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THE MODULUS OF POLYETHYLENE

by
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The Modulus of Polyethylene

In a previous article in this journal, we simultaneously measured shear modulus, density, and crystallinity for linear polyethylenes as a function of temperature in samples subjected to various annealing procedures.

At sufficiently high temperatures, the degree of amorphicity becomes appreciable and the modulus becomes lower than $7 \times 10^6$ dynes/cm$^2$. Under these conditions one can interpret the modulus as a rubber elasticity modulus. In the sample, under these conditions, the crystallites have a dual role: they act as crosslinks and also as filler particles. An equation has been proposed for the shear modulus:

$$G = \frac{(1-Q)d_kT}{T_m}(1+2.5Q+14.1Q^2)$$

In equation (1) $Q$ is the fractional crystallinity, $d$ is the density, $m$ is the molecular mass of the repeating link in the chain ($CH_2$ in this case,) $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $\bar{r}$ is the average number of $CH_2$ units in an amorphous sequence of the polymer chain connecting two crystallites. The term in parenthesis on the right hand side is a correction for the "filler effect."
Data obtained in reference (1) on $Q$, $d$ and $G$ at various temperatures enable us to compute $F$, a quantity which should be of use in characterizing crystalline polymers.

We believe that it is permissible to apply equation (1) based on rubber elasticity theory for values of $G$ less than $7 \times 10^8$ dynes/cm$^2$ and for values of $r$ equal to or greater than ten. This is suggested by our systematic studies of highly crosslinked polymers.

Table I shows the data for $T$, $d$, $Q$, and $G$ for sample (No. 491 $\bar{M}_v=2.8\times10^5$) of reference (1) together with the values of $r$ computed by equation (1).

It would, of course, be of great interest if other physical methods for measuring $\bar{r}$ could be developed.
Table I

Linear Polyethylene

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Density</th>
<th>Crystallinity</th>
<th>Modulus (dynes/cm²)</th>
<th>r</th>
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</thead>
<tbody>
<tr>
<td>115</td>
<td>0.918</td>
<td>0.76</td>
<td>6.53x10^8</td>
<td>10.0</td>
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<tr>
<td>120</td>
<td>0.912</td>
<td>0.70</td>
<td>4.95x10^8</td>
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<td>125</td>
<td>0.903</td>
<td>0.67</td>
<td>3.37x10^8</td>
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<td>130</td>
<td>0.892</td>
<td>0.51</td>
<td>7.8x10^7</td>
<td>70.6</td>
</tr>
<tr>
<td>133</td>
<td>0.795</td>
<td>0.30</td>
<td>6.9x10^7</td>
<td>95.8</td>
</tr>
</tbody>
</table>
References


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