Liquid Wood Rheology

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Abstract. “Liquid wood” is a biopolymer composite exhibiting a lignin matrix. Lignin is separated as a by-product of paper. Following research by German scientists from a production company, an invention was made that determines a new use of lignin, the capitalization of said product in this case being superior. This material combines lignin with other natural substances: resins, waxes, vegetable fibres etc. It results a polymer that exhibits certain physic-chemical properties which recommend it for large scale use, being able to substitute plastic materials. Some of the properties of “liquid wood” are: it is a thermo-injectable polymer, it is obtained from renewable resources and it is biodegradable. Existing injection or extruding machines, used for synthetic polymers such as polyethylene and polypropylene, can be employed to obtain various “liquid wood” parts. It has been observed that injection process parameters influence mechanical and physic – chemical properties of products obtained from “liquid wood”. In order to find the optimal injection parameters for an object that exhibits certain mechanical and physic – chemical properties, it is necessary to determine the rheological properties of “liquid wood”. In this paper, several “liquid wood” rheological properties have been determined, in order to assist the optimization of the injection process.

1. Introduction
A biopolymeric composite, “liquid wood” has a constitutive matrix made of lignin. This is an organic polymer containing mostly phenolic compounds. It is found in approximately 25 – 35% of vegetal biomass, [1]. Lignin exhibits a macromolecular structure and, considering some novel measurements, an empirical chemical formula that describes this product has been found: $C_{42}H_{30}O_8(\text{OCH}_3)_6(\text{OH})_4$. Lignin is essential when it comes to plants: it has a significant task in ferrying water and nutrients, [2].

“Liquid wood” is materialized in three distinct presentation forms. For every one of them, lignin is present in different proportions. They are: ARBOFORM® - lignin matrix (60%) improved with hemp fibres or vegetable flax, ARBOBLEND® - 99% lignin and 1% natural additives and ARBOFILL® - biopolymeric composite exhibiting a lignin matrix (60%) and blends of sawdust, natural fibres and petrochemical polymeric compounds such as polypropylene and polyethylene (40%), [3]. This article
seeks to determine the rheological behaviour of the “liquid wood”. The results’ analysis and the final remarks are very important, such that the injection and extruding processes could be optimized. Also, they reveal the behaviour in time of the “liquid wood” finite products, [4]. The tests that will be presented give information regarding injection process – related properties of the objects obtained by using “liquid wood”. They are very important, as available scientific literature on this subject seems to point out that, while “liquid wood” has a good overall workability, the injection parameters are of paramount importance to the overall quality of obtained samples. Therefore, the obtained results complete the determination of the optimal injection parameters, [5]. As such, the values of these injection parameters have a direct influence in the mechanical and physic – chemical properties of parts obtained from “liquid wood”, [6,7]. Consequently, by modifying several injection parameters, “liquid wood” parts with different mechanical and physic – chemical properties may be obtained, [8].

2. Analysis Method

The rheological determinations were carried out using a modular rheometer Physica MCR 501 (figure1) (Anton Paar, Austria), outfitted with an oven – type system CTD 600 that allows the adjustment of temperature in the interval -150 to 600 °C, [9].

The device is equipped with bearings containing airbags, which make it very sensitive in when studying very small stresses. All analyses can be performed by controlling the normal force. The device can function in CSR mode (constant shear speed), CSS mode (constant shear effort) and DSO mode (dynamic oscillatory deformation modulus), [10].

The measurements were taken on a plane – plane geometry. Both the upper and lower plates are made of stainless steel. The diameter of the employed plate is 25 mm. The distance (gap) between the plates was set at 3-5 mm. The results were interpreted with the help of RHEOPLUS v.3.40 software. For the tests concerning temperature sweep, the heating speed of the sample was set to 1°C/minute.

Both types of rheological tests were carried out – oscillatory tests and rotational tests. The reproducibility of the results was checked by carrying out the rheological tests on 3 samples of each analysed material.

2.1. Oscillatory tests

In the case of oscillatory tests, the upper plate goes back and forward, performing an oscillation movement, as presented in figure 2.

Figure 1. Physica MCR 501 rheometer and the used plane – plane device.

Figure 2. The back and forward movement of the upper plate.
2.1.1. Amplitude sweep. Oscillatory tests are very useful in describing the microstructure of viscoelastic materials, giving information about the material’s structure and elasticity. The measured rheological parameters are the accumulation modulus $G'$ (a measure of the deformation energy accumulated by the sample during shearing, representing the material’s elastic behaviour), the loss modulus $G''$ (a measure of the deformation energy used by the sample during shearing, representing the material’s viscous behaviour), phase angle $\delta$, damping or loss factor $\tan \delta = G''/G'$ (which describes the ratio between the viscous and the elastic component of a viscoelastic behaviour) and the complex viscosity $\eta^*$. 

In the case of the amplitude sweep test, the amplitude in a certain domain is varied and the frequency is kept constant (figure 3(a)). This test is carried out in order to determine the linear viscoelastic domain of the material (LVE), which helps in determining the correct parameters required for subsequent oscillatory tests (figure 3(b)).

![Figure 3. Amplitude sweep.](image)

The maximum deformation up until the accumulation modulus value $G'$ remains constant is called critical deformation and defines the limit of the linear viscoelastic domain (LVE – linear viscoelastic). The critical deformation indicates the minimum quantity of energy required to destabilize the material’s structure.

Amplitude sweep tests give the following information:

- The limit value $\gamma_L$ of the linear viscoelastic domain (LVE) (or the domain of reversible deformations). Above this limit, the $G'$ and $G''$ curves have deviated from the constant values of the plateau. The limit value of the shear effort $\tau$ at which the linear viscoelastic domain is overtaken (for example the point at which the value $G'$ starts to decrease), may be considered as a value of the tension threshold (yield point).
- The sample’s structure in the linear viscoelastic domain is expressed by comparing $G'$ and $G''$ values. If $G' > G''$, then the sample has a gel character (solid character) and if $G'' > G'$, then the sample has a liquid character.
- The structural strength of the sample.

2.1.2. Frequency sweep. In the case of frequency sweep tests, the amplitude is kept constant and the frequency is varied, the variation of shearing moduli ($G'$, $G''$) and of the tangent of loss angle on a large frequency domain being thus monitored.

Regarding the diagrams obtained following frequency sweep tests, the accumulation modulus ($G'$) describes the elastic behaviour of the sample, providing information regarding the stability and structural resistance of the sample ("rigidity"), while the loss modulus ($G''$) supplies information about the viscous behaviour ("flexibility"). The loss angle tangent, $\tan(\delta) = G''/G'$.

Frequency sweep gives useful information regarding the internal structure and the molecular mass of the analysed material. The large values of the accumulation modulus indicate the presence of a
stable internal forces’ network inside the sample. This is a measure of the samples’ mechanical and structural stability.

Applying the Carreau – Yassuda model for the results obtained by frequency sweep, the zero shear viscosity, \( \eta_0 \), and the infinite shear viscosity, \( \eta_\infty \), may be computed. A large value of the zero shear viscosity indicates a large average molecular mass and an increased mechanical stability of the sample.

2.1.3. Temperature sweep. Regarding the temperature sweep tests, the amplitude and the frequency are kept constant, only the temperature being modified in a certain domain. In this test, the variation of the shear moduli (\( G', G'' \)) and of the loss angle tangent is tracked in a certain temperature domain.

Temperature tests allow the determination of certain transition events of polymers. The behaviour of polymers is studied especially at melting and hardening, giving useful information about the material’s structure type.

2.2. Rotational tests

In contrast with oscillatory tests, rotational tests are relatively simple ones, in which the upper plate rotates and the lower plate is fixed. The final result of the rotational tests is represented by flow curves \( \dot{\gamma}(\tau) \) and viscosity curves \( \eta(\tau) \). The viscosity determined with the help of the rotational tests is termed shear viscosity or dynamic viscosity \( \eta \) and may be described by the relation (1):

\[
\eta = \frac{\tau}{\dot{\gamma}} \tag{1}
\]

Rotational tests are of two types: tests with controlled shear speed (CSR – controlled shear rate) and tests with controlled shear effort (CSS – controlled shear stress). In the case of CSR tests, the speed \( n \) or the shear speed \( \dot{\gamma} \) is controlled and in the case of CSS tests, the shear effort \( \tau \) or the torsion moment \( M \) is controlled. CSR tests are usually carried out at a flow speed specific to technological processes, for example the pipe flow or particle sedimentation phenomenon. CSS tests are employed in the case of phenomena caused by the action of some forces, for example blood flow.

2.2.1. Flow curves. One of the study domains of rheology is flow. Most rheometers have, as functioning principle, the axis relative rotation of three types of geometries: (a) concentric cylinders, (b) cone – plate or (c) – parallel plates (figure 4). The type of measurement geometry is specific to the sample’s nature and to the generated flow conditions.

![Figure 4. Types of measurement geometries for a rotational rheometer.](image)

The concentric cylinders are used for samples exhibiting low viscosity; the large contact surface renders a high sensitivity at low shearing speeds. Furthermore, this system may be used to measure materials presented as particles, as long as the distance between the cylinder and the cone is not critical. For high viscosity samples, cone – plate or parallel plates systems are used; the last system exhibits very low sensitivity to the distance variation between the plates, but a variation of the
shearing speed inside the sample exists. The cone-plate geometry eliminates this problem and is generally used for high viscosity pastes, gels and concentrated mixes.

A flow curve is the graphical representation of the materials’ flow behaviour, through which a sample is subjected to an either increasing or decreasing shearing force, with the shearing effort and viscosity being computed by the device’s parameters. The shape of the flow curves is indicative of the sample’s flow behaviour and it is usually one of the four cases described in figure 5.

![Flow Types](image)

Figure 5. Flow types (blue line – viscosity, red line – shearing effort).

For a Newtonian behaviour (a), the viscosity is constant along the entire domain of the shearing speed. When viscosity decreases with the shearing speed, a pseudo-plastic behaviour appears (b) (shear thinning). Distend behaviour (c) (shear thickening) appears when viscosity increases with the increase in shearing speed. The Bingham – type plastic behaviour (d) is characterized by a large value of viscosity, up until a critical value of the shearing effort (tension threshold) is reached, after which the sample begins to practically flow.

The flow type has consequences upon controlled-flow applications. Referring to materials with a distend behaviour, they cannot be easily pumped. In the case of paints, the aim is to obtain paints with a pseudoplastic behaviour, but they should have thixotropic properties as well, such that they may be applied on a vertical surface.

To sum up, a simple flow curve can be obtained by applying some series of shearing and by recording the obtained viscosity. The shape of the curve can be employed to predict the flow behaviour in different applications. By interpolating the values of viscosity, a value of shear speed outside the measurement domain of the apparatus can be obtained.

3. Results and discussions

The purpose of rheological tests is to obtain information about the mechanical properties of the analysed materials. Rheological measurements allowed the correlation of information regarding the viscoelastic behaviour with the employment capacity in the industry of "liquid wood"-type materials. The correlation between the microstructure and the macroscopic behaviour of a material can be shown with the help of oscillatory rheological tests. Thus, rheological measurements allow the estimation of the studied systems’ structural stability with the help of measured viscoelastic parameters: accumulation modulus $G'$, loss modulus $G''$, phase angle $\delta$, loss factor $\tan \delta$ and complex velocity $\ln^*1$.

The first oscillatory rheologic test made on studied samples was the amplitude sweep test, carried out in order to determine both the limit of the viscoelastic domain, and to estimate the materials’ structural stability. The tests were performed at a temperature of 150°C. In the case of this test, the frequency is maintained constant ($\omega = 10$ rad/s) and the deformation is varied between 0.001 and 100%. In figure 6, the structural stability of the samples, in the small deformations’ domain, at work temperature, may be observed. Arbofill and Arboform samples exhibit a high rigidity (accumulation
modulus $G'$ has high values) and the structure is more susceptible to deformations. The Arboblend sample exhibits a stable structure throughout the entire deformation domain, with a mainly liquid behaviour ($G'' > G'$). This is due to the strong links present between the macromolecules, which dictate a structured fluid behaviour.

![Figure 6. Temperature sweep for analysed materials at 150°C.](image6)

When doing the frequency sweep test, the amplitude is maintained constant in the limit of linear viscoelastic domain ($\gamma = 0.003 - 1\%$ at 150°C) and the frequency is varied in the $0.005 \div 500$ rad/s domain. This test gives information regarding the stability in resting state and the behaviour over time of the analysed materials. The $G'$ values are greater than $G''$ over the entire studied frequency domain, so the Arbofill and Arboform samples exhibit a solid – type behaviour at the temperature of 150°C (figure 7). The dynamic moduli are almost parallel and vary little with frequency, which suggests the existence of a stable network due to some interactions from the component macromolecule chains. In the case of the Arboblend sample, the dynamic moduli are parallel and frequency dependent, due to the existence of some physical links that break and reknit over the entire testing period.

![Figure 7. Frequency sweep for analysed materials at 150°C.](image7)

Furthermore, the structural stability and the fluidization degree of the analysed materials were highlighted with the help of rheological temperature tests, which were made at a constant frequency ($\omega = 10$ rad/s) and constant amplitude in the linear viscoelastic domain (figure 8).
Figure 8. Rheological temperature tests of the analysed materials.

The rotational tests were carried out in the 0.01 ÷ 100 s⁻¹ domain of shearing speeds. The large values of viscosity at zero shearing (table 1), computed with the Carreau–Yasuda model from the flow curves (figure 9), highlight the structural stability of the analysed materials.
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Table 1. Values of viscosity at zero shearing.

| Sample name | Viscosity at zero shearing (Carreau – Yasuda model) (Pa·s) |
|-------------|----------------------------------------------------------|
| Arboblend   | 1793.7                                                   |
| Arboform    | 104850                                                   |
| Arbofill    | 33325                                                    |

4. Conclusions

It is observed that for most of the „liquid wood” materials the phase transition happens within the 150-170°C temperature interval. This observation leads to the remark that the optimum injection temperature will be found in this specific temperature interval. The rheological tests indicate also the behaviour of the “liquid wood” material types, when they are exposed to mechanical forces. The tests presented in this paper showed the changes of the characteristic coefficients, such as the shear coefficient and the viscoelastic coefficient, depending on frequency, pressure and temperature interval. Following the results, the parameters’ values can be determined, with the purpose of optimizing the injection process – the temperature, pressure, speed, injection time etc. Moreover, the tests’ results indicate the parameters’ optimum values during the extrusion process.

5. References

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