The Viscous Flow of Molten Polypropylene

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The absolute relation between shear stress and shear rate of a molten polypropylene has been studied in the range of temperature from 240 to 280°C and of shear stress from $10^5$ to $10^7$ dyne/cm$^2$, using a capillary type viscometer. It is confirmed that the flow behavior of molten polypropylene exhibits strong non-Newtonian character and its tendency becomes more distinguishable as viscosity average molecular weight increases and as temperature is elevated.

The dependency of the flow behavior on the heterogeneity of molecular weights as well as on the average molecular weight is discussed. The so-called 3.5 power law of the relation between viscosity and weight average molecular weight at zero shear is supposed to be valid for a series of polymer sample of different isotacticities as well as that of different average molecular weights.

INTRODUCTION

The flow behavior of molten polymers has been extensively studied for scientific purpose as well as for industrial necessities and correlated with some molecular factors. In general, the molten liquid of a polymer such as polyethylene exhibits non-Newtonian character and there exists rather a complicated relation between shear stress and shear rate. In addition, it has been reported that the so-called end-effect is usually observed at the entrance of capillary if a capillary type viscometer is used.

We examine the relation between shear rate and shear stress of isotactic polypropylene under different conditions, using a capillary viscometer, and discuss the dependency of the flow behavior on temperature, molecular weight, isotacticity and other factors.

EXPERIMENT

Materials

The starting materials for samples used were two kinds of commercial products of polypropylene, Moplen AS and Avisun 1021. The samples of different molecular weights were obtained from Avison 1021 by pyrolysis, as will be described in a later section. Fractions extracted with n-heptane were also used in a part of the present work. Viscosity average molecular weights were obtained from intrinsic viscosity measurements in decalin at 135°C using the relation $\eta \approx 1.10 \times 10^{-4} M^{0.8}$ established by Kinsinger and Hughes. The

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densities of bulk crystallized specimens were measured at 30°C with a submerged float method using n-propanol and ethylene glycol. The density measurements were converted to the degree of crystallinity according to the relation given by Danusso, Moraglio and Natta and assuming the additivities of the specific volumes of the crystalline and amorphous phases, that is,

\[
\text{Crystallinity} = (0.983 + 9(t + 180) \times 10^{-4} - 1/d^4)/(4.8(t + 180)10^{-6}),
\]

where \(d\) is the density at \(t\)°C.

It was found that if molded film was annealed at 135°C for 2 hours, the crystallinity reached almost an equilibrium value under the given condition. Hence, the value for annealed film was used as a measure indicative of crystallizability for the samples.

**Viscometer for Molten Polymer**

A capillary type viscometer, the Koka Flow Tester, was employed to obtain the flow curve of molten polymers under different loads in a wide range of temperature. For this purpose around one gram of specimens was packed into the heating cylinder of the cross section area of 1.00 cm\(^2\) with the aid of a plunger, and allowed to perfect melt at a chosen temperature by heating it for 15 minutes, then extruded out through dies of different sizes under a fixed load at the temperature. The downwards speed of the plunger was automatically recorded, which provided the flow mass per unit period of time under the con-

![Fig. 1. Sketch of dies. (in mm.)](image)

**Table 1. Sizes and dimension of dies.**

<table>
<thead>
<tr>
<th>Die No.</th>
<th>Radius (R, \text{cm})</th>
<th>Length (L, \text{cm})</th>
<th>Ratio (L/R)</th>
<th>Depth of approach (\text{cm})</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>0.100</td>
<td>2.0</td>
<td>0</td>
<td>Flat</td>
</tr>
<tr>
<td>2</td>
<td>0.050</td>
<td>0.200</td>
<td>4.0</td>
<td>0</td>
<td>Flat</td>
</tr>
<tr>
<td>3</td>
<td>0.015</td>
<td>0.100</td>
<td>6.7</td>
<td>0</td>
<td>Flat</td>
</tr>
<tr>
<td>4</td>
<td>0.025</td>
<td>0.050</td>
<td>2.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>5</td>
<td>0.025</td>
<td>0.100</td>
<td>4.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>6</td>
<td>0.025</td>
<td>0.200</td>
<td>8.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>7</td>
<td>0.025</td>
<td>0.300</td>
<td>12.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>8</td>
<td>0.025</td>
<td>0.500</td>
<td>20.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>9</td>
<td>0.025</td>
<td>0.600</td>
<td>24.0</td>
<td>0.25</td>
<td>Approach</td>
</tr>
<tr>
<td>10</td>
<td>0.025</td>
<td>0.800</td>
<td>32.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
<tr>
<td>11</td>
<td>0.025</td>
<td>1.000</td>
<td>40.0</td>
<td>0.26</td>
<td>Approach</td>
</tr>
</tbody>
</table>

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The schematic diagram and dimensions of the dies used are shown in Fig. 1 and Table 1.

THE TYPICAL FLOW CURVES AND SO-CALLED END EFFECTS OF CAPILLARY VISCOMETER

We first consider the typical flow curves of two samples, Moplen AS and Avisun 1021 which were used as the starting material in this work. The intrinsic viscosities and maximum crystallinities of them are listed in Table 2.

Table 2. The properties of two polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density of annealed samples g/ml</th>
<th>Intrinsic viscosity [η], 100ml/g</th>
<th>Crystallinity of annealed samples, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moplen AS</td>
<td>0.900</td>
<td>4.03</td>
<td>60.5</td>
</tr>
<tr>
<td>Avisun 1021</td>
<td>0.902</td>
<td>3.33</td>
<td>62.5</td>
</tr>
</tbody>
</table>

Fig. 2. Typical Flow Curve of Two Polymers at Indicated Temperatures.

Fig. 2 shows the typical flow curves of these two samples, where extrusion mass per unit period of time is plotted against pressure at the indicated temperatures. It is readily ascertained from non-linearity of the curves that the viscous flows of the samples are of extremely strong non-Newtonian character over the temperature range examined.

According to the flow theory, the shear stress at the wall of a capillary when liquid flows through the capillary, \( F_r \) can be given as

\[
F_r = \frac{PR}{2L}. \tag{1}
\]

The apparent fluidity of the liquid, \( \phi_a \) and apparent shear rete, \( f_a(F_r) \) can be
defined as

\[ \dot{\theta}_a = \frac{8LQ}{\pi R^4}P \]

\[ f_s(F_r) = F_r \dot{\theta}_a \]

\[ = \frac{4Q}{\pi R^3}, \]

where \( P, R, L \) and \( Q \) represent the pressure difference of both ends of the capillary, the radius and the length of it and the mass extruded out through the capillary for unit period of time, respectively.

The apparent fluidity is a characteristic parameter of the liquid which may be decided uniquely by shear stress as shown in the next section regardless of whether the liquid is of Newtonian or not, whereas for the Newtonian case it is reduced to the real fluidity. Therefore, if the apparent shear rate \( \frac{4Q}{\pi R^3} \) was plotted against shear stress \( \frac{PR}{2L} \) from the flow data obtained by using several dies of different dimensions, \( i.e. \) of several pairs of \( L \) and \( R \), one unique curve should be obtained for a liquid at a chosen temperature, so far as the above mentioned relations are valid.

The results of Moplen AS at 280°C using three dies of different sizes are shown in Fig. 3. It can be easily seen that the relation of apparent shear rate against shear stress is greatly dependent on the size of dies used. This should be attributed to unvalidity of Eq. (1) for the present case.

![Fig. 3. Apparent shear rate vs. shear stress by eq. (1) of Moplen AS at 280°C, using dies; No. 1 (.), No. 2 (.), and No. 3 (O).](image)

Eq. (1) was introduced to the case that a liquid flows in a capillary stationarily throughout the whole path as a laminar flow. However, in a real flow in a capillary with a finite length, some irregularity caused from both of its ends must necessarily take place, which usually is called the end effect of a capillary flow.

In general, the end effect has been corrected for Newtonian flows by adding some multiple number of the capillary radius to the capillary length\(^{11}\). Thus, instead of Eq. (1), the corrected shear stress at the wall can be given as

\[ F_c = \frac{PR}{2(L+nR)}, \]

\[ (182) \]
where $n$ is a proper number for the liquid. It is well known that Eq. (4) is applicable widely for almost all of the Newtonian flow, while there has been only a few information for non-Newtonian flows, except that, for a molten polyethylene, the validity of Eq. (4) was reported. Therefore, we first examine Eq. (4) with a molten polypropylene.

Eq. (4) can be rearranged in the form: $P = 2(L/R)F_c + 2nF_c$. This equation predicts a linear relation between $P$ and $L/R$ at a constant value of $F_c$. In order to examine this relation, in Fig. 4 apparent shear rate $4Q/πR^3$ was first plotted against pressure $P$ with use of the original data, from which Fig. 3 had been obtained. Next, from the figure thus obtained were read off the pressures corresponding to a fixed apparent shear rate at several levels of the apparent shear rate, and these values were plotted against the value of $L/R$ in Fig. 5. Then, linear straight lines should be obtained, so far as Eq. (4) is valid, because a chosen apparent shear rate should correspond to a unique real shear stress regardless of whether the flow is Newtonian or not. As is shown in Fig. 5, fairly good straight lines are observed at the different levels of shear rate. The result may indicate that Eq. (4) is appropriate to use for the molten polypropylene of 280°C. In addition, the points, where the lines intercept the horizontal axis, provide the values of $n$ corresponding to apparent shear rates.

Using Eq. (4) and the values of $n$ obtained here for Moplen AS at 280°C, the apparent shear rate is plotted against the corrected shear stress in Fig. 6. It shows that all data comprise one unique curve within experimental error. Although the aboves are only an example for the flow of Moplen AS at 280°C, all results for the samples used ensured the appropriateness of Eq. (4) over the temperature range examined.

With these techniques we could calculate the corrected shear stress from the experimental flow curve obtained at different temperatures for all samples. It should be noticed here that the correction factor $n$ is not only dependent on
the sort of sample but also on the shear rate.

In Figs. 7 and 8, correction factor $n$ for Moplen AS and Avisun 1021 at different temperatures are plotted against the apparent shear rate.

As can be seen Fig. 7, the value of $n$ increases with decreasing of temperature, and with increasing of apparent shear rate, showing a tendency of leveling off at the higher apparent shear rates. The result in Fig. 8 for Avisun 1021 with the use of the approach dies of greater values of $L/R$ shows the same tendency for temperature and shear rate but smaller values of $n$ in the whole range of shear rate.

It should also be noticed here that the values of $n$ determined by using a series of dies of some range of $L/R$ did not always cover another series of dies whose $L/R$ values were extremely different from that of the former series. In addition, different values might be obtained for the different types of dies. As a matter of technique, therefore, one has to utilize the values of $n$ which have been determined with using a die series of same type covering the $L/R$ of the...
ABSOLUTE RELATION BETWEEN SHEAR RATE AND SHEAR STRESS

The absolute relation between shear rate and shear stress has scarcely been reported as yet for a non-Newtonian flow, mainly because of experimental difficulties, although it is of fundamental importance to describe the flow behavior of a liquid. However, now we can decide the absolute relation for molten polypropylene, since the real shear stress could be obtained by using the correction factor \( n \) as pointed out in the former section.

If we use the \( L_e \) in stead of \( L \) in Eq. (1), shear stress can be given as

\[
F_e = \frac{PR}{2L_e},
\]

where \( L_e = L + nR \). Then, the mass extruded out through a capillary for a unit time \( Q \) can be expressed as follows:

\[
Q = \int_0^R \pi r^2 f(F_e) \, dr = \frac{8\pi L_e^3}{P^4} \int_0^{F_e} F_e f(F_e) \, dF_e,
\]

where \( f(F_e) \) represents the real shear rate at the shear stress of \( F_e \). Therefore, if we re-define the apparent fluidity \( \phi_a \) as

\[
\phi_a = \frac{8L_eQ}{\pi R^4P},
\]

one finds the Eq. (7) with the aid of Eqs. (4)', (5) and (6), (Krieger and others):

\[
f(F_e)/F_e = \left[ 1 + \frac{1}{4} \frac{d \ln \phi_a}{d \ln F_e} \right] \phi_a
\]

Fig. 9. The absolute relation between shear rate and shear stress of two samples at indicated temperatures. Solid curve: Avisun 1021 at 280, 270, 260, and 240°C. Dotted curves: Moplen AS at 280, and 260°C, where experimental points are omitted to avoid confusion.
The values of $F_e$ and $\phi_n$ in the equation can be all obtained from experimental data, using Eqs. (4) or (4)' and (6). Eventually, we can obtain the real value of shear rate as a function of the shear stress from experimental data.

In Fig. 9 the shear rates of the two samples are plotted against the shear stress in logarithmic scale. Thus all viscous flows of the samples at a chosen temperature can be described by using the relation between shear stress and shear rate obtained here. In comparing the flow of Moplen AS with that of Avisun 1021, some differences are apparently observed. For example, Avisun 1021 shows to be more fluid than Moplen AS at lower shear stresses but the former becomes less fluid than the latter at higher shear stresses at equivalent temperatures.

On the other hand, according to Eq. (7), the term of $d \ln \phi_n / d \ln F_e$ may be considered to indicate a measure of deviation from the Newtonian character, so that the flow is reduced to a Newtonian one and $\phi_n$ to the real fluidity if the value goes to zero. Therefore, we plot $\ln \phi_n$ against $\ln F_e$ in Fig. 10 in order to examine the flow character in more detail.

There can be seen that every pair of experimental points seems to comprise a low curvature curve, each of which exhibits an inflexion point. In a region beyond those points the extruded molten polymers generally showed irregular shapes. Hence the points might be considered as an upper limit of the regular flow. However we will not further discuss the flow behavior of molten polymer in the range above the point for the time being, although it might be considered as a point characteristic of a polymer.

In Table 3 the slope $d \ln \phi_n / d \ln F_e$ and the ratio of shear rate to shear stress $f(F_e)/F_e$ at the shear stress of $3 \times 10^4$ dynes/cm$^2$ of two samples are listed. As
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Table 3. $d \ln \phi_a / d \ln F_e$ and $f(F_e)/F_e$ of two samples at $3 \times 10^5$ dynes/cm$^2$ of shear stress.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature $^\circ$C</th>
<th>$d \ln \phi_a / d \ln F_e$</th>
<th>$f(F_e)/F_e$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morplesn AS</td>
<td>260</td>
<td>0.91</td>
<td>1.23$\phi_a$</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.75</td>
<td>1.19$\phi_a$</td>
</tr>
<tr>
<td>Avisun 1021</td>
<td>240</td>
<td>1.05</td>
<td>1.26$\phi_a$</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.88</td>
<td>1.22$\phi_a$</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.52</td>
<td>1.13$\phi_a$</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.33</td>
<td>1.08$\phi_a$</td>
</tr>
</tbody>
</table>

* Calculated from the value of $d \ln \phi_a / d \ln F_e$, using eq. (7).

can be seen, Moplen AS has the higher value of $d \ln \phi_a / d \ln F_e$ than Avisun 1021 at corresponding temperatures, that may indicate the more non-Newtonian character of the former polymer.

Furthermore, the ratio of shear rate to shear stress shown in the last column of the table could be also of indicative to the character of the flow at the shear stress and the temperature. The lowest value of $d \ln \phi_a / d \ln F_e$ and $f(F_e)/F_e \cdot \phi_a$ of Avisun 1021 at the highest temperature 280°C might imply that the flow approached the Newtonian character in accordance with the increase of temperature (the former 0.33 and the latter 1.08).

THE FLOW OF MOLTEN POLYPROPYLENE OF DIFFERENT MOLECULAR WEIGHTS

We next consider the effects of the molecular factors of the polymer, such as average molecular weight, on the flow behavior. For the purpose several fractions of different average molecular weights were obtained from Avisun 1021 by mean of pyrolysis of the polymer through heating the kerosine solution at higher temperatures for chosen time periods. Some properties of the fractions used herein are listed in Table 4.

Here I, H, G and F are fractions extracted by n-heptane after the pyrolysis.

Table 4. Properties of pyrolized fractions from Avisun 1021.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[η], 100 ml/g</th>
<th>$M_x \times 10^{-5}$</th>
<th>Density*, g/ml</th>
<th>Crystallinity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.18</td>
<td>3.77</td>
<td>0.909</td>
<td>71.4</td>
</tr>
<tr>
<td>B</td>
<td>2.79</td>
<td>3.77</td>
<td>0.905</td>
<td>66.5</td>
</tr>
<tr>
<td>C</td>
<td>1.90</td>
<td>1.98</td>
<td>0.905</td>
<td>66.5</td>
</tr>
<tr>
<td>D</td>
<td>1.86</td>
<td>1.93</td>
<td>0.909</td>
<td>71.4</td>
</tr>
<tr>
<td>E</td>
<td>1.46</td>
<td>1.43</td>
<td>0.908</td>
<td>70.5</td>
</tr>
<tr>
<td>I</td>
<td>2.20</td>
<td>2.38</td>
<td>0.907</td>
<td>69.4</td>
</tr>
<tr>
<td>G</td>
<td>1.84</td>
<td>1.90</td>
<td>0.909</td>
<td>71.4</td>
</tr>
<tr>
<td>H</td>
<td>1.50</td>
<td>1.47</td>
<td>0.909</td>
<td>71.4</td>
</tr>
<tr>
<td>F</td>
<td>1.25</td>
<td>1.17</td>
<td>0.909</td>
<td>71.4</td>
</tr>
</tbody>
</table>

* The value for mold film of samples (annealed at 135°C for 2 hrs.) is shown.
By the extraction, contents less than 9% were removed but no increase in the crystallinity except in average molecular weight was observed. The extrusion experiments of molten liquid of those fractions were conducted at the temperature of 260°C with using different sizes of dies and the results provided the relations between apparent fluidity and corrected shear stress, which are shown in Figs. (11) and (12).

Each curve in the figures seems to comprise a curve having slightly upwards curvature in the range of lower shear stresses and usually rather distinct inflexion point beyond which irregular extrusions take place is recognized, similarly as in the case of the original commercial products in the previous sections.

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Fig. 11. The apparent fluidity vs. stress of samples of different molecular weight obtained from pyrolysis, designations of the specimens are listed in Table 4, where

--- A --- B --- C

--- D --- E

The experimental points are omitted to avoid confusion.

Fig. 12. The apparent fluidity vs. shear stress of n-heptane extracted samples after pyrolysis, the designations of the specimens are listed in Table 4, where experimental points are omitted to avoid confusion.

Fig. 13. The re-plot from Fig. 11 and 12 to compare E and D with G and H.
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There it can be also seen that the apparent fluidity generally becomes less as molecular weight increases. If we compare the results of D and E with that of H and G as re-plotted in Fig. (13) from the Figs. (11) and (12) for comparison, it can be seen that at lower shear stresses the difference between E and G and between D and H are not so distinguishable but at higher shear stresses E and D become larger than G and H. Here E and G, D and H have almost the same average molecular weight and crystallizability to each other as shown in the Table (4), but E and D are thought to have a wider distribution of molecular weights than G and H, because the latters were extracted by n-heptane after pyrolysis but no increase of crystallinity was recognized. Therefore, the higher fluidity of E and D in range of higher shear stresses should be attributed to the wider distribution of molecular weights. This is in good accordance with the results of J. F. Rudd1 about molten polystyrene that the fluidity at higher shear stresses depends not only on the viscosity average molecular weight but also on the number average of it, although the fluidity in zero shear stress usually is thought to depend only on the weight average molecular weight as well-known.

In order to study deviations of these results from the Newtonian character, \( \frac{d \ln \phi_o}{d \ln F_e} \) and the ratio \( f(F_e)/F_e \) at the shear stress of \( 3 \times 10^5 \) dynes/cm\(^2\) are listed in Table 5.

Table 5. Deviation factors of pyrolyzed fractions from Newtonian character at 260°C at the shear stress of \( 3 \times 10^5 \) dynes/cm\(^2\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \frac{d \ln \phi_o}{d \ln F_e} )</th>
<th>( f(F_e)/F_e )</th>
<th>( M_v \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.84</td>
<td>1.21( \phi_o )</td>
<td>2.38</td>
</tr>
<tr>
<td>H</td>
<td>0.69</td>
<td>1.17( \phi_o )</td>
<td>1.90</td>
</tr>
<tr>
<td>F</td>
<td>0.65</td>
<td>1.16( \phi_o )</td>
<td>1.47</td>
</tr>
<tr>
<td>G</td>
<td>0.35</td>
<td>1.09( \phi_o )</td>
<td>1.17</td>
</tr>
<tr>
<td>A</td>
<td>1.31</td>
<td>1.33( \phi_o )</td>
<td>3.77</td>
</tr>
<tr>
<td>B</td>
<td>1.25</td>
<td>1.31( \phi_o )</td>
<td>3.57</td>
</tr>
<tr>
<td>C</td>
<td>0.82</td>
<td>1.20( \phi_o )</td>
<td>1.98</td>
</tr>
<tr>
<td>D</td>
<td>0.81</td>
<td>1.22( \phi_o )</td>
<td>1.93</td>
</tr>
<tr>
<td>E</td>
<td>0.86</td>
<td>1.22( \phi_o )</td>
<td>1.43</td>
</tr>
</tbody>
</table>

The results show that the values of \( \frac{d \ln \phi_o}{d \ln F_e} \) and \( f(F_e)/F_e \phi_o \) increase generally with increasing the viscosity average molecular weight in comparing the data of two series, A-E and I-F. It means that the non-Newtonian character becomes larger with increasing of the viscosity average molecular weight. Furthermore, it may be also noteworthy that the non-Newtonian character of samples has been reduced by the n-heptane extraction so that the values of \( \frac{d \ln \phi_o}{d \ln F_e} \) and \( f(F_e)/F_e \phi_o \) of the series of I-F are smaller than those of the series of A-E at same viscosity average molecular weight. If it is considered that the series of I-F probably have a narrower distribution of molecular weights than that of A-E, the n-heptane extracted samples may indicate the less
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non-Newtonian character at an equivalent number average molecular weight as well as at an equivalent viscosity average molecular weight.

These consideration may suggest that the non-Newtonian character of molten polymer generally decreases as homogeneity of the polymer molecules increases.

DISCUSSION

By means of a capillary type viscometry and by using different kinds of the dies, we could obtain the absolute relation between shear stress and shear rate of molten polypropylenes. Furthermore, with the value of $d \ln \phi_a / d \ln F_\sigma$ in eq. (7), we could estimate the flow character of sample in comparison with Newtonian flows.

On the other hand, many kinds of relations between shear stress and shear rate have been experimentally proposed by several investigators for non-Newtonian flows. For example, the following equation was proposed by Spencer\(^{13}\) to indicate the dependency of shear stress on the apparent viscosity $\eta^*$ of a non-Newtonian flow.

$$\eta^* = \eta_0 \exp(-KF_\sigma)$$  \hspace{1cm} (8)

where, $\eta^* = 1/\phi_a$ and $\eta_0$ is the value of $\eta^*$ when $F_\sigma = 0$.

It is reported that $K$ is constant in a relatively wide range of $F_\sigma$ for some non-Newtonian liquids and it can be a measure indicative of the non-Newtonian character\(^{19}\). Eq. (8) alternatively can be expressed as

$$\ln \phi_a = \ln \phi_0 + KF_\sigma,$$  \hspace{1cm} (9)

where $\phi_0$ is the value of $\phi_a$ when $F_\sigma = 0$. In order to check the relation, the value of $\ln \phi_a$ of Avisun 1021 is plotted against shear stress $F_\sigma$ in the Fig. 14. As can be seen, the experimental points at each temperature seem to fall approximately on a common straight line in the lower range of $F_\sigma$. This may indicate the constancy of $K$ in Eq. (9).

On the other hand, from Eq. (9), $K$ can be expressed as

![Fig. 14. log $\phi_a$ against $F_\sigma$ of Avisun 1021, at 240°C ; 260°C ; 280°C.](190)
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\[ K = \frac{d \ln \phi_a}{d \ln F_e} = \frac{1}{F_e} \frac{d \ln \phi_a}{d \ln F_e} \] (10)

The term of \( \frac{d \ln \phi_a}{d \ln F_e} \) in the right hand in Eq. (10) is the value which we used as a measure for non-Newtonian character of a liquid according to the suggestion of Eq. (7). Therefore, eventually, Spencer’s \( K \) as a measure for the character of a liquid is quite identical with the value which can be obtained by dividing \( \frac{d \ln \phi_a}{d \ln F_e} \) by \( F_e \). Under these circumstances, it must be apparent that even if we use the value of \( K \) in Eq. (8) instead of that of \( \frac{d \ln \phi_a}{d \ln F_e} \) in Eq. (7), the consideration as to the non-Newtonian character of samples in the former sections must be quite similar.

The approximate linearity of the curves in Fig. 14 in the range of lower shear stresses may imply the possibility to obtain the apparent fluidity at zero shear \( \phi_a \) and hence its reciprocal \( \eta_a \) by extrapolating the lines to zero shear. Such attempts were conducted for samples of different molecular weights, A, B, C ......, and I by using the original data of Figs. 11, 12. As the results, it was found that \( \eta_a \) was approximately proportional to the 3.5 power of viscosity average molecular weight at the temperature of 260°C.

\[ \eta_a = KM^{a - 3.5} \] (11)

where \( K \) is a constant. If it is considered that \( M_a \equiv M_w \) for the polymers because of their relatively narrower molecular weight distributions which might be expected by the pyrolysis, Eq. (11) is reduced to the equation:

\[ \eta_a = KM^{w - 3.5} \] (12)

which is the one established experimentally by Fox, Rudd and others\(^{11,10}\) and confirmed theoretically by Bueche\(^{10}\). Therefore, our results may be of indicative that Eq. (12) will be also experimentally applicable to a series of polymers having different isotacticities and different molecular weights.

However, the range in isotacticities of the samples examined is not so wide as shown by their crystallinities in Table 4. Therefore, a further study will be necessary to confirm Eq. (12) for a series of polymer of different isotacticities in more detail.

REFERENCES