### **REVIEWS OF TOPICAL PROBLEMS**

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# Further research on the improvement of models and computer programs for the prediction and analysis of the physical properties of polymers

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Abstract. Investigations carried out in recent years on the development of models and computer programs for predicting and analyzing the physical properties of polymers are described. The method for constructing diagrams of compatibility of water permeability and the glass transition temperature, density, the thermal expansion coefficient, the cohesion energy, etc. is analyzed. Computer synthesis of network polymers and the possibility of predicting the thermal expansion coefficient of materials based on polyvinyl chloride and the elastic modulus of composites with a number of aromatic polymers are considered. The effect of a solvent (plasticizer) on strength and viscosity is analyzed. Considerable attention is paid to the use of self-oscillations excited during deformation of polymer films in

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Received 9 September 2021, revised 22 November 2021 Uspekhi Fizicheskikh Nauk **193** (6) 625–668 (2023) Translated by V L Derbov actuators of nanomechanical devices. The calculation of the viscosity of dispersions of spherical nanoparticles with an adsorption polymer layer in a polymer melt and in a low-molecular liquid is carried out. The principles of predicting the coefficients of molecular packing of amorphous-crystalline polymers and their solvents are stated, and the influence of the chemical structure of heat-resistant thermoplastics on friction against steel is also estimated.

**Keywords:** diagrams of compatibility of physical properties of polymers, computer synthesis of network polymers, glass transition temperature, cohesion energy, water permeability, thermal expansion coefficient, actuators of nanomechanical devices, strength and viscosity of plasticized polymers, molecular packing coefficients, friction coefficients

### 1. Introduction

In review [1], we considered the following characteristics of polymers: glass transition temperature, yield temperature of polymer nanocomposites, heat conductivity, boiling temperature of polymer solutions, water absorption and water permeability of polymers and nanocomposites, yield strength, viscosity, storage and loss moduli, and dielectric constant.





The present review is devoted to the development of a model and computer program for the automated construction of diagrams of compatibility of water permeability with a number of physical characteristics of polymers, including van der Waals volume and density, cohesion energy, glass transition temperature, and intense thermal degradation onset temperature. Diagrams of the compatibility of water permeability with a number of characteristics are constructed for polymers of various classes: polyethers, polyether ketones, polyamides, etc. In monographs [2, 4], the principle of constructing 'compatibility diagrams' is described. A compatibility diagram is schematically shown in Fig. 1.

As an example, Fig. 2 presents a diagram of compatibility of the glass transition temperature  $T_g$  and the intense thermal degradation onset temperature  $T_d$ . Formulae relating the parameters of the two properties are presented in monograph [5].

At present, much attention is being devoted to numerical methods of predicting polymer properties, which simplify the work of chemists dealing with synthesis. Many physical properties of polymers can be predicted in advance based on their chemical constitution, without lengthy and laborious experiments. Naturally, such work should be computerized, so that the properties are predicted after displaying the chemical constitution of the polymer repeat unit on a monitor. This is the so-called direct problem. The inverse problem is the computer synthesis of polymers possessing the required characteristics, belonging to the specified ranges of their variation input in the computer.

Currently, molecular modeling is becoming more and more sought after for studying the structure of macromolecules and various chemical reactions in which they are involved [6–20]. Methods of molecular modeling also allow studying and solving the problems of nanostructures [21] and creating new polymer materials [22–24].

Monographs and reviews [2–4] thoroughly describe and discuss molecular modeling methods and algorithms and present examples of studying the properties of polymers of various classes.

# 2. Formulae relating water permeability to other characteristics

Since the present review is devoted to obtaining diagrams of compatibility of polymer water permeability with such physical characteristics as glass transition temperature, intense thermal degradation onset temperature, cohesion energy, and density, let us derive the formulae relating these characteristics to water permeability.

Water permeability P of polymers was described in [25, 26] according to the general equation

$$P = P_0 \exp\left(-\frac{\Delta E}{RT}\right),\tag{1}$$

where  $P_0$  is a constant,  $\Delta E$  is the activation energy of the penetration process, R is the universal gas constant, and T is the absolute temperature.

The quantity  $\Delta E$  was described by the relation [25, 26]

$$\Delta E = \frac{\sum_{i} \Delta E_{i}^{**}}{N_{\rm A} \sum_{i} \Delta V_{i}},\tag{2}$$

where  $N_A$  is the Avogadro number,  $\sum_i \Delta V_i$  is the van der Waals volume of the repeat unit of the polymer, and  $\sum_i \Delta E_i^{**}$ is the energy of intermolecular interaction, including the energies of interaction of each atom and the specific groups of atoms, which give rise to dipole-dipole interaction or hydrogen bonds.

Then,

$$\ln P = \ln P_0 - \frac{\sum_i \Delta E_i^{**}}{N_A R T \sum_i \Delta V_i} \,. \tag{3}$$

After some transformations, we have

$$\frac{\sum_{i} \Delta E_{i}^{**}}{RT} - \left(N_{\rm A} \sum_{i} \Delta V_{i}\right) \ln P_{0} = -\left(N_{\rm A} \sum_{i} \Delta V_{i}\right) \ln P \,. \tag{4}$$

Atomic constants and parameters characterizing the energy of strong intermolecular interactions are presented in Refs [25, 26]. The value of  $\ln P_0$  equals 3.002 (20.16 barrer). The correlation coefficient used in the water permeability calculations is 0.98. The glass transition temperature was described by the equation

$$T_{\rm g} = \frac{\sum_i \Delta V_i}{\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 + \left(\sum_i K_i \Delta V_i\right)_{\rm p}},\tag{5}$$

where  $\sum_{i} \Delta V_{i}$  is the van der Waals volume of the repeating fragment of the polymer network,  $(\sum_i a_i \Delta V_i + \sum_i b_i)_1$  is the set of atomic constants for the repeat unit of internode chains, and  $(\sum_i K_i \Delta V_i)_p$  is the set of atomic constants for a network node (see [2] for the physical meaning of parameters  $a_i, b_j$ , and  $K_i$ ). Monograph [2] analyzes the glass transition temperature for 1050 polymers of various structures. The disagreement between the calculated and experimental data is 3-5%, although in a number of cases this value is below 3% or above 5%. The cases of increased discrepancy (>5%) are of primary importance for us, since they are associated with an inaccurate account for intermolecular interactions (dipoledipole and hydrogen bonds). These discrepancies are being eliminated in the new versions of the Kaskad program developed at the Nesmeyanov Institute of Organoelement Compounds (INEOS), Russian Academy of Sciences.

The intense thermal degradation onset temperature is determined from the relation

$$T_{\rm d} = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i} \,, \tag{6}$$

where  $K_i$  are the atomic constants related to the parameters of the Morse potential;  $K_i = (63/2)[R/(ad_0E)_i]$ , *a* and  $d_0$  are the parameters of the Morse potential, and *E* is the chemical bond energy.

In the literature, there are different values of  $T_{\rm d}$  for the same polymer. With this fact taken into account, the correlation coefficients are from 0.911 to 0.934. For copolymers, when calculating the glass transition temperature  $T_{\rm g}$ , the relation is valid in the form

$$T_{g} = \frac{\sum_{k=1}^{k=n} \alpha_{k} \left(\sum_{i} \Delta V_{i}\right)_{k}}{\sum_{k=1}^{k=n} \alpha_{k} \left(\sum_{i} \Delta V_{i}\right)_{k} / T_{g,k} + 0.03 \sum_{k=1}^{k=n} \alpha_{k} \left(1 - \alpha_{k}\right)}, \quad (7)$$

where  $a_k$  is the mole fraction of the *k*th component, *n* is the number of components,  $T_{g,k}$  is the glass transition temperature of the *k*th component, and  $\sum_i \Delta V_i$  is the van der Waals volume of the *i*th component.

The cohesion energy  $\Delta E^*$  is defined by the formula

$$\Delta E^* = \sum_i \Delta E_i^* \,, \tag{8}$$

where  $\Delta E_i^*$  is the contribution of each atom and type of intermolecular interaction to  $\sum_i \Delta E_i^*$ .

The cohesion energy of a repeat unit of a polymer is described by the equation [2]

$$\sum_{i} \Delta E_{i}^{*} = \delta^{2} N_{\rm A} \sum_{i} \Delta V_{i} \,, \tag{9}$$

where  $\delta$  is the solubility parameter (Hildebrand parameter).

For the solubility parameter, there are different values in the literature for the same polymer, because for polymers it is not possible to measure the hidden evaporation heat directly (polymers do not evaporate and are destructured under heating). To assess the parameter of polymer solubility experimentally, the characteristic viscosity is measured and its dependence is plotted versus the solubility of the liquids in which it was measured. The maximum of the dependence corresponds to the solubility parameter accepted for the polymer. With these circumstances taken into account, the correlation coefficients are from 0.958 to 0.971.

The density of polymers  $\rho$  is described by the relation

$$\rho = \frac{Mk}{N_{\rm A} \sum_i \Delta V_i} \,, \tag{10}$$

where *M* is the molecular mass of the repeat unit, and *k* is the molecular packing coefficient (the averaged value is k = 0.681).

The averaged value of the discrepancy between the calculated and experimental data amounts to 3.6%.

Let us derive the expressions relating the water permeability to the rest of the considered characteristics. It is possible, because all equations contain the van der Waals volume of the repeat unit of the polymer. The water permeability and glass transition temperature are related as

$$\ln P = 3.002 - \frac{\sum_i \Delta E_i^{**}}{N_A RTT_g \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)}.$$
 (11)

The water permeability and the intense thermal degradation onset temperature are related as

$$\ln P = 3.002 - \frac{\sum_i \Delta E_i^{**}}{N_{\rm A} R T T_{\rm d} \sum_i K_i \Delta V_i} \,. \tag{12}$$

The relation between the water permeability and the density has the form

$$\ln P = 3.002 - \frac{\rho \sum_{i} \Delta E_{i}^{**}}{RTMk} \,. \tag{13}$$

The water permeability is related to the cohesion energy as follows:

$$\ln P = 3.002 - \frac{\delta^2 \sum_i \Delta E_i^{**}}{RT \sum_i \Delta E_i^{*}}.$$
 (14)

### 3. Construction of compatibility diagrams

Let us consider the result of applying the 'compatibility diagram' method and the computer program obtained in Refs [27–29]. We present compatibility diagrams for different classes of polymers containing different numbers of basic fragments. Here, the notion of a basic fragment should be commented on. A basic fragment is the smallest chemical constitution, which cannot be imagined to be 'cut' along the structure axis. In particular, such structures are

$$+ \underset{CH_{3}}{\overset{+}{\underset{CH_{3}}{\overset{+}{\underset{O}}{\underset{O}}{\overset{+}{\underset{O}}{\overset{}}{\overset{+}{\underset{O}}{\overset{\bullet{}}{\overset{\bullet{}}{\overset{\bullet{}}{\overset{\bullet}{\overset{\bullet{}}{\overset{\bullet}{}}{\overset{\bullet}{\overset{}}{\overset{\bullet}{\overset{}}{\overset{}}{\overset{}}{\overset{}}{\overset{}}{\overset{}}{\overset{}}{\overset$$

and many others.

The characteristics and their dimension units in the compatibility diagrams are as follows:

- water permeability (barrer);
- glass transition temperature (K);
- van der Waals volume (nm<sup>3</sup>);
- intense thermal degradation onset temperature (K);
- density (g cm $^{-3}$ );
- cohesion energy (J mol<sup>-1</sup>).

In Refs [27–29], the minimum and maximum values of water permeability were calculated for polymers of different classes. The number of polymers 'synthesized' by means of a computer depends on the number of basic fragments introduced to construct the repeat units. For polyolefins, vinyl polymers, and polystyrenes, the repeat unit consists of two basic fragments. For polyketones, polyetherketones, complex polyethers, and polycarbonates, the number of basic fragments in the repeat units can exceed four. For the numerical calculations carried out, the number of basic fragments was chosen equal to five or six [27–29].

As an example, let us consider diagrams of the compatibility of water permeability with the above characteristics for polycarbonates having six basic fragments (the general number of structures being of the order of  $2 \times 10^3$ ): in the compatibility diagrams, a shift towards smaller values of water permeability is seen (Fig. 3a–d) in the distribution of characteristics.

The diagrams of compatibility of various properties of polymers were constructed using a computer program implemented in Python 3.9. This version is distributed under the free Python Software Foundation License that allows using it without limitations. Since Python 3.9 can work with any OS, including MS Windows, Mac OS, and Linux, as well as Android and iOS, the program can be assembled for any of the above operational systems.

Based on studies carried out in Refs [27-29], it is possible to make the following conclusions. The method of 'compatibility diagrams' allows choosing polymers that have the prescribed properties, namely, water permeability, density, cohesion energy, glass transition temperature, and intense thermal degradation onset temperature. Upon expanding the intervals for water permeability and increasing the number of basic fragments in the repeat unit, the number of structures approaches many tens of thousands. From a number of polymers (polyurethanes, polysulfones, polysulfides, simple and complex polyethers, polyamides, polyketones, and polyetherketones), it is possible to choose a huge number of structures possessing a relatively low water permeability. The choice of structures with high water permeability is substantially limited. For polyolefins, vinyl polymers, and acrylic and metacrylic polymers, the choice of structures with high and low water permeability is always limited. The reason, as was mentioned above, is that the repeat units in polymers of this group are synthesized from two basic elements, whereas for the remaining polymers they consist of five or six basic fragments.

Table 1 presents the number of structures falling within each of five intervals of water permeability, which differ depending on the maximum value of water permeability for each class of polymer [28, 29].



Figure 3. Diagrams of compatibility of water permeability with a number of characteristics for polycarbonates with six basic fragments [28, 29].

Polymer class		W	ater permeability interv	vals					
Complex polyethers	0–6000	6000-12,000	12,000-18,000	18,000–24,000	24,000-30,000				
	Number of structures								
	24,596	3368	979	476	81				
Polyketones,		W	ater permeability interv	vals					
polyetherketones	0-5100	5100-10,200	10,200–15,300	15,300-20,400	20,400-25,500				
	Number of structures								
	23,296	1552	372	200	80				
Polyolefins,	Water permeability intervals								
vinyl polymers	0–500	500-1000	1000-1500	1500-2000	2000–2570				
	Number of structures								
	12	5	3	2	2				
Polystyrenes	Water permeability intervals								
	0-30	30–60	60–90	90–120	120–150				
	Number of structures								
	7	14	1	3	0				
Polycarbonates		W	ater permeability interv	vals					
	0-800	800-1600	1600-2400	2400-3200	3200-4000				
			Number of structures						
	1567	342	159	76	16				

Table 1. Number of polymer structures in various intervals of water permeability.

From Table 1, it is seen that the maximum number of structures of polymer repeat units corresponds to the range of the lowest water permeability.

### 4. Computer synthesis of network polymers

References [30, 31] proposed the model and structural principle of the corresponding computer program for electronic synthesis of polymer networks having a specified interval of glass transition temperatures  $T_g$ . The repeating fragment of the network is synthesized from the smallest basic fragments connected with each other by means of the controlling matrix of interactions. Presented are 78 nodes of the network, as well as 54 basic fragments for constructing internode chains and the repeating fragments of network polymers, whose glass transition temperatures fall within the specified interval.

The problem of predicting the temperature  $T_g$  and other physical properties of network polymers based on their chemical constitution was thoroughly considered in monographs [2–5]. In monographs [32, 33], such an approach is absent: instead, only corrections to the methods of calculating linear polymers are made, which make it possible to estimate the values of  $T_g$  in network polymers.

Earlier, in Refs [2–5], a model and computer program that allowed implementing the computer synthesis of *linear* polymers were developed. The synthesis is performed using the smallest basic fragments, which cannot be 'cut' along the macromolecule axis. In Table 2, a number of such fragments are presented.

Table 2 also shows the chemical constitution of each basic fragment. The lengths of bonds with the neighboring

chemically bound atoms are indicated. The labels characterizing the possibility of chemical binding with this or that atom from the left and from the right during polymer chain formation are pointed out. Finally, in the last column of the table, a numerical value of the van der Waals volume of the basic fragment is given.

In Refs [30, 31] devoted to the computer synthesis of network polymers, linear chains are structural elements of a repeating fragment that connect the nodes. For fine-mesh polymers, the variety of repeating fragments of the network in the course of its computer synthesis is achieved by setting a relatively large number of basic fragments. In Refs [2–5], 96 basic fragments were used, partially presented in Table 2. The remaining basic fragments are introduced in the present review, and all the above calculations are carried out for them. The larger the number of basic fragments specified by the user before the beginning of computer synthesis, the greater the number of network structures that can be synthesized.

The possibility of attaching this or that atom to a basic fragment in the process of computer synthesis is determined by the so-called connection matrix, presented in Table 3.

In addition to what is mentioned above, in Refs [2–5] the influence of the uniform and nonuniform distribution of the number of repeat units in linear chains connecting the nodes was analyzed, and an analysis of the effect of network structure inhomogeneities (dangling chains and aliphatic cycles) on  $T_g$  was carried out.

Let us proceed to a direct consideration of the principles of computer synthesis of network polymers. In Refs [2–5], how the features of the chemical constitution of network

Fragment number	Chemical constitution of the fragment	Lengths with adjace	Lengths of bonds with adjacent atoms, Å			Van der Waals volume, Å <sup>3</sup>
		Left	Right	Left	Right	
1		1.48 1.54	1.48 1.54	1	1	17.1
		1.54	1.50	1	4	20.2
		1.50	1.50	4	4	23.3
		1.54	1.37	1	6	18.6
2	—{ сн_}	1.48 1.54	1.48 1.54	2	2	34.2
	ČH <sub>3</sub>	1.54	1.50	2	4	37.8
3	CH <sub>3</sub>	1.48 1.54	1.48 1.54	2	2	51.3
		1.54	1.50	2	4	54.9
4	← CH → └ CH <sub>2</sub> − CH <sub>3</sub>	1.48 1.54	1.48 1.54	2	2	51.3
5	CH- CH- O-CH <sub>3</sub>	1.48 1.54	1.48 1.54	2	2	43.9
6	CI CH	1.48 1.54	1.48 1.54	2	2	31.9
7	CI	1.48 1.54	1.48 1.54	2	2	46.8
		1.48 1.54	1.48 1.54	2	2	46.65
	CI	1.48 1.54	1.48 1.54	2	2	46.65
8	+ сн +	1.48 1.54	1.48 1.54	2	2	92.6
		1.54	1.50	2	4	96.2
9		1.48 1.54	1.48 1.54	2	2	107.5
10		1.48 1.54	1.48 1.54	2	2	109.8
11	F [ ]	1.48 1.54	1.48 1.54	1	1	27.1
		1.48 1.54	1.48 1.54	1	1	27.1

# Table 2. Table of basic fragments for constructing internode chains.

# Table 2. (continued)

Fragment number	Chemical constitution of the fragment	Lengths with adjace	of bonds nt atoms, Å	La	bels	Van der Waals volume, Å <sup>3</sup>
		Left	Right	Left	Right	
12		1.48 1.54	1.48 1.54	2	2	18.6
		1.54	1.37	2	6	20.1
	Ö	1.50	1.50	4	4	24.8
		1.37	1.37	4	4	17.6
13	$- \begin{bmatrix} CF_3 \\ I \\ C \\ I \\ CF_3 \end{bmatrix}$	1.48 1.54	1.48 1.54	2	2	81.1
14		1.48 1.54	1.48 1.54	2	2	55.0
15		1.48	1.48	3	3	75.6
		1.48	1.37	3	5	78.8
		1.37	1.37	5	5	82.1
		1.48	1.37	3	6	77.4
		1.37	1.37	5	6	80.6
		1.37	1.37	6	6	79.2
	~	1.76	1.48	7	3	76.8
		1.76	1.76	7	7	78.0
		1.76	1.37	7	6	78.6
		1.76	1.37	7	5	80.0
16		1.48	1.48	3	3	75.6
		1.48	1.37	3	5	78.8
		1.37	1.37	5	5	82.1
		1.48	1.37	3	6	77.4
		1.37	1.37	5	6	80.6
		1.37	1.37	6	6	79.2
		1.76	1.48	7	3	76.8
		1.76	1.76	7	7	78.0
		1.76	1.37	7	6	78.6
		1.76	1.37	7	5	80.0
17		1.37	1.37	5	5	115.5
18		1.50	1.50	8	8	3.4
		1.50	1.50	9	8	2.7
	ŢŸŢ	1.50	1.50	9	9	2.1
		1.64	1.64	10	10	0.5
19		1.54	1.50	2	8	25.1
		1.54	1.37	2	9	24.4

# Table 2. (continued)

Fragment number	Chemical constitution of the fragment	Lengths with adjace	of bonds ent atoms, Å	La	bels	Van der Waals volume, Å <sup>3</sup>
		Left	Right	Left	Right	
20		1.37	1.48 1.54	11	14	28.4
21		1.37	1.37	11	11	8.5
22	[- s -]-	1.76	1.76	12	12	16.5
23		1.76	1.76	12	12	26.1
24		1.37	1.37	11	11	144.6
25		1.37	1.37	11	11	190.2
26		1.37	1.37	5	11	113.4
		1.48	1.37	3	11	110.1
		1.76	1.37	7	11	111.3
27	NH 1	1.37	1.48	3	5	103.4
		1.76	1.48	7	3	101.3
28	$ \begin{array}{c} CH_3 \\ \downarrow \\ Si \\ \downarrow \\ CH_3 \end{array} $	1.64	1.64	13	13	71.6
29		1.37	1.37	11	11	25.6
30		1.37	1.37	6	6	124.8
		1.48	1.48	3	3	121.3
31		1.37	1.37	11	9	39.7
32		1.37	1.37	11	11	38.8
33		1.54	1.54	2	2	43.1
34		1.54	1.54	2	2	47.2
35	CF	1.54	1.54	2	2	37.0

# Table 2. (continued)

Fragment number	Chemical constitution of the fragment	Lengths with adjace	Lengths of bonds with adjacent atoms, Å		bels	Van der Waals volume, Å <sup>3</sup>
		Left	Right	Left	Right	
36	$\begin{array}{c} - \begin{array}{c} - \begin{array}{c} CH \end{array} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	1.54	1.54	2	2	79.5
37	$CH_{3}$ $- CH_{2}$ $CH_{3}$ $C$ $C$ $CH_{2} - CH_{3}$	1.54	1.54	2	2	96.5
38		1.54	1.54	2	2	62.5
39	CH CH C C C C C C C C C CH CH CH CH CH C	1.54	1.54	2	2	113.5
40	$ \begin{array}{c} CH_3 \\ \hline \\ C \\ \hline \\ C \\ \hline \\ \\ O \end{array} $	1.54	1.54	2	2	130.5
41	$CH_{3}$ $(CH_{3})$	1.54	1.54	2	2	79.5
42		1.54	1.54	2	2	73.9
43		1.54	1.54	2	2	59.0
44		1.48	1.48	3	3	47.7
45		1.54	1.54	2	2	120.5
46		1.54	1.54	2	2	120.5
47		1.54	1.54	2	2	120.5

### Table 2. (conclusion)

Fragment number	Chemical constitution of the fragment	Lengths with adjace	of bonds nt atoms, Å	La	bels	Van der Waals volume, Å <sup>3</sup>
		Left	Right	Left	Right	
48	CI CI	1.54	1.54	2	2	106.5
49		1.54	1.54	2	2	106.5
50		1.54	1.54	2	2	106.5
51		1.54	1.54	2	2	98.0
52		1.37	1.37	9	9	30.25
		1.50	1.50	8	8	31.65
53	F F	1.48	1.48	3	3	95.6
	[ F F	1.37	1.37	6	6	100.25
54	F $F$ $F$ $F$ $F$ $F$	1.48 1.54	1.48 1.54	2	2	121.1
55	t c t o	1.48	1.48	3	3	108.5
		1.54	1.54	2	2	108.52
56	+c+	1.48	1.48	3	3	156.0

polymers affect their properties is thoroughly analyzed, in particular, the glass transition temperature  $T_g$ . The value of  $T_g$  is calculated using the following formula:

$$T_{\rm g} = \frac{\left(\sum_i \Delta V_i\right)_{\rm r.f.}}{\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 + \left(\sum_i K_i \Delta V_i\right)_{\rm c.p.}},\tag{15}$$

where  $(\sum_i \Delta V_i)_{r.f.}$  is the van der Waals volume of a repeating fragment of the network,  $(\sum_i a_i \Delta V_i + \sum_j b_j)_1$  is the set of atomic constants  $a_i$  and increments  $b_j$  for linear chains contained in the repeating fragment of the network, and  $(\sum_i K_i \Delta V_i)_{c.p.}$  is the set of atomic constants for the nodes of the network.

Labels	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	1	1	1	0	0	0	0	0	0	0	0	0	0	0
2	1	0	1	0	0	0	0	0	0	0	0	0	0	0
3	1	1	1	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	1	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	1	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	1	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	1	0	0
8	0	0	0	1	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	1	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	1	0
11	0	0	0	0	0	1	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	1	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	1	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	1

**Table 3.** Matrix of labels controlling the computer synthesis of polymers.

The values of  $a_i$ ,  $b_j$ , and  $K_i$  are present in Refs [2–5], where the definition of a network node (i.e., of which atoms a node consists) is also given. Table 4 shows a number of atoms and atomic structures giving rise to chain branching. There is a total of 27 such structures forming nodes of polymer networks in this review.

Table 4. Chemical constitution of a network node.\*

As an example, let us choose an interval of glass transition temperatures for network polymers from 450 to 480 K. The program 'synthesizes' a variety of repeating fragments of polymer networks, from which we choose, for example, only five structures (Table 5). All the values of  $T_g$  fall within the given interval of temperatures.

Therefore, Refs [30, 31] show a possibility in principle of carrying out the electronic synthesis of not only linear polymers, which we have developed earlier [2–5], but also network polymers. Further work in this area is related to considering the network topology. Indeed, with a similar chemical constitution of basic fragments and their number, as well as similar nodes, the chemical constitutions of polymer networks can be different. This depends on where the links of the chains are located, to say nothing of the structure defects (the formation of cycles, the presence of branching chains, one end of which is not attached to the network structure, etc.). Here is an example of this effect. For radiation cross-linked polymer chains of polyethylene, the following structure is possible:



Fragment of network node		Bond lengt	h, Å (labels)	Van der Waals	$\sum_{i} K_i \Delta V_i$ ,		
	Left	Right	Bottom	Тор	volume, A <sup>3</sup>	K A	
ССН—С	1.54 (2)	1.54 (2)	1.54 (2)	_	11.0	15.00	
CN   N	1.54 (14)	1.40 (6)	1.40 (6)		14.1	18.53	
NN       	1.40 (14)	1.40 (6)	1.40 (6)		17.6	20.25	
CC	1.40 (11)	1.40 (11)	1.40 (11)	_	1.5	3.78	
ССн—С   0	1.54 (2)	1.54 (2)	1.50 (4)		14.2	15.00	
ССНС	1.54 (2)	1.54 (2)	1.40 (11)		12.6	15.00	
CC	1.54 (2)	1.54 (2)	1.54 (2)	1.54 (2)	5.0	5.75	

# Table 4. (continued)

Fragment of network node Bond length, Å (la					Van der Waals	$\sum_{\mathbf{K}_i} K_i \Delta V_i$ ,	
	Left	Right	Bottom	Тор	volume, A <sup>3</sup>	$K^{-1} A^3$	
CC	1.8 (2)	1.88 (2)	1.64 (13)	1.64 (13)	27.6	24.84	
CO CO C C	1.64 (13)	1.64 (13)	1.88 (2)		49.6	58.9	
OO	1.64 (13)	1.64 (13)	2.32 (10)		49.6	58.9	
СС	1.48 (3)	1.48 (3)	1.37 (5)		72.5	90.32	
CC	1.48 (3)	1.48 (3)	1.37 (6)	_	71.1	88.71	
сс сс	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	63.1	77.08	
сс сс	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	63.1	77.08	
NN NN	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	70.2	85.36	
	1.48 (3)	1.48 (3)	1.48 (3)		83.3	126.7	
CC F C	1.48 (3)	1.48 (3)	1.48 (3)	_	84.3	102.5	
CC CC CI	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	90.7	159.7	

Fragment of network node		Bond lengt	h, Å (labels)	Van der Waals	$\sum K_i \Delta V_i$ ,	
	Left	Right	Bottom	Тор	volume, A <sup>3</sup>	$K^{-1} A^3$
CC CC F	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	73.1	87.86
СС	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	108.6	134.15
сс сс	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	108.6	134.15
NN NN	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	115.8	142.43
NN NN	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	115.8	142.43
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	164.0	299.3
cs	1.48 (3)	1.76 (7)	1.48 (3)		70.5	88.02
	1.40 (11)	1.40 (11)	1.40 (11)	_	70.35	122.17
* In the table, we indicate the lengths of the	1.37 (5)	1.37 (5)	1.37 (5)		65.7	98.52

(16)

### Table 4. (conclusion)

This network is four-functional, i.e., four chains come out from its node. For such a network, the glass transition temperature is calculated according to the relation

 $T_{\rm g}$ 

$$=\frac{2(m-2)\left(\sum_{i}\Delta V_{i}\right)_{1}+4\left(\sum_{i}\Delta V_{i}\right)_{1}^{*}+\left(\sum_{i}\Delta V_{i}\right)_{cr,p}}{2(m-2)\left(\sum_{i}a_{i}\Delta V_{i}+\sum_{j}b_{j}\right)_{1}+4\left(\sum_{i}a_{i}\Delta V_{i}+\sum_{j}b_{j}\right)_{1}^{*}+\left(\sum_{i}K_{i}\Delta V_{i}\right)_{cr,p}},$$

where  $(\sum_{i} a_i \Delta V_i + \sum_{j} b_j)_1$  is the set of atomic constants and increments for the repeat unit of linear internode chains,  $(\sum_{i} a_i \Delta V_i + \sum_{j} b_j)_1^*$  is the same for the end units directly attached to cross-linked points,  $(\sum_{i} K_i \Delta V_i)_{\text{cr.p}}$  is the set of atomic constants for the network nodes, and *m* is the number of repeat units in internode chains.

Using the proposed approach and the appropriate equations, it is possible to construct polymer networks of various topologies with an unchanged chemical constitution.

No.	Chemical constitution of repeating fragment	Glass transition temperature $T_{g}$ , K
1	$\begin{array}{c} + CH_2 - CH CH_2 - H_2 \\ I \\ CH_2 \\ CH_2 \\ CH_2 \\ + \end{array}$	474
2	$+CH_2 - + + + + + + + + + + + + + + + + + + $	479
3	$\begin{array}{c} CH_2-CH_2-CH_2 \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	457
4		473
5	+ NH + NH + NH - CH <sub>2</sub> -CH <sub>2</sub> +	465

 Table 5. Repeating fragments of polymer networks and their glass transition temperature.

# **5.** Possibilities of predicting thermal expansion coefficient of materials based on polyvinyl chloride

Polyvinyl chloride (PVC) is one of the main polymers used to obtain a variety of materials. In the present review, we consider the problem of reducing the thermal expansion coefficient of polyvinyl chloride by mixing it with heatresistant polymers possessing a high glass transition temperature: polyimides, complex polyethers, polyetherketones, polysulphides, and polyphenylene oxides. The prediction of the thermal expansion coefficient based on polyvinyl chloride is of importance because, in a number of technical applications, a minimum distortion of dimensions with a change in temperature is required. Based on Refs [2–5], we derived an equation for calculating the thermal expansion coefficient of polymers,

$$a_{\rm L} = \frac{1}{3} \frac{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \alpha_i \Delta V_i + \sum_j \beta_j\right)_k}{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k} , \qquad (17)$$

where  $\alpha_i$  are the coefficients of volume thermal expansion caused by the weak dispersion interaction of the *i*th atom with the neighboring atoms,  $\beta_j$  are parameters characterizing the contribution of each type of specific intermolecular interaction (dipole–dipole, hydrogen bonds) to the thermal expansion coefficient,  $\sum_i \Delta V_i$  is the van der Waals volume of the repeat unit of the polymer or the repeating fragment of the polymer molecular network,  $\alpha_k$  is the molar fraction of the component *k*, and *n* is the number of components. The coefficient of linear thermal expansion of a polymer can be expressed in terms of the values of the analogous coefficients  $\alpha_{G,k}$  for the components:

$$\alpha_{\rm L} = \frac{1}{3} \frac{\sum_{k=1}^{k=n} \alpha_k \alpha_{\rm G,k} \left(\sum_i \Delta V_i\right)_k}{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k} \,. \tag{18}$$

To reduce the thermal expansion coefficient of PVC, it is possible to prepare mixtures of PVC with other polymers. This is allowed by the criterion of compatibility of polymers, described in detail in Refs [2–5]. The criterion is based on the analysis of surface forces arising upon merging the polymer body in a liquid, as well as on considering the specific intermolecular interactions between the polymer and the solvent. The criterion looks like this:

$$\mu \leqslant 1.374 \Phi \left( \Phi - \sqrt{\Phi^2 - 1 + a} \right), \tag{19}$$

where  $\mu = \delta_p^2/\delta_s^2$ ,  $\delta_p$  and  $\delta_s$  are the solubility parameters of the polymer and solvent, respectively,  $a = \gamma_{sp}/\gamma_s$ ,  $\gamma_s$  is the surface tension of the solvent, and  $\gamma_{sp}$  is the interphase tension between the polymer and the solvent.

The interphase tension is calculated using the formula

$$\gamma_{\rm sp} = \gamma_{\rm s} + \gamma_{\rm p} - 2\Phi(\gamma_{\rm s}\gamma_{\rm p})^{0.5}, \qquad (20)$$

where  $\gamma_p$  is the surface energy of the polymer,

$$\Phi = \frac{4(V_{\rm p}V_{\rm s})^{1/3}}{\left(V_{\rm s}^{1/3} + V_{\rm p}^{1/3}\right)^2},\tag{21}$$

and  $V_p$  and  $V_s$  are the molar volumes of the polymer and the solvent, respectively.

Substituting Eqn (20) into Eqn (21), we obtain

$$\mu \leqslant 1.374 \Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_p}{\gamma_s} - 2\Phi \left(\frac{\gamma_p}{\gamma_s}\right)^{0.5}} \right).$$
 (22)

When analyzing the compatibility of two polymers, variants are possible. If one polymer is introduced in a small amount into the other polymer, then, in criterion (22), the first of them is considered a 'polymer' and the second a 'solvent' and vice versa. Let us introduce the notation

$$\beta_{1} = \Phi \left( \Phi - \sqrt{\Phi^{2} + \frac{\gamma_{p1}}{\gamma_{p2}} - 2\Phi \left(\frac{\gamma_{p1}}{\gamma_{p2}}\right)^{0.5}} \right), \qquad (23)$$

$$\beta_2 = \Phi \left( \Phi - \sqrt{\Phi^2 + \frac{\gamma_{p2}}{\gamma_{p1}} - 2\Phi \left(\frac{\gamma_{p2}}{\gamma_{p1}}\right)^{0.5}} \right), \qquad (24)$$

where  $\gamma_{p1}$  and  $\gamma_{p2}$  are the surface energy of polymers 1 and 2, respectively,

$$\Phi = \frac{4(V_{p1}V_{p2})^{1/3}}{\left(V_{p1}^{1/3} + V_{p2}^{1/3}\right)^2},$$
(25)

and  $V_{p1}$  and  $V_{p2}$  are the molar volumes of polymers 1 and 2, respectively.

Here, different situations are possible.

1. If when using criterion (22) it happens that in all cases the left-hand side of the criterion is greater than the righthand one, then an absolute incompatibility takes place. By 'all cases' we mean such cases in which the first polymer is introduced in small amounts into the second one or, vice versa, the second polymer is introduced into the first one in small amounts. The compatibility criterion then takes the form

- for the first polymer introduced into the second one,

$$\mu_1 = \frac{\delta_{p_1}^2}{\delta_{p_2}^2} > 1.374\beta_1 \,, \tag{26}$$

— for the second polymer introduced into the first one,

$$\mu_2 = \frac{\delta_{\rm p2}^2}{\delta_{\rm p1}^2} > 1.374\beta_2 \,. \tag{27}$$

Here,  $\delta_{p1}$  and  $\delta_{p2}$  are the solubility parameters of polymers 1 and 2, respectively.

Since the left-hand side of criteria (26) and (27) is greater than the right-hand side, the polymers are incompatible.

2. Upon introducing a small amount of the first polymer into the second one, criterion (22) shows that the compatibility is observed, i.e.,

$$\mu_1 = \frac{\delta_{\rm p1}^2}{\delta_{\rm p2}^2} < 1.374\beta_1 \,. \tag{28}$$

However, when introducing the second polymer into the first one, it may happen that compatibility is absent, i.e.,

$$\mu_2 = \frac{\delta_{\rm p2}^2}{\delta_{\rm p1}^2} > 1.374\beta_2 \,. \tag{29}$$

This result, paradoxical at first glance, is actually possible, as demonstrated in Ref. [2]. For the considered case, when the first polymer is compatible with the second and the second is incompatible with the first, the dependence of the glass transition temperature on the composition has the form schematically presented in Fig. 4 (curve I). The character of the curves in Fig. 4 is thoroughly analyzed in Ref. [2]; the difference between curve I and curve 2 is due to interphase stratification and improving the compatibility of microphases upon changing the content of the initial polymers in them.

3. The case corresponding to absolute compatibility of polymers, i.e., the first polymer 'dissolves' in the second and the second in the first.



**Figure 4.** Schematic plot of glass transition temperature  $T_g$  versus the mixture composition ( $\alpha$  is the molar fraction on one of the components). *I* — partially compatible polymers, *2* — fully compatible polymers [2].

The compatibility criterion takes the form for the first polymer introduced into the second one,

$$u_1 = \frac{\delta_{p_1}^2}{\delta_{p_2}^2} < 1.374\beta_1 \,, \tag{30}$$

- for the second polymer introduced into the first one,

$$\mu_2 = \frac{\delta_{p2}^2}{\delta_{p1}^2} < 1.374\beta_2 \,. \tag{31}$$

In this situation, one more glass transition temperature  $T_g$  appears, and the dependence of  $T_g$  on the mixture composition has the form schematically shown in Fig. 4 (curve 2).

Thus, the compatibility criterion consists of two parts:  $\mu$  and 1.374 $\beta$ . If the left-hand side of criterion  $\mu$  is smaller than the right-hand side, 1.374 $\beta$ , then the polymers are compatible; if not, then incompatible. Table 6 presents data on the compatibility of PVC with a number of polymers. The signs -- mean that the polymer is incompatible with PVC, the signs -+ mean that this polymer is partially compatible with PVC, and the signs ++ mean the complete compatibility of the polymer with PVC.

The calculated properties of all analyzed polymers are summarized in Table 7.

Structure	Structure is introduced into PVC	PVC is introduced into the structure	Interphase tension, mN m <sup>-1</sup>	$\mu_1$	1.374 β <sub>1</sub>	$\mu_2$	1.374 β <sub>2</sub>
Poly-4-chlorostyrene	+	+	1.52	1.02	1.28	0.98	1.29
Poly-2,6-dichlorostyrene	+	+	2.12	1.11	1.18	0.90	1.26
Polyetheretherketone	+	+	0.60	1.05	1.32	0.95	1.34
Polyetherketone	+	+	0.69	1.09	1.28	0.91	1.31
Polyphenylene sulphide	-	+	7.12	1.16	0.76	0.86	0.96
Ultem	+	+	1.12	1.13	1.25	0.89	1.29
2,6-dimethylphenylene oxide	+	+	2.94	0.89	1.03	1.12	1.12
Polycarbonate	+	+	0.40	1.00	1.34	1.00	1.32
Polysulfone	+	+	1.15	1.17	1.23	0.85	1.27

**Table 6.** Compatibility of PVC with a number of polymers.

Structure	$V_{\rm m},{\rm cm}^3~{ m mol}^{-1}$	$\delta$ , (J cm <sup>3</sup> ) <sup>0.5</sup>	$\gamma, mN m^{-1}$	$T_{\rm g},{ m K}$	<i>T</i> <sub>d</sub> , K	$\alpha_G,10^4\;K^{-1}$	$\alpha_L,10^4\;K^{-1}$
PVC	43.3	19.4	34.2	340	530	2.81	0.94
Poly-4-chlorstyrene	109	19.6	34.4	410	550	2.34	0.78
Poly-2,6-dichlorstyrene	121	20.4	38.4	405	515	2.37	0.79
Polycarbonate	211	19.4	33.0	431	717	2.23	0.74
Polyimide ULTEM	460	20.6	37.4	500	730	1.91	0.64
Polyetheretherketone	232	19.9	35.3	420	780	2.31	0.77
Polyetherketone	157	20.3	36.9	430	760	2.23	0.74
Polysulfone	353	21.0	38.8	467	679	2.05	0.68
Polyphenylene sulphide	83.5	20.9	69.0	363	726	2.64	0.88
Poly-2,6-dimethylphenylen oxide	104	18.3	48.9	442	703	2.17	0.72
Polyarylate F-2	345	21.0	39.6	578	683	1.67	0.56
$*V_{\rm m}$ — mole volume, $\delta$ — solubility parameter, $\gamma$ — surface energy, $\alpha_{\rm G}$ — volume thermal expansion coefficient, $\alpha_{\rm L}$ —linear thermal expansion coefficient.							

Table 7. Calculated properties of polymers.\*



Figure 5. Dependence of linear thermal expansion coefficient (LTEC) on the weight fraction of the second polymer in the mixture with PVC. (a) 1 - poly-4-chlorstyrene, 2 - polycarbonate, 3 - poly-2,6-dimethylphenyleneoxide, (b) 1 - poly-2,6-dichlorstyrene, 2 - Utem, 3 - polyetherketone, (c) 1 - polyetheretherketone, 2 - polysulfone, 3 - polyphenylene sulphide [34].

The calculated values of the linear thermal expansion coefficient (LTEC) are presented in Table 8.

From Table 8, it is seen that the preparation of a mixture of PVC with a number of commercial polymers leads to a substantial reduction in LTEC. Dependences of LTEC on the content of the second polymer in the mixture with PVC are presented in Fig. 5.

Thus, the possibility of a prognosis about the thermal expansion coefficient of materials based on mixtures of polymers with PVC is demonstrated. The calculations have shown that there are many polymer structures that are compatible with PVC or form technological mixtures. All these mixtures possess a reduced value of LTEC as compared to that of the initial PVC. The reduction reaches from 6% to 52%. The higher the glass transition temperature of the polymer added to the mixture with PVC, the greater the decrease in LTEC. Experiments have shown good agreement of calculated and experimental data [34].

**Table 8.** Structures and van der Waals volumes of repeat units  $\sum_i \Delta V_i$  and  $\alpha_L$ .

Structure	$\sum_{\substack{i \\ \text{Å}^3}} \Delta V_i,$	$10^4K^{-1}$
Polyvinylchloride (PVC) $+CH_2-CH_2-CH_1$ CI	48.9	0.94
Poly-4-chlorostyrene +CH <sub>2</sub> -CH	96.4	0.78
Poly-2,6-chlorostyrene $+CH_2-CH_2$ Cl	107	0.79
Polyphenylene sulphide	73.8	0.88

Structure	$\sum_{\substack{i \\ \text{\AA}^3}} \Delta V_i,$	$\overset{\alpha_L,}{10^4}K^{-1}$
Poly-2,6-dimethylphenylen oxide + $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$	92	0.72
Polycarbonate + 0 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -	239	0.74
Polyetheretherketone $+ \swarrow - c - \checkmark - o - \checkmark - o - + \circ - \circ - + \circ - \circ - \circ - \circ - \circ - \circ - \circ$	262	0.77
Polyetherketone $+ \left( \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	178	0.74
Polysulfone $+ \circ - \swarrow - \downarrow_{C+}^{CH_3} \longrightarrow - \circ - \swarrow - \Downarrow_{S}^{0} - \swarrow - \downarrow_{S}^{0}$	399	0.68
Polyarylate F-2 + c	390	0.56
Polyimide Ultem	520	0.64

#### Table 8. (conclusion)

# 6. Predicting the elasticity modulus of composites based on a mixture of polyvinyl chloride and a number of aromatic polymers

Let us consider the methods of predicting the modulus of elasticity of materials based on mixing compatible and incompatible polymers. These materials comprise fine dispersions of one of the polymers in a polymer matrix of another polymer. The following variants will be analyzed: a dispersion of a solid amorphous polymer with a definite chemical constitution in a solid amorphous matrix of a polymer with another chemical constitution; a dispersion of particles of a mineral filler in a matrix of a composite based on a mixture of organic polymers. The dependences of the elasticity modulus on the molar, weight, and volume fraction are determined by the van der Waals volume of the components, the molecular mass of the repeat units, and the density of the components. Let us plot the dependences of the elasticity modulus of polyvinyl chloride mixtures with a number of polymers, including aromatic polyethers, polyetherketones, polysulfone, and polycarbonate. The maximum increase in the modulus of elasticity from 2400 to 3980 MPa is provided by the aniline phthaleine polypyromellitimide.

At present, new polymer materials, as a rule, are being developed by mixing known polymers. The mechanical properties (strength, elasticity modulus, etc.) are currently being studied in a large number of polymer mixtures, but only some studies deal with calculation prognosis methods. Let us briefly consider these studies. For mixtures of polystyrene and ABS plastic, it was found that their mechanical properties are better than the similar properties of the constituent components [35]. The authors explain this fact by the good compatibility of these polymers. Reference [36] considers various calculation methods for estimating the dependence of the elasticity modulus on the mixture composition. These dependences are often extremal and possess maxima, i.e., the elasticity moduli of mixtures can exceed average values for various compositions.

The morphology and properties of mixtures of polystyrene and a copolymer of styrene and acrylonitrile were studied. The measured elasticity moduli of mixtures were compared with the calculated values, which were described using the Doi theory [37]. It was found that the main role is played by an increase in the size of particles due to the change in the interphase tension and viscosity of mixtures. The effect of interphase tension in incompatible mixtures of polymers was studied in a number of papers [38–42]. Much attention was paid to the morphology of mixtures, the dimensions of particles, attempts to prepare finedispersed mixtures, and the effect of all these factors on the modulus of elasticity and other mechanical properties [43–46].

In spite of the large number of papers devoted to the structure and mechanical properties of mixtures, the issues analyzed in the present review do not always find adequate consideration. First, this is related to the possibility of predicting the compatibility of polymers based on their chemical constitution and phase state and an evaluation of the elasticity modulus of the mixture allowing for the phase and physical state of the mixed polymers (dispersion of a solid polymer in an elastomer, dispersion of two solid, glassy or crystalline polymers). In this case, chemical interaction between microphases is possible. All factors mentioned above affect the modulus of elasticity of materials based on polymer mixtures. In this review, we consider a dispersion of solid polymer 1 in solid polymer 2.

To analyze the elasticity modulus E of a mixture of polymers, we use the formula obtained in Ref. [4] and transform it:

$$E = \frac{\alpha_{m,p1} (\sum_{i} \Delta V_{i})_{p1} + \alpha_{m,p2} (\sum_{i} \Delta V_{i})_{p2} + \dots + \alpha_{m,pn} (\sum_{i} \Delta V_{i})_{pn}}{\alpha_{m,p1} (\sum_{i} \Delta V_{i})_{p1} / E_{1} + \alpha_{m,p2} (\sum_{i} \Delta V_{i})_{p2} / E_{2} + \dots + \alpha_{m,pn} (\sum_{i} \Delta V_{i})_{pn} / E_{n}}$$
(32)

In Eqn (32),  $(\sum_i \Delta V_i)_{p1}$ ,  $(\sum_i \Delta V_i)_{p2}$ ,  $(\sum_i \Delta V_i)_{pn}$  are the van der Waals volumes of the repeat units (or repeating network fragments) of polymers 1, 2, and *n*;  $\alpha_{m,1}$ ,  $\alpha_{m,2}$ , and  $\alpha_{m,n}$  are the molar fractions of polymers 1, 2, and *n*; and *E*<sub>1</sub>, *E*<sub>2</sub>, and *E*<sub>n</sub> are the elasticity moduli of polymers 1, 2, and *n*, respectively.

In a more compact form, Eqn (32) is written as

$$E = \frac{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k}{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k / E_k},$$
(33)

where  $\alpha_k$  is the molar fraction of the *k*th component,  $(\sum_i \Delta V_i)_k$  is the van der Waals volume of the *k*th

No.	Polymer	Elasticity modulus <i>E</i> , MPa	Van der Waals volume, $\left(\sum_{i} \Delta V_{i}\right)_{2}, \text{\AA}^{3}$	$\frac{\left(\sum_{i}\Delta V_{i}\right)_{2}}{\left(\sum_{i}\Delta V_{i}\right)_{1}}$	$\frac{M_{\rm p2}}{M_{\rm p1}} \frac{\rho_{\rm p1}}{\rho_{\rm p2}}$
1	Polyetherketone + $         -$	2350	178	3.574	3.613
2	Polyetheretherketone +	2110	205	4.192	5.351
3	Polysulfone $+\circ \longrightarrow \overset{C_{H_3}}{\underset{C_{H_3}}{\overset{C_{H_3}}{\longleftarrow}}} \circ \longrightarrow \overset{0}{\underset{0}{\overset{U}{\longrightarrow}}} \to \to \to $	2280	312	6.380	8.165
4	Polyarylate F-2 + c	2790	390	7.975	7.940
5	Poly-2,6-dimethylphenylene oxide + $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$	1890	92	1.881	2.383
6	Polycarbonate $+ 0 - \sqrt{\begin{array}{c} C \\ C $	1780	187	3.824	4.877
7	Anilinephthalein polypyromellitimide $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$ $\rightarrow$	3980	409	8.364	8.314
8	Polyvinylchloride $- \begin{bmatrix} -CH_2 - CH_1 \end{bmatrix}$ $C_1$	2400	48.9	1.000	
$*\rho_{\rm p1}$ and	d $\rho_{p2}$ are the densities of polymers 1 and 2, respectively.				

Table 9. Moduli of elasticity for a number of polymers.\*

component, and  $E_k$  is the elasticity modulus of the kth component.

Allowing for the fact that for a two-component system we have  $\alpha_{m1} + \alpha_{m2} = 1$ , Eqn (33) can be presented in the form

$$E = \frac{1 + \alpha_{m2} \left[ (\sum_{i} \Delta V_{i})_{2} / (\sum_{i} \Delta V_{i})_{1} - 1 \right]}{1/E_{1} + \alpha_{m2} \left[ (\sum_{i} \Delta V_{i})_{2} / ((\sum_{i} \Delta V_{i})_{1} E_{2}) - 1/E_{1} \right]}.$$
 (34)

In Eqn (34),  $(\sum_i \Delta V_i)_1$  and  $(\sum_i \Delta V_i)_2$  are the van der Waals volumes of the repeat units (or repeating network fragments) of polymers 1 and 2,  $\alpha_{m1}$  and  $\alpha_{m2}$  are the mole fractions of polymers 1 and 2, and  $E_1$  and  $E_2$  are the moduli of elasticity of polymers 1 and 2, respectively.

To obtain the dependence of the elasticity modulus on the weight fraction  $\alpha_w$  of polymers, we use the relation between the molar and weight fractions

$$\alpha_{\rm m2} = \frac{1}{1 + M_{\rm p2}/M_{\rm p1} \left(1/\alpha_{\rm w2} - 1\right)} , \qquad (35)$$

where  $M_{p1}$  and  $M_{p2}$  are the molecular masses of the repeat units of polymers 1 and 2.

Then, the dependence of the elasticity modulus on the weight fraction of the second polymer  $\alpha_{w2}$  will be expressed as

$$E = \frac{1 + \frac{\left(\sum_{i} \Delta V_{i}\right)_{p2} / \left(\sum_{i} \Delta V_{i}\right)_{p1} - 1}{1 + \left(M_{p2} / M_{p1}\right) \left(1 / \alpha_{w2} - 1\right)}}{\frac{1}{E_{1}} + \frac{\left(\sum_{i} \Delta V_{i}\right)_{p2} / \left(\left(\sum_{i} \Delta V_{i}\right)_{p1} E_{2}\right) - 1 / E_{1}}{1 + \left(M_{p2} / M_{p1}\right) \left(1 / \alpha_{w2} - 1\right)}}.$$
(36)

Let us estimate the dependences of the elasticity modulus on the molar fraction of the second polymer, added to the mixture with polyvinyl chloride. The estimates are carried out using Eqn (34), which includes a number of physical parameters. These parameters are presented in Table 9 for polymers of various classes, compatible with polyvinyl chloride, according to data from Ref. [34]. Since the review topic is predicting the elasticity moduli for mixtures of polymers, we will estimate all physical parameters of the polymers by calculations. The elasticity modulus upon stretching is calculated by the Bicerano method [32] using the DWT PDtools computer program. The van red Waals volume ( $\sum_i \Delta V_i$ ) and density  $\rho$  of the polymers are calculated by means of the Kaskad program.



**Figure 6.** Dependence of elasticity modulus on molar fraction of the second polymer. Curve numbering corresponds to polymer numbering in Table 9 [34].

The obtained dependences of the elasticity modulus on the molar fraction of the second polymer are shown in Fig. 6. It is seen that a number of polymers (nos 1, 2, 3, 5, 6) somewhat decrease the polyvinyl chloride elasticity modulus when introduced into the mixture composition. Other polymers (nos 4, 7) increase the elasticity modulus. At relatively low concentrations, the modulus of elasticity rapidly grows upon increasing the concentration of the added polymer, and then the growth slows down.

Let us now analyze the dependences of E on the volume fraction of polymer 2. The molar fraction is related to the volume fraction as

$$\alpha_{\rm m,2} = \frac{1}{1 + (M_{\rm p2}/M_{\rm p1}) (\rho_{\rm p1}/\rho_{\rm p2}) (1/\beta_2 - 1)}, \qquad (37)$$

where  $M_{\rm p1}$  and  $M_{\rm p2}$  are the molecular masses of the repeat units of polymers 1 and 2,  $\rho_{\rm p1}$  and  $\rho_{\rm p2}$  are their densities, and  $\beta_2$  is the volume fraction of polymer 2.

Substituting Eqn (37) into Eqn (34) allows describing the dependence of the elasticity modulus on the volume fraction of polymer 2:

$$E = \frac{1 + \frac{\left(\sum_{i} \Delta V_{i}\right)_{p2} / \left(\sum_{i} \Delta V_{i}\right)_{p1} - 1}{1 + \left(M_{p2} / M_{p1}\right) \left(\rho_{p1} / \rho_{p2}\right) \left(1 / \beta_{2} - 1\right)}{\frac{1}{E_{1}} + \frac{\left(\sum_{i} \Delta V_{i}\right)_{p2} / \left(\left(\sum_{i} \Delta V_{i}\right)_{p1} E_{2}\right) - 1 / E_{1}}{1 + \left(M_{p2} / M_{p1}\right) \left(\rho_{p1} / \rho_{p2}\right) \left(1 / \beta_{2} - 1\right)}}.$$
(38)

Figure 7 demonstrates the dependences of E on  $\beta_2$ . These dependences are qualitatively similar to those of the elasticity modulus on the molar fraction of the second polymer. It can be seen from them that the elastic modulus can increase by a relatively small amount, but in most cases it decreases when a second polymer is introduced into the mixture.

In Ref. [34], the elasticity modulus is also calculated using Eqn (36) for all concentrations of a mineral filler and a comparison with experimental data is carried out. As a result, the dependence of the elasticity modulus on the  $CaCO_3$  concentration is obtained, as shown in Fig. 8. It can be concluded that the experimental values of the elasticity modulus coincide with the calculated values.

Thus, the possibility of calculating elastic moduli of materials based on polymer mixtures is demonstrated by the example of a dispersion of solid polymer 1 in solid polymer 2,



**Figure 7.** Dependence of elasticity modulus on the volume fraction of the second polymer. Curve numbering corresponds to polymer numbering in Table 9 [34].



**Figure 8.** Dependence of elasticity modulus on the weight fraction of CaCO<sub>3</sub> with respect to the wood filler. Curve —calculated results; squares — results of experiment [34].

as well as by the example of a dispersion of a mineral filler in a solid polymer matrix. The dependences of elasticity moduli on the molar and volume fraction have different forms associated with the van der Waals volume of the components, the molecular mass of the repeat units, and the density of components. It is established that the modulus of elasticity grows when increasing the concentration of polymers having a high glass transition temperature in the mixture with PVC. The addition of a mineral filler to the mixture of PVC with natural polymers facilitates an increase in the modulus of elasticity.

# 7. Effect of a solvent (plasticizer) on yield strength and viscosity

In Ref. [47], the effect of chemical composition and concentration of components in a polymer-solvent (plasticizer) mixture on the yield strength and viscosity is analyzed and the appropriate calculation scheme is developed. The chemical constitution of the polymer and solvent, intermolecular interaction between the polymer and solvent, the van der Waals volume and molecular mass of the repeating polymer unit and the solvent molecule, and the solvent concentration are taken into account. Temperature dependences of the viscosity are obtained. The calculation scheme is computerized and included in a separate option of the Kaskad program.

Parameter	PMMA	DBP
Van der Waals volume, $Å^3$	96.4	280
Yield strength, MPa	62.3 (at 40 °C)	—
Molecular mass, $M_0$	100 (for a repeat unit)	278

Table 10. Physical parameters of the PMMA-DBP system.

Rheological properties of polymer solutions are important for both theory and practice, the latter due to their solutions being used in a number of processes of polymer recycling. Some polymer materials, such as polyvinyl chloride, are practically always used in the plasticized form. Therefore, issues related to the development of computation schemes that allow predicting such polymer properties as the yield strength and viscosity, depending on the chemical constitution of the polymer and solvent (plasticizer), remain relevant.

First, let us dwell on the analysis of the yield strength. The term *yield strength* is applicable to the glassy state of polymers. Therefore, it is first necessary to determine the interval of solvent (or plasticizer) concentration ensuring a glassy state of the plasticized polymer. As an example, consider the polymethyl methacrylate (PMMA) and dibutyl phthalate (DBP) system. For this system, we have the parameters presented in Table 10, which allow determining the dependence of glass transition temperature on the concentration of plasticizer. The calculations were carried out using the Kaskad program.

The dependence of softening temperature  $T_s$  on the weight fraction of DBP is shown in Fig. 9 (obtained by scanning the monitor screen). It can be seen that the introduction of the weight fraction 0.23 of DBP in PMMA leads to the appearance of a highly elastic state at room temperature, since at such DBP concentration the glass transition temperature is  $T_g = 293$  K.

The next step of the calculation consists in estimating the yield strength  $\sigma_{e,T}$ , both at the given temperature and at the temperature of the glassy state, close to the glassy transition temperature. Such an estimate can be obtained using a simplified expression [32], according to which

$$\sigma_{\mathrm{e},\,T} = 0.028 E_T\,,\tag{39}$$

where  $E_T$  is the Young modulus of a glassy polymer at temperature *T*, calculated as

$$E_T = 2(1 + v_T) G_T = 3(1 - 2v_T) B_T.$$
(40)

Here,  $G_T$  is the shear modulus of the glassy polymer at temperature T,

$$G_T = \frac{3(1-2\nu_T)}{2(1+\nu_T)} B_T, \qquad (41)$$

 $B_T$  is the volume modulus, depending on T,

$$B_T = 8.23333 E_{\rm coh} \left( \frac{5V_{\rm M,0}^4}{V_{\rm M,T}^5} - \frac{3V_{\rm M,0}^2}{V_{\rm M,T}^3} \right),\tag{42}$$

where  $V_{M,0}$  is the molar volume at T = 0,  $V_{M,T}$  is the molar volume at temperature  $T, E_{coh}$  is the molar cohesion energy

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Figure 9. Dependence of the PMMA yield temperature  $T_s$  on the weight fraction of DBP [4].

(which can be calculated by means of the Kaskad program),  $v_T$  is the Poisson coefficient (of the glassy state) depending on *T*:

$$v_T = v_0 + \frac{50T}{T_g} \left\{ 0.00163 + \exp\left[0.459\left(T - T_g - 13\right)\right] \right\}, \quad (43)$$

$$v_0 = v_{298 \,\mathrm{K}} - \frac{14900}{T_{\mathrm{g}}} \left\{ 0.00163 + \exp\left[0.459 \left(285 - T_{\mathrm{g}}\right)\right] \right\}, \quad (44)$$

$$v_{298\,\mathrm{K}} = 0.513 - 3.054 \times 10^{-6} \, \frac{V_{\mathrm{w}}}{I_{\mathrm{m}}} \, ,$$

 $V_{\rm w}$  is the van der Waals volume, and  $I_{\rm m}$  is the length of a repeat unit of the polymer in the completely stretched-out conformation.

The estimate shows that the yield strength at T = 40 °C equals 63 MPa and at T = 75 °C (close to the PMMA glass transition temperature) it amounts to 10.6 MPa. According to the principle formulated in Refs [48–50], the yield strength is determined from the following equation:

$$\sigma_{\rm e} = \frac{\left(1 - \alpha_{\rm m,s}\right) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} + \alpha_{\rm m,s} \left(\sum_{i} \Delta V_{i}\right)_{\rm s}}{\left(1 - \alpha_{\rm m,s}\right) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} / \sigma_{\rm e,p} + \alpha_{\rm m,s} \left(\sum_{i} \Delta V_{i}\right)_{\rm s} / \sigma_{\rm e,s}},$$
(45)

where  $\alpha_{m,s}$  is the molar fraction of the solvent,  $(\sum_i \Delta V_i)_p$  is the van der Waals volume of the repeat unit of the polymer,  $(\sum_i \Delta V_i)_s$  is the van der Waals volume of a molecule of solvent,  $\sigma_{e,p}$  is the yield strength of the polymer at the given temperature, and  $\sigma_{e,s}$  is the 'yield strength' of the solvent.

Since the value of the yield strength is measured in the glassy state of a system (in our case, the polymer–solvent system), Eqn (45) holds only in a fixed interval of solvent concentrations, and it should be transformed into the following formula:

$$\sigma_{e} = \frac{(1 - \alpha_{m,s+p}) \left(\sum_{i} \Delta V_{i}\right)_{p} + \alpha_{m,s+p} \left(\sum_{i} \Delta V_{i}\right)_{s+p}}{(1 - \alpha_{m,s+p}) \left(\sum_{i} \Delta V_{i}\right)_{p} / \sigma_{e,p} + \alpha_{m,s+p} \left(\sum_{i} \Delta V_{i}\right)_{s+p} / \sigma_{e,s+p}},$$
(46)

where  $\alpha_{m,s+p}$  is the molar fraction of the polymer–solvent mixture;  $(\sum_{i} \Delta V_i)_{s+p}$  is the van der Waals volume of the



Figure 10. Dependence of yield strength on molar fraction of DBP.  $T = 40^{\circ}$  [4].

above mixture, which is critical, i.e., if the solvent concentration exceeds the critical one, then the mixture transitions to a rubbery state; and  $\sigma_{e, s+p}$  is the yield strength for the polymer– solvent system, possessing a critical concentration of the solvent.

In our case, the critical weight fraction of the solvent is 0.23, as can be seen from Fig. 9. The molar concentration  $\alpha_m$  is related to the weight concentration  $\alpha_w$  by Eqn (35). It follows that the critical molar concentration of the solvent is  $\alpha_m = 0.097$ .

Formula (46) is valid in the interval of  $\alpha_{e,s+p}$  from 0 to 1 and at  $\alpha_m = 0.097$ , the van der Waals volume being calculated as

$$\left(\sum_{i} \Delta V_{i}\right)_{s+p} = (1 - 0.097) \left(\sum_{i} \Delta V_{i}\right)_{p} + 0.097 \left(\sum_{i} \Delta V_{i}\right)_{s} = 114.2 \text{ Å}^{3}. \quad (47)$$

According to Eqn (46), the following expression should be written taking into account all physical parameters, calculated above:

$$\sigma_{\rm e} = \frac{96.4 + 183.5\alpha_{\rm m,s}}{1.547 + 48.3\alpha_{\rm m,s}} \,. \tag{48}$$

Expression (48) is valid in the interval of  $\alpha_{m,s}$  from 0 to 0.097. The dependence of the yield strength on the mole fraction of the solvent (plasticizer) is shown in Fig. 10.

To express Eqn (48) in terms of the weight fraction of the solvent  $\alpha_{w,s}$ , one should substitute Eqn (35) into Eqn (48):

$$\sigma_{\rm e} = \frac{96.4 + \frac{183.5}{1 + (M_{\rm s}/M_{\rm p})(1/\alpha_{\rm w,s} - 1)}}{1.547 + \frac{48.3}{1 + (M_{\rm p2}/M_{\rm p1})(1/\alpha_{\rm w,s} - 1)}} \,. \tag{49}$$

Relation (49) is valid within the interval of  $\alpha_{w,s}$  from 0 to 0.23 for the considered PMMA + DBP system. Keeping in mind that in the considered example  $M_s = 278$  and  $M_p = 100$ , we get

$$\sigma_{\rm e} = \frac{96.4 + 183.5/(2.78/\alpha_{\rm w,s} - 1.78)}{1.547 + (48.3/2.78/\alpha_{\rm w,s} - 1.78)} \,. \tag{50}$$



Figure 11. Dependence of yield strength on weight fraction of DBP.  $T = 40 \circ C$  [4].



Figure 12. Dependences of yield strength on molar fraction of DBP. Numbers on the curves denote temperature:  $1 - 20^{\circ}$ C,  $2 - 30^{\circ}$ C,  $3 - 40^{\circ}$ C,  $4 - 50^{\circ}$ C,  $5 - 60^{\circ}$ C [4].

The dependence of the yield strength on the weight fraction of the solvent is shown in Fig. 11. Such dependences can be obtained in any temperature interval of the glassy state for polymer–solvent (plasticizer) systems.

In the case of PMMA and DBP, Eqn (46) transforms into the following:

(

$$\sigma_{\rm e} = \frac{96.4 + 183.5\alpha_{\rm w,s}}{(\sum_i \Delta V_i)_{\rm p}/\sigma_{\rm e} + 48.3\alpha_{\rm w,s}},$$
(51)

where  $(\sum_i \Delta V_i)_p$  is the van der Waals volume of the polymer repeat unit,  $\sigma_e$  is the yield strength of the polymer, and  $\alpha_{m,s}$  is the molar fraction of the solvent.

Formula (51) is valid in the interval of  $\alpha_{m,s}$  from 0 to 0.097. The value of  $\sigma_e$  depends on temperature and can be calculated by means of the PDTools program using the Bicerano method [32]. The values of the yield strength for PMMA at various temperatures are presented in Table 11.

Using the values from Table 11, one can calculate the values of the yield strength as a function of the DBP plasticizer concentration. These dependences are shown in Fig. 12. The temperature dependences of the yield strength are presented in Fig. 13.

Thus, an analysis of the effect of temperature, chemical constitution of the components of the polymer–plasticizer mixture, and their concentration on the yield strength is shown to be quite possible.

Temperature °C	Yield strength, MPa
20	91.6
30	77.0
40	62.3
50	47.6
60	33.0
70	18.3

Table 11. Calculated values of  $\sigma_e$  at various temperatures for PMMA.



**Figure 13.** Temperature dependences of the yield strength. Numbers on curves denote the molar fraction of the DBP plasticizer [4].

### 8. Viscosity of plasticized polymers

Now, let us consider an analysis of viscosity depending on the concentration of solvent (plasticizer). According to Ref. [51], the dependence of viscosity on the solvent volume fraction is described by the relation

$$\ln \frac{\eta}{B} = 4 \ln \rho + \left\{ \alpha_{\rm v, p} \left[ 0.025 + \Delta \alpha \left( T - T_{\rm g, p} \right) \right] + (1 - \alpha_{\rm v, p}) \left[ 0.025 + \alpha_{\rm s} \left( T - T_{\rm g, s} \right) \right] \right\}^{-1},$$
(52)

where *B* is a combined constant, including the molecular mass,  $\rho$  is the polymer concentration,  $\alpha_{v,p}$  is the difference between thermal expansion coefficients at temperatures  $\Delta \alpha$  greater and smaller than the glass transition temperature *T* of the polymer,  $T_g$ ,  $\alpha_s$  is the thermal expansion coefficient of the solvent (plasticizer),  $T_{g,s}$  is the glass transition temperature of the solvent,  $\Delta \alpha = \alpha_L - \alpha_G$ , and  $\alpha_L$  and  $\alpha_G$  are the coefficients of the polymer thermal expansion in the highly-elastic and glassy state, respectively.

The value of  $\rho$  is determined by the expression

$$\rho = \frac{g_{\rm p}}{v_{\rm p} + v_{\rm s}} = \frac{g_{\rm p}}{g_{\rm p}/\rho_{\rm p} + g_{\rm s}/\rho_{\rm s}} = \frac{1}{1/\rho_{\rm p} + g_{\rm s}/(\rho_{\rm s}g_{\rm p})}, \quad (53)$$

where  $g_p$  is the polymer weight in the solution,  $g_s$  is the solvent weight,  $\rho_p$  is the polymer density,  $\rho_s$  is the solvent density,  $v_p$  is the polymer volume, and  $v_s$  is the solvent volume.

Let us express  $\rho$  in terms of the polymer volume fraction:

$$\alpha_{\rm v,p} = \frac{v_{\rm p}}{v_{\rm p} + v_{\rm s}} = \frac{1}{1 + v_{\rm s}/v_{\rm p}} = \frac{1}{1 + g_{\rm s}\rho_{\rm p}/(\rho_{\rm s}g_{\rm p})}.$$
 (54)

From Eqn (54), we have

$$\frac{g_{\rm s}}{g_{\rm p}} = \frac{\left(1/\alpha_{\rm v,p} - 1\right)\rho_{\rm s}}{\rho_{\rm p}} \,. \tag{55}$$

Substituting Eqn (55) into Eqn (54), we obtain

$$\rho = \rho_{\rm p} \alpha_{\rm v, \, p} \,. \tag{56}$$

The value of *B* can be determined from Eqn (52) if the viscosity  $\eta$  is known at the given temperature *T* for the initial polymer, containing no solvent. In this case,  $\alpha_{v,p} = 1$  and Eqn (52) transforms into the following:

$$\ln \frac{\eta}{B} = 4 \ln \rho_{\rm p} + \left[ 0.025 + \Delta \alpha \left( T - T_{\rm g, p} \right) \right]^{-1}.$$
 (57)

The viscosity  $\eta$  can be calculated using the Bicerano equation [32]; for the interval  $T_g < T < 1.2T_g$ , the following equation is used to calculate the zero shear viscosity  $\eta_{cr, T}$  depending on *T*:

$$\log_{10} \frac{\eta_{\rm cr, T}}{\eta_{\rm cr, 1.2T_g}} = 26.32 \left(\frac{T_g}{T}\right)^2 - 11.11 \frac{T_g}{T} - 9.02.$$
(58)

For  $T > 1.2T_g$ , the following relation is used:

$$\log_{10} \frac{\eta_{\rm cr, T}}{\eta_{\rm cr, 1.2T_g}} = \frac{(T_g - T)E_{\eta}}{2.3RT_g} , \qquad (59)$$

where  $\eta_{cr,1,2T_g}$  is the zero shear viscosity at  $1.2T_g$ ,  $E_\eta$  is the viscous flow activation energy,

$$E_{\eta} = \left(\frac{H_{\eta}}{M}\right)^3,\tag{60}$$

 $H_{\eta} = H_{\eta}^{\text{sum}} + H_{\eta}^{\text{str}}$  is the viscosity temperature function,  $H_{\eta}^{\text{sum}} = 177.7J + 2.2N_{\text{H}\eta}$  is a sum of group contributions to the molar viscosity temperature function,  $N_{\text{H}\eta} = 5N$  (complex ether group in acryl polymers) -N (all other types of complex ether groups) -20N (carbonate group) -7N (amid group) +6N (simple ether group)  $-3N_{\text{Cl}} - N_{\text{Br}} + 5N$  (sulphone group)  $-10N_{\text{Si}} + 3N$  (hexagonal nonterminal aromatic rings)  $+8N_{\text{C=C}} + 4N$  (carbon atoms, linked to four nonhydrogen atoms, i.e., with  $\delta = \delta^{v} = 4$ ) +2N (carbon atoms, linked to three nonhydrogen atoms and one hydrogen atom, i.e., with  $\delta = \delta^{v} = 3$ ),

$$J = 1.474N - 0.929N_{\rm H} + 4.1128^{\,0}\chi^{\rm v} + 0.9778N_k \,,$$

 $N_k = 5N$  (amide group) +7N (cyanide group) +15N (carbonate group)  $+5N_{Cl} + 13N_{Br} + 4N$  (hydroxyl group) -3N(simple ether group)  $-5N_{C=C} + 3N$  (sulphone group) -3N(complex ether group in acryl polymers) -5N (isolated saturated aliphatic hydrocarbon cycle, i.e., cyclohexyl or cyclopentyl;  ${}^0\chi^{v}$  is the *n*th-order valence connectivity index. (See [32] for details).

The ultimate equation for calculating viscosity depending on the polymer volume fraction reads

$$\ln \frac{\eta}{B} = 4 \ln \rho_{\rm p} \alpha_{\rm v, p} + \left\{ \alpha_{\rm v, p} \left[ 0.025 + (\alpha_{\rm L} - \alpha_{\rm G})(T - T_{\rm g, p}) \right] + (1 - \alpha_{\rm v, p}) \left[ 0.025 + \alpha_{\rm s} \left( T - T_{\rm g, p} \right) \right] \right\}^{-1}.$$
(61)

Temperature, K	Viscosity, $\ln (\eta [N s m^{-2}])$
390	19.69
400	17.45
410	15.39
420	13.48
430	11.72
440	10.09
450	8.58
460	4.06

Table 12. PS viscosity values.



Figure 14. Dependence of PS viscosity on polymer volume fraction. Numbers on curves denote the temperature in kelvins [4].



**Figure 15.** Temperature dependences of shear viscosity. Numbers on curves denote polymer volume fraction  $\alpha_{v,p}$ : *I* – 1.0, *2* – 0.95, *3* – 0.90 [4].

The polymer parameters  $\rho_p$ ,  $T_{g,p}$ ,  $\alpha_L$ , and  $\alpha_G$  are calculated by means of the Kaskad program. The viscosity  $\eta$  at a given temperature *T* is calculated by the Bicerano method [32]; the value of  $\alpha_s$  is taken from experiment or is accepted to be  $\alpha_s \approx 1 \times 10^{-3} \text{ K}^{-1}$ .

Let us consider an example of a polystyrene (PS)-toluene system. For this system at T = 410 K,  $\ln (\eta [N \text{ s } m^{-2}]) = 15.386$ ,  $\ln B = 11.1$ ,  $\rho_p = 1.06$  g cm<sup>-3</sup>,  $T_{g,p} = 376$  K,  $T_{g,s} = 178$  K,  $\alpha_L = 6.41 \times 10^{-4}$  K<sup>-1</sup>,  $\alpha_G = 2.55 \times 10^{-4}$  K<sup>-1</sup>,  $\alpha_s = 1.07 \times 10^{-3}$  K<sup>-1</sup>.

The dependence of  $\log \eta$  on the PS volume fraction  $\alpha_{v,p}$  is shown in Fig. 14.

The parameter *B* in Eqn (52) can be calculated using Eqn (57) if the viscosity  $\eta_0$  for the initial polymer is known. The values of viscosity  $\eta$  determined at different temperatures are given in Table 12. The calculation results for the PS-toluene system are shown in Fig. 15.

Thus, an analysis of the effect of temperature, chemical composition, and content of both components on the yield strength and viscosity can be carried out for various polymer–solvent mixtures. Computer calculations allow performing the analysis in automated mode after displaying the chemical constitution of the polymer and the solvent.

## 9. On using auto-oscillations excited due to deformation of polymer films in actuators of nanomechanical devices

Reference [52] analyzed the polymers that can be used in actuators of nanomechanical devices. Methods for increasing their service life and the thermal effects upon the excitation of self-oscillations in the frequency range of 200–250 Hz were considered. There are a number of problems whose solution requires executive micro- or nanomechanical devices that allow transforming one type of mechanical motion (say, translation) into another (say, vibration). Such devices transforming the energy of the input signal (electrical, optical, mechanical, etc.) into an output signal (e.g., a controlled motion) were called actuators [53].

Common types of micro- and nanomechanical devices include piezoelectric actuators [54], widely used in acoustics. As a rule, in macroscopic devices, ceramic piezoelectrics are applied (lead zirconate-titanate, PZT), whose operation requires high voltage ( $\sim 150$  V). Typical examples of such actuators are considered in Ref. [55].

In the case of autonomous nanodevices that exclude the use of high voltage, other solutions are necessary. One of the ways is to develop polymer systems, in which self-oscillations are continuously excited in the frequency range of 200–250 Hz. Below, based on experimental material on studying self-oscillations in various polymers, we formulate the requirements for their glass transition temperatures and consider ways of implementing systems supporting such oscillations with a minimal expenditure of energy.

Reference [56] presents the results of studying selfoscillations in a number of polymers: polyamide (PA-6), polyvinyl chloride (PVC), and amorphous polyethylene terephthalate (PETP). The choice of polymers was determined by the fact that the authors used the results of experiments using no metallic springs to stretch the samples (see the comment about using springs after Table 13). PA-6 was an exception, for which the experimental results were corrected using the data for PVC and PETP. Since the authors who studied the above polymers were interested in their own problems, we will try to reduce these data to a critical stretching rate  $v_{str}$ , at which the self-oscillations are excited, and the corresponding frequency  $\omega$ .

To determine  $\omega$  and  $v_{\text{str}}$ , we use the data from Ref. [57], where, based on a nonlinear model comprising two Aleksandrov–Lazurkin elements connected at a certain angle [58], analytical expressions for  $v_{\text{str}}$  and  $\omega$  were obtained in the steady-state mode (when the amplitude and frequency of oscillations do not change with time).

Polymer	$T_{\rm g}, { m K}$	Initial sample length <i>l</i> <sub>0</sub> , mm	Sample thickness, $\delta$ , mm	Critical rate of stretch- ing**, mm min <sup>-1</sup>	Self-oscillation frequency, Hz	
PA-6 (with an additional spring)*	335	20	0.2	22.8 (50)	0.2	
PVC (without a spring)	355	30	0.9	15.8 (40)	2.7	
PETP (without a spring)	353	50	0.25	14.4 (30)	$\sim 1$	
* Since at a very high sample compliance no self-oscillation is excited, a soft spring was installed in sequence with the sample [59]. ** Rate of sample stretching is indicated in parentheses.						

Table 13. Self-oscillation parameters of some polymers according to data in Ref. [60].

Table 14. Dependence of the rate of sample stretching to excite self-oscillations at a frequency of 250 Hz on the glass transition temperature of polymers.

Polymer	<i>T</i> <sub>g</sub> , K	Relaxation time $\tau_1$ , min	Critical rate of stretching, mm min <sup>-1</sup>	Rate of stretching, mm min <sup>-1</sup>	Initial sample length, <i>l</i> <sub>0</sub> , mm
PETP	353	0.044	14.4	474	50
PC	422	8.93	0.014	6.6	10
PMS	436	26.24	0.0048	3.87	10

According to Ref. [57], expressions for  $\omega$  and  $v_{\rm str}$  have the following form:

$$\omega \simeq \frac{0.3}{4\tau_1} \left(3 + \frac{K_3}{K_1}\right) \left(\frac{v}{v_{\text{str}}}\right)^2,\tag{62}$$

$$v_{\rm str} = \frac{3l_0}{8\tau_1} \left[ 3\left(1+3\frac{K_1}{K_3}\right) \right]^{0.5} \frac{K_1}{K_3} \,, \tag{63}$$

where  $\tau_1$  is the polymer relaxation time;  $K_3$  and  $K_1$  are the elasticity coefficients, related to the deformation of elastic links both inside a macromolecule and between macromolecules, respectively; v and  $v_{str}$  are the rate of stretching the polymer and the stretching rate value at which self-oscillations begin to get excited, respectively; and  $l_0$  is the linear size of the region where self-oscillations are excited.

Let us perform some estimates. Let the elasticity coefficient  $K_3$  be due to a deformation of chemical bonds and  $K_1$  be due to a deformation of van der Waals links; then,  $K_1/K_3 \ll 1$  and Eqns (62) and (63) can be simplified:

$$\omega \simeq \frac{0.075}{\tau_1} \frac{K_3}{K_1} \left(\frac{v}{v_{\text{str}}}\right)^2,\tag{64}$$

$$v_{\rm str} = \frac{0.65l_0}{\tau_1} \frac{K_1}{K_3} \,. \tag{65}$$

From Eqns (64), (65), it is possible to obtain the following relation for estimating  $v_{str}$  as a function of the sample stretching rate v, self-oscillation frequency  $\omega$ , and initial sample length  $l_0$ :

$$v_{\rm str} = \frac{0.115v^2}{l_0\omega} \left(\frac{K_3}{K_1}\right)^2.$$
 (66)

Assuming that in further estimates the ratio  $K_1/K_3$  in polymers is of the same order of magnitude, let us use Eqn (66) to evaluate  $K_1/K_3$  at  $v/v_{\text{str}} = 1$ . For  $l_0 = 10$  mm (the length of the sample working length),  $v_{\text{str}} = 12.4$  mm min<sup>-1</sup> = 0.207 mm s<sup>-1</sup>,  $\omega_{\text{str}} = 2\pi/T_{\text{str}}$ , and  $T_{\text{str}} \sim 1$  s, according to [59] for PETP, we obtain  $K_1/K_3 = 0.0195$ , and expression (66) takes the form

$$v_{\rm str} = \frac{302 \, v^2}{l_0 \omega} \,.$$
 (67)

Table 13 presents the results of estimates of  $v_{str}$  and frequencies of oscillations excited at  $v_{str}$  for the considered polymer systems.

The estimates show that, with an increase in glass transition temperature  $T_g$  of a polymer, the critical rate of exciting self-oscillations decreases, which means that in attenuator drives one should use polymers in which  $T_g > 355$  K. Examples of such polymers are polymethyl styrene ( $T_g = 436$  K) and polycarbonate ( $T_g = 422$  K).

Let us estimate the stretching rate v at which selfoscillations with a frequency of 250 Hz are excited in samples of polymethyl styrene (PMS) and polycarbonate (PC). The appropriate expression that can be derived from Eqn (67) will have the following form:

17.65 
$$\left(\frac{l_0}{v_{\rm str}}\right)^{0.5} = \frac{v}{v_{\rm str}},$$
 (68)

where the rates have the dimension [mm min<sup>-1</sup>], and  $l_0$  is measured in millimeters.

To evaluate v from Eqn (68), the value of  $v_{\rm str}$  should be known, which in the general case could be determined from Eqn (65). However, whereas for polymers presented in Table 13, all necessary parameters can be extracted from experimental data, for PMS and PC, only their  $T_{\rm g}$  is known. Therefore, to estimate the relaxation times  $\tau_1$  of PMS and PC, we will make use of the theory of absolute reaction rates, the dependence of activation energy on  $T_{\rm g}$  [61], and the experimental data on PA-6 and PETP. The calculations using Eqn (65) yield  $\tau_1^{\rm PA-6} = 0.011$  min,  $\tau_1^{\rm PET} = 0.044$  min, and in the general case

$$\ln \frac{\tau_1^{\text{new}}}{\tau_1^{\text{PET}}} = 0.077 \left( T_g^{\text{new}} - T_g^{\text{PET}} \right), \tag{69}$$

where  $\tau_1^{\text{new}}$  is the relaxation time of the new polymer.

Table 14 presents the relaxation times calculated using Eqn (69) and the rates of sample stretching to excite self-

oscillations at a frequency of 250 Hz. In the case of PMS, upon stretching the sample by 1.5 times, it is possible to excite self-oscillations in 1.3 min.

To determine the sample temperature T corresponding to the found relaxation times (see Table 14) for PETP and PMS, we use the Williams–Landel–Ferry equation

$$\ln a_T = -C_1 \, \frac{T - T_g}{C_2 + T - T_g} \,, \tag{70}$$

where  $a_T = \tau(T)/\tau(T_g)$ ,  $T_g$  is the glass transition temperature of the studied polymer, and  $C_1$  and  $C_2$  are constants of the material.

Below, when determining *T*, we take for  $C_1$  and  $C_2$  their average values  $\langle C_1 \rangle$  and  $\langle C_2 \rangle$ , calculated based on data from Ref. [60] for polymers. In Eqn (70),  $C_1 = 39$ , and  $C_2 = 52$  K. To determine  $a_T$ , we take for  $\tau(T_g)$  its average value  $\langle \tau(T_g) \rangle$  according to data from Ref. [62] for amorphous polymers, i.e.,  $\langle \tau(T_g) \rangle = 40$  s.

Calculations using Eqn (69) under the above assumptions yield for PETP T = 381 K (heating to a temperature of 108 °C, almost as in Ref. [59], when the polymer transits to a highly elastic state), and, for PMS, T=437, K = 164 °C, i.e., sample heating occurs as the self-oscillations become excited.

Thus, the mechanism of exciting self-oscillations by stretching polymers considered above quite adequately describes the appropriate processes. By selecting a polymer material in which the self-oscillations are excited in a polymer film with specified geometric dimensions, one can ensure the operation of an actuator with minimal energy expenditures. In PVC, where oscillations of two types are observed [60], preference was given to a higher frequency, since the lower one corresponds to a critical rate exceeding the stretching rate. To assess the critical stretching rate in PA-6, the following procedure was used. Since the self-oscillation frequency obtained in testing the sample with a spring corresponds to a critical stretching rate  $v_{\rm str}$  exceeding the really attainable stretching rate, the value of  $v_{\rm str}$  was determined via the average value of  $\langle v/v_{\rm str} \rangle \sim 2.3$ , found from the data for PVC and PETP and the stretching rate of the PA-6 sample.

# 10. Calculation of viscosity of dispersions of spherical nanoparticles with an absorbing polymer layer in a polymer melt and in a low-molecular liquid

In Ref. [63], expressions are obtained for the dynamic viscosity of a polymer melt in the presence of spherical nanoparticles with an adsorption polymer layer and without it. Also obtained was an expression for the relative viscosity of a dispersion of spherical nanoparticles with an adsorption layer of an amphiphilic copolymer-stabilizer in an aqueous medium. These expressions relate the viscosity of dispersed systems with the molecular mass and chemical constitution of the polymer, as well as the concentration and the radius of nanoparticles with the presence of a polymer adsorbing layer taken into account. The mean value of the radius of silver nanoparticles with an adsorption layer of an amphiphilic copolymer of ethylene and maleic acid in an aqueous medium was calculated. The calculated values of radii were compared with the experimental values obtained by the method of dynamic light scattering, and good agreement between them was found.

In the production of nanocomposite construction polymer materials and thin films with a prescribed set of properties, of great importance are such parameters as the viscosity of melts and solutions of polymers, the molecular mass of the polymers, as well as the concentration, shape, dimensions and adhesion properties of nanoparticles and their distributions in the volume of the disperse medium.

Also known is the effect of a viscosity decrease in solutions and melts of polymers in the presence of a small number of nanoparticles due to the adsorption of polymers in a surface layer, which is accompanied by violation of the polymer solution structure [64-67]. The presence of attraction or repulsion between the polymer and nanoparticles increases or reduces the polymer relaxation time in the surface layer, which is reflected in the glass transition temperature and strength properties of the composite material [68, 69]. The size of metallic nanoparticles affects their diffusion in a polymer melt [69]. The diameter of disperse filler particles in a melt affects the process of forming chain disperse structures, substantially changing the rheological properties of nanocomposite systems: the reduction in disperse particle size increases the probability of formation of chain structures; as a result, the increased viscosity of the system elongates the period during which these structures are formed [70]. By the example of adding low concentrations of fullerene and carbon nanotubes (with a volume concentration of  $\sim 0.05$ ), the effect of the nanoparticle shape on the viscosity and surface tension of the polymer nanocomposite melt was established [71].

Much attention is devoted to the simultaneous investigation of heat conductivity and viscosity of nanoliquids, i.e., dispersions of chemically stable metals, metal oxides, and carbon tubes of nanosize range in heat-conducting liquids (e.g., in water, ethylene glycol, and their mixtures or polymer solutions). The interest in such systems is due to the fact that even minor concentrations of nanoparticles can substantially change the thermophysical properties of the basic liquid. The resulting increase in heat conductivity of nanoliquids is temperature-dependent, namely, with an increase in temperature, the heat conduction coefficient increases. The practical use of nanoliquids is associated with the possibility of a liquid heat carrier for high-efficiency cooling of various electronic systems (e.g., servers) at room temperature of the cooling liquid, in contrast to traditional low-temperature coolers. However, along with the change in heat conduction, the introduction of nanoparticles into a liquid also affects other thermophysical properties. The most important characteristic is viscosity, since the advantage due to an increase in heat conductivity can be lost because of the increased energy costs of the circulation of a viscous nanoliquid through a cooling system [72].

The viscosity of a dispersion containing spherical particles has been repeatedly described in the literature. Various models and equations based on them were proposed relating the viscosity of a disperse system with the volume fraction of disperse particles. Let us briefly consider these models.

One of the equations describing the viscosity of a dispersion containing spherical particles is the Einstein equation

$$\eta = \eta_0 \left( 1 + 2.5\varphi \right), \tag{71}$$

where  $\eta$  is the suspension viscosity,  $\eta_0$  is the viscosity of the pure liquid,  $\varphi$  is the disperse phase volume, and 2.5 is the parameter used only for spherical particles.

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Another highly popular useful semiempirical equation for the concentration dependence of dispersion viscosity was proposed by Moony [73],

$$\eta = \eta_0 \exp\left[\frac{2.5\varphi}{1 - (\varphi/\varphi^*)}\right],\tag{72}$$

where  $\varphi^*$  is the so-called critical concentration. The physical meaning of  $\varphi^*$  is the ultimate value of the degree of filling with hard particles. This quantity depends on the particle shape and packing mode, i.e., on the packing coefficient. For example,  $\varphi^* = 0.74$  in the case of hexagonal packing of hard spherical particles. Among other popular models and corresponding equations, the Krieger–Dougherty model [74],

$$\eta = \eta_0 \left( 1 - \frac{\varphi}{\varphi^*} \right)^{2.5\varphi^*},\tag{73}$$

and the Quemada model [75],

$$\eta = \eta_0 \left( 1 - \frac{1}{2} \, K \varphi \right)^{-2},\tag{74}$$

are worth mentioning, where K takes values from 2.54 to 3.71.

Concentrated suspensions [76–78] and emulsions [78–81] were studied by R Pal. In these papers, a large amount of experimental data is collected, which can be used to check the performance of various models describing the behavior of the relative viscosity of suspensions and emulsions in a wide range of concentrations.

Let us consider current models in more detail. Reference [82] considers the role of normal stresses in curved flows of suspensions. The resulting equation describing the relative viscosity depending on the volume fraction of the disperse phase has the form

$$\eta = \eta_0 \left[ 1 + 2.5\varphi \left( 1 - \frac{\varphi}{\varphi^*} \right)^{-1} + 0.1 \left( \frac{\varphi}{\varphi^*} \right)^2 \left( 1 - \frac{\varphi}{\varphi^*} \right)^{-2} \right].$$
(75)

The model proposed by Zarraga et al. [83] is intended for concentrated suspensions containing spherical particles. The equation for the dependence of suspension viscosity on the volume fraction of dispersed particles reads

$$\eta = \eta_0 \exp\left[k\varphi \left(1 - \frac{\varphi}{\varphi^*}\right)^{-3}\right].$$
(76)

Review [84] analyzes the nature of divergence in colloid dispersions of hard spheres under conditions of low shear viscosity. Later reviews [85, 86] analyze the viscosity of concentrated suspensions of hard monosized particles and bimodal spheres. The following relation is proposed:

$$\eta = \eta_0 \left( \frac{1 - \varphi}{1 - \varphi/\varphi^*} \right)^{2.5\varphi^*/(1 - \varphi^*)}.$$
(77)

Reference [87] considers effective viscosities of concentrated suspensions of soft particles under static and highfrequency impact. The following relation is obtained:

$$\eta = \eta_0 \left( 1 - \frac{1}{1 + 1/\varphi - 1/\varphi^*} \right)^{-2.5}.$$
(78)

In papers in recent years, multiple models aimed at describing the relative viscosity of suspensions are discussed [87, 88]. Faroughi [88] proposed and substantiated a generalized equation for suspensions and emulsions experiencing a steady flow at low Reynolds numbers. For suspensions containing hard particles, the equation is written as

$$\eta = \eta_0 \left(\frac{\phi^* - \phi}{\phi^* (1 - \phi)}\right)^{2.5\phi^*/(1 - \phi^*)}.$$
(79)

Dörr et al. [89] considered a discrete model describing the relative viscosity of polydisperse suspensions, with substantial attention devoted to the maximum value of the packing coefficient.

In review papers devoted to the study of viscous properties of nanodimension disperse systems [90–92], it was shown that nanoliquids possess a number of specific features. Their viscosity coefficients depend not only on the packing density (volume fraction  $\varphi$ ) of nanoparticles, according to the Einstein equation and its modifications applicable to high  $\varphi$ , but also on the shape [93], size [94, 95], level of aggregation [96], temperature [97], pH value of the medium [98], and even the nature of the particles [99]. These parameters were introduced into a number of equations describing the viscosity of nanoliquids.

According to Graham's equation [100] considering the diameter of particles  $(d_p)$  and the distance between particles (h) at small  $\varphi$ , the viscosity of nanoliquids can be represented as

$$\eta = \eta_0 \left( 1 + 2.5\varphi + 4.5 \left[ \frac{1}{(h/d_p) \left(2 + h/d_p\right) \left(1 + h/d_p\right)^2} \right] \right).$$
(80)

Chen et al. [101] modified the Krieger–Dougherty equation, taking into account the influence of aggregates of disperse particles on the packing:

$$\eta = \eta_0 \left( 1 - \frac{\varphi_a}{\varphi_m} \right)^{-2.5\varphi_m},\tag{81}$$

where  $\varphi_a = \varphi(a_a/a)^{3-D}$ ,  $a_a$  and a are the size of aggregates and initial particles, respectively, D = 1.8 is the fractal index for a nanoliquid, and  $\varphi_m$  is the maximum volume of the fraction of particles, determined experimentally.

Masoumi et al. [102] proposed a new theoretical model to determine the viscosity of nanoliquids, based on the Brownian motion of nanoparticles in a disperse medium:

$$\eta = \eta_0 \left( 1 + \frac{\rho_N V_{\rm b} d_N^2}{72 C \delta \eta_0} \right),\tag{82}$$

where  $\rho_N$  is the density,  $d_N$  is the diameter of the particles,  $\delta$  is the distance between particles, *C* is the correction factor elated to the particle diameter, and  $V_b$  is the Brownian velocity, related to temperature:  $V_b = (1/d_p)[18k_BT/(\pi\rho_p d_p)]^{1/2}$ , where  $k_B$  is the Boltzmann constant,  $d_p$  is the particle diameter,  $\rho_p$  is the particle density.

This model can be used to calculate the effective viscosity taking into account the diameter, density, and volume of the particle fraction.

However, classical theoretical models are unable to predict the viscosity of nanoliquids with sufficiently high accuracy. As shown by Rudyak et al., this is due to the range of nanoparticle size from 1 to 100 nm [103, 104]. The smallest particles in this range exceed the size of common inorganic molecules only by 2–3 times. Therefore, their movement in the disperse medium can be described by a system of Boltzmann kinetic equations. At the same time, the transfer of the largest particles of this range obeys the laws of Brownian motion. The difference between mechanisms of particle motion determine the influence of their size on the viscosity, as well as the effect of increasing viscosity coefficient with a decrease in the particle size. All nanoliquids manifest non-Newtonian properties earlier at some threshold concentration of particles when there is a higher volume concentration and smaller size of particles. In this case, it is assumed that, with the growth of nanoparticle diameter, the dependence of nanoliquid viscosity on the particle size becomes weaker.

The dependence of the viscosity coefficient of non-Newtonian nanoliquids with nanoparticles of medium size at volume concentrations not higher that 10–15% is approximated well by the quadratic dependence on  $\varphi$ :

$$\eta = \eta_0 \left( 1 + k_1(D)\phi + k_2(D)\phi^2 \right),$$
(83)

where *D* is the diameter of nanoparticles. The constants  $k_1$  and  $k_2$  not only are functions of density of the disperse medium but also depend on the ratio of masses and sizes of nanoparticles and molecules of the liquid [105].

Some equations for calculating the viscosity coefficient of nanodimension disperse systems consider not only the volume fraction and diameter of nanoparticles but also the thickness of the disperse medium layer adsorbed on the particle surface. Hosseini et al. [90] proposed an empirical equation for calculating the relative viscosity of aluminum oxide nanoparticles in water nonstabilized by a polymer taking into account the volume concentration, nanoparticle size, and the temperature and thickness of the layer coating the particles:

$$\eta = \eta_0 \exp\left[m + \alpha \left(\frac{T}{T_0}\right) + \beta\left(\varphi_{\rm h}\right) + \gamma\left(\frac{d}{1-r}\right)\right], \quad (84)$$

where  $\varphi_h$  is the hydrodynamic volume of the fraction of nanoparticles, *d* is the nanoparticle diameter, *r* is the thickness of the coating layer of the disperse medium,  $T_0$  is the etalon temperature, *T* is the measured temperature of the nanoliquid, *m* is a factor depending on the system properties (hardness of nanoparticles, disperse medium density, interparticle interaction), and  $\alpha$ ,  $\beta$ ,  $\gamma$  are constants determined experimentally.

Syzrantsev et al. [106] modified the known Batchelor equation [107] describing the dependence of relative viscosity of micrometer-size suspensions on the volume concentrations of particles. In the modified form applicable to calculations of relative viscosity of nanoliquids, it reads

$$\frac{\eta}{\eta_0} = 1 + 2.5\varphi \left(1 + K\right) + 6.25\varphi^2 \left(1 + K\right)^2,\tag{85}$$

where

$$K = \delta \sigma_{\rm p} S_{\rm sp} + \frac{\pi}{8} (\delta \sigma_{\rm p} S_{\rm sp})^2 + \frac{\pi}{48} (\delta \sigma_{\rm p} S_{\rm sp})^3$$

In Eqn (85), the parameter  $\varphi_{\text{eff}} = \varphi(1 + K)$  is used, which is the effective volume concentration of nanoparticles taking into account the adsorption layer of the disperse medium with thickness  $\delta$  (comparable to the diameter of particles *D*), density  $\rho_p$ , and size distribution of particles f(D). It is assumed that  $\delta$  and  $\rho_p$  do not depend on the size of the particles. In the case of micrometer-size suspension particles, the specific surface  $S_{sp}$  and the adsorption layer  $\delta$  are decreased. At  $\delta \ll D$ , the value of K tends to zero and Eqn (85) takes the traditional form. This modification extends the applicability of the classical Batchelor mode for a nanosize region of dispersed particles, when K tends to unity and the attached volume of the disperse medium is comparable to the volume of the disperse phase.

The considered models describe the dependence of the relative viscosity of disperse systems in different intervals of concentrations and at different sizes of dispersed particles depending on their volume fraction. However, these models do not allow calculating the relative viscosity of disperse systems where the dispersed particles are stabilized by polymer coatings (with known chemical constitution and molecular mass) adsorbed on the surface of the particles. Two options can be considered. In one of them, the disperse particles are inert, and in the other one they exhibit strong intermolecular interaction with the molecules of the disperse medium. In this connection, the aim of Ref. [64] was to develop a calculation scheme for determining the character of relative viscosity dependence on the volume fraction of spherical nanoparticles in a disperse system, taking into account the adsorbed polymer layer. Silver nanoparticles stabilized with the amphiphilic copolymer of ethylene and maleic acid were considered.

In the cited paper, computation schemes are presented that relate the disperse system viscosity parameters to the concentration and radius of nanoparticles, taking into account the chemical constitution and molecular mass of the adsorbed polymer layer. In this case, two problems are solved:

(1) the direct problem, i.e., the calculation of the relative viscosity of a disperse system taking into account the concentration, size, and molecular mass of nanoparticles in the adsorbed polymer layer. Such a calculation can be performed using any of the above equations involving the volume fraction  $\varphi$  of the dispersed particles;

(2) the inverse problem, i.e., the calculation of the size of nanoparticles with the adsorption layer of a polymer based on the measurements of the disperse system relative viscosity. In this case, for nanocomposite polymer melts and low-mole-cular liquids, single-layer and multilayer polymer coatings of nanoparticles were evaluated.

For the analysis, the classical Einstein (71) and Moony (72) equations were used. Note that Eqn (71), as well as Eqn (72), becomes inapplicable when, as a result of strong intermolecular interaction between the molecules of the liquid and the disperse particles, a stable adsorption layer is formed.

First, let us consider the dependence of viscosity  $\eta$  on  $\varphi$  for inert solid nanoparticles. If we have a polymer melt, then the viscosity  $\eta_0$  is calculated using the Bicerano method [32]. For example, for polyethylene, the viscosity is  $\eta_0 = 5.9 \times 10^{-4}$  Pa s at T = 430 K. The dependence of viscosity on the volume fraction of spherical nanoparticles is shown in Fig. 16.

The ultimate concentration  $\varphi = 0.1$  is introduced because the Einstein equation is valid at a low concentration of nanoparticles. The Moony equation is valid in a wider concentration interval. For polystyrene, the dependences of viscosity on the volume fraction of spherical nanoparticles are shown in Fig. 17.



**Figure 16.** Dependence of viscosity on volume fraction of nanoparticles at low concentration. Dependence is calculated using the Einstein equation (71) [63].



Figure 17. Dependence of viscosity on volume fraction of nanoparticles within a wide range of concentrations. I — dependence calculated using the Moony equation (72), 2 — dependence calculated using the Einstein equation (71) [63].

As can be seen, within a narrow interval of concentrations (< 0.1), both dependences are close to each other; however, they rapidly diverge in a wide interval of concentrations of nanoparticles. The above examples demonstrate a situation when a strong intermolecular interaction between polar groups located on the surface of nanoparticles and the molecules of solvent or melt is absent.

Now let us consider the calculation of the viscosity dependence on the weight fraction of nanoparticles, when a strong intermolecular interaction takes place between polar groups on the surface of nanoparticles and the solvent or melt molecules. In this case, the adsorption layer is formed around a nanoparticle. The surface area of one nanoparticle is

$$S_{\rm np} = 4\pi R_{\rm np}^2 \,, \tag{86}$$

where  $R_{np}$  is the nanoparticle radius.

The volume of one spherical nanoparticle is

$$v_{\rm np} = \frac{4}{3} \,\pi R_{\rm np}^3 \,. \tag{87}$$

The number of nanoparticles in the system is

$$n_{\rm np} = \frac{c_{\rm np}}{g_{\rm np}} \,, \tag{88}$$

where  $c_{np}$  is the weight of all nanoparticles,  $g_{np}$  is the weight of one nanoparticle,

$$g_{\rm np} = \rho_{\rm np} v_{\rm np} \,, \tag{89}$$

 $\rho_{\rm np}$  is the density of a nanoparticle,  $v_{\rm np}$  being its volume.

Consider 1 g of a system containing a polymer melt and nanoparticles. In this composition,  $c_{np}$  is the mass of the nanoparticles and  $(1 - c_{np})$  is the melt mass. Then, the number of repeat units of the polymer in the composition is

$$N_{\rm c} = \frac{1 - c_{\rm np}}{M_0} \, N_{\rm A} \,, \tag{90}$$

where  $M_0$  is the molecular mass of the repeat unit.

The number of repeat units per macromolecule is

$$N = \frac{M}{M_0} , \qquad (91)$$

where M is the polymer molecular mass.

If the melt structure is globular, then the globule volume is expressed as

$$V_{\rm g} = \frac{\left(\sum_i \Delta V_i\right)_{\rm p} N}{k} \,, \tag{92}$$

where  $(\sum_i \Delta V_i)_p$  is the van der Waals volume of a polymer repeat unit, and k is the molecular packing coefficient. Usually, for polymer melts, k = 0.64.

The globule radius can be calculated using the formula

$$R_{\rm g} = \sqrt[3]{\frac{3V_{\rm g}}{4\pi}} = \sqrt[3]{\frac{3(\sum_{i} \Delta V_{i})_{\rm p} N}{4\pi k}}.$$
(93)

The area occupied by one globule on the surface of a nanoparticle is

$$S_{\rm g} = \pi R_{\rm g}^2 = \pi \sqrt[2/3]{\frac{3\left(\sum_i \Delta V_i\right)_{\rm p} N}{4\pi k}}.$$
(94)

The total surface of one nanoparticle is calculated using Eqn (86). The relation that determines the ultimate number of globules which can be distributed over the surface of a single nanoparticle is

$$n_{\rm gl} = \frac{S_{\rm np}}{S_{\rm g}} = \frac{4\pi R_{\rm np}^2}{\pi^{2/3} \sqrt{3 \left(\sum_i \Delta V_i\right)_{\rm p} N / (4\pi k)}}$$
$$= \frac{4R_{\rm np}^2}{0.518^{2/3} \sqrt{\left(\sum_i \Delta V_i\right)_{\rm p} N}}, \qquad (95)$$

with k = 0.64. Taking into account Eqn (91), we can write

$$n_{\rm gl} = \frac{7.72 R_{\rm np}^2}{\sqrt[2/3]{\left(\sum_i \Delta V_i\right)_{\rm p}} \frac{M}{M_0}}.$$
(96)

As an example, let us consider a nanocomposite polymer system based on polyamide, the parameters of which are presented in Table 15.

If the nanoparticle radius is equal to 50 Å (5 nm) and the polymer molecular mass is M = 14,000, then the value of  $n_{gl}$ 

 Table 15. Parameters for a nanocomposite system of melt of polyamide-6 with nanoparticles.

Parameters	Value
Molecular mass of repeat unit, $M_0$	113
Polymer molecular weight, M	14,000
Van der Waals volume of the polymer repeat unit $(\sum_i \Delta V_i)_p$ , Å <sup>3</sup>	116
Molecular packing coefficient of the melt, $k$	0.64
Weight of nanoparticles per gram of composition $c_{np}$ , g	0.10
Radius of nanoparticles $R_{\rm np}$ , Å	50
Density of nanoparticles $\rho_{\rm np}$ , g cm <sup>-3</sup>	1.54
Zero shear viscosity of polyamide-6 (at $T = 463$ K) $\eta$ , 10 <sup>-4</sup> Pa s	15.20

calculated using Eqn (91) amounts to 32.6 units. Obviously, the radius of one nanoparticle together with the polymer adsorption layer equals

$$R_{\rm np+ad.l} = R_{\rm np} + 2R_{\rm gl} = R_{\rm np} + 2\sqrt[3]{\frac{3(\sum_{i} \Delta V_{i})_{\rm p} N}{4\pi k}}$$
  
=  $R_{\rm np} + 1.44\sqrt[3]{\left(\sum_{i} \Delta V_{i}\right)_{\rm p} \frac{M}{M_{0}}}.$  (97)

The volume of one nanoparticle together with the adsorption layer

$$v_{\rm np+ad.l} = \frac{4}{3} \pi \left( R_{\rm np} + 1.44 \sqrt[3]{\left(\sum_{i} \Delta V_{i}\right)_{\rm p} \frac{M}{M_{0}}} \right)^{3}.$$
 (98)

The volume fraction of nanoparticles without adsorbed layers can be calculated as

$$\varphi = \frac{v_{\rm np} n_{\rm np}}{v_{\rm np} n_{\rm np} + V_{\rm p}} \,, \tag{99}$$

where  $V_{p}$  is the volume of a polymer in the composition.

The volume fraction of nanoparticles containing adsorption layers can be calculated using the following formula:

$$\varphi_{\rm np+ad.l} = \frac{v_{\rm np+ad.l} n_{\rm np}}{v_{\rm np+ad.l} n_{\rm np} + V_{\rm p} - v_{\rm ad.l} n_{\rm np}} , \qquad (100)$$

where  $v_{\text{ad.1}}$  is the volume of the adsorption layer per nanoparticle,

$$V_{\rm p} = \frac{G_{\rm p}}{\rho_{\rm p}} \,, \tag{101}$$

 $G_{\rm p}$  is the polymer weight in the composition, and  $\rho_{\rm p}$  is the polymer density.

If we analyze 1 g of the composition, then  $G_p = 1 - c_{np}$ , where  $c_{np}$  is the mass of nanoparticles in 1 g of the composition. The polymer density is calculated using the formula [2, 3]

$$\rho_{\rm p} = \frac{kM_0}{N_{\rm A} \left(\sum_i \Delta V_i\right)_{\rm p}} \,. \tag{102}$$

Thus, we obtain

$$V_{\rm p} = \frac{(1 - c_{\rm np}) N_{\rm A} \left(\sum_{i} \Delta V_{i}\right)_{\rm p}}{k M_{0}} \,. \tag{103}$$

The volume of the adsorption layer is expressed as

$$V_{\rm ad.l} = n_{\rm gl} \, V_{\rm gl} \,. \tag{104}$$

Substituting Eqns (92) and (96) into Eqn (104), we find

$$v_{\rm ad.1} = \frac{7.72 R_{\rm np}^2 \sqrt[3]{\left(\sum_i \Delta V_i\right)_{\rm p}}}{k} \,. \tag{105}$$

Substituting Eqns (88), (89), (98), and (105) into Eqn (100), we arrive at the expression for the volume fraction of nanoparticles with the adsorption polymer layer:

$$\varphi_{\rm np+ad,l} = \left[ \left( R_{\rm np} + 1.44 \sqrt[3]{\frac{M}{M_0} \left( \sum_i \Delta V_i \right)_{\rm p}} \right)^3 \frac{c_{\rm np}}{\rho_{\rm np} R_{\rm np}^3} \right] \\ \times \left[ \left( R_{\rm np} + 1.44 \sqrt[3]{\frac{M}{M_0} \left( \sum_i \Delta V_i \right)_{\rm p}} \right)^3 \frac{c_{\rm np}}{\rho_{\rm np} R_{\rm np}^3} \right. \\ \left. + \frac{(1 - c_{\rm np}) N_{\rm A} (\sum_i \Delta V_i)_{\rm p}}{kM_0} - \frac{7.72 \sqrt[3]{\left( \sum_i \Delta V_i \right)_{\rm p}} 3c_{\rm np}}{4\pi \rho_{\rm np} R_{\rm np}} \right]^{-1}.$$
(106)

Let us consider examples of calculations.

The initial polymer is polyamide-6. The parameters of this polymer are presented in Table 15. If there is no adsorbed layer, the volume fraction of nanoparticles is calculated as

$$\varphi = \frac{c_{\rm np}/\rho_{\rm np}}{c_{\rm np}/\rho_{\rm np} + (1 - c_{\rm np})/\rho_{\rm np}} = \frac{c_{\rm np}/\rho_{\rm np}}{c_{\rm np}/\rho_{\rm np} + \left[ (1 - c_{\rm np}) N_{\rm A} \left( \sum_{i} \Delta V_{i} \right)_{\rm p} / (kM_{0}) \right]} .$$
(107)

Substituting the parameters from Table 15 into Eqn (107), we get  $\varphi = 0.0695$ . If an adsorbed layer has formed on the surface of the particle, then, using all parameters from Table 15 and Eqn (106), we obtain  $\varphi_{np+ad,l} = 0.2226$ .

Let us now find the dependence of viscosity on the weight fraction of nanoparticles. The type of this dependence is determined by the possibility of forming the polymer adsorption layer on the nanoparticle surface.

1. There is no strong intermolecular interaction between the polymer chains and the polar groups located on the surface of the nanoparticles. Then, substituting all parameters of the system from Table 15 into Eqn (71), we obtain

$$\eta = 15.2 \left( 1 + \frac{1.6225c_{\rm np}}{0.966 - 0.317c_{\rm np}} \right).$$
(108)

2. There is a strong intermolecular interaction between the polymer chains and polar groups localized on the surface of the nanoparticles. Then, we obtain the following expression:

$$\eta = 15.2 \left( 1 + \frac{7.9763c_{\rm np}}{2.0419c_{\rm np} + 0.9661} \right).$$
(109)

Figure 18 demonstrates the dependence of viscosity on the mass of nanoparticles contained in 1 g of the composition. All calculations are carried out using Eqns (108) and (109).



**Figure 18.** Dependence of viscosity on the mass of nanoparticles in 1 g on a composite containing polyamide-6 and nanoparticles: I — strong interaction between polymer chains and polar groups located on the surface of nanoparticles is absent; 2 — strong interaction between polymer chains and polar groups located on the surface of nanoparticles is present. Calculations are carried out using the Einstein equation (71) [63].

Now, let us calculate similar dependences using the Moony equation (72). When the strong intermolecular interaction between polymer chains and polar groups located on the surface of nanoparticles is absent, we substitute the parameters from Table 15 into Eqn (72) at  $\varphi^* = 0.74$  (hexagonal packing) and obtain

$$\eta = 15.2 \exp\left(\frac{1.6225c_{\rm np}}{0.966 - 1.194c_{\rm np}}\right).$$
(110)

When the strong intermolecular interaction appears, we obtain the following expression:

$$\eta = 15.2 \exp\left(\frac{7.9763c_{\rm np}}{0.966 - 2.2695c_{\rm np}}\right).$$
(111)

The dependences of viscosity on the concentration of nanoparticles, calculated using the Einstein equation (71), are shown in Fig. 18. The dependences of viscosity on the concentration of nanoparticles, calculated using the Moony equation (72), are presented in Fig. 19.

Let us now calculate the dependence of viscosity on the polymer molecular mass. Substituting all parameters from Table 15, except M, into Eqn (71), we obtain

$$\eta = 15.2 \left( 1 + \frac{1.2975 \times 10^{-6} \left( 50 + 1.453 \sqrt[3]{M} \right)^3}{0.519 \times 10^{-6} \left( 50 + 1.453 \sqrt[3]{M} \right)^3 + 0.8513} \right).$$
(112)

The substitution of all parameters, except M, into Eqn (72) yields

$$\eta = 15.2 \exp\left(\frac{1.2975 \times 10^{-6} \left(50 + 1.453 \sqrt[3]{M}\right)^3}{0.8513 - 0.1823 \times 10^{-6} \left(50 + 1.453 \sqrt[3]{M}\right)^3}\right).$$
(113)

The dependences of viscosity on the molecular mass of polyamide-6 calculated using Eqns (71) and (72) are shown in Fig. 20.

Let us calculate the dependence of viscosity on the radius of spherical nanoparticles. When there is no adsorption layer, the viscosity is independent of the nanoparticle size. If the



**Figure 19.** Dependence of viscosity on the mass of nanoparticles in 1 g on a composite containing polyamide-6 and nanoparticles: I — strong interaction between polymer chains and polar groups located on the surface of nanoparticles is absent; 2 — strong interaction between polymer chains and polar groups located on the surface of nanoparticles is present. Calculations are carried out using the Moony equation (72) [63].



**Figure 20.** Dependence of viscosity on the molecular weight of polyamide-6: 1 — calculated using the Einstein equation (71), 2 — calculated using the Moony equation (72) [63].

adsorption layer is formed, then the formulas for describing the dependence of viscosity on the nanoparticle radius (taking into account all parameters presented in Table 15) take the following form:

$$\eta = 15.2 \left( 1 + \frac{0.16225 \left[ (R_{\rm np} + 35)/R_{\rm np} \right]^3}{0.0649 \left[ (R_{\rm np} + 35)/R_{\rm np} \right]^3 + 0.8685 - 0.912/R_{\rm np}} \right)$$
(114)

with the Einstein equation, and

$$\eta = 15.2 \exp\left(\frac{0.16225 \left[(R_{\rm np} + 35)/R_{\rm np}\right]^3}{0.8685 - 0.912/R_{\rm np} - 0.0228 \left[(R_{\rm np} + 35)/R_{\rm np}\right]^3}\right)$$
(115)

with the Moony equation.

The dependences of viscosity on the radius of nanoparticles are shown in Fig. 21. We can see that, in agreement with the Moony equation, the viscosity sharply increases when the size of nanoparticles decreases.

In Ref. [64], a disperse system is also considered, consisting of a low-molecular liquid and nanoparticles, the surface of which contains a modifying polymer layer,



Figure 21. Dependence of viscosity on the radius of nanoparticles with an adsorbed polymer layer: 1 — calculated using the Einstein equation (71), 2 — calculated using the Moony equation (72) [63].

executing the function of a stabilizer of particles in the disperse medium. The area  $S_m$  of one macromolecule of the polymer modifier is expressed as

$$S_{\rm m} = 2R_{\rm m}nl_0 = 2R_{\rm m}\frac{M}{M_0}\,l_0\,, \tag{116}$$

where  $R_m$  is the cross section radius of the macromolecule, *n* is the number of repeat units, *M* is the molecular weight of the modifier,  $M_0$  is the molecular weight of the repeat unit, and  $l_0$  is the length of the repeat unit. In the first approximation,  $l_0 = 2R_m$ . Then, from Eqn (116), it follows that

$$S_{\rm m} = 4R_{\rm m}^2 \,\frac{M}{M_0}\,. \tag{117}$$

The radius of a macromolecule of the polymer modifier is

$$R_{\rm m} = \sqrt[3]{\frac{3\sum_i \Delta V_i}{4\pi}},\tag{118}$$

where  $\sum_i \Delta V_i$  is the van der Waals volume of a repeat unit of the polymer macromolecule. Then,

$$S_{\rm m} = 4 \left(\frac{3\sum_{i} \Delta V_{i}}{4\pi}\right)^{2/3} \frac{M}{M_{0}} \,. \tag{119}$$

The ultimate number  $n_{\rm m}$  of macromolecules that can be distributed over the surface of one nanoparticle is expressed as

$$n_{\rm m} = \frac{S_{\rm np}}{S_{\rm m}} = \frac{\pi^{5/3} R_{\rm np}^2 M_0}{M (0.75 \sum_i \Delta V_i)^{2/3}} , \qquad (120)$$

where  $S_{np}$  is the area of a nanoparticle surface, and  $R_{np}$  is the nanoparticle radius.

The radius of a nanoparticle with the adsorbed layer of the modifier has the form

$$R_{\rm np+ad.l} = R_{\rm np} + 2R_{\rm m} = R_{\rm np} + 1.241 \left(\sum_i \Delta V_i\right)^{1/3}.$$
 (121)

The volume of a nanoparticle with the adsorption layer is expressed as

$$v_{\rm np+ad.l} = \frac{4}{3} \pi \left[ R_{\rm np} + 1.241 \left( \sum_{i} \Delta V_i \right)^{1/3} \right]^3.$$
 (122)

The volume fraction 
$$\varphi_{np}$$
 of nanoparticles without the adsorbed layer is

$$\rho_{\rm np} = \frac{v_{\rm np} n_{\rm np}}{v_{\rm np} n_{\rm np} + V_{\rm s}} \,, \tag{123}$$

where  $v_{np}$  is the volume of a nonmodified nanoparticle,  $n_{np}$  is the number of nanoparticles in the system,  $V_s$  is the volume of the liquid.

The volume fraction  $\varphi_{np+ad,l}$  of nanoparticles with an adsorption layer has the form

$$\varphi_{\rm np+ad.l} = \frac{v_{\rm np+ad.l} n_{\rm np}}{v_{\rm np+ad.l} n_{\rm np} + V_{\rm s}} , \qquad (124)$$

where the liquid volume  $V_s$  is determined in the usual way:

$$V_{\rm s} = \frac{G_{\rm s}}{\rho_{\rm s}} \,, \tag{125}$$

where  $G_s$  is the weight of the liquid,  $\rho_s$  is its density. The number of nanoparticles is expressed as

$$n_{\rm np} = \frac{G_{\rm np}}{g_{\rm np}} = \frac{G_{\rm np}}{\rho_{\rm np} v_{\rm np}} \,, \tag{126}$$

where  $G_{np}$  is the weight of the nanoparticles, and  $\rho_{np}$  is the nanoparticle density.

From Eqn (111), it follows that

$$\varphi_{\rm np+ad.l} = \frac{1}{1 + V_{\rm s}/(v_{\rm np+ad.l} \, n_{\rm np})} \,. \tag{127}$$

Taking into account Eqns (122), (123), (126), we can write (127) in the form

$$\varphi_{\rm np+ad.l} = \left\{ 1 + \frac{0.239G_{\rm s}\rho_{\rm np}v_{\rm np}}{\rho_{\rm s} \left[ R_{\rm np} + 1.241 \left( \sum_{i} \Delta V_{i} \right)^{1/3} \right]^{3} G_{\rm np}} - \frac{1}{0.74} \right\}^{-1}.$$
(128)

Substituting expression (128) into Eqn (72), we obtain

$$\frac{\eta}{\eta_0} = \exp\left\{2.5 \times \left(1 + \frac{0.239G_{\rm s}\rho_{\rm np}v_{\rm np}}{\rho_{\rm s}G_{\rm np}\left[R_{\rm np} + 1.241\left(\sum_i \Delta V_i\right)^{1/3}\right]^3} - \frac{1}{0.74}\right)^{-1}\right\},\tag{129}$$

where  $\eta$  and  $\eta_0$  are the viscosity of the sol of nanoparticles and of the initial solvent, respectively,  $G_s$  and  $G_{np}$  are the weight of the disperse medium and of the nanoparticles,  $v_{np}$  is the mean volume of one nanoparticle,  $\sum_i \Delta V_i$  is the van der Waals volume of a repeat unit of a polymer macromolecule, and  $\rho_s$ and  $\rho_{np}$  are the densities of the disperse medium and nanoparticle, respectively. Expression (129) allows estimating the radius of a nanoparticle with the adsorption polymer layer from the experimentally obtained relative viscosity of the disperse system.

Substituting the above values from Table 16 into Eqn (129), it is possible to calculate the radii of disperse silver particles with the adsorption layer of a copolymer of ethylene and maleic acid at different concentrations of Ag–EMA in an aqueous solution in the interval of 0.1-1.0 g dl<sup>-1</sup> (Fig. 22, curve 2). At lower concentrations, the values of relative viscosity diverge from the linear dependence, apparently due to the effect of polyelectrolyte swelling of copolymer molecules. This effect has been found, for example, in diluted

 
 Table 16. Parameters for an Ag-copolymer disperse system of ethylene and maleic acid (EMA).\*

Parameters	Value
Molecular mass of a repeat unit, $M_0$	144
Molecular mass of polymer, M	25,000
Van der Waals volume of a repeat unit of polymer $(\sum_i \Delta V_i)_p$ , Å <sup>3</sup>	120
Solvent weight $G_s$ , g	99.00
Weight of Ag nanoparticles per g of composition, $G_{np}$ , g	0.429
Weight of EMA adsorption layer per g of the composition, g	0.571
Radius of silver nanoparticles according to data from trans- mission electron microscopy (TEM) $R_{np}$ , Å	10.00
Density of silver nanoparticles $\rho_{\rm np}$ , g cm <sup>-3</sup>	10.50
Density of solvent $\rho_s$ , g cm <sup>-3</sup>	1.002
Volume of a single silver nanoparticle $v_{\rm np}$ , Å <sup>3</sup>	4187
Relative viscosity $\eta/\eta_0$	3.93
* $c = 1$ g dl <sup>-1</sup> , 0.1M glycine buffer, pH = 9, $T = 25$ °C.	

aqueous solutions of flexible chain copolymers at an ionic strength of 0.1 M [108].

From Fig. 22, it is seen that the relative viscosity of the EMA solution (curve 1) considerably exceeds the viscosity of nanoparticles with an Ag–EMA polymer adsorption layer under similar conditions (curve 2) due to the adsorption of flexible chain macromolecules of an amphiphilic copolymer on the surface of spherical silver nanoparticles.

From the parameters presented in Table 17, it follows that the calculated mean radius ( $R_{np}$ ) of silver nanoparticles with an adsorption layer of copolymer stabilizer amounts to  $103 \pm 6$  Å.

The mean value of  $R_{Ag-EMA} = 103 \pm 6$  Å differs from the value experimentally found using the method of dynamic light scattering (DLS) for the main fraction of nanoparticles,  $R_{np} = 74 \pm 4$  Å, in a 0.05M glycerol buffer (pH = 9, T = 25 °C). The differences among radii of nanoparticles can be due to the presence of a second fraction of larger particles in the disperse system, which are associates of nanoparticles with  $R_{np}$  being about 830 Å (established by means of the DLS method [109]).

![](_page_31_Figure_8.jpeg)

**Figure 22.** Dependences of relative viscosity on concentration: 1 - EMA, 2 - Ag-EMA in 0.1M glycine buffer, pH = 9,  $T = 25^{\circ}\text{C}$ . Equations describing these dependences, respectively, have the form y = 34.538x + 2.6756 ( $R^2 = 0.9565$ ) for EMA and y = 1.3624x + 1.5704 ( $R^2 = 0.9521$ ) for Ag-EMA [63].

Since it is known that  $R_{Ag} = 10$  Å, the thickness of the Ag–EMA polymer adsorption layer under these experimental conditions is about 90 Å. This value highly depends on the pH and ionic strength of the solvent because of the polyelectrolyte nature of the amphiphilic copolymer stabilizer of nanoparticles. For example, earlier, it was shown in [109] that in a neutral medium (0.05 M solution of NaNO<sub>3</sub>), when the degree of ionization of carboxyl groups of maleic acid residuals decreases, the radius of the main fraction of disperse Ag–EMA particles decreases twofold to the value of  $54 \pm 2$  Å, the thickness of the adsorption polymer layer being about 46 Å (at  $R_{Ag} = 10$  Å).

Thus, in contrast to the adsorption layer of a liquid on the surface of nonstabilized nanoparticles in nanoliquids, the adsorption polymer layer of particles stabilized with amphiphilic polyelectrolytes considerably exceeds the dimensions of the nanoparticles. The thickness of this layer is strongly affected by the ionic composition of the disperse medium.

Table 1	7. (	Calculation	of the 1	mean radius of	f nanopartic	les of silv	er with ar	1 absorption	layer o	f EMA*	* copolymer f	from vise	cometry	data
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$c_{Ag-EMA}$ , g dl <sup>-1</sup>	$\eta_{\rm red} = \eta_{\rm sp}/c = 1.3624x + 1.5704$	$\eta_{\rm rel} = \eta/\eta_0 = \eta_{\rm red}  c + 1$	$\ln \eta_{\rm rel}$	$G_{Ag}$ , g in 1 dl	$G_{\rm s}$ , g in 1 dl	$R_{Ag-EMA}, Å$
0.1	1.7064	1.1706	0.1576	0.0429	99.9	108.5
0.2	1.8344	1.3669	0.3125	0.0858	99.8	107.1
0.3	1.9784	1.5935	0.4659	0.1287	99.7	106.3
0.4	2.1144	1.8458	0.6129	0.1716	99.6	105.1
0.5	2.2504	2.1252	0.7539	0.2145	99.5	103.8
0.6	2.3874	2.4324	0.8889	0.2574	99.4	102.5
0.7	2.5224	2.7657	1.0173	0.3003	99.3	101.2
0.8	2.6584	3.1267	1.1400	0.3432	99.2	99.9
0.9	2.8214	3.5393	1.2639	0.3861	99.1	98.8
1.0	2.9304	3.9304	1.3687	0.4290	99.0	97.5
* 0.1 M — glycine	buffer, pH = 9, $T = 25 ^{\circ}$ C.		•	•	•	•

The inverse problem is to find the coefficient of relative viscosity of polymer-stabilized nanoparticles of known radius. For example, for Ag-EMA with the mean value  $R_{\rm np} = 103 \pm 6$  Å at c = 0.5 g dl<sup>-1</sup>, the calculated value of relative viscosity amounts to  $1.95 \pm 0.11$ , the experimentally obtained value being 2.12 (see Table 17). As the concentration of nanoparticles in the system increases to 1 g  $dl^{-1}$ , the calculated value of the relative viscosity (5.23) declines more sharply from the experimental value (3.93). This discrepancy can be a consequence of increasing the proportion of largesize aggregates of nanoparticles ( $R_{np} = 830$  Å) [109] upon increasing the initial concentration of nanoparticles in the system. Calculations using Eqn (129) show that, at the disperse phase concentration of 1 g  $dl^{-1}$  with the content, for example, of a 10% fraction of nanoparticle aggregates and, therefore, 90% of the main Ag-EMA fraction with  $R_{\rm np} = 103$  Å and  $G_{\rm Ag} = 0.3861$  g (see Table 17), the relative viscosity  $\eta_{rel}$  reduces to 4.28, approaching the experimental value. In this case, the contribution to the total amount of viscosity from the calculated relative viscosity of the fraction of aggregates with  $R_{np} = 830$  Å is insignificant.

Thus, the theoretical calculations presented are based on the classical rheological equations, which relate the value of relative viscosity with the concentration and radius of spherical nanoparticles with a polymer of known chemical constitution and molecular mass, adsorbed on their surface. The obtained dependence allows calculating the relative viscosity of a nanocomposite disperse system in a polymer melt or a solution of low-molecular liquid at the known parameters of dispersed particles (radius of particles and their concentration). It also makes it possible to solve the inverse problem, i.e., to calculate the particle radius with the adsorbed polymer layer from the experimental value of relative viscosity.

### 11. Analysis of molecular packing coefficients of amorphous-crystalline polymers and their solvents

The analysis of molecular packing coefficients is important for understanding many physical properties of polymer systems. The molecular packing coefficient is a ratio of the van der Waals volume  $\sum_i \Delta V_i$  of the polymer repeat unit or a molecule of the liquid to the molar volume:

$$k = \frac{\sum_{i} \Delta V_i}{M/d}, \qquad (130)$$

where M is the molecular mass of the repeat unit of the polymer or a molecule of the liquid, and d is the density.

In Ref. [110], the influence of the amorphous-crystalline state on the packing coefficients of polymers is considered. The structure of the amorphous-crystalline state of polymers is specified and the boundaries of the change in the crystalline and amorphous components are determined. An expression for the packing coefficient of solvents is obtained. Its analysis showed that the liquids consist of a dense and a loose fraction with the packing coefficients  $k_{de}$  and  $k_{lo}$ , respectively, which vary within the following limits:  $0.558 < k_{de} < 0.6$ ;  $0.364 < k_{lo} < 0.539$ .

Earlier, in Ref. [110], it was shown that, taking into account the fluctuations in the packing coefficients of polymers in the amorphous state, it is possible to describe the change in the ratio of the glass transition temperature  $T_g$  to the melting temperature  $T_m$  of polymers  $(T_g/T_m)$  in the entire range of the real variation in the packing coefficient  $k_{0, cr}$  in the

crystalline state. Further studies carried out in Ref. [110] show that the expression for  $\langle T_g/T_m \rangle$  obtained in [111] allows estimating the contributions from the packing coefficients of dense  $k_1$  and loose  $k_2$  components to the amorphous-crystalline state of polymers, evaluating their degree of crystallicity  $\xi$ and, after appropriate transformation, establishing the relation between  $T_g/T_m$  and the packing coefficients of solvents.

The ratio  $T_g/T_m$  is known to be independent of the polymer stereoisomeric composition. Moreover, the polymerization conditions themselves (temperature, pressure) affect  $T_g$  and  $T_m$ . A special place is occupied by copolymers consisting of two or more structural units, as an example of which proteins are analyzed in [109] whose molecules consist of 20 amino acid residuals. The specific feature of these proteins is that their molecules form different structures (globular or having the form of tied rods), depending on the sequence of amino acid residuals.

Studies in recent years have shown that the low-frequency Raman spectra of polymethyl methacrylate (PMMA) and polycarbonate (PC) possess an interesting property—the presence of boson peaks [112] (excess density of vibrational states [113], exceeding the Debye density by a few times depending on the material). In glasses [114], the boson peaks manifest themselves in the temperature region of 3–15 K. The excess density of vibrational states manifests itself in lowenergy spectra of inelastic scattering of neutrons, lowfrequency spectra of Raman scattering (from 0.6 to 800 GHz), far-infrared absorption, as well as low-temperature heat capacity and heat conduction. In a similar region of temperatures ( $T_0 = 6$  K), there is a crossing point of temperature dependences of packing coefficients of polymers [2, 3].

Below, using the most characteristic polymers and liquids as an example, we will consider the influence of the factors listed above on the packing factors. Considering these factors is necessary when assessing the conditions for the dissolution of polymers, density, refractive index, etc. First, we consider the definition of the packing coefficients in dense and loose components of a polymer in an amorphous-crystalline state. The dependence of  $\langle T_g/T_m \rangle$  in the entire real range of packing coefficient  $k_{0,cr}$  variation in the crystalline state, proposed in Ref. [111], can be used to analyze the packing coefficients of dense and loose structures of polymers. Let us write it in the following form:

$$\left\langle \frac{T_{\rm g}}{T_{\rm m}} \right\rangle = \frac{k^* - 0.732}{15.625 \left(k^* - 0.7313\right) \left(k^* - 0.6025\right)} \,,$$
(131)

where  $k^*$  is the packing coefficient of the amorphouscrystalline polymer, the meaning of which will be clarified below.

Let us briefly dwell on the nature of the amorphouscrystalline state of polymers. According to Refs [115, 116], a polymer molecule, depending on the degree of polymerization, can form a globule consisting of a dense core (analogous to the crystalline state) and a 'margin' (analogous to the coiled state). Such a globule upon a temperature change will undergo two transitions: the transition of the edge from a glassy state to a rubbery state at temperature  $T_g$  and, with the further growth of temperature, globule core melting at  $T_m$ . A polymer in the block state formed by such globules will be characterized by a certain degree of crystallicity.

Let us evaluate the influence of the crystallicity degree  $\xi$ and degree of polymerization N on the packing coefficient of

Polymer	Forms of polymers	$T_{\rm g}, {\rm K}$	$T_{\rm m}, {\rm K}$	$T_{\rm g}/T_{\rm m}$	$k_1$	$k_2$	ξ <sub>exp</sub>	$k^*$
	PEHD (high density)	253	393–408	0.644-0.62	0.73	0.705-0.709	0.7–0.85	0.723-0.727
Polyethylene (PE)	PELD (low density)	248	376–388	0.66-0.64	0.73	0.702-0.705	0.5-0.65	0.716-0.721
Polystyrene (PS)	Isotactic	378	513	0.737	0.73	0.691	0.3–0.35	0.703-0.705
Polymethyl metha-	Isotactic	323	433	0.746	0.73	0.69	—	—
crylate (PMMA)	Syndiotactic	388	473	0.82	0.73	0.682	—	—
Lysozyme	Protein	331	346	0.957	0.73	0.67	0.49	0.699

**Table 18.** Values of packing coefficients for dense  $k_1$  and loose  $k_2$  components and  $k^*$  for a number of amorphous-crystalline polymers.

an amorphous-crystalline polymer. The volume of a macromolecule consists of the volume of the dense core and the volume of the edge. Considering an amorphous-crystalline polymer as a homogeneous mixture of amorphous and crystalline parts, the packing coefficient of the amorphouscrystalline polymer  $k^*$  can be expressed as [2, 3]

$$k^{*} = \frac{\left[\xi(\sum_{i} \Delta V_{i})_{\rm cr} + (1 - \xi)(\sum_{i} \Delta V_{i})_{\rm a}\right] N_{\rm A}}{\left[\xi M_{\rm cr} + (1 - \xi)M_{\rm a}\right]/d}, \qquad (132)$$

where  $\xi$  and  $(1 - \xi)$  are the molar fractions of the crystalline (degree of crystallicity) and amorphous part in the amorphous-crystalline polymer, respectively.  $(\sum_i \Delta V_i)_{\rm cr}$  and  $(\sum_i \Delta V_i)_{\rm a}$  are the van der Waals volumes of the repeat unit of the crystalline and amorphous parts of the polymer,  $M_{\rm cr}$ and  $M_{\rm a}$  are the molecular masses of these components, respectively, and *d* is the density of their mixture.

Since  $(\sum_i \Delta V_i)_{cr} = (\sum_i \Delta V_i)_a$ ,  $d = \xi d_{cr} + (1 - \xi)d_a$ , where  $d_{cr}$  and  $d_a$  are the densities of the polymer in the crystalline and amorphous states and  $(\sum_i \Delta V_i)_{cr} N_A / (M_{cr}/d_{cr}) = k_1$ , expression (132) can be reduced to the form

$$k^* = k_1 \left[ \xi + (1 - \xi) \frac{d_a}{d_{\rm cr}} \right] = \xi k_1 + (1 - \xi) k_2 , \qquad (133)$$

where  $k_2 = k_1(d_a/d_{cr})$ , and  $k_1$  and  $k_2$  are the packing coefficients of the dense and loose components of the polymer, respectively. Usually,  $0.3 \le \xi \le 0.7$  [117].

Using expression (133), it is possible to evaluate  $k^*$  of polymers in the amorphous-crystalline state based on experimental data  $T_g$ ,  $T_m$ , and  $\xi_{exp}$  and the values of  $k_1$  and  $k_2$ , calculated by means of expression (131). Table 18 summarizes these values for a number of polymers.

For the case of PMMA (Table 19), for which  $\xi_{exp}$  is unknown, the values of  $k^*$  were calculated for the degree of crystallicity  $0.3 \leq \xi \leq 0.7$  [117].

The spread of the  $k^*$  value in amorphous-crystalline polymers presented in Table 18 may be due to the methods of sample preparation and the degree of polymerization of molecules (with a decrease in the degree of polymerization, the size of the amorphous region decreases [115, 116]). For example, in the case of PMMA, depending on the stereoisomeric composition of the polymer, substantial changes in  $k^*$  occur depending on the value of  $\xi$  (see Table 19).

The above estimations were carried out for synthetic polymers. In biopolymers, e.g., globular protein lysozyme, the dense core consists of  $\alpha$ -spirals,  $\beta$ -folds, and turns. To calculate  $k_1$  and  $k_2$ , we use data from Ref. [118] on  $T_g$ ,  $T_m$  ( $T_m = T_{dn}$  is the temperature of protein denaturation). To estimate  $\xi$ , we assume that  $\xi \sim N_{nuc}/(N_{nuc} + N_{marge})$ , where  $N_{nuc}$  and  $N_{marge}$  are the number of units in the core and the margin of the lysozyme globule, respectively. We take these

**Table 19.** Change in the packing coefficient of the amorphous-crystalline PMMA  $k^*$  depending on the degree of crystallicity  $\xi$ .

Polymer	Forms of polymer	٣ζ	$k^*$
	Isotactic	0.3–0.7	0.715-0.723
РММА	Syndiotactic	0.3–07	0.696-0.715

data from Ref. [118]. Then,  $\xi = 0.49$  and  $k^* = 0.699$  (see Table 18); the latter is close to the value of the packing coefficient of lysozyme obtained in Ref. [58] ( $k_{58|}^* = 0.691$ ). In practice,  $\xi$  is estimated based on spectroscopy data (the ratio of the area of peaks corresponding to the crystalline part to the total area of peaks corresponding to both amorphous and crystalline components). Since the core of the globule consists of amino acid residuals of different constitutions, the real value of  $\xi$  will differ from the experimental  $\xi_{exp}$ . Estimates show that, to obtain  $k^* = 0.691$ , the value of  $\xi$  should be  $\xi = 0.35$ .

The values of  $k_1$  and  $k_2$  presented in Table 18 show that in the Lifshitz–Rosenzweig approximation the maximum value is  $\langle k_1 \rangle^{\text{max}} = 0.73$  and the minimum value is  $\langle k_2 \rangle^{\text{min}} = 0.67$ . Keeping in mind that the maximum value of the packing coefficient of crystalline polymers is  $\langle k_1 \rangle^{\text{max}} = 0.745$  [58], we can determine the difference  $\delta$  between the real ultimate values of the packing coefficient and its maximum value, determined by the corresponding approximation, i.e.,  $\delta = k_1^{\text{max}} - \langle k_1 \rangle^{\text{max}} = 0.015$ . From here, it is possible to specify the minimum value of the packing coefficient for polymers in an amorphous state  $k_2^{\text{min}} = \langle k_2 \rangle^{\text{min}} - \delta = 0.655$ , which is realized in copolymers like proteins.

Let us proceed to an analysis of packing coefficients of organic liquids and water. Expression (131) can be used to specify the packing coefficients of organic liquids and water  $k_{lq}$ . In this case, we will follow these considerations. Since the constant 0.6025 in the denominator of expression (131) determines the upper bound for the packing coefficients of nonspherical molecules of the liquid [119, 120], we will retain it in the modified expression (131).

Let us present the modified expression (131) in the form

$$\left\langle \frac{T_{\rm g}}{T_{\rm m}} \right\rangle = \frac{k_{\rm lq} - a}{A \left( k_{\rm lq} - b \right) \left( k_{\rm lq} - 0.6025 \right)} \,.$$
(134)

To determine the coefficients A, a, and b, we make use of the data on  $T_g/T_m$  and  $k_{lq}$  taken for toluene, ethylbenzene, and ethanol (Table 20).

As a result, we obtain a = 0.6113, b = 0.172, A = 5.1334, and expression (134) takes the form

$$\left\langle \frac{T_{\rm g}}{T_{\rm m}} \right\rangle = \frac{k_{\rm lq} - 0.6113}{5.1334 (k_{\rm lq} - 0.172)(k_{\rm lq} - 0.6025)}.$$
 (135)

No.	Liquids	$T_{\rm g}, { m K}$	$T_{\rm m}, { m K}$	$T_{\rm g}/T_{\rm m}$	$k_{1q}^{de}$	$k_{ m lq}^{ m lo}$
1	Water	134	273	0.491	0.596	0.364
2	Pyridine	116	231.4	0.503	0.594	0.386
3	Acetic acid	150	290	0.517	0.587	0.426
4	Chloroform	111	209.5	0.531	0.581	0.483
5	Ethanol	96	159	0.604	0.558	0.539
6	Isobutyl chloride	88	142	0.620	0.569	0.519
7	Ethylbenzene	111	178	0.624	0.570	0.515
8	Toluene	113	178	0.635	0.574	0.507
9	Glycerol	186	291	0.639	0.575	0.504
10	N-pentyl benzene	128	198	0.646	0.577	0.499
11	Isoamyl bromide	105	161	0.652	0.578	0.495
12	N-propanol	98	146	0.671	0.581	0.484
13	Isopropyl benzene	125	177	0.706	0.585	0.466
14	3-bromopentane	108	147	0.735	0.587	0.453
15	Propylene glycol	167	213	0.782	0.589	0.434

**Table 20.** Dependence of  $k_{lq}^{de}$  and  $k_{lq}^{lo}$  on  $T_g/T_m$  of liquids.

An analysis of Eqn (135) shows that only the condition  $T_g/T_m < 1$  is physically meaningful, which holds at  $0.36 < k_{lq} < 0.6$ . With the considered values of the parameters *a*, *b*, and *A*, expression (135) has a minimum at  $k_{lq} = 0.549$ .

In Table 20, the values of  $k_{lq}$  for organic liquids calculated from the  $T_g/T_m$  data are presented. The values of  $T_g$  are taken from Refs [121–123] and  $T_m$  are taken from the reference data.

As is shown by the calculations using Eqn (135), each value of  $T_g/T_m$  of the liquid corresponds to two packing coefficients, the dense packing coefficient  $k_{lq}^{de}$  and the loose packing coefficient  $k_{lq}^{lo}$ . In the region  $0.604 \leq T_g/T_m \leq 0.782$ , expression (135) describes well the variation in  $k_{lq}$  [3]. However, in the region where  $T_g/T_m$  varies from 0.531 to 0.491, expression (135) does not work. To make Eqn (135) capable of describing this region as well, it is necessary to correct the coefficient A. For example, to describe  $k_{lq}$  of water, the coefficient A in (135) should equal 11; this can be taken into account by introducing the following dependence of A on  $T_g/T_m$ :

$$A = 11 \left[ 1 - 10.23 \left( \frac{T_{\rm g}}{T_{\rm m}} - 0.491 \right) \right].$$
(136)

Furthermore, at  $T_g/T_m \ge 0.604$ , we have A = 5.1334.

When approximating the dependence (136), we used as a reference point the loose component packing coefficient  $k_{\rm sl}^{\rm lo} = 0.364$  for water, obtained as a result of computer simulation of water by methods of molecular dynamics (MD) and statistical geometry [124].

The MD method allows studying water from the point of view of the spatial arrangement of certain structural elements of the system (Delone simplexes, i.e., the tetrahedrons formed by a group of four nearest atoms making an elementary cavity in the studied system), whose shape is substantially distorted upon the action of hydrogen bonds.

As a result, a dense fraction is formed in water due to joining regular tetrahedrons by the adjacent faces and a loose fraction formed by irregular distorted tetrahedrons. Thus, water can be considered a totality of two systems (dense in the form of branching chains, whose basic element is a perfect tetrahedral configuration, and loose, with a disordered arrangement of atoms).

As a density parameter, the packing coefficient  $k_f = V_p/V_f$  was used, where  $V_p$  is the volume occupied by spherical particles within the fraction,  $V_f$  is the fraction volume.

Since the fractions consist of Delone simplexes, the volumes  $V_p$  and  $V_f$  expressed via the appropriate parameters of the simplexes have the following form:

$$V_{\rm f} = \sum_{i} V_{i},$$
$$V_{\rm p} = \frac{1}{3} R_0^3 \sum_{i} \omega_{i},$$

where  $V_i$  is the volume of the *i*th simplex of the considered fraction,  $V_0$  and  $R_0$  are the volume and the radius of a single spherical particle, respectively,  $\omega_i$  is the sum of trihedral solid angles at the vertices of the *i*th simplex of the fraction, and the packing coefficient of the fraction is

$$k_{\rm f} = \frac{1}{3} R_0^3 \frac{\sum_i \omega_i}{\sum_i V_i} \,.$$

In Ref. [124], the molecules of water were approximated by a sphere with effective radius  $R_0 = 1.4$  Å (oxygen atom). As a result, the following topologic feature of the microstructure of the modeled liquid water was revealed [124]: water consists of a dense fraction and a loose one with the packing coefficients  $k_{de} = 0.5049$  and  $k_{lo} = 0.3640$ , respectively. It should be noted that, according to our calculations (see Table 20),  $k_{de} = 0.596$ . However, since the main contribution to the packing coefficient of water comes from the loose fraction, the error in the determination of the packing

![](_page_35_Figure_2.jpeg)

**Figure 23.** Dependence of packing coefficients for dense  $k_1$  and loose  $k_2$  fraction of polymers (p) and liquids (lq) on  $T'_g/T'_m$  [117].

coefficient of water will be only 2.8%. Moreover, the found discrepancy in  $k_{de}$  can help in correcting the criteria of selecting the dense fraction simplexes.

Figure 23 shows the dependences of the packing coefficients of the dense  $k_1$  and loose  $k_2$  fractions of polymers and liquids on  $T_g/T_m$ , plotted using the data from Table 18 and Table 19. It is seen that in polymers within  $0.62 < T_g/T_m < 0.957$  the value of  $k_1$  is practically unchanged ( $k_1 \sim 0.73$ ), whereas  $k_2$  in the same range of  $T_g/T_m$  decreases from 0.709 to 0.67. In the case of liquids, we have, first, smaller values of the coefficients  $k_1 = k_{lq}^{de} = k_{de}$  and  $k_2 = k_{lq}^{lo} = k_{lo}$  and, second, a clearly expressed minimum of  $k_1$  and maximum of  $k_2$  in the region of  $T_g/T_m = 0.6$ . Moreover, while in polymers at a certain density and  $k^*$  the main contribution is due to the ordered part with  $\xi \sim 0.7$ , in liquids it is due to the disordered part with  $\xi \sim 0.1$  [124].

Now, let us turn to the behavior of polymers and liquids in the case of small  $T'_g/T'_m$  and the appearance of a boson peak. Note preliminarily that, in the general case in Eqn (135), according to [125], the left-hand side had the following form:  $T'_g/T'_m$ , where  $T'_g = T_g - T_0$ ,  $T'_m = T_m - T_0$ ,  $T_0 = 6$  K. However, since in Ref. [110] we were interested in values  $T_g \ge T_0$  and  $T_m \ge T_0$ , we ignored the quantity  $T_0$  and used equations like (131), (135), (136). In the present section, we are interested in the region of low characteristic temperatures, when the quantity  $T_0$  cannot be ignored. Therefore, using Eqns (135) and (136), we will take  $T_g/T_m$  instead of  $T'_g/T'_m$ . In this case, Eqns (135) and (136) with the introduced corrections taken into account will be applicable to the study of packing coefficients of polymers and liquids in the region of small values of  $T'_g/T'_m$ . Table 21 presents the dependences of  $T'_g/T'_m$  on k at  $0.21 \le T'_g/T'_m \le 0.491$ .

**Table 21.** Coefficients  $k_1$  and  $k_2$  in the region of small values\* of  $T_g/T_m$ .

Below, we will try to clarify the physical meaning of new points in Table 21 (by the example of  $T'_g/T'_m = 0.25$ ) within the research on boson peaks. As shown by experimental studies, in the temperature range from 3 to 15 K in glasses, there is an excess density of vibrational states (compared to the Debye density), which manifests itself as a boson peak in spectral measurements. Such peaks are observed in studies of PMMA and polyisobutylene (PIB), as well as silicate glasses.

Let us perform a number of estimates for syndiotactic PMMA at

$$\frac{T'_{\rm g}}{T'_{\rm m}} = 0.25\,. \tag{137}$$

For this purpose, we reduce expression (137) to the following form:

$$T_0 = \frac{T_{\rm m}}{3} \left( \frac{4T_{\rm g}}{T_{\rm m}} - 1 \right).$$
(138)

Since in the syndiotactic PMMA  $T_g/T_m = 0.82$  and  $T_0 = 6$  K, we obtain  $T_m = 7.89$  K, i.e., a value considerably lower than the melting temperature of PMMA (see Table 18), but close to the temperature of the relaxation transition related to reorientation of methyl groups in PMMA [128], equal to 13.8 K. This means that the methyl groups of PMMA form a rotational isomer subsystem inside the PMMA chain, where rearrangements occur upon the vibration of the rest atoms of the chain. Such a subsystem is characterized by its own glass transition temperature. While for the low-temperature transition  $T_g = 13.8$  K, its  $T_m = 16.83$  K (in this case, it is assumed that in PMMA the ratio  $T_g/T_m$  is unchanged for all transitions).

According to Ref. [127], the activation energy of the low-temperature transition  $\Delta E^*$  is estimated as

$$\Delta E^* = 26kT_{\rm g}\,,\tag{139}$$

which at  $T_g = 13.8$  K yields  $\Delta E^* = 0.115$  kJ mol<sup>-1</sup>, with the corresponding frequency of a transition over the potential barrier  $f^* = 7.6$  THz. Indeed, during the rearrangement of the rotational isomer subsystem formed by methyl groups, they transit from the trans to the gauche state and back, which is determined by the energy difference  $\Delta E$  between rotational isomers. Since in these states CH<sub>3</sub> groups have different polarizabilities, according to [128] the excitation of Raman transition frequencies  $f_{\text{max}}$  occurs, which are recorded by the method of Raman scattering, i.e.,  $\Delta E = h f_{\text{max}}$ . As in PMMA, the maximum of the Raman scattering spectrum is  $f_{\text{max}} = 400$  GHz [128], and we have  $\Delta E/\Delta E^* = f_{\text{max}}/f^* = 0.053$  (which is close to the corresponding ratio for a  $\gamma$ -transition [58]).

No.	$T_{\rm g}, { m K}$	$T_{\rm m}, { m K}$	$T_{ m g}^{\prime}/T_{ m m}^{\prime}$	$T_{\rm g}/T_{\rm m}$	A	$k_1$	$k_2$			
1	134	273	0.491	0.491	11	0.596	0.364			
2		_	0.29		33.62	0.599	0.277			
3	4.2	5.12	0.25	0.82	38.12	0.599	0.279			
4	_	_	0.21		42.62	0.599	0.287			
* I1	* In the case of water (No. 1), instead of $T'_{g}/T'_{m}$ we took $T_{g}/T_{m}$ . In all other cases (Nos 2–4), the ratio $T'_{g}/T'_{m}$ has the above meaning.									

Thus, estimates of the packing coefficients of polymers and liquids carried out in Ref. [111] by means of the relation  $\langle T_g/T_m \rangle = f(k)$  proposed in [111] and data from computer experiments made it possible to describe the dependence on  $(T_g - T_0)/(T_m - T_0)$  in the entire range of its variation  $(0 < (T_g - T_0)/(T_m - T_0) < 0.734)$  for the packing coefficients of the dense  $k_1$  and loose  $k_2$  fractions. This is reflected in Fig. 23. It is shown that the packing coefficients  $k_1$  and  $k_2$  of polymers and liquids change within a limited range as the temperature varies in a wide range up to the vacuum temperature. In polymers,  $0.745 < k_1 < 0.71$ ,  $0.655 < k_2 < 0.7$ , in liquids,  $0.558 < k_1 < 0.6$ ,  $0.364 < k_2 < 0.539$ . The analysis carried out is of importance for specifying the conditions of the solubility of polymers and calculating dielectric properties and surface tension coefficients of polymers and solvents.

# **12.** Effect of chemical constitution of heat-resistant thermoplastics on friction with steel

At present, a number of new heat-resistant thermoplasts of various chemical constitution are being synthesized. Such thermoplasts, in particular, were used as a binding material for filled composites in friction units: crystalline polyether ether ketones (PEEKs) [130–132], polyphenylene sulphide (PPS) [133, 134], and amorphous heat-resistant polymers — polysulfones (PSPs) [135] and poly(arylene ether ketones) (PAEKs) synthesized in recent years [136].

Reference [130] shows advantages of using in friction units PEEKs with higher molecular mass in the case of similar crystallicity. Of no less importance is the conclusion about the possible nonsymbasis of varying the PEEK friction coefficient upon increasing the wear resistance. Reference [132] establishes a correlation between the polymer molecular mass and the tribological properties of PEEKs. It is important to note that this is done by comparing three properties: the molecular mass, strength indicators, and the tribological properties.

Polysulfone of various molecular masses was used as a polymer binder of carbon-filled plastics [135]. In the paper, the conclusion is made that the molecular mass is a key factor in the exploitation of products made of polysulfone.

During thermal processing of amorphous PEEKs at T=180-300 °C, the dependence of the physical-mechanical and tribological properties on the degree of crystallization of the obtained coatings was discovered [137]. The developed

semi-crystalline coatings have increased hardness and decreased wear; the friction coefficient reaches the value f = 0.33.

It should be noted that increasing the molecular mass as a way to achieve better tribological indicators is not a universal means for polymers of various chemical constitutions. Reference [138] devoted to the study of friction in aliphatic polyamide-66 shows an inverse dependence between the molecular mass indicator and tribological properties of the studied polymer. At the same time, in all papers concerning tribological properties of a polymer of a different chemical constitution, a PEEK, it is proved that increasing the molecular mass and crystallicity of this polymer is a way to improve its tribological indices.

The reasons why such a correlation is not present in polymers of different chemical constitutions have been earlier shown in Ref. [139]. Using the example of numerous representatives of various classes of polymers, a systematization of tribochemical behavior was proposed with a division of polymers into tribochemically active ones, to which among thermoplasts the aliphatic polyamides were attributed, and tribochemically stable ones, including polyimides, polyphenylchinoxalines, polyphenylenoxide, and polyoxadiasoles.

In Ref. [140], an attempt is made to use the calculation method of computer simulation to explain the tribological behavior of reinforcing fibers of polyamide (Kevlar—polyparaphenylene terephthalamide, Nomex—poly(meta-phenyleneisophthalamide) and polyoxadiosole (POD). It is shown that, in spite of the high rigidity and wear resistance, polyamides retain high tribochemical activity and cannot be applied under conditions of dry friction as antifriction materials.

The purpose of Ref. [141] was to establish the effect of the chemical constitution and physical state (structure) of a number of heat-resistant thermoplasts, both amorphous and crystalline, on their friction against steel within a unified approach. In Ref. [141], the calculation method of computer materials science was exploited, widely used in polymer chemistry to determine a number of functional properties, such as the glass transition temperature, fluidity, heat resistance, and volume expansion coefficient. For thermoplasts, the intermolecular interaction energy ( $E_{IMI}$ ) and its components, i.e., the energy of dipole-dipole interaction and hydrogen bonds ( $E_{dip-dip}$  and H-bond), are determined, as is the energy of dispersion interaction ( $E_{disp}$ ) (Table 22).

 Table 22. Values of intermolecular interaction energy for heat-resistant polymers.

		Amorphous		Crystalline					
Parameter	PAEK	PAEK-F	PSF	PEEK	PFS	Kevlar	Nomex	POD	
	Blocks					Reinforcing fibers			
Intermolecular interaction energy, kJ mol <sup>-1</sup>	421	444	461	258	73	308	249	144	
Ratio of the energy of dipole-dipole interaction and hydrogen bonds to the total energy, %	18	25	32	9	9	45	45	37	
Ratio of the energy of dispersion interaction to the total energy, %	82	75	68	91	91	55	55	63	
Friction coefficient (average), P = 10 MPa, $v = 0.5$ m s <sup>-1</sup>	0.4	0.75	0.8	0.6	0.45	0.35	0.45	0.25	

# 13. Studies of the effect of the molecular mass of the amorphous poly(arylene ether ketone) on friction and wear

The study of the influence of the intermolecular interaction energy on the friction of polymers is based on an assumption [141] that, under the conditions of shear, the high value of the weak dispersion interaction  $E_{disp}$  as compared to the strong dipole-dipole interaction  $E_{dip-dip}$  must relieve the shear efforts. It is also obvious that, in the presence of friction,  $E_{disp}$  should correlate with the molecular component of the friction force  $F_{mol}$ . For the studied thermoplasts, the obtained dependences of high  $E_{disp}$ , as opposed to  $E_{dip-dip}$ , evidence the possibility of obtaining materials with a reduced friction coefficient based on them.

However, this is only a possibility rather than a guaranty of obtaining an antifriction wear-resistant material. The reason is that the friction force is the sum of mechanical and molecular components ( $F_{\rm fr} = F_{\rm mech} + F_{\rm mol}$ ). In dry friction, when the polymer material itself is both a bearing surface and a lubricant, the high value of  $E_{disp}$  leads to a sharp increase in  $F_{\text{mech}}$ . In the process of friction, due to low surface hardness, the depth of the deformed layer increases, which gives rise to an increase in the total magnitude of the friction force  $F_{\rm fr}$  with an increase in both  $F_{mech}$  and  $F_{mol}$ . In this connection, the problem of creating a material with a lower friction coefficient in the case of PAEKs reduces to searching for a way to decrease  $F_{mech}$ without changing the chemical structure and introducing additional components. In the case of heat-resistant thermoplasts, to get the desired effect, it is reasonable to study one of two methods of changing the physical state: to try to crystallize the polymer or to increase maximally its molecular mass.

Experimental tests of PAEK samples with the reduced viscosities  $\eta_{red} = 0.75$  and 0.53 dl g<sup>-1</sup> were carried out using the I-47 friction machine with a spherical counterbody 5 mm in diameter at a pressure of 10 MPa for friction of the polymer with steel [141]. The results of several experiments were unsatisfactory (Fig. 24). The friction coefficient increased to 0.7 in the sample with higher rather than lower molecular mass. The negative results obtained upon increasing the molecular mass could be evidence of either a complex interrelation between the two variables  $F_{mech}$  and  $F_{mol}$  of the friction force or the impossibility in principle of obtaining samples of PAEKs with the friction coefficient lower than f = 0.5 and simultaneously with an increased wear resistance. Therefore, the final friction experiments were performed with a wide range of objects, in six samples, where  $\eta_{\rm red}$  varied in the interval from 0.4 to 2.49 dl  $g^{-1}$  (see Fig. 24).

It is reasonable to divide the dependences of tribological properties (wear, friction coefficient) on the index  $\eta_{red}$  obtained in the experiment into three regions as  $\eta_{red}$  grows.

In the first region, with PAEK friction in the range  $\eta_{red}$  from 0.4 to 0.53 dl g<sup>-1</sup>, a noticeable decrease in wear occurs while maintaining the value of the friction coefficient f = 0.55, which is explained by a certain enhancement of physical and mechanical parameters: an increase in relative elongation and tensile strength of the polymer.

In the second region with  $\eta_{red}$  from 0.75 to 1.0 dl g<sup>-1</sup>, the change in tribological parameters is accompanied by an increase in the friction coefficient and a decrease in the wear. Such a behavior of these coefficients frequently occurs in polymer tribological materials and is probably explained by nonsymbasis in the change in the mechanical and molecular components of the friction force.

![](_page_37_Figure_9.jpeg)

Figure 24. Dependence of the coefficient of friction and wear on  $\eta_{red}$  in pressed PAEK samples [141].

![](_page_37_Figure_11.jpeg)

**Figure 25.** Dependence of friction coefficient on test duration: I — PAEK-F with  $\eta_{red} = 0.5$  dl g<sup>-1</sup>, 2 — PSF with  $\eta_{red} = 0.5$  dl g<sup>-1</sup>, 3 — PAEK with  $\eta_{red} = 0.5$  dl g<sup>-1</sup>, 4 — PAEK with  $\eta_{red} = 2.49$  dl g<sup>-1</sup> [141].

In the third region at high values of  $\eta_{red}$ , the most significant results were obtained upon increasing the PAEK molecular mass to  $200 \times 10^3$  Da ( $\eta_{red} = 2.49$  dl g<sup>-1</sup>), where a substantial decrease in the friction coefficient to 0.4 occurs and simultaneously minimum wear is ensured.

Experiments have shown that, in the friction of heatresistant amorphous PAEK thermoplasts, there are two reference factors relating chemical constitution to the tribological properties. The character of behavior of thermoplasts under friction is determined by the energy of intermolecular interaction and the physical state of the polymer, in the case considered, the PAEK molecular mass.

Based on the established dependence, it is possible to hypothesize that the friction coefficient of polysulfone (PSF) with steel at a value of reduced viscosity comparable to that of PAEKs should demonstrate a higher value of the friction coefficient due to the lower value of  $E_{\text{disp}}$  (see Table 22). Experimental data on the friction of PAEKs and PSF with the same reduced viscosity ( $\eta_{\text{red}} = 0.5 \text{ dl g}^{-1}$ ) confirmed this hypothesis (Fig. 25).

It seems of interest to consider the tribological properties of the amorphous PAEK, containing F atoms and having the same reduced viscosity as the analog. As a rule, polymer analogs differing only by the substitution of H atoms for F atoms demonstrate a reduction in the friction coefficient, as takes place in polyethylene. In the study of friction in PAEKs based on bisphenol A, having a propyl group (polymer 3), and PAEKs based on bisphenol AF with a hexafluoropropyl group (polymer 1), it is seen that the friction coefficient of polymer 1 increases to f = 0.8, whereas in polymer 3f = 0.55 (see Fig. 25).

The reasons for such a behavior are probably due to the sharp change in one of the most important physicalmechanical parameters affecting antifriction properties of polymers: relative elongation under stretching ( $\varepsilon$ %). In PAEKs based on bisphenol AF with a hexafluoropropyl group,  $\varepsilon$ % decreases depending on  $\eta_{red}$  to 25–80% compared with the analog. This leads to the fact that, under friction, the sharp reduction in deformability facilitates a significant increase in the wear and friction coefficient.

### 14. Partially crystalline polymers

The group of tribostable polymers includes both amorphous and partially crystalline representatives: polyetheretherketone (PEEK) and polyphenylene sulphide (PPS). To understand the nature of friction in crystalline thermoplasts, the same approaches were used as for amorphous ones (see Table 22).

It can be seen that in these polymers the ratio of dispersion interaction energy to the total energy of intermolecular interaction is higher (> 90% for polyaryletherketone) than in the case of amorphous ones (70–80%), which evidences the possibility of creating antifriction materials with low friction coefficients based on them.

However, experimental results (Fig. 26) show that the friction coefficients of both crystalline polymers are higher than those of the high-molecular amorphous PAEK and nearly coincide with the friction coefficient of the PAEK having a lower reduced viscosity ( $\sim 0.5-0.75$  dl g<sup>-1</sup>). Such a tribological behavior of partially crystalline thermoplasts (PEEK, PPS) is probably due to the presence of a significant amount (to  $\sim 70\%$ ) of amorphous structure consisting of the polymer with decreased molecular mass in their composition. This is confirmed by thermomechanical studies — both crystalline polymers have lowered values of the glass transition temperature: 140–143 °C in PEEKs and 90–100 °C in PPS.

The constitution of partially crystalline thermoplasts offers reasons to believe that the origin of friction in these polymers, as well as in amorphous ones, is based on the same factor of chemical structure that determines the value  $E_{disp}$  of the intermolecular interaction energy, not to mention the indexes of molecular mass of the amorphous-crystalline structure of thermoplasts. It is possible to hypothesize that, upon increasing the molecular mass of the polymer with

 $f_{\rm fp} \frac{0.8}{0.7}$ 

0.6

0.5

0.4

0.3

subsequent crystallization, more tribostable crystalline thermoplasts than those studied in the experiment could be obtained.

### 15. Specific tribochemical behavior of polymers

As was shown above, using computer simulation methods, it is possible to obtain information about the chemical constitution of polymers. Nevertheless, this approach is at present unable to provide exhaustive information about the specific tribological properties of polymers. A number of polymers, for example, PEEKs and PPS with completely coincident indicators of chemical constitution and crystallicity, demonstrate different tribological behaviors. For example, they noticeably differ in values of the friction coefficient: 0.6 in PEEKs and 0.45 in PPS (see Fig. 26).

Perhaps, in this case, the different tribological behavior of PEEKs and PPS is explained by some specific tribological properties associated primarily with PPS. In spite of the high value of heat resistance, in the process of friction, this polymer can manifest weakly expressed properties of selflubrication [142]. Even with the friction of PPS powder between two steel conterbodies, the adhesion of transfer films on the steel surfaces occurs.

The material in Ref. [141] does not claim to develop a semiempirical method for calculating the friction coefficient of polymers. The paper only reports the results of using the indicators of intermolecular interaction energy obtained by computer simulation to create a general approach to understanding the complex nature of friction in heat-resistant tribostable thermoplasts. This approach allowed revealing two main factors determining the character of friction in heatresistant thermoplasts against steel: the dispersion component of the intermolecular interaction energy and the polymer molecular mass. The crystallicity only increases the temperature boundaries for exploiting the polymers with lowered molecular mass but does not ensure low-temperature stability.

The conclusions are based on a study of 14 samples of polymers with different chemical constitutions and molecular masses. The developed universal formalized approach cannot describe the entire complex process of dry friction of some polymers that expose the effects of self-lubrication, tribochemical lubrication, sharp degradation of a number of physical-mechanical properties, etc. in the process of friction. Such specific behavior is considered by the example of introducing S and F atoms into a repeat unit of thermoplasts.

### 16. Conclusion

Thus, in this review, we considered models and a computer program that allows automated construction of diagrams of compatibility of water permeability with a van der Waals volume, density, cohesion energy, glass transition temperature, and intense thermal degradation onset temperature. The diagrams of compatibility of water permeability with a number of physical characteristics are constructed for polyethers, polycarbonates, polystyrenes, polyesters, polyetherketones, polyamides, polyimides, etc. All this is in the mainstream of numerical methods of predicting polymer properties, since they simplify the research of synthetic chemists.

Much attention is paid to network polymers, widely used in engineering. A model and a principle of the appropriate

![](_page_38_Figure_17.jpeg)

computer program for electronic synthesis of polymer networks having a prescribed interval of glass transition temperatures  $T_g$  are proposed. The chemical constitution of 78 network cross-linked points and 122 basic fragments are represented to construct the internode chains. Such an approach to the prediction of properties of network polymers has been applied to scientific research for the first time.

The problem of reducing the thermal expansion coefficient of polyvinylchloride by mixing with heat resistant polymers possessing a high glass transition temperature is considered. The prediction of the thermal expansion coefficient of polyvinylchloride-based materials is important, because this polymer is widely used in a number of technical applications, and it is necessary to minimize the size distortions of polyvinylchloride products with a change in temperature. It is demonstrated that the expansion coefficient of polyvinylchloride can be reduced by 52% using mixing with heat-resistant polymers. Another problem, related to polyvinylchloride, is to predict the compatibility of this polymer with other polymers and assess the elasticity modulus of the mixture allowing for the phase and physical state of the mixed polymers. In this case, chemical interaction between microphases is taken into account.

Substantial attention is devoted to the influence of plasticization on the strength and viscosity of plasticized polymers, and an appropriate calculation scheme is developed. The chemical constitution of the polymer and solvent, intermolecular interaction between the polymer and the solvent, van der Waals volume, and molecular mass of the repeat unit of the polymer and solvent molecule, as well as the solvent concentration, are taken into account. Temperature dependences of viscosity are obtained. The calculation scheme is computerized and included as a separate option in the Kaskad program (Institute of Organoelement Compounds, Russian Academy of Sciences). The rheological properties of polymer solutions are important for the processes of polymer recycling carried out with the use of their solutions. Moreover, some polymer materials, such as polyvinyl chloride, are practically always used in plasticized form. Therefore, issues related to developing computation schemes for predicting such properties of polymers as strength and viscosity depending on the chemical constitution of the polymer and the solvent (plasticizer) remain relevant. In this review, these issues are analyzed in detail by a number of examples using methods developed by both the authors of the present review and other researchers.

In the cited new papers on predicting and analyzing physical properties, polymers that can be used in actuators of nanomechanical devices were studied. Ways to increase their service life and the thermal effects arising upon exciting self-oscillations in the frequency range of 200–250 Hz are presented. The predicted polymers can be used for the computerization of actuators.

Also presented are theoretical calculations based on the classical rheological equations relating the value of relative viscosity with the concentration and radius of spherical nanoparticles having a polymer with the known chemical constitution and molecular mass adsorbed on their surface. The obtained dependence allows calculating the relative viscosity of a nanocomposite disperse system in a polymer melt or solution in a low-molecular liquid at known parameters of the dispersed particles (radius and concentration), as well as solving the inverse problem of calculating the radius of particles with the polymer adsorption layer from the experimental value of relative viscosity.

The review discusses such an urgent problem as assessing the temperature dependence of molecular packing coefficients of polymers and liquids. By means of computer experiments, it was possible to describe the dependence of packing coefficients for dense  $k_1$  and loose fraction  $k_2$  on temperature. The analysis carried out is important for specifying the conditions of polymer solubility and calculating the dielectric properties and surface tension coefficients of polymers and solvents.

Finally, we touch upon an important physical subject of how the chemical constitution of thermoplasts affects their friction with steel. Such thermoplasts, in particular, are used as binders for filled composites in friction units: crystalline polyetheretherketones, polyphenylene sulphide, polysulfones, and polyaryletherketones, synthesized in recent years. Studies of these polymers allowed a better understanding of the mechanism of friction with steel and assessing the possibility of predicting the friction coefficient and wear.

In general, the topics covered in the review can help the successful application of polymers in a number of technical devices and facilitate the development of new medical materials related to the treatment of wounds and burns. The obtained data are within the framework of large projects carried out by the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS) and the Moscow State University of Civil Engineering (MGSU).

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