Some studies on melt flow behaviour of poly(ethylene terephthalate)

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The flow behaviour of poly(ethylene terephthalate) melt has been studied on a capillary rheometer in the temperature range 275-295°C. The intrinsic viscosities of the extrudates were also determined. The melt flow data was corrected for the molecular weight reduction that occurs in the rheometer during the measurement with the help of the intrinsic viscosity data. An empirical equation relating the zero shear melt viscosity to the intrinsic viscosity of the polymer has been derived and it is shown to predict the measured melt viscosity quite accurately. The activation energy for flow has been estimated to be 16.5 kcal/mol. The viscosity profiles along the capillary radius have been graphically illustrated. The present analysis shows that PET melt flowing through a capillary is Newtonian close to the capillary axis and pseudo-plastic close to the wall of the capillary.

Keywords: Capillary rheometer, Intrinsic viscosity, Newtonian fluid, Poly(ethylene terephthalate), Rabinowitsch fluid, Zero shear melt viscosity

1 Introduction

One of the most critical parameters in melt spinning is the melt viscosity of the polymer which shows a strong dependence on the molecular weight and its distribution. In industry, the molecular weight is most conveniently and quickly assessed by measuring the limiting solution viscosity of the polymer in a suitable solvent. But it is the melt viscosity of the polymer which determines its flow behaviour and is of greater practical importance. However, for the measurement of melt viscosity, a rheometer is required. In addition to molecular weight, the melt viscosity is also dependent on the shear rate. Therefore, the need has been felt to relate the solution viscosity (intrinsic viscosity) of the polymer to its melt viscosity. A number of empirical relationships have been proposed which can all be generalized by the following type of relationship:

$$\eta_0 = k \langle \eta \rangle^n$$  \hspace{1cm} (1)

where \(\eta_0\) is the melt viscosity at zero shear rate; \(k\) and \(P\), the constants; and \(\langle \eta \rangle\), the intrinsic viscosity of the polymer. Some researchers have proposed such relationships for poly(ethylene terephthalate) (PET) also. These relationships are generally empirical in nature and are based on the intrinsic viscosity data of PET chips. It is worth pointing out that PET can degrade in the molten state and this may result in a reduction in the molecular weight of the polymer during the transport of the melt. Hence, no investigation or correlation can be taken as completely dependable unless the effect of degradation is accounted for. This is important since comparisons can be made only between the data obtained for polymers of identical characteristics. Any difference in the intrinsic viscosity values of the polymer due to degradation would only weaken the validity of such correlations.

The present work endeavours to relate melt viscosity to the molecular weight of the extrudate and not to the molecular weight of the chips. An empirical rheological equation of state of the Arrhenius type has been developed for molten PET which allows direct calculation of the zero shear melt viscosity using the intrinsic viscosity of the extrudate. This information has further been used to describe the flow of the polymer melt and its response within a capillary by taking into account its non-Newtonian behaviour. This information could be valuable in optimizing extrusion parameters and also for designing melt-spinning equipment. The present work aims at achieving a clear insight into some of these
factors and their effect on the flow behaviour of PET melt.

The rheological studies have been carried out on a 'Rheograph 2001' which is of the capillary extrusion type. Steady-state conditions of flow are not readily obtainable with this type of viscometer, but they simulate actual conditions of extrusion and are hence useful and popular for carrying out rheological studies.

2 Non-Newtonian Behaviour of Polymer Melts

Polymer melts in general are non-Newtonian, or more specifically pseudo-plastic (shear thinning), and do not follow Newton's law of viscous flow which states that

\[ \tau = \eta \gamma \]  ... (2)

where \( \tau \) is the shear stress; \( \eta \), the viscosity of the fluid; and \( \gamma \), the shear rate.

The non-Newtonian nature of polymer melts is principally due to the conformational changes of the macromolecules and to a breakdown of the network structure upon deformation. Consequently, the viscosity of the polymer shows a dependence on the rate of deformation. The most generalized and widely used model to represent non-Newtonian flow is the Rabinowitsch model. A convenient simplification of the model leads to the Power-law or Ostwald de-Waele equation:

\[ \tau = \kappa \gamma^n \]  ... (3)

where \( \kappa \) is the consistency parameter; and \( n \), the flow index.

This model represents the data adequately over a limited range of shear rates. But for very high and very low shear rates, the model fails since the fluid response may be Newtonian in these regions. The typical behaviour of a polymer melt is shown in Fig. 1. It indicates that in the initial region, the melt flow behaviour is Newtonian and then gradually diverges from Newtonian response and is better approximated by an ideal Rabinowitsch fluid. The viscosities for an ideal Newtonian and an ideal Rabinowitsch fluid are also shown in the figure for comparison. The actual behaviour of the polymer can be considered to be Newtonian at low shear rates followed by non-Newtonian like that of a Rabinowitsch fluid at high shear rates. In the modified fluid, the transition occurs at a shear rate of \( \gamma_{\text{transition}} \) (Fig. 1) and at shear rates above this value, the fluid response is that of a Rabinowitsch fluid and is characterized by the flow index \( n \). Because of the shear rate dependence of viscosity, the viscosity across the capillary during extrusion may not be constant. During actual extrusion conditions, the response of the fluid near the core would be Newtonian due to the low shear rates prevailing in that region, while towards the capillary walls, the flow pattern could be non-Newtonian. If the throughput rate \( Q \) is estimated on the assumption of pure Newtonian or pure non-Newtonian (Rabinowitsch) flow behaviour, it would not be representative of actual throughput rate. These idealized flow behaviours are represented by Eqs (4) and (5).

\[ Q = C_0 (\Delta P)^{1/n} \]  ... (4)

and

\[ Q = C_1 (\Delta P)^{1/n} \]  ... (5)

where \( \Delta P \) is the pressure drop; and \( C_0 \) and \( C_1 \), the constants.

The modified fluid more closely approximates the throughput, which shows the following type of dependence on the pressure drop:

\[ Q = C_2 (\Delta P)^{1/n} + \frac{C_3}{(\Delta P)^{2/n}} \]  ... (6)

where \( C_2 \) and \( C_3 \) are constants.

3 Materials and Methods

3.1 Sample Specifications

Poly(ethylene terephthalate) chips supplied by Modipon (India) Ltd, Modinagar, having the following specifications were used:

- Bright cylindrical shape
- Length, 4-5 mm
- Diameter, 3-5 mm
- Intrinsic viscosity, 0.63 dl/g
- Diethylene glycol content, 0.725 wt %

3.2 Measurement of Melt Viscosity

The polymer chips were dried at 130°C in a vacuum oven for 24 h to avoid hydrolytic degradation.
during testing. Extrusion measurements were carried out in 'Rheograph 2001' of M/s Gottfert which gives data on the piston speed, test pressure, melt temperature, apparent shear stress, apparent shear stress, apparent viscosity, etc. This equipment is microprocessor-controlled and allows the measurements to be made at different rates of throughput in a single run. But in the present investigation, the measurements were made at only one extrusion rate in a single run. This was done to enable the polymer to reach a steady state. The time for melting of PET chips allowed in each test was 3 min. Thermo-oxidative degradation was minimized by carrying out the test in a medium of nitrogen. The capillary of the Rheograph has a radius of 0.05 cm and is 3 cm long.

3.3 Measurement of Intrinsic Viscosity

The PET extrudates obtained as a result of each extrusion run were collected. Their intrinsic viscosities were measured using an Ubbelohde viscometer. The solvent system used was a mixture of phenol and 1,1,2,2-tetrachloroethane in the ratio of 60:40 (wt %) and the measurements were made at 30 ± 0.01°C. AR grade chemicals were used. They were further purified by distillation; phenol at 180°C and tetrachloroethane at 145-146°C.

3.4 Determination of DEG Content

The DEG content in PET was determined using the procedure adopted by Goodyear, USA.

4 Results and Discussion

The values of shear rate, shear viscosity, shear stress, etc. as given by the Rheograph are the apparent values. Moreover, they do not take into account the true nature of their variation within the capillary. Hence, the information cannot be used to characterize the rheological behaviour of molten PET. The only true values are \( Q \) and \( \Delta P \) and these are shown in Table 1. Fig. 2 is a log-log plot of \( \Delta P \) vs. \( Q \) obtained for various temperatures of extrusion.

The plots clearly indicate two linear regions with certain degree of scatter. In the first region, at low rates of throughput, the behaviour is Newtonian with unit slope \((n = 1)\) while in the second region, the average slope is given by \( n = 0.613 \), where the behaviour is non-Newtonian (pseudo-plastic).

4.1 Analysis of Extrudate

The extrudate obtained from each run was collected and its intrinsic viscosity measured. The re-
The results are given in Table 1. In the absence of oxidative and hydrolytic degradation (section 3.2), the only other possible mechanisms could be thermal and mechanical. Mechanical degradation is possible at very high shear rates, leading to cleavage of molecular chains. But the data in Table 1 precludes its presence in the range of throughput rates used in the present investigation as at higher extrusion rates; the degradation shown is less. This further confirms that there is no mechanical degradation. This would suggest that the degradation is mainly due to thermal and hydrolytic effects. At higher extrusion rates, the residence time of the polymer in the molten state is less and the resulting degradation is also less.

The scatter of data points in Fig. 2 could be explained as follows. The intrinsic viscosities of the extrudates obtained at various temperatures of extrusion and at different extrusion rates are not the same as shown in Table 1 ($\eta'_{\text{sample}}$). This implies that the molecular weights of the samples are not the same. The scatter in the data is apparently because the data points relate to materials differing in molecular weights. The throughput rate values were therefore normalized to a reference intrinsic viscosity. This was achieved by using the following empirical relationship:

$$Q_{\text{norm}} = Q_{\text{sample}} \left( \frac{\eta'_{\text{ref}}}{\eta'_{\text{sample}}} \right) = Q_{\text{sample}} \left[ \frac{\eta'_{\text{sample}}}{\eta'_{\text{ref}}} \right]^{5.145}$$

where $Q_{\text{norm}}$ is the normalized or corrected throughput rate with respect to the reference intrinsic viscosity $\eta'_{\text{ref}}$ (0.56 dl/g) for an extrudate sample whose intrinsic viscosity is $\eta'_{\text{sample}}$ and which has a throughput rate of $Q_{\text{sample}}$, and $\eta'_{\text{ref}}$ and $\eta'_{\text{sample}}$, the Newtonian melt viscosities of the respective samples. The data on corrected throughput $Q_{\text{norm}}$ are also given in Table 1. The values of $Q_{\text{norm}}$ are plotted against $\Delta P$ in Fig. 3 and it is interesting to see that the scatter of the data points is now
reduced. The Newtonian region again yields a flow index \( n = 1 \) for the slope and the non-Newtonian region gives an average value of \( n = 0.635 \). These values are more dependable since they do not carry the error introduced by the comparison of polymer extrudates with dissimilar molecular weights.

4.2 Activation Energy

To account for the effect of temperature on the melt viscosity, an Arrhenius type of dependence has been assumed, viz.

\[
\eta_0 = A \exp \left( \frac{E}{RT} \right)
\]  

... (8)

where \( \eta_0 \) is the zero shear rate viscosity; \( A \), a constant; \( E \), the activation energy; \( R \), the universal gas constant; and \( T \), the absolute temperature in K.

An accurate determination of the activation energy is very important. The value of activation energy changes with temperature and hence some precautions are necessary in its evaluation. Melt viscosity measurements have been made at five different temperatures. Zero shear rate viscosity or the limiting viscosity has been obtained in the region where \( Q \) is proportional to \( \Delta P \). The logarithm of limiting viscosity is plotted against \( 1000/T \) (Fig. 4) and the value of activation energy obtained from the slope of the plot which is equal to \( E/R \). If the non-limiting viscosity values are used for obtaining activation energy, the activation energy so obtained will be erroneous. The activation energy with respect to limiting shear rate is the only absolute value. Fig. 4 gives a value of 16.5 kcal/mol for the activation energy which compares well with the activation energy for dried PET obtained by most of other workers (Table 2).

4.3 Rheological Equations

The melt viscosity of a polymer depends on its molecular weight, temperature and shear rate. An Arrhenius type of relationship can be assumed since the mobility at high temperatures is closely approximated by an activated rate process. A number of workers have proposed empirical relationships for the melt viscosity of PET, most prominent among them being Gregory and Manaresi. For the present analysis, the starting point has been Gregory's equation [Eq. (9)] and Gregory's equation as modified by Manabe to include the effect of diethylene glycol on the viscosity [Eq. (10)].

\[
\eta_0 = \mathcal{F}^{1.145} \exp \left( \frac{6802.1}{t + 273} - 2.321 \right)
\]  

... (9)

where \( t \) is the temperature of the melt in °C and DEG is the wt % of diethylene glycol in PET.

In the present investigation, \( \mathcal{F}^{1.145} \) has been measured using a mixture of phenol and 1,1,2,2-tetrachloroethane in the ratio of 60:40 (wt %) at 30°C. Manaresi et al. measured \( \mathcal{F}^{1.145} \) using ortho-chlorophenol solution at 25°C. The \( \mathcal{F}^{1.145} \) value obtained from the latter method is higher than that obtained in the present investigation by 0.010. Taking this into account, the equation of Manaresi et al. can, therefore, be written, for purposes of comparison, with the present results as

\[
\eta_0 = (\mathcal{F}^{1.145} + 0.010)^{1.145} \exp \left( \frac{8565.6}{t + 273} - 5.5182 \right)
\]  

... (11)

The present investigation yields the following equation:

\[
\eta_0 = \mathcal{F}^{1.145} \exp \left( \frac{6802.1}{t + 273} - 2.321 \right)
\]  

... (9)
Table 3 - Measured Newtonian melt viscosity of the extrudates and the values predicted by different equations given in the text

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>275</td>
</tr>
<tr>
<td>Chip intrinsic viscosity, 0.63 dl/g</td>
<td>0.557</td>
</tr>
<tr>
<td>Chip DEG content, 0.725 wt%</td>
<td>0.725</td>
</tr>
<tr>
<td>Intrinsic viscosity of extrudate, dl/g</td>
<td>0.557</td>
</tr>
<tr>
<td>DEG, wt%</td>
<td>0.725</td>
</tr>
<tr>
<td>Experimental</td>
<td>1527</td>
</tr>
<tr>
<td>Eq. (9)</td>
<td>1180</td>
</tr>
<tr>
<td>Eq. (10)</td>
<td>1295</td>
</tr>
<tr>
<td>Eq. (11)</td>
<td>1438</td>
</tr>
<tr>
<td>Eq. (12)</td>
<td>1550</td>
</tr>
</tbody>
</table>

Eq. (12) approximates the melt viscosity more closely than its previous versions. The intrinsic viscosity of the extrudate rather than that of the chips has been used in the present investigation. The melt viscosity values computed using some of the other relationships along with the melt viscosity values predicted by the equation proposed in this paper are given in Table 3.

4.4 Viscosity Distribution within the Capillary

During flow in a capillary, the shear stress is not constant along its radius. PET shows shear rate dependent viscosity and there exists a distribution of viscosity within the capillary. For a Newtonian fluid, the response of the sample is independent of the shear rate. But for a non-Newtonian fluid, the response is more complex. Fig. 5 shows the calculated viscosity profiles assuming Newtonian response for PET, which indicates only temperature dependence. Fig. 6 shows the viscosity of PET along the capillary radius if a Rabinowitsch type of response is assumed with a flow index of 0.635. For a modified fluid, the definition of \( n \) as referred to in Eq. (3) changes as follows.

\[
\eta = \eta_0 \left( \frac{\varphi}{\eta_{\text{transition}}} \right)^{n-1} \quad \ldots (13)
\]

or

\[
\eta = \eta_0 \left( \frac{r \Delta P}{2L \tau_c} \right) \quad \ldots (14)
\]

where \( \eta \) is the melt viscosity at shear rates more than \( \eta_{\text{transition}} \) (poise); \( \eta_{\text{transition}} \) the critical shear rate (s\(^{-1}\)).
5.3 The activation energy has been obtained with respect to the zero shear rate viscosity of the polymer and comes out to be 16.5 kcal/mol.

5.4 The empirical rheological equation incorporating the intrinsic viscosity of the chips does not result in good agreement between the experimental and predicted viscosity values.

5.5 The empirical rheological equation incorporating the intrinsic viscosity of the extrudate and the activation energy with respect to limiting shear viscosity values yields the following relationship for the melt viscosity and gives good fit with the experimental data.

$$\eta_0 = \eta_0^{1.45} \exp \left( \frac{8286}{T+273} - 4.6434 - 0.159(\text{DEG}) \right)$$

5.6 Pseudo-plastic behaviour of polymer melts is more closely approximated by the modified fluid model. Its use in approximating the flow behaviour of PET is found to yield more realistic flow profiles.

References
5. T Manabe (unpublished work).