DEGRADATION OF POLYETHYLENE MOLECULE
BY HIGH PRESSURE JET.

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Introduction.

Formerly, for the purpose of preparing the emulsion of cod liver oil, the authors reported the way of jet by high pressure." In that case, it was confirmed from the subsequent experiments that the spouted liquid was shattered by the friction with the neighbouring fluid in high speed flying.17 It is anticipated that the molecule of polymer may be shattered by high pressure jet. The authors spouted the polyethylene molecule dissolved or suspended in tetraline and examined the effects of pressure, temperature and the distance between the nozzle and the crashing plate.

Apparatus and Experimental Method.

The apparatus used is the same as in the case of emulsion, but in this case the area ratio of pistons is 1:10 and it is possible to apply 5000 atm. The experimental method is all the same and the number of times of jetting are respectively 9, 17 and 37. The nozzle diameter is 0.42 mm and the experimental conditions are given in Table 1.

Samples.

The molecular weight of the polyethylene used, colourless and transparent, is 26900, its softening point being about 105°C. The boiling point of tetraline used is 205–207°C. The concentration of polyethylene is 1%, and it is dissolved completely in tetraline at a temperature of 80°C and spouted at given temperatures.

Table 1.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Press. (atm)</th>
<th>Distance of nozzle and crashing plate (mm)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2000</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>470</td>
<td></td>
</tr>
</tbody>
</table>

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(1) R. Kiyama, H. Kinoshita and K. Suzuki, This Journal, 21, 82 (1951).

Method for the Determination of the Molecular Weight.

The molecular weight of polyethylene is determined from the viscosity, namely, the equation of Staudinger (molecular weight: $M$, concentration: $C$ and specific viscosity: $\eta_s$)

$$\lim_{C \to 0} \frac{\eta_s}{C} = K_M \times M$$

is used. The temperature of measuring viscosity is $75^\circ$C and $K_M = 0.93 \times 10^{-3}$. The concentrations of 1, 0.5, 0.25, 0.1 and 0.05% are measured.

Experimental results.

![Graph showing the relation between molecular weight and number of times.](image)

Fig. 1 Relation between molecular weight and number of times.

The molecular weight is measured for the samples that are experimented under the condition given in Table 1, and the results are illustrated in Fig. 1.

Considerations.

It is effective in the case of preparing emulsion at high pressures and at a long distance between the nozzle and the crashing plate. In the case of crashing substances, such as polyethylene, high pressure is required, but the short distance between the nozzle and the crashing plate is effective. The authors considered the effects of pressure, temperature and the distance between the nozzle and the crashing plate as follows.

(1) Pressure effect. At the same distance between the nozzle and the crashing plate (2 mm), the molecular weights in the case of 37 times jettings by pressures of 2000 and 4000 atm, are respectively 26610 and 25660 at $10^5$C, and 22120 and 20620 at $100^5$C. It is clear that the molecular weight becomes smaller as the pressure.

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becomes higher. In other words, as in the case of emulsion, it is effective to make the speed of jetting higher.

(2) Temperature effect. At 10°C, a 1% tetraline solution of polyethylene consists of a white, unstable, and viscous colloids, but over 70°C it seems transparent and colourless, so it is possible to consider that it is a solution. In Exps. No. 1 and 3, (pressure: 2000 atm), the temperatures are respectively 10°C and 100°C, and the molecular weights after 37 times-jetting are respectively 26610 and 22120, and in Exps. No. 2 and 4, (pressure: 4000 atm), at the same temperatures the molecular weights are 25660 and 20620 respectively. This shows that the molecular weight becomes smaller as the temperature becomes higher. From these results, it is clear that the polyethylene molecule is more easily crashed in the case of solution than in the colloidal state under the same conditions.

(3) Effect of the distance between the nozzle and the crashing plate. In Exps. No. 4, 5, 6 and 7, where the pressure is 4000 atm, the temperature is 100°C and the distances between the nozzle and the crashing plate are changed as 2, 10, 100 and 470 mm, the molecular weights after 17 times-jetting are respectively 21740, 21670, 22390 and 23030. When the distance between the nozzle and crashing plate is 10 mm, the molecular weight is slightly small as compared with that in the case of 2 mm, but in the cases of 100 mm and 470 mm, the molecular weight gradually becomes large. It seems that the decrease of the molecular weight depends on mechanical crashing by the collision with the crashing plate. But, it is not reasonable to consider that the crashing is due to the plate collision only because of nearly equal effectiveness in the cases of the distance 2-10 mm. It may be considered that the decrease of molecular weight is caused by the friction in high speed flying in fluid as in the case of emulsion.

The decrease of the molecular weight by high speed flying becomes greater as the distance between the nozzle and the crashing plate becomes longer. On the contrary, the decrease of the molecular weight by collision becomes greater as the distance becomes shorter. In the present experiment, the crashing by plate collision is powerful and that by flying is less effective.

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