

Effect of Molecular Weight on Viscosity of Polypropylene Melt by Capillary Rheometry

Daniel N. Njoroge

Department of Mechanical and Manufacturing Engineering
Aalborg University
Fibigerstraede 16, DK-9220
Aalborg East - Denmark

ABSTRACT

This study is based on characterization of Polypropylene melt by capillary rheometry. It includes operating the twin bore capillary rheometer, preparation of samples, measurement of rheological properties of polymer melts. In this study, samples of PP pellets of 3 different molecular weights were investigated. The samples were subjected to well-defined strain rate and pressure drop recorded. Their stress responses were derived from the recorded pressure readings. The effect of molecular weight on rheological properties of PP was analysed.

Keywords :— Capillary rheometry, Viscosity, Shear rate.

I. INTRODUCTION

Rheological properties of polymer melts are measured using rheometers. Typical rheological properties are viscosity, modulus, compliance, yield stress, and relaxation times. These properties depend on the microstructure of the material and, hence, depend on stress or strain-induced structural changes, and on time [1].

In rheometry, the test sample is mounted into the rheometer and subjected to well-defined stress or strain. In strain-controlled experiments, the strain or strain rate is prescribed and the stress response gets recorded whereas, for stress-controlled instruments the stress is prescribed and the strain is recorded [2].

The pressure drop, Δp , for flow in a capillary (of radius R , length L) at a volume flow rate, Q , depends on the shear viscosity, η as shown in (1) provided that the flow is laminar. Equation (1) is used to describe capillary rheometry for both Newtonian and also non-Newtonian fluids [1]–[3].

$$\eta = \frac{\Delta p \pi R^4}{L 8Q} \quad (1)$$

As the piston pushes the polymer melt through the die of constant cross section (circular). The volume flow rate, Q , and the pressure gradient, P' , in the region of fully developed flow are measured for determining the shear viscosity. Q is determined from the measured piston speed, v_p , and the piston cross sectional area, A_p as given in (2).

$$Q = A_p v_p \quad (2)$$

II. MATERIALS AND METHODS

A. Materials

Polypropylene (PP) polymer pellets of different molecular weight: HG265FB (molecular weight 180,000), HG365FB (molecular weight 230,000) and HB600TF (molecular weight 460,000) were used as received.

B. Acquisition of Rheological Properties

The twin bore capillary rheometer was used in this experiment. The temperature controlled housing which is wrapped by heaters was heated and maintained at 220°C . The PP pellets were then fed in through the feed system. The pellets were compressed during the filling of the bore so as to hold as much material as possible. The pistons were lowered to push the pellets as they got heated where the piston force was increased gradually. With time, the polymer melted and flowed through the measurement die. The experiment was conducted on shear rates of $10 - 10,000 \text{ s}^{-1}$. With prescribed shear rates, the pressure transducers recorded the pressure responses in the fully developed flow region.

C. Characterization

The overall purpose of the capillary flow experiment is the measurement of the steady shear viscosity, η of non-Newtonian fluid (polymer melt) as given in (3), where τ is the shear stress and $\dot{\gamma}$ the shear rate [4].

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3)$$

From the experiment, neither τ nor $\dot{\gamma}$ is measured directly; hence they are derived from the pressure readings and the measured volume flow rate. The data analysis depends on the geometry of the capillary. For a circular capillary of radius, R

the cross-section area is given by (4). Both the shear stress and the shear rate vary throughout the capillary cross-section.

$$A = \pi R^2 \quad (4)$$

1) **Shear stress Estimation:** The pressure gradient, P' can be approximated from the measured pressure drop, Δp over the entire capillary length, L as shown in (5).

$$P' = -\frac{\Delta p}{L} \quad (5)$$

This approximate, P' value, includes pressure losses at the inlet and the outlet of the capillary and can be corrected using **Bagley's correction** [2]. The maximum shear stress at the capillary walls, τ_w is given by (6).

$$\tau_w = -\frac{R}{2} P' \quad (6)$$

Substituting (5) in (6), we get an expression of shear stress at the walls in-terms of pressure drop as shown in (7).

$$\tau_w = -\frac{\Delta p R}{2L} \quad (7)$$

The shear stress in fully developed capillary flow grows linearly with the distance from the centre of the capillary ($r = 0$) to its maximum value, τ_w at the walls ($r = R$) as shown in (8) [5].

$$\tau(r) = \frac{\tau_w r}{R} = \frac{\Delta p r}{2L} \quad (8)$$

2) **Shear rate Estimation:** Shear thinning fluids, such as polymer melts, adopt a shear rate as given in (9) known as **representative shear rate** [3].

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (9)$$

Equation (9) is valid for Newtonian fluids only and represents the apparent shear rate. For non-Newtonian flows which are experienced by polymer melts, the shear rate can be corrected using **Weissenberg-Rabinowitsch correction** [2].

3) **Viscosity Estimation:** Viscosity of the polymer melt was estimated using (10), where τ is the estimated shear stress after pressure gradient correction and $\dot{\gamma}_{corr}$ is the true shear rate after wall shear rate correction [6]–[7].

$$\eta = \frac{\tau}{\dot{\gamma}_{corr}} \quad (10)$$

III. RESULTS AND DISCUSSION

A. Pressure Gradient Correction using Bagley's Plots

The pressure gradient approximated using (5) overestimates the real P' value since it includes pressure losses at the inlet and the outlet of the capillary. These so-called 'end effects' can be subtracted out using Bagley's correction.

Using (7) for shear stress, and making the pressure drop as the subject, we get (11) which is used in Bagley correction.

$$\Delta p = 2\tau_w \frac{L}{R} \quad (11)$$

Fig. 1 was plotted using (11) for PP with 180,000 molecular weight. The value of $2\tau_w$ is constant at fixed $\dot{\gamma}$. Similarly, Fig. 2 and 3 shows the bagley plots for PP with 230,000 and 460,000 molecular weight respectively. The slopes of the plots are equal to twice the shear stress for various apparent shear rates. The intercepts represent the entrance pressure losses, Δp_{ent} .

Table I, II and III shows the equations from the Bagley's plots at different shear rates and the analysed data after Bagley's correction for PP with 180,000 molecular weight, 230,000 molecular weight and 460,000 molecular weight respectively.

B. Wall Shear Rate Correction using Weissenberg-Rabinowitsch plots

The shear rate given in (9) is only true for Newtonian fluids, polymer melts exhibit non-Newtonian behavior, therefore the equation can be corrected using Weissenberg-Rabinowitsch (WR) plot. Equation (12) represents a corrected shear rate.

$$\dot{\gamma}_{corr} = \frac{4Q}{\pi R^3} \left[\frac{1}{4} \left(3 + \frac{d \ln \dot{\gamma}}{d \ln \tau_w} \right) \right] \quad (12)$$

For PP with different molecular weight, Fig. 4 was obtained using (12). The Curve fits was done with linear approximation to yield (13)–(15) for the 3 types of PP with 180,000, 230,000 and 460,000 molecular weights respectively.

$$y = 1.5x - 9.3 \quad (13)$$

$$y = 2.3x - 19 \quad (14)$$

$$y = 3.2x - 31 \quad (15)$$

For PP with 180,000 molecular weight, slope of the plot was obtained by getting a derivative of the fitting curve to yield (16), which is used as WR correction value for correcting the shear rate. Similarly, (17) and (18) were obtained for PP with 230,000 and 460,000 molecular weights respectively.

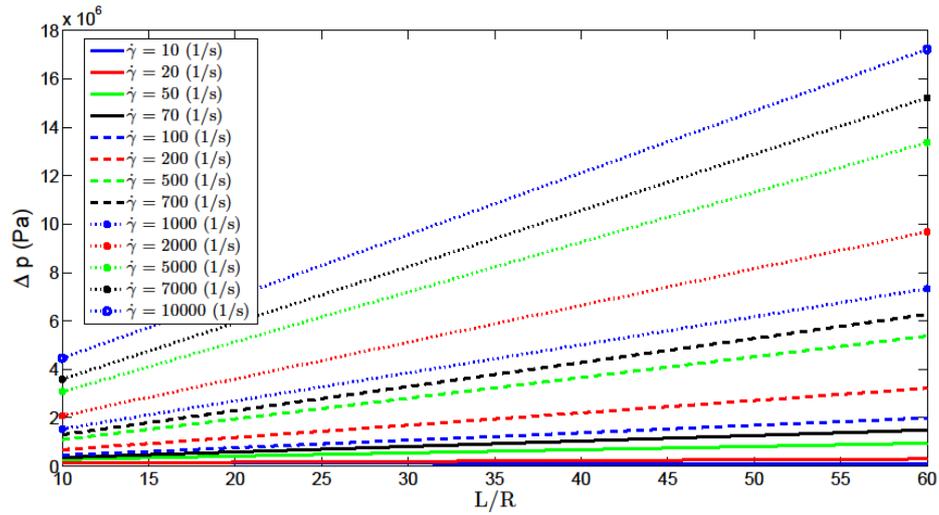


Fig. 1 Bagley plot (a) 180,000 MW.

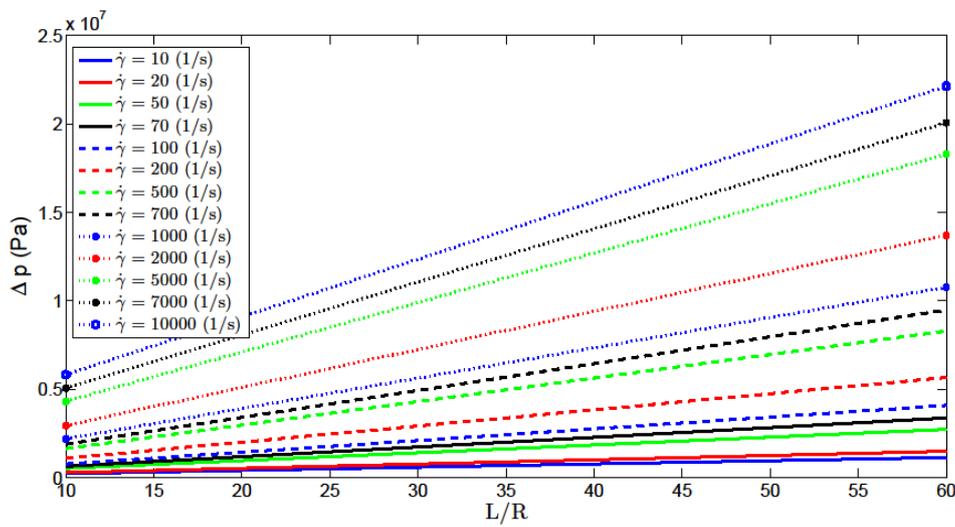


Fig. 2 Bagley plot (b) 230,000 MW.

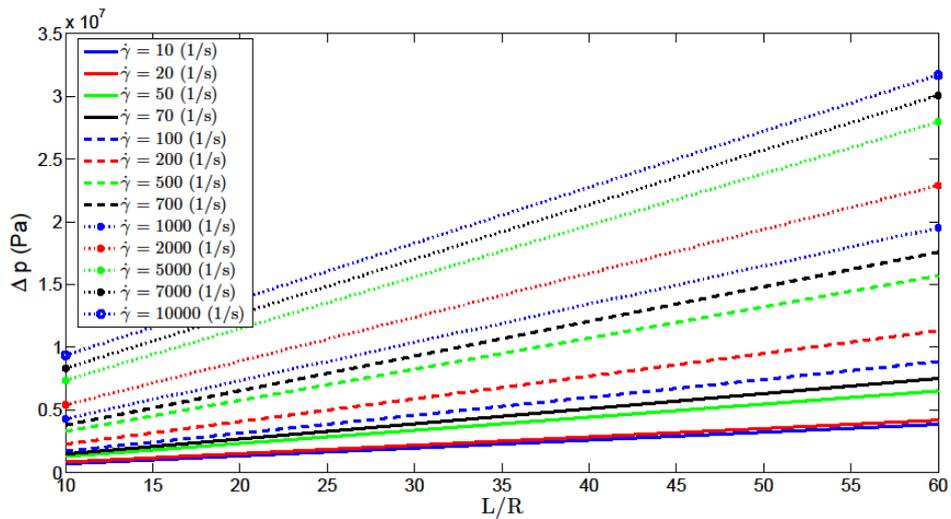


Fig. 3 Bagley plot (c) 460,000 MW.

TABLE I
ANALYSED DATA AFTER BAGLEY AND WR CORRECTIONS - PP 180,000 MW.

$\dot{\gamma}$ 1/s	Equations	Δp_{ent} Pa	Slope Pa	τ Pa	$ln(\tau)$	$ln(\dot{\gamma})$	WR correction	$\dot{\gamma}_{corr}$ 1/s	η Pas	$log \dot{\gamma}_{corr}$	$log \eta$
10	y=-500x + 129000	129000	-500	-250	-	2.3026	1.5	11.25	-22.2222	1.0512	-
20	y=3480x + 89200	89200	3480	1740	7.4616	2.9957	1.5	22.5	77.3333	1.3521	1.8883
50	y=13320x + 145800	145800	13320	6660	8.8039	3.9120	1.5	56.25	118.4000	1.7501	2.0734
70	y=22740x + 128600	128600	22740	11370	9.3387	4.2485	1.5	78.75	144.3810	1.8963	2.1595
100	y=30760x + 145400	145400	30760	15380	9.6408	4.6052	1.5	112.5	136.7111	2.0512	2.1358
200	y=50800x + 171000	171000	50800	25400	10.1425	5.2983	1.5	225	112.8889	2.3522	2.0527
500	y=85660x + 236400	236400	85660	42830	10.6650	6.2146	1.5	562.5	76.1422	2.7501	1.8816
700	y=99480x + 303200	303200	99480	49740	10.8146	6.5511	1.5	787.5	63.1619	2.8963	1.8005
1000	y=115940x + 377600	377600	115940	57970	10.9677	6.9078	1.5	1125	51.5289	3.0512	1.7121
2000	y=151800x + 566000	566000	151800	75900	11.2372	7.6009	1.5	2250	33.7333	3.3522	1.5281
5000	y=205940x + 1017600	1017600	205940	102970	11.5422	8.5172	1.5	5625	18.3058	3.7501	1.2626
7000	y=232480x + 1267200	1267200	232480	116240	11.6634	8.8537	1.5	7875	14.7606	3.8963	1.1691
10000	y=255360x + 1902400	1902400	255360	127680	11.7573	9.2103	1.5	11250	11.3493	4.0512	1.0550

TABLE III
ANALYSED DATA AFTER BAGLEY AND WR CORRECTIONS - PP 230,000 MW.

$\dot{\gamma}$ 1/s	Equations	Δp_{ent} Pa	Slope Pa	τ Pa	$ln(\tau)$	$ln(\dot{\gamma})$	WR correction	$\dot{\gamma}_{corr}$ 1/s	η Pas	$log \dot{\gamma}_{corr}$	$log \eta$
10	y=18340x + 40600	40600	18340	9170	9.1237	2.3026	2.3	13.25	692.0755	1.1222	2.8402
20	y=24080x + 44200	44200	24080	12040	9.3960	2.9957	2.3	26.5	454.3396	1.4232	2.6574
50	y=44140x + 81600	81600	44140	22070	10.0020	3.9120	2.3	66.25	333.1321	1.8211	2.5226
70	y=54760x + 89400	89400	54760	27380	10.2176	4.2485	2.3	92.75	295.2022	1.9673	2.4701
100	y=66300x + 109000	109000	66300	33150	10.4088	4.6052	2.3	132	250.1887	2.1222	2.3983
200	y=91380x + 176200	176200	91380	45690	10.7296	5.2983	2.3	265	172.4151	2.4232	2.2366
500	y=132980x + 311200	311200	132980	66490	11.1048	6.2146	2.3	662.5	100.3623	2.8212	2.0016
700	y=151780x + 374200	374200	151780	75890	11.2370	6.5511	2.3	927.5	81.8221	2.9673	1.9129
1000	y=171480x + 483200	483200	171480	85740	11.3591	6.9078	2.3	1325	64.7094	3.1222	1.8110
2000	y=215000x + 801000	801000	215000	107500	11.5852	7.6009	2.3	2650	40.5660	3.4232	1.6082
5000	y=279440x + 1518600	1518600	279440	139720	11.8474	8.5172	2.3	6625	21.0898	3.8211	1.3241
7000	y=300100x + 2066000	2066000	300100	150050	11.9187	8.8537	2.3	9275	16.1779	3.9673	1.2089
10000	y=326220x + 2566800	2566800	326220	163110	12.0022	9.2103	2.3	13250	12.3102	4.1222	1.0903

TABLE IIIII
ANALYSED DATA AFTER BAGLEY AND WR CORRECTIONS - PP 460,000 MW.

$\dot{\gamma}$ 1/s	Equations	Δp_{ent} Pa	Slope Pa	τ Pa	$ln(\tau)$	$ln(\dot{\gamma})$	WR correction	$\dot{\gamma}_{corr}$ 1/s	η Pas	$log \dot{\gamma}_{corr}$	$log \eta$
10	y=63020x + 58800	58800	63020	31510	10.3581	2.3026	3.2	15.5	2032.9032	1.1903	3.3081
20	y=66800x + 163000	163000	66800	33400	10.4163	2.9957	3.2	31	1077.4194	1.4914	3.0324
50	y=104760x + 219400	219400	104760	52380	10.8663	3.9120	3.2	77.5	675.8710	1.8893	2.8299
70	y=120680x + 257200	257200	120680	60340	11.0078	4.2485	3.2	108	556.1290	2.0354	2.7452
100	y=142780x + 272200	272200	142780	71390	11.1759	4.6052	3.2	155	460.5806	2.1903	2.6633
200	y=180940x + 448600	448600	180940	90470	11.4128	5.2983	3.2	310	291.8387	2.4914	2.4651
500	y=248440x + 785600	785600	248440	124220	11.7298	6.2146	3.2	775	160.2839	2.8893	2.2049
700	y=276220x + 1005800	1005800	276220	138110	11.8358	6.5511	3.2	1085	127.2903	3.0354	2.1048
1000	y=304480x + 1246200	1246200	304480	152240	11.9332	6.9078	3.2	1550	98.2194	3.1903	1.9922
2000	y=350160x + 1882400	1882400	350160	175080	12.0730	7.6009	3.2	3100	56.4774	3.4914	1.7519
5000	y=411940x + 3240600	3240600	411940	205970	12.2355	8.5172	3.2	7750	26.5768	3.8893	1.4245
7000	y=435300x + 3958000	3958000	435300	217650	12.2906	8.8537	3.2	10850	20.0599	4.0354	1.3023
10000	y=446940x + 4881600	4881600	446940	223470	12.3170	9.2103	3.2	15500	14.4174	4.1903	1.1589

$$\text{slope} = \frac{d \ln \dot{\gamma}}{d \ln \tau_w} = 1.5 \quad (16)$$

$$\text{slope} = \frac{d \ln \dot{\gamma}}{d \ln \tau_w} = 2.3 \quad (17)$$

$$\text{slope} = \frac{d \ln \dot{\gamma}}{d \ln \tau_w} = 3.2 \quad (18)$$

For PP with 180,000 molecular weight, the analysed data is presented in Table I. Table II and III shows the analysed data for PP with 230,000 molecular weight and 460,000 molecular weight respectively.

Equation (10) and viscosity data analysed in Tables I – III were used to plot Fig. 5 that analyses how the viscosity, η varies with the true shear rate, $\dot{\gamma}_{corr}$ in all the 3 types of PP investigated. Finally the viscosity plots were fitted to a linear approximation and resulted to models given in Table IV.

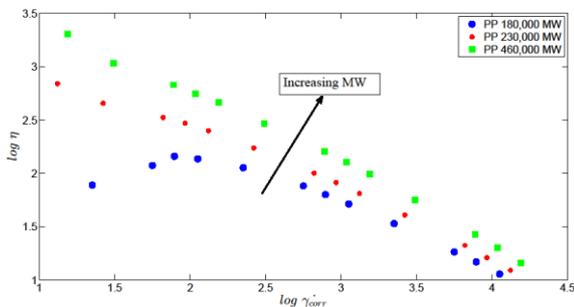


Fig. 4 Viscosity plots for PP of different MW.

TABLE IVV
VISCOSITY MODELS.

PP Type	Model
PP 180,000 MW	$y = -0.39x + 2.8$
PP 230,000 MW	$y = -0.58x + 3.6$
PP 460,000 MW	$y = -0.7x + 4.2$

IV. CONCLUSIONS

Three types of PP with different molecular weights were characterized by capillary rheometry. The rheological properties of PP melts was measured and the effect of molecular weight analysed.

From the analysed data, information in Table V can be deduced, as the effect of molecular weight (MW) on rheological properties of PP melt. Experimental trends are also included in Table V.

In addition, the molecular weight was also found to affect the pressure losses. As molecular weight increased, the pressure entrance losses were seen to increase.

TABLE V

EFFECTS OF MOLECULAR WEIGHT AND EXPERIMENTAL TREND ON PP MELT.

Basis	Trend	Shear stress	Viscosity
MW	Increasing MW	Increasing	Increasing
$\dot{\gamma}$	Increasing $\dot{\gamma}$	Increasing	Decreasing

ACKNOWLEDGMENT

This work was supported by Department of mechanical and manufacturing Engineering, Aalborg University, Denmark.

REFERENCES

- [1] Winter, H.H., *Capillary Rheometry*. Encyclopedia of Life Support Systems (EOLSS). 2008, USA: UNESCO Publishers Co Ltd.
- [2] Morrison, P.F., *Shear Viscosity Measurement in a Capillary Rheometer*. 2014: Michigan Technological University.
- [3] Morrison, F.A., *Understanding Rheology*. 2001: Oxford University Press.
- [4] A. D. Gotsis, B.L.F.Z., *Effect of long branches on the rheology of polypropylene*. Journal of Rheology 48, 895 (2004), 2004. **48**: p. 895.
- [5] Astasuain, M., C. Sarmoria, and A. Brandolin, *Controlled rheology of polypropylene: Modeling of molecular weight distributions*. Journal of Applied Polymer Science, 2003.
- [6] Sugimoto, M., et al., *Melt rheology of polypropylene containing small amounts of high molecular weight chain. I. Shear flow*. Journal of Polymer Science Part B: Polymer Physics, 2001. **39**(21).
- [7] Utracki, L.A. and A. Luciani, *Rheology of polypropylene, in Polypropylene: An A-Z reference*, J. Karger-Kocsis, Editor. 1999, Springer Netherlands: Dordrecht. p. 715-720.