Rheological characterization of PVC corncob composites. Effect of molecule weight of PVC

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Abstract. The flow behaviors of different poly (vinyl chloride) and corncob flour composite were characterized using a Göttfert 20 extrusion rheometer. The rheological characterization includes extrusion experiments at different temperatures and screw speeds. By evaluation of flow rate and die pressure the flow properties and the activation energy of the flow can be determined. This also provides insight into the internal structure/organization of the prepared composite and gives information about process ability and processing window parameters. The flow of the melt is mostly determined by the molecular weight of the polymer but for PVC the higher organization of the polymer as tertiary and quaternary structures have also a significant effect. Moreover, the molecular weight affects not only the viscosity but also the relaxation times. This flow behavior of the polymer has changed significantly by shearing time and thermal history of the materials. PVC composites compounded from raw PVC powder of various K values (molecule weight) were prepared and examined via a complete rheological analysis. The PVC composite’s morphology mostly depends on the concentration of the components, the material matrix and the corncob additive. The viscosity of the composites, the Rabinovich exponent, and flow-viscosity curves were determined in this paper. The results of the rheological tests can help us to make comprehensive conclusion about the composite structures, processing possibilities and applicability.

Keywords: PVC, corncob, melt rheology

1. Introduction

Nowadays, the environmental awareness is the most important. Thereby, the majority of researchers trying to make plastics to be more “natural” therefore using natural fillers for easier biodegradation [1]. The new composites need to be developed to have excellent properties for technical applications. However, before testing of the mechanical properties, it is also necessary to study the viscosity of the materials. As the fields are only concerned with plastics but also using metals, alloys and ceramics, so it is also necessary to carry out the rheological tests too [2, 3]. In order to determine the rheological properties of different materials, the first step is to study the models which are describing their behavior [4].

The rheology of polymer generally refers to the deformation process and flow above the glass transition of temperature [5]. Poly (vinyl chloride) can be characterized by rheological properties. Due to the special structure of PVC, furthermore as in this case when use filler (corncob) and additives to knowing the rheological parameters of the composite is quite important. These additives always
forming separate solid phases, therefore the polymer melt has higher viscosity than without additives. Moreover, the PVC depending on its fusion grade can also flow as a particle flow, i.e. the PVC melt is inherently a two-phase system. The flow properties are changed by thermal history of the compound. The polymeric flow is partly caused through particle sliding. The viscosity and relaxation time of the composites depend on the molar mass and the temperature. The melt elasticity of polymers decreases with increasing of the molecular mass contrary to viscoelastic theories. The molecular weight also significantly influences the values of the activation energy [6, 7].

Some researchers have already investigated the viscosity modifying effects of natural fillers. Mantina et al. analyzed that the mechanical and viscosity changing properties of soft wood, homonym plant and sago starch with polypropylene. The viscosity of the natural composites was higher than the base matrix viscosity. This effect was further enhanced by increasing the amount of natural fillers [8]. Other researchers has also described the viscosity enhancing effect of the woods filler [9, 10] Maiti et al. examined that the wood flour concentration has a rheological modifier effect to isotactic-polypropylene. This case, the shear stress rate follows the power laws and the viscosity curves show shear thinning property when the natural filler component was increased in the composites [11]. Li and Wolcott did similar examinations, they also investigated the effect of the natural fillers to the wall slip of the die [12].

2. Materials and Methods
Commercially available PVC powders have been provided by BorsodChem Zrt. To prepare the composites PVC resins and additives were used. The additives were the following: corncob, Ca-Zn based solid stabilizer, paraffin based external- and partial glycerol ester type internal lubricants, ground CaCO₃ filler. The corncob filler was at a 200 – 300 μm particle size. The content of the corncob 20 phr (per hundred resin) for all three composites. Three different types of PVC from K = 56; 58; 64 molecular weight were mixed with corncob thoroughly in a turbo mixer. The mixing process was maintained about 15 minutes until it reached a temperature of 140 °C. The resulting powder had been extruded by Göttfert Extrusiometer 20 laboratory extruder. The barrel diameter was 20 mm, the length was 20D (400 mm). A continuous compression screw of 1:4 compression rate was used. The length of dies (capillaries) were 15; 20; 25 mm. The temperature of die and barrel in front of the die were set 160 to 180°C. All data (3 pressure date, 3 steel temperatures, 3 mass temperatures; output, torque) were recorded at 20, 40, 60, 80, 100 rpm.

3. Rheological Measurement and Results
For the rheological measurements on the extruder the exact geometry of the capillaries has to be known and in case of pressure measurement in front of the capillary, the pressure drop in the inlet of the capillary needs to be also considered. In the first step the Bagley correction was determined using capillaries of the same diameter, same inlet geometry and different active length. As described in the paragraph materials and methods, the determination method is shown in Fig.1 where the pressure drop is plotted as function of relative length (L/D) of the capillary.

| Table 1. Physical and adjusted lengths of the capillaries |
|----------------------------------------------------------|
| Physical length [mm] | Adjusted length [mm] |
| 15                     | 19.66                 |
| 20                     | 24.66                 |
| 30                     | 34.66                 |
The straight lines meet at 1.0 pressure drop and the equivalent length of the inlet. Therefore, a longer capillary length had to be calculated than the physical capillary length.

After determined the Bagley correction factors the extrusion experiments with longer capillaries were carried out. For determination of melt viscosity the longest die (30 mm phisical length capillary) at screw speeds of 20, 40, 60, 80 and 100 u/min were used.

The pressure drop and the output work was tabulated and from the data examined the exponent is the Rabinovich equation.

\[ n = \frac{d \lg Q}{d \lg \Delta P} \]  

Where: \( n \) - flow exponent (Rabinovits correction), \( Q \) - volumetric speed \([m^3/s]\), \( \Delta P \) - pressure drop on the capillary \([Pa]\).

**Figure 2.** Determination of \( n \) (Rabinovich exponent) for composites made from K=56 resin
Using the n values the output was corrected with the density of the material, the shear rate (eq. 2) and shear stress values (eq. 3) were calculated. The shear rate of the wall could be determined by the following equation:

$$\dot{\gamma} = \frac{6 Q}{h^2 w} \left(\frac{n+2}{3}\right)$$

(2)

Where: $\dot{\gamma}$-calculated shear rate [1/s], $Q$-volumetric speed [m³/s], h-thickness of the gap [mm], w-width of the gap [mm]. To determine the viscosity, needed to calculate the shear stress (eq.3) on the capillary wall.

$$\tau = \frac{h\Delta P}{\left(\frac{h}{w} + 1\right)2l}$$

(3)

Where: $\tau$-shear stress [MPa], h-thickness of the gap [mm], W-width of the gap [mm], $\Delta P$-pressure drop on the capillary [Pa], l-length of the gap [mm].

From the eqs. 2 and 3 the viscosity can be determined.

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}$$

(4)

Where: $\eta$ – viscosity [Pas].

Plotting the calculated viscosity as a function of shear rate we graphically demonstrated by Fig.3

![Figure 3. Composite of 56 and 58 with different die length](image)

The dependence of the temperature and the viscosity was also investigated at Fig. 4.
In addition, in case of K=64 composite the graph in Fig. 5. The composite of K = 56 its viscosity curve is similar than to K=58, the difference are larger for the K = 64 composites. Of which a possible explanation is that this materials considerably slipping on the die therefore the flow is not a pure shear flow. The lower is the polymers molecular weight, the better is its compatibility with the additives, and this causes the slipping as the amount of external lubricant is negligible. Clearly that visible below the shear rate of 1000 – 1500 sec⁻¹ the temperature dependence of viscosity follows the expectations, that the higher is the temperature the lower is the viscosity, but over 1500 sec⁻¹ the difference between the viscosities is below the determination error. So practically, the viscosity lines run into one line.

Plotting the viscosity values, as function of shear rate and the parameter is the K-values is the PVC resin used. The difference between the K=56 and 58 is very low (although measurable) but true the molecular weight are very near to each other and the K = 64 is obviously higher.
For PVC resins of 58 and 64 value the \( r^2 \) (coefficient of determination) was over 0.99, however, the viscosity values function of temperature were scattered and gave a poor correlation (\( r^2 \) only 0.77) for resin K=56. Therefore, we do not consider this data as reliable and not plotted here (Fig.6).

Figure 6. Activation energy of 58 and 64 composite

4. Conclusion

The PVC/Corncob flour composite rheologically can be handled as normal polymer melt. It follows the general rheological laws. It seems that the energy of the activation is dependent on the molecular weight i.e. the K-value of the PVC resin. The results were verified by viscosity measurements of samples. Demonstrated by real flow viscosity and flow activation energy curves, because of the good fitting of the viscosity data as function of die length see in Fig.3. The Bagley correction proved reliable, it can be used for obtaining real rheological data. The results show that these natural composites behave rheological as normal polymeric materials.

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