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Rheological behavior of wood flour filled poly(lactic acid): temperature and concentration dependence

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ABSTRACT

The aim of this study is to evaluate the influence of temperature and filler concentration on the rheology of wood fiber filled poly(lactic-acid). After measuring complex viscosity for various filler amounts (0-30 wt.%) and temperatures (155-175°C), it has been found that a single master-curve can be obtained by shifting the curves diagonally onto the one of the neat matrix at a reference temperature. Considering only the complex viscosity of the neat matrix at all temperatures, the resulting pure thermal shifts can be fitted by a Williams–Landel–Ferry equation. The same procedure can be employed considering the complex viscosity of all composites at the reference temperature. Here, the concentration shifts are approximated by a Krieger–Dougherty equation. We propose that these two pure shift factors can be combined together, independently of each other, for predicting the complex viscosity of the composites at any temperature and filler amount. The main assumption of this procedure is that temperature and filler concentration effects must be disjoint. For validation, the predicted shift factors have been compared with the experimental ones related to composites tested at temperatures other than reference. The agreement is satisfactory, thus the hypotheses at the basis of this methodology are justified.

INTRODUCTION

The increasing awareness about the importance of environmental sustainability has attracted considerable attention towards plastics that are environmentally friendly. An example of these are the “green composites” based on commodity thermoplastics filled with natural fibers, e.g. wood fibers or flour [1-2]. These materials, known as wood polymer composites (WPC), are possible substitutes of wood, as they look similar but have better moisture resistance. Moreover, wood fibers are cheap and abundantly available as a byproduct of the wood transformation industry [3], while the processing temperatures of the commodity polymers are low enough to prevent wood fibers thermo-oxidative degradation during processing [4].

The use of biodegradable or compostable matrices increases the sustainability of these materials even further. Interesting applications are those that are characterized by a short life span of the material, e.g. packaging [5,6]. Among biodegradable plastics, poly(lactic acid) or PLA is one of the most widely used. It is based on lactic acid and belongs to the family of the aliphatic polyesters produced out of renewable resources. Degradation occurs by hydrolysis of the ester bond, and in the appropriate environment the polymer can be completely dissolved in 8 – 12 weeks [7].

PLA is typical for products where both adequate mechanical properties and biodegradability are required [8]. On the other hand, the major disadvantage is its high cost if compared with the most common petroleum-based plastics [9]. From this point of view, wood fibers are a perfect candidate to be compounded with PLA: this filler is compostable and inexpensive, thus it decreases the total cost, while keeping biodegradability.

In the recent scientific literature there is quite a large number of papers about the characterization of wood fiber filled PLA (from now on W-PLA). The research work is mainly concerned with aspects such as the influence of wood fibers on the mechanical properties [10-12], degradation [13,14], improvement of interfacial adhesion [15-18] and effects of fiber chemical treatments [19]. Not enough attention has been paid to the rheological characterization: to the authors' knowledge, the rheology of W-PLA is treated only in one paper [20], in which the flow properties are investigated as a function of the maleic anhydride content at 190 °C.

In the present work W-PLA composites, filled with different percentages of wood fibers (0, 10, 20 and 30 wt.%) have been characterized with the parallel plate rheometer in oscillatory mode at different testing temperatures (155, 165 and 175 °C). The aim is to describe the influence of both filler content and temperature on the rheological properties.

According to the time temperature superposition, the influence of temperature can be described by a unifying approach, in which the complex viscosity curves are shifted diagonally in a bi-logarithmic plot until a single master curve is obtained. The resulting shift factors depend on temperature and can be fitted, for example, by the Williams-Landel-Ferry equation. The influence of the filler content can also be described in a similar way, as reported in [21,22]. Again, the viscosity curves can be shifted diagonally in a viscosity – frequency bi-logarithmic plot and the corresponding shift factors can be fitted by various models, such as the Einstein's equation for very dilute suspensions, or the Krieger – Dougherty equation for more concentrated ones. The Krieger – Dougherty equation has already been used for natural fiber filled polymer systems in [23,24]. All these relations consider filler content in terms of volume concentration, thus care should be taken in transforming mass fractions into the corresponding volume fractions.

In this work, the two pure shift factors, i.e. temperature and concentration, will be first obtained by considering complex viscosity of neat PLA at all temperatures and complex viscosity of W-PLA at all concentrations at a suitable single reference temperature. Next, the two pure shift factors will be combined together to predict the shift factors of the complex viscosity curve of W-PLAs at any concentration and any temperature within the tested range. The whole procedure will be validated by comparison with the experimental measurements.

MATERIALS AND METHODS

Materials

The matrix is a poly(lactid acid) that has been purchased from Nevicolor S.p.A, Luzzara (RE), Italy, under the commercial name of NEVIBIO PLA 0509. The melting temperature is 150 °C, density is 1.22 g/cm³ at 23 °C and melt index is 5 g/10min (tested at 190 °C, 2.16 kg). The filler is wood fibers from spruce having a bulk density of 1.4 g/cm³. Its commercial name is JELUXYL HW 50/100 and is provided by JELU, Rosenberg, Germany.

Pellets of 30 wt.% composite have been prepared by compounding fibers and matrix using a twin screw extruder (screw diameter 26 mm). The mass fraction has been controlled through a gravimetric feeder. During compounding, a uniform temperature distribution of 155 °C has been maintained in the extruder barrel and die in order to prevent thermal degradation. A screw speed of 100 RPM has been used to insure a short residence time. Both, wood fibers and PLA, have been dried at 85 °C for 24 hours before processing to prevent PLA heat induced hydrolysis.

Rheometer specimen preparation

Slabs of 2 mm thickness of 30 wt.% W-PLA have been extruded through a starve fed single screw extruder (screw diameter 50 mm, length over diameter ratio 40). Again, a flat 155 °C temperature profile has been imposed during extrusion and the screw speed has been kept at 100 RPM. Slabs of 10 wt.% and 20 wt.% W-PLA have also been obtained by feeding the extruder with 30 wt.% and neat PLA pellets mixed together in the hopper in suitable proportions, as to obtain the desired mass fraction. Notice that this procedure makes sure that all composites specimens received the same number of thermo-mechanical cycles.

Composites specimens have been obtained by punch cutting 25 mm diameter discs from the extruded slabs, while 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 procedure included a 10 minutes warm up period and a 5 minutes stage in order to eliminate trapped air to achieve good compaction.

Preliminary analyses

As processing may modify filler shape and dimensions, wood particles have been isolated and measured after the second extrusion: the PLA matrix has been dissolved in chloroform (purchased from Sigma-Aldrich) at room temperature, then the fibers have been sieved, dried and observed at the optical microscope (LEICA MEF4M 5x magnification). A sample fiber is shown in Fig. 1, the mean and standard deviation of length, diameter and length over diameter ratio (L/D) of the fibers are listed in Tab. 1.

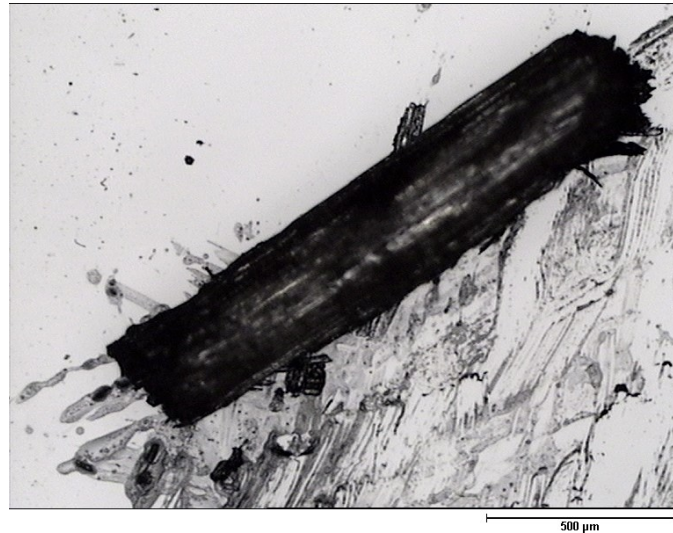


Fig. 1– Optical micrograph of wood fibres after PLA matrix dissolution

Tab. 1 - Mean and standard deviation (in parentheses) of length, diameter and L/D of the fibres

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

PLA matrix dissolution has also been used to verify the effective mass fraction of the 10 and 20 wt.% composites, which were obtained without using a gravimetric feeder: after sieving and drying, the fibers have been weighed using a precision scale, thus the weight ratio with respect to the original composite weight could be calculated. The effective mass fractions of the 10 wt.% and 20 wt.% composites have been measured at 12.6 wt.% and 19.5 wt.%, respectively.

Rheometry methods

All rheometry tests have been performed in nitrogen atmosphere using a strain controlled parallel plate rheometer (ARES, Rheometric Scientific) equipped with 25 mm diameter titanium plates. All specimens have been dried at 75 °C for 24 hours in a vacuum oven before performing the measurements. PLA is extremely sensitive to hydrolytic degradation in the presence of heat and moisture [25], while wood fibers have a low thermal resistance due to oxidative degradation [26],

thus it is necessary to verify that the samples do not degrade during testing. To this aim, time sweep measurements have been performed using a 30 wt.% W-PLA at the maximum temperature that would be used later (175 °C), and at 3 rad/s frequency and 0.2% shear strain. Maintaining these parameters constant, dynamic shear moduli and torque have been monitored for 30 minutes.

Next, small amplitude oscillatory shear measurements have been performed at 155, 165 and 175 °C. For each filler concentration and temperature, the linear viscoelasticity domain has been probed with a strain sweep test at a fixed frequency of 3 rad/s in a 0.02-50% shear strain range. This has indicated the most convenient shear strain values to be used for the subsequent frequency sweep testing: 0.05% for the 30 wt.% and the 19.5 wt.%, 0.1% for the 12.6 wt.%, and 1% for neat PLA. These strain values are within the linear viscoelastic region and have been chosen in such a way that all materials are loaded with the same torque, which is sufficiently higher than the instrument sensitivity.

The frequency sweep test has provided the response of the materials in terms of the dynamic moduli, i.e. the storage modulus G' and the loss modulus G'' . The frequency ω has been varied between 0.1 and 100 rad/s and the complex viscosity

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

has been determined as a function of frequency.

Density measurements

In order to transform the mass fractions into the corresponding volume fractions at the various temperatures, it is necessary to evaluate the densities of the various compounds at the temperatures of interest. The density of the neat matrix has been measured using a melt flow indexer (SANS, ZRZ1452) in agreement with the ISO 1133 part B norm. The material in pellets has been placed inside the barrel, which has been heated to the required temperature while stirring gently to avoid bubbles formation. The piston has then been loaded with a 2.16 kg weight to extrude the material through the 2.095 mm diameter die. The instrument measures the piston displacement l thanks to an encoder, the extrudate has then been weighed with a precision scale to measure its mass m , so that the density ρ can be evaluated through:

$$\rho = \frac{m}{0.711 l} \quad (2)$$

The measurement has been repeated three times and averaged.

The same procedure has been used also for measuring the 30 wt.% W-PLA density at 155 °C, the only difference with respect to the neat PLA being the use of a 5.0 kg mass instead of 2.16 kg. This density value will be used to estimate the wood flour density at the relevant temperatures. This will

be assumed constant over the temperature range considered. The remaining compound densities will be obtained through mixture rule using PLA and wood flour densities and the known mass fractions.

RESULTS AND DISCUSSION

Density measurements

Neat PLA melt density average and standard deviation (in parentheses) are reported in Tab. 2 at all tested temperatures. As expected, density decreases with temperature. The coefficient of thermal expansion of PLA can be estimated from the slope of the density vs. temperature curve (Fig. 2), and is equal to $2.0 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$. This value is of the same order of magnitude of the one in [27].

Tab. 2 - PLA density and standard deviation (in parentheses) as function of temperature

Temperature ($^\circ\text{C}$)	Density (g/cm^3)
155	1.04 (0.01)
165	1.02 (0.03)
175	1.00 (0.03)

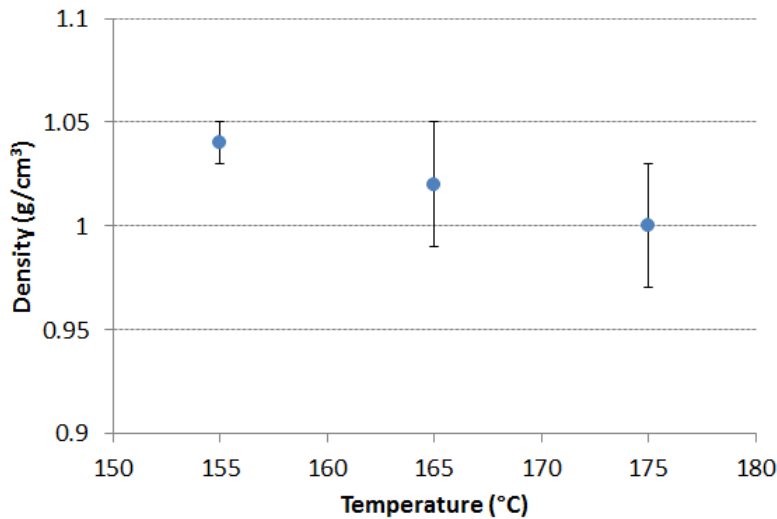


Fig. 2 – PLA density as a function of temperature. Error bars represent standard deviations.

The mean density of the 30 wt.% W-PLA at 155 $^\circ\text{C}$ is $1.11 \text{ g}/\text{cm}^3$ with a standard deviation of $0.04 \text{ g}/\text{cm}^3$. This value can be used to obtain the wood flour density ρ_w through mixture rule:

$$\frac{1}{\rho(\mu)} = \frac{\mu}{\rho_w} + \frac{1-\mu}{\rho_{PLA}}, \quad (3)$$

in which μ is the mass fraction, ρ and ρ_{PLA} are the composite and neat matrix densities. The wood flour density is the only unknown. Solving for ρ_w one obtains that wood flour density at 155 $^\circ\text{C}$ is

equal to 1.32 g/cm^3 , which is in reasonable agreement with wood flour density at room temperature (1.4 g/cm^3) and will be supposed constant over the temperature range considered.

From mixture rule written in terms of the volume fraction ϕ :

$$\rho(\phi, T) = \phi \rho_w + (1 - \phi) \rho_{PLA}(T) \quad (4)$$

one can get the relationship between mass and volume fractions by comparison with Eq. (3). The result is:

$$\frac{1}{\phi(T)} = 1 + \frac{\rho_w}{\rho_{PLA}(T)} \left(\frac{1}{\mu} - 1 \right). \quad (5)$$

Notice that volume fraction is temperature dependent through the temperature dependence of PLA density. Mass fraction, obviously, is not.

Rheology measurements

The results of the time sweep rheological tests are shown in Fig. 3. Torque and dynamic moduli are plotted as a function of time for the 30 wt.% W-PLA. During the test all monitored values have been sufficiently stable, indicating that the composite would not degrade for the entire duration of the subsequent tests. Temperatures higher than 175°C have not been considered because of lack of stability in the time sweep test.

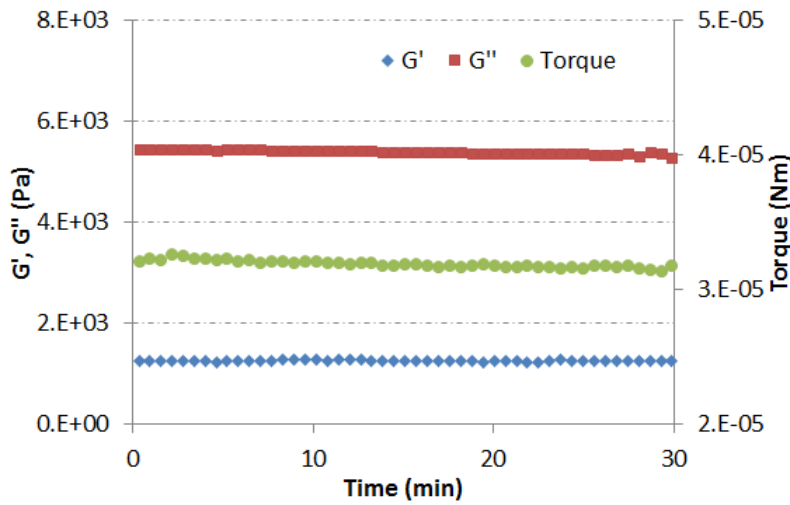


Fig. 3 – G' , G'' and torque as a function of time for the 30 wt.% at constant strain and frequency.

The frequency sweep measurements have been performed in the linear viscoelastic region at 155, 165 and 175°C for all materials. As an example, Fig. 4 shows the storage and loss moduli as a function of frequency at 155°C for neat PLA and W-PLA at 12.6 wt.% and 30 wt.%: both dynamic moduli increase with concentration and frequency, in agreement with [11], and there is a transition from fluid-like ($G'' > G'$) to solid-like ($G' > G''$) behavior between 10 and 100 rad/s. The crossover frequency between G' and G'' shifts at lower values as the wood fiber percentage increases,

indicating that the mechanical response becomes more solid-like at higher filler content, as should be expected. The behavior at 165 °C and 175 °C (not shown) is very similar, except that in the frequency range that has been analyzed, the transition from fluid- to solid-like behavior is not visible: at higher temperatures the behavior is only fluid-like in the tested frequency range.

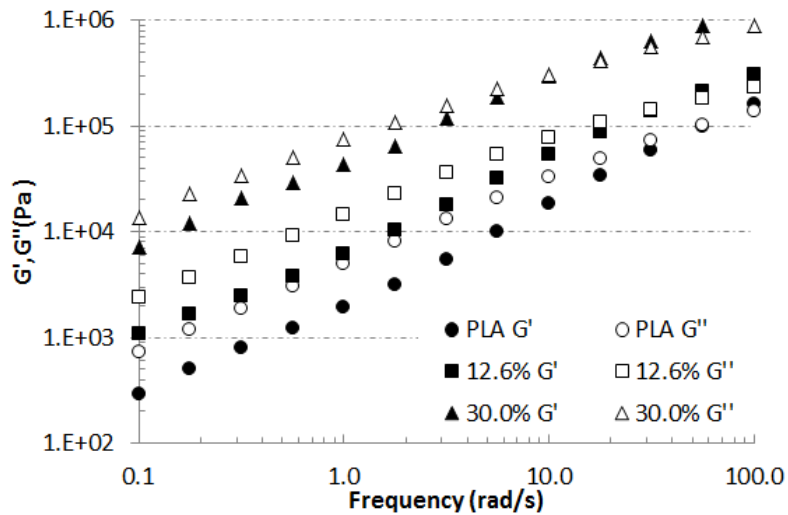


Fig.4 – G' and G'' as a function of frequency for neat PLA (circle), 12.6 wt.% (square) and 30 wt.%(triangle) at 155°C. Only 3 materials are shown for clarity.

The effect of wood fibers on complex viscosity is presented in Figs. 5 - 7 for all temperatures. Complex viscosity of all W-PLAs increases with fiber content and decreases with frequency after a short plateau, much in the same way as shear viscosity varies with shear rate (shear thinning behavior). The identification of complex viscosity with shear viscosity is part of the so called Cox-Merz rule, whose validity is still a subject of debate for filled materials [28]. This is particularly relevant when filler is in the form of fibers that would orient themselves during steady shear flow, while in oscillatory conditions randomness would be preserved. As a consequence, the results that have been found in this work are valid only as complex viscosity vs. frequency and should not be generalized to steady shear properties. On the other hand, as reported in Tab. 1, the wood fibers aspect ratio is rather small, thus fibers orientation may play a less significant role.

Looking at Figs. 5 - 7 in more detail, the right end of the complex viscosity plateau moves to lower frequencies as the fibers concentration increases. The influence of temperature on complex viscosity cannot be inferred directly from Figs. 5 – 7, nonetheless, comparing the homologous curves in the various figures, it can be seen that complex viscosity decreases with temperature, as expected.

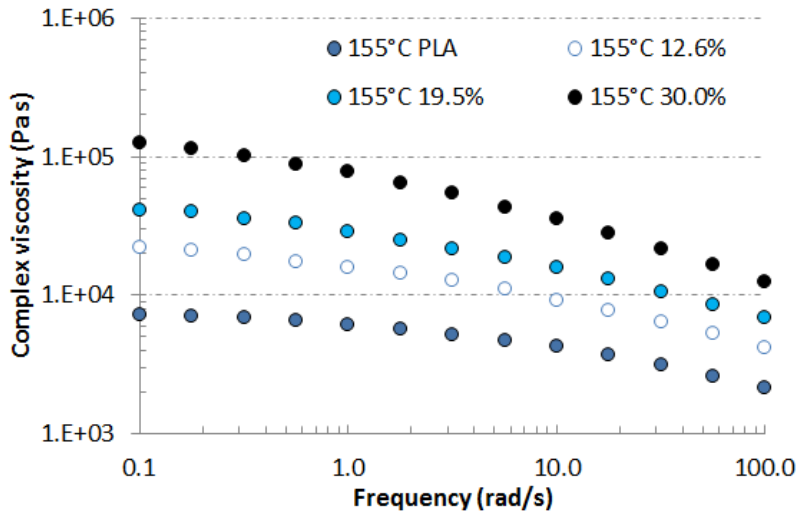


Fig. 5 – Complex viscosity as a function of frequency for different percentages of filler at 155°C.

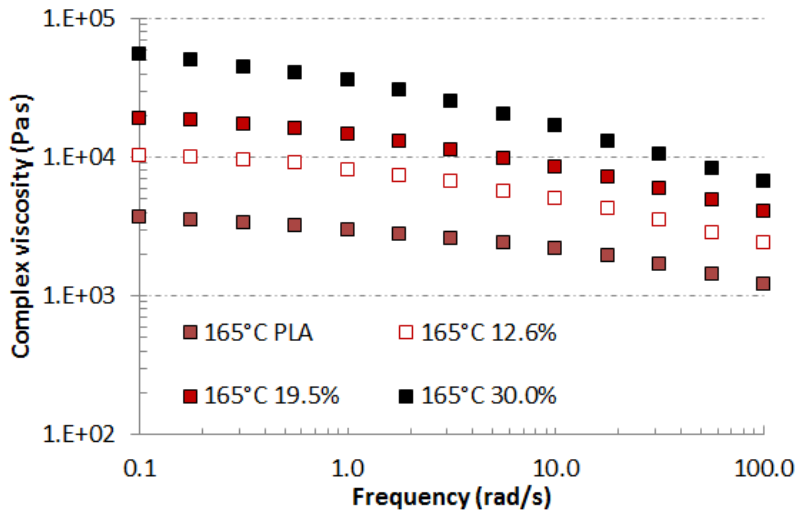


Fig. 6 – Complex viscosity as a function of frequency for different percentages of filler at 165°C.

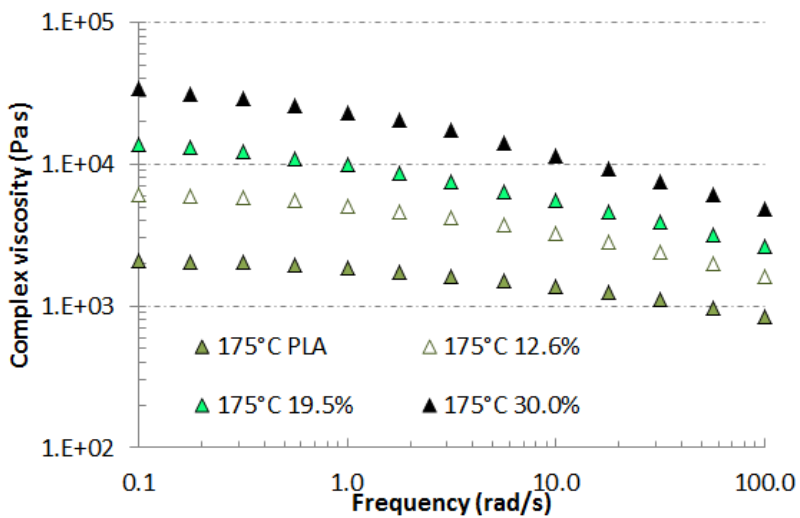


Fig. 7 - Complex viscosity as a function of frequency for different percentages of filler at 175°C.

It is well known that, as a consequence of the time temperature superposition, a single master curve can be obtained by shifting the complex moduli curves horizontally in a log-log plot. This procedure is equivalent to shifting the complex viscosity curves as a function of frequency diagonally, again in a bi-logarithmic plot. This diagonal shift is constructed by the superposition of a horizontal shift and a vertical shift, which are of the same value but opposite in sign.

Let us now consider only the complex viscosity curves of neat PLA at the three tested temperatures. These can be shifted onto the complex viscosity curve at the reference temperature, here chosen to be 155 °C. The shifting is successful in that a single master curve is obtained (Fig.8), which extends the neat PLA complex viscosity curve at 155 °C at lower frequencies.

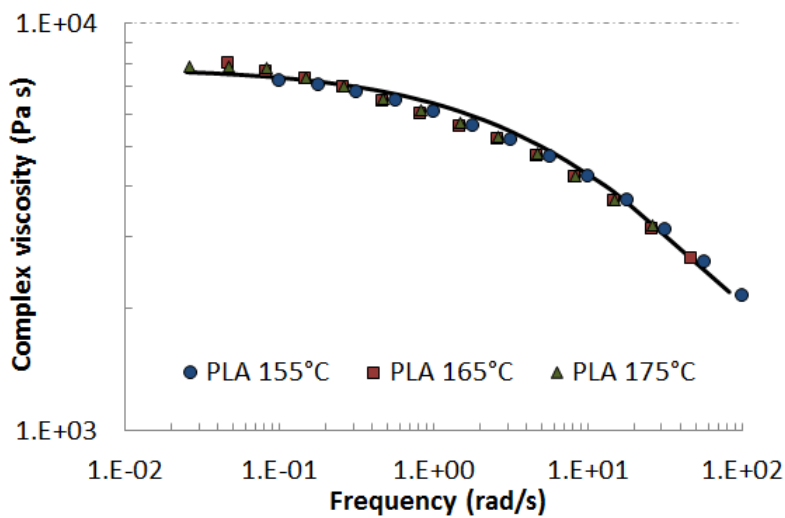


Fig. 8 - Complex viscosity master curve obtained from neat PLA at 155 – 165 – 175 °C fitted with Carreau – Yasuda equation (solid line) Eq. (8).

Indicating with a_T the thermal shift factors, the dependence of a_T on temperature is reported in Tab. 3 and also shown in Fig. 9. These values can be fitted using the Williams-Landel-Ferry equation

$$\log (a_T) = -\frac{C_1(T-T_0)}{C_2+T-T_0} \quad (6)$$

in which C_1 and C_2 are fitting parameters and T_0 is the reference temperature (i.e. 155 °C). A good fitting can be achieved with $C_1 = 1.97$ and $C_2 = 47.93$ °C.

Tab. 3 - PLA thermal shift factors as a function of temperature

Temperature (°C)	Logarithmic thermal shift factor $\log(a_T)$	Thermal shift factor a_T
155	0	1
165	- 0.340	0.457
175	- 0.580	0.263

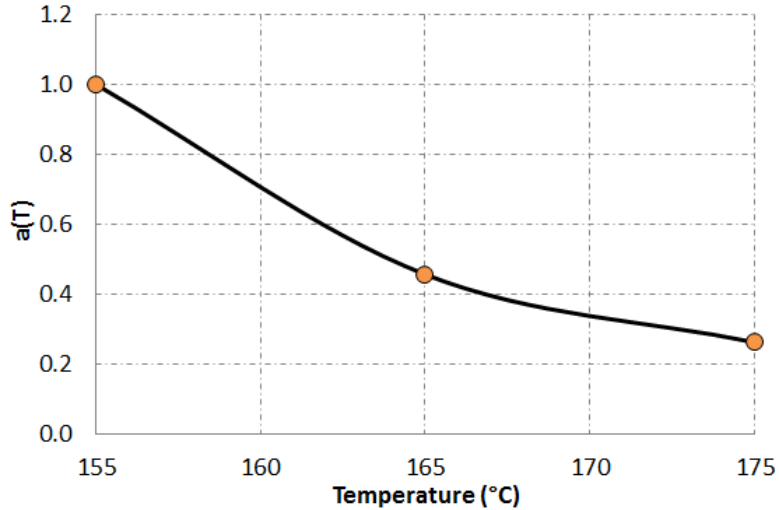


Fig. 9 – Temperature shift factor a_T vs. temperature and curve fitting using Williams-Landel-Ferry Eq. (6).

The same master curve can be obtained by shifting the complex viscosity curves of the three W-PLAs measured at the reference temperature onto the one of neat PLA at the same temperature. Again, the shifting is intended to be diagonal. For the case of wood fiber filled composites this procedure has already been used for PP/wood flour [23, 24] and PE/wood flour [29]. In Fig. 10 it is shown that the master curve is very well fitted by the shifted viscosity curves of the composites. The whole procedure provides a remarkable extension at higher frequencies: comparing Fig. 8 with Fig. 10 it is evident that concentration has a much stronger effect than temperature.

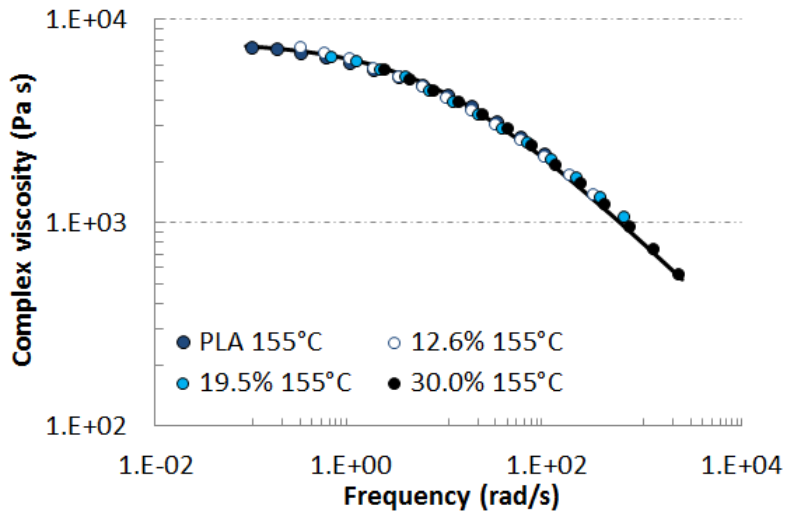


Fig. 10 - Complex viscosity master curve obtained by shifting 12.6 – 19.5 – 30 wt.% W-PLA curves at 155°C onto the neat PLA one. Fitting with a Carreau – Yasuda equation (solid line) Eq. (8).

The concentration shift factor will be indicated with b_ϕ and depends on filler volume fraction ϕ , thus in order to evaluate the dependence of the concentration shift factor on filler content, one must

first transform the mass fractions into volume fractions at the reference temperature, using Eq. (5). The plot of the concentration shift factors as a function of volume fraction is pictured in Fig. 11 and reported also in Tab. 4. The functional dependence can be described by a Krieger – Dougherty equation:

$$b_{\phi} = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-m} \quad (7)$$

where ϕ_{max} is the maximum packing volume fraction and m is supposed to be equal to $\phi_{max} [\eta]$, where $[\eta]$ is the intrinsic viscosity. Very often m assumes a value around 2 for many diverse situations [22], nevertheless it is customary to treat it as a fitting parameter: its value is chosen such that the experimental data can be fitted in a satisfactory way. In the case at hand, Fig. 11 shows that a good fit can be obtained with $\phi_{max} = 0.85$ and $m = 8.816$. Values of the exponent that are higher than 2 are quite common for highly filled materials. In particular, in the case of natural fibers, values around 4 have already been found in the literature [23] and a justification has been given in terms of the very irregular shape and size of the wood particles [24].

The complex viscosity master curve that has been obtained can be fitted with a Carreau-Yasuda equation:

$$\eta_{PLA,155^{\circ}} = \frac{\eta_0}{(1+(\lambda \omega)^c)^{\frac{1-n}{c}}}, \quad (8)$$

the best fit values being $\eta_0 = 7800$ Pa s, $\lambda = 0.14$, $n = 0.54$ and $c = 0.6$. It is shown as a solid line together with the shifted experimental curves in Figs. 8 and 10.

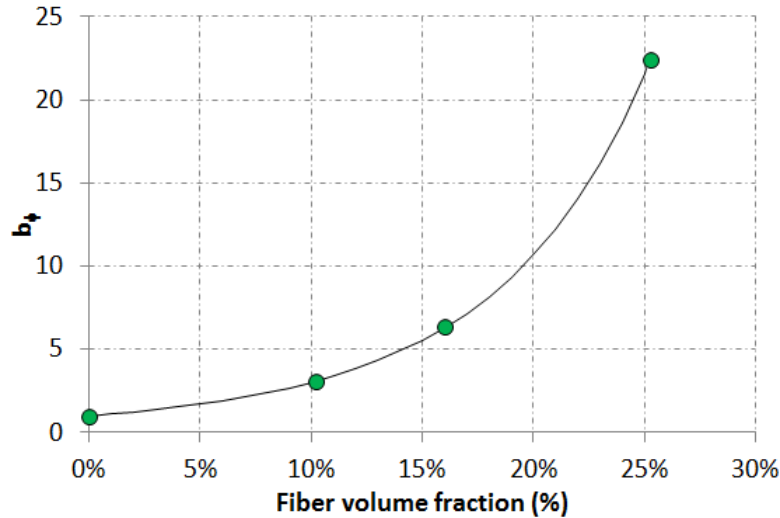


Fig. 11 – b_{ϕ} vs. fiber volume fraction ϕ and curve fitting using Eq. (7).

Tab. 4 – Diagonal shift factor as a function of the filler volume fraction at 155°C

μ mass fraction wt. %	ϕ volume fraction vol. %	Logarithmic concentration shift factor $\log(b_\phi)$	Concentration shift factor b_ϕ
0	0	0	1
12.6	10.2	0.482	3.034
19.5	16.03	0.803	6.353
30.0	25.24	1.350	22.387

So far we have considered only a pure thermal shift factor and a pure concentration one. Mazzanti and Mollica [30] have proposed a methodology to combine together the two pure shift factors for predicting the effect of temperature and filler concentration on the viscosity of the PP/wood flour system. The effect of the two shift factors was assumed to be disjoint, in the sense that they can be composed as if they were occurring separately. From the microstructural viewpoint, a consequence is that the temperature effect on polymer-polymer interactions is assumed to be stronger than the one on filler-filler and filler-polymer interactions.

In mathematical terms, denoting with η_{ref}^* the master-curve, the complex viscosity at any temperature T and filler volume fraction ϕ is

$$\eta^*(T, \phi, \omega) = a_T b_\phi \eta_{ref}^*(a_T b_\phi \omega). \quad (9)$$

In [30], the interest to link temperature and filler concentration effects stemmed from the difficulty of measuring complex viscosity of filled materials at relatively high temperatures, because of an insufficiently large linear viscoelastic region. This methodology has not been validated in the PP/wood system, because it was not possible to study the composites at a temperature other than the reference one [31]. In the present case, the PLA/wood system allows to check for validation using the experimental complex viscosity curves of W-PLA at 165 °C and 175 °C.

In Fig. 12 the complex viscosity curves for all filler concentrations at 165 and 175 °C have been shifted onto the master-curve in a very satisfactory way. The numerical values of the logarithmic experimental shifts $\log(k_{T\phi})$ are reported in Tab. 5. In order to validate the methodology proposed through Eq. (9), the difference between the experimental shift factors $k_{T\phi}$ and the ones determined by composing thermal and concentration shifts as $a_T b_\phi$ must be quantified.

A word of caution must be spent for the calculation of the concentration shift factors. The volume fraction, which is needed to calculate b_ϕ , must be determined at the temperature of interest, not at the reference temperature. Thus, one must first determine the volume fraction ϕ at the desired temperature using Eq. (5). This requires the knowledge of PLA density at the same temperature. Once the volume fraction is known, b_ϕ can be obtained from the Krieger-Dougherty Eq. (7).

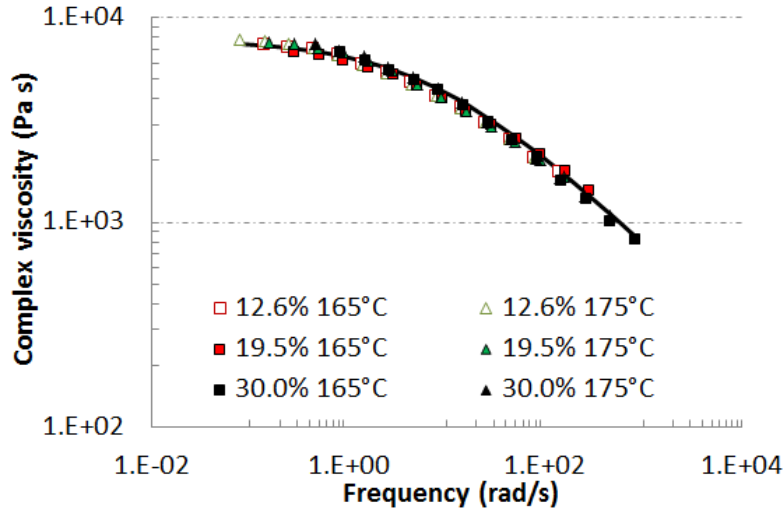


Fig. 12 – Comparison between the master curve and the W-PLA diagonally shifted curves at temperatures other than the reference temperature. Agreement is very satisfactory.

Tab. 5 – Comparison between logarithmic diagonal shift factors as a function of the filler volume fraction and temperature obtained with the proposed methodology and experimentally

	12.6 wt.%			19.5 wt.%			30.0 wt.%		
	Eq. (9)	Experiment	Error	Eq. (9)	Experiment	Error	Eq. (9)	Experiment	Error
	$\log(a_T b_\phi)$	$\log(k_T \phi)$	%	$\log(a_T b_\phi)$	$\log(k_T \phi)$	%	$\log(a_T b_\phi)$	$\log(k_T \phi)$	%
165 °C	0.140	0.135	3.88	0.445	0.440	1.20	0.985	0.905	8.88
175 °C	-0.109	-0.105	3.45	0.191	0.198	-3.46	0.722	0.658	9.79

A useful parameter to evaluate the proposed methodology is the error percentage defined as:

$$\text{Error \%} = \frac{\log(a_T b_\phi) - \log(k_T \phi)}{\log(k_T \phi)} * 100. \quad (10)$$

As can be seen from Tab. 5, the difference is very small, especially at lower volume fractions. In any case, maximum discrepancy is below 10%, which can be considered a good validation.

The temperature range that has been investigated is bounded from below by the PLA melting temperature and from above by the W-PLA thermal stability evaluated through time sweep testing. As this range is only 20 °C wide, the described shifting procedure may suffer of lack of generality. One can be confident that results are accurate only if interpolating within the temperature range that was investigated.

CONCLUSIONS

In this article, W-PLAs at various wood fiber content and temperatures have been characterized at the parallel plate rheometer in oscillatory mode. The main result is that the complex viscosity curves of all materials collapse onto a single master curve by shifting them diagonally in a bi-

logarithmic plot. The master curve corresponds to the complex viscosity of the neat matrix at a specified reference temperature. This master-curve can be used to predict the complex viscosity of W-PLA for any temperature and concentration, using the thermal shift factors of neat PLA combined with the concentration shift factors of the W-PLAs at the reference temperature. This is true at least within the bounds that have been investigated. The main assumption at the basis of the proposed methodology is no interaction between temperature and concentration effects. From the good comparison between experimental and theoretical predicted data, one can conclude that this assumption is verified within a reasonable experimental uncertainty.

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