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OF MECHANICAL ENERGY LOSSES IN POLYMERS

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THERMOSTIMULATED CREEP FOR THE STUDY OF MECHANICAL ENERGY LOSSES IN POLYMERS

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Abstract.- A detailed study of molecular motions has been performed by Thermostimulated Creep (TSC). The great advantage of the TSC technique for this investigation is its high resolving power. Data obtained on polypropylene will be presented as example. Between -30 °C and +40°C, two retardation modes can be distinguished. The one observed around the glass transition temperature is characterized by mechanical retardation times following an Arrhenius equation. They have the peculiarity to take the same value = 2.8 sec. at the compensation temperature -T = 23 °C. This behavior has been found to be characteristic of the glass transition; it may arise from amorphous chains free from restraints caused by the presence of crystallites. Another retardation mode is observed 50 °C above the glass transition temperature. It has also been, experimentally, resolved into "elementary" processes but, contrarily to the preceding ones, the corresponding retardation times do not follow an Arrhenius equation. As they can be described by a Vogel equation, they have been assigned to the fluidification of the amorphous chains.

1. THERMOSTIMULATED CREEP SPECTRAS. -We briefly recall the principle of Thermostimulated Creep. The sample is subjected to a mechanical stress at a given temperature Ta, for a time allowing some orientation of the mobile retardation units; the temperature is then lowered to a temperature T0 << Ta at which certain molecular motions are frozen and then, the stress is removed. Next, the sample is heated at a monotonous rate so that the mobile units can disorientate. The response y, its time derivative y', and the temperature T are recorded as a function of time. TSC spectra of isotactic polypropylene are represented on Figures 1 and 2: The solid line corresponds to the resin free from antioxidant, the dashed line, for the same resin with 1,000 ppm of Ionox 330. For both sets of experiments, the heating rate was 0.072 °C/sec. Spectra of Figure 1 correspond to samples annealed at room temperature for 48 hours; spectra of Figure 2 have been registered after a series of quenching from room temperature until liquid nitrogen temperature. In all polypropylene samples - with or without antioxidant - the "low temperature" peak is not affected by the thermal history of the sample; while the "high temperature" one has strongly decreased after a series of quenching. The "low temperature" peak may arise from amorphous chains free from constraints from crystallites, the "high temperature" one to amorphous chains under restraints caused by the presence of...
Figure 1: Thermostimulated Creep of Polypropylene (PP) after an annealing at room temperature for 48 hours.

Figure 2: Thermostimulated Creep of Polypropylene (PP) after a series of quenching between room temperature and liquid nitrogen temperature.

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Figure 3 shows the evolution of the TSC spectra of polypropylene with antioxidant between the annealed state (solid line) and the quenched state (dashed line). The intermediate state (dotted line) has been taken 16 hours after a quench. For this series of experiments, the heating rate was 0.090 °C/sec. The difference between the behavior of the two peaks observed on annealed polypropylene is striking: The temperature position of the low temperature peak is independent of the thermal history while the one of the high temperature peak is strongly affected. The shift towards lower temperatures of the high temperature peak indicates a decreasing of its average activation energy.

These observations may be explained by the existence of constrained amorphous regions where a given order would be induced by the presence of crystallites. It may be expected that such morphological entities disappear after quenching. Experimental evidences of such an ordered amorphous phase in polypropylene have been yet published by Beck et al. (1) and Wada et al. (2). X-ray studies now in progress (3) ascertain the previous hypothesis.

\[ \text{Figure 3: Thermostimulated Creep of Polypropylene (PP)} \]

--- after an annealing at room temperature for 48 hours.
--- after a series of quenching between room temperature and liquid nitrogen temperature.
....16 hours after a quench.
(intermediate state)

--- arbitrary units
--- quenched
--- 16h

-50 0 50

°C

(3) A. Douillard; Private Communication.
2. EXPERIMENTAL RESOLUTION OF TSC SPECTRA. -The complex TSC spectra obtained in polypropylene have been resolved experimentally by using fractional loading programs. The stress was applied at the temperature $T_a$ for 2 minutes so that the units having a retardation time $\tau$ or lower than $\tau$ were oriented. Then, the temperature was lowered to $T_a-10^\circ$ at which the stress was removed. Before heating as in a usual cycle of TSC, the temperature was kept constant for 2 minutes in order to randomize the units having a retardation time shorter than $\tau$. For the next fractional loading program, the stress was applied at $T_a+10^\circ$. Each "elementary" peak was well described by making the hypothesis of a single retardation time. Then, the mechanical retardation time $\tau$ is given by:

$$\tau(T) = \frac{\gamma(T)}{\gamma(T)}$$

We shall report here data obtained on polypropylene with antioxidant. The variations of the retardation times versus the reciprocal temperature for the various elementary peaks isolated between $-30^\circ$ and $+40^\circ$ have been plotted on Figure 4. The small arrows indicate the temperature of the TSC maximum ($T_m$).

Figure 4: Arrhenius diagram of mechanical retardation times isolated by fractional loading programs in polypropylene with 1,000 ppm of Ionox.

The TSC peaks observed at -19°C, -1°C, +5°C, +9°C, and +41°C are characterized by retardation times following an Arrhenius equation:

$$\tau(T) = \tau_0 \exp \left( \frac{U}{kT} \right)$$

where \( \tau_0 \) is the preexponential factor,

\( k \) the Boltzmann constant,

and \( U \) the activation energy.

The values of \( \tau_0 \) and \( U \), deduced from the Arrhenius plot of Figure 4, are listed in Table 1.

<table>
<thead>
<tr>
<th>Tm(°C)</th>
<th>U (eV)</th>
<th>( \tau_0 ) (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-19</td>
<td>0.53</td>
<td>( 3.10^{-9} )</td>
</tr>
<tr>
<td>-1</td>
<td>0.88</td>
<td>( 3.10^{-15} )</td>
</tr>
<tr>
<td>+5</td>
<td>1.15</td>
<td>( 7.10^{-20} )</td>
</tr>
<tr>
<td>+9</td>
<td>1.57</td>
<td>( 4.10^{-27} )</td>
</tr>
<tr>
<td>+41</td>
<td>1.25</td>
<td>( 1.10^{-18} )</td>
</tr>
</tbody>
</table>

**Table 1**

The peaks observed between +15°C and +33°C can be characterized by retardation times following a Vogel equation:

$$\tau(T) = \tau'_0 \exp \left( a(T-T_m) \right)$$

where \( \tau'_0 \) is the preexponential factor,

\( a \) the thermal expansion coefficient of the free volume,

and \( T_m \) the critical temperature at which the mechanical retardation time would become infinite.

The Vogel plot of Figure 5 shows that it exists such a critical temperature, linearizing the variation of \( \ln \tau \) versus \( (T-T_m)^{-1} \). The values of \( \tau'_0, a, \) and \( T_m \) are listed in Table 2.

<table>
<thead>
<tr>
<th>Tm(°C)</th>
<th>( a(°)^{-1} )</th>
<th>( T_m(°C) )</th>
<th>( \tau'_0 ) (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+15</td>
<td>( 2.1x10^{-3} )</td>
<td>-38</td>
<td>( 6.0x10^{-3} )</td>
</tr>
<tr>
<td>+16</td>
<td>( 4.8x10^{-3} )</td>
<td>-20</td>
<td>0.21</td>
</tr>
<tr>
<td>+25</td>
<td>( 1.3x10^{-2} )</td>
<td>0</td>
<td>3.7</td>
</tr>
<tr>
<td>+31</td>
<td>( 4.6x10^{-3} )</td>
<td>-10</td>
<td>0.43</td>
</tr>
<tr>
<td>+33</td>
<td>( 1.0x10^{-2} )</td>
<td>0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

**Table 2**
3. DISCUSSION - The elementary processes isolated between $-19^\circ C$ and $+9^\circ C$ take the same value $\tau_c = 2.8$ sec at the compensation temperature $-T_c = 23^\circ C$. Thermostimulated Currents studies of polypropylene (5) have shown that an analogous compensation law was followed by the dielectric relaxation times constituting the low temperature component of the glass transition. Such a behavior is not characteristic of polypropylene since it has been observed in other polymers (6). So, the processes corresponding to the retardation times obeying the compensation law may be due to microbrownian motions of amorphous chains free from restraints from crystallites.

The mechanical processes obeying a Vogel equation have probably the same origin than the dielectric processes having an analogous temperature dependence (5). Such a transition being also observed in completely amorphous polymers, it may arise from the fluidification of the amorphous chains.
