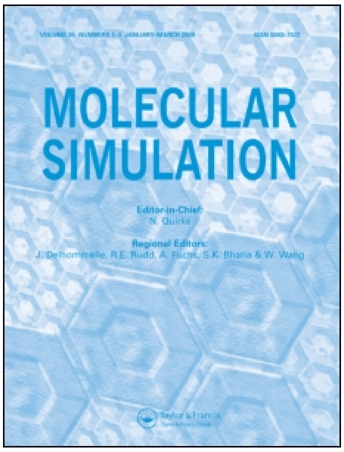

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Influence of network topology on mechanical properties of network polymers

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We studied theoretically how the network topology influences the mechanical properties of polymers. We used conclusions of thermofluctuation theory of fracture and graph theory. The long-term strengths of monofunctional and polyfunctional networks were compared. The cross-link functionality distribution of the polyfunctional networks is a power function. All other conditions being equal, the long-term strengths of the polyfunctional polymer networks are some three to four times the long-term strengths of the monofunctional networks.

Keywords: Polymer; Network topology; Mechanical properties

1. Introduction

Most of the experimental and theoretical studies of the mechanical properties of polymeric materials aim at finding correlations between the strength, strain, and long-term strength, on one hand, and factors such the molecular mass of the polymer, its phase and relaxation states, polymer-network density, and the nature and concentrations of plasticizers and fillers, on the other [1–5]. Here, we attempted to ascertain how the topology of a three-dimensional polymer network influences the mechanical characteristics of the polymer.

The topology of a polymer network will be described using a distribution of the type

$$P = P(f)$$

where f is the functionality of a cross-link of the polymer network; P is the fraction of the f-functional cross-links. Our attention will be focused on comparison of the mechanical properties of two types of polymer networks. One type is a monofunctional network with the distribution law

$$\begin{aligned} &P = 1, \quad \text{if} \quad f = l; \\ &P = 0, \quad \text{if} \quad f < l \quad \text{or} \quad f > l \end{aligned} \tag{1}$$

The other type is a polyfunctional network with the distribution law

$$P = Af^{-\nu} \tag{2}$$

Here A and ν are factors whose physical meaning will be considered below.

The networks having distribution (1) have been addressed repeatedly. They are synthesized in manufacturing of various polymeric materials. In most cases, $f = 3$ or 4. The polymer networks having distribution (2) have not yet been analyzed. Meanwhile, power distribution law (2) applies to describe the topology for a wide scope of communication, ecologic, metabolic and social networks [6–9]. Such networks, which are also referred to as scale-free networks, are highly reliable and resistant toward unfavorable external impacts. Comparing the mechanical properties of polymer networks with distribution laws (1) and (2), we will ascertain whether a scale-free network is a concept applicable to manufacturing of polymer materials.

2. Results and discussion

Consider two network polymer samples: sample 1 has distribution (1), and sample 2 has distribution (2).

Let the subchains of the polymer network in samples 1 and 2 have the same chemical nature, concentrations

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per unit volume (network density) and molecular-mass distributions. The samples are free of defects. Constant and equal mechanical stresses are applied to both samples.

Repeated investigations [4] showed that in the very general case, polymer degradation develops by the following scenario: microdefect generation, microdefect accumulation, microdefect growth and coagulation to macrodefects, destruction of the material. Consider the generation of a microdefect of volume V in samples 1 and 2.

Let there be N subchains of the polymer network in microvolume V. Of them, N_d subchains are destroyed when a microdefect is formed. Then,

$$\Delta_\mathrm{d} = \frac{N_\mathrm{d}}{N},$$

$$\Delta_\mathrm{r} = 1 - \Delta_\mathrm{d}$$

Here Δ_d and Δ_r are, respectively, the fractions of the subchains destroyed and undestroyed upon the formation of a microdefect.

The Δ_d and Δ_r for samples 1 and 2 will be estimated using the tools of the graph theory [9].

Regard the polymer network of sample 1 in microvolume V as a random graph. In this case, the network destruction criterion can be written in the form of

$$p_\mathrm{cr} = \frac{1}{k} \tag{3}$$

where k is the number of cross-links in microvolume V, and p_cr is the critical connection probability. On the other hand,

$$p_\mathrm{cr} = \frac{N - N_\mathrm{d}}{N^{\Sigma}}, \tag{4}$$

$$N^{\Sigma} = \frac{k(k-1)}{2}, \tag{5}$$

$$N = \frac{kf}{2} \tag{6}$$

Here, N^{Σ} is the maximal possible number of connections formed by k cross-links of the network. Simple transformations convert expressions (3)–(6) to

$$\Delta_\mathrm{d} = 1 - \frac{1}{f}, \tag{7}$$

$$\Delta_\mathrm{r} = \frac{1}{f} \tag{8}$$

The results obtained using equations (7) and (8) for the most frequent polymer network functionalities are compiled in table 1.

From results obtained in [8–10] it is possible to draw a conclusion that, if the network is a scale-free graph with distribution (2) and if the break down of any of its connections is equiprobable, the network retains the power distribution upon degradation. During the network degradation, ν increases from its initial value ν' to reach critical value ν^* at which the network is destroyed.

Table 1. Characteristics and comparison of long-term strengths for mono and polyfunctional polymer networks.

Network type	f	Δ_d	Δ_r	δ_τ
Monofunctional network	3	0.667	0.333	3.51
Monofunctional network	4	0.750	0.250	2.78
Network in compliance with the Zhurkov and Bueche model	–	0.632	0.368	3.86

Consider the polymer network of sample 2 in microvolume V as a scale-free graph. In this case, the equation [9]

$$F(\nu^*) = \sum_{f=1}^{f_m} f(f-2) f^{-\nu^*} = 0 \tag{9}$$

where f_m is the maximal junction-point functionality, can serve as the network destruction criterion. The results of solving equation (9) for f_m varying in the range 10–30 are displayed in table 2.

The values of $f = 1$ and 2 may be interpreted as dangling ends and linear subchains of the polymer network. Take that the number of cross-links k remains unchanged as the network progressively degrades. The degradation of a separate cross-link is accompanied by a reduction in its functionality due to the destruction of the subchains connected to this cross-link. For example, a five-functional cross-link of the starting network transforms to a cross-link having a functionality of 4, 3, 2 (a linear subchain), or 1 (a dangling end). The number of the subchains of the polymer network in sample 2 corresponding to the current ν value is

$$N(\nu) = k \sum_{f=2}^{f_m} A(\nu) f^{-\nu} \frac{f}{2} = \frac{A(\nu)k}{2} \sum_{f=2}^{f_m} f^{1-\nu}$$

Find $A(\nu)$ from normalization conditions

$$\sum_{f=1}^{f_m} A(\nu) f^{-\nu} = 1,$$

$$A(\nu) = \frac{1}{\sum_{f=1}^{f_m} f^{-\nu}}$$

Table 2. Characteristics of polyfunctional polymer networks.

f_m	ν^*	ν'_3	ν'_4	ν'_zh
10	2.89	2.05	1.84	2.12
15	3.07	2.27	2.05	2.35
20	3.16	2.39	2.21	2.46
25	3.21	2.46	2.28	2.53
30	3.25	2.49	2.33	2.57

In this case, Δ_d is

$$\Delta_\mathrm{d} = \frac{k}{2N}\left(A(\nu')\sum_{f=2}^{f_m} f^{1-\nu'} - A(\nu^*)\sum_{f=2}^{f_m} f^{1-\nu^*}\right) \quad (10)$$

Figure 1 shows Δ_d versus ν' plots calculated from equation (10) (curves (1)–(5)). One can see that Δ_d increases as ν' decreases or f_m increases. The straight lines corresponding to Δ_d for monofunctional networks with $f = 3$ and 4 are also shown in figure 1 (lines (6) and (7)). The abscissas of the points at which curves (1)–(5) intersect straight lines (6) and (7) (ν'_3 and ν'_4) are listed in table 2. If $\nu' < \nu'_3$ and $\nu' < \nu'_4$, then the Δ_d of the polymer network in sample 2 is greater than in sample 1 with their networks having three- and four-functional cross-links, respectively.

Figure 2 shows the cross-link functionality distributions for sample 2 calculated for various exponent indices. Figure 3 shows the effect of ν on the ratio

$$\delta_f(\nu) = \frac{k_f(\nu)}{k_f(\nu')} = \frac{N_f(\nu)}{N_f(\nu')}$$

where $k_f(\nu')$, $N_f(\nu')$, and $k_f(\nu)$, $N_f(\nu)$ are the number of f-functional cross-links and the number of the corresponding subchains for the starting and current states of the degrading polymer network.

Clearly, the cross-links with functionality $f = 1$ increase in number with increasing ν, since the number of dangling ends increases as a result of degradation of subchains. The starting network contains few high-functionality cross-links (about 2% for $f = 30$). Such cross-links form some type of framework. Therefore, their percentage decreases most strongly as the network degradation progresses. For example, at the moment when the network is destroyed ($\nu = \nu^*$), there remains as little as about 1.5, 0.22 and 0.07% of the starting amount of the cross-links with $f = 10$, 20 and 30, respectively. The concentration of the cross-links having $f = 3$–5 passes through a maximum. The transient increase in the amount of these cross-links results from the degradation of cross-links having higher functionalities.

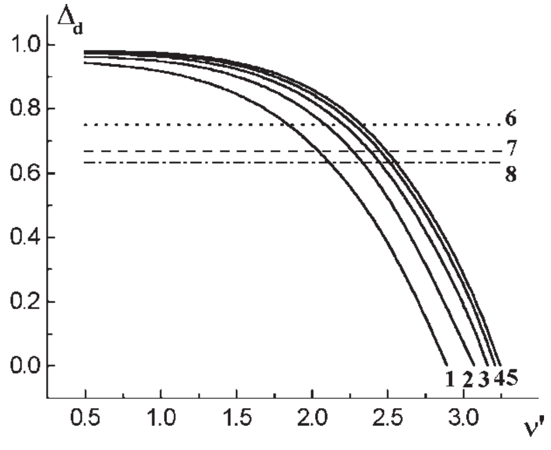

Figure 1. Δ_d versus ν plots for (1–5) polyfunctional polymer networks with f_m = (1) 10, (2) 15, (3) 20, (4) 25, and (5) 30; for (6, 7) monofunctional networks with f = (6) 4 and (7) 3; and for (8) a network that satisfies the Zhurkov and Bueche model.

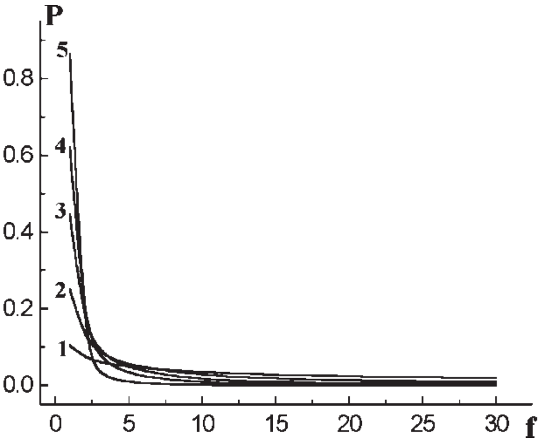

Figure 2. Cross-link functionality distribution curves for polyfunctional polymer networks with $f_m = 30$ and ν = (1) 0.5, (2) 1, (3) 1.5, (4) 2 and (5) 3.

Compare τ, the time required for a microdefect to form in samples 1 and 2. To this end, obtain an equation to relate τ with Δ_d (or Δ_r). Let mechanical stress σ exist in microvolume V and let it be related to average stress σ_av, which is applied to the network polymer sample, through overstress factor β:

$$\sigma = \beta\sigma_\mathrm{av}$$

Let β have a small value and let this value be the same in samples 1 and 2. In accordance with the thermofluctuation theory [2,4], the destruction probability of a subchain of the polymer network during period $\mathrm{d}\tau$ equals

$$W = W_0 e^{-U(\sigma)/RT} \quad (11)$$

Here $U(\sigma)$ is the activation energy of bond rupture per mole of chemical bonds, which is a function of stress σ; R is universal gas constant; T is temperature. Set $\mathrm{d}\tau = \tau_0$ (where τ_0 is the period of thermal oscillations of atoms) and $W_0 \approx 1$. Break the time elapsed from the moment at which the stress was applied into n intervals. In view of equation (11), the amount of the subchains of the polymer network degraded during the 1st, 2nd and i-th intervals as a function of time is, respectively,

$$N_\mathrm{d}^{(1)} = Ne^{-U(\sigma)/RT},$$

$$N_d^{(2)} = \left(N - N_d^{(1)}\right)e^{-U(\sigma)/RT} = N\left(1 - e^{-U(\sigma)/RT}\right)e^{-U(\sigma)/RT},$$

$$N_\mathrm{d}^{(i)} = \left(N - \sum_{k=1}^{i-1} N_d^{(k)}\right)e^{-U(\sigma)/RT} = N(1 - e^{-U(\sigma)/RT})^{i-1}e^{-U(\sigma)/RT}$$

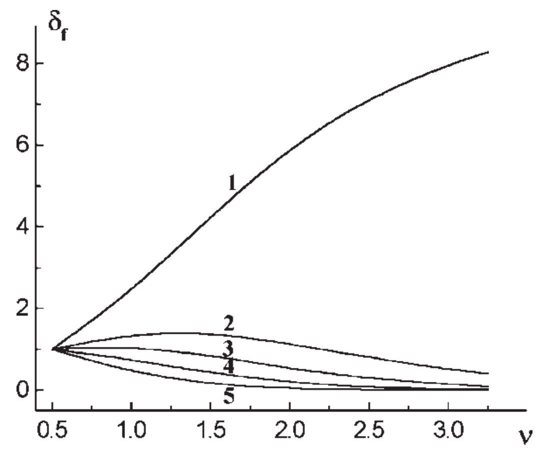

Figure 3. δ_f versus ν plots. Cross-link functionality: f = (1) 1, (2) 3, (3) 5, (4) 10 and (5) 30.

Then,

$$N_{\mathrm{d}} = \sum_{i=1}^{n} N_{\mathrm{d}}^{(i)}$$

$$= Ne^{-U(\sigma)/RT} \sum_{i=1}^{n} (1 - e^{-U(\sigma)/RT})^{i-1}, \qquad (12)$$

$$n = \frac{\tau}{\tau_0}$$

Equation (12) includes the sum of the first n terms of the geometric progression with base 1 and denominator $1 - e^{-U(\sigma)/RT}$. Use the expression for the sum of the terms of a geometric progression. Rewrite equation (12) in the form of

$$\Delta_{\mathrm{d}} = \frac{N_{\mathrm{d}}}{N} = 1 - (1 - e^{-U(\sigma)/RT})^n$$

After several transformations, we arrive at

$$\tau = \tau_0 \frac{\ln \Delta_{\mathrm{r}}}{\ln(1 - e^{-U(\sigma)/RT})} \qquad (13)$$

Expand the denominator of equation (13) into a series and write an equation that relates the microdefect formation time to the fraction of the undegraded subchains:

$$\tau = \tau_0(-\ln \Delta_{\mathrm{r}}) e^{U(\sigma)/RT} \qquad (14)$$

In most cases, the major contributor to the long-term strength of a material is the time required for microdefects to appear and pile-up. On the other hand, the appearance of microdefects (the loss of continuity) in the material during exploitation is frequently unacceptable. Therefore, equation (14) is applicable to ascertain the long-term strength of a network polymer.

Note that, if

$$U(\sigma) = U_0 - \gamma\sigma$$

(where U_0 is the activation energy of bond rupture at $\sigma = 0$; γ is a structural factor) and if

$$\Delta_{\mathrm{d}} = 1 - e^{-1} = 0.632,$$

$$\Delta_{\mathrm{r}} = e^{-1} = 0.368,$$

$$\ln \Delta_{\mathrm{r}} = -1$$

then equation (14) converts to the Zhurkov [11] and Bueche [12] equation for the long-term strength of polymers:

$$\tau = \tau_0 e^{U_0 - \gamma\sigma/RT}$$

The plot for $\Delta_{\mathrm{d}} = 0.632$ is line (8) in figure 1. The abscissas at which this line intersects curves (1)–(5), ν'_{zh}, which are analogues of ν'_3 and ν'_4, are listed in table 2.

From equation (14), it follows that for identical τ_0, $U(\sigma)$ and T the long-term strengths of samples 1 and 2 can be compared using the relationship

$$\delta_\tau = \frac{\tau^{(2)}}{\tau^{(1)}} = \frac{\ln \Delta_{\mathrm{r}}^{(2)}}{\ln \Delta_{\mathrm{r}}^{(1)}}$$

where $\tau^{(1)}$, $\Delta_{\mathrm{r}}^{(1)}$ and $\tau^{(2)}$, $\Delta_{\mathrm{r}}^{(2)}$ are the long-term strengths and the fractions of the undegraded subchains upon microdefect formation in samples 1 and 2, respectively. The δ_{r} is calculated for the $\Delta_{\mathrm{r}}^{(1)}$ corresponding to three- and four-functional polymer networks and to a network satisfying the Zhurkov and Bueche model ($\Delta_{\mathrm{r}} = 0.368$). The $\Delta_{\mathrm{r}}^{(2)}$ corresponds to a polyfunctional network with $f_m = 30$ and $\nu' = 0.5$ ($\Delta_{\mathrm{r}}^{(2)} = 0.021$). The results of the calculations are displayed in table 1. One can see from the data displayed in table 1 that the long-term strength of sample 2 is 2.8–3.9 times the long-term strength of sample 1. Thus, we may infer that it is advisable to synthesize scale-free polyfunctional networks in manufacturing of polymer materials.

There are two concluding remarks concerning synthesis of polyfunctional polymer networks.

As polyfunctional cross-links of polymer networks it is expedient to use oligomers containing as reactive and neutral monomer units. Reactive units are evenly distributed along oligomer chain. Their quantity determines functionality of network cross-link. Neutral units reduce concentration of reactive units and allow avoiding steric and conformational difficulties at formation of network cross-link.

Polyfunctional polymer network with discrete distribution $P = P(f)$ is the simplest to synthesize. However, the degradation of high-functionality cross-links makes the distribution continuous. Therefore, the conclusions drawn in this work hold.

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