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Investigations of the Rheology and Reactivity of Extrudable Wood-Resin Compounds

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Summary. The extrusion of wood composites based on thermosetting resins is a new application in the field of wood plastic composites. To enable the extrusion of wood thermosetting compounds, it is necessary to know their reactivity and rheology well beforehand, to prevent the system curing inside the extruder. This study shows the different techniques that were adapted to allow in combination an estimation of the processing behaviour of wood-resin compounds in extrusion.

Keywords. Crosslinking; Extrusion; Melamine resin; Rheology; Wood plastic composites.

Introduction

In recent years extruded wood plastic composites (WPC) have received considerable attention from the industry resulting in a tremendous growth in market shares. These commercially available WPCs are usually based on polyethylene or polypropylene. For the extrusion of WPCs based on thermosetting resins no commercial applications are known until now due to the unsuitable rheological behaviour of thermosettings, even though their properties are superior to those of thermoplastics. Extrudable wood-melamine-resin composites combine the advantages of conventional WPC with those of thermosetting wood composites. They have better thermal properties like higher creep resistance, high-temperature strength, higher tensile and bending strength, and improved stiffness and hardness [1].

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Special melamine resins have been developed by Agrolinz Melamine International GmbH showing thermoplastic-like behaviour with well-tuned melt-characteristics to enable the extrusion of wood-melamine-resin compounds [2]. As these compounds are highly reactive systems, where the crosslinking of the resin is catalyzed by wood [3] it is important to know their rheology and reactivity beforehand to prevent them disintegrating, clumping, or even curing inside the extruder.

Since every step during the extrusion process influences the reactivity and hence the rheology of the mixture, and due to the fact that composites with such a high amount of filler (up to 70% of wood) cannot be tested on common devices (*e.g.* plate-plate-rheometer, DMTA) a range of different tests had to be developed to obtain the required information.

This study shows the different techniques that were adapted to enable an estimation of the processing behaviour of wood-resin composites, as there are:

- the high-pressure capillary rheometer with slit die to obtain information on the rheological behaviour
- the modified *Brabender* test in the batch mixer, giving the reactivity, process window and flowability in dependency of temperature, wood type, shear rate and composition under kneading conditions
- the ultrasonic observed pressing where the speed and progress of crosslinking under pressing conditions is determined

Results and Discussion

As mentioned before special melamine resins have been developed to improve the flow behaviour of wood-melamine-resin compounds. Hence these compounds show thermoplastic behaviour, comparable with that of *PP*-based ones, as presented in Fig. 1. The plastification of the resin is achieved by the insertion of chemical compounds with long and bendable chains in between the melamine molecules during synthesis, as described by *Wirpsza* [4]. As a result the resin can be processed like a thermoplast but only in a defined temperature range below which flow is impossible due to the resin not being melted and above which crosslinking will start. This processing window is influenced by the presence of wood, which catalyzes the crosslinking depending on its acidity [3]. While processing, the processing window is even more narrowed due to the local heating caused by the shearing of the melamine resin and wood splinters.

The shear dependent viscosity of the wood-resin compounds – as obtained from measurements with the high-pressure capillary rheometer – is still higher than that of wood-*PP* compounds but nevertheless they are extrudable. At a shear rate of $100\,s^{-1}$ they show viscosities of about $1500\,Pa \cdot s$, which is much lower than those of the compounds based on the first generation of resins, which were as high as $2 \times 10^4\,Pa \cdot s$ at $100\,s^{-1}$ [2]. As indicated in Fig. 1 the rheology of wood-resin compounds can be determined for temperatures up to 130°C allowing measurements at shear rates as high as $300\,s^{-1}$. The values of the compound depicted in Fig. 1 can be described with the *Ostwald-deWaele* approximation with values for $n = 0.4$ and $k = 2.7 \times 10^4\,Pa \cdot s^n$ at 110°C, which is comparable with results *Hristov et al.* published for low-filled (25%) wood-polyethylene compounds ($n = 0.43$ and $k = 3.2 \times 10^4\,Pa \cdot s^n$ at 180°C) [5]. At 130°C the power-law model parameters for the wood-resin compound are $n = 0.25$ and $k = 4.2 \times 10^3\,Pa \cdot s^n$.

In the following the importance of taking into account more than one method will be demonstrated on the example of two wood-melamine-resin compounds, which are similar in every aspect except the types of resin differing in their reactivity. Even though the flow curves determined at 110°C of these two compounds are quite similar (Fig. 2), the results gained in the *Brabender* test at 130°C show how the processing window is affected (Fig. 3). Only by changing the type of resin, leaving everything else the same (kneading conditions, amount and type of wood) the effect on the reactivity is tremendous: the curing peak of compound **B** is higher and more distinctive than the one of compound **A**, indicating that the resin in **B** is more sensitive to shear induced local heating causing a higher reactivity. The earlier onset of crosslinking and curing of compound **B** results in a processing window that is reduced by app 25%, which has to be taken into consideration for the extrusion process.

The ultrasonic observed pressing provides even more information on the differences in the curing behaviour of these two compounds. The speed of crosslinking under pressing conditions is determined giving an estimate for what happens in the extrusion

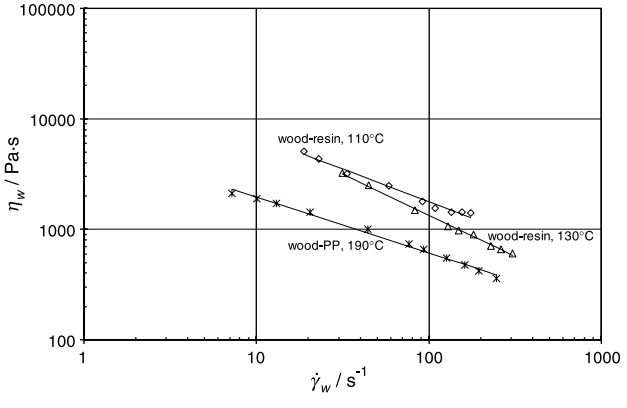

Fig. 1. Viscosity curves for wood-resin (squares – at 110°C; triangles – at 130°C) and wood-*PP* compounds (stars); the symbols represent the values of η_w, and the lines the corresponding *Ostwald-deWaele* approximations.

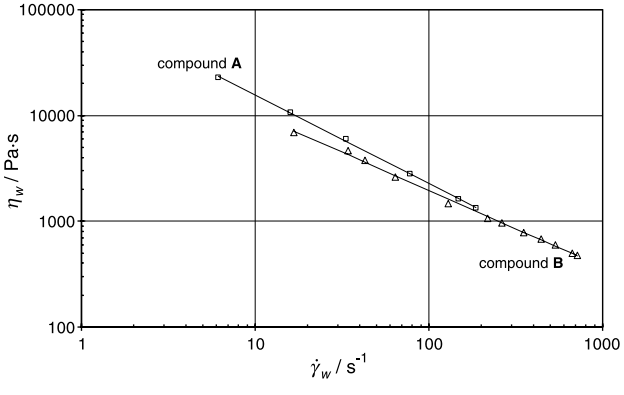

Fig. 2. Flow curves of two wood resin-compounds, based on two different resins (**A** and **B**), squares – compound **A**; triangles – compound **B**, measured at the same temperature (110°C)

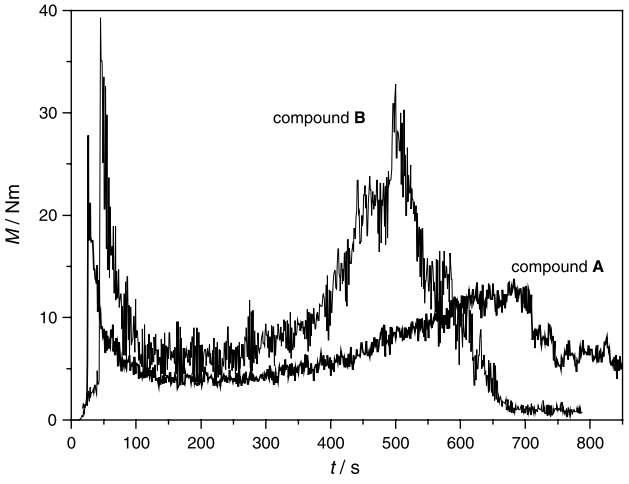

Fig. 3. Influence of the resin on the processing window as determined with the *Brabender* test at 130°C

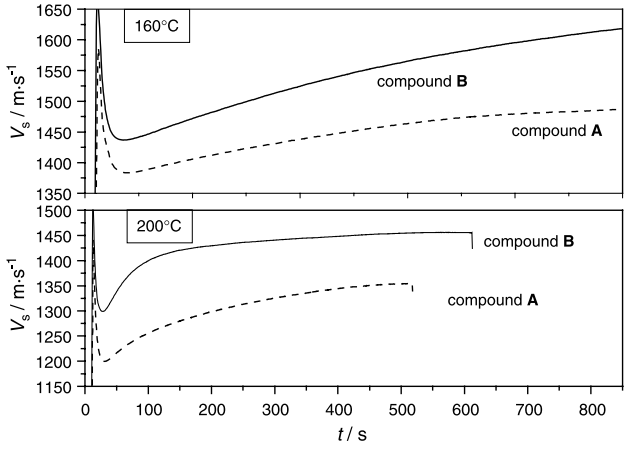

Fig. 4. US-curves of the pressings of wood-resin compounds (dotted line – compound **A**; full line – compound **B**) based on two different resins taken at two different temperatures (160 and 200°C)

tool. As can be seen in Fig. 4 compound **B** shows a stronger thermal dependency of reactivity than compound **A**. Whereas the slope of the curve of compound **A** is only slightly steeper at 200°C, compared to 160°C, and the platform that marks the end of curing is not reached in the specified time at either temperature, the curve of compound **B** shows a significant change of shape at the higher temperature (Fig. 4 bottom). The initial slope after the softening-minimum of compound **B** at 200°C is double the value than that of compound **A**, and the plateau is reached. It means for the extrusion that compound **B** will be cured faster in the mould at higher temperatures than A.

Taking into account the results of the three different methods one can conclude that the processing of these two compounds despite their comparable rheological behaviour will be very different. Whereas the extrusion of compound **B** will be more challenging due to its smaller processing window, compound **A** will produce composites with inferior properties as they may not be completely cured.

Conclusions

Highly filled wood-melamine-resin compounds are complex in terms of processing behaviour: they are sensitive systems, where every change of parameter like temperature and resin type (as well as the type of wood and composition [3, 13]) influences the reactivity and therefore rheology and leads to tremendous changes in their processing behaviour. High-pressure capillary rheometry with slit die is proven to be a suitable method to characterize the rheological behaviour of wood-melamine-resin compounds, which is comparable to that of wood-thermoplastic composites. To estimate the extrudability of WPCs based on thermosetting resins it is not enough to rely on the results from rheological investigations, but to know their reactivity as well. Therefore different techniques were adapted to gain additional information on the flowability, crosslinking and curing behaviour.

As this study shows, the three methods described in this paper (high-pressure capillary rheometry, *Brabender* test and ultrasonic observed pressing) in combination enable one to assess the prospects of a successful extrusion of wood-melamine-resin compounds of different compositions.

Materials and Methods

Materials

The two melamine resins, called **A** and **B**, used in this study, differ in their reactivity, and are special tailored ones (HIPE®ESIN, type MPER; AMI) to ensure their applicability in extrusion; whereas the woods are commercially available wood-splinters of different well-defined sizes and types.

Methods

Different authors have reported results on rheological measurements of either a way to monitor the crosslinking of thermosettings [6] or wood-filled thermoplastic compounds [5, 7, 8]. Whereas rheology studies on highly filled wood-plastic composites are scarce and usually carried out with either *PP* [7] or *HDPE* [5, 8] as matrix, basically no work

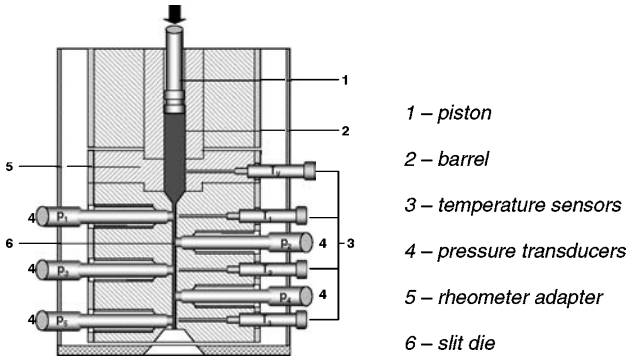

Fig. 5. Schematic picture of the high pressure capillary rheometer

dealing with the application of highly filled wood-thermosetting compounds could be found in open literature.

The measurements on the high-pressure capillary rheometer with slit die were carried out at the Montanuniversity in Leoben to get information on the rheological behaviour of the wood-resin compounds. Figure 5 shows the schematic set-up of the device [2, 9].

Calculation method [9]

The pressure drop inside the slit die at an applied shear rate is measured.

For the shear stress τ follows:

$$\tau_w = \frac{\Delta p \cdot (H \cdot B)}{2 \cdot L \cdot (B + H)} \tag{1}$$

with τ_w the shear stress at the wall, Δp the pressure drop, B the width, H the height and L the length of die.

The true shear rate $\dot{\gamma}_w$ is calculated using the *Weissenberg-Rabinowitsch* correction for slit dies [10]:

$$\dot{\gamma}_w = \frac{\dot{\gamma}_{\text{app}}}{3} \cdot \left(2 + \frac{d \lg \dot{\gamma}_{\text{app}}}{d \lg \tau_w}\right) \tag{2}$$

Leading to the true viscosity η_w:

$$\eta_w = \frac{\tau_w}{\dot{\gamma}_w} \tag{3}$$

with $\dot{\gamma}_{\text{app}}$ the apparent shear rate.

In the case of wood-resin compounds the viscosity curves can be well described using the *Ostwald-deWaele* model:

$$\eta = k\dot{\gamma}^{n-1} \tag{4}$$

with k being the flow consistency index and n the flow behaviour index.

The modified *Brabender* test was carried out in a batch mixer (ThermoHaake Polylab System Rheomix/Rheocord 540p) in which the wood-resin compound is subjected to the kneading of two roller rotors under defined conditions [10]. Therefore an acceleration of the curing reaction caused by shear induced local heating is taken into account. The rheometer is set up in a low-shear mode in order to mimic the action of a twin screw extruder. The resulting torque and energy are measured as a function of time and temperature.

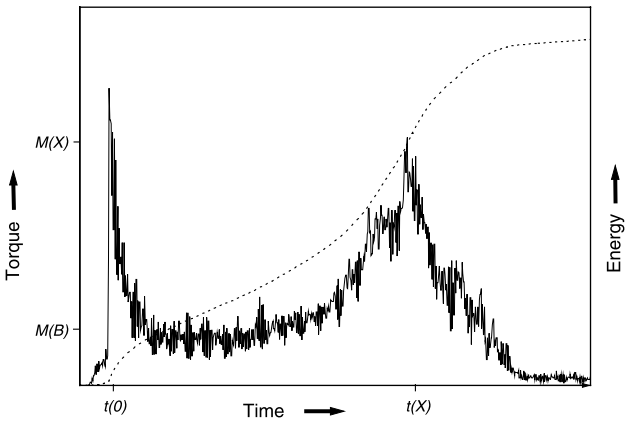

Fig. 6. Typical torque (full line) and energy (dotted line) -time plot (Rheogramme) of a wood-resin compound

Figure 6 shows a rheogramme of the isothermal mixing of a typical wood-resin compound: After the initial maximum – representing the filling of the mixing chamber – the torque drops to a minimum ($M(B)$) corresponding to the melting of the resin. A rapid rise in the torque marks the onset of curing. The time difference between the filling ($t(0)$) and the curing-maximum ($M(X)$ at $t(X)$) gives the processing window. After the compound is cured the torque drops again because of the hardened composite being ground up.

The ultrasound technology has been developed for the use in industry as a non-destructive cure monitoring technique [11]. This method makes use of the fact that an ultrasonic pulse signal which is transmitted through the compound excites molecule segments that start oscillating resulting in an attenuation of the ultrasonic waves. Thus, the ultrasonic sound velocity is closely related to the elastic moduli of materials. During crosslinking reactions molecules of low molecular weight convert into a network of macromolecules which is accompanied by strong changes in the viscoelastic properties resulting in changes of the velocity of ultrasound transmitted through it. The ultrasound measurements are made with ultrasonic sensors fixed within opposite sides of the press with the transmitter in the plunger and the receiver in the mould.

During pressing, the velocity first decreases, corresponding to the softening (decrease of elastic modulus) as the material is heated by contact to the mould. The minimum indicates the point, where the material is melted and starts curing. With the start of the curing the increasing density of the material enables the sound to propagate more rapidly. The shape of the curve reflects the rate of the chemical reaction. As the crosslinking reactions slow down, the increase in the sound velocity also diminishes until a plateau is reached, indicating that the compound is cured [12].

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