RELAXATION SPECTRA IN POLYMERS

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Methods of determining the continuous and discrete relaxation spectra are analyzed with the object of choosing a characteristic describing the actual relaxation processes. It is shown that the discrete spectrum is a physically sounder characteristic and makes it possible to distinguish the most probable elementary relaxation processes. Problems of predicting the relaxation processes in real polymers can be simplified by using the discrete relaxation spectrum.

Polymeric materials are characterized by the presence of relaxation processes with a broad range of relaxation times. Consequently, the mechanical behavior of real polymeric materials cannot be described by a mathematical model containing only one relaxation time [1]. Theoretically, the stress relaxation process is determined with any desired degree of accuracy by means of the rheological relation following from the Boltzmann superposition principle and containing the continuous relaxation spectrum:

$$\sigma(t) = \varepsilon_0 \frac{E(t)}{\varepsilon_0} = \frac{E(t)}{\varepsilon_0} \int_{-\infty}^{\infty} E(\tau) \exp \left( \frac{-t}{\tau} \right) d\tau,$$

where \( \sigma(t) \) is the relaxing stress; \( \varepsilon_0 \) is the given strain; \( E(\tau) \) is a continuous nonnegative function called the relaxation spectrum. In practice, for polymers on a broad time interval the relaxation spectrum is not monotone; certain fluctuations, which make it possible to distinguish the most probable relaxation processes, are observed. Thus, the discrete relaxation spectrum is sometimes used to characterize the relaxation processes [2, 3]. In this case the relaxation spectrum is represented by a sum of delta functions [4]

$$E(\tau) = \sum_{i=1}^{n} E_i \delta(\tau - \tau_i).$$

Hence the total relaxation process is expressed as a sum of exponentials:

$$\sigma(t) = \varepsilon_0 \frac{E(t)}{\varepsilon_0} = \sum_{i=1}^{n} E_i \exp \left( -\frac{t}{\tau_i} \right),$$

where \( E_i \) is a coefficient indicating the contribution of the \( i \)-th relaxation process; \( \tau_i \) is the relaxation time of the \( i \)-th elementary process.

In particular, for black-filled rubbers the discrete spectra have been used [2, 3] to distinguish three principal groups of elementary relaxation processes — physical relaxation of the polymer chains, relaxation in the black-rubber component, and chemorelaxation of the polymer chains or vulcanization network. An investigation of the slow stage of the polyethylene creep process has also revealed [5] the presence of three regions of partial compliances characterized by a different distribution of relaxation times.

We have now investigated the relaxation processes in a filled rubber with the aid of the discrete and continuous relaxation spectra and have also made an analysis of these methods.


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We experimentally determined the long-term stress relaxation in a uniaxially compressed specimen.

The cylindrical specimens measured 8 × 10 mm and were composed of vulcanizate based on SKN-40 butadiene-nitrile rubber filled with 100 parts by weight DG-100 carbon black and vulcanized with sulfur and diphenylguanidine. The stress relaxation (Fig. 1) was measured in the relaxation apparatus described in [6] at a temperature of 50 ± 1°C and a static compressive strain of 20%.

1. Description of the Relaxation Processes: Discrete Spectrum

The graphoanalytic method of Tobolsky-Murakami [7] and Bartenev-Bryukhanov [8] has recently been widely used for calculating the discrete spectrum from the experimental data. This method is based on the assumption that the real relaxation process consists of individual elementary relaxation processes, i.e., at t/τ >> 1 the dependence of ln E(t) on t for t > τ_n becomes a straight line; the greatest relaxation time τ_n is determined from the slope of this segment; the intercept made by extrapolation to the ordinate axis is equal to ln E_n. Then the dependence of ln[E(t)−E_n exp (−t/τ_n)] on time t is plotted and the time τ_{n-1} is similarly obtained; followed by the other relaxation times τ_i and coefficients E_i. In [2, 3] it was shown that this method is applicable if the experiment lasts long enough for the physical relaxation processes to be completed and a linear segment is observed on the chemical relaxation curve.

The parameters of the discrete spectrum are presented in Table 1, from which it is clear that the total stress relaxation process for the rubber investigated consists of five elementary processes and can be described in accordance with Eq. (3) by a sum of five exponentials.

TABLE 1. Parameters of the Discrete Relaxation Spectrum for a Filled Rubber

<table>
<thead>
<tr>
<th>Relaxation time τ_i of the elementary process, min</th>
<th>E_i kgf/cm^2</th>
</tr>
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<tbody>
<tr>
<td>4,4</td>
<td>11,2</td>
</tr>
<tr>
<td>21,6</td>
<td>7,9</td>
</tr>
<tr>
<td>1,3 × 10^3</td>
<td>3,8</td>
</tr>
<tr>
<td>1,3 × 10^3</td>
<td>24</td>
</tr>
<tr>
<td>1,74 × 10^4</td>
<td>17,6</td>
</tr>
</tbody>
</table>

Fig. 1. Long-term stress relaxation curve for a filled rubber at T = 50°C; O) experimental values of σ(t); ●) values of σ(t) calculated from Eq. (3).

Fig. 2. Discrete (1-5) and continuous (6, 7) relaxation spectra determined from the experimental data of Fig. 1: 1-5) E'(τ) from Eq. (2); 6) H_2(τ) from relation (4); 7) H_2(τ) from Eq. (5).