SOME PECULIARITIES OF THE BEHAVIOUR OF HIGHLY CROSSLINKED EPOXY-AMINE NETWORKS IN THE GLASSY STATE

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Abstract — Some peculiarities of the behaviour of glassy densely crosslinked epoxy-amine networks (yield behaviour, glass transition, Young's modulus, packing density) as a function of curing reaction conditions have been studied. Networks prepared by curing diglycidyl ethers of resorcinol or bisphenol-A with aromatic amines have been considered. Experimental data, which are impossible to explain within the framework of the conventional free-volume concept, have been found. The interpretation of transport properties employs a model in which the glassy state possesses holes of different sizes. Different conditions of polymer curing lead to redistribution of excess free volume over holes of different sizes. The processes of merging and dissociation of holes have been considered. It has been suggested that the properties of a polymeric glass essentially depend not only on a free-volume fraction, but also on the ratio between holes of "large" and "small" sizes as well as on the type of size distribution function of holes.

INTRODUCTION

Epoxy networks formation from rather simple diglycidyl ethers of some bisphenols and aromatic diamines has been investigated in recent years at the Institute of Chemical Physics, the USSR Academy of Sciences (1, 2, 3, 4).

$$\text{H}_2\text{N}-\text{R}_1-\text{NH}_2+\text{H}_2\text{C}-\text{CH}_2-\text{O}-\text{R}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{NH}_2+\text{H}_2\text{O} \rightarrow \text{R}_1-\text{NH}-\text{CH}_2-\text{CH}_2-\text{N}-\text{R}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{R}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}-\text{R}_1$$

$$\text{R}_1 = \text{R} \quad \text{and} \quad \text{R}_2 = \text{SO}_2$$

These systems, based on diglycidyl ethers of resorcinol (DGER) and bisphenol-A (DGEBA), have proved to be rather suitable from several points of view. Thus, from the chemical point of view, at moderate temperatures ($T = 80 - 120°C$) and especially with methaphenyldiamine (mPhDA) as a curing agent, the curing reaction proceeds practically without side-reactions, such as polymerization of epoxy groups, reactions of secondary hydroxyl groups with epoxy ones and with each other, etc. (2).

The molecular structure of the formed networks imply that the ratio of the rate constants of the first ($k_1$) and the second ($k_2$) addition reactions

$$\text{HN-Ph} + \text{H}_2\text{N-Ph} \xrightarrow{k_1} \text{HN-Ph;} \quad \text{HN-Ph} + \text{HN-Ph} \xrightarrow{k_2} \text{Ph} \quad \text{under given conditions is close to one:} \quad k_1/k_2 = 0.8 - 1.0.$$

This means that network formation reaction in this case does not proceed by formation of long linear macromolecules which then have to crosslink each other.
Statistical-topological models of the network structures describe nicely both the kinetics of their formation and equilibrium elasticity of rubbery state (4). These facts are rather important since they clearly indicate the absence of so called spatial heterogeneity of the chemical cross-links in the volume of the network. If heterogeneity exists, it may lead to weak bonding of densely crosslinked regions of networks (clusters), which, in turn, according to (5), may result in low mechanical properties of network polymers.

It has been shown (1—4) that the kinetics of epoxy—amine networks formation is nicely described by normal statistics taking into account diffusion limitations of the curing reaction. The subject of our interest in the present paper is the structure and properties of such epoxy—amine networks in the glassy state at 40 – 110°C below $T_g$.

We dwell at length on the above—mentioned results since they provide a good characteristic of the networks considered both from chemical and topological viewpoints.

At room temperature, network epoxy—amine polymers resulted from the curing reaction are rather dense homogeneous glasses with high mechanical characteristics (strength, rigidity). Ultimate glass transition temperatures $T_g$ for stoichiometric networks range from 135 to 160°C.

In Table 1 are shown molecular packing characteristics of several network polymers estimated at 22°C. Mean packing density $K$ (literature data) for a large number (about 100) of linear glassy (6,7) and some crystalline (7,8) polymers is also presented for comparison:

**TABLE 1. Densities $d$ and molecular packing coefficients $K$ for some polymers estimated at 22°C**

<table>
<thead>
<tr>
<th>Networks</th>
<th>$d$ (g/cm³)</th>
<th>$K$</th>
<th>Linear polymers</th>
<th>$d$ (g/cm³)</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGER—mPhDA (1:1)</td>
<td>1.293</td>
<td>0.717*</td>
<td>DGER—aniline</td>
<td>1.246</td>
<td>0.712</td>
</tr>
<tr>
<td>DGER—mPhDA (1:1.4)</td>
<td>1.299</td>
<td>0.727</td>
<td>Other linear glassy polymers</td>
<td>1.298</td>
<td>0.720</td>
</tr>
<tr>
<td>DGER—mPhDA (1.4:1)</td>
<td>1.298</td>
<td>0.705</td>
<td>Crystalline polymers (7,8):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGER—DAP (1:1)</td>
<td>1.295</td>
<td>0.705</td>
<td>Polyethylene</td>
<td>1.280</td>
<td>0.708</td>
</tr>
<tr>
<td>DGER—DAPhS (1:1)</td>
<td>1.340</td>
<td>0.711</td>
<td>Polypropylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGERA—mPhDA (1:1)</td>
<td>1.280</td>
<td>0.708</td>
<td>Polytetrafluoroethylene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*For stoichiometric networks are calculated for the curing reaction conversion $\alpha = 0.92$. ** $K = 0.681$ — mean value for linear polymers.

The values of $K$ in the Table 1 are comparable since they were estimated from the same van der Waals' radii for similar atoms in different polymers. From the Table 1 it is evident that epoxy networks are markedly better packed than glassy linear polymers, i.e. the high concentration of chemical cross-links does not create noticeable kinetic obstacles for good packing of an intermodular chain.

It is also of interest that fairly essential deviations of the network composition from the stoichiometric one do not affect the packing density. Undoubtedly, the dense packing of the networks is due to hydrogen bonding. This is clear from high packing density of a model linear polymer prepared by condensation of DGER with m-PhDA (see Table 1). However, chemical cross—links also lead to better packing of the networks.

As it is well-known (2,3), in the formation of dense networks curing reaction in stoichiometric mixtures cannot proceed until complete conversion of functional groups. It is connected with random character of the curing process. At rather large $\alpha$ unreacted monofunctional groups of the forming network cannot interact being spatially separated.

In Fig. 1 are shown ultimate curing conversions $\alpha_u$, which may be reached in DGER—mPhDA (1:1) system at different temperatures of isothermal curing.
At $T > 110^\circ C$ the reaction reaches its topological limit $\alpha = 0.92 \pm 0.1$ (according to our data). Increasing the $T_c$ up to 170°C does not increase $\alpha$. During isothermal curing at $T_c < 110^\circ C$ the reaction reaches certain limits determined by diffusion which depend on $T_0$. The reaction essentially stops when the reactant system wholly solidifies at the given $T_c$. In the vitrified polymer unreacted functional groups do not possess enough mobility to interact with reactive neighbours.

The polymers under consideration have rather high values of static mechanical properties. The results, testifying to this, are given in Fig. 2.

**Fig. 1.** Ultimate conversions $\alpha_u$ reached at different curing temperatures $T_c$ (isothermal curing) by the system DGER-mPhDA (1:1). Curing time $t \to \infty$.

In Fig. 2a are presented typical stress-strain diagrams (stretching) of glassy(curves 1,2) and rubber-like network polymers (curve 3) based on DGER - mPhDA (1:1). These diagrams exhibit usually yield behaviour. We have managed to prove that stress-strain behaviour of samples showing a quasi-brittle character of fracture, often observed for densely crosslinked glassy networks, is due to their macroscopic defects. As it is seen from curves 1,2 (Fig. 2a), the high concentration of chemical cross-links in a glassy
polymer does not hinder it from yielding. These defects may be removed from the sample by means of suitable thermal treatment (discussed later). In this case the apparent quasi-brittle fracture of network glasses disappears and the yield point may be clearly seen in the stress-strain diagrams. That is why, it was natural to choose the yield point as a value characterizing the static mechanical behaviour of the investigated glasses.

Values of $G_2(22°C)$ for epoxy-amine networks of different compositions are given in Fig. 2b (curves 1, 2). In all cases the samples were cured up to $\alpha_u$. From Fig. 2b it is seen that $G_2$ of the network glasses weakly depends on the amount of unreacted functional groups of both amine and epoxy types over a rather wide range of their concentrations, or, in other words, $G_2$ of the network glasses is practically independent of the curing conversion $\alpha_u > 0.83$. It is essential that in the rubbery state* (curve 3, Fig. 2b) the ultimate strength of the networks is proportional to the concentration of chemical cross-links, being maximum for stoichiometric ratio. This fact shows that in the glassy state network mechanical behaviour is determined not by chemical factors (for example, curing conversion or network composition), but by the physical structure of the glass, and most of all by its packing. If we remember that the perfection of the molecular packing of the investigated glasses is not increased in non-stoichiometric polymers, then, the independence of the yield point $G_2(22°C)$ of the concentration of unreacted functional groups becomes clear.

It is obvious, that the studied glasses are well organized, the absolute level of $G_2$ being fairly high, though it can be raised by another 15% more by post-cure thermal treatment. High values of the Young's modulus, to be discussed later, are also typical for glassy epoxy-amine networks. Investigating the relationship between the glassy state structure and macroscopic properties of the studied polymers, we have found some phenomena, which, in our opinion, cannot be even qualitatively rationalized within the conventional free-volume concept for amorphous polymers.

Here, I would like to explain what is implied by "conventional free-volume concept". If we speak about the kinetic properties of glassy substances, such as, the position and the character of glass transition, yield behaviour, diffusion coefficient etc., or, what is just the same, if we consider transport processes (e.g. transfer of mass, heat or electricity), we see that the increase of free-volume fraction in the glass always leads to increasing molecular mobility, making the transport processes easier. This means that any increase of both $T_g$ and $G_2$ is connected with a decrease of mobility or free volume (packing improvement) and vice versa. Such a viewpoint is, of course an oversimplification. However, it qualitatively presents the real relationship between some macroscopic properties and the packing structure of the glasses.

As I have already mentioned, our results do not fall within the framework of these concepts. So, let us proceed to some of the "unusual" results.

THE DESCRIPTION OF SOME "UNUSUAL" EXPERIMENTAL RESULTS

Curing at lowered temperatures. As we have already stated, during isothermal curing at $T_0 < 100 - 110°C$ the reaction stops at $\alpha_u < \alpha_g$ due to polymer vitrification. It is natural to suggest that at heating such a polymer it will soften at $T_g \approx T_C$ if measurements of $T_g$ are taken at the frequencies corresponding to the effective frequency of the chemical reaction ($\nu_{eff} \approx 10^4 s^{-1}$). This is confirmed experimentally.

In Fig. 3 are shown the results of heat capacity measurements for the networks obtained by isothermal curing at $T_0 = 80, 100, 130°C$ respectively. $T_g$ for each of them was rather close to the corresponding $T_C$. The somewhat higher values of $T_g$ in comparison with $T_C$ are due to the effective frequency of the scanning calorimetry ($\nu_{eff} \approx 10^3 s^{-1}$), which is a little bit higher than the effective frequency of the curing reaction. Polymers resulting from isothermal curing at each $T_0$ are not only of different composition (different $\alpha_u$), but also have a different structure of the glassy state. Both different $T_g$ and different values of endothermic peaks of $C_p$ for the networks of each composition was measured separately.

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* $T_g$ for the networks of each composition was measured separately.
Behavour of glassy crosslinked epoxy-amine networks

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$T$, °C

100 110 120 130 140 150 160

3.0

2.8

2.6

2.4

2.2

2.0

1.8

1.6

1.4

DGER-mPhDA (1:1)

Heat capacity $C_p$, J.K$^{-1}$.g$^{-1}$

Fig. 3. Heat capacity for networks DGER-mPhDA (1:1) prepared under different $T_c$. $T_c$: 1 - 80; 2 - 100; 3 - 130°C. $T_g$ ($T_g^2$; 3) - the glass transition temperature of each sample. $C_p$ - the heat capacity of networks at $T > 110$°C.

It is well-known that the larger the area under an endothermic peak of $C_p$, the larger is the energy absorbed by the glass for the formation of new holes during the glass-rubber transition. From Fig. 3 it is clear that the lower $T_c$, the higher is the endo-peak of $C_p$, i.e. the structure of glass obtained at low $T_c$ is more perfect than that of the glass obtained at high temperatures (enthalpy of such glass is lower). To a certain extent this fact is in itself contradictory. On the one hand, at low $T_c$ we obtain a glass with more perfect structure, but, on the other hand, this glass softens at lower temperature.

We have managed to establish that the glass structure is being formed when the reacting system vitrifies in the course of curing (so called liquid-glass transition). The lower the rate of vitrification, the better is the structure of the glass (lower enthalpy) forming in the process.

Let us examine another important kinetic property of glasses, namely, the yield point.

In Fig. 4 are shown the values of $\xi$ (22°C, stretching, $\xi$ = 1 mm/min) for polymers with different $T_g$ (that is, for polymers, obtained at different $T_c$). In spite of the fact that the networks cured at a lower $T_c$ have smaller $T_g$, their mechanical properties ($\xi$) are essentially higher.

In Fig. 5 we assemble some other results. In this Figure is shown the dependence of the Young's modulus on the testing temperature for a number of network polymers. The curves correspond to polymers obtained at $T_c$ equal to: 43°C (1); 90°C (2) and 110°C (3). From Fig. 5 it is clear that the polymers with higher modulus in the glassy state have the lowest $T_g$. These results also require special explanation.

Young's modulus. The other "unusual" experimental fact is connected with the polymer glass rigidity, which may be characterized either by the effective Young's modulus $E$ or by shear modulus $G$. It is well-known that the Young's modulus of glasses essentially depends on the excess of free volume in them. Recent theoretical calculations (9,10) (computer simulation) have revealed that the Young's moduli of densely packed amorphous and crystalline solids, composed of similar particles, satisfy as $E_{amorphous} = 0.57 E_{cr}$ (crystalline). This ratio nicely agrees with experimental results available in literature. The estimation of the magnitude of the Young's modulus for molecular crystals from van der Waals' interactions of molecules gives $E_{cr} \approx 5.5-6.0$ GN/m² (10,11). This means that real moduli for polymer glasses have to be about 3.0 GN/m². In Table 2 are assembled the values of Young's moduli for some glassy polymers at room temperature.
Fig. 4. Changes of yield point $\sigma_y$ (22°C) (1), Young's moduli $E$ (22°C) (2) and density $d$ (22°C) (3) for glassy networks DGER-mPhDA (1:1), cured under different $T_c$ and having different $T$. $T_c$ were determined from Fig. 3.

Fig. 5. Changes of Young's moduli of networks DGER-mPhDA (1:1) with temperature. The samples (1, 2, 3) were cured at different temperatures of isothermal curing $T_c$ up to corresponding $T_e$. $T_c$ for the samples: 1 — 43°C; 2 — 90°C; 3 — 110°C.
TABLE 2. Effective Young's moduli for some polymers (stretching)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E, \text{GN/m}^2$</th>
<th>Polymer</th>
<th>$E, \text{GN/m}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (atactic)</td>
<td>2.8 - 3.32</td>
<td>Delrin</td>
<td>2.65</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>2.95 - 3.21</td>
<td>&quot;Capton&quot; (aromatic polyimide)</td>
<td>3.1</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1.89 - 2.09</td>
<td>Polymethyl-terephthalate</td>
<td>3.9</td>
</tr>
<tr>
<td>Polysulfone (aromatic)</td>
<td>2.6</td>
<td>Network DGER−mPhDA (1:1)</td>
<td>3.3</td>
</tr>
<tr>
<td>Polycrystal of polyethylene (9)</td>
<td>5.05</td>
<td>Network DGER−-mPhDA (1:1)</td>
<td>5.5</td>
</tr>
<tr>
<td>Oxide</td>
<td>2.6 - 2.8</td>
<td>Polyethylene chain flexure</td>
<td>$2.6 \times 10^2$</td>
</tr>
</tbody>
</table>

Although the modulus depends on the temperature and frequency of measurement, in all the cases, given in Table 2, glass transition temperatures are rather high and the temperature dependence of $E$ (stretching) in this case may be neglected. As far as the frequency of measurements is concerned, all the values of $E$ correspond to deformational rates, at which the frequency (rate) dependence becomes insignificant. Two facts are of interest in Table 2.

1. All the values of $E$ are really close to 30 GN/m$^2$, which nicely agrees with theoretical estimates.

2. The moduli of all the polymers are very close to each other.

In Table 1 we quote also a modulus for a network based on DGER−mPhDA (1:1), $E (22°C) = 3.3 \times 10^2$ GN/m$^2$. First of all, this value shows that the rigidity of glassy networks is determined not by chemical bonds, but by van der Waals' interactions between chains, i.e. it is dependent on the packing density. Secondly, the network has an elevated modulus, as compared to linear polymer glasses, which is due to its higher dense packing. The independence of the moduli of linear polymers on their chemical structure can be easily explained within the framework of a packing concept. Thus, it is well-known that packing density for a large number of linear polymers is $K (22°C) = 0.68 \pm 0.01$. This fact is macroscopically reflected in the similar values of the glass moduli.

In Fig. 4 (curve 2) are shown the values of $E (22°C)$ for some glassy networks (DGER−mPhDA, 1:1) prepared at different $T_C$. From this Figure it is clear that $E (22°C)$ linearly grows with the decrease of $T_C$, and at $T_C = 43°C$ it reaches $E (22°C) = 55$ GN/m$^2$. This value is close to the theoretical one of molecular crystals. How can this be understood? Polymer remains amorphous with approximately the same quantity of excess free volume in it. It is absolutely obvious that this result cannot be explained within the framework of conventional concepts, it requires a new approach.

Relaxation of endothermic peak of heat capacity. It is well-known that the perfection of the structure of glasses, including polymer glasses, depends on the thermal prehistory, and in particular on the rate of cooling. The structure of a polymer glass may be improved, that is, its specific volume or enthalpy may be decreased by slow cooling of the melt or by prolonged isothermal annealing near $T_g$.

Figure 6. shows such results for linear (Fig. 6a) and network (Fig. 6b) polymer glass. During isothermal annealing of linear polymers the improvement of glass packing takes place, which is reflected in the growth of the endothermic peak of $C_p$ with annealing time. The growth of the endothermic peak of $C_p$ is also observed for networks. It is obvious that, from the point of view of the free volume concept, only densification process may proceed spontaneously.
Fig. 6. Change of the heat capacity $C_p$ (a) of polyvinylacetate (Ref. 17) and (b) network DGER-mPhDA (1:1), annealed at different time. Annealing temperature $T_a$ for PVA is equal to 21°C; for DGER-mPhDA: (1) the quenched sample; (2) $T_a = 120°C$, annealing time 90 h.; (3) the sample cooled from 110°C to room temperature for 9 hours.

Figure 7 demonstrates the data on $C_p$ relaxation for the network on the basis of DGER-mPhDA (1:1) prepared at $T_c = 90°C$. After curing the sample has been exposed to physical ageing at room temperature in an atmosphere of dry argon (curve 2) and air (curve 3).

Fig. 7. Relaxation of endo-peak of heat capacity for the network DGER-mPhDA (1:1) cured at $T_c = 90°C$. Time of storage at temperature 23°C: (1) 0 h.; (2) 350 h. (argon); (3) 350 h. (air); $C_p^r$ - the level of $C_p$ of the rubbery network cured at $T_c = 120°C$ up to $\alpha_h^r$. 

$C_p$, J K$^{-1}$ g$^{-1}$
From Fig. 7 it is seen that the endo-peak of $C_p$ decreases with ageing time. This does not agree with the densification processes which have to proceed under these conditions.

**Effect of post-cure thermal treatment on the yield behaviour of glassy networks:** In Fig. 8 are shown stress-strain (σ-ε) curves (σ is the actual stress) for the networks based on DGER-DAP (1:1) cured at 100°C and then heated up to 170°C. Starting at 170°C the samples were either slowly ($\approx 10^0$C/h) cooled (annealing) or quickly cooled to low temperature (0 - 10°C) (quenching).

**Figure 8.** Stress-strain curves (stretching) for the network DGER-DAP (1:1) at different temperatures. (a) the annealed samples. (b) the quenched samples; strain rate = 10$^{-2}$ min$^{-1}$.

Figure 8 shows that the sets of samples behave in a different way (different $\sigma_y$, $\epsilon_{break}$), the difference remaining up to rather high temperatures. Different curves, undoubtedly, reflect the different structures of the quenched and annealed samples. The annealed samples are characterized by a larger rigidity, elevated $\sigma_y$ and relatively small $\epsilon_{break}$. The quenched samples are essentially more plastic with far larger break elongations.

It is essential that this phenomenon is reversible. The 5–7-fold repetition of annealing-quenching operations leads to reversible $\sigma$-ε diagrams. It turned out that the observed yield of the studied network polymers was not connected with the breaking of chemical bonds, i.e. this was not a chemically controlled yield. Thus, repeated loadings of relaxed samples, preliminarily loaded up to elongations slightly larger than $\epsilon_y$, show the diagrams of the first loading (with the shift on the value $\sigma_y$) and a stable level of $\sigma_y$ values. If annealing causes the growth of a glassy polymer density, this always leads to the above-mentioned changes of the mechanical properties. Annealing-quenching thermal treatment always result in typical changes of stress-strain curves. However, such changes are not always accompanied by the changes of polymer density.

Two facts, in our opinion, are noteworthy here.

1. In a number of cases network polymers change their mechanical properties (stress-strain curves) without marked changes in macroscopic density; Even when the density of glassy polymers was practically constant, we found rather large changes in $\sigma_y$ level.

2. Lowering of isothermal curing temperature (for DGER-mPhDA 1:1) leads to a markedly larger increase of $\sigma_y$ (see Fig. 5) than the process of annealing. However, the density $\rho$ (22°C) of networks DGER-mPhDA, cured in the range of $T_c$ from 100 to 55°C, is practically constant for all $T_c$.

Both these facts suggest to us that the changes of $\sigma_y$ during the thermal treatment of these polymer glasses are not necessarily connected with the change of the total free volume in the polymer.

Thus, concluding this part of the paper, we would like to emphasize once
more that all the above-mentioned experimental results, obtained while investigating densely crosslinked epoxy-amine network glasses, are difficult to explain solely from the point of view of differences in free volume fractions.

INTERPRETATION OF THE GIVEN EXPERIMENTAL RESULTS WITHIN THE FRAMEWORK OF A HOLE MODEL OF POLYMER GLASSES

Since liquids, including polymer ones, keep in their structure a short-range order, typical for a corresponding crystalline body, it is logical to come to the following conclusion about the hole structure of glassy bodies. As a matter of fact, there is at present no other structural alternative for the description of such subjects.

Frenkel introduced the hole concept into solid state physics (12). This concept was further developed for polymers in the works of Eyring (13) and other authors (14).

The holes of an amorphous body concentrate the total excess free volume of a polymer glass, i.e., the volume which is excess in relation to a polymer crystal composed of macromolecules of the same chemical structure.*

Two classes of holes, configurational and fluctuational, should be distinguished in an amorphous polymer. The former are connected with the existence of configurational (stereochemical) defects in a regular structure of macromolecules. These defects arise at the moment of a monomer (oligomer) "erroneous" addition to the growing species. The experience indicates that the following types of addition: "head-to head", "tail-to-tail" heterotactic addition etc., lead to defects in a configurational sense.

The other class of holes - fluctuational holes, have a kinetic nature, being due to the "freezing-in" in the glass of a certain amount of relatively high-energy conformational sequences of macromolecular fragments.

In principle, the large fraction of fluctuational holes may be removed from an amorphous polymer by infinitely slow cooling. At the same time configurational holes cannot be removed from a polymer without breaking chemical bonds in macromolecules.

Proceeding from this classification of holes, the total volume of a polymer body, unoccupied by atoms may be presented as

\[ V_{am} = V_{cr} + N_{fl} V_{fl} + N_{cf} V_{cf} \]

where \( V_{cr} \) the unoccupied volume of a corresponding crystal; \( N_{fl}, N_{cf} \) the number of fluctuational and configurational holes in the body; \( V_{fl}, V_{cf} \) the average volumes of holes of both classes.

In relation to transport processes in the glassy state the holes have different properties. Thus, configurational holes at any dynamic transitions, occurring in a polymer, cannot separate from their parent chain and migrate in the space of the sample. Migrations of such holes occur only with the parent chain to which they are attached. At the same time fluctuational holes may migrate in the sample due to consequent conformational transformations in macromolecules and disappear at the free surface of the sample. In this sense and from the point of view of transport processes in polymer, fluctuational holes may be called dynamic, and configurational ones - static.

As it is known, the rate of transport processes depends on the moving rate of holes (frequency of jumps) in the sample. That is why, in the remainder we shall be mainly interested in fluctuational holes, although configurational holes can make certain contributions to kinetic properties of a glassy body. This phenomenon will be considered later.

Brownian motion of fluctuational "holes" in the sample proceeds by the mechanism of "exchanging places" (by analogy with the movement of vacancies in an atomic lattice with defects). Usually, the holes move in the sample due to conformational transitions of the corresponding chain fragments. The vector of this transition, on the average, is directed perpendicularly towards the chain axis. The movement of holes along the chain is possible only in rare cases. Thus, the movement of holes is a process characteristic of an ensemble of chains, but not of one chain.

* For epoxy-amine networks we can imagine only hypothetic crystal since constituent chains are unable to crystallize because of stereochemical defects statistically distributed through N-atoms.
The number \( N_{kl} \) and size \( V_i \) of holes of \( i \)-th type are determined by

\[
N_{kl} = N_0 \exp \left( \frac{\Delta G}{kT} \right) - \exp \left( \frac{\Delta S}{k} \right) \exp \left( \frac{1}{kT} \right) \frac{p_i V_1}{k T}
\]

where \( N_0 \) is the number of segments in the system; \( \Delta G \) is the free energy; \( \Delta S \) is the entropy of the mixture of holes with segments, and \( N_{kl} \) is the energy of one hole, which consists of elastic energy of the hole environment \( W_{el} \) and of the surface energy of the hole \( W_{sf} \)

\[
W_{h} = W_{el} (V_i) + W_{sf} (V_i)
\]

Within the framework of the dislocation theory (18) and taking into consideration only elastic terms, it may be written as

\[
W_{el} (V_i) = \frac{\mu}{4\pi (1 - \nu)} \ln \left( \frac{r_i}{r_0} \right)
\]

where \( \mu \) is the shear modulus, \( \delta \) is the Burgers' vector, \( \nu \) is the Poisson's ratio, \( r_0 \) is the radius of the dislocation nucleus, and \( r_i \) is the distance from the centre of the nucleus (hole).

For \( W_{sf} \) it may be presented as

\[
W_{sf} = \frac{4\pi r^2 \gamma_0}{1 - \frac{\rho_0}{\rho_i}} = 4\pi \gamma_0 (r^2 - \delta^2)
\]

where \( r \) is the radius of a hole, \( \gamma_0 \) is the coefficient of surface tension and \( \delta \) is the minimum possible distance between the walls of a "nucleus" hole. It is appropriate to mention here that the calculation of \( W_{sf}(V_i) \) is a complex problem. Naturally, \( W_{sf} \) has to be essentially different from macroscopic surface tension. To estimate this magnitude one should take into consideration the real structure of the macromolecular fragment with appropriate conformation and configuration on the surface of this hole. At present, such calculation is probably possible only with the help of a computer within the frame of molecular dynamics methods.

The values of \( W_{sf} \) are assumed to be estimated in terms of a purely elastic approach as it is seen from the equation. However, in reality, the viscoelastic behaviour of the material near the hole should be taken into account. Unfortunately, this has not yet been done for polymer bodies.

The literature on the study of molecular mobility in polymers by different methods (15) shows that practically all the polymers have a temperature-discrete spectrum (at \( \nu = \text{const} \)) of molecular motions, whose nature is similar for all polymers. This fact allows us to suggest that in the range of dynamic molecular transitions the mobility of the corresponding holes unfreezes. At each transition (\( \alpha, \beta, \gamma \) etc.) we have defreezing of the corresponding holes. It means that the total fluctuational free volume of a polymer is discretely distributed through the holes of different types - \( V_{\alpha}, V_{\beta}, V_{\gamma} \) and \( V_0 \), where indices correspond to the conventional classification of molecular motions in polymers (15). Such holes have the following size hierarchy \( V_0 > V_\beta > V_\gamma > V_\alpha \).

On heating an amorphous polymer in a certain range of temperatures \( \Delta T \) (\( 1 = \beta, \gamma, \alpha \)) there usually appear mechanical or dielectric losses. And it is in this range, \( \Delta T_i \), that unfreezing of \( i \)-th type holes motions takes place. Starting at low temperatures \( \delta, \beta, \gamma \) holes and, finally, \( \alpha \)-type holes gradually unfreeze.*

As soon as fluctuational holes begin to move in the sample, they interact, merging into multiplets, which, in their turn, split into singlets and smaller multiplets.

Merging of holes is an advantageous process since the specific energy on a unit surface of a hole decreases with increasing hole size. Such a decrease is caused by the decrease of surface tension with the growth of the hole radius. Merging of holes into multiplets proceeds until the decrease of mixing entropy of holes exceeds the energetic term resulting from the increase of the hole size.

According to this, we have suggested that for each temperature of an amor-

*Strictly speaking, in each region of \( \Delta T_i \) is being observed a slight increase of free volume of a polymer due to the origination of new holes. However, for \( \beta, \gamma \) processes the increase of volume is insignificant. The account of newly appearing holes should be undertaken only in the glass transition region.
phous polymer there is a corresponding thermodynamically equilibrium size distribution of holes. Such a suggestion means that in any amorphous polymer glass in non-equilibrium state there exist at least two relaxation processes, i.e., the tendency towards decreasing of excess free volume of a polymer (densification) and the tendency towards the equilibrium hole size for the relaxation temperature.

The rate of the first process is determined by the amount of excess free volume $\Delta V_e$ and by $\Delta T$ – the difference between the temperature of relaxation and the temperature of unfreezing of the corresponding molecular motions. The rate of the second process depends not only on the difference in temperatures, but also on the time history of the sample, which influences the deviation of the system from the equilibrium structure at the preceding temperature.

Since the movement of holes is a kinetic process, it is logical to suggest that the frequency of the hole jumps is a function of their sizes $r_1$

$$\tau = \tau_0 \exp \left[-\frac{u}{kT} (r_1)^{1/kT}\right]$$

where $u$ is the barrier, which the hole has to overcome to change a place. The larger the hole, the longer is the time $\tau$ of its settled life. It means that holes merge into multiplets, but merging always "slows down" the velocity of motions (jumping frequencies) in the sample.

Configurational holes cannot move on their own (they move only together with the chain, to which they are "attached"). However, they can capture fluctuational holes merging with them. That is why, configurational holes, in average, limit the mobility of the fluctuational ones, i.e. they are traps for the latter.

Since macromolecules or their fragments cannot migrate in the space unoccupied by other molecules, any "mass redistribution" in a polymer may occur only in the presence of holes, or in other words, all the processes of mass transfer in polymers are due to directed transition of holes.

Let us consider some properties of the studied polymers in the framework of a hole model. As an example we shall consider only the holes of $V(1)$-type since these are the holes of this type, that make the greatest influence upon the properties under consideration. For other holes the analysis is similar.

Shear viscosity and plasticity. It is well-known that the rate of viscous shear flow is determined by the rate of hole jumps at the constant concentration of holes. In accordance with the above, shear viscosity for the given body will be smaller, the smaller is the average size of holes responsible for shear flow, other things being equal. When the mechanical straining of a glassy polymer reaches the yield point, than a process similar to shear flow occurs in a local zone of the polymer (shear band). It means that "splitting" of holes in the polymer to smaller ones takes place in the shear band. This is the change of the material structure at yielding. The energy for such a process $W(\tau)$ appears due to the work of effective shear stress

$$W(\tau) \sim V_{sh} \tau_{eff}$$

where $V_{sh}$ is the shear activation volume.

It is such a transformation of a polymer glass structure which takes place at its plastic deformation.

Fig. 9 shows the changes of the shear activation volume $V_{sh}$ during deformation.

Fig. 9. The change of $V_{sh}$ at stretching DG-PhLA (1:1.5) network. $T_{exp} = 343^\circK$. Strain rates $\varepsilon$, $\text{min}^{-1}$: 1 – $10^{-4}$; 2 – $10^{-3}$; 3 – $10^{-2}$.
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tion of a glassy network based on DGER-mPhDA (1:1,3). The shear activation volume $V_{sh}$ was calculated on the basis of the model of thermally activated stress-biased viscous flow given by Eyring (16). It is seen that $V_{sh}$ decreases with increasing stress and deformation, and, when the stress in the sample approaches $\sigma_y$, $V_{sh}$ becomes constant. The result shows that the average volume of the "molecular flow fragment" near $\sigma_y$ decreases by a leap, which favours yielding.

Fracture. For yielding the great role is played by the width of the hole size distribution function. If $F(r)$ is wide, small holes begin to move at rather small $\sigma$ (low proportionality stress). However, this process quickly stops due to the capture of small holes by large ones. Too large stresses are needed for the consideration of large holes, and fracture process, which is parallel to deformation, "outruns" yielding. Such processes probably occur in the "plastic zones" of the polymer before cracks begin to grow.

Annealing and quenching of polymer glasses. The rise in temperature always favours the decrease of an average size of holes, surface tension $\gamma_0$ reducing with temperature as

$$d \gamma_0 / dT \sim -B (d/M_1)^{2/3}$$

where $d$ is the density and $M_1$ is the molecular weight of a fragment, which transforms through the $i$-th type hole. Large holes are entropically not favoured in the polymer melt, that is why, fast cooling of high-temperature polymer melts leads to freezing-in of a larger fraction of small holes, which makes the process of plastic deformation easier (small $\sigma_y$ large $\delta_{br}$). On annealing the average size of holes increases, which results in large $\sigma_y$. These phenomena may occur both with a change of the total free volume of the system and without it. The latter is possible only because in a glassy polymer there always exist pores, whose surface is the source of nucleation or trapping of holes. However, the process of pore loss in the sample (the decrease of a polymer specific volume) is, apparently, a permanent process because of their great size. The dynamic exchange between pores and holes may lead to the fact that such properties of the sample as $\sigma_y$ and $T_g$ can change at almost constant density of the polymer.

Formation of polymer properties in the course of curing reaction. As it has been shown the properties of glassy polymers essentially depend on the rate of vitrification in the course of curing. It is natural to assume that at vitrification of the reacting system the hole structure formation takes place, and at slow vitrification $F(r)$ has time to come nearer to equilibrium. Fast vitrification (high $T_g$) leads to a glass with very non-equilibrium hole size distribution, resulting in rather low $\sigma_y$. The softening temperature of the sample depends, in the first place, on the concentration of large holes since only large holes permit the transitions of large segments. At low $T_g$ (slow vitrification) of the sample the formation of large holes takes place in the process of curing, which leads to reduced $T_g$. However, large holes cannot move easily under stress, and the mechanical behaviour of the sample is defined by another "tail" of the size distribution function $F(r)$ of small holes. These processes explain the concurrent behaviour of $T_g$ and $\sigma_y$. $F(r)$ of holes may influence kinetic parameters of a glass transition process. Thus, a certain increase of activation energy of the $\alpha$-transition with temperature may be caused by a gradual involvement of larger hole motions. This means that the size of segments, whose mobility heating of polymer glasses, is determined not by the property of a single macromolecule (its rigidity), but by the sizes of holes existing in the glass. In this case the size distribution of holes is the physical basis of the usually observed distribution of relaxation times.

CONCLUSIONS

Densely crosslinked epoxy-amine polymers appeared to be rather interesting objects of study from the point of view of the structure of the polymer glassy state. This is due not only to the fact that networks form fairly homogeneous closed packed glasses, but also because of the possibility of change in the structure and properties of glasses under isothermal conditions. In usual studies of the glass-transition phenomenon in a polymer, the investigator has to change the temperature of the sample to observe this transition. On curing the networks considered in this work one can observe the glass transition under isothermal conditions, and kinetic parameters of this transition depend on the rate of the molecular weight increase of a polymer in a chemical reaction. Since the rate of the chemical reaction may be changed by introducing catalysts into the system, at the same tempe-
nature one can obtain glasses with different structures and thus with different properties. We think that, using this approach, we can receive new information on the nature of the glass transition and the changes of the polymer structure in this transition. As far as the above-mentioned hole model is concerned, it is necessary to have experimental data on the sizes of holes in a polymer to answer the question concerning the real value of the model. Unfortunately, these data have not been available in literature.

There are as yet no good experimental methods of defining hole sizes. We hope this can be done by the analysis of the form (width) of the endothermic peak of heat capacity. However, this work is still to be done.

Theoretical analysis of the energy of different types of holes requires reliable information on the hole physical structure. Unfortunately, such data are also not available.

It is impossible to give a general solution of the problem here, and in this sense the situation is similar to that in the theory of dislocations (16), in which the structure of a dislocation core is still unknown. However, in spite of this, the theory of dislocations has greatly contributed to the understanding of the nature of the mechanical behaviour of solids. That is why, the development of hole concepts for polymer glasses does not seem hopeless to us.

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