Manifestation of molecular mobility of polymers of different classes over a wide temperature range

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Translation submitted by P. Curtis

One of the most important problems tackled by modern polymer science is establishing the relationship of the macroscopic physical properties of polymers in bulk with their structure and the nature of thermal flow of the corresponding kinetic units. Understanding the molecular mechanism of manifestation of particular macroscopic properties of polymers means the possibility of influencing them in the necessary direction, i.e. learning to create polymeric materials with specified properties.

Most information for solving the problem formulated can be obtained by a complex study of the molecular relaxation processes in polymers by different physical methods of relaxation spectrometry.

The mechanical losses at $T > T_0$, just like the modulus, depend greatly on the molecular weight. The magnitude of the minimum of mechanical losses at $T > T_0$ decreases with increase in molecular weight. The minimum of mechanical losses is observed close to the centre of the high elasticity plateau, where there is an inflection on the temperature dependence of the modulus. It was established that the mechanical losses are a function of the number-average and weight-average molecular weight. It was also established that the breadth of the minimum of losses increases with increase in polydispersity, i.e. with increase in the ratio of the weight-average and number-average molecular weight. The values of moduli $G'$ and $G''$ in the high elasticity (rubbery) region do not depend on the molecular weight since the molecular weight between entanglements is constant for the given polymer (ref. 1). However, with increase in molecular weight, the plateau covers a wider range of frequencies. When $T < T_g$, the molecular weight has only a very slight effect on the dynamic properties of the polymers.

The most common types of polymer are those possessing a three-dimensional network. The most important characteristic of such polymers is their degree of crosslinking: $\nu = P/M_{cr} = N_{net}/N_A$ (1)

where $M_{cr}$ is the molecular weight of the chain section between two neighbouring crosslinked points, $N_{net}$ is the number of chains of the network per unit volume, and $N_A$ is Avogadro’s number. The kinetic theory of high elasticity (ref. 2) makes it possible to establish the relationship between the equilibrium modulus $E_0$ and the degree of crosslinking:

$$E = 3pRT/M_{cr} = 3\nu RT$$ (2)

For non-ideal networks, instead of (2), use is occasionally made of the expression

$$E_0 = 3\Phi_0\nu RT$$

where $\Phi_0$ is the coefficient (shape factor) taking into account the non-ideality of the three-dimensional network.

It can be maintained (ref. 1) that, for all organic polymers, the equilibrium modulus measured in the region of the high elasticity plateau increases with increase in the crosslink density of the three-dimensional network. Such a dependence of the elastic modulus on the degree of crosslinking is encountered most frequently and is assumed to be normal (Fig. 1).

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Examples of densely crosslinked polymers are cured epoxy and phenol-formaldehyde resins. Investigations of certain crosslinked epoxy resins were carried out by the present authors. Bisphenol A resins ED-5, ED-6, and ED-L, which have an identical chemical structure but different contents of epoxy groups in the uncured state, and ethylchlorohydrin-based E-181 epoxy resin were studied. Epoxy resins cured by metaphenylenediamine had the initial characteristics given in Table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Content of epoxy groups, wt.%</th>
<th>Molecular weight</th>
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<tbody>
<tr>
<td>ED-5</td>
<td>20.79</td>
<td>410</td>
</tr>
<tr>
<td>ED-6</td>
<td>16.48</td>
<td>520</td>
</tr>
<tr>
<td>ED-L</td>
<td>8.76</td>
<td>980</td>
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The results of measuring Young’s dynamic modulus and the tangent of the angle of mechanical losses \( \tan \delta \) of the three cured bisphenol A resins are given in Fig. 1. From an analysis of the experimental data obtained it can be seen that there are at least two regions where relaxation processes are most intense. In the first low-temperature region from \(-150^\circ\)C to \(+50^\circ\)C, several relaxation processes are observed. This region is characterised by a marked fall in dynamic modulus \( E' \) with increase in temperature. The second region of relaxation (50–170°C) corresponds to transition from the glassy to the high-elastic (rubbery) state. In this temperature range there is a sharp decrease in \( E' \) with decrease in temperature. The mechanical losses in this region are very high (ref. 1). Table 2 gives the main characteristics of the polymers investigated and the temperatures of their transitions.

From Table 2 it can be seen that, for polymers with an identical chemical structure, the glass transition temperature increases with increase in the concentration of epoxy groups in uncured resin from 66°C (ED-L) to 149°C (ED-5).

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
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</tr>
<tr>
<td>ED-5</td>
</tr>
<tr>
<td>ED-6</td>
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<tr>
<td>ED-L</td>
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Such increase in \( T_g \) is undoubtedly due to increase in the density of the three-dimensional network. Common to all the polymers studied is the \( \beta \)-transition (\(-50^\circ\)C). The part of the molecule common to all epoxy resins is responsible for the relaxation process corresponding to this transition. It is possible that this relaxation process with an activation energy of about 10 kcal/mol is due to the mobility of the chain element:

\[
\text{O} \quad / \quad -\text{CH}_2\text{-C-CH}_2\text{-O} \quad \backslash
\text{H}
\]

For all the polymers investigated, there is a temperature transition in the range from \(-80\) to \(-90^\circ\)C (\( \delta \)-transition).

It is natural to assume that the \( \delta \)-transition is due to unfreezing of the mobility of phenyl groups of bisphenol A in the main chain of the polymer.

The most interesting result obtained in the investigation of the epoxy resins is the abnormal dependence of the dynamic elastic modulus on the density of the three-dimensional network in epoxy polymers in the glassy state.

From Fig. 2 it can be seen that, in the glassy state, the highest dynamic modulus \( E' \) is possessed by ED-L resin, for which the degree of crosslinking was minimum. The lowest value of \( E' \) in the glassy state is possessed by resin ED-5, which has the densest three-dimensional network. Above the glass transition temperature there is the normal dependence of \( E' \) on the degree of crosslinking: \( E' \) increases with increase in the number of crosslinks. The abnormal dependence of \( E' \) on the degree of crosslinking is due to the fact that, in the glassy state, the crosslinks prevent any decrease in the distance between the kinetic elements of neighbouring chains with decrease in temperature, thereby lowering the effectiveness of intermolecular interaction. As a result of this, in the glassy state \( E' \) may decrease with increase in the degree of crosslinking. This explanation of the abnormal dependence of \( E' \) on \( \nu \) is confirmed by the results of measuring the mechanical losses of \( \tan \delta \) as a function of temperature. As can be seen from Fig. 2, the greatest distance of the energy of acoustic vibrations in the glassy state is observed in ED-5 resin which has the
greatest degree of crosslinking. The smallest losses in the
glassy state are possessed by ED-L, which is characterised by
the lowest density of the three-dimensional network. Thus, in
the glassy state of the epoxy polymers examined the mechanical
losses increase with increase in the density of the three-
dimensional network formed by chemical crosslinks. In addition,
it is well known that the mechanical losses increase with
increase in molecular mobility. Consequently, the results of
studying the relationship \( \tan \delta = f(T) \) indicate that, in the glassy
state, the polymers with a greater degree of crosslinking have
greater molecular mobility. Meanwhile, it is well known that
intensification of intermolecular interaction leads to damping
of molecular motion and therefore to reduction in the tangent
of the angle of mechanical losses. Consequently, a study of the
temperature dependence of mechanical losses leads to the
conclusion that, below the glass transition temperature, there is a gradual increase in chain
orientation in the amorphous regions (ref. 3). Such a
dependence of the glass transition temperature on the degree
of crystallinity is encountered most frequently and is considered
normal.

The changes in the peaks of mechanical losses on specimens
of the same polymer with different degrees of crystallinity are
normally used to explain the mechanism of relaxation
processes. Normally, the peak of the tangent of the angle of
mechanical losses that corresponds to unfreezing of the
segmental motion of the amorphous regions decreases with
increase in the degree of crystallinity, and in very strongly
crystallised specimens it degenerates entirely (Fig. 3).

The elastic modulus of crystallising polymers increases with
increase in the degree of crystallinity (Fig. 4) owing to the
influence of crystals as macrocrosslinked points or particles of

\[
\chi = \frac{(\rho - \rho_2)}{(\rho_1 - \rho_2)}
\]

where \( \rho \) is the density of the polymer, \( \rho_1 \) is the density of the
crystallites, and \( \rho_2 \) is the density of the amorphous phase of
the polymer. Formula (3) has an approximate nature.

Crystallinity affects the glass transition temperature of the
amorphous regions. Normally, the glass transition temperature
of a weakly crystalline polymer (\( \chi = 0.1 \)) practically coincides
with the glass transition temperature of an entirely amorphous
polymer. With increase in crystallinity, the glass transition
temperature of the amorphous regions is displaced towards
higher temperatures. This displacement is attributed in Adam-
Gibbs theory (ref. 2) to the fact that, with increase in the
degree of crystallinity, there is a gradual increase in chain
orientation in the amorphous regions (ref. 3). Such a
dependence of the glass transition temperature on the degree
of crystallinity is encountered most frequently and is considered
normal.

Fig. 2 Temperature dependences of dynamic elastic shear modulus
and damping factor of polypropylene with different degree of crystallinity,
increasing from 0 to 0.65 with increase in density of polymer:
1 - 0.870 mg/ m\(^3\); 2 - 0.875 mg/ m\(^3\); 3 - 0.894 mg/ m\(^3\); 4 - 0.905
mg/ m\(^3\)

Fig. 3 Temperature dependences of dynamic characteristics G and tan
\( \delta \) of partially crystalline polytetrafluoroethylene of different degree of
crystallinity: 1, 1' - degree of crystallinity 92%; 2, 2' - degree of
crystallinity 48%
rigid filler. This is manifested particularly clearly in the temperature range \( T_g < T < T_m \). In addition to the peak of mechanical losses that is related to the glass transition temperature of the amorphous phase, in crystalline polymers one or several peaks can also appear that are governed by processes occurring in the crystalline phase. Here, the mechanical losses are governed mainly by molecular motion in the amorphous phase of the polymer.

Change in the degree of crystallinity is manifested clearly in the nature of the temperature dependences of the dynamic elastic modulus and the factor of mechanical losses, just as for polytetrafluoroethylene. From Fig. 4 it can be seen that a reduction in the degree of crystallinity leads to a consistent reduction in \( G \) and to the separate appearance of maxima of mechanical losses, which indicates less difficult unfreezing of the motion of kinetic units of different size. Occasionally, an additional peak related to molecular motion in the crystalline phase appears at very low temperatures (refs. 1 and 4).

Plasticisers are introduced mainly to lower the glass transition temperature of rigid glassy polymers, to increase their plasticity and elasticity, and also to facilitate the processing of the polymers. Plasticisers not only displace the inflection on the temperature dependence of the elastic modulus and the \( \alpha \)-peak of mechanical losses towards lower temperatures but also expand the regions of maximum losses during glass transition (Figs. 5 and 6).

The poorer the plasticiser as a solvent, the greater is the degree to which this peak expands. Thus, in PVC, the poor 'solvent' dibutyl phthalate gives a broader and lower peak compared with that observed when the 'good' solvent diethyl phthalate is used (ref. 1). The peak of mechanical losses in the PVC–diethylhexyl succinate system reaches its maximum width with a plasticiser content of about 40%, and with further increase in the plasticiser content it narrows slightly (Fig. 6).

As shown in Fig. 5, for this system the plasticiser broadens the high elasticity plateau and lowers the elastic modulus. The reduction in the elastic modulus is due to dilution of the polymer and to increase in the length of the segment of chains between physical entanglements, while the increase in the breadth of the plateau is due to the fact that the plasticiser lowers the glass transition temperature more than it lowers the melting point of the PVC crystals. The dynamic properties of copolymers are similar to those described above for plasticised polymers, with the exception of the high elasticity plateau of copolymers of a crystallising monomer with a non-crystallising monomer, which decreases with increase in the content of the latter rather than increasing, as in the case of an increased plasticiser content, and the formation of copolymers broadens the peak of mechanical losses.

This is due to the chemical heterogeneity of the macromolecules of the copolymers. The introduction of plasticisers into polymers often causes complex effects associated with secondary relaxation transitions (ref. 1). Here, the position of the secondary transitions may be displaced towards higher or lower temperatures. The peak of mechanical
losses may disappear entirely, or a new peak may appear. In some polymers such as polycarbonate and polyvinyl chloride, a marked secondary transition is observed in the glassy state. When certain plasticisers are introduced into such polymers, along with a reduction in the glass transition temperature, there is a reduction in intensity or the complete disappearance of the secondary transition. When the secondary transition disappears, the elastic modulus increases in the temperature range between the glass transition temperature and the secondary glass transition temperature, and failure of the polymer occurs not by a plastic but by a brittle mechanism (ref. 1).

The dynamic mechanical properties of polymers can be changed considerably by heat treatment of the specimens, the effect of heat treatment being considerably smaller for amorphous glassy polymers than for crystallising polymers. The quenching of amorphous polymers, in contrast to annealing, normally leads to an increase in mechanical losses. Quenching lowers the temperature at which the maximum of mechanical losses is observed in the region of glass transition and broadens the region of the low-temperature peak of mechanical losses (Figs. 7 and 8). Annealing at a temperature close to the glass transition temperature after abrupt cooling of the melt lowers the mechanical losses and increases the elastic modulus. Parts produced by injection moulding have a complex thermal prehistory which is superimposed on different orientation effects. It was established that additional maxima of losses, disappearing during annealing, appear in such parts manufactured from amorphous glassy polymers.

The dynamic mechanical properties of crystalline polymers are particularly sensitive to the thermal prehistory of specimens. Slow cooling or annealing increases the elastic modulus and the temperature of $\alpha$-transition in the amorphous phase by comparison with quenching. Figs. 9 and 10 show the typical effect for crystalline polymers. In this case it is obvious that $\alpha$-transition has two components, the high-temperature component being displaced to a greater degree than the low-temperature component when the heat treatment conditions are changed.
Some polymers, such as PETP and polyurethanes, remain entirely amorphous during quenching, but during annealing or heat ageing above the glass transition temperature they are partially crystallised. Their crystallisation is accompanied with a sharp increase in the elastic modulus when \( T > T_g \) and with a change in the shape of the temperature dependence of the mechanical losses. In some polymers, crystallisation causes no change in the glass transition temperature, while in others it leads to an increase in the glass transition temperature. In polypropylene, quenching raises the glass transition temperature more than annealing does.

Oriented polymers are anisotropic materials and are characterised by three elastic moduli: Young's longitudinal modulus \( E_z \), Young's transverse modulus \( E_t \), and the longitudinal–transverse elastic modulus \( G_{zt} \).

Oriented polymers are produced in the following way: by drawing of the polymer at a temperature above the glass transition temperature with subsequent cooling, by cold drawing of crystalline polymers with an elastic amorphous phase, and by rolling of plastic polymers. Drawing in one direction produces uniaxially oriented polymers, while drawing in two directions produces biaxially oriented polymers. Quantitatively, the degree of orientation is fairly difficult to assess. The birefringence can be used as the simplest qualitative measure of orientation. Other optical methods can also be used to assess the degree of orientation. Young's dynamic longitudinal modulus is normally greater than the Young's modulus of non-oriented polymers. In highly oriented fibres produced by cold drawing, the longitudinal elastic modulus can exceed the elastic modulus of a non-oriented polymer by tens of factors. The degree of orientation is roughly equal to \( 1 - E_n / E_z \), where \( E_n \) is the elastic modulus of the non-oriented polymer. Change in the mechanical prehistory affects the relaxation effects in the polymers, again through change in the degree of crystallinity of the polymers. Drawing of polyethylene specimens at various temperatures in a direction longitudinal to their longitudinal axis leads to an increase in molecular ordering, which determines a reduction in the maxima (Fig. 10). Drawing of specimens in the perpendicular direction leads to a reduction in their degree of crystallinity (amorphisation), facilitating molecular mobility and increasing the maxima.

REFERENCES


(No date given)