



Effect of molecular weight on secondary Newtonian plateau at high shear rates for linear isotactic melt blown polypropylenes



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ABSTRACT

In this work, three melt blown grades of isotactic linear polypropylenes, with weight average molecular weights between 56 250–75 850 g/mol, have been characterized at 230 °C over a very wide shear rate range ($10\text{--}10^7$ 1/s) by using conventional rotational and twin bore capillary rheometry equipped with novel orifice die, and by an instrumented capillary nozzle on an injection molding machine. A low shear rate primary Newtonian plateau, a pseudoplastic region and a well developed secondary Newtonian plateau (occurring between $2\cdot 10^6\text{--}7\cdot 10^6$ 1/s) were identified for all the polypropylene melts. Flow activation energy at low (E_0) and high (E_∞) shear rates was found to be 56.590 kJ/mol and 25.204 kJ/mol, respectively. Considering the typical value of pressure sensitivity coefficient for polypropylene melt, $\beta = 20.00\text{ GPa}^{-1}$, and measured flow activation energy at the secondary Newtonian plateau, $E_\infty = 25.204$ kJ/mol, it was found that the effect of viscous dissipation and pressure is mutually cancelled, i.e. that the measured viscosity data can be considered as the true material property within the whole applied shear rate range. For the first time, it has been revealed that the secondary Newtonian viscosity, η_∞ , depends linearly on the weight average molecular weight, M_w , in log-log scale as $\eta_\infty = 1.19\cdot 10^{-6} M_w^{1.084}$. The observed slope close to 1 between η_∞ and M_w suggests that polymer chains in the melt are disentangled at the secondary Newtonian plateau region. This conclusion is supported by the experimental observation that the high shear rate flow activation energy E_∞ for given PP melts is comparable with the flow activation energy of PP like oligomer (squalane, $\text{C}_{30}\text{H}_{62}$; 2,6,10,15,19,23-hexamethyltetracosane). The measured flow data were fitted by six different viscosity models, from which two, namely Modified Carreau and Quemada models, were suggested here for the first time. It has been found that the accuracy of utilized models to describe the measured data is the highest for the newly suggested models and decreases in the following order: Modified Quemada model, Modified Carreau model, Carreau-Yasuda model, Cross model, Generalized Quemada model and Carreau model.

1. Introduction

Melt blowing is a fabrication process typically used in the production of nonwoven polymer micro-fibers. Low viscosity polymers are extruded through a spinnerette die containing several hundred holes. At the end of the die, an air manifold is located to provide hot and compressed high velocity air, which stretches the melt creating fibers when it leaves the spinnerette (see Fig. 1). 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 a special die where orifice diameters, D , are very small (0.064 mm–0.125 mm) and length-to-diameter ratio, L/D , is very large (20/1–1000/1) [4–6]. Thus, it is possible to produce nanofibers at reasonable rates, and provide melt blown

fibers of the same size range as those previously exclusive to the domain of electrospinning technology [3,6–8].

Polypropylene is the most widely used polymer in the melt blown technology due to its low cost, ease of processing, good mechanical properties, and chemical inertness [9–12]. In order to understand the formation of nanofibers and process stability, it is necessary to know rheological behavior of these polymers. Probably the first researcher to perform a detailed rheological characterization of melt blown PPs was Yizhong Wang [13]. Wang characterized two ExxonMobil Escorene melt blown PPs (MFI of 400 and 1200 g/10 min) at 185–240 °C using an Advanced Rheometric Expansion System (ARES, frequency range 0.1–100 rad/s) and advanced capillary extrusion rheometer covering shear rates in the range 1 to 10^5 1/s. Later, Rajkishore Nayak [14] investigated the rheological behaviour of four melt blown PPs (MFI of

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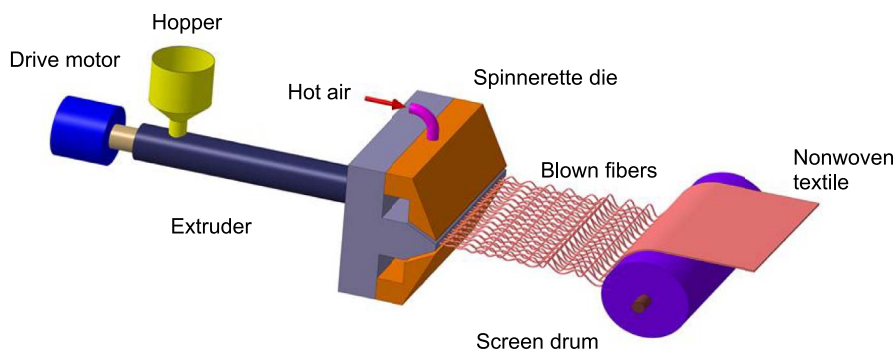


Fig. 1. Schematic of the melt blown process.

100, 300, 1000 and 2000 g/10 min with M_w of 100 875, 77 590, 60 238 and 55 509 g/mol) between 180–210 °C utilizing an ARES in dynamic mode and low frequency range (0.1–100 rad/s). Both authors showed that conventional rheological tools can be used for rheological characterization of very low viscosity melt blown PPs but, such tools are limited in being unable to cover extreme deformation rate range typical for melt blown technology, i.e. 10^6 – 10^7 1/s [1,15], which significantly limits optimization of this process.

There are only a few papers reporting shear viscosity measurements for polymer melts at such high shear rate range utilizing specially designed rheological equipment such as hydraulically powered capillary rheometer [16] or an instrumented injection molding machine [17,18–20]. With respect to polyolefins (such as polypropylene, PP, high-density polyethylene, HDPE, and ultra-high-molecular-weight polyethylene, UHMWPE), the following key conclusions have been found.

Firstly, HDPE and UHMWPE exhibit a Newtonian behaviour between about $3 \cdot 10^6$ – $5 \cdot 10^6$ 1/s [16] whereas at higher shear rates, the second shear thinning region was observed. In this flow regime, shear viscosity decreases with the shear rate mainly due to polymer chain scission, which was confirmed via monitoring of weight average molecular weight, M_w , of extruded HDPE at high shear rates. Secondly, a well-developed secondary Newtonian plateau was found for four different polypropylenes between approximately $1 \cdot 10^6$ – $8 \cdot 10^6$ 1/s [16–20]. In this case, no second shear thinning or thickening region was detected within whole applied high shear rate range. On the other hand, it was found that the secondary Newtonian plateau for specific PP grade can be followed by the shear thickening behaviour occurring at the highest shear rates if the effect of pressure prevails over the effect of viscous dissipation [17].

Finally, Takahashi et al. [16] compared flow curves, containing secondary Newtonian plateau, for HDPE and UHMWPE samples (having about an order of magnitude different M_w) and concluded that the viscosity dependence on M_w is small at high shear rates. Kelly et al. [17] provided similar comparison for two PPs with different M_w (192 000 and 283 000) with the suggestion that ‘...molecular size or structure may influence the observed high strain plateau’.

With the aim to understand flow behaviour of melt blown polymers in more detail, three linear isotactic PP samples with melt flow rate between 450–1200 g/10 min were characterized over a very wide deformation rate range (10 – 10^7 1/s) by using rotational and capillary rheometry as well as by the instrumented injection molding machine

equipped with interchangeable dies. In the second part of this work, the fitting capability of different simple shear viscosity models were evaluated for all tested polymer samples.

2. Experimental

In this work, linear isotactic PP Borflow HL504FB (76k), HL508FB (64k) and HL512FB (56k) produced by Borealis Polyolefine have been used. Basic characteristics of their pellets are summarized in Table 1.

Low shear rate viscosity data were measured on an Advanced Rheometric Expansion System (ARES 2000 model, Rheometrics Scientific, USA) at 190, 210 and 230 °C in parallel plate mode. The aluminium bottom plate with the overflow channel was used to prevent polymer melt leakage flow out of the geometry. A 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 [21–22]. 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. In this work, three long dies (length to diameter ratio, L/D , equal to 16, $D_1 = 0.15$ mm, $D_2 = 0.5$ mm, $D_3 = 1$ mm) and three orifice dies with the same diameters were used. Close fitting piston tips of the instrument were made from polyether ether ketone (PEEK). The PEEK piston tips are used in order to prevent any possible polymer melt leakage flow between the piston tips and the barrel due to very low shear viscosity of the melt blown samples. Furthermore, it was found necessary to use polytetrafluoroethylene tape to prevent polymer melt leakage flow between the die holder and capillary rheometer barrel as it is shown in Fig. 2.

The measurements were performed in a constant piston speed mode at the shear rate range of (30–640,000) s^{-1} and 230 °C. In our measurements we used pressure transducers (Dynisco, USA) in ranges of (10,000) PSI (68.9476 MPa), (1500) PSI (10.3421 MPa), (500) PSI (3.4473 MPa). To improve accuracy of measured data at low shear rates range the highly sensitive pressure transducer (250) PSI (1.7237 MPa) calibrated to its resolution limit was used for recording pressure at the entrance to the orifice capillary die. The compressed air based device, CCS 20 from AMV Messgeräte GmbH, was used to calibrate this pressure transducers by using 69 calibration points.

For high strain rate rheometry at 190, 210 and 230 °C, a high accuracy Fanuc Roboshot S-2000i electric high-speed injection molding

Table 1
Basic characteristics of utilized melt blown polypropylenes (pellets).

Sample Name	Melt flow index at 2.16 kg and 230°C (g.10min ⁻¹)	DSC peak melting point (°C)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_z (g mol ⁻¹)	M_{z+1} (g mol ⁻¹)	M_w/M_n (-)
HL504FB	450	161–165	20,100	112,500	284,500	510,500	5.60
HL508FB	800	156–160	17,050	104,500	282,000	533,000	6.13
HL512FB	1200	156–160	16,950	90,950	220,500	384,500	5.37

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