Journal of Engineering Physics and Thermophysics, Vol. 77, No. 1, 2004

PREDICTION OF THE PARAMETERS OF THE SUPERMOLECULAR STRUCTURE OF NETWORK POLYMERS WITHIN THE FRAMEWORK OF FRACTAL MODELS

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UDC 669.017

A fractal model enabling one to predict the parameters of the supermolecular structure of network polymers based on the cross-link density has been proposed. A cluster model of the amorphous state of polymers has been employed for quantitative description. Good agreement between theory and experiment has been obtained.

As is well known [1–3], computer modeling of the processes of formation of network polymers has suggested that at the gelation point, the cross-linked skeletons of these polymers are fractal structures; an increase in the cross-link density ν_c leads to an increase in the fractal dimension of such a skeleton. However the latter parameter is not very convenient from the practical viewpoint, although one prefers to characterize glassy network polymers at present precisely with the quantity ν_c [4]. Nonetheless, it has been shown in [5] that one can obtain different properties, for example, different values of the glass-transition temperature, for one and the same network polymer when the quantity ν_c is constant. This is attributed to the change in the supermolecular (cluster) structure of the network polymer in the process of physical aging, namely, to the increase in the degree of local order [5]. The latter effect has quantitatively been described within the framework of the cluster model of the structure of an amorphous polymeric state [6, 7]. In turn, the degree of local order determines the value of the fractal dimension d_f of the supermolecular polymeric structure [8]. Thus, it becomes possible to predict, from the level of chemical cross-linking, the structural characteristics (consequently, the properties) of network polymers in the glassy state, to the gelation point. One possible variant of solution of the problem indicated will be considered below with the example of the typical representatives of the class of network polymers — epoxy polymers of amine and anhydride cross-linking.

We have employed epoxy polymers (EPs) produced by hardening of epoxydian oligomer ÉD-22 by 3,3′-dichloro-4,4′-diaminodiphenylmethane (EP-1) and isomethyltetrahydrophthalic anhydride (EP-2) with a varied hardener:oligomer proportion in moles (equivalents) K_{st}. A variation of 0.50 to 1.50 in K_{st} enabled us to vary the quantity ν_{cr} within $(2–17)\cdot 10^{26}$ m^{-3}. The samples were produced both at atmospheric pressure (EP-1 and EP-2) and under the conditions of unilateral compression at a pressure of 200 MPa (EP-1-200 and EP-2-200). The details of manufacture of the samples have been presented in [9]. The value of ν_{cr} was calculated from the results of thermomechanical tests of epoxy polymers [10]. The samples of the epoxy polymers were tested for uniaxial compression at a temperature of 293 K and a deformation rate of $\sim 5.6\cdot 10^{-3}$ sec^{-1}. The value of the Poisson coefficient μ was evaluated using the relation [11]

$$\frac{\sigma_y}{E} = \frac{1 - 2\mu}{6\,(1 + \mu)}\,. \tag{1}$$

The fractal dimension d_f of the epoxy-polymer structure has been calculated as follows [12]:

$$d_f = (d - 1)\,(1 + \mu)\,. \tag{2}$$

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To derive the relation between ν_{cr} and d_f of the epoxy polymers under study we have employed the model (proposed in [13]) whose essence is as follows. The competitive processes of nucleation and growth of a crystal were described within the framework of two kinetic equations:

$$\frac{dR}{dt} = k_1 c^m , \tag{3}$$

$$\frac{dR}{dt} = k_2 c^\rho . \tag{4}$$

The employment of (3) and (4) for description of the nucleation and growth of the regions of local order (clusters) in epoxy polymers is based on the fact that clusters are in their physical essence an analog of crystallites with extended chains [6, 7]. The characteristic dimension of a cluster is taken to be equal to the length of the segments involved, i.e., to the statistical-segment length l_{st}, which in turn is evaluated as [14, 15]

$$l_{st} = l_0 C_\infty . \tag{5}$$

Just as in [13], we have $m = 1$, since the growth of a cluster represents the addition of a single segment of length l_{st} [6], and $\rho > 1$, since the nucleation of a cluster requires that two or more segments be present at the nucleation site. However the application of Eq. (3) to a single epoxy taken separately necessitates serious modification. If we take $R = l_{st}$, Eq. (3) will, apparently, lose its meaning since l_{st} = const and $dR/dt = 0$ for each epoxy polymer under study, which implies the impossibility of cluster growth. Then Eq. (3) will be written in the form

$$\frac{dn_{cl}}{dt} = k_1 c . \tag{6}$$

The limiting value of n_{cl} is limited by the nucleation of new clusters of thermofluctuation origin [13]; therefore, we have

$$l_{st} = \frac{dn_{cl}/dt}{dN/dt} . \tag{7}$$

It is apparent that the fraction of macromolecular segments C capable of forming clusters must decrease with time, as the clusters are being formed, and the quantity n_{cl} must also decrease, with allowance for the condition l_{st} = const for each epoxy polymer. This explains the presence of unstable clusters which have lower values of n_{cl} in the structure of the amorphous state of the polymers [8, 9, 16]. This also explains the self-similarity of the cluster structure in the interval of scales of its existence. We note once again an important fact — the system of Eqs. (3) and (4) is applicable to the set of all the epoxy polymers under study, whereas system (4) and (6) is applicable to each of these polymers taken separately.

For the set of epoxy polymers under study we can write the following relations [13]:

$$N\,(l_{st}) = \left(\frac{dN_{cl}}{dt}\right) t_{gel} , \tag{8}$$

$$l_{st} \sim \frac{dl_{st}/dt}{dN_{cl}/dt} . \tag{9}$$

Equation (9) predicts that, as the cross-link density ν_{cr} increases, C_∞ and consequently l_{st} decrease. This leads to an intensification of the nucleation of new clusters, i.e., to a growth of N_{cl}.

Setting $R = l_{st}$ and $m = 1$ and dividing Eq. (3) by (4), we obtain

$$l_{\mathrm{st}} \sim \frac{dl_{\mathrm{st}}/dt}{dN_{\mathrm{cl}}/dt} \sim \frac{c}{c^{\rho}} = c^{1-\rho} , \tag{10}$$

since k_1 and k_2 are constants.

Equation (8) in combination with (4) on condition that t_{gel} = const, k_2 = const, and $N = N_{\mathrm{cl}}$ yields that

$$N_{\mathrm{cl}}\,(l_{\mathrm{st}}) = k_2 t_{\mathrm{gel}} c^{\rho} , \tag{11}$$

or, since $k_2 t_{\mathrm{gel}}$ = const:

$$N_{\mathrm{cl}}\,(l_{\mathrm{st}}) \sim c^{\rho} . \tag{12}$$

Equations (2) and (4) enable us to determine c as

$$c \sim l_{\mathrm{st}}^{-1/(\rho-1)} , \tag{13}$$

or

$$c \sim N_{\mathrm{cl}}^{1/\rho} . \tag{14}$$

Equating the right-hand sides of (13) and (14), we obtain

$$N_{\mathrm{cl}}^{1/\rho} \sim l_{\mathrm{st}}^{-1/(\rho-1)} \tag{15}$$

or

$$N_{\mathrm{cl}}\,(l_{\mathrm{st}}) \sim l_{\mathrm{st}}^{-\rho/(\rho-1)} . \tag{16}$$

It has been indicated in [13] that the classical theory of nucleation requires that ρ be less than 2, which results in the condition

$$\frac{\rho}{\rho - 1} \geq 2 . \tag{17}$$

Furthermore, there is another constraint — the volume of the clusters must not exceed the total volume of the polymer, which yields another condition:

$$\frac{\rho}{\rho - 1} \leq 3 . \tag{18}$$

Thus, the index in relation (9) has the same limits as the fractal dimension of an object in a three-dimensional space [17]. We can obtain the exact interrelation of $\rho/(\rho - 1)$ and d_{f} by comparing (9) to that obtained in [8]:

$$N_{\mathrm{cl}}\,(l_{\mathrm{st}}) \sim l_{\mathrm{st}}^{-d_{\mathrm{f}}} . \tag{19}$$

As is well known, the quantity N_{cl} can be written as follows [7]:

$$N_{\mathrm{cl}} = \frac{V_{\mathrm{link}}}{n_{\mathrm{cl}}} = \frac{2V_{\mathrm{link}}}{F} . \tag{20}$$

Since a cluster is an analog of a crystallite with an extended chain, we have [7]

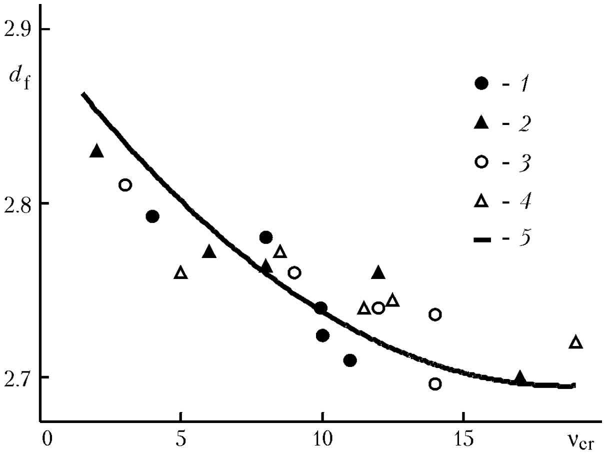

Fig. 1. Fractal dimension d_f of the epoxy-polymer structure vs. cross-link density ν_{cr}: 1) EP-1; 2) EP-2; 3) EP-1-200; 4) EP-2-200; 5) for all the epoxy polymers [1–4) calculated from Eq. (2); 5) calculation from (17)]. $\nu_{cr}\cdot 10^{-26}$, m^{-3}.

$$F = 2n_{cl}\,. \tag{21}$$

Noteworthy is another important fact. A comparison of Eqs. (4) and (19) shows that the maximum rate of formation of clusters is attained for $\rho = 2$ or $d_f = 2$. To put it differently, the maximum level of local order is assumed to correspond to the minimum fractal dimension of the polymer structure.

Within the framework of the cluster model [6, 7], a network polymer can be considered as a superposition of two skeletons — a network of chemical-cross-link sites and a cluster network of physical linkages with densities ν_{cr} and V_{link} respectively. Setting each of these skeletons perfect (i.e., disregarding the effect of end chains), we can write [18]

$$M_{cr}^{ef} = \frac{M_{cr} f}{2}\,, \tag{22}$$

$$M_{link}^{ef} = \frac{M_{link} F}{2}\,. \tag{23}$$

With account for (20), (22), and (23), relation (19) will have the form

$$\frac{2\nu_{cr}}{f} \sim l_{st}^{-d_f}\,. \tag{24}$$

We have obtained in [19] an expression relating the parameters C_∞ and d_f:

$$C_\infty = \left(\frac{d_f}{3\,(3-d_f)} + \frac{4}{3}\right). \tag{25}$$

A combination of (24) and (25) enables us to obtain the following equation:

$$l_0^{d_f}\left(\frac{d_f}{3\,(3-d_f)} + \frac{4}{3}\right)^{d_f} = 3.75\cdot 10^{28}\,\frac{f}{\nu_{cr}}\,, \tag{26}$$

where the empirical numerical coefficient on the right-hand side of the equation has been obtained by equating the d_f values calculated from (2) and (26) for $\nu_{cr} = 10^{27}$ m^{-3}.

The values of d_f (calculated from Eqs. (2) and (26)) as a function of ν_{cr} for the epoxy polymers under study are compared in Fig. 1 (on condition that l_0 = 1.25 Å [8] and f = 4), from which it is clear that a good agreement of the two sets of fractal dimensions has been obtained. This means that the increase in the fractal dimension of the skeleton to the gelation point [3] leads to a decrease in the fractal dimension d_f of the supermolecular structure of a network polymer in the glassy state. We note that knowledge of the value of d_f enables one to predict the properties of an epoxy polymer [20]. Thus, varying K_{st} or arresting the reaction at a certain stage, one can produce polymers with desired properties. However, the employment of the stoichiometric value K_{st} = 1.0 is more preferable from the practical viewpoint, which gives the most stable systems [12], including network polymers [21]. In this case, variation of the properties of the final product can be attained by changing the functionality of the cross-linking agent f or the molecular characteristics of the epoxy oligomer.

Thus, the use of a fractal analysis enables us to obtain the interrelation of the characteristics of a network polymer to the gelation point (or at this point) and in the glassy state. We note that this is true only of a freshly produced polymer. Subsequently the quantity d_f will change because of the process of physical aging, which is inevitable by virtue of the thermodynamically nonequilibrium nature of glassy polymeric state. Nonetheless, the methodology proposed enables us to predict the properties of glassy network polymers even in the stage of the reaction of cross-linking. Furthermore, the model considered quantitatively predicts the effects assumed earlier, namely: the existence of unstable clusters [9, 16], the self-similarity of the cluster structure [21], and a decrease in d_f, as the degree of local order increases [21].

NOTATION

E, elastic modulus; d, dimension of the enveloping Euclidean nested space, in the present case it is equal to three; R, crystal size; t, running time; k_1 and k_2, equilibrium constants; K_{st}, stoichiometric quantity; N, number of crystals; c, molecular concentration on the surface; m and ρ, indices; l_0, length of the skeleton bond in the main macromolecular chain; l_{st}, length of the statistical segment; C_∞, characteristic ratio that is the index of statistical rigidity of the chain; n_{cl}, number of segments in one cluster; t_{gel}, time interval of gelation; M_{cr}^{ef} and M_{link}^{ef}, effective molecular masses of the portions of chains between chemical-cross-link sites and clusters; M_{cr} and M_{link}, calculated values of the indicated molecular masses; f and F, functionalities of a chemical-cross- link site and a cluster respectively; V_{link}, density of the cluster network of molecular linkages which is equal as a first approximation to the number of segments in clusters per unit volume; μ, Poisson coefficient; ν_{ef}, cross-link density; σ_y, yield strength. Subscripts and superscripts: f, fractal; cl, cluster; gel, gelation; ef, effective; cr, cross-link; link, linkage; y, yield; st, statistical.

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