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Rheological and mechanical characterization of PP-based Wood Plastic Composites

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Abstract

The aim of this paper is to investigate the influence of filler content and temperature on the rheological, mechanical and thermal properties of wood flour polypropylene composites (WPCs). Testing WPCs at high temperatures and percentages of filler is extremely challenging because of reduced linear viscoelastic region, high viscosity and degradation. In this work a complete characterization of WPCs with different filler percentages (0 – 70%wt.) has been made. Rheological tests are performed at 170°C for the WPCs and in the 170 - 200°C range for neat PP. A single master curve is obtained using two shift factors that can be described by a modified Eilers model and a Williams - Landel - Ferry equation. This mastercurve, fitted with a Carreau – Yasuda model, can be very useful for predicting the viscosity of WPCs at temperatures that are typically used during processing and for any percentage of filler.

Keywords

Wood plastic composites (WPC), Polypropylene, Rheology, Mechanical properties, Thermal properties

1. Introduction

In recent years Wood Plastic Composite (WPC) has attracted great interest in decking, fences, indoor furniture and outdoor building products. This material is a polymer filled with natural fibers of ligno - cellulosic origin and can be a convenient substitute for wood or plastics.

The presence of the polymeric matrix imparts several advantages with respect to natural wood. WPC products can be manufactured in complex shapes easily and rapidly using forming techniques typical of plastics, such as extrusion and injection molding. For instance, WPC can be extruded as solid or hollow boards with an engineered design. At the same time, profiles can also be shaped using conventional woodworking tools like saw and drill. Coloring can be obtained quite easily through pigmentation, hence painting is not necessary, although possible. Moreover, thanks to

the hydrophobic character of the polymer, WPC products require less maintenance than wood, especially in terms of a better durability in wet environment. Aesthetics and mechanical properties are not as good as natural wood, but if compared to other engineered wood products, such as Middle Density Fiberboard (MDF) or particleboard, WPC performs better. Lastly, WPC is recyclable like all thermoplastics: although it may be difficult to reprocess, Viksne and Rence [1] and Shahi et al. [2] have found that the mechanical properties don't decay too much with the number of reprocessing cycles.

With respect to plastics the main advantages are low cost and reduced environmental impact due to the presence of the cheap natural fibers that can be obtained out of waste materials produced locally. In order to achieve maximum cost reduction and sustainability, WPCs should be made using recycled plastics [3] and the filler quantity maximized to limit the usage of the more expensive polymer. This motivates the interest towards highly filled WPC. In fact, high percentage loadings (50%wt. or more) are commercially available, especially for extrusion grades WPC. Moreover, if compared to glass fibers and ceramic powders, natural fibers have lower density and are less abrasive: the composite is thus comparably lighter and wear of processing machineries is reduced.

Nevertheless WPC has several drawbacks. First of all, the hydrophilic natural fibers are incompatible with the hydrophobic polymeric matrix: fiber - fiber interaction is preferred to fiber - matrix interaction, and this leads to agglomeration and reduced dispersion of the fibers. Macroscopically it results in mixing problems but also in lower mechanical properties due to the weak nature of the fiber - matrix interface.

Improving the mechanical behavior is an important research topic. Many papers deal with coupling agents (e.g. maleic anhydride modified polymers) to increase the adhesion between polymer and natural fibers [4 – 11]: the mechanical properties generally increase with the amount of coupling agent up to a certain threshold value. The length and orientation of the fibers are parameters that play an important role in the mechanical performance, as noted by Migneault et al. [12] and Beckermann and Pickering [13], with properties increasing with the fiber length. Also, activating the wood surface with chemical modification agents (silanes, alkali, isocyanate, ester) [8, 14 – 17] for decreasing fiber hydrophilicity has a positive effect on mechanical properties as well as reducing the filler - filler interaction (silica fillers) [17, 18].

Another negative consequence of the natural fibers hydrophilicity is moisture absorption, which causes swelling and distortion as well as fiber pull out in the finite products, but also during processing there are absorption related problems, like water

vapor cavities formation and the consequent decay in the mechanical properties of the material. This effect is clearly more severe for high fiber content. In order to prevent these difficulties, it is necessary to dry the material before processing and, in the case of extrusion, to use a venting zone equipped extruder.

The major limitation of the materials filled with natural fibers, though, is oxidative degradation during processing. Natural fibers are mainly composed of lignin, hemicellulose and cellulose. The starting degradation temperatures of these components are 110°C, 196°C and 255°C, respectively [19 - 21]. It is commonly assumed that the processing temperature should not exceed 200°C and this in turn reduces the choice of the polymers that can be used as matrix (usually polyolefins and polyvinylchloride). In any case, the processing window is narrow because it is limited not only by the thermal stability of the fibers but also by the melting temperature of the polymer.

If the material is processed at a temperature close to the melting temperature, the viscosity of the neat polymer can be considerably high and the presence of large quantities of filler increases the viscosity even further. Thus, WPC processing generally requires more power and the localized heating induced by viscous dissipation can worsen degradation problems. Therefore, although high natural fiber percentage is desirable to achieve sustainability and low material cost, processing may become a challenging task.

In order to gain a better control on the many processing variables it is necessary to characterize the material from the rheological point of view. The number of papers dedicated to the rheological characterization of natural fiber filled composites is increasing, and this testifies the interest towards these materials. If polyethylene (high density polyethylene or HDPE) is used as matrix, thermal stability is a less critical issue due to the melting temperature (about 135°C) that is much lower than natural fiber degradation. Many authors, in fact, have studied the rheological properties of HDPE - based WPC, even with a high percentage of filler. Li and Wolcott [22] and Carrino et al. [23] have studied the shear flow of HDPE - based WPC using capillary rheometry with a particular attention to wall slip phenomena and surface tearing. Hristov et al. [24, 25] have also used capillary rheometry measurements with extrudate distortions evaluations, in conjunction with rotational rheometry performed in oscillatory mode. Other authors [14, 26, 27] have characterized the viscosity of HDPE - based WPC with the rotational rheometer varying the filler concentration. In particular, Godard et al. [27] obtained a mastercurve valid for a wide range of filler concentrations (0%wt. - 60%wt.)

and fitted it using a Carreau – Yasuda model. The curve of the shift factor as a function of concentration was fitted with a Krieger – Dougherty equation, which is one of the most widely used models for concentrated suspensions.

Polypropylene (PP) has a melting temperature that is higher than polyethylene by 30°C at least. The processability range is thus only about 20°C wide (180°C - 200°C), and this makes processing particularly difficult at high fiber volume fractions. Nevertheless, the mechanical properties of PP - based WPC are generally higher than HDPE - based ones, as can be seen by comparing the main results of papers dealing with HDPE - based WPC [4, 6, 14, 28 - 30] with those dealing with PP - based WPC [5, 31, 32]. In particular, Englund et al. [33] make a comparison between the mechanical properties of various polymer matrix WPCs and find that among PP, PVC and HDPE, PP - based ones offer a good compromise between adequate strength and stiffness and good ductility.

The ease of degradation of PP – based WPC (from now on PP-WPC) may prevent getting a good quality product, but can also invalidate the results of material characterization, since the material may be kept at high temperatures in the presence of oxygen for long times. Such a drawback, in principle, can be solved by reducing the testing temperatures and performing tests in controlled atmosphere or in vacuum. Capillary viscometry can be used in this way, but it is well known that measurements on wood filled materials are affected by extensive wall slip [23, 34 - 36] and other flow instabilities [24, 25] that may render the experimental procedures more difficult. Moreover, highly filled materials display too high a viscosity for capillary flow. Another possibility is to characterize the material in oscillatory mode, thus obtaining the flow curve using the Cox – Merz rule but one must ensure that the material be loaded within the linear viscoelasticity range (LVR). This is difficult, because the testing temperature must be anyway sufficiently low and it is known that at high filler contents the LVR size is reduced [25]. It is thus clear that characterizing this material at the usual processing temperatures may be very difficult.

Perhaps for this reason rheological properties of PP-WPC have been measured only in a few papers, usually with moderate filler content. Maiti et al. [37] have studied the shear flow of i-PP - wood fiber composites at 220°C using capillary rheometry, with a fiber concentration between 0 – 32.2 vol %. Marcovich et al. [38] have investigated the behavior of PP-WPC (0 – 50%wt. wood content) at 200°C with a parallel plate rheometer in oscillatory mode. The dynamic moduli were scaled with respect to the filler content with horizontal shift factors obtaining a single master curve, that has been

modeled using a generalized Maxwell model. Azizi and Ghasemi [39] have investigated the properties of PP-WPC at 190°C using a parallel plate rheometer relating the complex viscosity to wood and coupling agent content (0 – 60%wt. and 0 – 4% respectively). Soury et al. [30] have studied PP-WPC at three different wood contents (50 – 60 – 70%wt.) and at two temperatures (175 - 195°C) using a rotational rheometer generating a large body of interesting experimental data, but fail to show their results in a clear graphical format. Ares et al. [40] have investigated the effect of recycled PP on the rheological properties of PP-WPC at 200°C with a 0 – 30%wt. wood filler content. Other authors, like Gonzàles - Sànchez et al. [41] and Le Moigne et al. [34] have studied PP based composites with different type of filler other than wood i.e. kraft pulp and molten flax, respectively.

In this work we will characterize PP-WPC in oscillatory mode in nitrogen atmosphere and at low temperature (170°C), in order to gain reliability of the measured quantities. The flow curves at higher temperatures, that are more useful for processing, will be estimated by mathematical modeling, using a master-curve obtained from measurements on WPCs at various fiber volume fractions (0%, 30%, 50% and 70% wt.) and on neat PP at various temperatures (170°C, 180°C, 190°C and 200°C).

The rheological characterization will be completed with capillary viscometer measurements. Static and dynamic mechanical properties will also be measured to verify the quality of the final product, while thermal measurements, using differential scanning calorimetry, are convenient for assessing degradation during characterization and for obtaining information on the material.

The paper is organized in the following 5 sections. Section 2 deals with the description of the material and the samples preparation, while Section 3 details the experimental procedures of thermal, rheological, optical and mechanical tests. Section 4 lists the results which are discussed in Section 5, where the master-curve at various fiber volume fractions and temperatures is obtained. In the last Section 6, the conclusions are drawn and future developments are introduced.

2. Material:

Commercial wood-flour polypropylene composites (WPC) have been purchased from PlasticWOOD S.r.l., Mazzantica di Oppeano (VR), Italy. The materials used for the study contain 30, 50, and 70% natural fibers in mass from white fir. The 30% wt. (commercial name PP 30 S) and the 70% wt. (commercial name PP CO 68/BZ) have been acquired from the producer as compounds, while the 50% wt. has been obtained by processing the two commercial compounds in equal weight percentage, as

described below. The producer has also supplied the neat polypropylene (PP) used as the matrix of the composites. The bulk density, as declared by the producer, is 909 kg/m³ for neat PP, 1067 kg/m³ for the 30% wt. WPC and 1183 kg/m³ for the 70% wt. WPC. The bulk density for the 50% wt. (1125 kg/m³) is the average of the two commercial compounds. In Tab. 1 length, diameter and L/D ratio of the fibers are listed.

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

Length (μm)	Diameter (μm)	L/D
166.1	16.0	10.2
(65.1)	(2.5)	(3.1)

2.1 Samples preparation

Neat PP, 30% wt. and 70% wt. WPC samples are produced either from pellets directly or from extruded profiles, while 50% wt. WPC samples are obtained only from extruded profiles by mixing 30% wt. and 70% wt. in equal percentages. The extruded profiles are produced using a single screw extruder (P.R.T. SERVICE & INNOVATION S.r.l., Sant'Agostino (FE), Italy) with a screw diameter of 50 mm and L/D ratio of 40. The extruder is equipped with a breaker to improve compaction and with a venting zone to help degasification of water vapor. The die is a 50 x 3 mm slit (Fig. 1). During extrusion, a uniform temperature distribution of 190°C has been maintained along the barrel, while the die temperature has been set at 180°C and the screw speed at 60 RPM. All samples have been dried at 90°C in a vacuum oven for 12 hours to reduce the moisture content prior to testing.

3. Experimental procedures

3.1 Degradation of natural fibers

Wood fibers have a low thermal resistance, therefore it is necessary to prevent degradation during measurement. The phenomenon of thermal degradation depends not only on temperature but also on residence time, therefore it is interesting to evaluate the behavior of WPC at a fixed high temperature for a long time. Only the 70% wood flour WPC has been tested because it is the one that would degrade most easily. A differential scanning calorimeter test using a DSC 823 (Mettler Toledo) under a nitrogen atmosphere has been performed in isothermal conditions to investigate, as a function of time, the degradation of samples obtained from extruded profiles. The temperature has been increased from 25 up to 180°C at a heating rate of 20°C/min,

kept at 180°C for 60 minutes and finally decreased down to room temperature at 20°C/min.

A time sweep measurement under a nitrogen atmosphere has been performed using a strain controlled rheometer (ARES, TA Instruments) to evaluate the thermal stability of the samples during the rheological measurements. The temperature has been set at 180°C, the frequency at 3 rad/s and the shear strain at 0.2%. Maintaining these parameters constant, the dynamic shear moduli and the torque have been monitored for 35 minutes.

3.2 Thermal characterization

All calorimetry measurements (DSC 823 Mettler Toledo) have been carried out under nitrogen atmosphere. The DSC scans have been performed on 6 - 10 mg samples contained in aluminum sealed pans.

In the ramp test neat PP and WPCs have been analyzed to measure their thermal properties. Compound pellets have been used for the tests. The sample temperature has been increased from 25°C up to 220°C at a heating rate of 10°C/min and held in the molten state for 5 min to erase the thermal history of the specimens and to eliminate residual moisture and voids. After being cooled at 10°C/min down to room temperature, the samples have been reheated to 220°C at 10°C/min. The crystallization temperature, melting temperature, specific heat capacity, melting and crystallization enthalpy have been obtained from the cooling and the second heating scan.

3.3 Rheological characterization

3.3.1 Parallel plate rheometer

The rheological characterization has been performed with a smooth surfaces parallel plate rheometer (ARES, TA Instruments) in dynamic oscillation and strain controlled mode. The samples in the form of 25 mm diameter disks have been cut from extruded profiles using a punch cutter.

The disk specimens have been placed between the parallel plates with a 2.5 mm gap to carry out the rheological measurements. Three types of rheological experiments have been done on WPC specimens: time, strain and frequency sweep, all of them under nitrogen atmosphere at 170°C. For neat PP the strain and frequency sweeps have been performed also at different temperatures, i.e. 170, 180, 190, 200°C.

In the strain sweep test the response of the material to increasing strain amplitudes has been measured at constant frequency and temperature. This experiment allows to

determine the linear viscoelastic region (LVR) of the materials, which is important for performing the frequency sweep test correctly. For each material three different frequencies (1, 3, 10 rad/s) have been evaluated and the shear strain has been in the 0.02% – 5% range.

In the frequency sweep test it is possible to observe the response of the material as a function of frequency at constant strain and temperature. The strain value is chosen within the LVR. Different strain values have been chosen for the experiments, i.e. 0.01%, for the WPC 50% wt. and WPC 70% wt., 0.02%, for the WPC 30% wt. and 5% for neat PP. The frequency has been varied between 0.1 and 100 rad/s. The storage modulus G' and the loss modulus G'' can be measured as a function of frequency. These values are used to calculate the damping factor:

$$\tan \delta = \frac{G''}{G'} \quad (1)$$

and the complex viscosity:

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

where ω is frequency.

3.3.2 Capillary rheometry

A capillary rheometer (RHEOTESTER 1500 - GÖTTFERT) has been used to study the shear flow behavior directly. The barrel of the rheometer has a 12 mm diameter reservoir and an effective working length of 200 mm. A mercury-filled pressure transducer of 0.2% precision with a 1000 bar full-scale has been used to measure the pressure drop. The transducer is located above the capillary die entrance. The tests have been set up using different values of the piston velocity in the range 0.01 - 5 mm/s.

Only two materials have been tested, i.e. neat PP and the WPC 30% wt. A smooth tungsten carbide die with 1 mm diameter has been used for neat PP, while for the 30% wt. WPC a rough tungsten carbide die with 2 mm diameter has been used. All measurements have been made at 170°C. Once the pressure drop ΔP is measured, knowing the geometry and the speed of the piston it is possible to calculate the wall shear stress τ_w and the apparent shear rate $\dot{\gamma}_a$ as follows:

$$\tau_w = \frac{\Delta P R}{2 L} \quad (3)$$

$$\dot{\gamma}_a = \frac{4 Q_m}{\pi R^3} \quad (4)$$

where Q_m is the volumetric flow rate, R and L are the radius and length of the die, respectively. Three different capillary lengths (10, 20, 30 mm) have been used in each capillary measurement to correct for entrance effects using the Bagley procedure.

3.4 Scanning Electron Microscopy (SEM)

WPC samples with 30% wt. and 70% wt. wood fiber content have been fractured from an extruded profile. The x - direction corresponds to the extrusion direction while the zy - plane is the cross section (Fig. 1). Two fracture surfaces have been observed: one obtained from the xy - plane and the other from the zy - plane.

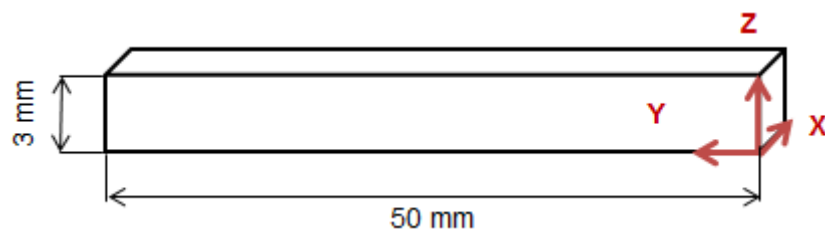


Fig. 1 - Extruded profile geometry

The ZEISS EVO MA 15 scanning electron microscope (SEM) has been employed to characterize the morphology of the composites.

3.5 Mechanical characterization

3.5.1 Static mechanical analysis

The mechanical measurements have been performed in tension on a universal testing machine (INSTRON 4467) at room temperature. All samples have been obtained from extruded profiles and have been loaded in the extrusion direction.

The tests have been performed according to the EN ISO 527-1 standard at 2 mm/min crosshead speed and with a 500N load cell. Five dog bone samples have been tested for each material and the average values of the relevant mechanical parameters (Young's modulus and yield strength) and their standard deviations have been reported.

3.5.2 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis has been conducted in simple tension mode using the RSAIII (TA instrument) to carry out the tests. All specimens have been obtained from extruded profiles. Specimens dimensions are 2 x 2.5 x 43 mm and have been determined on the basis of the recommended size range suggested by the instrument manufacturer. Each sample has been clamped at its top and bottom and placed in tension. Dynamic temperature scans have been made from 25°C up to 200°C, with a heating rate of 2°C/min. The frequency used has been 1 Hz. The E' and E'' moduli have been measured as a function of temperature.

4. Results

4.1 Wood fibers degradation

Tests for evaluating wood fibers degradation have been performed first. In Fig. 2 the heat flow is reported as a function of time for the 70% wt. WPC. The thermogram shows an endothermic peak due to melting, after which the heat flow remains constant until the exothermic peak of the cooling phase appears. The constant heat flow during the 60 minutes in which the material is kept at 180°C shows that the material does not degrade in the conditions at which the test was performed.

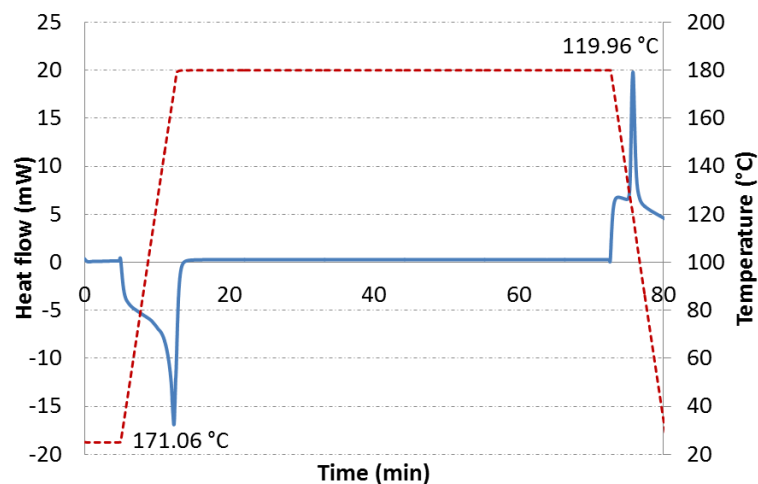


Fig. 2 - Heat flow (continuous blue line) and temperature (red dotted line) as a function of time for the 70%wt. WPC

In Fig. 3 the torque and the loss and storage moduli are reported as function of time. It is evident that a stable plateau is reached during the test, thus the 70% wt. WPC does not degrade for the whole duration of the test.

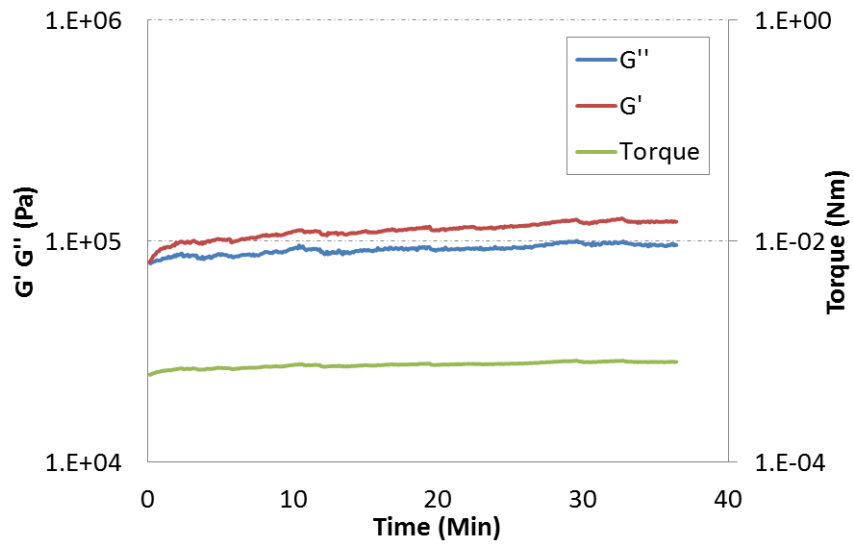


Fig 3 - G' , G'' and torque as a function of time for the 70% wt. WPC at constant strain and frequency to evaluate the possibility of degradation during rheological tests.

4.2 Thermal characterization

The neat PP DSC curves are reported in Fig. 4. The melting and crystallization peaks are clearly visible; a second order transition is also present and located at around 110°C in heating (around 80°C in cooling). In Table 2 the relevant thermal parameters are listed: solid and liquid specific heat capacity (c_{p_s} and c_{p_l} respectively), crystallization and melting enthalpy (ΔH_c and ΔH_m respectively), crystallization and melting temperature (T_c and T_m respectively), for neat PP and all WPCs.

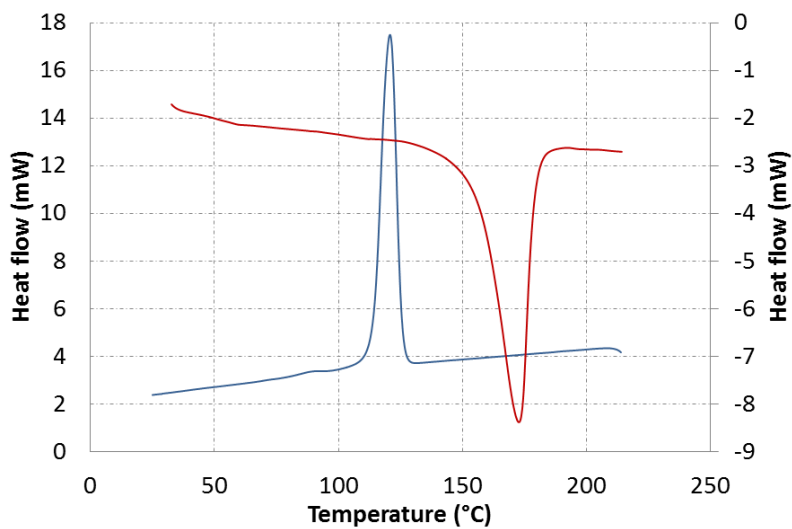


Fig. 4 - DSC thermograms of neat PP in the “as received” granule form. Cooling (blue line) and second heating (red line).

Tab. 2 - Thermal properties of PP and WPCs measured with the DSC.

Thermal properties	PP	30% wt.	50% wt.	70% wt.
cp_s (J/kg/°C)	1961	1653	1443	1230
cp_l (J/kg/°C)	1924	1727	1516	1354
ΔH_c (kJ/kg)	78	45	35	29
ΔH_m (kJ/kg)	76	36	29	21
α_{PP} (%)	36.7	25.0	27.8	31.0
T_c (°C)	122.5±0.2	124.8±0.2	125.6±0.2	126.1±0.2
T_m (°C)	165.1±0.2	165.8±0.2	165.7±0.2	165.6±0.2
T_g (°C)	- 20.24±0.2	//	//	//

Cristallinity α_{PP} is obtained as the ratio of the melting enthalpy of the specimen ΔH_m , calculated using only the weight of the PP, and the latent heat of fusion of a pure polypropylene crystal, assumed to be $\Delta H_0 = 207\text{J/g}$ [42]:

$$\alpha = \frac{\Delta H_m}{\Delta H_0} \quad (5)$$

4.3 Mechanical characterization

The tensile strength σ_y , stiffness E (Young's modulus) and density ρ for each compound are reported in Tab.3. In Fig. 5 a representative stress strain curve in tension is shown. All WPCs show brittle behavior.

Tab 3. - Mean and standard deviation (in parentheses) of static mechanical properties and density of WPC with different percentages of filler

Material	Tensile properties		Density ^a
	σ_y (MPa)	E (GPa)	ρ (kg/m ³)
70% wt.	16.8 (0.8)	5.6 (0.5)	1183
50% wt.	18.3 (0.9)	4.1 (0.5)	1125
30% wt.	16.6 (0.5)	3.6 (0.7)	1067
0% wt.	19.9 (0.8)	0.9 (0.02)	909

^a Data supplied by the producer

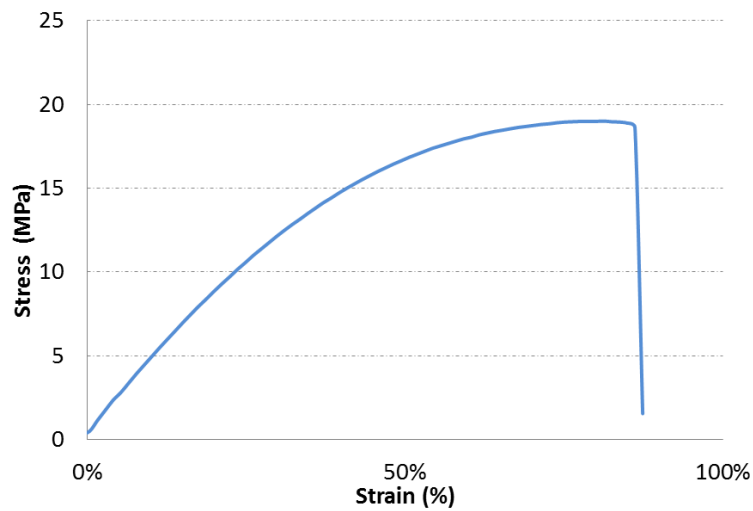


Fig. 5 - Typical stress-strain curve for the 50% wt. WPC during tension tests.

The storage modulus (E'), loss modulus (E'') and damping factor ($\tan \delta$) of WPCs have been measured as a function of temperature (25°C up to 200°C). The moduli precision is $\pm 1\%$. Fig. 6 shows the plot of E' as a function of temperature for each of the WPCs and neat PP. The storage modulus decreases with temperature. The moduli of the WPCs show no important variations with the addition of the fibers, although the 70%wt. has a more stable behavior after melting. The neat PP storage modulus is lower than the WPCs moduli.

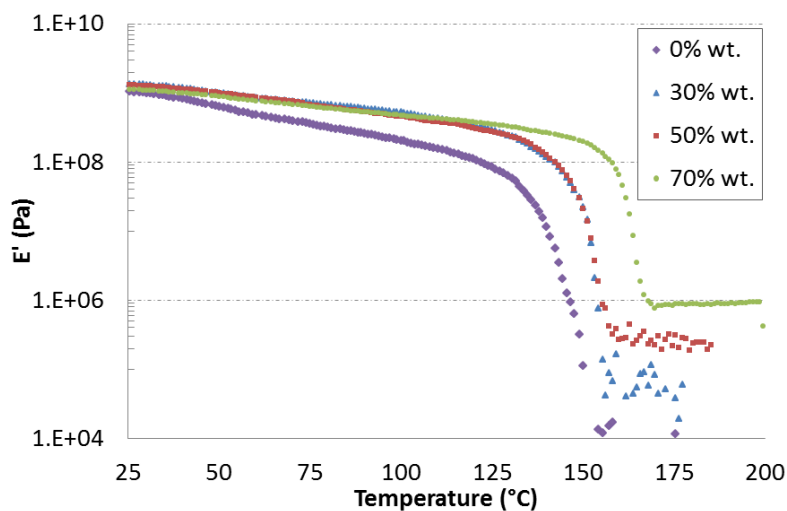


Fig. 6 - Storage modulus (E') as a function of temperature for different percentage of fibers WPC and neat PP.

In Fig. 7 $\tan(\delta)$ is plotted as a function of temperature. The curves of all materials increase with temperature. A relaxation peak is observed around 70 - 80°C. The increase in the fibers percentage shifts this relaxation peak to higher temperatures.

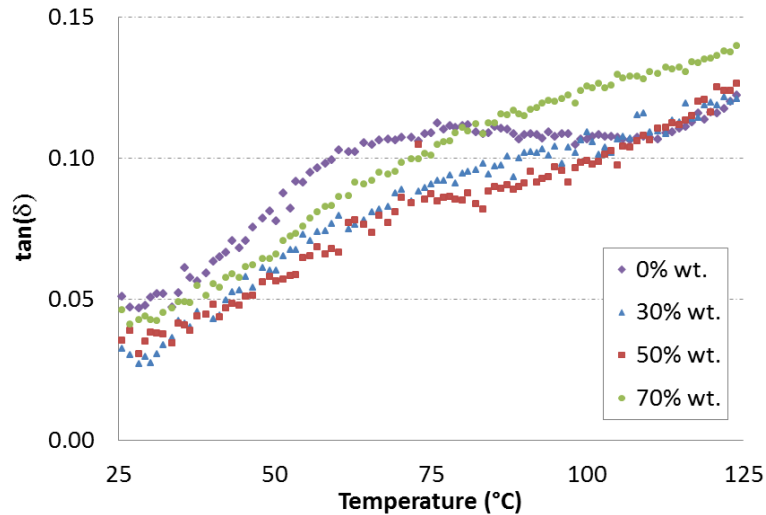
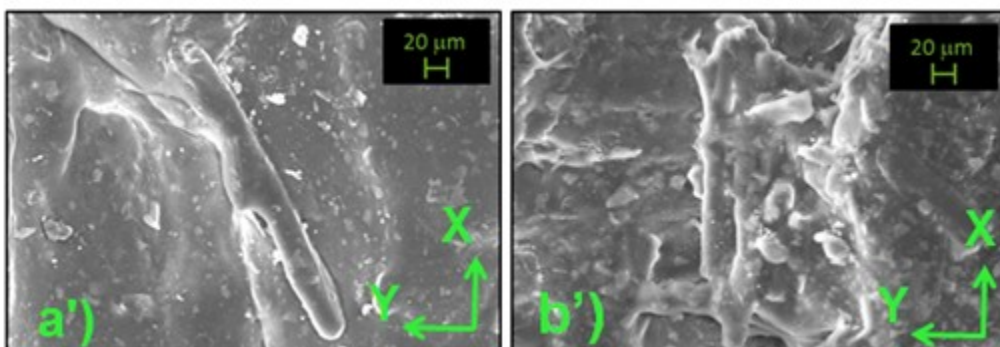


Fig. 7 - Mechanical loss factor ($\tan(\delta)$) as a function of temperature (25 – 125 °C) for different WPCs and neat PP.

4.4 Scanning Electron Microscopy (SEM)

Fig. 8 shows the SEM micrographs of fractured surfaces of (a) 30% wt. and (b) 70% wt. WPC. The x - direction corresponds to the extrusion direction, while the zy - plane is the cross section. The SEM images show a good interfacial bond and compaction between fibers and the PP matrix. There are no voids or pull-out traces within the structure. The 30% wt. WPC shows a relatively smoother surface with respect to the 70% wt. WPC.



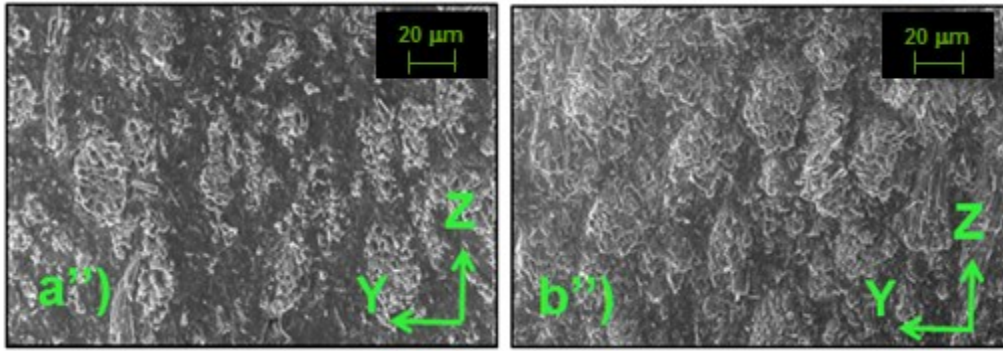
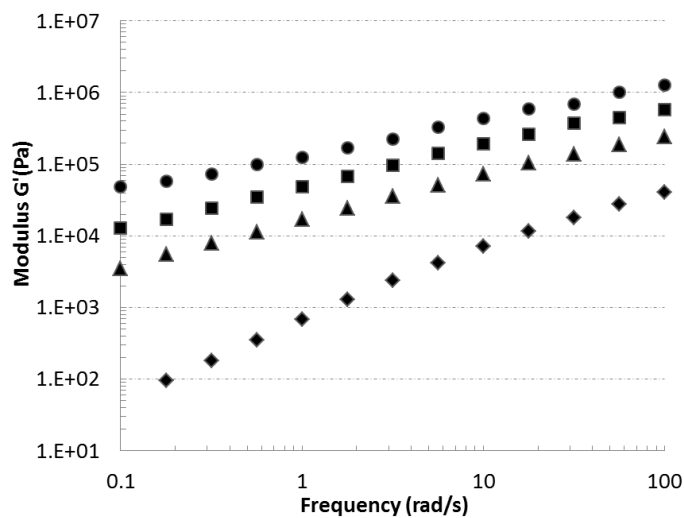


Fig. 8 - SEM micrograph of a') 30% wt.in the extrusion direction, a'') 30% wt.in the cross section direction, b') 70% wt. in the extrusion direction and b'') 70% wt. in the cross section direction.

4.5 Rheological characterization

4.5.1 Rotational rheometry

The measurements of the WPC samples have been performed in the linear viscoelasticity region at 170°C. Fig. 9 provides the storage and loss moduli as a function of frequency. Both moduli increase with the percentage of fibers and with frequency. At low frequencies neat PP and all WPCs show a liquid viscoelastic behavior ($G'' > G'$), at higher frequencies that of a viscoelastic solid ($G'' < G'$). **The crossover between G' and G'' shifts at lower frequencies as the wood fiber percentage increases. Unlike neat PP, the WPCs show storage and loss moduli that are always of the same order of magnitude.**



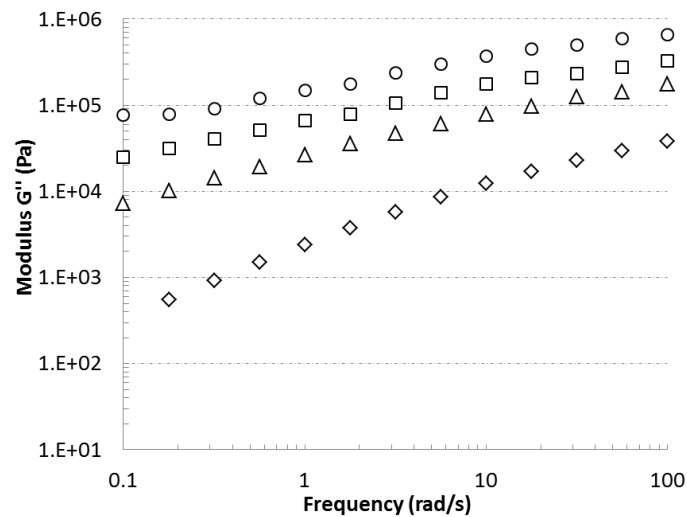


Fig. 9 - G' (black) and G'' (white) as a function of the frequency of neat PP (diamond), 30% wt. (triangle), 50% wt. (square) and 70% wt. (circle).

The effect of natural fibers on complex viscosity at 170°C is presented in Fig. 10. Complex viscosity increases with the percentage of fibers. All materials show a shear-thinning behavior, but neat PP has a Newtonian plateau at low shear rates. Increasing the temperature the viscosity of neat PP (Fig. 11) decreases keeping the same qualitative behavior.

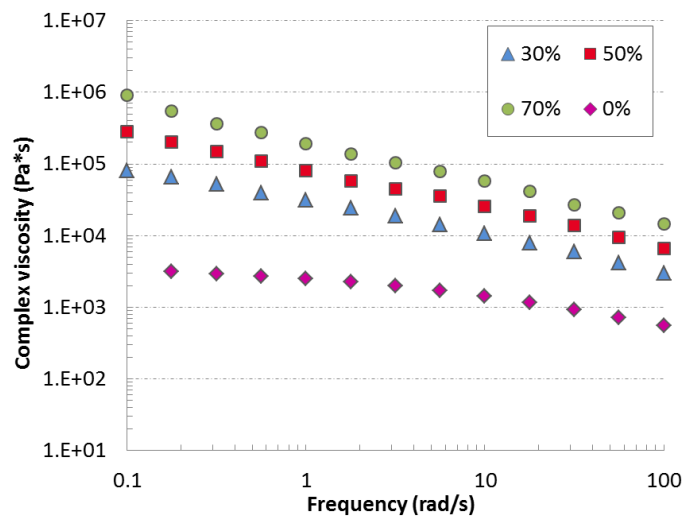


Fig. 10 - Complex viscosity as a function of frequency for different percentages of fibers.

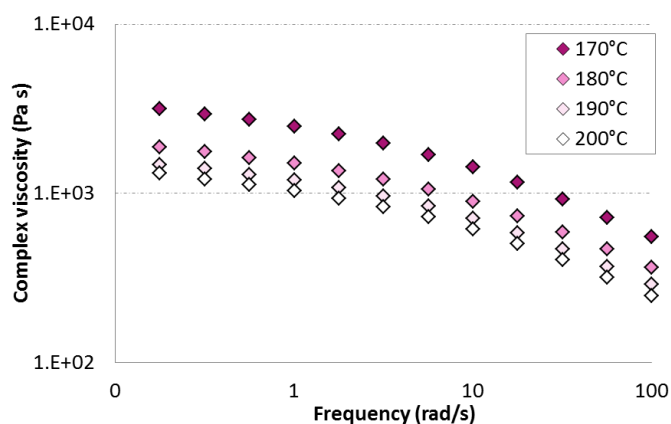


Fig. 11 - Complex viscosity of neat PP as a function of frequency at various temperatures.

4.5.2 Capillary viscometry

Shear viscosity vs. shear rate at 170°C for neat PP and 30% wt. WPC is presented in Fig. 12. The range of apparent shear rate examined is 12 – 3456 s⁻¹ for neat PP and 1 - 432 s⁻¹ for the 30% wt. WPC. The shear viscosity decreases with shear rate, confirming the shear-thinning behavior that was already observed in the rotational rheometry tests. The $\tau(\dot{\gamma}_a)$ data has been treated following the Rabinowitch procedure to obtain the shear viscosity data corrected for shear thinning effects. The shear viscosity range is 10² - 10⁴ Pa s for neat PP and 10¹ - 10³ Pa s for the 30% wt. WPC. At low strain rates it is possible to appreciate the beginning of the Newtonian plateau in the neat PP specimen.

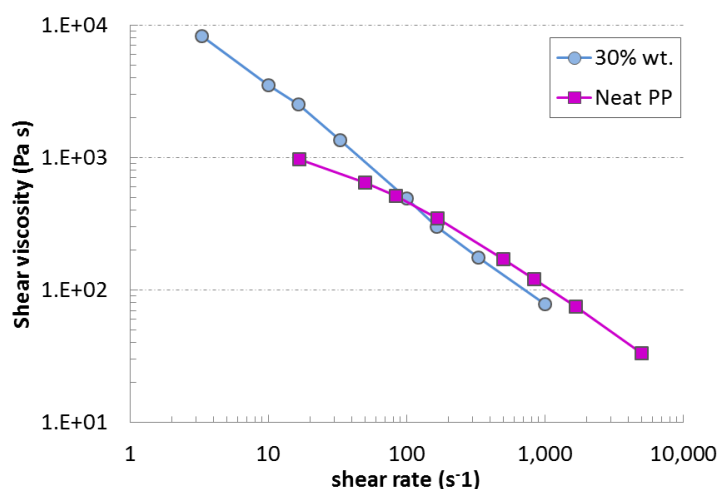


Fig. 12 - Shear viscosity as a function of shear rate at 170°C for neat PP and 30% wt. WPC.

The shear viscosity from the capillary rheometer and the complex viscosity from the parallel plate rheometer of neat PP and the 30% wt. WPC are shown together in Fig. 13 and Fig. 14. For neat PP the two viscosities match perfectly in the region where data from both rheometers are available. The 30% wt., on the other hand, shows a shear viscosity from capillary measurements that is consistently lower than that obtained with the rotational rheometer.

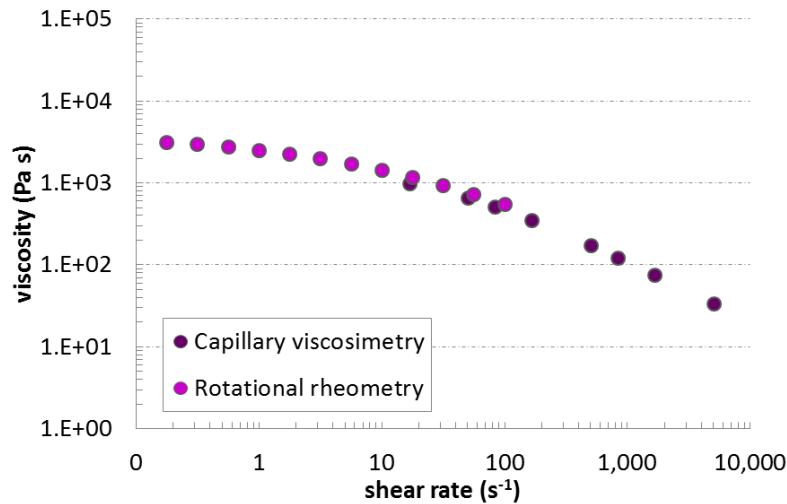


Fig. 13 - Complex viscosity obtained from rotational rheometry and shear viscosity obtained from capillary measurements for neat PP

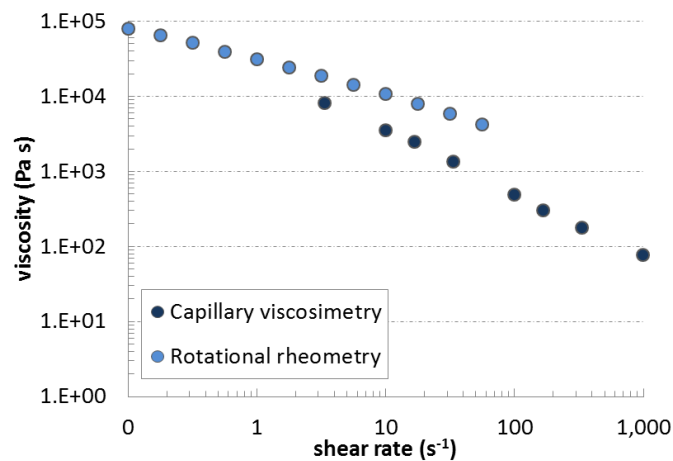


Fig. 14 - Complex viscosity obtained from rotational rheometry and shear viscosity obtained from capillary measurements for 30% wt. WPC

5. Discussion

An important starting point to study the thermal, mechanical and rheological properties of WPC is to exclude wood degradation during testing. Degradation is a phenomenon

that depends on temperature, residence time and presence of oxygen. For this reason a nitrogen atmosphere has been always used, but this may not be sufficient to solve the problem completely: many samples have been prepared using extruded profiles and it is not possible to exclude the presence of oxygen within the samples, for example caught within voids or in areas that were not fully compacted during extrusion. Neglecting lignin degradation, thermal degradation of natural fibers occurs as a two-stage process at two different temperatures: hemicellulose degradation starts at 195°C while cellulose at 255°C, as reported by Bouafif et al. [20]. The temperature of hemicellulose degradation onset is commonly assumed as the upper limit for WPC processing and has also been chosen as the maximum temperature for testing.

The results presented in Figs. 2 and 3 confirm the reliability of the tests used to characterize the material. In Fig. 2 the constancy of the heat flow is an indication that natural fibers do not degrade at the testing temperature and for the whole duration of the test: exothermal peaks would be present if degradation occurred. Thermal stability is also clear from Fig. 3 where loss and storage moduli and torque as a function of time for the 70% wt. WPC are reported. The values are basically constant during the period of testing. In particular, the time (35 minutes) and temperature (180°C) of the test were greater than those of any subsequent test on WPC samples.

In order to define the test temperature, it is necessary not only to know the upper limit temperature, where the measurements are unaffected by degradation, but also the lower limit, i.e. the melting temperature of the compounds. The DSC tests are used to find the melting temperature, which is the same for all materials (165°C). This value is in agreement with typical values for PP. In the DSC curves of PP it is possible to appreciate two melting and crystallization peaks: these indicate that the PP that is used as the matrix of WPC is a block copolymer; the secondary peak, being centered at around 135°C in heating, probably indicates the presence of ethylene as a comonomer. Moreover, it is possible to barely appreciate a second order transition around 60 – 80 °C. The thermal properties of the WPCs and neat PP are listed in Tab. 1. The solid and liquid specific heat capacity decrease by increasing the filler content. The specific heat capacity of neat PP at the melting temperature was 1966 J/kg/°C, in general agreement with the theoretical value of 1900 J/kg/°C [43]. Knowing the specific heat capacity of neat PP ($c_{p,PP}$), of the WPCs ($c_{p,WPC}$) and the mass fractions of fibers (x_f) and matrix (x_{PP}), it is possible to estimate the specific heat capacity of the natural fibers ($c_{p,f}$) using the rule of mixtures as follows:

$$c_{p,WPC} = x_f c_{p,f} + x_{PP} c_{p,PP} \quad (6)$$

The three specific heat capacities of the natural fibers, calculated in this way from each of the WPCs, coincide and are equal to 920 J/kg/°C, in agreement with literature values [44]. The WPCs crystallization degree is lower than the neat PP value, although it increases slightly with the wood flour percentage in the composites in agreement with [40]. As expected, the melting and crystallization temperatures remain basically constant despite the increase in the filler content since only the polymeric matrix has a melting point.

5.1 Mechanical characterization

It is well known that wood fibers and polypropylene are incompatible. Filler - filler interactions are preferred to filler – matrix interactions, especially at high wood fiber contents, and this leads to the formation of wood fibers agglomerates as discussed by Huang and Zhang [26]. The polymer - filler interfacial interaction and its quality are the most important factors that influence the mechanical properties of the composite. A good bond between wood and polymer improves the stress transfer and as a result the mechanical properties, as reported by Shahi et al., Tasdemir et al. and Godard et al. [2, 27,32].

In Fig. 8 the SEM micrographs of 30% wt. and 70% wt. WPCs are presented. Both compounds show a good fiber dispersion and a satisfactory adhesion between matrix and fibers without voids; this is due to the presence of an appropriate compatibilizer in the composite formulation. The mechanical and physical properties of the WPCs that are listed in Tab. 2 confirm this observation, in particular in the values of the Young's modulus, which increases with the amount of filler and this is explained by the higher stiffness of the filler.

Concerning the strength results, all the composites have a similar value of the yield stress between 17 – 18 MPa, with brittle failure shortly after (Fig. 5), while neat PP shows an yield strength of about 19 MPa, slightly greater than WPCs, in agreement with Bouza et al. [45]. In spite of the good adhesion seen in the SEM micrographs, fibers and matrix are anyway incompatible and this prevents a significant improvement of strength with increasing the fibers percentage. Moreover, wood fibers may introduce defects or stress intensity regions that embrittle the material, even if the chemical bonds between the compatibilizer and the filler - polymer interface may be adequate. This results in WPCs displaying a brittle behavior, while neat PP is definitely more ductile.

Among the WPCs, the highest strength is obtained with the 50%wt., although the dispersion of the results does not allow to consider such a result significant from a statistical point of view.

Fig. 6 shows the plot of the storage modulus (E') of the WPCs and the neat PP as a function of temperature. As we can see, the storage modulus of each of the WPCs has the same order of magnitude, is higher than the value of neat PP and is a decreasing function of temperature, but as the melting temperature is reached, the storage modulus drops quickly. Interestingly, such a drop occurs for the less filled materials first. This may be due to the formation of fibers agglomerates at higher filler content.

At higher temperatures, the 70% wt. WPC keeps a minimal mechanical performance. The damping factor (Fig. 7) increases with temperature in the 25 – 125 °C range. At higher amounts of filler, the $\tan(\delta)$ value decreases and a relaxation peak between 70°C and 80°C is also visible, although smaller than the one of neat PP. The relaxation peak could be explained by the melting of some PP crystallites as found also by Paul et al. [46].

5.2 Rheological characterization

As previously mentioned, the temperature range in which the parallel plate test can be safely performed on the WPCs is between 165°C and 200°C. The results obtained from the strain sweep test are important to determine the linear viscoelastic region (LVR) and this limits the frequency sweep test temperature: for temperatures above 170°C the WPCs have not shown a sufficiently wide linear viscoelastic domain. Fig. 9 presents the storage modulus G' and the loss modulus G'' as a function of frequency for neat PP and the various WPCs. Both moduli increase with frequency and with the filler content and the crossover between G' and G'' shifts at lower frequencies at higher wood fiber percentage. This has been observed also by Godard et al. [27] for the case of HDPE - based WPC: the transition from fluid - like to solid - like behavior occurring at lower frequencies with increasing the wood fibers percentage indicates that the response of the material tends to become more elastic at higher fiber volume fractions, which is reasonable.

The complex viscosity curves are presented in Fig 10. As expected, the complex viscosity increases with the fibers concentration and shows a shear thinning behavior. The neat PP curve displays the transition from a Newtonian plateau to a power law like behavior at 10 rad/s, while the 30% wt. WPC has the same transition at a much lower frequency (less than 1 rad/s). The other composites do not show the Newtonian plateau in the frequency range that has been investigated. Shear thinning is typical of

the polymeric matrix, as the polymer chains at high frequencies or shear rates do not have enough time to recreate secondary links for reorganizing the original arrangement. The Newtonian plateau, evident in the neat PP curve, shifts at lower and lower frequencies, as the WPC filler content increases, and eventually disappears from the frequency range that has been analyzed. This result has been found also by Ares et al.[40], who ascribe it to the disruption of fiber agglomerates.

For better understanding the shear thinning behavior of the materials, the viscosity curves for neat PP and the WPCs have been fitted with a power law model:

$$\eta = m \dot{\gamma}^{n-1}. \quad (7)$$

The power law exponent n and the consistency index m are reported in Tab. 4 for all materials. In the case of neat PP and the 30% wt. WPC, that display the Newtonian plateau in the frequency range considered, curve fitting has been performed for sufficiently high frequencies, in particular between 10 – 100 rad/s for the 30% wt. WPC and 30 – 100 rad/s for neat PP.

Interestingly, n basically has the same value irrespective of the wood fiber content, with a very slight decrease. This can be easily explained because the shear thinning behavior depends on the polymeric matrix, not on the filler. The value that is found (around 0.4) is in general agreement with Ares et al. [40], in the case of high filler volume fractions. The consistency index, on the other hand, increases with the percentage of fibers, as viscosity normally increases with filler quantity.

Tab 4 - Power law parameters at 170 °C in a frequency range between 10 – 100 rad/s for the WPCs and 30 – 100 rad/s for PP neat.

Composition	m (Pa s ^{n})	n
0% wt	9.00E+03	0.353
30% wt.	3.02E+04	0.445
50% wt.	8.25E+04	0.402
70% wt.	2.06E+05	0.398

Compared to the rotational rheometer, the capillary viscometer is useful for measuring viscosity at higher shear rates. Figs. 13 and 14 show in the same graph the viscosity of neat PP and the 30% wt. WPC obtained both with the rotational rheometer as a function of frequency and with the capillary viscometer as a function of shear rate (the Cox-Merz rule is utilized). The perfect match of the neat PP curve indicates that the results obtained using the Cox-Merz rule are accurate for this material and allow the

determination of viscosity in the full range of shear rates between $0.1 - 1000 \text{ s}^{-1}$. In the graph of the 30% wt., on the other hand, the curve from capillary measurements and from the parallel plate rheometer don't match, and moreover, looking at Fig. 12, the WPC curve is below the neat PP one, which is unreasonable. This behavior can only be explained with the presence of slip during capillary viscometry measurements, even if rough surface capillaries were used for testing the 30%wt. WPC.

Slip in capillary dies is caused by the lubricating effect given by the alignment of natural fibers along the capillary axis and by the formation of a lubrication layer between the capillary walls and the molten WPC. The natural fibers, in fact, tend to migrate towards the interior of the capillary die, leaving a thin layer of polymer that acts as a "lubricant" that reduces the viscosity at the wall, thus giving rise to an apparent slip phenomenon, which is often observed with filled polymers as reported by Barnes [47]. A similar behavior, specific for natural fibers filled systems, was observed also by Le Moigne et al.[34] and Hristov et al. [24].

A single master-curve could be obtained for the viscosity of all WPCs at various fiber percentages and temperatures. This can be very useful for predicting the flow curves of WPCs at temperatures that are more typically in the processing range ($180^{\circ}\text{C} - 200^{\circ}\text{C}$). Testing at such temperatures is extremely difficult because of slip, degradation and too high viscosity problems when capillary rheometry is used, or the LVR being too small when the parallel plate rheometer is employed.

Let us consider temperature effects on the master-curve first. The viscosity of neat polypropylene has been measured at different temperatures, in particular between 170°C and 200°C , which is a range that is wide enough to contain the usual WPC processing temperatures. Fig. 11 shows that the complex viscosity decreases with temperature, which is a well-known effect and can be modeled by shifting the viscosity curves diagonally in a log viscosity – log shear rate plot. By doing this, one can obtain the single curve of Fig. 15, which represents the viscosity curve of neat PP at 170°C .

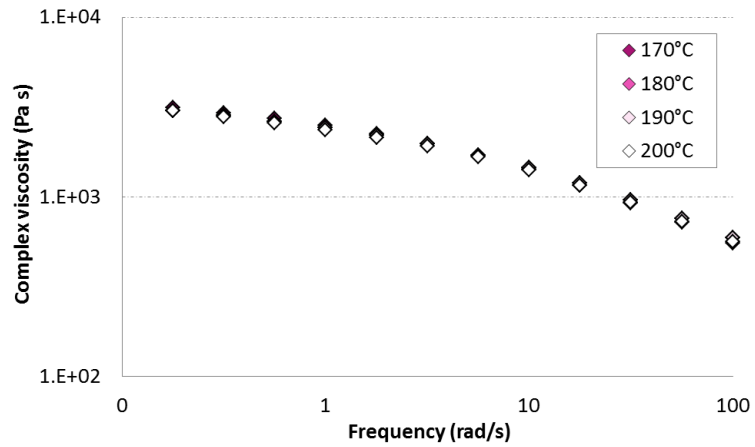


Fig. 15 - Complex viscosity master - curve at different temperature for neat PP

The diagonal shift factors are listed in Tab. 5 and are also shown as a function of temperature in Fig. 16. The temperature shift factors $\log(a_T)$ are fitted using a Williams-Landel-Ferry (WLF) equation:

$$\log(a_T) = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (8)$$

in which C_1 and C_2 are fitting parameters and T_0 is the reference temperature, here 170°C. A good fitting can be obtained for the following values: $C_1 = 0.57$ and $C_2 = 16^\circ\text{C}$.

Tab. 5 Diagonal shift factor as a function of temperature

Temperature ($^\circ\text{C}$)	Diagonal Shift factor $\log(a_T)$
170	0
180	0.21
190	0.31
200	0.36

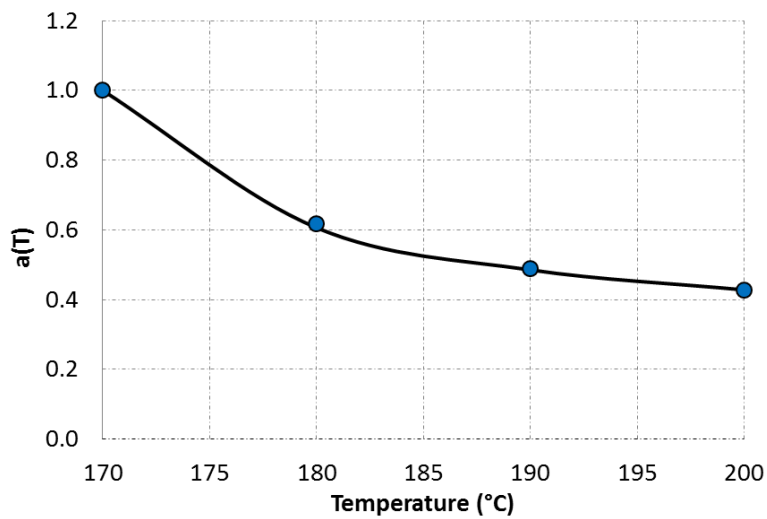


Fig. 16 - Function $a(T)$ vs. temperature T and curve fitting using Eq. 8.

Concerning the influence of the filler content, as introduced by Highgate and Whorlow [48] and reported also by Barnes [47], a single master curve can be obtained by shifting the viscosity curves diagonally in a viscosity – shear stress bilogarithmic plot. It is possible to show that such a procedure is equivalent also to shifting the flow curves in a log viscosity - log shear rate plot, but in a 45° diagonal direction, in which an horizontal shear rate shift is superimposed onto the diagonal shift. The two shifts would have the same value but opposite sign. Notice that this procedure is the same as the one used by Trappe and Weitz [49] and, in the case of natural fiber filled composites, also by Marcovich et al. [38] and by Godard et al. [27].

The 170°C flow curves of neat PP and all WPCs (Fig. 10) have been shifted diagonally until they matched the curve for neat PP (Fig. 17), thus this master-curve is really relative to the viscosity of the unfilled system at 170°C and will be denoted by $\eta_{PP,170^\circ}$. This curve has been fitted with a Carreau – Yasuda model:

$$\eta_{PP,170^\circ} = \frac{\eta_0}{(1 + (\lambda \omega)^c)^{\frac{1-n}{c}}} \quad (9)$$

where ω is frequency, η_0 is the viscosity value at the Newtonian plateau for neat PP at 170°C, n is related to the slope of the shear thinning portion of the curve in a log-log plot and λ and c are fitting parameters. The constants used in the Carreau - Yasuda model are listed in Tab. 6.

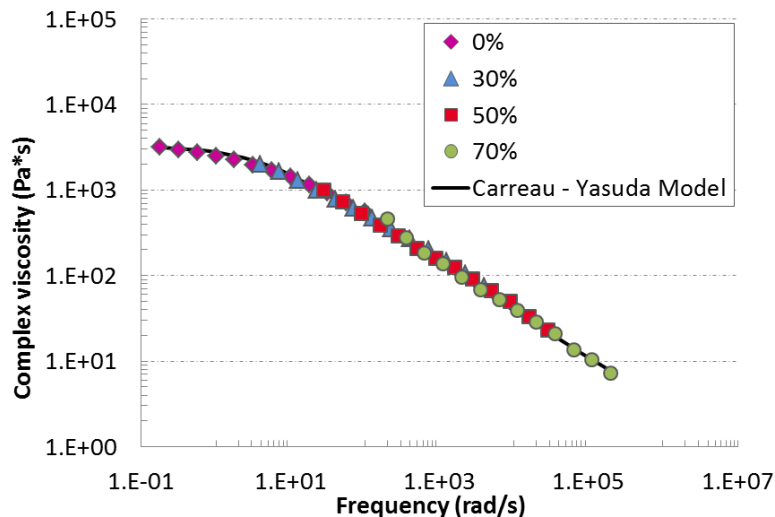


Fig. 17 - Complex viscosity master-curve at 170°C for neat PP and all WPCs fitted with a Carreau - Yasuda model

Tab. 6 - Fitting parameters used in the Carreau – Yasuda model

Fitting Parameters	
λ	0.3
c	1
n	0.45
η_0	3200

The values used for the diagonal shift factor, that will be indicated with $\log(b_\phi(\phi))$, are listed in Tab. 7. The function $b_\phi(\phi)$ is the ratio of the viscosity of the WPC with filler volume fraction ϕ and that of neat PP at constant shear stress, thus it represents a sort of relative viscosity at 170°C, keeping the shear stress constant. In Fig. 18 $b_\phi(\phi)$ is plotted as a function of the filler volume fraction ϕ and fitted using a modified Eilers model [50]:

$$b_\phi(\phi) = \left[1 + \xi \frac{\phi}{1 - \frac{\phi}{\phi_{max}}} \right]^2 \quad (10)$$

where the model parameters are $\phi_{max} = 0.79$ and $\xi = 14.55$. The ϕ_{max} parameter is the maximum possible volumetric loading of wood fibers in the PP matrix and the ξ parameter should be half of the intrinsic viscosity of the wood fiber - PP mixture, according to [50]. In the case of rigid spheres in a dilute solution such a value is 2.5 according to the well-known Einstein relation, in the present case this value is much higher due to the non-spherical shape and deformability of the particles.

Tab. 7 – Diagonal shift parameter as a function of the filler volume fraction

WF mass fraction % wt.	ϕ WF volume fraction % vol.	Diagonal shift factor $\log(b_\phi)$	Relative viscosity b_ϕ
0	0	0	1
30	27	1.60	40
50	44	2.45	251
70	61	3.20	1585

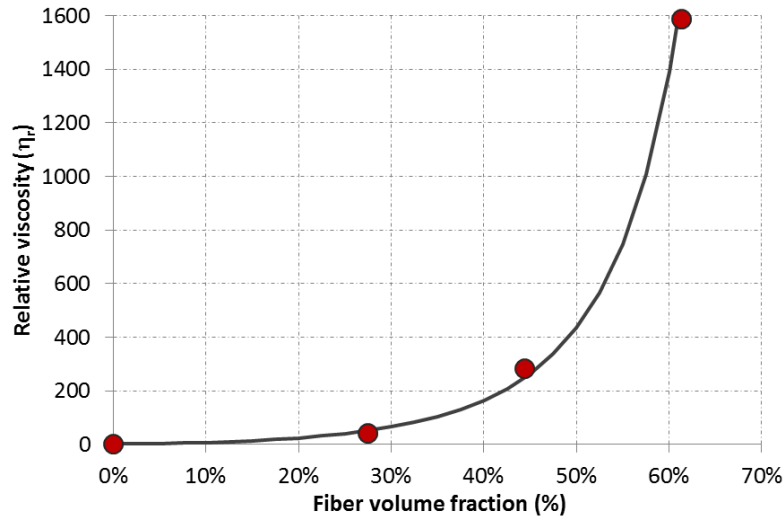


Fig. 18 – Relative viscosity $b_\phi(\phi)$ as function of fiber volume fraction ϕ and curve fitting using Eq. 10

Now, considering both shifts, i.e. the diagonal thermal shift and the diagonal volume fraction shift, the master curve that is proposed takes the following form:

$$\eta(T, \phi, \dot{\gamma}) = a_T(T) b_\phi(\phi) \eta_{PP,170^\circ}(a_T(T) b_\phi(\phi) \dot{\gamma}) \quad (11)$$

in which the functions a_T , b_ϕ and $\eta_{PP,170^\circ}$ have been introduced in Eq. (8), (9) and (10). Despite Eq. (11) has been obtained only for neat PP at various temperatures and only at 170°C for the various filler volume fractions, we propose that such a curve may be used in general to estimate the viscosity of PP - WPC in the whole range of temperatures and filler volume fractions. For such an hypothesis to hold, it must be assumed that the net response on viscosity of temperature and filler volume fraction is the sum of the effects which would have been caused by each of these variables individually. This is reasonable if the influence of temperature on filler – filler and filler – polymer interactions is negligible, thus the most significant effect of temperature is only on the PP viscosity.

The other models for natural fiber filled polymeric composites that have been proposed in the recent literature [27, 38] have also been able to construct a single master curve that is valid for a wide range of filler volume fractions. Such models are constructed in the same way as the one which is proposed in the present article, concerning the filler volume fraction dependence. To our knowledge, though, the model that is presently proposed is the first one that takes into account both, temperature and natural fibers percentage. The interest in combining temperature and filler fraction effects in a single model stems from the possibility of producing the flow curve of the materials by running

tests at lower temperatures, where degradation problems are less relevant and also the linearity in the viscoelastic response is guaranteed.

6. Conclusions and future developments

In this paper we have characterized PP - WPC at various wood fiber percentages. The mechanical testing shows that wood fibers make the composite stiffer without lowering strength values too much, while thermal properties have confirmed that the processing window of this material is rather narrow, being limited upwards by wood fiber degradation and downwards by the melting temperature, which is around 165°C.

Rheological measurements on WPCs have been performed both with parallel plate and capillary rheometer at 170°C. Such a temperature is imposed by the possibility of performing the parallel plate testing within the linear viscoelasticity region, but the data that are measured are not directly useful for processing, as a convenient minimum temperature should be around 180°C – 190°C. In order to obtain the WPC viscosity at typical processing temperatures, we propose to use the model presented in Eq. 11. This model makes use of the WPC viscosity measured at 170°C at various wood quantities and of neat PP viscosity measured at various temperatures in the 170°C – 200°C range. These measurements are used to create shift factors that allow to estimate the WPC viscosity on the basis of neat PP viscosity, temperature and wood fibers content. The main simplifying hypothesis involved in the realization of such a model is that the effects of temperature and filler content on the composite viscosity are assumed to be disjoint.

In order to validate the model, it is necessary to evaluate the flow curve of at least one PP - WPC material at a temperature other than 170°C. This could not be done at this stage, mainly because the LVR was insufficient to obtain reliable results. We are currently working towards measuring the viscosity of PP - WPC using an instrumented extruder slit die, which would allow the determination of the flow characteristics of the material in a condition that is very similar to the actual processing conditions.

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