On Pressure and Temperature Affected Shear Viscosity Behaviour of Poly(Lactid) Acid Melt

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Abstract: Rheological properties of a poly(lactid) acid (PLA) as one of the most important bio-base sustainable polymer potentially applicable for medical applications had been studied. Shear flow behaviour of PLA melt was determined using capillary rheometer modified by backpressure device directly connected to the main rheological apparatus. The device employed increases pressure actuating on polymer melt stream in capillary reservoir through restricting valve resulting in an increase of melt viscosity. The temperature and pressure sensitivity coefficients were determined through the viscosity data fitting with the Carreau-Yasuda model. The study revealed that shear viscosity of tested PLA melt is strongly affected by temperature and pressure.

Key-Words: Rheology, Shear Viscosity, Pressure Coefficient, Temperature Coefficient, Poly(lactid) acid, Carreau-Yasuda model

1 Introduction

As it is indicated by an increasing number of research papers in a past decade, poly(lactic) acid (PLA) which is produced from natural renewable sources become an alternative sustainable material in near future [1]. This fact is connected namely with high reproducibility of PLA production (comparing to common biopolymers), and controllable degree of biodegrade-ability.

PLA is aliphatic polyester which can be produced by ring opening polymerization of lactic acid (LA) monomer naturally occurred in many food production industries. It was shown that semi-crystalline structure of this thermo-plastic polymer depends on the content of l-LA and d-LA stereo isomers, particularly d-LA decreases the crystallization rate of PLA, note that 12-15% of d-LA could even make PLA completely amorphous. Physical appearance and properties of PLA are usually compared with polystyrene (PS) or poly(ethylene terephthalate) (PET) in term of its strength, rigidity, transparency, and processing conditions, while its biodegradability warrants an important potential advantage especially for its single-use applications exploitable, for example, in medical application, food packaging, and agricultural films.

Generally, PLA can be formed employing either of polymer process such as extrusion, injection moulding, blow-moulding, etc. Processing flow behaviour of PLA melts have been thus studied in several investigations [2-6] describing shear and elongational viscosities with the focus to solve the flowing problems arisen in conventional processes, as it was done before with other similar thermoplastic polymers.

Since the precise simulations of polymer processes play important role in industrial problem solutions, the pressure coefficient, commonly omitted up to now in flow behaviour simulation, is being more essential, particularly for high pressure processes, such as injection moulding. An investigation of the pressure coefficient has been proposed by Maxwell and Jung [7] and studied continuously since 1950s. One of the most practical used methodologies are using a conventional capillary rheometer with different length of dies [8-9] or a die blockage at the exit [10-13] in order to generate different pressure build up in melt stream. Moreover, some mathematical models have been chosen for the pressure influence evaluation. Reported values of pressure coefficient presented in research papers proved acceptable deviation concerning various methodologies currently employed for its determination. Up to now, the mostly conventional polymers such as polystyrene (PS), polypropylene (PP), polyethylene (PE), polymethyl methacrylate (PMMA), Polycarbonate (PC), poly-α-methylstyrene-co-acrylo-nitrile (PαMSAN), and acrylonitrile-butadiene-styrene (ABS) [8-13] were investigated, while the rheological properties of PLA and its blends have been focused only on routine shear and elongational viscosity behaviour description at chosen temperatures conditions.

ISBN: 978-1-61804-022-0

In present work, the pressure affected flow behaviour of a PLA was investigated by means of capillary rheometer equipped with backpressure device designed at Tomas Bata University and in details described by Sedlacek in [11]. Obtained flow curves at various temperature and pressure conditions were described by the Carreau-Yasuda model determining in this way the both temperature and pressure sensitivity coefficients.

2 Experimental

2.1 Material and Thermal Analysis

A commercial available PLA grade Ingeo4060D produced by NatureWorks (USA) was chosen for an investigation. The resin granules had been dried in an oven at 55℃ for 4 hrs prior to experiment and then kept in the oven at 45℃ along the experiment in order to prevent moisture sorption causing significant degradation of PLA.

Thermal analysis of used polymer was carried out using differential scanning calorimeter (DSC 1, Mettler Toledo, Switzerland) at temperature range from -40 to 210℃ and heating and cooling rate of 20℃/min. While the first heating scan was performed in order to remove stress and thermal history of the sample, characteristics temperature, namely glass transition, melting temperature, and temperature of crystallization, were determined from the second heating scan.

2.2 Flow Behaviour Determination

The pressure dependent shear flow behaviour of the PLA was measured using a capillary rheometer (Goettfert 2001, Goettfert Inc., Germany) modified with device consisting of regulated pressure chamber and restriction needle valve located at the exit of the chamber. Applied backpressure device for determination of pressure influence on viscosity behaviour was designed at Tomas Bata University in Zlin, while its functionality was successfully verified in several research works [11, 14-16]. Pressure profile during experiments was recorded by the means of the pressure transducer MDA 462-1/2 (Dynisco, USA) with nominal range of 700 bars attached to the lower chamber in order to record pressure build up (exit or backpressure) and the entrance pressure transducer GFT 048B (Goettfert, Germany) with nominal range of 2000 bar monitoring pressure conditions in the reservoir above the capillary die entrance.

Two dies of two L/D (length/diameter) ratios were selected in order to evaluate appropriate corrections of viscosity behaviour: pressure profile determined using 1/20 capillary was corrected for an entrance pressure loss utilizing 0.12/1 orifice die. The experiments were performed at two different temperatures 170, and 190°C keeping constant along the reservoir and capillary zone. An additional external temperature control was used for the pressure regulated chamber. The experiment was carried out at different constant apparent shear rates covering range from 35-2500 s^{-1}. Pressure effect was determined from the measurements comprising five different adjustments of needle valve at each temperature and repeated several times in order to calculate mean value of viscosity in further evaluation. The resin melting time of three minutes was kept in order to prevent polymer degradation from long residue time.

2.1 Temperature and Pressure Coefficient Evaluation

The following equations were used to calculate the true shear stress (σ_c), and shear rate ($\dot{\gamma}_c$) according to Bagley and Rabinowitch corrections, respectively, while the negligible exit pressure loss was assumed in this calculations:

$$\sigma_{\mathrm{C}} = \frac{(\Delta P_C - \Delta P_E)R}{2L} \tag{1}$$

$$\dot{\gamma}_C = \frac{4Q}{\pi R^3}\left(\frac{3n+1}{4n}\right) \tag{2}$$

where R and L are the radius and length of a capillary, respectively, and Q stands for flow rate. The correlated entrance pressure drop measurement was determined based on the difference in capillary and orifice die pressure profile, where a capillary pressure drop

$$\Delta P_C = P_{Cen} - P_{Cex} \tag{3}$$

and entrance pressure drop

$$\Delta P_E = P_{Oen} - P_{Oex} \tag{4}$$

are employed. While the subscripts O means orifice die, C stands for capillary die, *en* and *ex* correspond to entrance and exit pressure, respectively. The parameter n was obtained from the slope of log-log plot between true shear stress and apparent shear rate. The shear viscosity η_c can then be calculated from:

$$\eta_{\mathrm{C}} = \frac{\sigma_C}{\dot{\gamma}_C} \tag{5}$$

Assuming linear pressure profile in the capillary die, mean pressure (P_m) can be determined from:

$$\mathrm{P_m} = \frac{P_{Cen} + P_{Cex}}{2} \tag{6}$$

ISBN: 978-1-61804-022-0

Finally, the determination of temperature coefficient (α) and pressure coefficient (β) were determined by fitting the viscosity data with Carreau-Yasuda model:

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

where η_0, $\dot{\gamma}$, and $\eta_{(\dot{\gamma})}$ are zero-shear viscosity, shear rate, and shear rate dependent viscosity, respectively, K_1, n, a are empirical constants. The simple explanation of temperature and pressure function, f, used in polymer engineering calculation for determination of the α and β are:

$$f = e^{-\alpha(T-T_r)} \quad (8)$$

$$f = e^{\beta(P_m-P_r)} \quad (9)$$

where P, and T, stands for gauge pressure and temperature, respectively, while r means reference point. Both pressure and temperature functions could be combined as follow:

$$f = e^{-\alpha(T-T_r)+\beta(P_m-P_r)} \quad (10)$$

This sensitivity function was used to calculate the average pressure and temperature coefficients from the experimental data.

3 Results & Discussion

The DSC scanning micrograph of used PLA is shown in Figure 1.

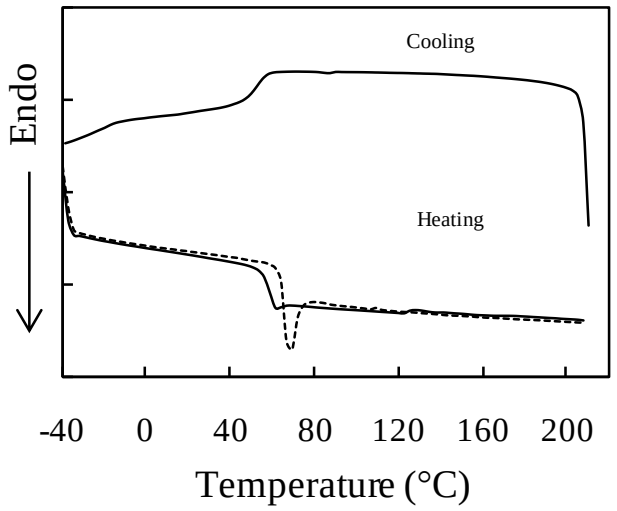

Figure 1. DSC data of PLA4060D at 20°C/min heating and cooling rate (the solid lines refer 2nd scan and the dash line refer 1st scan)

It is clear that PLA4060D is an amorphous polymer performing by both cooling and heating ramps. There is only one transition which can be determined during the both heating and cooling periods. Next to the first scan, the second heating was performed. Obviously a small shift of transition temperature comparing to the first heating ramp was revealed due to erasing of stress and thermal history in the polymer resin together with utter evaporation of water. The glass transition temperature evaluated from the second heating scan is around 57.7°C. Similar to the first scan, no further temperature effects were determined on the curve thus indicating an absence of crystallinity portion in the resin.

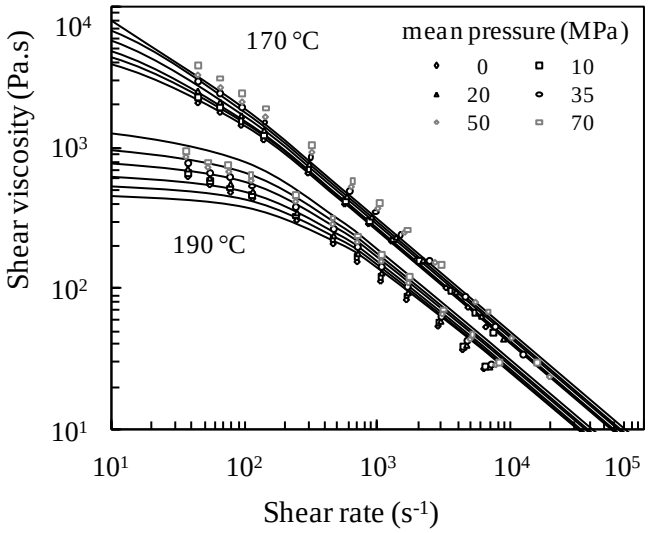

Figure 2. Pressure affected shear viscosity data of PLA4060D at temperatures of 170, and 190°C; symbols stand for experimental data, while the solid lines represent data fitting by the Carreau-Yasuda model

The flow behaviours of tested PLA at different mean pressures and temperatures are presented in Figure2. While pressure melt growth induces the obvious viscosity increase, as it is clear on the contrast of experimental shear viscosities data at various mean pressures as indicated by different symbols in the graph, flow data set at temperature of 190°C has significantly lower values of viscosity in the whole range of shear rate compared to the flow behaviour of tested PLA at 170°C. Furthermore, shear viscosity of tested PLA decline with increasing shear rate for the each mean pressure indicating a preservation of shear thinning behaviour typical for a common thermoplastic polymer. Thus it can be concluded that the pressure increase in the PLA melt did not influence the shear thinning behaviour while it effects only on the magnitude of viscosity.

The pressure-temperature-dependent flow curves fitting experimental data are presented by solid lines in Figure 2. The numerical calculation results employing

least squares method were determined utilizing the Carreau-Yasuda model (see Eq. 7) with the sensitivity function expressed by Eq. 10. Temperature of 170°C and pressure of 0.1 MPa were used here as the reference values. The calculated parameters of Carreau-Yasuda model determined in the described procedure are summarized in Table 1.

TABLE 1. Fitting parameter of Carreau-Yasuda model determined for PLA4060.

η_0 (Pa.s)	n (-)	K_1 (s^{-1})	a (-)	β (GPa^{-1})	α ($10^{-3}.°C^{-1}$)
3668	0.1966	0.0285	1.219	15.40	107.23

From the table, it can be concluded that tested PLA has relatively high sensitivity to both pressure and, especially, temperature. Comparing the experimental data and fitting curves it could seen that they do not fit each other in absolute values. It should be mentioned here that observed discrepancies could be fairly withdraw by the means of discrete fitting of individual investigated effects, in other words description of flow behaviour under particular pressure and temperature condition will assure accurate result. Nevertheless, in this way the advantage of unique set of fitting parameters for further modelling purposes will be lost. Clearly, pertinence of determined flow behaviour description is sufficient enough for estimation of flow behaviour dependencies, moreover even for the purposes of flow situation simulations in the range of common processing conditions.

4 Conclusion

Pressure and temperature sensitivity of PLA4060D was investigated by means of the modified capillary rheometer. The backpressure device providing different pressure levels allowed determination of pressure influence on flow behaviour of the PLA melts. Determined shear viscosity data was evaluated utilizing the Carreau-Yasuda model with a sensitivity function. The effect of pressure increase and temperature change on flow behaviour was described by the mean of the temperature and pressure sensitivity coefficients. It was proved that even the PLA shear thinning behaviour at selected temperature conditions was not affected by an actuating pressure, the shear viscosity of tested PLA melt is significantly influenced by the both effects. Pressure and temperature coefficients having values of 15.40 (GPa^{-1}) and 107.23 ($10^{-3}.°C^{-1}$), respectively, have been found to be appropriate to describe the shear flow behaviour of PLA4060D in adequate manner.

Acknowledgment:

Present article was created within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111). The Ministry of Industry and Trade of the Czech Republic (project 2A-1TP1/126) and the Ministry of Education, Youth and Sports of the Czech Republic, (Grant. No. MSM 7088352101) are acknowledged for the financial support.

References:

[1] Rafael A., Loong-Tak L., Susan E.M. S., and Hideto T., *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*, Wiley Series on Polymer Engineering and Technology, 2010

[2] Fang Q., and Hanna M. A., *Rheological properties of amorphous and semicrystalline polylactic acid polymers*, Industrial Crops and Products, Vol.10, 1999, pp. 47-53

[3] Palade L.-I., Lehermeier H. J., and Dorgan R. J., *Melt Rheology of High L-Content Poly(lactid acid)*, Macromolecules, Vol.34, 2001, pp.1384-1390

[4] Lehermeier HJ., and Dorgan JR., Melt rheology of poly(lactid acid): Consequences of blending chain architectures, *Polymer Engineering and Science*,Vol.41, 2001, pp.2172-2184

[5] Liu J., Lou L., Yu W., Liao R., Li R., and Zhou C., Long chain branching polylactide: Structures and properties, *Polymer*, Vol.51, 2010, pp.5186-5197

[6] Mihai M., Huneault M. A., and Favis B. D., Rheology and Extrusion Foaming of Chain-Branched Poly(lactid acid), *Polymer Engineering and Science*, Vol.50, pp. 629-642

[7] Maxwell B., and Jung A., Hydrostatic pressure effect on polymer melt viscosity, *Modern Plastics*, Vol.35, 1957, pp.174-182

[8] Liang J.-Z., Pressure effect of viscosity for polymer fluids in die flow, *Polymer*, Vol.42, 2001, pp.3709-3712

[9] Pantani R., and Sorrentino A., Pressure Effect on Viscosity for Atactic and Syndiotactic Polystyrene, *Polymer Bulletin*, Vol.54, 2005, pp.365-376

[10] Binding D.M., Couch M.A., and Walters K., The pressure dependence of the shear and elongational properties of polymer melts, *Journal of Non-Newtonian Fluid Mechanics*, Vol.79, 1998, pp.137-155

[11] Sedlacek T., Zatloukal M., Filip P., Boldizer A., and Saha P., On the Effect of Pressure on the Shear and Elongationla Viscosities of Polymer Melts, *Polymer Engineering and Science*, Vol.44, 2004, pp.1328-1337

[12] Cardinaels R., Puyvelde P. V., and Moldenaers P., Evaluation and comparison of routes to obtain pressure coefficients from high-pressure capillary rheometry data, *Rheologica Acta*, Vol.46, 2007, 495-505

[13] Aho J., and Syrjälä S., Measurement of the Pressure Dependence if Viscosity of Polymer Melts Using a Back Pressure-Regulated Capillary Rheometer, *Journal of Applied Polymer Science*, Vol.117, 2010, 1076-1084

[14] Hausnerova B., Sedlacek T., Filip P., and Saha P., The effect of powder characteristics on pressure sensitivity of powder injection moulding compounds, *Powder Technology*, Vol.206, 2011, 209-213

[15] Sedlacek T., Zatloukal M., Filip P., Boldizar A., and Saha P., On the effect of pressure on the shear and elongational viscosities of polymer melts, *Polymer Engineering and Science*, Vol.44, 2004, 1328-1337

[16] Piyamanocha P., Sedlacek T., Polaskova M., Filip P., and Saha P., Rheological Behaviour of Polypropylene Blends utilized in Foaming Process, *Latest Trends on Engineering Mechanics, Structures, Engineering Geology*, Mathematics and Computers in Science and Engineering, 2010, 275-278