

Theoretical Modeling of Mechanical Resistance and Stability and Related Characteristics of Polymeric Systems with Branching/Cross-Linking

Freddy Romm¹ and Oleg Figovsky

Polymate Ltd., P.O. Box 73, 10550 Migdal Emek, Israel

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A theoretical (thermodynamic) method for the estimation of mechanical characteristics of polymeric systems is proposed. This method uses the statistical polymer method for modeling of branched/cross-linked structures. The weak interaction between macromolecules is modeled in the approach of their mutual interpenetration. The proposed method is used for the estimation of mechanical resistance and stability of microporous polymeric materials. An engineer method for the evaluation of mechanical stability and resistance of polymeric materials is derived. © 2002

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INTRODUCTION

The problem of estimation of mechanical properties of polymeric materials with branching (and cross-linking) is one of the most important but is difficult to solve in terms of the physical chemistry of the solid state. Many existing constructive materials are polymeric, and the evaluation of their mechanical characteristics is extremely important for their practical use. Moreover, forecasting the properties of new materials (at the stage of their elaboration) may seriously reduce the costs of the experimental studies and tests, due to the preliminary evaluation of mechanical characteristics of the projected microporous material, based on the relationship between its preparation conditions, structure, and properties.

Existing theoretical methods for the study of the mechanical stability/resistance of materials are based on traditional theories of solid state. A brief analysis of these methods was given in (1), where a similar problem was solved for pyrolytically prepared microporous materials.

¹To whom correspondence should be addressed. E-mail: cerafr@technix.technion.ac.il.

In the present paper, we propose a theoretical (thermodynamic) method for the evaluation of mechanical characteristics of polymeric structures, first their mechanical stability and resistance, and a related engineer method for forecasting the mechanical resistance of a polymeric material, based on the conditions of its preparation.

Let us solve this problem in two stages: (1) mechanical properties of a single macromolecule, and (2) properties of a structure composed of multiple interacting macromolecules.

As was shown in (2), the results of any tests related to any deformation can be generalized for every kind of deformation, due to using an exponential formula. Therefore, it is enough to build a model containing a single kind of deformation, as was done for pyrolytically prepared microporous materials in (1). For this reason, we use below an approach similar to that employed in (1).

MODELING OF BRANCHED POLYMERS

The main problem in modeling of branched structures is due to their enormous number. Hence, each model of branching needs, first, to reduce the number of structures.

According to the rule of computing, models are divided into analytical and numerical ones. Numerical models do not need an analytical solution but replace it with numerical simulations.

According to the main assumption about several specifications of the treated structures, existing models can be divided into fixing structure (architecture) and nonfixing structure ones. The fixation of considered structures, based on several physical considerations, reduces significantly the number of treated structures, but may sometimes lose the correctness of the description of branched macromolecular systems.

The majority of existing models of branching is based on several fixations of treated structures: stars, quasichains, etc. (3, 4).

Many numerical models do not need such specifications, but they have difficulties in the treatment of structures

with a moderate or high degree of polymerization (see below).

According to the approach regarding the mechanism of polymer formation, models are classified into kinetic and statistical ones.

Numerical Models

This method of solution of problems of branching avoids numerous complicated equations, due to the limitation of the degree of polymerization. Numerical models allow, in principle, evaluation of every characteristic parameter of a considered system.

Numerical simulations are very useful in studies of conformational properties of branched polymers having a low degree of polymerization. Monte Carlo, molecular dynamics, and Brownian dynamics methods are employed to simulate the equilibrium and dynamic behavior, and also to reproduce hydrodynamic properties. The simulations are performed on several polymer models. Different Monte Carlo algorithms are devised for lattice and off-lattice models. Numerical models are effective in the description of uniform homopolymer stars as single chains, or in non-diluted solutions and melts, employing a variety of techniques, models, and properties. Other important structures, such as stars with different types of monomer units, combs, brushes, dendrimers, and absorbed branched polymers, have also been the subject of specific simulation studies (3–5).

Nevertheless, numerical models have the following shortcomings:

(1) Numerical models are very sensitive to initial data, error of calculations, and selection of the random number generator.

(2) The physical sense of obtained numerical results is not always clear.

(3) It is difficult to distinguish physical tendencies, as they are calculated, from eventual errors.

Below, we consider only analytical models.

Statistical Models

The statistical approach is based on the Flory–Stockmayer concept of branching trees. The mathematical techniques of this approach use probability generating functions. The building (monomer) units and molecules are represented by graphs. The collection of branched molecules in the system is represented by a collection of molecular trees composed of monomers. This collection is transformed into a collection of rooted trees by choosing every monomer unit (node) for the root with the same probability and placing it on generating zero (6). The covalently bound units appear in the first, second, etc. generations with respect to the unit in the root. This transformation provides two

principal consequences: (1) the distribution of units in the root represents the distribution of units in the system, and (2) an N -mer is rooted N times so that it appears in the collection of rooted trees—the rooted forest— N times. The transformation into the rooted trees is performed in order to be able to generate the trees using simple probabilistic considerations (6). The monomer units differ in the number of reacted functional groups. For a single-component system, this distribution is sufficient for building trees. It is assumed that the reactivity of a group in a unit does not depend on the state of groups in neighboring units (6).

Thus, in the mathematical sense, the main characteristic of a polymeric system (in the statistical approach) is a probability generating functions (PGF), which is defined for the number of bonds issuing from an f -functional monomer in the root $F_0(z)$ as

$$F_0(z) = \sum_{i=1}^f p_i z^i. \quad [1]$$

In Eq. [1], p_i is the probability of finding a monomer unit in the root having i issuing bonds. This probability is equal to the fraction of units with i reacted functional groups; z is a variable of the generating function through which the operations with PGF are performed (6).

The statistical approach is applicable to two opposite kinds of systems: polymers in equilibrium, for which the sequence of reactions leading to their formation is not important, and polymers formed due to eventual interaction of radicals. Obviously, in real practice, the equilibrium situation is much more important, especially for aggregates.

One of the principal shortcomings of the statistical approach is due to the assumption that structures having various shapes are formed with the same probability. Other drawbacks of this approach will be considered below.

Another statistical method for the study of branched structures, based on the assumption of a given configuration of branched polymers on the lattice uniquely characterized by specifying of the total number of monomers, the number of chemical bonds, the total number of k -functional sites ($k = 1, 2, 3, \dots$), the total number of loops in all the polymers, and the number of polymers was developed in (5, 7–11). In many cases, the equilibrium distribution of the polymers is assumed (7–10). This approach allows solution of some problems regarding the behavior of polymers on the interface. However, not all assumptions in this approach seem acceptable (for example, the applicability of the lattice model is sometimes doubtful).

Kinetic Approach

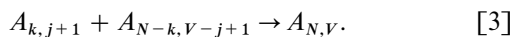
This approach was developed by Kuchanov (12). The polymeric system is described by an infinite set of

differential equations for the concentration of each N -mer. There are two principal schemes realizing this approach.

1. Random irreversible step polyaddition of an f -functional monomer. Each macromolecule is characterized by its degree of polymerization N and the number of unreacting groups $V(N)$. For a tree structure, V is found from the following equation (6, 12):

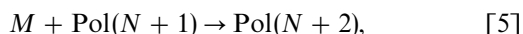
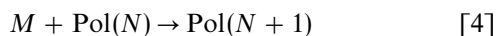
$$V(N) = N(f - 2) + 2. \quad [2]$$

The formation of an N -mer having V unreacting groups ($A_{N,V}$) is described by the following equation:



The system is described by corresponding kinetic equations for the change of $C_{N,V}$ with time (6, 12).

2. Initiated living polymerization. This process is important for such substances as epoxy resins and described by the following reaction scheme,



where $\text{Pol}(N)$ means N -mer. Also for this case, kinetic equations in the differential form are written and solved (6, 12).

The kinetic approach is applicable only to systems in nonequilibrium, for which the reverse reaction (decomposition of macromolecules) is neglected. As result, this approach cannot be used for derivation/evaluation of thermodynamic functions. Also, in this approach, the problem of equivalence of all shapes of macromolecules (as was mentioned for the statistical approach) persists.

Both statistical and analytical approaches can be employed not only in analytical but also in numerical forms.

The complexity and the large number of equations in the kinetic approach make it less used by researchers, in comparison with the statistical approach.

For both statistical and kinetic approaches, we mention the methodological problem: there is no conjugation between them or with the model describing chain structures (13). A system transformed from nonequilibrium to equilibrium cannot be described by the statistical approach (which is invalid for nonequilibrium) nor by the kinetic approach (which is not applicable to equilibrium). Hence, before the application of such an approach, the researcher must know whether or not the system he deals with is in equilibrium.

In contrast to kinetic and statistical approaches, the statistical polymer method (SPM) considered below brings the necessary conjugations automatically.

Statistical Polymer Method

The concept of statistical polymer method comprises three levels of modeling: (1) single macromolecules with branching (no cross-links), (2) simple macromolecular systems (equilibrium mixtures of macromolecules having branched/cross-linked structure), with estimation of their additive parameters, and (3) complex macromolecular systems, with nonequilibrium, nonadditive parameters.

The statistical polymer method was experimentally tested indirectly (against existing curves of adsorption isotherms measured on microporous materials having branched cross-linked structure (14)) and indirectly (with reproduction of the Trommsdorf effect (15)).

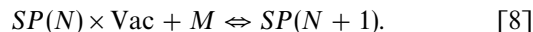
Statistical polymer is defined as the average structure including all possible (taking into account their probability) structures of polymers containing the same number of monomers. This definition allows formulation of all processes in polymeric mixtures in terms of statistical polymers. Reactions of polymerization/destruction (decomposition, depolymerization) are written as



where M is the monomer, and $SP(N)$ is an N -meric statistical polymer (16).

An equilibrium situation is described by a number of independent reactions. Reactions between statistical polymers and monomers [6] and their reverse are chosen as the basis of independent reactions (16).

The capability of an N -mer to accept an additional monomer is characterized by the occurrence of unreacting bonds (defined as *vacancies*), their number being found (for a non-cross-linked situation) as $V_{\Sigma}(N) = (f - 2)N + 2 = (m - 1)N + 2$, where f is the functionality, and $m = (f - 1)$ the number of branching. Independent reactions [6] are written as reactions of occupation of vacancies:



The reverse reaction (transformation of $(N + 1)$ -mer to N -mer) is characterized by removal from the $(N + 1)$ -mer of a monomeric unit having one single bond only with the rest of polymer (otherwise no N -mer obtained but two new polymers). Such monomeric units are defined as *extreme units*. Their number (in the non-cross-linked case) is found from recursive equation:

$$U_{\Sigma}(N + 1) = U_{\Sigma}(N) + 1 - \frac{mU_{\Sigma}(N)}{V_{\Sigma}(N)}. \quad [9]$$

Obviously, $U_{\Sigma}(1) = 1$, $U_{\Sigma}(2) = U_{\Sigma}(3) = 2$.

Below, we use the statistical polymer method for studies of mechanical properties of macromolecular systems.

The rates of direct and reverse reactions [6] are found, respectively, from

$$\begin{aligned} W_+(N+1) &= K_+ V_\Sigma(N) C_1 C_N, \\ W_-(N+1) &= K_- U_\Sigma(N+1) C_{N+1}, \end{aligned} \quad [10]$$

where C_1 and C_N are concentrations of monomers and N -mers, respectively, and K_+ , K_- are constants of direct and reverse reactions [6], respectively. The condition of equilibrium is given by (16)

$$W_+(N+1) = W_-(N+1) \Rightarrow \frac{C_{N+1}}{C_1 C_N} = \frac{K_+ V_\Sigma(N)}{K_- U_\Sigma(N+1)}. \quad [11]$$

For classical polymeric systems, polymerization in equilibrium is not typical. The solution of this problem is much more important for various aggregates. Probably for this reason, no experimental data about weight distribution in equilibrium are found in the literature. However, aggregates such as polymer-like adsorbents were described by the statistical polymer method, and this model was used for treatment of adsorption isotherms; the correlation between experimental and theoretical data was excellent (15).

Cross-Link Formation

The statistical polymer method describes cross-links as internal bonds in polymers; hence, their formation is determined by the same vacancies which cause polymerization. The number of possibilities for cross-link formation is found from (14, 15)

$$C_r = \frac{1}{2} V_\Sigma(N) [N - 1 - B_{0\Sigma}(N)], \quad [12]$$

where $B_{0\Sigma}$ is the number of monomeric units having no vacancies, found from a recursive equation analogous to [9]. The rates of reaction of cross-link formation and destruction are given by the following equations, respectively,

$$W_{c+} = K_{c+} C_r, \quad W_{c-} = K_{c-} G_r, \quad [13]$$

where G_r is the number of cross-links, and K_{c+} and K_{c-} are constants of cross-link formation and destruction, respectively. In equilibrium, the left parts of equations [13] are equal:

$$\begin{aligned} W_{c+} = W_{c-} &\Rightarrow K_{cr} = G_r / C_r \\ &= 2G_r / V_\Sigma(N) / [N - B_{0\Sigma}(N) - 1]. \end{aligned} \quad [14]$$

Let us note that Eqs. [12], [13] are basic not only for equilibrium but also for nonequilibrium system description.

Thermodynamic Functions

Equation [11] can be rewritten as follows

$$\Delta S^0(N) = \Delta S_e^0 + R_g \ln [V_\Sigma(N) / U_\Sigma(N+1)], \quad [15]$$

where $K_0 = K_+ / K_-$. The heat effect of polymerization is $\Delta H^0 = \Delta E_a$, $\Delta H^0 = 2\varepsilon_0$. From Eq. [15] we obtain

$$\Delta S^0(N+1) = R_g [\ln K_0 + \ln V_\Sigma(N) - \ln U_\Sigma(N+1)]. \quad [16]$$

For the case of dimerization:

$$\Delta S^0 = R_g [\ln K_0 + \ln V_\Sigma(1) - \ln U_\Sigma(2)]. \quad [17]$$

From Eqs. [15], [17] follows (15)

$$\Delta S^0(N+1) = \Delta S^0(2) + R_g \ln \left[\frac{2V_\Sigma(N)}{(m+1)U_\Sigma(N+1)} \right]. \quad [18]$$

The chemical potential of the statistical N -mer is found from (15)

$$\mu(N) = \mu^0(N) + R_g T \ln C(N) \quad [19]$$

$$\mu^0(N) = \varepsilon_0 V_\Sigma(N) - M \quad [20]$$

$$M = T \left[NS^0(1) + N\Delta S^0(2) + \sum_{n=1}^N R_g \ln \left[\frac{2V_\Sigma(n-1)}{(m+1)U_\Sigma(n)} \right] \right], \quad [21]$$

where $S^0(1)$ is the entropy of monomer (17, 18).

Evaluation of Additive Parameters of the Polymeric System

All additive parameters are found from the following equation,

$$\Pi_\Sigma = \sum_{N=1}^{\infty} C(N) \Pi(N), \quad [22]$$

where $\Pi(N)$ is the value of evaluated parameter Π for the N -mer.

Fractal Properties

The statistical approach allows description of fractal properties of polymeric structures, comprising percolation

(19). Fractal properties of branched macromolecules with cross-linking can be analyzed by the statistical polymer method as was done in (15). In such a case, both size and volume of the statistical N -mer are found by the statistical polymer method, and then the fractal dimensionality is evaluated from

$$d_f = (\log_{10}(V_2/V_1))/(\log_{10}(R_2/R_1)), \quad [23]$$

where V_1 and V_2 are volumes of N_1 - and N_2 -mers, respectively (both $N_1, N_2 \rightarrow \infty, V_1 = N_1, V_2 = N_2$), and R_1, R_2 are their characteristic sizes.

In the analysis of physical properties of separate macromolecules (presented below) we use the statistical polymer method.

Estimation of Polymer Size in the Statistical Polymer Method

The polymer size estimation is based on the structural considerations in the statistical polymer method presented in (14–16).

A monomer unit in the statistical polymer is chosen as a basis. All other monomer units can be divided into groups located the same distances from the basis. Such distance is expressed in monomer units. The group located at the distance of K monomer units from the basis is characterized (by definition) by $(K + 2)$ -th level. The basis corresponds to the first level, its neighbors form the second level, etc. The total number of levels in the statistical N -mer is N . Each level is characterized by the number of monomer units $R_k(N)$ and vacancies $V_k(N)$. These parameters are found from the following equations (15, 16):

$$R_k(N + 1) = R_k(N) + (mV_{k-1}(N) - V_k(N))/V_2(N) \quad [24]$$

$$V_k(N) = mR_{k-1}(N) - R_k(N) \quad [25]$$

$$R_1(N) = 1, \quad V_1(N) = 0. \quad [26]$$

Equations [24]–[26] allow the evaluation of the characteristic size (“diameter”) of the statistical N -mer, that being defined as (15)

$$Z(N) = \sum_{k=1}^N W_k(N) \quad [27]$$

$$W_k(N) = 1 \text{ if } R_k(N) \geq 1 \quad [28]$$

$$W_k(N) = R_k(N) \text{ if } R_k(N) < 1. \quad [29]$$

Figures 1a, 1b present the dependence of the characteristic size of statistical polymers of different weight on the

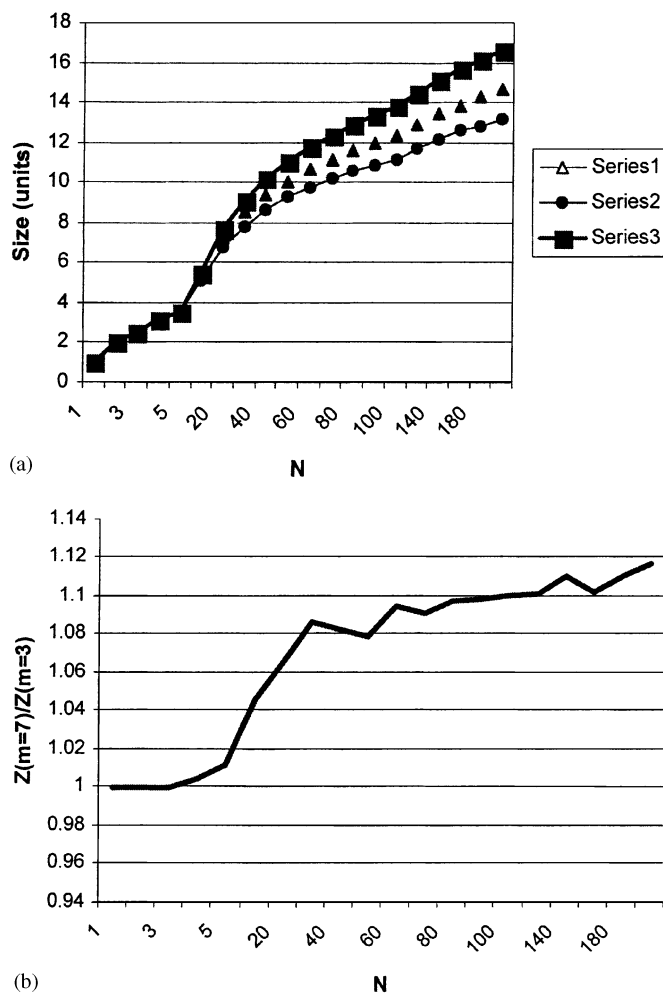


FIG. 1. (a) Characteristic size of statistical N -mer: $m = 3$ (series 1), $m = 7$ (series 2), and $m = 2$ (series 3). (b) Relationship between sizes for $m = 3$ and $m = 7$.

degree of polymerization, for branching numbers 2, 3, and 7; these numbers are frequently found in polymeric and aggregated systems (corresponding to functionality or coordination number 3, 4, or 8, respectively).

We may note that, as follows from Figs. 1a and 1b, the divergence between the curves for $m > 2$ is not large; hence, the number of branching does not influence much the characteristic size. Let us note that, in the practical aspect, the situations $m = 3$ and $m = 7$ are most important; hence, an error in the estimation of m does not cause catastrophic faults in the evaluation of the characteristic size of branched macromolecules.

Equations [24]–[26] are useful also for the evaluation of other averaged structural parameters of branched polymers, e.g., moment of inertia. Rotation of a statistical polymer is characterized by the two following parameters:

$$I_1 = \frac{\sum_{k=1}^N kR_k(N)}{N}; \quad I_2 = \frac{\sum_{k=1}^N kR_k(N)k^2}{NI_1}. \quad [30]$$

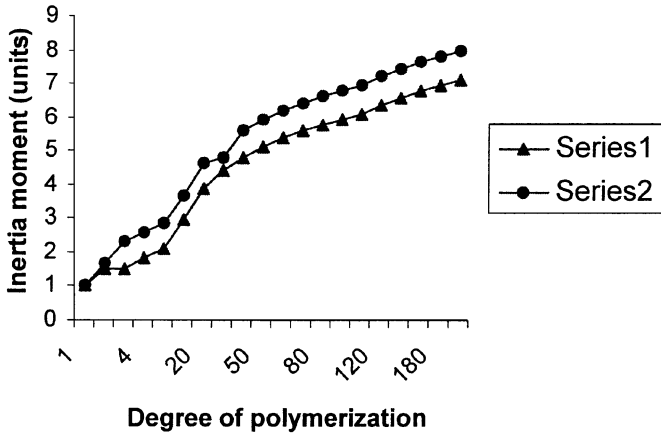


FIG. 2. Inertia moments of rotation of trees ($m = 3$). Series 1, I_1 ; series 2, I_2 .

Figure 2 presents I_1 and I_2 as functions of N at $m = 3$. As follows from Fig. 2, the inertia moments do not significantly change with N at a high degree of polymerization.

Influence of Cross-Linking on the Characteristic Size of the Statistical Polymer

Cross-link formation between monomeric units belonging to k_1 -th and k_2 -th levels ($k_1 < k_2$) is equivalent to the transfer of the unit from the k_2 -th level onto the $(k_1 + 1)$ -th one. Hence,

- (1) cross-linking between the k -th and $(k + 1)$ -th levels does not change the characteristic size;
- (2) if $k_2 > (k_1 + 1)$, all units having more k_2 level and connected with the linked unit on the k_2 -th level are "moved" onto the corresponding levels.

Of course, the assumption of no change of the characteristic size because of cross-linkages inside the k -th level or between the k -th and $(k + 1)$ -th levels is an approximation, but the fraction of such cross-links is so low that the error can be neglected.

The probability of getting cross-linkage between the k_1 -th and k_2 -th levels is

$$P(k_1, k_2) = \alpha_c R_{k_1}(N) R_{k_2}(N) \tag{31}$$

$$\alpha_c = \frac{1}{\sum_{k_1=1}^N \sum_{k_2=1}^N R_{(k_1)}(N) R_{(k_2)}(N)}, \tag{32}$$

where α_c is the normalization coefficient.

The influence of cross-linking on the characteristic size is equivalent to the change of the values of $R_k(N)$,

$$\delta R_k(N) = u_{k+} - u_{k-} \tag{33}$$

$$u_{k+} = \sum_{k_1=k+2}^N v_{(k_1)} \tag{34}$$

$$u_{k-} = \sum_{k_2=1}^{k-2} v_{(k_2)}, \tag{35}$$

where $v_{k_1} = P(k, k_1)$, and $v_{k_2} = P(k, k_2)$.

The change of the characteristic size because of formation of C cross-links in a statistical polymer is equivalent to C times repeated transformation given by Eqs. [31]–[35].

The change of the characteristic size because of cross-linking is given by Fig. 3. We note that, as follows from Fig. 3, the number of cross-links is not as important as their existence itself (meaning even the existence of one single cross-link): even one cross-link changes the characteristic size much more than the formation of second and third links.

Correlation between the Characteristic Size and the Entropy

A statistical N -mer having characteristic size $L(N)$ is able to occupy any position in volume $V(L) = L^3$; hence, a larger value of L means more available microstates and higher entropy. This is found from the following equation:

$$S(L) = R_g [N \ln(V/N) + (V - N) \ln(V/(V - N))]. \tag{36}$$

Cross-linkage reduces the characteristic size ($L \rightarrow L'$, $L' < L$) and, respectively, the entropy,

$$\delta S = R_g [N \ln(V'/V) + (V' - N) \ln(V'/(V' - N)) - (V - N) \ln(V/(V - N))], \tag{37}$$

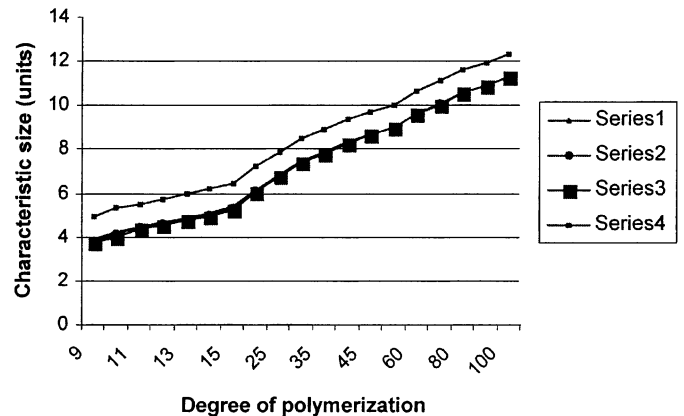


FIG. 3. Size of cross-linked polymers. Series 1, one cross-link; series 2, two cross-links; series 3, three cross-links; series 4, no cross-links.

where $V' = V(L')$. Taking into account that the volume fraction occupied by the macromolecule is not too large in any case, Eq. [37] can be rewritten approximately:

$$\delta S = R_g N \ln(V'/V). \quad [38]$$

Cross-linking delivers energy of two vacancies getting linkage; therefore, the resulting change of free energy is

$$\delta G = 2\varepsilon_0 + T\delta S. \quad [39]$$

The above analysis concerns a single macromolecule with branching and cross-linking. For a system consisting of a number of such macromolecules, their interaction needs to be accounted for.

Inertial and thermodynamic characteristics considered above are additional parameters (or related to several additional parameters); therefore, after they are estimated for separate macromolecules, their values for polymeric mixtures are found from Eq. [22]. However, such properties as mechanical resistance and stability cannot be found without analysis of interactions between macromolecules in mixtures.

Bonds in the Macromolecular Structure

The considered macromolecular system is characterized by the following interior bonds:

(1) intermonomer bonds forming the macromolecules (not cross-linkage);

(2) cross-links, which influence the form and the characteristic size of macromolecules—in their energy of formation they are similar to intermonomer bonds, but their formation reduces much the system entropy, and cross-links may get eventual tension because of the steric factor;

(3) weak intermacromolecular bonds, which form the structure from macromolecules.

Under an exterior pressure, intermacromolecular bonds are destroyed first, this process being completely or partly irreversible. If the pressure loading is accompanied by heating, many cross-links are broken too, also a reversible process. Intermonomer bonds and the rest of the cross-links (that eventually do not cause steric problems to their macromolecules) are destroyed under much higher pressures.

Structure of Macromolecular System

A macromolecular system with branching and without numerous cross-links may have a very high porosity. For several systems, that can be more than 80% (e.g., silica gel (20)). If a macromolecular mixture is treated under pressure, two factors are found reducing the porosity: additional cross-link formation, and interpenetration of macro-

molecules. Interpenetration is understood as a form of interaction of macromolecules that results in finding monomeric units belonging to a macromolecule inside the volume limited by monomeric units belonging to another macromolecule. The physical sense of interpenetration is the occupation of voids inside several macromolecules by other macromolecules.

The condition of additional cross-link formation is given by the same equations [12]–[14], while interpenetration of two or more (μ) macromolecules is possible under condition that

$$\mu < M = 1/(1 - \xi), \quad [40]$$

where ξ is the maximal available local porosity (this corresponds to a system containing infinite macromolecules without cross-links, nor interpenetration); $\xi = (Z^3 - Z^{d_t})/Z^{d_t}$ (Z is found from Eq. [27], $Z \rightarrow$ infinity; d_t is found from Eq. [23]).

A macromolecular system acted on by an exterior pressure P is described by the following equation,

$$P dV_{mm} = dE_{mm}, \quad [41]$$

where dV_{mm} and dE_{mm} are the changes of the volume and the interior energy of the macromolecular system, respectively,

$$dV_{mm} = dV_{cl} + dV_{ip}, \quad [42]$$

$$dE_{mm} = dE_{cl} + dE_{ip}, \quad [43]$$

where the terms with indices “cl” and “ip” mean cross-linking and interpenetration, respectively. For many systems, the cross-linkage does not significantly depend on pressure, and the deformation is determined mostly by interpenetrations.

The whole volume of the macromolecular system can be divided into M zones containing (each) μ interpenetrating macromolecules. For the zones in which interpenetration is not found, we assume (by definition) $\mu = 1$, whereas the maximal available value of μ is M (see Eq. [40]). The value of M is estimated by the statistical polymer method, as described above.

The system is characterized by the distribution function $F(\mu)$ presenting the fraction of monomeric units found in zones of μ times interpenetration. The amount of monomeric units, the volume, the energy, and the entropy are estimated from the following equations:

$$v_\Sigma = \sum_{\mu=1}^M F(\mu) \quad [44]$$

$$V_\Sigma = \sum_{\mu=1}^M \frac{\xi F(\mu)}{\mu} \quad [45]$$

$$E_{\Sigma} = \sum_{\mu=1}^M \varepsilon \mu F(\mu) \quad [46]$$

$$S_{\Sigma} = -R_g \left(\sum_{\mu=1}^M F(\mu) \ln(F(\mu)) \right), \quad [47]$$

where ζ is the averaged porosity, and ε the energy of a single weak bond. Let us assume that the porosity of macromolecules does not directly depend on μ (meaning that the interpenetration does not change the form of macromolecules). For a system close to equilibrium, the entropy is at a maximum; therefore, a little variations of the left terms in Eqs. [44]–[47] gives

$$\sum_{\mu=1}^M \delta F(\mu) = 0 \quad [48]$$

$$\sum_{\mu=1}^M \frac{\delta F(\mu)}{\mu} = 0 \quad [49]$$

$$\sum_{\mu=1}^M \mu \delta F(\mu) = 0 \quad [50]$$

$$\sum_{\mu=1}^M \delta F(\mu) (\ln(F(\mu) + 1)) = 0. \quad [51]$$

From Eqs. [48]–[51] we obtain

$$\sum_{\mu=1}^M \delta F(\mu) \left(\ln F(\mu) + \gamma_1 + \mu \gamma_2 + \frac{\gamma_3}{\mu} \right) = 0 \quad [52]$$

or

$$F(\mu) = A_F \exp(\beta_v/\mu + \beta_e \varepsilon \mu). \quad [53]$$

Equations [48]–[53] provide the complete description of a macromolecular structure with interpenetration.

If interpenetration is accompanied by cross-linking, the contribution of each process to the total mechanical resistance is estimated from the following equations for volume, energy, and entropy:

$$\delta V_{\Sigma} = \delta V_{ip} + \delta V_{cl} \quad [54]$$

$$\delta E_{\Sigma} = \delta E_{ip} + \delta E_{cl} \quad [55]$$

$$\delta S_{\Sigma} = \delta S_{ip} + \delta S_{cl} = \text{maximum} \rightarrow \delta S_{ip} = \delta S_{cl}. \quad [56]$$

Figure 4a presents the value of pressure needed for cross-linking of different macromolecules. As follows from Fig. 4a, the greatest contribution to the mechanical resistance of polymeric materials is due to low-degree macromolecules.

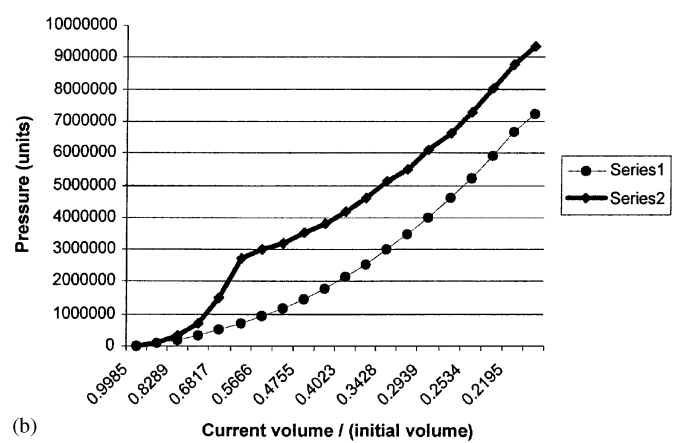
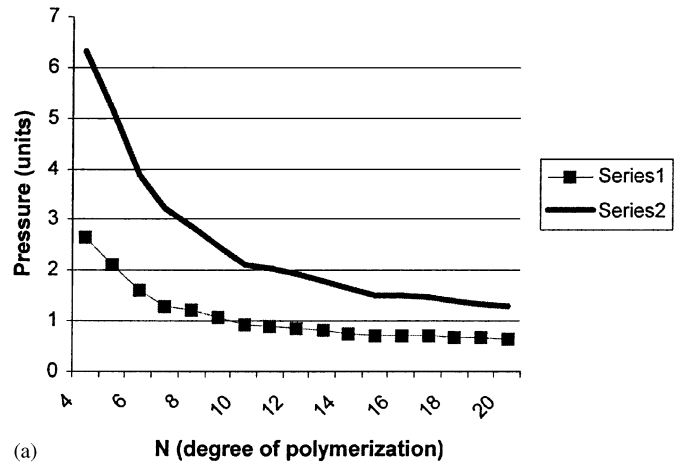


FIG. 4. (a) Pressure needed for cross-linking of macromolecules ($m = 3$). Series 1, energy of cross-linking 10 units; series 2, energy of cross-linking 100 units. (b) Pressure vs volume. Series 1, IP without cross-linking; series 2, cross-linking + IP.

Since cross-linking is high-energy process (in contrast to interpenetration, which is a low-energy process, as noted above), cross-linking takes place mostly under lower pressures (compare to Fig. 4b).

As follows from Fig. 4b, the initial rising of curve 2 is caused by two processes: (1) cross-linking of hard macromolecules, and (2) initial interpenetration. The sharp rising of curve 2 is due to cross-linking of light molecules, while the further rising is due only to interpenetration.

Engineer Evaluation of the Mechanical Resistance of a Polymeric System

The present engineer method is based on the above approach and comprises the following stages of computing:

1. Characterization of separate macromolecules: the initial parameters are the number of branching m (or functionality f), constants of the direct and reverse reactions K_+ ,

K_-, K_{c+}, K_{c-} , (or, for equilibrium, K_0 and K_{cr}). All values $V_{\Sigma}(N)$, $U_{\Sigma}(N)$, C_N , C_r , $\Delta S^0(N)$, $\mu^0(N)$ are found from Eqs. [8]–[21].

2. Characterization of the interior structure of separate macromolecules: values $R_k(N)$ and $Z(n)$ are found from Eqs. [24]–[27]. If necessary, values I_1 and I_2 are found from Eq. [24].

3. Evaluation of the fractal dimensionality and related parameters: the fractal dimensionality is found based on Eq. [23]. The maximal porosity ζ and the maximal number of interpenetration M are then calculated.

4. Evaluation of interpenetration parameters: the interpenetration distribution function is found from Eq. [53]. The function $P(V)$ is computed based on Eqs. [41]–[53].

CONCLUSIONS

A theoretical (thermodynamic) method for the estimation of mechanical characteristics of polymeric systems has been proposed. This method uses the statistical polymer method for modeling of branched/cross-linked structures. The weak interaction between macromolecules has been modeled in terms of the approach of their mutual interpenetration. The proposed method has been used for the estimation of mechanical resistance and stability of microporous polymeric materials. An engineer method for the evaluation of mechanical stability and resistance of polymeric materials is derived.

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