

On Pressure Affected Shear Viscosity of Poly(Lactic) Acid

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Abstract. Evaluation of pressure coefficient of polymer melt viscosity has become important parameter taken into account for flow behavior prediction in polymer processing simulation software. In this paper, the pressure coefficient of biodegradable polymers, poly(lactic) acid (PLA), was investigated. A capillary rheometer equipped with back pressure device controlling pressure in polymer melt during flow was employed for experiments. Pressure sensitivity was evaluated through pressure coefficient calculated via fitting of obtained viscosity data by the help of Carreau-Yasuda model. It was found that pressure coefficient of PLAs is strongly affected by the internal structure of tested polymer.

Keywords: Pressure dependent viscosity, Rheology, Poly(lactic) acid.

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INTRODUCTION

Investigation of pressure influence on polymer melt viscosity has increasing tendency in the last decades. Pressure effect, which was often overlooked in the past, becomes a more important parameter nowadays. Since it has a significant effect on melt viscosity behavior particularly in high pressure processes such as injection moulding and powder injection moulding [1-3] it was incorporation into several softwares providing simulation of polymer processes.

Generally, there are several techniques for determination of influence of pressure on flow behavior. It could be studied through viscosity and PVT data relation using Simha-Somcynsky [4-6] or modified Miller [7] equations. Furthermore an investigation of pressure affected viscosity employing modified rheometers and followed by evaluation of flow behavior by the help of pressure coefficient using some mathematical models could be employed. The pressure coefficient was incorporated into several nonlinear models such as Barus-Arrhenius combination [8-9], White-Metzner [10], Cross-Vogel [11], modified power law [12], WLF equation [13] and Carreau-Yasuda [1, 14]. The accuracy and reliability of different techniques available for determination of pressure influence has been reported by Goubert et al. [15] and H. E. Park et. al. [16]. It was demonstrated that the pressure coefficient obtained from analysis of temperature affected viscosity and PVT data fairly agree with robust method. Further it was shown that pressure coefficient evaluated from non-linearity in pressure profile determined using standard capillary rheometer is not

precise due to the combining and hardly separable effect of temperature, pressure, and slip. On the other hand, double-piston slit-die close system rheometer [17] and sliding plate rheometer [16], as the most robust methods, were proved to provide the most precise results, since the shear stress, shear rate and pressure in the system can be directly investigated [17]. Nevertheless, these robust methods require very complex and commercially unavailable instruments. Finally, a relative simple methodology is an enhancement of capillary rheometer by back-pressure device providing results with 10% error as reported Goubert et al. [15].

Up to now the most of the mentioned research studies have been focused on petroleum based polymer while none of them investigated the pressure coefficient of natural based polymer which is becoming an alternative sustainable material in the future. Therefore, in this work, the pressure dependent flow behaviors of three various grades of poly(lactic) acid (PLA, polylactide) were studied. For this purpose, the standard capillary rheometer with back pressure device as present in Sedlacek et al. [10] was used for determination of pressure affected viscosity of PLA melt, while obtained flow curves were evaluated by means of the Carreau-Yasuda model.

EXPERIMENT

General purpose biopolymer grades Ingeo 2002D, Ingeo 4042D and heat seal grade Ingeo4060D based on PLA (the chemical structure is shown in Figure 1) and produced by NatureWorks, USA, was chosen for our study. PLA granules were dried in an oven at recommended conditions (90, 80, and 45°C, respectively) before rheological experiments and kept at an appropriated elevated temperature (45°C) during experimental period to prevent moisture absorption causing drastically PLA degradation in any process.

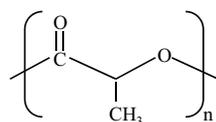


FIGURE 1. Chemical structure of poly(lactic) acid (PLA).

The pressure dependent rheological behavior of PLA at temperature of 190°C was studied using a capillary rheometer, Göttfert Rheograph 2001, Germany equipped with back-pressure device. Back-pressure device designed at Polymer Centre of Tomas Bata University in Zlin, Czech Republic, and described in more details in the paper of Sedlacek et al. [10] (its schematic diagram is shown in Figure 2) was used for modification of standard rheometer in order to generate pressure increase in tested polymer melts. Pressure level in polymer melt is controlled by the mean of an adjustable needle valve restricting outflow channel which is horizontally altered in a range of micro meter.

Two pressure values were taken; one above the entrance of capillary and another one in the secondary chamber. The entrance pressure was recorded via Göttgert GFT 048B transducer while the exit pressure was indicated by Dynisco MDA 462-1/2 transducer with 140 MPa nominal ranges.

Two 180° entrance plane capillaries of 1 mm diameter with various lengths were utilized in the experiments. A capillary with length to diameter (L/D) ratio of 20 and an orifice capillary with L/D of 0.12 were employed in order to determine the entrance pressure drop. The schematic of dies used in experiments can be seen in Figure 3.

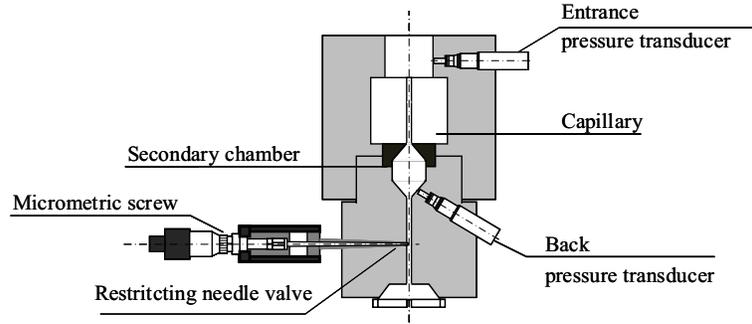


FIGURE 2. Schematic of capillary rheometer with back pressure device.

Before the rheological measurement was performed, PLA granules were filled into the reservoir of both rheometer and back pressure chamber. Viscosity measurements of tested materials were then conducted at shear rate ranges of 35-2500 s^{-1} . The needle valve position was fixed for each set of experiment and, then, at least for six times relocated to change pressure level in polymer melts. Pressure drop across capillary and orifice dies were recorded and evaluated as follows.

Entrance (ΔP_E) and capillary (ΔP_C) pressure drops can be calculated from following equations:

$$\Delta P_E = P_{Oen} - P_{Oex} \quad (1)$$

$$\Delta P_C = P_{Cen} - P_{Cex} \quad (2)$$

where the subscripts *en* and *ex* correspond to entrance and exit, respectively, while *o* and *c* stand for orifice and capillary type of dies. These pressure drops are functions of temperature and mean pressure. Assumed linear pressure profile in the die, then the mean pressure can be determined from:

$$\Delta P_m = \frac{P_{Cen} + P_{Cex}}{2} \quad (3)$$

True shear stress (σ_c) with Bagley correction and true shear rate ($\dot{\gamma}_c$) can be derived from following equations:

$$\sigma_c = \frac{(\Delta P_C - \Delta P_O)R}{2L} \quad (4)$$

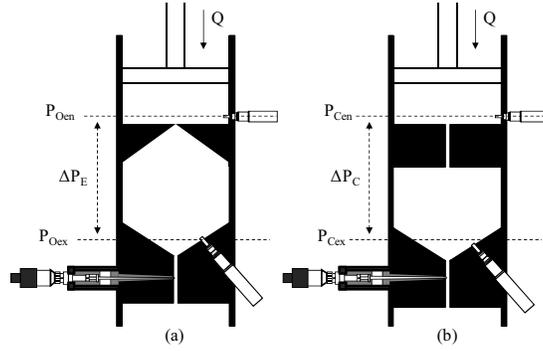


FIGURE 3. Schematic of orifice and capillary dies used in experiment. (a) orifice and (b) capillary die.

$$\dot{\gamma}_c = \frac{4Q}{\pi R^3} \left(\frac{3n+1}{4n} \right) \quad (5)$$

where R , L , and Q are capillary radius and length, and volume flow rate respectively. The value of Rabinowitch parameter (n) is obtained from the slope of log-log plot of true shear stress versus apparent shear rate. Consequently, true shear viscosity (η_c) is then calculated from a proportion between shear stress and shear rate.

$$\eta_c = \frac{\sigma_c}{\dot{\gamma}_c} \quad (6)$$

Pressure dependent shear viscosity can be determined by shear viscosity data fitting at different value of mean pressure using Carreau-Yasuda model which is:

$$\eta_{(\dot{\gamma})} = \frac{\eta_0 f}{1 + [(K_1 f \dot{\gamma})^a]^{(1-n)/a}} \quad (7)$$

where η_0 , $\dot{\gamma}$, and $\eta_{(\dot{\gamma})}$ are zero-shear viscosity, shear rate, and shear dependent viscosity, respectively. K_1 , n , and a are empirical constants while f is an exponential function of pressure sensitivity defined as:

$$f = e^{\beta(P-P_0)} \quad (8)$$

here P , P_0 , and β are mean and reference pressures, and pressure coefficient, respectively.

RESULTS AND DISCUSSION

The pressure dependent viscosity data determined at different mean pressures is represented in Figure 4 as symbols while solid lines present obtained data fits via Carreau-Yasuda model with pressure exponential function. Software employing least square method was employed for fitting parameters calculation. The obtained values of parameters are summarized in Table 1.

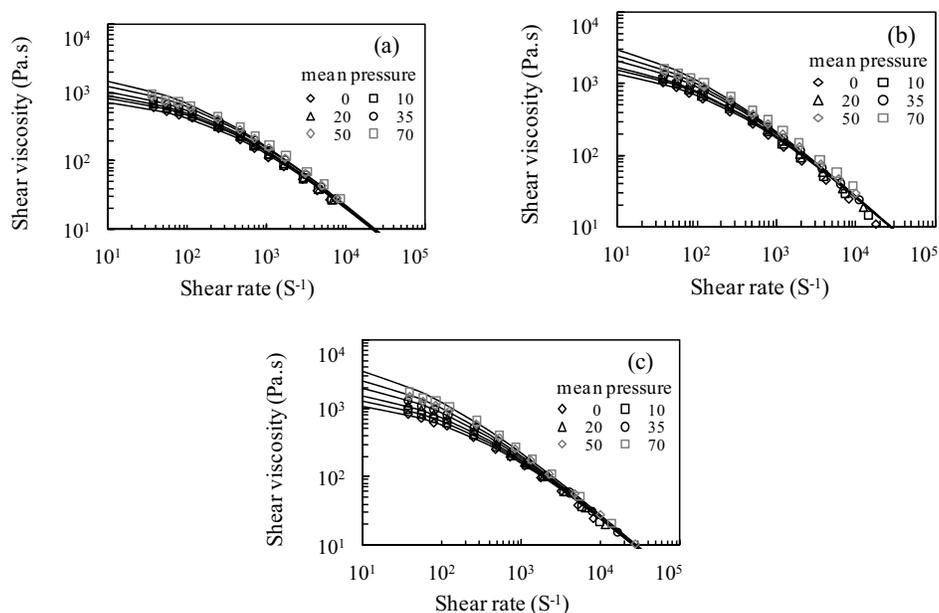


FIGURE 4. Pressure-dependent viscosity versus shear rate of PLAs (a)4060D, (b)4042D, and (c)2002D at 190°C. Solid lines represent data fitting by the Carreau-Yasuda model.

As can be seen from Figure 4, shear viscosity data of all tested PLA grades are in the whole experimental range of shear rate in good agreement with constructed fitting curves. Furthermore, it is clear from the figure that PLA melt viscosity decline with shear rate increased indicating shear thinning behavior of tested materials. Moreover, obviously viscosity growth as mean pressure is increased signifies positive influence of pressure on flow behavior.

TABLE 1. Fitting parameter of Carreau-Yasuda model.

Material	η_0 (Pa.s)	n (-)	K_1 (s ⁻¹)	a (-)	β (GPa ⁻¹)
Ingeo 4060D	923	0.0207	0.0039	0.5869	11.841
Ingeo 4042D	1887	0.0003	0.0064	0.5495	15.051
Ingeo 2002D	1523	0.0052	0.0052	0.5552	21.471

From numerical results presented in Table 1, it is obvious that the zero shear viscosity of Ingeo 4060D is significantly lower than that of the others grades, particularly, in comparison with zero shear viscosity of Ingeo 4042D it is approximately half. Determined results could be connected with significant difference in molecular weight of tested materials. Graphical result describing significant

variation in shear viscosity behavior is clearly visible in Figure 5 where the master curves of reduced viscosity versus reduced shear rate are shown. While the time-pressure superposition was applied in order to construct mentioned master curve, reduced quantities employed here were determined from following equations:

$$\eta_r = \frac{\eta}{f} \quad (9)$$

$$\dot{\gamma}_r = f\dot{\gamma} \quad (10)$$

where η_r , and $\dot{\gamma}_r$ are reduced shear viscosity and reduced shear rate, respectively.

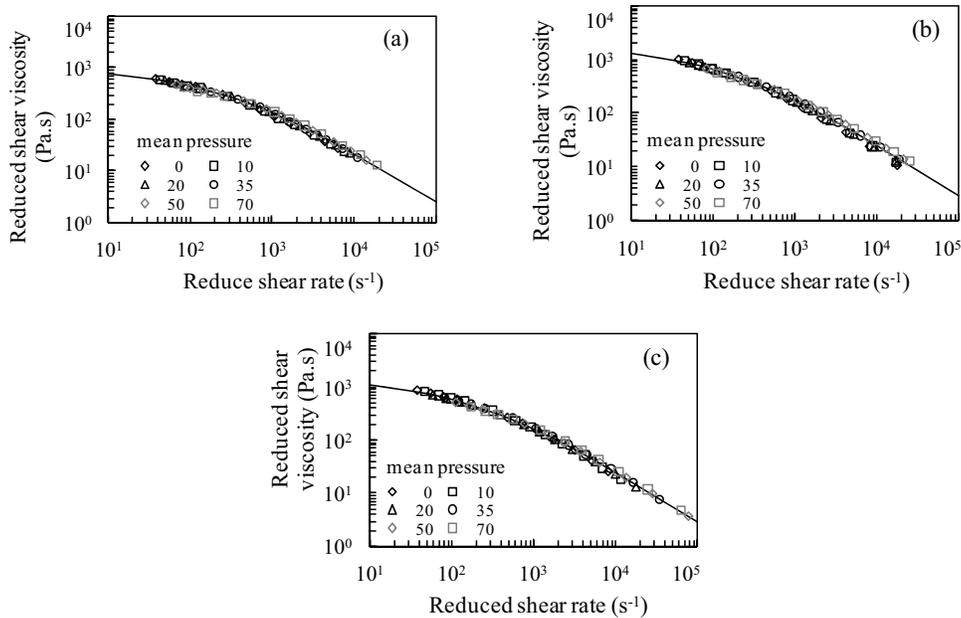


FIGURE 5. Corrected shear viscosity versus corrected shear rate of PLAs (a) 4060D, (b) 4042D, and (c) 2002D at 190°C. Solid lines represent data fitting by the Carreau-Yasuda model.

Concerning pressure sensitivity, it was clear from Table 1 that influence of pressure is the lowest for Ingeo 4060D, while value of pressure coefficient of Ingeo 2002D is almost two times higher. The variation in pressure sensitivity comes from divergence in molecular structure of tested PLA grades connected with variation in molecular weight of backbone and branches, as well as in amount of branching units. As reported by Sedlacek et al. [10], the pressure sensitivity of polyethylenes (low density, LDPE, linear low density, LLDPE, and high density, HDPE) melt viscosity is significantly influenced by their molecular structure. While linear structure of HDPE is connected with the lowest value of pressure coefficient (found to be approximately 10 GPa^{-1}), linearly structured macromolecules of LLDPE with short branches has only slightly higher pressure sensitivity (approximately 12 GPa^{-1}), in the case of long chain branches of LDPE pressure sensitivity coefficient increased significantly up to value of 20 GPa^{-1} . Based on this fact, it might be possible to assume that the structures of

tested PLA grades could vary from highly branched to linear structures as value of β is ordered Ingeo 2002D>4042D>4060D. However, the verification of such presumption needs to be checked by the means of available methods.

CONCLUSION

Pressure sensitivity to viscosities of three various biopolymers grades based on poly(lactic) acid was investigated via standard capillary rheometer equipped with back pressure device. The built up pressure in polymer melt streams were altered and precisely controlled by the help of a needle valve. The Carreau-Yasuda model was successfully employed for evaluation of the PLA flow behavior and calculation of pressure sensitivity coefficients. The results revealed that zero shear viscosities of tested PLA grades vary significantly from one grade to another. Moreover it was shown that also increase of viscosity with pressure growth in polymer melt diverge significantly between tested grades. The order of pressure coefficient values was found to be ordered as follows: Ingeo 2002D>4042D>4060D. It is assumed that observed variation in biopolymer structure notably affects the values of pressure coefficient.

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