In-line rheometry of polypropylene based Wood Polymer Composites

2 authors:

Valentina Mazzanti
University of Ferrara
34 PUBLICATIONS **271** CITATIONS

SEE PROFILE

Francesco Mollica
University of Ferrara
84 PUBLICATIONS **1,604** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Natural fibers/ Poly (lactic acid) composites View project

3D Printing of Natural Fibers Reinforced Polymers View project

In-line rheometry of polypropylene based Wood Polymer Composites

V. Mazzanti, F. Mollica

Dipartimento di Ingegneria, Università degli Studi di Ferrara, Via Saragat 1, I - 44122 Ferrara, Italia

Corresponding author F. Mollica, francesco.mollica@unife.it, +39 3297506547

ABSTRACT

A completely satisfactory off–line rheological investigation of Wood Polymer Composites (WPC) is often impossible at processing temperatures: when using parallel plate rheometry in oscillatory mode, the linear viscoelastic region is too small, while in capillary rheometry the sieving effect of the fibres may invalidate the results. Moreover, all off–line tests present the risk of wood degradation.

To this aim, an in–line extrusion rheometer (slit die) has been developed. The major advantages are that the measurements are made in real processing conditions and degradation problems are less severe thanks to a reduced presence of oxygen inside the extruder barrel.

In order to verify the methodology, tests have been conducted on a commercial polypropylene based WPC with 30wt% white fir fibres and compared with off–line measurements performed at a lower temperature on the same material. For comparison, a temperature shift factor has been used, that has been estimated by characterizing the polypropylene matrix alone.

KEYWORDS Rheology, Wood Polymer Composites, In-line rheometer, Slit die

1. INTRODUCTION

Wood Polymer Composites (WPC) are thermoplastic polymers filled with wood flour at various concentrations and have attracted both research and commercial interest because of their environmental friendliness, especially if recycled plastics and waste originating wood flour are used [1 - 3]. Natural fibres offer many advantages when used as fillers for plastics: low cost, easy obtainability, low density, biodegradability, low abrasiveness against processing machineries and high filling levels capability.

Compared to natural wood, WPC products show good durability in wet environment thanks to the hydrophobic character of the polymeric matrix, which allows them to substitute wood in outdoor applications. From the technological point of view, WPC products can be manufactured easily, rapidly and with great variety of shapes using forming techniques that are typical of thermoplastic polymers, such as extrusion or injection moulding.

On the other hand, processing is also the source of a few drawbacks of these materials. First, the processing temperature window is rather narrow, being limited downwards by the melting temperature of the polymer and upwards by the degradation temperature of the natural fibres. These are mainly composed of lignin, hemicellulose and cellulose, whose degradation temperatures are 110°C, 196°C and 255°C, respectively [4 - 6]. Since the upper bound processing temperature is chosen on the basis of hemicellulose degradation, polyolefins, polyvinylchloride or polystyrene are generally used as WPC matrices. However, the processing temperature must be relatively low, thus the viscosity of the polymeric matrix is rather high and the presence of large quantities of filler increases viscosity even further. Among polyolefins, polypropylene (PP) has the advantage of having attractive mechanical properties [7], on the other hand, the processability range is only about 20°C wide (180°C - 200°C). PP-based WPC processing is thus challenging in that it requires more power than other thermoplastics and can present localized heating phenomena induced by viscous dissipation that may lead to material degradation. In order to control processing related issues, the precise knowledge of the rheological properties is very helpful.

WPC flowing behaviour may be very difficult to characterize with standard off-line rheological techniques [8]. If rotational rheometry is used in continuous mode, the maximum shear rate obtainable is usually below values that are significant for processing. This is mainly due to the need for maintaining a sufficiently large gap compared to the average filler size [9]. The shear rate range can be increased by running tests in oscillatory mode and using the Cox-Merz rule. The shear rate is assumed to be equal to the oscillation frequency and this allows one to bring the measuring range to levels that are more interesting for processing purposes. For oscillatory mode to be performed correctly, though, the material must be tested within its linear viscoelasticity range (LVR), and this poses severe restrictions to the application of this technique to molten WPCs, as their LVR is often insufficiently narrow at normal processing temperatures [8, 10]. As a result, a complete rheological characterization at typical processing temperatures is almost impossible with a rotational rheometer.

With capillary rheometry there are no limitations coming from the LVR and the shear rates are sufficiently high, but still the presence of the fibres creates a few difficulties. In fact, the capillary orifice could "sieve" the WPC melt in such a way that the filler volume fraction that is extruded through the capillary would be smaller than the nominal fraction (a filler fraction greater than nominal would remain inside the reservoir) [11]. The problem cannot be solved by simply increasing the diameter of the capillary, because feeding a large capillary requires a quantity of material that may not be available in the reservoir. This, in fact, must be small enough that the polymer can be brought to melting in a reasonable time. Moreover, in literature it is well known that WPC slips at the wall [12], thus the Mooney procedure for slip correction is also limited by the effective availability of a number of capillary diameters that are sufficiently large to exclude sieving

phenomena. In any case, all off-line tests at high temperatures and percentages of filler are affected by the problem of wood flour oxidative degradation, which imposes to carry out testing in a controlled atmosphere.

Many problems encountered with traditional off-line rheometry can be solved all at once using a process rheometer. In particular, there are no LVR issues nor limitations on the reservoir size, as the material loading is the output of an extruder, which ensures an adequate and continuous flow rate. Moreover, degradation issues are less severe due to the effective oxygen reduction during processing and the characterization is independent of samples preparation, as in-line methods have the clear advantage of studying the material in the same conditions at which it is processed. This is particularly important for a material that is non–homogenous like WPC.

In the past, a good number of process rheometers have been developed in conjunction with extruders [13 - 21] or injection moulding machines [22 - 24] in order to characterize molten polymers. In this paper we will concentrate on process rheometers connected to extruders. These can be divided into on-line and in-line instruments. On-line rheometers take a side stream of melt from the main process flow, usually by the action of a by–pass and a gear pump. After measurement, the sample can be discarded as waste or reintroduced into the main stream. In-line rheometers are installed directly into the process main stream, thus abrupt changes of direction are not needed to pick up the fluid samples, and the instrument flow rate coincides with the extruder flow rate. The slit is the preferential geometry, usually with two or more flush mounted pressure transducers to measure the pressure drop along the channel directly, i.e. without the need to perform the Bagley correction.

In-line and on-line rheometers have been widely used in the literature to characterize unfilled materials. Lodge and de Vargas [13] were among the first ones to develop a slit on-line apparatus for measuring the rheological properties of two low density polyethylenes (LDPE). Their results agreed with traditional off-line measurements. Similar results were found also by other authors [14 , 15] for polyolefins and polystyrene using in-line and on-line equipment, while other researchers [16, 17] gave evidence of shear viscosity values that were lower compared with off-line measurements. A possible explanation of this phenomenon is a fluidity increase of the polymer melt due to viscoelastic effects generated by the plasticating extruder [18].

In-line rheometers are particularly well suited for studying easily degrading materials, such as polyvinylchloride (PVC). Coates et al. [19] used an in-line rheometer to monitor and control the gelation levels in PVC compounding. The pressure drop in a slit measured with two flush mounted pressure transducers allowed the accurate prediction of the gelation level. An interesting work has been published by Glomsaker et al. [20] about different PVC formulations using a variable slit height in-line rheometer. The measurements showed significant geometry dependency but the experimental data did not fit into the Mooney plot. PVC was also investigated by Thorsteinsen et al. [21] who used an instrument composed of a dual slit adapted to a twin screw extruder.

The objective of this work is to design and to test a process rheometer device that enables to characterize a temperature sensitive and highly viscous material, such as PP-based WPC, directly during processing. This apparatus permits to carry out the measurements at the processing temperature and compare the viscosity values with those obtained with standard off-line techniques and reported in a previous study [8]. To the authors' knowledge, this is the first work where in-line rheometry is used to characterize natural fibres filled polymers.

2. EXPERIMENTAL

2.1 Material

Commercial wood flour filled polypropylene (commercial name PP 30 S) has been purchased from PlasticWOOD S.r.l., Mazzantica di Oppeano (VR), Italy. This material contains 30% white fir wood fibres in mass. The bulk density at room temperature, as declared by the producer, is 1067 kg/m^3. The shape and dimensions of the wood fibres were measured by dissolving the PP matrix in toluene at 105°C for 12 hours at a total concentration of 10 mg/ml. Subsequently, the fibres were sieved, dried and observed at the optical microscope (Zeiss Axiovert 200, 20x magnification (Fig. 1). The mean and standard deviation of length, diameter and length over diameter ratio (L/D) are listed in Tab. 1.
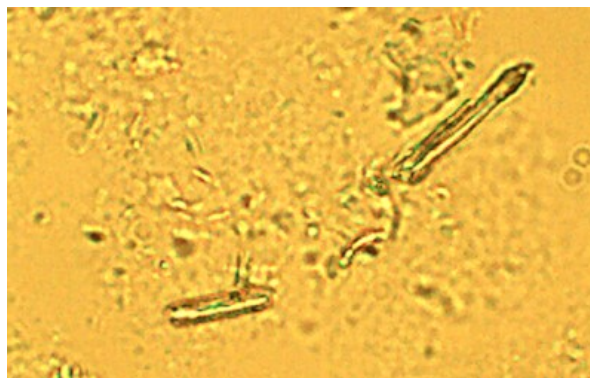

Fig. 1 – Optical micrograph of white fir fibres after PP matrix dissolution

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

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

2.2 Apparatus

The rheological measurements are performed using a slit die in-line rheometer connected to a single screw extruder (P.R.T. SERVICE & INNOVATION S.r.l., Sant'Agostino (FE), Italy). The drive motor allows a screw speed range of 0 – 110 RPM. The extruder barrel has six thermal sections, while the screw is 50 mm in diameter, with a length to diameter ratio of 40 and a

compression ratio of 1.23. The extruder is also equipped with a breaker to improve compaction and with a venting zone to help degasification of water vapour.

18NiCrMo5 steel (EN10027 standard), carburized and tempered to HRC 61 was used for the slit die. The measuring apparatus is pictured in Fig. 2, where also a schematic drawing is shown, and is composed of six parts: an extruder die (blue component), an adapter (green component), two separators (light blue components) and upper and lower halves that create the main body of the die (red components). The two halves are bolted together with eight M10 screws and constitute the top and bottom surfaces of the slit. The slit thicknesses used are 1.31, 1.95, 4.04 mm depending upon the separators used and have been measured with a micrometre.
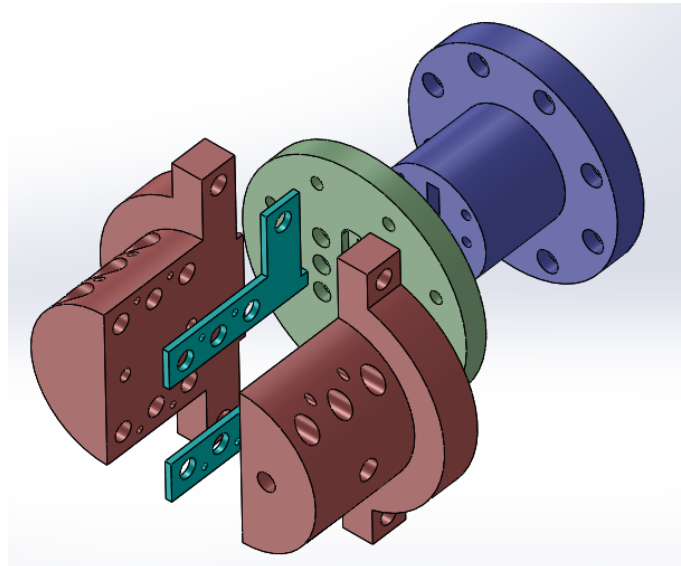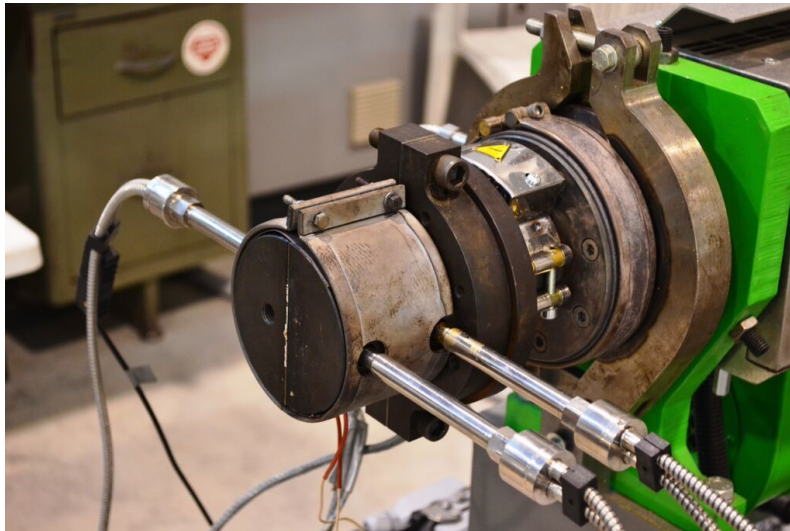

Fig. 2 – Picture and exploded view of the instrumented slit die with the three pressure transducers

The die channel is 50 mm wide and 105 mm long. Three pressure transducers (GEFRAN M32 mercury – filled transducers, ± 0.25% full scale accuracy) are flush mounted along the slit length, allowing pressure drop measurements along the die. In order to ensure a fully developed flow, the first pressure transducer is placed 40 mm from the slit entrance. The remaining two transducers

are located 25 mm apart, hence at 65 and 90 mm from the entrance. The first two transducers have a 500 bar pressure full scale, the one closer to the die exit has a 100 bar pressure full scale. Heating is achieved by three external resistance heaters with two control thermocouples located within the slit die body, close to the melt. To increase reliability, the polymer temperature is also checked with thermocouples (J-type, ± 0.1°C accuracy) contained inside the pressure transducers, capable of measuring the melt temperature directly. However, due to the in–process nature of the system, accurate temperature control is difficult during extrusion, and shear heating generally makes the melt temperature higher. The modularity of this apparatus allows the complete disassembling and cleaning of the system.

Analogic signals from the process instrumentation are conditioned and interfaced to a PC using a NI CompactDAQ 9178 (National Instruments) modular interface unit. This unit consists of eight interchangeable slots where suitable acquisition modules can be inserted. Here, two modules have been used: NI 9923 for pressure analogic signal conditioning and acquisition and NI 9211 for temperature analogic signal acquisition. Labview 2013 has been used to acquire and record data.

2.3 Experimental procedures

The 30 wt.% WPC pellets have been dried at 80°C in a drying system for 24 hours prior to performing extrusion and rheological measurements, in order to reduce the moisture content. During extrusion, a uniform temperature distribution of 195°C± 2.0 °C has been maintained along the barrel and the slit die. The volumetric flow rate Q has been controlled through the extruder screw speed and determined by dividing the mass flow rate by the known density of the fluid at the testing temperature (915 kg/m^3). The mass flow rate has been measured by dividing the throughput weight (100 g minimum) by the time needed to extrude it.

3. RESULTS

The wall shear stress is calculated from the pressure drop measurements along the die length as

$$\tau_w = \frac{h}{2}\frac{\Delta P}{L}, \tag{1}$$

where $\Delta P/L$ is the pressure gradient along the slit of length L and height h. The pressure profiles obtained from the flush mounted transducers have always been linear, as shown in Fig. 3, where some typical pressure profiles (h = 1.95 mm) for various mass flow rates are pictured. The linear fit approximation has displayed a coefficient of determination (R^2) of 0.99 at least for all measurements.
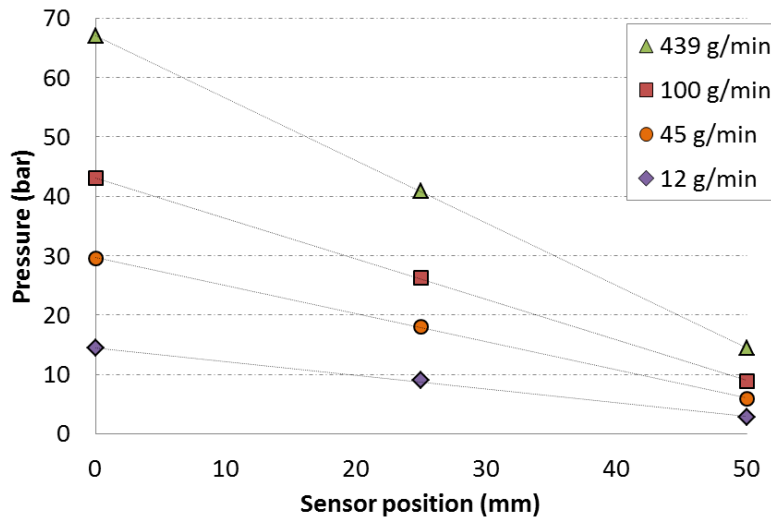
Fig. 3 - Pressure profiles vs. sensor position at different mass flow rates

The apparent shear rate $\dot{\gamma}_a$ in a rectangular slit is

$$\dot{\gamma}_a = \frac{6Q}{wh^2},$$ (2)

where w is the slit width and Q is the volumetric flow rate.

A few temperature profiles of the melt are shown in Fig. 4. Non-uniformity results from cooling, as the melt approaches the slit die exit, or from localised heating due to viscous dissipation effects. The in-line configuration does not reduce the temperature variations introduced by the extruder and can cause some temperature control problems [17]. The results given in Fig. 4 are considered to be acceptable given such difficulties.
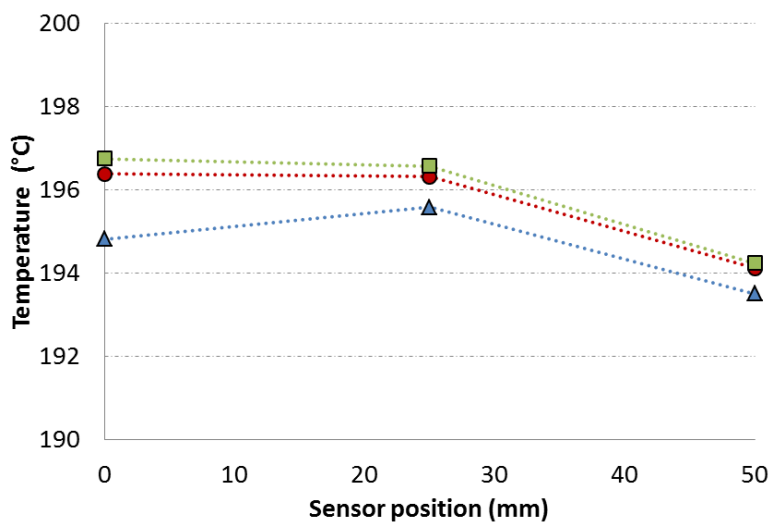

Fig. 4 – Some typical temperature profiles along the die plotted vs. sensor position

Fig. 5 shows the shear stress versus apparent shear rate for the three different slit heights. From the plot it is evident that the curves are not coincident: at a given shear stress, the flow rate, and thus the apparent shear rate, is higher for smaller heights, and this can be explained by wall slip [25].
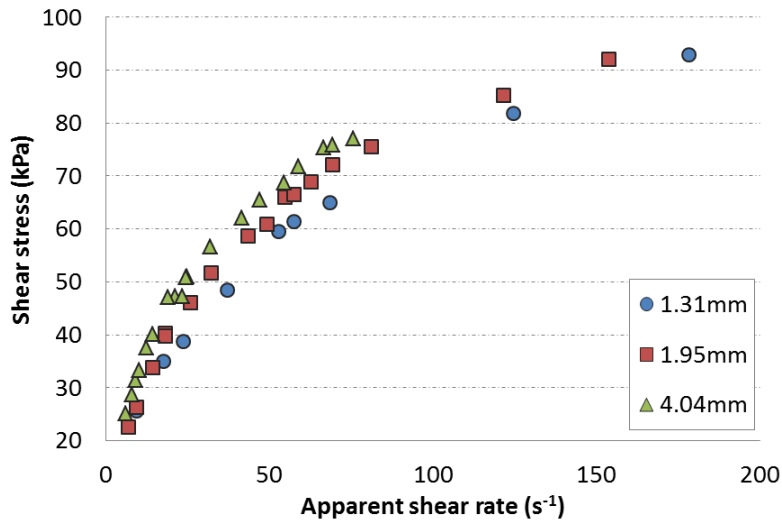

Fig. 5 - Shear stress vs. apparent shear rate for the various slit heights

The Mooney analysis has been performed as shown in Fig. 6, by plotting the apparent shear rate against 1/h, in order to evaluate wall slip effects. The material shows positive intercepts on the flow rate axis for all available levels of shear stress, the linear fit has a good agreement with a coefficient of determination not less than 0.97, thus the standard Mooney procedure is valid. From the slopes and intercepts of the Mooney plots it is possible to find the slip velocity and the apparent shear rate corrected for slip.
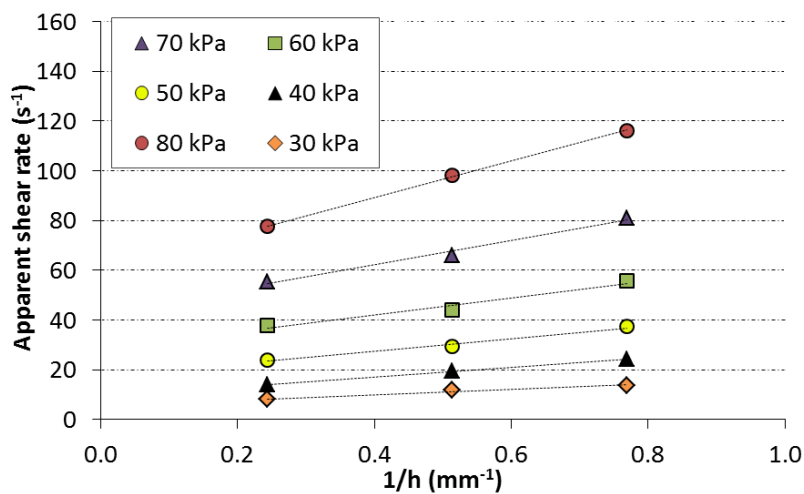

Fig. 6 – Mooney plot

The shear stress dependent values of wall slip velocity are presented in Fig. 7. Slip velocity varies between 1.76 – 12.22 mm/s and increases with shear stress. Such a trend agrees with similar studies present in the literature and performed with capillary viscometer [26, 27]. The curve can be fitted with a power law:

$$v_s = k\tau^n ,$$

(3)

the fitting parameters being k = 3.0148E-03 mm/s and n = 1.87.
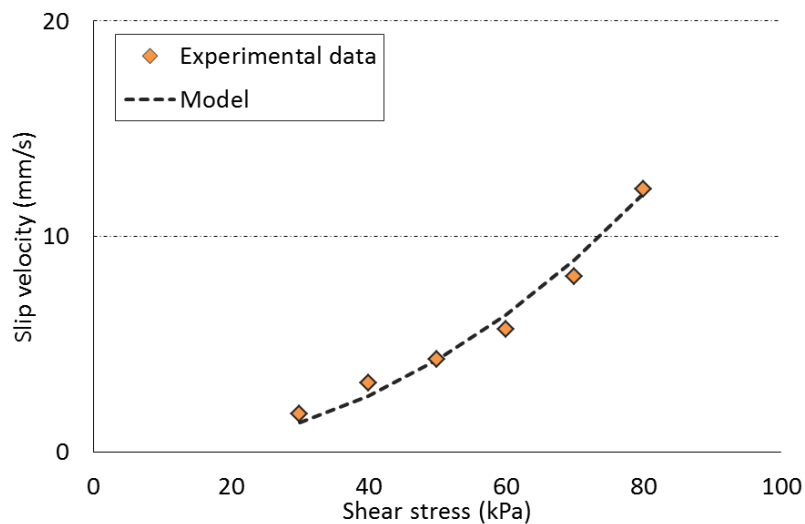

Fig. 7 – In-line slip velocities obtained from the slopes of the Mooney plot lines

Next, the apparent shear rate is corrected for non-Newtonian effects using the Rabinowitsch procedure. In Fig. 8 the plot of the shear viscosity versus the true shear rate is presented. Viscosity decreases with the shear rate showing a shear thinning behaviour.
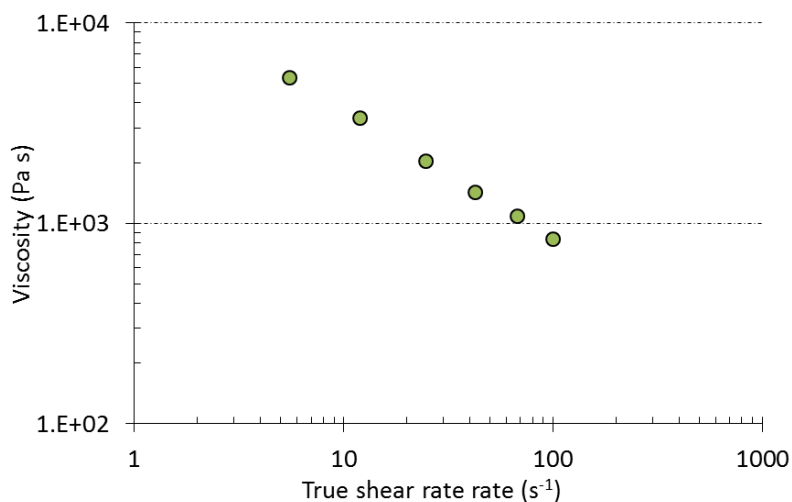

Fig. 8 – Shear viscosity vs. true shear rate

The curve has been fitted with a power law model

$$\eta = m\,\dot{\gamma}^{n-1}\,,$$ (4)

where $n = 0.36$ is the exponent of the power law and $m = 15700$ Pa s^n is the consistency index. In Fig. 9 the shear stress versus true shear rate plot is shown. The behaviour of the material does not seem to show the presence of an yield stress and thus confirms the reliability of the tests.
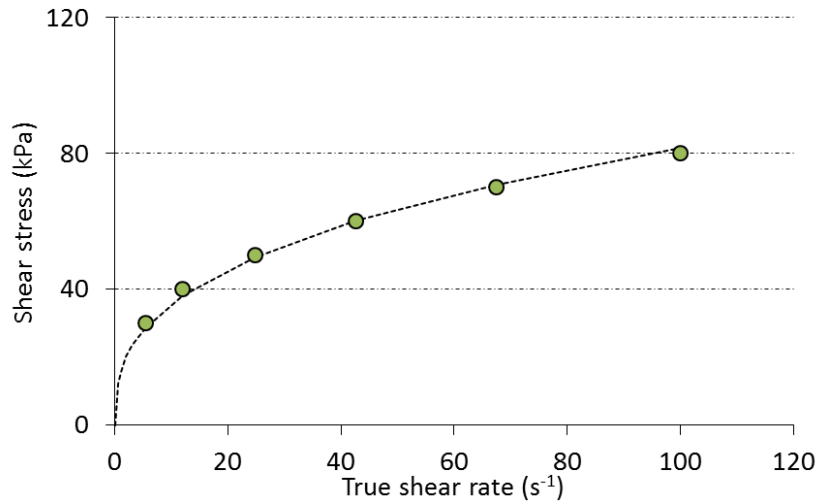

Fig. 9 - Shear stress vs. shear rate

4. DISCUSSION

In order to quantify the reliability of the results obtained with the in-line rheometer, the total uncertainties on shear stress τ and apparent shear rate $\dot{\gamma}_{app}$ and the relative uncertainties of their parameters have been analysed in agreement with ISO/IEC Guide 98 [28].

The total uncertainties on τ and $\dot{\gamma}_{app}$ are 7.1% and 4.6%, respectively. These values are satisfactory for this type of measurement and have been calculated for the condition of greater uncertainty. In Tab. 2 the uncertainty contributions for each of the parameters involved in the calculations are listed.

Tab. 2 – Shear stress and apparent shear rate parameters and corresponding relative uncertainties

Shear stress parameters	Relative uncertainties
slit height h	0.8%
slit length L	0.08%
pressure drop ΔP	5.0%

Apparent shear rate parameters	Relative uncertainties
mass flow rate $\dot{m}$	2.0%
slit width w	0.02%
slit height h	1.5%
density ρ	2.0%
time t	3.3%

Notice, though, that the corrections for slip (Mooney procedure) and non – Newtonian behaviour (Rabinowitsch correction) are necessary and introduce additional uncertainties related to the fitting that is involved in the procedures, nevertheless both are well known and widely accepted in the scientific community.

In order to validate in-line testing, literature studies have often compared in-line rheological characterization with traditional off-line methods, as already described in the Introduction (Section 1). In the case of this material, the off-line rheological characterization has been published in [8] with parallel plate geometry (ARES, TA instruments) in dynamic oscillation mode (0.1 - 100 rad/s frequency range).

The strain amplitude (0.02%) has been chosen within the LVR, but this limited testing to 170°C and makes it impossible to compare the in-line and off-line results directly. Nevertheless, the viscosity curves of the WPC using the off-line rotational rheometer at 170°C and the in-line process rheometer at 195°C are shown in Fig. 10. The curves have the same qualitative trend, both showing a shear thinning behaviour and decreasing with temperature in agreement with the literature [10, 29, 30].
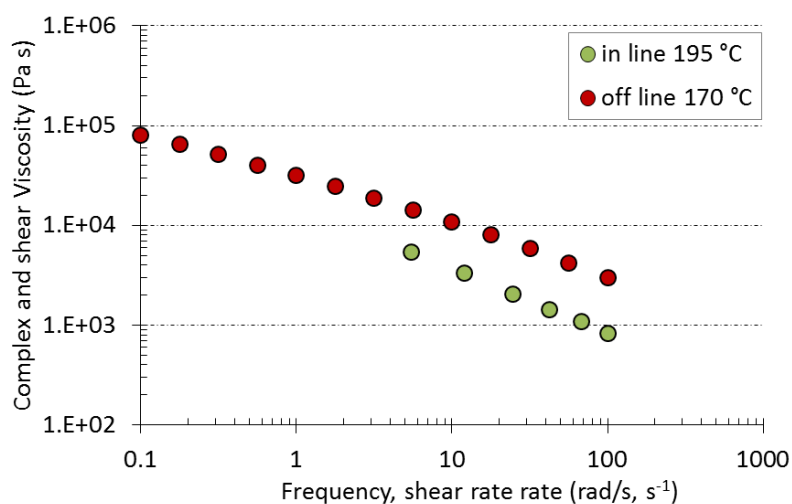
Fig. 10 – Shear viscosity vs. shear rate calculated with in-line rheometer at 195°C compared with complex viscosity vs. frequency measured with standard off-line rheometer at 170°C

In order to quantify comparison, both viscosity curves shown in Fig. 11 have been fitted with a power law model (Eq. 4). The fitting parameters are reported in Tab. 3.

Tab. 3 – Power law fitting parameters for the in-line and off-line flow curves

Test type		Fitting parameters	
Instrument	Temperature (°C)	m (Pa s^n)	n
In-line rheometer	195	15700	0.36
Off-line rheometer	170	30200	0.44

Clearly, the largest difference is in the consistency index while the power law exponent is similar for both temperatures. In fact, temperature dependence of viscosity can be modelled by shifting the viscosity curves diagonally in a log viscosity – log shear rate plot, and this procedure would leave the power law exponent unchanged. The consistency index, on the other hand, will be reduced by the vertical downward shift corresponding to the temperature increase. In our case, the value of the diagonal shift factor obtained by displacing the upper curve downwards is equal to 0.36.

Interestingly, in [8] the same polypropylene used as the matrix for the WPC compound of the present article has been investigated. The viscosity curves have been measured at different temperatures, in particular in the 170 – 200 °C range, using a rotational rheometer (ARES G2, TA Instruments) in oscillation mode with a parallel plate geometry. In that paper it was possible to create a single mastercurve applying time – temperature superposition. The diagonal shift factors as a function of temperature were fitted using a Williams-Landel-Ferry equation

$$\frac{\eta}{\eta_r} = -\frac{C_1(T-T_r)}{C_2+T-T_r},$$ (5)

with the following best fit values: $C_1 = 0.57$, $C_2 = 16°C$ and the reference temperature $T_r = 170°C$, with η_r being the viscosity corresponding to the reference temperature. Using this interpolation, the diagonal shift factor that is necessary to shift the neat PP viscosity curve from 170°C down to 195°C is equal to 0.41.

Comparing the values of the shift factors obtained from the diagonal shift of the 30 wt.% WPC (0.36) and the neat PP viscosity curves (0.41), they are very close as their difference is around 12%. Such a value is interesting since this difference is of the same order of magnitude of the apparent shear rate and the shear stress total uncertainties, hence the shift factor could be considered to be the same for the WPC and for the neat PP. This would mean that the diagonal thermal shift factor is independent of the filler volume fraction within the WPC compound.
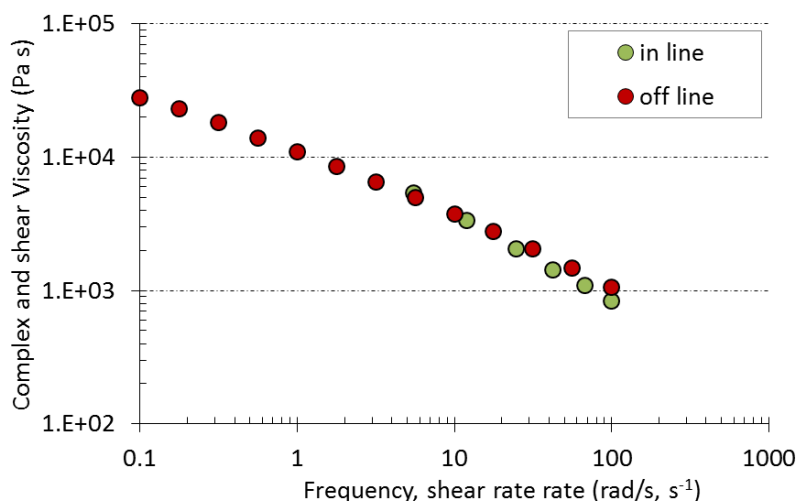
Fig. 11 – In-line viscosity and shifted off-line viscosity curves for the 30 wt.% WPC at 195°C

The results from in-line viscometry and the shifted off-line flow curve (Fig. 11) are in reasonably good quantitative agreement, taking into account the measurement uncertainties. Nevertheless, the curves do not match perfectly: the one obtained with the in-line rheometer shows a slope that is slightly greater than the one from the off-line rheometer. Rauwendaal and Fernandez [18] gave a possible reason for this behaviour, as a substantial amount of shearing deformation prior to measurement, caused by the action of the single screw extruder on the polymer, reduces viscosity by shear thinning and viscoelastic effects. The amount of this effect depends on the environment, the shear rate and the time elapsed between the preshearing and the measurement.

5. CONCLUSIONS

This paper presents the development of an instrumented slit die rheometer mounted on a single screw extruder, which has been used to measure the rheological properties of a polypropylene compound filled with 30 wt.% wood flour. Since a complete off-line rheological characterization at temperatures typical of processing conditions is often impossible, the in–process methodology is the only way to characterize this material.

The results show that the in-line rheometer is able to determine the shear viscosity as a function of shear rate with a good reliability for a range of different shear rates. Slip velocities have also been determined using the Mooney procedure. The viscosity curve obtained with the in-line rheometer at 195°C agrees with the viscosity curve measured with parallel plate rheometry at 170°C and shifted at 195°C using the shift factor calculated for the pure matrix. This is an indication that, for this material, thermal shift factors are independent of the filler amount, taking into account the measurement uncertainties and the effect of shear due to the plasticating extruder.

REFERENCES

[1] J. Markarian, Wood-plastic composites: current trends in materials and processing, Plastics Additives and Compounding, 2008; 4: 20–25

[2] H. Cheung, M. Ho, K. Lau, F. Cardona, D. Hui. Natural fibre-reinforced composites for bioengineering and environmental engineering applications, Composites: Part B, 2009; 40: 655 – 663

[3] E. Zini, M. Scandola, Green composites: An overview, Polym. Comp., 2011; 32: 1905–1915

[4] M. V. Ramiah, Thermogravimetric and differential thermal analysis of cellulose, hemicellulose, and lignin, J. App. Polym. Sci., 1970; 14: 1323-1337

[5] H. Bouafif, A.Koubaa, P. Perré, A. Cloutier, B. Riedl, Wood particle/high-density polyethylene composites: thermal sensitivity and nucleating ability of wood particles, J. App. Polym. Sci., 2009; 113: 593-600

[6] H. Jeske, A. Schirp, F. Cornelius, Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wood flour and polypropylene in wood plastic composites (WPC) Termochim. Acta, 2012; 543: 165-171

[7] K. Englund, V. Villechevrolle, Flexure and water sorption properties of wood thermoplastic composites made with polymer blends, J. App. Polym. Sci., 2011; 120: 1034-1039

[8] V. Mazzanti, F. Mollica, N. El Kissi, Rheological and mechanical characterization of polypropylene-based wood plastic composites, Polym. Comp., 2016, 37: 3460-3473

[9] H. A. Barnes, A review of the rheology of filled viscoelastic system, Rheology Review, 2003; 1-36

[10] N. E. Marcovich, M. M. Reboredo, J. Kenny, M. I. Aranguren, Rheology of particle suspensions in viscoelastic media. Wood flour-polypropylene melt, Rheol. Acta, 2004; 43: 293-303

[11] U. Yilmazer, C. Gogos, D. Kalyon, Mat formation and unstable flows of highly filled suspensions in capillaries and continuous processors, Polym. Comp., 1989; 10: 242

[12] T. Q. Li, M. P. Wolcott, Rheology of HDPE-wood composites. I. Steady state shear and extensional flow, Polym. Eng. Sci., 2005; 45: 549-559

[13] A.S. Lodge, L. Vargas, Positive hole pressures and negative exit pressures generated by molten polyethylene flowing through a slit die, Rheol. Acta, 1983; 22:151 – 170

[14] A.L. Kelly., M. Woodhead, P.D. Coates, D. Barnwell, K. Martin, In-process rheometry studies of LDPE compounds: Part I: Unfilled resin, Int. Polymer Processing, 2000; 4: 355 – 360

[15] P.F. Teixeira, L. Hilliou, J. Covas, J.M. Maia, Assessing the practical utility of the hole-pressure method for the in-line rheological characterization of polymer melts, Rheol. Acta, 2013; 52: 661 – 672

[16] A. Pabedinskas, W. R. Cluett, S. T. Balke, Process control for polypropylene degradation during reactive extrusion, Polym. Eng. Sci., 1991; 31: 365 – 375

[17] M. Padmanabhan, M. Bhattacharya, In-line measurement of rheological properties of polymer melts, Rheol. Acta, 1994; 33: 71–87

[18] C. Rauwendaal, F. Fernandez, Experimental study and analysis of a slit die viscometer, Polym. Eng. Sci., 1985; 25 : 765–771

[19] P.D. Coates, R.M. Rose, B. Wilkinson, In-process measurements for monitoring and control of gelation levels in UPVC compounding, Plast. Rubb. Compo. Process. App.1995; 23: 295–303

[20] T. Glomsaker, E. L. Hinrichsen, P. Thorsteinsen, In-line versus off-line rheological measurements on S-PVC formulations relevant for flow in extrusion dies, Polym. Eng. Sci, 2001; 41: 2231 - 2248

[21] P. Thorsteinsen, E. L. Hinrichsen, T. Glomsaker, Document A dual slit in-line die for measuring the flow properties of S-PVC formulations, J. vinyl & additive tech., 2003; 9: 188-197

[22] J. Aho, S. Syrjälä, Shear viscosity measurements of polymer melts using injection machine with adjustable slit die, Polym. Testing, 2011; 30: 595-601

[23] G. Gou, P. Xie, W. Yang, Y. Ding, Online measurement of rheological properties of polypropylene based on an injection molding machine to simulate the injection-molding process, Polym. Testing, 2011; 30: 826-832

[24] N. Zhang, M.D. Gilchrist, Characterization of thermo-rheological behavior of polymer melts during the micro injection moulding process, Polym. Testing, 2012; 31:748-758

[25] M. Mooney, Explicit formulas for slip and fluidity, J. Rheol., 1931; 2:210

[26] T. Q. Li, M. P. Wolcott, Rheology of HDPE-wood composites. I. Steady state shear and extensional flow, Composites: Part A, 2004; 35: 303-311

[27] L. Carrino, S. Ciliberto, G. Giorleo, U. Prisco, Effect of filler content and temperature on steady-state shear flow of wood/high density polyethylene composites, Polym. Comp., 2011; 32: 796-809

[28] ISO/IEC Guide 98, A Guide to Expression of Uncertainty in Measurement 1995

[29] A. Ares, R. Bouza, S. G. Pardo, M. J. Abad, L. Barral, Rheological, mechanical and thermal behaviour of wood polymer composites based on recycled polypropylene, J. Polym Environ, 2010; 18: 318-325

[30] N. Le Mogne, M. Van Den Oever, T. Budtova, Dynamic and capillary shear rheology of natural fiber-reinforced composites, Polym. Eng. Sci., 2013; 53: 2582–2593