MEASUREMENT AND MODELING OF FLOW BEHAVIOUR FOR MELT BLOWN POLYMER MELT IN VERY WIDE DEFORMATION RATE RANGE

Martin Zatloukal¹, Jiri Drabek¹ and Mike Martyn²

¹Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 275, 760 01 Zlin, Czech Republic
²IRC in Polymer Engineering, School of Engineering, Design & Technology, University of Bradford, Bradford BD7 1DP, UK

Abstract

In this work, linear PP Borflow HL504 FB, having melt flow rate equal to 450 g/10min, has been characterized by using rotational and capillary rheometry as well as by the instrumented injection molding machine. The measured data, that shows first as well as second Newtonian plateau, were consequently fitted by four conventional models (Cross, Carreau, Generalized Quemada and Carreau-Yasuda models) as well as by two novel viscosity models (modified Quemada and Carreau models) suggested here for the first time. It has been revealed that the modified 5-parametric Quemada model shows the highest flexibility to describe the flow viscosity curve for the investigated polymer melt in comparison with the other utilized models.

Introduction

Melt blown is the process at which very low viscosity polymers are extruded through the die nosepiece containing several hundred holes. At the end of the die, the air manifold is located to provide hot and compressed high velocity air, which stretches created fibers when it leaves the die (see Figure 1).

Figure 1. Visualization of the melt blown process.

It has been reported that polymeric nanofibers can also be produced by melt blown technology through, firstly, changing of processing conditions [1], secondly, by the polymer modification [2-3], and finally, by utilizing of special die where orifice diameters, D, are very small (0.064mm-0.125mm) and length to diameter ratio, L/D, is very large (20/1-1000/1) [4-6]. In more detail, Ellison et al. [1] produced average fiber diameter less than 500nm for PBT, PP and PS by reduced throughput and increased air flow rate. Nayak at al. [2] produced PP nanowebs (diameter of 438nm-755nm) by lowering molecular weight of PPs (100-300 melt flow index, MFI) by the injection of air and water at the vent port of the extruder. Zuo et al. [3] has shown that it is possible to produce PBT and PECTFE nanofibers, with average diameters as small as 70nm from melt blown fiber-in-fiber polymer blends. A special stacked plate die design with an orifice of 0.064mm diameter was used to fabricate nanofibres with average diameter of 320-470nm for a wide range of melt flow index PPs (35-1200 MFI) [4]. Brang et al. [5] fabricated nanofibres (average fiber diameter for most of the fibres less than 500nm) from PP, PET, PA, PE, PLA, Co-PA, PFE by meltblowing using a modified die with plate edge profile having very large length-to-diameter ratio (L/D=0.12/1) to achieve high web uniformity and small orifice diameters (D=0.12mm). Hills inc. (West Melbourne) produced meltblown nanowebs from low viscosity homopolymers (1500–1800 MFI) with average diameter of 250 nm and a range between 25 and 400nm. According to Hills, apart from the low viscosity, smaller diameter orifices, high spin hole density (100 holes per inch) and extremely high length-to-diameter ratios enable the production of these nanofibers at reasonable rates, and put meltblown production in the same size range that was previously the exclusive domain of electrospinning technology [3, 6-8].

One of the key problem connected to melt blowing processes optimization is utilization of extremely low viscosity polymers at extremely high deformation rates, for which rheological characterization is very complicated [9-11] or practically impossible by using standard rheological tools. With the aim to understand flow behavior of melt blown polymers in more details, PP samples with melt flow rate equal to 450 g/10min was characterized in wide deformation rate range by using rotational and capillary rheometry equipped by novel orifice die design as well as by the instrumented injection molding machine. In the second part of this work, the
fitting capability of different simple shear viscosity models were evaluated for the tested polymer samples.

**Experimental**

In this work, linear PP Borflow HL504 FB (Melt Flow Rate = 450 g/10min at 230°C/2.16 kg) produced by Borealis Polyolefine have been used. Low shear rate viscosity data were measured on Advanced Rheometric Expansion System (ARES 2000 model, Rheometrics Scientific, USA) at 230°C in parallel plates mode. In order to capture Newtonian plateau, shear creep measurements were performed at the given temperature. Rosand RH7-2 twin bore capillary rheometer, together with Bagley and Rabinowitsch corrections, has been utilized for the determination of shear viscosities at medium shear rates by using a novel patented orifice die [12]. The main advantage of the utilized orifice die is the open downstream region design which eliminates any possibility for artificial pressure increase due to polymer melt touching the downstream wall.

Due to the fact that the melt index of the chosen melt blown sample is extremely high, polyether ether ketone (PEEK) piston tips rather than copper ones have been used. The PEEK piston tips have been used in order to prevent any possible melt leakage flow between the piston tips and the barrel due to very low shear viscosity of the melt blown samples. The comparison between the PEEK and copper piston tips for the capillary rheometer is provided in Figure 2.

![Figure 2. Comparison between conventional copper piston tip (left) and PEEK piston tip (right) for the RH7-2 capillary rheometer.](image)

The measurements were performed in a constant piston speed mode at the shear rate range of (10-80,000) s⁻¹. In our measurements we used pressure transducers (Dynisco, USA) in ranges of (10,000) PSI (68.9476 MPa), (1,500) PSI (10.3421 MPa), (500) PSI (3.4473 MPa). In order to obtain the most accurate data at low shear rates range, the highly sensitive pressure transducer (250) PSI (1.7237 MPa) calibrated into its down resolution limit was used for pressure recording at the entrance to the orifice capillary die.

For high strain rate rheometry, a Fanuc Roboshot S-2000i injection molding machine was used, with screw diameter 22 mm and a maximum barrel pressure rating of 260 MPa. The machine was operated in air-shot mode using a capillary die in place of the nozzle. Melt pressure was measured at entrance to the capillary die at a frequency of 100 Hz using pressure transducer a Kistler 4021A. Injection screw position and speed were also monitored at the same frequency. Polymer was injected at a range of speeds from 2.6 mm/s to 220 mm/s first through a capillary die of length 10 mm and diameter 0.5 mm, then this test was repeated with an orifice die of the same diameter. Polymer was plasticized in the screw of the molding machine at a screw rotation speed of 2.83 revolutions per second with at back pressure of 0.1 MPa. Injection was initiated following a dwell time of 30 s. Process data were collected using a LabView SC2345 data acquisition unit triggered by a 24 V signal from the injection molding machine at the start of injection.

**Theory**

In this work, the following simple shear viscosity models with capability to describe the first and the second Newtonian plateau via \( \eta_0 \) and \( \eta_v \) parameter, respectively, were utilized.

**4-parametric Cross model [13]**

\[
\eta(\dot{\gamma}) = \eta_v + \frac{\eta_0 - \eta_v}{1 + (\dot{\gamma} \lambda)^{a}}
\]

where \( \eta_0 \), \( \eta_v \), \( \lambda \) and \( a \) are model parameters.

**4-parametric Carreau model [14]**

\[
\eta(\dot{\gamma}) = \eta_v + \frac{\eta_0 - \eta_v}{1 + (\dot{\gamma} \lambda)^{n}}
\]

where \( \eta_0 \), \( \eta_v \), \( \lambda \) and \( n \) are model parameters.

**4-parametric Generalized Quemada model [15-16]**

\[
\eta(\dot{\gamma}) = \left[ \frac{\eta_v}{\eta_v + \frac{\eta_0 - \eta_v}{1 + (\dot{\gamma} \lambda)^{n}}} \right]^a \left[ 1 + \frac{t_s}{1 + (\dot{\gamma} \lambda)^{n}} \right]^{1-a} \]

where \( \eta_0 \), \( \eta_v \), \( a \) and \( t_s \) are model parameters.
5-parametric Carreau-Yasuda model [17]

\[ \eta(\dot{\gamma}) = \eta_s + \frac{\eta_0 - \eta_s}{\left[1 + (\dot{\gamma}/\lambda)^{\alpha}\right]^{n/\alpha}} \]

(4)

where \( \eta_s, \eta_0, \alpha, \lambda, a \) and \( n \) are model parameters.

Suggested 5-parametric Modified Quemada

\[ \eta(\dot{\gamma}) = \eta_s + \frac{\eta_0 - \eta_s}{\left[1 + (\dot{\gamma}/\lambda)^{\alpha}\right]^{n/\alpha}} \]

(5)

\[ 1 - \frac{1}{\left[\eta_0 / \eta_s\right]^{1/\alpha}} \frac{1}{1 + (\dot{\gamma}/\lambda)^{\alpha}} \]

where \( \eta_s, \eta_0, \alpha, a \) and \( \lambda \) are model parameters.

Suggested 5-parametric Modified Carreau model

\[ \eta(\dot{\gamma}) = \eta_s + \frac{\eta_0 - \eta_s}{\left[1 + (\dot{\gamma}/\lambda)^{\alpha}\right]^{n/\alpha}} \]

(6)

\[ f = \left[\frac{\tanh[\eta(\dot{\gamma})]}{\tanh(\eta_0)}\right]^{(\alpha n - 1)} \]

(7)

where \( \eta(\dot{\gamma}) \) is given by Eq.2, and \( \eta_s, \eta_0, \alpha, a \), and \( n \) are model parameters.

**Results and Discussion**

Measured shear viscosity data plotted as the function of the shear rate for investigated melt blown polymer sample is provided in Figure 3.

It can be seen that the first as well as the second Newtonian plateau can clearly be identified. In order to evaluate selected rheological models, two different approaches were selected. In the first case, the model parameters characterizing the first and the second Newtonian plateau (i.e. \( \eta_0 \) and \( \eta_s \)) were determined directly from the Figure 3. Then, all shear viscosity models were used to fit the measured data keeping the \( \eta_0 \) and \( \eta_s \) parameters fixed. In the second case, all model parameters, i.e. including \( \eta_0 \) and \( \eta_s \), were allowed to vary in order to reach the best fit. Comparison between the measured data and model fitting line for both chosen approaches is provided in Figures 4-5.

Fitting error for each model and studied case was evaluated via the Root Mean Squared Error (RMSE) defined as

\[ RMSE = \sqrt{\frac{1}{\delta} \sum_{i=1}^{\delta} (\log(\eta_i) - \log(\hat{\eta}_i))^2} \]

(8)

where \( \delta \) is the number of measured points, \( \eta_i \) and \( \hat{\eta}_i \) represent measured and predicted shear viscosity points at given shear rate (see Tables 1-2). All model parameters are summarized in Tables 3-4.

**Table 1.** Fitting error (Root mean squared error – RMSE) for each utilized model sorted from the best to the worst and the case No.1 (\( \eta_0 \) and \( \eta_s \) are fixed).

<table>
<thead>
<tr>
<th>Model name</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Quemada model</td>
<td>0.075666</td>
</tr>
<tr>
<td>Modified Carreau model</td>
<td>0.099055</td>
</tr>
<tr>
<td>Carreau-Yasuda model</td>
<td>0.126494</td>
</tr>
<tr>
<td>Cross model</td>
<td>0.127832</td>
</tr>
<tr>
<td>Generalized Quemada model</td>
<td>0.137738</td>
</tr>
<tr>
<td>Carreau model</td>
<td>0.161172</td>
</tr>
</tbody>
</table>

**Table 2.** Fitting error (Root mean squared error – RMSE) for each utilized model sorted from the best to the worst and the case No.2 (all model parameters are varied including \( \eta_0 \) and \( \eta_s \)).

<table>
<thead>
<tr>
<th>Model name</th>
<th>RMSE</th>
</tr>
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<tbody>
<tr>
<td>Modified Quemada model</td>
<td>0.073852</td>
</tr>
<tr>
<td>Modified Carreau model</td>
<td>0.078111</td>
</tr>
<tr>
<td>Carreau-Yasuda model</td>
<td>0.095626</td>
</tr>
<tr>
<td>Cross model</td>
<td>0.098904</td>
</tr>
<tr>
<td>Carreau model</td>
<td>0.105846</td>
</tr>
<tr>
<td>Generalized Quemada model</td>
<td>0.106348</td>
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</table>

Based on the Tables 1-2 and Figures 3-4, the following conclusions can be formulated.
• 5-parametric viscosity models are more capable to describe the measured data than 4-parametric models, as expected.
• Modified Quemada model and Cross model has the highest capability to describe the measured data from all utilized 5-parametric and 4-parametric models, respectively, independently to the utilized fitting methodology.
• With respect to 5-parametric models, modified Quemada and modified Carreau models shows higher capability to describe the measure data than Carreau-Yasuda model.

Table 3. Model parameters for the case No.1 (η₀ and η∞ are fixed).

<table>
<thead>
<tr>
<th>Model name</th>
<th>η₀ (Pa.s)</th>
<th>λ (s)</th>
<th>a (-)</th>
<th>n (-)</th>
<th>η∞ (Pa.s)</th>
<th>t_c (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross model</td>
<td>23.06276</td>
<td>0.000395</td>
<td>0.860477</td>
<td>-</td>
<td>0.229452</td>
<td>-</td>
</tr>
<tr>
<td>Carreau model</td>
<td>23.06276</td>
<td>0.008855</td>
<td>-</td>
<td>0.259637</td>
<td>0.229452</td>
<td>-</td>
</tr>
<tr>
<td>Carreau-Yasuda model</td>
<td>23.06276</td>
<td>0.00007567</td>
<td>0.774417</td>
<td>0.072987</td>
<td>0.229452</td>
<td>-</td>
</tr>
<tr>
<td>Generalized Quemada model</td>
<td>23.06276</td>
<td>0.00000157</td>
<td>0.742976</td>
<td>0.210652</td>
<td>0.00000257587</td>
<td>-</td>
</tr>
<tr>
<td>Modified Quemada model</td>
<td>23.06276</td>
<td>0.001741</td>
<td>2.587889</td>
<td>0.269199</td>
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<td>0.0014739787</td>
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<tr>
<td>Modified Carreau model</td>
<td>23.06276</td>
<td>0.0001741</td>
<td>0.278740</td>
<td>0.842597</td>
<td>0.805099</td>
<td>0.320041</td>
</tr>
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</table>

Table 4. Model parameters for the case No.2 (all model parameters are varied including η₀ and η∞ parameters).

<table>
<thead>
<tr>
<th>Model name</th>
<th>η₀ (Pa.s)</th>
<th>λ (s)</th>
<th>a (-)</th>
<th>n (-)</th>
<th>η∞ (Pa.s)</th>
<th>t_c (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross model</td>
<td>23.71444</td>
<td>0.000043</td>
<td>0.790466</td>
<td>0.168589</td>
<td>0.229452</td>
<td>-</td>
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<tr>
<td>Carreau model</td>
<td>22.77779</td>
<td>0.001135</td>
<td>-</td>
<td>0.320041</td>
<td>0.118781</td>
<td>-</td>
</tr>
<tr>
<td>Carreau-Yasuda model</td>
<td>24.07324</td>
<td>0.0005799</td>
<td>1.937899</td>
<td>0.208478</td>
<td>0.146068</td>
<td>-</td>
</tr>
<tr>
<td>Generalized Quemada model</td>
<td>24.07324</td>
<td>0.0005799</td>
<td>1.937899</td>
<td>0.208478</td>
<td>0.146068</td>
<td>-</td>
</tr>
<tr>
<td>Modified Quemada model</td>
<td>22.72441</td>
<td>0.0018049</td>
<td>0.850099</td>
<td>0.22879</td>
<td>0.008555</td>
<td>0.00000051505</td>
</tr>
<tr>
<td>Modified Carreau model</td>
<td>25.05447</td>
<td>0.001062</td>
<td>1.619827</td>
<td>0.718784</td>
<td>0.106899</td>
<td>-</td>
</tr>
</tbody>
</table>

Conclusion

In this work, linear PP Borflow HL504 FB (Melt Flow Rate = 450 g/10min at 230°C/2.16 kg) has been characterized in very wide deformation rate at 230°C by using rotational and capillary rheometry equipped by novel orifice die design as well as by the instrumented injection molding machine. The measured data were consequently fitted by six different viscosity models, from which two of them were suggested here for the first time. It has been found that, firstly, the used experimental instruments and procedures allow determining first and second Newtonian plateau as well as the region of pseudoplastic behavior. Secondly, the 5-parametric models show higher fitting flexibility than 4-parametric models, as expected. Finally, modified Quemada model was found to be the most flexible model for the given material in comparison with modified Carreau model as well as with conventional models such as Carreau-Yasuda model, Cross model, Carreau model and Generalized Quemada model.

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References

Figure 4. Comparison between experimentally determined shear viscosity data and model predictions for PP Borflow HL504 FB sample at 230°C and for fixed $\eta_0$ and $\eta_\infty$ parameters (the case No.1).
Figure 5. Comparison between experimentally determined shear viscosity data and model predictions for PP Borflow HL504 FB sample at 230°C where all model parameters were varied, including $\eta_0$ and $\eta_\infty$ parameters (case No.2).