Investigation of mechanical properties and swelling of scale-free polymer networks

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Abstract: We studied experimentally and theoretically how the network topology influences the mechanical properties and swelling of polymer networks. The properties of monofunctional and polyfunctional networks were compared. The cross-link functionality distribution of the polyfunctional networks is a power function. Such networks are also called scale-free networks. The ultimate tensile strength and ultimate tensile strain of a polyfunctional network appeared to be 1.4 and ~2 times as high as the respective parameters for a monofunctional network. For assessing the long-term strength of polymer networks, we used cyclic straining. The number of cycles from the onset of an experiment to the breakdown of the test sample for a scale-free polymer network was 56 to 60 times the number of cycles for a monofunctional network. We used the lattice-type model of solutions and derived an equation relating the chemical potential of the solvent or plasticizer in a swollen scale-free polymer network to the network parameters and the volume fraction of the polymer. The experimental results verified the validity of our theoretical analysis.

Keywords: Polymer, Network Topology, Scale-Free Networks, Mechanical Properties, Swelling of Polymer Networks

1. Introduction

This work was intended to experimentally and theoretically study how the topology of a three-dimensional network of a polymer material influences the mechanical properties and swelling of the material.

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 and P is the fraction of the f-functional cross-links. We will compare the mechanical properties and swelling of two types of polymer networks. One type is a monofunctional network with the distribution law

$$P = 1, \text{ if } f = l;$$

$$P = 0, \text{ if } f < l \text{ or } f > l \tag{1}$$

The other type is a polyfunctional network with the distribution law

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

Here, A and ν are factors. The value of ν influences both the topology and the properties of a polymer network. The value of A is found from the normalization conditions.

Networks with distribution law (1) were the subject matter of many studies [1–5]. They are synthesized in producing of different polymeric materials. In most cases, $f = 3$ or 4. Theoretical analysis of polymer networks with distribution law (2) was carried out in our earlier work [6]. We showed in [6] that the long-term strength of a POLYFUNCTIONAL network can several times exceed the long-term strength of a MONOFUNCTIONAL network with distribution law (1).

This work involves an experimental comparison of the ultimate tensile strength, ultimate tensile strain, and long-term strength between polymer networks of close compositions, one with distribution law (1) and the other with distribution law (2). This work also involves theoretical and experimental study of the swelling of Polyfunctional networks with distribution law (2).

Recall that the power distribution law (2) describes topology for a wide range of communication, environmental, metabolic, and social networks [7–10]. Such networks, which

are also called scale-free networks, are very reliable and stable toward harmful external influence. The results of this work prove the expedience of applying the scale-free network concept to the manufacture of polymer materials.

2. Experimental

The subject matters chosen to be studied in this work were polymer networks based on transformer oil plasticized butyl rubber. A commercial butyl rubber sample contained 1.85 wt % of isoprene. The polymer molecular weight was 300 000 g/mole. The butyl rubber was cured with p-benzoquinone dioxin ester. The composition of the monofunctional polymer network and the polyfunctional polymer network are listed in Table 1.

Table 1. Composition of polymer networks (wt %)

Components	Monofunctional network	Polyfunctional network
Butyl rubber	46.51	46.51
Transformer oil	46.51	45.84
Blend of butadiene oligomers		0.67
p-benzoquinone dioxin ester	6.98	6.98

To obtain the polyfunctional network, part of the transformer oil was replaced by a blend of butadiene oligomers with molecular weight of 2600, 3000, and 6000 g/mole, which functioned as polyfunctional cross-links. The concentration of the oligomer blend in the material was chosen such that the number of double bonds in the oligomer blend and in the butyl rubber was equal.

Presumably, the functionality of a polybutadiene molecule is proportional to its molecular weight. The oligomer fraction in the blend was calculated from

$$P = AM^{-v} \qquad (3)$$

where M is the oligomer molecular weight. According to the conclusions of [6], v was set equal to 0.5. The results of the calculations by equation (3) are displayed in Figure 1.
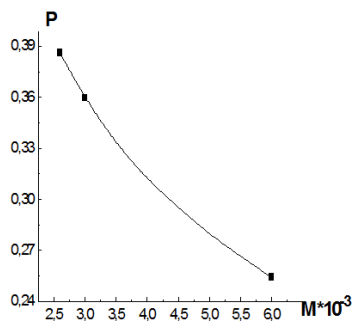

Figure 1. Dependence of a oligomer fraction in a blend from its molecular weight.

Polymer network samples were prepared as films about 2 mm thick from a 5% solution in toluene (all network components listed in Table 1 are well soluble in this solvent). The solution was poured onto a Teflon substrate. Toluene was

removed via evaporation under a hood for several days followed by evacuation for 1 h. The amount of the remnant volatile solvent in the samples as determined gravimetrically did not exceed 1%. Following the evacuation, the samples were cured for 1 week at 90ºC. The polymer network was formed as a result of the reaction of double bonds of butyl rubber, butadiene oligomers, and p-benzoquinone dioxin ester. The functionality of monofunctional networks was $f = 4$.

The mechanical properties of polymer networks were studied on an R-5 tensile testing machine. The working part of the scapula was 20 mm long. The linear straining rate was 20 mm/min. The cycling straining rate was 30 cycles per minute. Network swelling in toluene was studied by a gravimetric method.

3. Results and Discussion

Let us consider the results obtained from the mechanical studies of polymer networks. Figure 2 displays strain – stress ($\varepsilon - \sigma$) curves recorded during linear straining of networks having distribution law (1) or (2). Table 2 displays the characteristics of the polymer networks. The cross-link density of the network n_c and the molecular weight between network cross-links M_c were assessed using the following relationships [11]:

$$\sigma = RTn_c \left(\varepsilon - \frac{1}{(\varepsilon+1)^2} + 1 \right)$$

$$n_c = \frac{d}{M_c} \varphi_2^0$$

where d is the polymer density, φ_2^0 is the volume fraction of the polymer in the unperturbed state of the network at the moment of network formation, R is the universal gas constant, and T is temperature. n_c and M_c were calculated for the strain $\varepsilon = 1$ (100%).
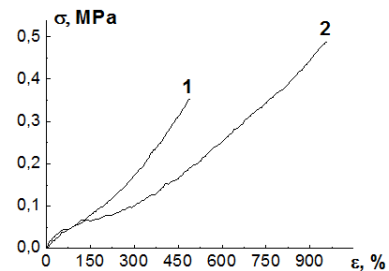

Figure 2. Strain – stress curves of monofunctional (1) and polyfunctional (2) networks.

From Table 2 one can see that the values of n_c and M_c are virtually the same for the monofunctional network and the scale-free polymer network. With this, the ultimate tensile strength and the ultimate tensile strain of the polyfunctional network are 1.4 and ~2 times the respective values for the monofunctional network. In this way, varying the topology of a polymer network offers a means for considerable improving the mechanical properties of the network.

Table 2. *Properties of polymer networks.*

Type of polymer network	n_c mole /m³	M_c g/mole	Ultimate tensile strength σ, MPa	Ultimate tensile strain ε, %
Monofunctional network	12.8	35938	0.35	490
Polyfunctional network	12.7	36220	0.49	960

In [6], the long-term strengths of networks with distribution laws (1) and (2) were compared under static stress. In this work, cyclic stress is employed to ascertain the long-term strength of polymer networks. Dynamic tests provide more visible results. In most cases, data gained by static and dynamic methods correlate with each other and may be compared in terms of the Bailey criterion [3].

Table 3 displays the numbers of cycles N from the onset of an experiment to the breakdown of the sample for various stress amplitudes (maximal strain ε_{max}) and for the maximal

Table 3. *Results of dynamic tests of polymer networks.*

Type of polymer network	ε_{max}, %	σ_{max}, MPa	Number of cycles N
Monofunctional network	300	0.17	373
	350	0.22	35
	400	0.26	14
Polyfunctional network	400	0.14	2250 <
	500	0.20	2102
	600	0.25	794
	750	0.34	459

stress σ_{max} achieved under ε_{max}. Clearly, for close σ_{max} values, N for a scale-free polymer network is 56 to 60 times greater than for a monofunctional network. Thus, the topology of the polymer network considerably influences its long-term strength. This inference agrees with the results obtained in [6]. Let us proceed with the results obtained from studying swelling of polymer networks. Before addressing experimental data, it is expedient to carry out a theoretical analysis of swelling of scale-free polymer networks. Flory [12] proposed their classical equation for the chemical potential of a solvent in a swollen monofunctional polymer network:

$$\frac{\Delta\mu_1}{RT} = \ln(1-\varphi_2) + \varphi_2 + \chi_1\varphi_2^2 + n_c\overline{V_1}\left(\left(\frac{\varphi_2}{\varphi_2^0}\right)^{1/3} - \frac{2\varphi_2}{f\varphi_2^0}\right) \quad (4)$$

Here, φ_2 is the volume fraction of the polymer in the current state of the network, χ_1 is the Huggins parameter, $\overline{V_1}$ is the partial molar volume of the solvent.

Equation (4) may be written as the following sum of terms:

$$\Delta\mu_1 = \Delta\mu_1^l + \Delta\mu_1^{el} + \Delta\mu_1^f$$

Here $\Delta\mu_1^l$ is a term characterizing the thermodynamic affinity of the solvent to the linear polymer, $\Delta\mu_1^{el}$ is associated with the transition of the network subchains into an extended state upon swelling, and $\Delta\mu_1^f$ is the due to the decrease in the system's entropy induced by cross-linking.

Equations for $\Delta\mu_1^l$ and $\Delta\mu_1^{el}$ are the same regardless of whether the polymer network is monofunctional or scale-free. The expressions for $\Delta\mu_1^f$ are substantially different.

The equation for $\Delta\mu_1^f$ of monofunctional networks, offered in [12], looks like

$$\frac{\Delta\mu_1^f}{RT} = n_c\overline{V_1}\frac{2\varphi_2}{\varphi_2^0}\left(1 - \frac{1}{f}\right) \quad (5)$$

Let us derive an equation to relate $\Delta\mu_1^f$ to the parameters of a scale-free polymer network. For this purpose, we will use the lattice-type model of solutions and the procedure proposed in [12].

Let us consider two cases.

In one case, the formation of a polymer network may be regarded as the interaction of ends of subchains with a molecular weight of M_c in the network. The cross-link size of a polyfunctional network is commensurate to the volume of one cell of the lattice (Δ).

Let K' be the number of free ends of subchains that remain in the system at a certain moment of the reaction. In this case, the thermodynamic probability of formation of an f-functional cross-link is

$$(f-1)!\left(\frac{K'\Delta}{V}\right)^{(f-1)} \quad (6)$$

where V is the system's volume.

For the thermodynamic probability of formation of K cross-links whose functionalities fall in the range from f_{min} to f_{max}, we may write

$$W = \prod_{f_{min}}^{f_{max}} ((f-1)!)^{K_f}\left(\frac{\Delta}{V}\right)^{K_f(f-1)} \Pi_f$$

Here, K_f is number of units with functionality f and Π_f

is the product of K integers.

The decrease in the system's entropy upon network formation is

$$\Delta S^f = k \ln W = k \left(\sum_{f_{min}}^{f_{max}} K_f (f-1) \ln V^{-1} + C_f \right)$$

where k is the Boltzmann constant and C_f is a function of f, K_f, Π_f, and Δ.

$\Delta \mu_1^f$ and ΔS^f are related through

$$\Delta \mu_1^f = -T \left(\frac{\partial \Delta S^f}{\partial n_1} \right)_{T,P} = -T \left(\frac{\partial \Delta S^f}{\partial \varphi_2} \right)_{T,P} \left(\frac{\partial \varphi_2}{\partial n_1} \right)_{T,P}$$

Here, n_1 is the amount of solvent moles in the system. After simple transformations, we arrive at

$$\left(\frac{\partial \varphi_2}{\partial n_1} \right)_{T,P} = -\frac{\overline{V_1}}{V} \varphi_2$$

$$\left(\frac{\partial \Delta S^f}{\partial \varphi_2} \right)_{T,P} = \frac{k}{\varphi_2} \sum_{f_{min}}^{f_{max}} K_f (f-1)$$

$$\Delta \mu_1^f = kT \frac{\overline{V_1}}{V_0} \frac{\varphi_2}{\varphi_2^0} \sum_{f_{min}}^{f_{max}} K_f (f-1) \qquad (7)$$

where V_0 is the system's volume corresponding to the unperturbed state of the network at the moment of its formation.

In accordance with equation (2), valid is

$$K_f = KAf^{-\nu}$$

$$N_c = \frac{KA}{2} \sum_{f_{min}}^{f_{max}} f^{1-\nu}$$

Here, N_c is the number of network subchains in the system. Then, expression (7) transforms into

$$\frac{\Delta \mu_1^f}{RT} = n_c \overline{V_1} \frac{2\varphi_2}{\varphi_2^0} \left(1 - \frac{\sum_{f_{min}}^{f_{max}} f^{-\nu}}{\sum_{f_{min}}^{f_{max}} f^{1-\nu}} \right) \qquad (8)$$

Comparing expressions (5) and (8), we may introduce a new parameter f^* as an effective cross-link functionality of a scale-free polymer network:

$$f^* = \frac{\sum_{f_{min}}^{f_{max}} f^{1-\nu}}{\sum_{f_{min}}^{f_{max}} f^{-\nu}}$$

Physically, f^* means that a scale-free polymer network behaves during swelling like a monofunctional polymer network with a cross-link functionality of f^*.

In the other case, a polymer network is formed as a result of the reaction between polymer macromolecules and oligomer molecules, the latter performing as polyfunctional cross-links of the network. Such a network has been obtained in the present work. Oligomer molecules have reactive and neutral units. Reactive units are evenly distributed along the oligomer chain. Their quantity determines the functionality of a network cross-link. Neutral units reduce the concentration of reactive units and allow avoiding steric and conformational hindrances to cross-linking.

For this network, equation (6) may be rewritten as

$$f! \left(\frac{K'\Delta}{V} \right)^f$$

By simple transformations according to the scheme above, we obtain an expression for $\Delta \mu_1^f$:

$$\frac{\Delta \mu_1^f}{RT} = n_c \overline{V_1} \frac{\varphi_2}{\varphi_2^0} \qquad (9)$$

Comparing expressions (5) and (9), we will write down for the effective functionality of a scale-free polymer network: $f^* = 2$.

Table 4. *Results of swelling of polymer networks*

Type of polymer network	φ_2^0	φ_2^*	χ_1	f
Monofunctional network	0.5	0.096	0.46	4
Polyfunctional network	0.5	0.084	0.46	1.81

Table 4 displays experimental data on equilibrium swelling of a monofunctional polymer network and a polyfunctional polymer network in toluene (φ_2^* is equilibrium volume fraction of the polymer). For the equilibrium swelling of a polymer network, $\Delta \mu_1 = 0$. As a result of solving equation (4) for a monofunctional network (with $f = 4$ and n_c taken from Table 2), the Huggins parameter was obtained as $\chi_1 = 0.46$. This value agrees well with $\chi_1 = 0.48$ found in [13] for the polyisobutylene–toluene system. As a result of solving equation (4) for a polyfunctional network (with $\chi_1 = 0.46$ and n_c taken from Table 2), the effective functionality of the polymer network was obtained as $f^* = 1.81$. This value agrees well with the results of our theoretical analysis.

4. Conclusions

The results of the mechanical tests obtained in this work prove the expedience of manufacturing scale-free polymer networks. The expressions derived for the effective functionality of networks, together with experimental swelling data, may serve to monitor the structure of scale-free polymer networks after synthesis.

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