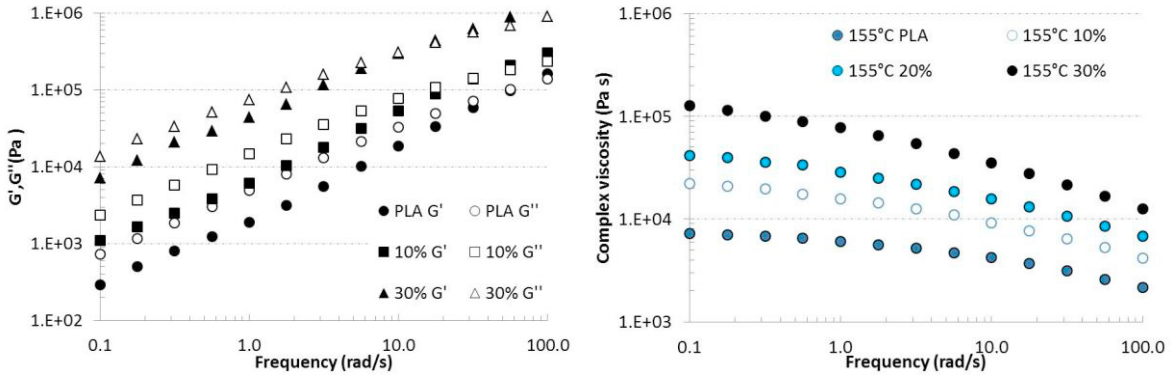


Fig. 1. (a) The dynamic moduli at 155°C; (b) complex viscosity at 155°C.

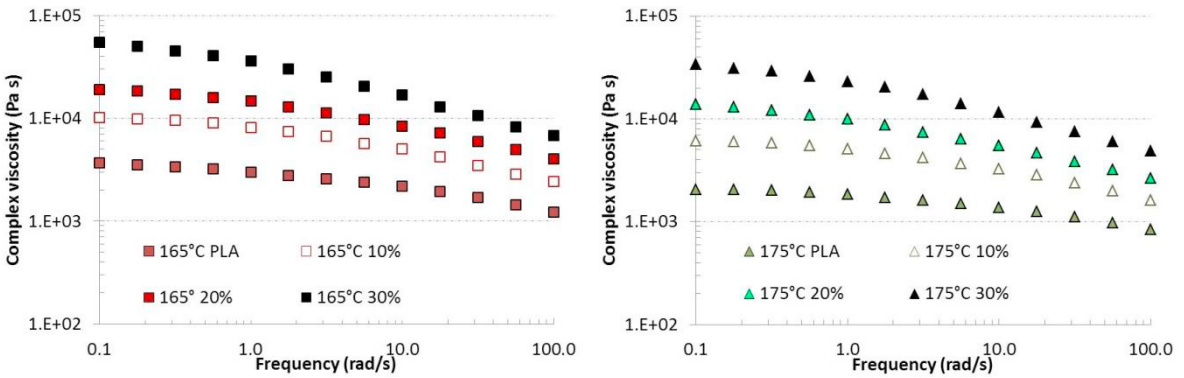


Fig. 2. (a) Complex viscosity at 165°C; (b) complex viscosity at 175°C.

The thermal shift factors depend on temperature and are pictured in Fig. 4a. Curve fitting can be performed with the Williams-Landel-Ferry equation:

$$\log(a_T) = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \tag{3}$$

Analogously, the concentration shift factors depend on concentration but it is customary to express this dependence in terms of volumetric concentration, not mass concentration. Thus the mass percentages have to be transformed into the corresponding volume fractions. Density of filler and matrix at the relevant temperatures must be known. These will be estimated on the basis of literature data [9]. In particular, we will assume 1.35 g/cm³ for wood fiber density at all temperatures, while for PLA at 155°C, 165°C and 175°C we will assume 1.14 g/cm³, 1.13 g/cm³ and 1.12 g/cm³, respectively. The volume fractions are: 8.6% for the 10 wt.%, 17.4% for the 20 wt.% and 26.6% for the 30 wt.%. The dependence of the concentration shift factors on volumetric concentration can be expressed in terms of the Krieger-Dougherty equation:

$$b_\phi = \left(1 - \frac{\phi}{\phi_m}\right)^m \quad (4)$$

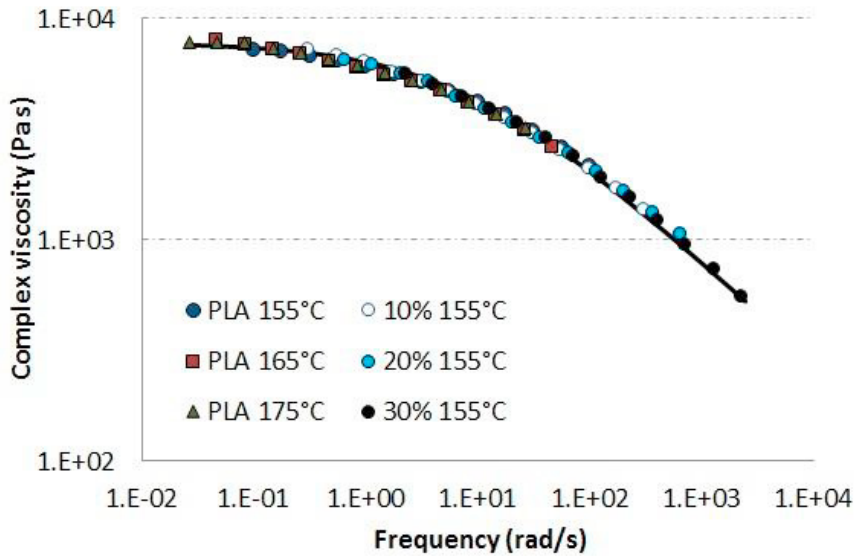


Fig. 3. The master curve obtained by shifting diagonally the complex viscosity curves.

The comparison between the experimental shift factors and the best fit through Eq. (4) is pictured in Fig. 4b. At this point we propose to combine the two single shift factor together to predict the complex viscosity of any composite at any temperature, using the master curve and the two pure shift factors. The main assumption at the basis of this procedure is that the effects of temperature and filler volume fraction on viscosity are disjoint. Such a model can be expressed as follows:

$$\eta^*(T, \phi, \omega) = a_T b_\phi \eta_{PLA,155}^*(a_T b_\phi \omega) \quad (5)$$

The complex viscosity curves of the composites at temperatures different from the reference temperature have been also translated onto the master curve for validation purposes. The result is pictured in Fig. 5. The comparison between the experimental shift factors and the composition of the pure shift factors obtained with Eq. (3) is reported in Tab. 2. As can be seen from the table values, the model prediction and the experimentally calculated shift values are reasonably close.

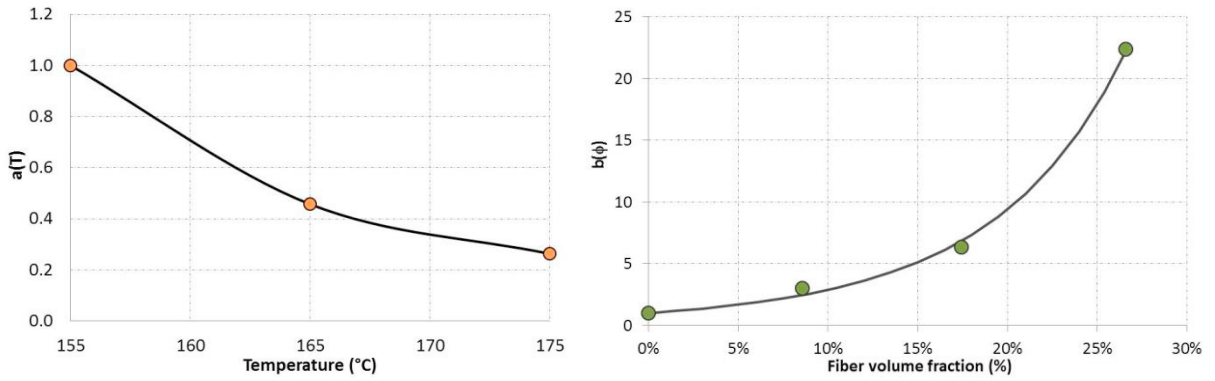


Fig. 4. (a) Thermal shift factors; (b) Concentration shift factors.

Table 2. Comparison between experimental shifts and shifts predicted by the model of Eq. (5)

Temperature	10%		20%		30%	
	Model	Experimental	Model	Experimental	Model	Experimental
165°C	0.142	0.135	0.463	0.440	1.010	0.905
175°C	-0.098	-0.105	0.223	0.198	0.770	0.658

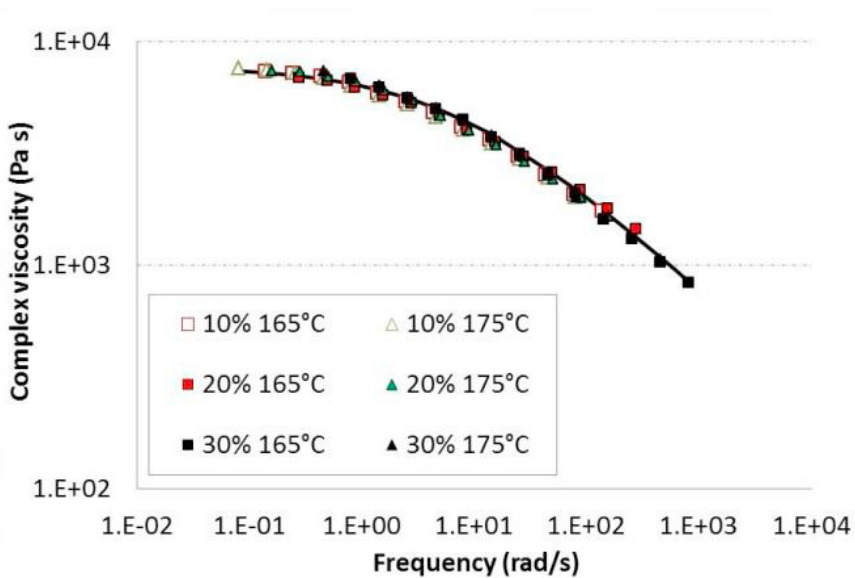


Fig. 5. Model validation.

4. Conclusions

Considering the good agreement between the experimental shift factors and the ones obtained using the model of Eq. (5), one can conclude that the hypotheses at the basis of the model are reasonable. In this work we measured the complex viscosity of the various materials. The identification of complex viscosity with shear viscosity may be problematic for filled materials [10]. For charactering the viscosity of easily degrading material, such as natural fiber filled polymers, the best method is in-line rheometry [11-12]. This work is currently underway and will be published elsewhere.

References

- [1] R. Datta, S.-P. Tsai, P. Bon Signore, S.-H. Moon, J. R. Frank, Technological and economic potential of poly(lactic acid) and lactic acid derivatives, *FEMS Microbiology Reviews* 16 (1995) 221-231
- [2] E. Zini, M. Scandola, Green composites: An overview, *Polym Comp* 32 (2011) 1905–1915.
- [3] Á. Csikós, G. Faludi, A. Domján, K. Renner, J. Móczó, B. Pukánszky, Modification of interfacial adhesion with a functionalized polymer in PLA/wood composites, *European Polymer Journal* 68 (2015) 592–600
- [4] V. Mazzanti, F. Mollica, N. El Kissi, Rheological and mechanical characterization of polypropylene-based wood plastic composites, *Polym Comp* 37 (2016) 3460–3473
- [5] V. Speranza, A. De Meo, R. Pantanti, Thermal and hydrolytic degradation kinetics of PLA in the molten state, *Polymer Degradation and Stability*, 100 (2014) 37-41
- [6] C.W. Macosko, *Rheology. Principles, measurements and applications*. Wiley 1994
- [7] D. J. Highgate, R. W. Whorlow, Rheological properties of suspensions of spheres in non-Newtonian media, *Rheologica Acta*, 9 (1970) 569–576
- [8] H. A. Barnes, A review of the rheology of filled viscoelastic system, *Rheology Review* (2003) 1-36.
- [9] D. R. Witzke, *Introduction to Properties, Engineering, and Prospects of Polylactide Polymer*, Ph.D. thesis, Chemical Engineering, Michigan State University, 1997.
- [10] W. Gleissle and B. Hochstein, Validity of the Cox–Merz rule for concentrated suspensions, *J of Rheology*, 47, (2016) 897-910
- [11] V. Mazzanti, F. Mollica, In-line rheometry of polypropylene based Wood Polymer Composites, *Polym Testing* 47 (2015) 30-35.
- [12] V. Mazzanti, F. Mollica, In-Process Measurements of Flow Characteristics of Wood Plastic Composites, (in press) *J of Polymers and the Environment* DOI 10.1007/s10924-016-0876-2