

# Application of cluster model for the description of epoxy polymer structure and properties

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## Abstract

A study was made of the structure and physico-mechanical properties of epoxy polymers obtained using different curing agent–oligomer ratios. The results were analysed within the framework of the cluster model of structure of the polymer amorphous state. It was shown that the model under consideration can be used for determining the quantitative structure–property relationships for cross-linked polymers. © 1998 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Wide application of epoxy polymers (EP) in various fields of engineering has stimulated the studies of their structure and properties. Having a complicated structural hierarchy, the EP require the analysis of structure–property relationships for specific levels of structural organization. In the present paper this analysis was done for the topological (segmental) level using the cluster model of structure of the polymer amorphous state [1–3].

It is known that amorphous polymers are typical of the existence of the network of macromolecular entanglements. This network determines the mechanical behaviour at temperatures above the glass transition temperature  $T_g$ .

According to the cluster model, in amorphous polymers there exists another kind of entanglement, which are regions of local ordering clusters, consisting of collinear close-packed segments of various macromolecules by analogy with crystallites with extended chains. As distinct from molecular entanglements, the cluster network exists only in a glassy state and fully disintegrates at the temperatures above  $T_g$ . Thus, in a glassy state there are two types of the segments packing: loose packing, where molecular entanglements are concentrated, and close packing, connected with clusters.

Earlier in terms of the cluster model a quantitative description of some properties of amorphous and semicrystalline polymers has been drawn [3–5]. The cluster

theory agrees well with the kinetic theory of fluctuational free volume [3] and fractal theory of plasticity [4]. The comparison of the calculated and experimental data can allow estimation of the applicability of the cluster theory to cross-linked polymers, which are the object of our investigation.

## 2. Experimental

Use was made of epoxy compositions (EC) based on diglycidyl ether of bisphenol A (DGEBA). The curing was performed by 3,3'-dichloro-4,4'-diaminodiphenylmethane (EC-1 composition) and methyltetrahydrophthalic anhydride in the presence of a catalyst three(dimethylaminomethyl)-2,4,5 phenol (EC-2). The ratio of curing agent to epoxy oligomer reactive groups ( $K_{st}$ ) was varied at 0.50–1.50. Thus it was possible to produce a number of EP specimens with different topologies of polymer networks. Detailed characteristics of reagents, curing conditions and chemical structure of the EP are given elsewhere [6].

Thermomechanical analysis (TMA) was performed under the uniaxial compression at 1.2 MPa at the temperature change rate of 2 K min<sup>-1</sup>. By applying the technique described in Ref. [6] to the TMA data we determined the mean statistical molecular mass of the chain between the cross-links:

$$M_s = \frac{3\rho RT_{he}\Delta\epsilon}{P\epsilon_0} \quad (1)$$

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where  $\rho$  is the polymer density;  $R$  is the characteristic gas constant;  $T_{he}$  is the initial temperature of the forced high elasticity,  $K$ ;  $\Delta\epsilon$  is the quasiequilibrium high elastic deformation;  $\epsilon_0$  is the specimen initial height;  $P$  is the specific load on specimen. The magnitude of  $M_s$  allowed us to calculate the effective density of the network sites ( $\nu_s$ ) by means of the following relationship [6]:

$$\nu_s = \frac{2\rho N_A}{3M_s} \quad (2)$$

where  $N_A$  is the Avogadro number.

The density was measured by hydrostatic weighing to four decimal places. The strain–stress characteristics were studied under the uniaxial compression at the crosshead displacement rate of  $5 \text{ mm min}^{-1}$ . The microhardness was measured at 0.5 N load by 15...20 indentations.

The X-ray study was performed by the Bragg–Brentano method in the angle range of  $2\Theta = 10...30^\circ$  using copper radiation and a nickel filter.

### 3. Results and discussion

Table 1 gives the results of the studies of the EP structure and properties:  $\nu_s$ ,  $\rho$ , yield stress ( $\sigma_y$ ), elasticity modulus ( $E$ ), microhardness ( $H_\mu$ ). For the both systems  $\rho$  is seen to grow with the increase in  $K_{st}$ . Dependencies of  $\nu_s$  and  $T_g$  on  $K_{st}$  pass through the maximum reaching the highest values at the stoichiometric ratio of the reagents,  $\sigma_y$  changes only insignificantly in this range of  $K_{st}$ .  $E$  shows the extremal behaviour with the minimum in the vicinity of  $K_{st} = 1.25$  (EC-1) and  $K_{st} = 0.75$  (EC-2). Dependence of  $H_\mu$  on  $K_{st}$  goes through the maximum (EC-1) or minimum (EC-2) near  $K_{st} = 1$ .

We do not go into details of the qualitative explanation of the obtained properties here since it has been done in Ref.

[6] and discuss them in the context of the structural model considered here [1,2].

#### 3.1. Determination of the density of cluster network of macromolecular entanglements

Cluster network density ( $V_e$ ) can be found in two ways. The first [1] is based on the fact stated in Refs [7,8] that amorphous glassy and semicrystalline polymers exhibit behaviour similar to that of rubbers at the plateau portion flow of the strain–stress curve ( $\sigma$ – $\epsilon$ ). Thus, one can determine  $V_e$  by means of the Mooney–Rivlin equation in the form [8]:

$$\sigma^t = K(\lambda^2 - \lambda^{-1}), \quad (3)$$

where  $\sigma^t$  is the true stress,  $K$  is the constant,  $\lambda$  is the drawing ratio. Eq. (3) is given for the compression strain.

At the linear dependence  $\sigma^t = K(\lambda^2 - \lambda^{-1})$ , one can easily determine the value of  $K$  and then, similarly to Eq. (1), the molecular mass ( $M_e$ ) of the chain fragment between the entanglement sites using the following formula[8]:

$$M_e = \frac{3\rho RT}{K} \quad (4)$$

where  $T$  is the test temperature.

Magnitudes  $M_e$  and  $V_e$  are interrelated in the similar way Eq. (2):

$$V_e = \frac{\rho N_A}{M_e} \quad (5)$$

The other technique is based on the existence of the unambiguous relation between the structure of the amorphous polymer described quantitatively by parameter  $V_e$  and the Poisson's ratio ( $\mu$ )[9]:

$$\mu \approx 0.5 - \frac{3 \cdot 10^{-10} \sqrt{191.11_m V_e}}{4\pi} \quad (6)$$

Table 1  
Structural and physico-mechanical properties of the EP

Composition	$\nu_s 10^{-20}$ ( $\text{cm}^{-3}$ )	$T_g$	$T_g^c$	$\rho$ ( $\text{g cm}^{-3}$ )	$E 10^{-3}$	$\sigma_y$	$\sigma_y^c$	$\Delta\sigma$	$H_\mu$	$V_e^{(1)} 10^{-21}$	$V_e^{(2)} 10^{-21}$	$d$ ( $\text{\AA}$ )
			(K)				(MPa)				( $\text{cm}^{-3}$ )	
EC-1												
$K_{st} = 0.5$	1.7	326	335	1.227	4.2	<sup>a</sup>			159			4.62
$K_{st} = 0.75$	5.4	366	392	1.234	3.9	140	154	22	205	2.05	1.9	4.63
$K_{st} = 1.0$	17.0	423	444	1.237	2.3	142	109	0	207	2.47	2.7	4.83
$K_{st} = 1.25$	12	405	396	1.244	2.0	131	107	0	197	3.41	3.5	4.80
$K_{st} = 1.5$	8.0	390	367	1.254	3.0	128	137	0	194	1.98	2.0	4.72
EC-2												
$K_{st} = 0.5$	4	342	362	1.207	3.6	120	114	11	220	1.15	1.2	4.55
$K_{st} = 0.75$	10	372	342	1.207	2.7	120	105	23	200	2.04	1.8	4.72
$K_{st} = 1.0$	11	399	358	1.208	2.8	131	134	22	190	2.92	2.8	4.80
$K_{st} = 1.25$	10	378	387	1.210	2.5	129	103	26	192	2.20	2.1	4.67
$K_{st} = 1.5$	8	343	390	1.213	3.0	121	95	32	235	1.31	1.2	4.67

<sup>a</sup>Brittle failure.

where  $l_m$  is the length of a monomeric link along the chain.

The magnitude of  $\mu$  can be determined by the results of the mechanical tests using the following equation [10]:

$$\sigma_y = \frac{1 - 2\mu}{6(1 + \mu)} E \quad (7)$$

The data presented in the table allow one to compare the values of  $V_c^{(1)}$  and  $V_c^{(2)}$  obtained by the first and the second methods. While determining  $V_c^{(1)}$  by means of Eqs. (3)–(5) we made use of the nominal stress  $\sigma$  rather than the true stress of the flow plateau  $\sigma^l$ . This simplification does not produce a considerable error due to small magnitudes of  $\lambda$  (up to  $\lambda \approx 1.3$ ) used in the calculations. One can see a rather good agreement between the values of  $V_e$  found by different techniques. This confirms the equal values of the latter ones and shows that relationship  $\sigma_y/E$  is controlled by parameter  $V_e$ .

One can, quite naturally, expect a certain correlation between  $\nu_s$  and  $V_e$ . In fact, the increase in  $\nu_s$  gives rise to the growth of  $V_e$  (see Table 1). And one observes two peculiarities in the  $V_e(\nu_s)$  dependences. Firstly, determination of  $V_e$  from Eqs. (6) and (7) gives a smaller spread of the results; therefore, the second technique used to determine  $V_e$  is more preferable and we shall use it in what follows. Secondly, one can easily show that dependences  $V_e(\nu_s)$  at  $\nu_s = 0$  are extrapolated to a non-zero value  $V_e$ . The latter fact becomes quite clear if one takes into consideration the existence of a local order in oligomers [11].

### 3.2. Chemical cross-linking effect on EP molecular parameters

In the case of linear polymers there is a correlation between molecular characteristics such as macromolecule cross-section area ( $S$ ), chain rigidity ( $\sigma_m$ ) and macroscopic properties [12–15]. Table 1 shows that variation of  $\nu_s$  changes the macroscopic characteristics of the EP. One can believe that the chemical cross-linking effects the polymer molecular parameters as well.

To check the validity of this assumption we studied the integral molecular parameter  $(S/C_\infty)^{1/2}$ , where  $C_\infty$  is the characteristic ratio [16]. Its physical essence is similar to that of  $a/\sigma_m$  ( $a$  is the chain ‘thickness’) used previously in Refs [12,13]. The value of  $C_\infty$ , however, is of a less indefinite character than  $\sigma_m$  [14]. This is due to the determination of parameters  $\sigma_m$  and  $C_\infty$ . The former depends on the macromolecule valent bond angles whereas the latter one depends on the length of these bonds. Usually the bond lengths can be determined much more accurately than the valent angles. This might explain why  $C_\infty$  has been widely used recently as a molecular characteristic [17,18].

Fig. 1 presents dependence  $T_g = f[(S/C_\infty)^{1/2}]$  constructed for linear polymers on the basis of the literature data [16,19]. Analytically it is expressed in the following way:

$$T_g \approx 129(S/C_\infty)^{1/2} \quad (8)$$

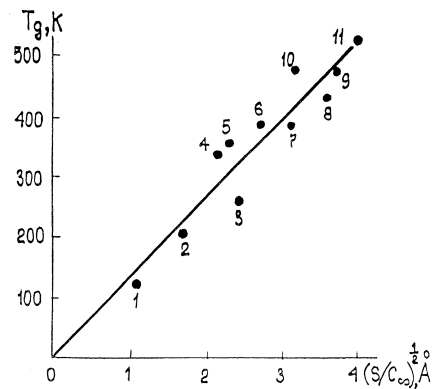


Fig. 1. Glass transition temperature  $T_g$  as a function of molecular parameter  $(S/C_\infty)^{1/2}$  for linear polymers: polytetrafluoroethylene (1), high density polyethylene (2), polypropylene (3), polyethyleneterephthalate (4), polyvinylchloride (5), polystyrene (6), polymethylmethacrylate (7), polycarbonate (8), polysulfone (9), polyarylate (10), polyarylatarylenesulfonoxide (11).

where  $T_g$  is measured in  $K$  and  $S$  in  $\text{\AA}^2$ . It is seen that this correlation holds even for polystyrene and polymethylmethacrylate usually exhibiting an anomalous behaviour [12,14]. It can be assumed that Eq. (8) should satisfy the EP as well, since it is true for their linear analogue, i.e. polycarbonate.

To estimate the magnitude of  $S$  in the case of the EP under consideration one can use the techniques described in Ref. [15] based on the wide angle X-ray diffraction. According to Ref. [15], the Bragg interval ( $d$ ) calculated by the position of the amorphous halo vertex and the macromolecule diameter ( $D$ ) are interrelated as

$$D \approx d^{1,22} \quad (9)$$

Table 1 gives the magnitudes of  $d$  for the investigated compositions. Dependence  $d(K_{st})$  exhibits the maximum at  $K_{st} = 1.0$  corresponding to that of the similar dependences  $T_g$  and  $\nu_s$ . Consequently, both the magnitude of  $D$  and the cylinder simulated macromolecule cross-section area  $S$  also change extremely.

The estimate of  $T_g$  by Eq. (8) provided  $C_\infty = \text{const}$  ( $C_\infty \approx 5$ ) shows that the obtained glass transition temperatures are smaller than the experimental ones [16]. Thus, at  $K_{st} = 1.0$  the calculated  $T_g$  is 347K, whereas the experimental value is 423K (the case of EC-1). For the EC-2 the respective values are 349K and 389K. Hence, it follows that the change in  $T_g$  cannot be explained by the variation of  $S$  only. One can assume that the change in  $S$  is accompanied by the change in  $C_\infty$ , i.e. the value characterizing the macromolecular coil compactness degree [16].  $C_\infty$  can be easily found from Eq. (8) using the experimental values of  $T_g$  (see Table 1). The calculations show that there is an extreme decrease in  $C_\infty$  within 5.0–3.3 with the minimum at  $K_{st} = 1.0$ . That is, the chemical cross-linking results in the increase in the effective macromolecule cross-section area and, consequently, makes a macromolecule more rigid [14], and a macromolecule coil more compact.

An independent check of the correctness of the quantitative estimates of  $S$  and  $C_\infty$  can be performed in the following way. Within the framework of the fractal concept of plasticity [4,20] and cluster model [1–3] it is shown that the yield process occurs in close-packed regions (clusters). And the relative fraction of clusters  $\varphi_c$  is equal to probability  $(1 - \chi)$  of the yield process realization given in Ref. [20] and the magnitude of  $\varphi_c$  can be easily determined from Eq. (3):

$$\varphi_c = \sqrt{3/2SC_\infty} l_m V_e \quad (10)$$

If magnitudes of  $S$  and  $C_\infty$  are calculated correctly the following condition should be met[4]:

$$\varphi_c \approx 1 - \chi \quad (11)$$

In Eq. (11) presence of the approximate equality sign is due to the fact that it is empirical one and has been obtained in Ref. [4] by comparing values of  $\varphi_c$  and  $(1 - \chi)$  found by using different techniques. As follows from the data presented in Fig. 2 Eq. (11) is actually met, that is, the obtained magnitudes of  $S$  and  $C_\infty$  correspond to the real state of the polymer.

Fig. 3 presents the dependence of density  $V_e$  of the macromolecule entanglement cluster network on the molecular parameter  $(S/C_\infty)^{1/2}$  obtained for the investigated polymer compositions. It is seen that there is a definite correlation between the order parameter  $V_e$  and the molecular structure characteristics.

Thus, the above results allow one to assume the following scheme of the chemical cross-linking effect on the structural arrangement and properties of the epoxy polymers. The cross-linking results in the increase of  $S$  and the decrease of  $C_\infty$ , the changes being the more pronounced the higher  $\nu_s$ . These changes effect the forming of the polymer segmental structure, namely, they control the order parameter  $V_e$ . Value  $V_e$  determines, in its turn, the physico-mechanical properties of the EP. The proposed model allows both qualitative and quantitative estimates of these changes as will be shown in the following sections.

### 3.3. EP elasticity modulus

The comparison of the magnitudes of  $\nu_s$ ,  $E$ ,  $V_e^{(2)}$  (see

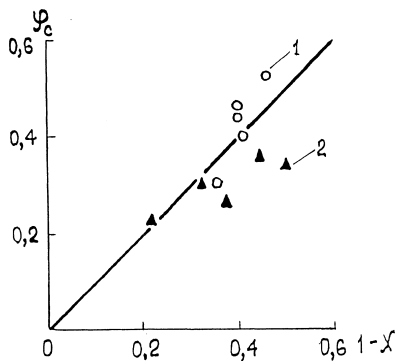


Fig. 2. Relationship between the relative fraction of clusters  $\varphi_c$  and probability of the yield processes  $(1 - \chi)$  for the EC-1 (1) and EC-2 (2).

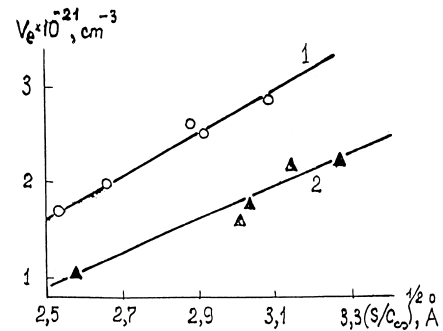


Fig. 3. Density  $V_e$  of the macromolecular entanglement cluster network as a function of molecular parameter  $(S/C_\infty)^{1/2}$  for the EC-1 (1) and EC-2 (2).

Table 1) shows that the best analogy is observed for dependences  $E(K_{st})$  and  $V_e(K_{st})$ . This fact makes it necessary to consider the behaviour of  $E$  within the framework of the cluster model discussed here.

According to Ref. [10] the value of  $E$  is determined by the contributions of both clusters and loose-packed matrix. The entire fluctuation free volume ( $f$ ) of the polymer is concentrated just in a loose-packed matrix and due to this it can be considered as a characteristics of its structure. For a glassy polymer the fraction  $f$  can be evaluated in the following way[21]:

$$f \approx 0.017 \left( \frac{1 + \mu}{1 - \mu} \right) \quad (12)$$

To make separate estimates of the cluster and loose-packed matrix contributions one must determine their respective fractions  $\varphi_c$  and  $\varphi_m$ . The former value is calculated by means of Eq. (10) and  $\varphi_m = 1 - \varphi_c$ . Fig. 4 shows dependence  $f(\varphi_m)$  for the both systems under study. It is linear and extrapolated at  $\varphi_m = 0$  to  $f = 0.024$ . The obtained result differs radically from that observed for the linear amorphous polymers where extrapolation of the  $f(\varphi_m)$  dependence to  $\varphi_m = 0$  gives a zero value of  $f$ . In the cross-linked polymers there seems to be some additional free volume  $f^a$  due to the presence of the chemical bond network sites. And the magnitude of the proper fluctuation free volume,  $f' = f - f^a$  is less than in linear polymers. It also follows from Fig. 4 that  $f'$  is determined by the association (dissociation) of segments into clusters, the free volume fraction in a loose-packed matrix is constant and amounts to  $f'$  (0.088

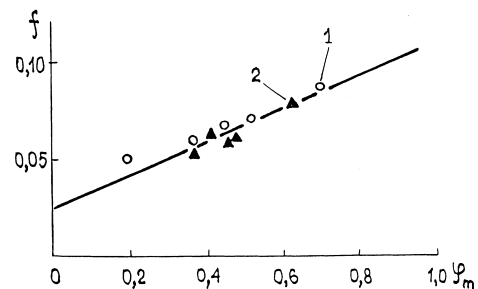


Fig. 4. Relative fluctuation free volume  $f$  as a function of loose-packed matrix fraction  $\varphi_m$  for the EC-1 (1) and EC-2 (2).

(or  $f = 0.112$  which is in a good agreement with the Boyer concept [22]) and the magnitude  $f$  is controlled only by  $\varphi_m$ .

Elasticity modulus  $E$  can be calculated using the values of  $H_\mu$  of the investigated polymers. The following relationship between  $H_\mu$  and  $E$  is proposed in Ref. [10]:

$$H_\mu = \frac{1 - 2\mu}{6(1 + \mu)} E \quad (13)$$

Eqs. (7) and (13) seem identical, since according to Ref. [10], both  $H_\mu$  and  $\sigma_y$  are equal to the internal pressure, for which Eq. (7) has actually been obtained in Ref. [10]. However, they given different values  $H_\mu$  and  $\sigma_y$  because of the difference in  $\mu$  values corresponding to different ranges of polymer deformation. Eqs. (12) and (13) yield:

$$E \approx 35.3 f H_\mu \quad (14)$$

We used this expression to obtain the calculated dependences  $E(K_{st})$ . Comparison of the calculated and experimental dependences of  $E$  for the EC-1 system (Table 1, Fig. 5) shows that they change in a similar way. The use of  $f'$  values in the calculations gives a better quantitative agreement between the compared dependences than in the case of  $f$ . The similar results have been obtained for the EC-2 system.

Figs 4 and 5 allow us to guess why the best analogy is observed between  $E$  and  $V_e$  values rather than between  $E$  and  $\nu_s$ . We think that in the elastic strain region the EP mechanical properties are determined not by the entire fluctuation free volume  $f$  but only by that fraction ( $f'$ ) which is connected with the association (dissociation) of segments into clusters.

It should be noted that at various forming stages the polymer properties are determined by structural regions. Thus, in elasticity ( $E$ ) and local plasticity ( $H_\mu$ ) ranges mostly loose-packed matrix ( $f'$ ) works, whereas at macroscopic yield ( $\sigma_y$ ) there is also an additional work of chemical cross-links ( $f = f' + f^a$ ). It is this fact that explains different values of  $\sigma_y$  and  $H_\mu$  obtained from Eqs. (7) and (13) in spite of the formal resemblance of the latter ones.

### 3.4. EP glass transition mechanism

In epoxy polymers one can observe various types of behaviour of  $E$  and  $T_g$  (Table 1 and Ref. [6]). The causes of this behaviour can be found within the framework of the

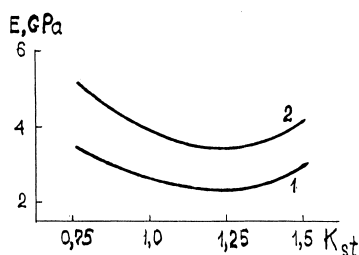


Fig. 5. Calculated dependences of elasticity modulus  $E$  as a function of the curing agent-oligomer ratio  $K_{st}$  for EC-1: (1) calculation by  $f'$ , (2) —  $f$ .

recent concepts [23] according to which the glass transition in amorphous polymers is associated with the formation of the ‘frozen’ local order. Thus, to describe the glass transition process one can use the cluster model.

According to Ref. [24] for a liquid in an equilibrium state corresponding to the polymer state at  $T > T_g$ , density fluctuation  $\psi(\nu)$  at volume  $\nu \rightarrow \infty$  is

$$\psi(\infty) = \rho k T \chi_T \quad (15)$$

where  $k$  is the Boltzmann’s constant;  $\chi_T$  is the isothermal compressibility. Eq. (15) shows that the density fluctuations are due to thermal mobility of atoms with energy  $k_T$  but are limited by the bulk rigidity  $\chi_T^{-1}$ .

The evaluation of  $\psi(\infty)$  for different polymers on the basis of the literature data [25] shows that  $\psi(\infty)$  is almost the same at  $T_g$ . This fact leads us to conclude that once a certain critical magnitude  $\psi(\infty) = \psi_c$  is reached, the ‘frozen’ local order regions, i.e. fluctuation network of macromolecular entanglements, cannot be formed due to high thermal mobility of macromolecules (density  $V_e$  of this network at  $T_g$  is zero [1,3]).

As a result, Eq. (15) can be transformed in the following way:

$$\psi_c = \frac{\rho K T_g}{K_T} \quad (16)$$

where  $K_T$  is the isothermal uniform compression modulus. Values  $K_T$  and  $E$  are interrelated as [10]:

$$K_T = \frac{E}{3(1 - 2\mu)} \quad (17)$$

Eqs. (16) and (17) imply that the criterion of constant  $\psi_c$  cannot be applied to the glass transition in the EP under consideration. In this case the decrease in  $E$  must result in the reduction of  $T_g$  which does not agree with the experimental data. To explain this discrepancy we assume that the chemical bond network sites restrict the segment fluctuations in a cluster, thus decreasing the density fluctuations. We retain here the main postulate of the model—that polymer going out of the glassy state is due to the decay of the ‘frozen’ local order. Similar ideas were developed by Flory [26] who assumed that in rubbers, physical entanglements, considered by a number of researchers as ‘long-term’ local order regions, limit the fluctuations of the chemical cross-linkage units.

It is difficult to express analytically the effect of  $\nu_s$  on  $\psi_c$ . One can, however, assume that with the growth of  $\nu_s$  the restrictions of  $\psi_c$  become larger, i.e.  $\psi_c$  becomes lower. The account of these restrictions was taken by us (just as by Flory [26]) empirically, namely, by introduction of factor  $C\nu_s^n$  into the right-hand side of Eq. (16), where  $C$  and  $n$  are the constants. In this case Eq. (16) for the cross-linked systems with the account of Eq. (17) acquires the form:

$$\psi_c = \frac{3\rho k T_g (1 - 2\mu)}{E C \nu_s^n} \quad (18)$$

In view of the fact that  $\psi_c$  is about the same for different polymers we can find it using, for example, the well-known data for polycarbonate [25]. Since, according to the made estimates, the best agreement with the experiment is shown by  $n \approx 1/2$  we shall use this magnitude in what follows. Magnitude  $C$  can be determined using  $T_g$  for one of the EP given in the table by means of fitting (matching the theoretical curve and experimental data). As a result, Eq. (18) is transformed to

$$T_g \approx 4.45 \cdot 10^{-3} K_T \nu_s^{1/2} \quad (19)$$

Table 1 gives dependences  $T_g(K_{st})$  calculated by means of Eq. (19) for the EP under investigation which show, in general, a good agreement with the experiment. The discrepancy observed in the case of the EC-2 system seems to be due to the approximate calculation of  $\mu$  by Eq. (7). The result obtained confirms the correctness of the chosen approach.

Thus, the presence of the chemical cross-linkage network effects not only the local order degree ( $V_e$ ) but also restricts the thermal fluctuations of the segments in clusters. This effect determines, to a great extent, the cross-linked system properties. Thus, in particular, it allows one to explain the different change of  $E$  and  $T_g$ .

### 3.5. Yield stress in EP

At present the fact of the similar change of the elasticity modulus and yield stress of polymers due to varying structure or external conditions (elongation rate, temperature, etc) is well recognized. The explanation is that the elasticity and yield processes are controlled by the same factor, namely, by the intermolecular interaction forces. However, this rule does not work here for the systems under investigation (see Table 1). This result can hardly be explained within the framework of 'homogeneous' structural models of amorphous polymers like the 'felt model' by Flory [27]. Within the cluster model this discrepancy is quite acceptable because magnitude  $\sigma_y$  is determined only by the local order degree ( $V_e$ ) and  $E$  depends on the properties of both clusters and loose-packed matrix.

To describe the yield processes in amorphous polymers a wide use has been made of the theories taking into account various defects present in polymers [28]. The principal correctness of these approaches is doubtless. There are some doubts as to the frequent mechanical application of the concept of a defect in a crystal to amorphous state. These states possess principally different perfect defect free structures. Thus, for a crystalline state this is a single crystal (long-range order). For an amorphous state, however, according to Flory [27] the perfect structure is represented by interpenetrating macromolecular coils (disorder). So in view of different perfect structures one needs different approaches to the definition of a defect. In crystalline solids a defect is the break of an order (dislocations), whereas in amorphous

materials a defect is the break of a disorder (cluster, crystallites) [29]. Within this treatment the segments forming clusters can be regarded as linear defects (dislocation analog), which makes it possible to apply the mathematical apparatus of the dislocation theory to describe the yield process in polymers.

According to [29], the relationship between  $\sigma_y$  and  $E$  can be described by Eq. (20):

$$\frac{\sigma_y}{\sqrt{3}} = \frac{Eb\sqrt{\rho_d}}{4\pi(1+\mu)} \quad (20)$$

where  $b$  is the Buegers vector,  $\rho_d$  is the linear defect density. To evaluate magnitude  $b$  in amorphous polymers there is a number of methods. In this paper we use an empirical equation [9]:

$$b \approx \left( \frac{52.2}{C_\infty} \right)^{1/2}, \text{ \AA} \quad (21)$$

Magnitude  $\rho_d$  is calculated in the following way. The number of segments in clusters per a unit volume of a polymer was taken equal to  $V_e$  [1,4] and the length of each segment equal to the statistical length [30]:

$$l_s = \sqrt{3/2} l_m C_\infty \quad (22)$$

Consequently:

$$\rho_d = \sqrt{3/2} l_m C_\infty V_e \quad (23)$$

The comparison of the experimental yield stress values of the investigated compositions and those calculated by means of Eq. (20) shows their satisfactory agreement (Table 1). It follows from Eq. (20) that a similar character of  $E$  and  $\sigma_y$  change is not the general rule and holds only at constant monotonously changing values  $\rho_d$ . This rule does not hold for the systems investigated here: dependences  $V_e(K_{st})$  and, consequently,  $\rho_d(K_{st})$  are extreme and this is the reason for different behaviours of  $\sigma_y$  and  $E$ . Different nature of defects in amorphous and crystalline states causes the different yield mechanisms. In crystals the yield proceeds through the defect forming mechanism whereas in amorphous polymers yield is caused by defect annihilation. The cluster model presupposes the presence of two cluster types in amorphous polymers: those possessing larger functionality  $F$  (larger quantity of segments in a cluster) and therefore being more stable and those with lower  $F$  which keep a loose-packed matrix in a glassy state. Polymer deforming up to the yield stress results in decay of less stable clusters and their relative fraction determines the difference  $\Delta\sigma$  of  $\sigma_y$  and flow plateau stress  $\sigma_p$  values. Since  $V_e$  can be found from magnitudes  $\sigma_p \leq \sigma_y$  (see Section 3.1) this causes the specific difference between  $\sigma_y$  and  $\sigma_y^c$ : in seven cases out of nine the experimental values of  $\sigma_y$  exceed or coincide with the theoretical ones (Table 1).

#### 4. Conclusion

The results obtained show that the cluster model of structure of the polymer amorphous state makes it possible to give a quantitative description of a number of properties of epoxy polymers. The proposed model does not require any adjusting, with the exception of Eq. (18). This model can be applied for obtaining quantitative structure–property relationships of cross-linked polymers.

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