Latest developments of models and calculation schemes for the quantitative analysis of the physical properties of polymers

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<u>Abstract.</u> The latest models and calculation schemes for the quantitative analysis of a number of physical properties of polymers are described. Among the physical properties are the glass transition temperature, flow temperature of polymer nanocomposites, thermal conductivity, boiling point of polymer solutions, water absorption and water permeability of polymers and nanocomposites, strength, viscosity, storage and loss moduli, refractive index, and dielectric constant. All calculation schemes are based on the structure of linear and cross-linked polymers; their degree of crystallinity, free volume, the influence of temperature, the composition of copolymers, and homogeneous mixtures of polymers are taken into account. In the case of nanocomposites, the concentration angles, the structure of analysis and orientation angles, the structure of analysis of the structure of temperature.

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Received 25 September 2018, revised 6 November 2018 Uspekhi Fizicheskikh Nauk **190** (2) 179–210 (2020) Translated by Yu V Morozov; edited by V L Derbov ture of polar groups grafted to the surface of nanoparticles, and the energy of intermolecular interactions are taken into account. Spherical nanoparticles, rectangular plates, and nanofibers are considered. The calculation scheme for the refractive index and the dielectric constant takes into account the effect of the plasticizing action of the remnants of the synthesis products, the solvent, and the nonlinearity on the Clausius–Mossotti function, the composition of the nanoparticles, and the temperature. All calculation schemes are computerized and allow automatic calculations after inputting into the computer the structure of the repeating unit of the polymer, as well as the shape and dimensions of the nanofillers.

Keywords: glass transition temperature, flow temperature, thermal conductivity, ebullioscopic constant, water absorption, water permeability of polymers and nanocomposites, yield strength, viscosity, storage modulus and loss modulus, refractive index, dielectric constant

1. Introduction

The latest review [1] of calculation schemes allowing a qualitative estimate of the physical properties of polymers from the chemical structure of their repeating units was published in 2015. Considered in Ref. [1] are over 60 physical properties of polymers, including thermal characteristics

(such as the glass transition and melting temperatures, initial temperature of intense thermal degradation, flow temperature, thermal expansion coefficient, heat conductivity), mechanical characteristics (elastic modulus, equilibrium rubber-like elasticity modulus), volumetric characteristics (van der Waals volume, molar volume, density), energy characteristics (cohesive energy, intermolecular interaction energy), surface characteristics (surface tension, interphase tension energy), optical and dielectric characteristics (refractive index, dielectric constant, dielectric loss tangent, stressoptical coefficient, molar refraction and molar polarizability, dipole moment), and barrier properties (carbon dioxide, oxygen, and nitrogen permeability). In many cases, the temperature dependences of these characteristics are estimated, as is their dependence on the degree of crystallinity, free volume, and molecular mass.

In addition, calculation schemes for predicting the solubility of polymers in organic solvents and their compatibility with each other are considered taking into account the chemical structure, molecular mass, and degree of orientation. The energy of intermolecular interaction is subdivided into weak dispersion interaction, strong dipole–dipole interaction, and hydrogen bond energies.

All calculation schemes are computerized and allow automatic numerical estimation. Problems of two types are solved, viz. (1) the direct problem, i.e., calculation of the physical properties of polymers from the structure of their repeating units displayed on the screen by the user, (2) the inverse problem or computer-assisted synthesis of polymers with predetermined properties in the interval chosen at the discretion of the user.

New methods have been proposed since 2014 and used to develop novel calculation schemes that made up the subject of the present review.

2. Glass transition temperature

At present there are a large number of calculation schemes for determining the glass transition temperature of linear and cross-linked polymers from the chemical structure of their repeating units [2–7]. Their analysis demonstrated that the same atoms and atomic groups localized in the main and side chains are involved in different intermolecular interactions and have different effects on the glass transition temperature. The models proposed by Van Krevelen [2], Bicerano [3], and Askadskii [4–7] for taking account of this influence make use of various corrections to improve computational accuracy.

In recent publications [8–10], new atomic constants and energies of dipole–dipole interaction and hydrogen bonds are introduced for atoms and atomic groups in the main and side chains. Also used is the model describing polymer glass transition temperature T_g reported in Refs [4–7]. The value of T_g in a linear polymer is defined as

$$T_{\rm g} = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_j b_j},\tag{1}$$

where a_i are atomic constants related to the weak dispersion interaction energy, b_j are constants related to dipole–dipole interaction b_{dd} and hydrogen bond b_h energies, and $\sum_i \Delta V_i$ is the van der Waals volume of a repeating unit.

Experiments show that the main and side chains formed by the same atoms or their groups may differ in rigidity, which results in different glass transition temperatures. If they refer to the main (m) and side (s) chains a_i values are denoted by $a_{i,m}$ and $a_{i,s}$, respectively.

To find the numerical values of these constants, the authors of [8–10] derived, based on Eqn (1), an overdetermined set of equations with the use of so-called polymer standards for which the glass transition temperature was multiply measured. Constants a_i and b_j obtained in Refs [8–10] for each atom and type of intermolecular interaction are presented in Table 1.

Van der Waals volumes of repeating units were calculated using the Cascade computer program developed at the A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS). A comparison of theoretical end experimental T_g values for a variety of polymers showed that the correlation coefficient is equal to 0.999. A correlation diagram containing over 50 polymers is presented in Fig. 1 and demonstrates good agreement between calculated and experimental data within the range of T_g values from -150 to 520 °C.

Thus, the separation of atomic constants for elements and groups localized in the main and side chains made it possible

 Table 1. Atomic constants and characteristics of intermolecular interactions in the main and side chains.

No.	Constants	Conventional symbols	Numerical values
1	Carbon in the main chain	a _{C,m}	-1.48
2	Carbon in the side chain	a _{C,s}	-1.72
3	Hydrogen in the main chain	a _{H,m}	28.42
4	Hydrogen in the side chain	a _{H,s}	26.89
5	Oxygen in the main chain	a _{O,m}	26.81
6	Oxygen in the side chain	a _{O,s}	14.21
7	Nitrogen in the main chain	a _{N,m}	2.75
8	Nitrogen in the side chain	a _{N,s}	-49.31
9	Silicon in the main chain	a _{Si, m}	7.17
10	Silicon in the side chain	a _{Si,s}	0.77
11	Chlorine	$a_{\rm Cl}$	3.91
12	Fluorine	a _F	7.50
13	Sulphur in the main chain	a _{S,m}	-8.08
14	Sulphur in the side chain	a _{S,s}	2.79
15	Double bond in the main chain	$b_{d,=}$	172.0
16	Dipole-diploe interaction	b _{dd}	-89.0
17	Hydrogen bond in aliphatic polyamides	$b_{ m h, al}$	-289.0
18	Hydrogen bond in aromatic polyamides	$b_{ m h, ar}$	-165.0
19	Hydrogen bond in the side chain	b _{h,s}	-232.0
20	Para-substitution	b _{para}	30.0
21	Meta-substitution	b _{meta}	83.0
22	Ortho-substitution	borto	83.0
23	Aliphatic cycle	b _{al.cycle}	-274.0



Figure 1. Correlation diagram of T_g^{exp} and T_g^{calc} —experimental and theoretical values of glass transition temperatures, respectively [10].

to accurately calculate glass transition temperatures of polymers differing in chemical structure without the use of a large number of correction coefficients.

3. Flow temperature of polymer nanocomposites

The flow temperature T_f of polymer nanocomposites is presently considered to be one of the main thermal characteristics of polymer systems. The model and the calculation scheme for the quantitative description of this characteristic were proposed in Ref. [11] taking into account the chemical structure of both polymers and nanoparticles, intermolecular interaction between them during modification of the particle surface by polar groups, the van der Waals volume and molecular mass of the polymer, and the shape and the concentration of the nanoparticles. The dependences of T_f on the nanoparticle radius, concentration, and number of surface polar groups are presented. The calculation scheme is computerized.

The most detailed analysis of the influence of nanoparticles on the physical properties of nanocomposites is presented in Ref. [12], where their structural, thermal, and mechanical characteristics are considered. Reference [11] poses the problem of creating such a calculation scheme for determining the flow temperature of nanocomposites taking account of all the aforementioned factors.

The presence of polar groups on the surface of nanoparticles gives rise to an additional intermolecular interaction between the polymer and the filler. This fact is taken into account by introducing an additional term in Eqn (1) for calculating glass transition temperature T_g needed to estimate the flow temperature T_f . For linear polymers, the following equation in used in Refs [4–7, 13–16]:

$$T_{gj} = \frac{\sum_{i} \Delta V_{i}}{\sum_{i} a_{i} \Delta V_{i} + \sum_{j} b_{j} - b_{j} \beta}, \qquad (2)$$

where β is the number of polar groups on the nanoparticle surface per repeating unit of the polymer. Quantities a_i and b_j are presented in the tables in Refs [4–7, 13–16].

The value of β is determined based on the following considerations. The number of spherical nanoparticles n_{np} in 1 g of a nanocomposite is expressed as

$$n_{\rm np} = \frac{m_{\rm np}^{\Sigma}}{m} = \frac{3m_{\rm np}^{\Sigma}}{\rho_{\rm np} 4\pi R_{\rm np}^3},$$
 (3)

where m_{np}^{Σ} is the total mass of nanoparticles in the nanocomposite, *m* is the mass of a single nanoparticle, and R_{np} is its radius.

The number of polar groups N_{pg} on the surface of all nanoparticles in this system is

$$N_{\rm pg} = \frac{n_{\rm pg} 3m_{\rm np}^{\Sigma}}{\rho_{\rm np} 4\pi R_{\rm np}^3} \,, \tag{4}$$

where n_{pg} is the number of polar groups on the surface of a single nanoparticle.

The total number of repeating units $N_{\rm ru}$ in the system under consideration is

$$N_{\rm ru} = 0.6023 \times 10^{24} \, \frac{w_{\rm pol}}{M_0} \,, \tag{5}$$

where w_{pol} is the polymer weight and M_0 is the molecular mass of a repeating unit. Then, the number of polar groups per repeating unit is expressed as

$$\beta = \frac{n_{\rm pg} 3m_{\rm np}^{\Sigma} M_0}{0.6023 \times 10^{24} \rho_{\rm np} 4\pi R_{\rm np}^3 w_{\rm pol}} \,. \tag{6}$$

Substituting (6) into Eqn (2) yields

$$T_{gj} = \left(\sum_{i} \Delta V_{i}\right) \left[\left(\sum_{i} a_{i} \Delta V_{i} + \sum_{j} b_{j}\right) - b_{j} \frac{n_{\text{pg}} 3m_{\text{np}}^{\Sigma} M_{0}}{0.6023 \times 10^{24} \rho_{\text{np}} 4\pi R_{\text{np}}^{3} w_{\text{pol}}} \right]^{-1},$$
(7)

where $b_j = 55 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}$ if polar groups of any type are localized on the surface of nanoparticles, $b_j = 27 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}$ when phenyl groups are localized on the nanoparticle surface, and $b_j = 140 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}$ in the presence of groups with hydrogen bonds. The calculation is performed for 1g of the composite.

If the nanoparticles are bar-shaped rather than spherical, Eqn (7) takes the form

$$T_{gj} = \left(\sum_{i} \Delta V_{i}\right) \left[\left(\sum_{i} a_{i} \Delta V_{i} + \sum_{j} b_{j}\right) - b_{j} \frac{n_{\text{pg}} m_{\text{np}}^{\Sigma} M_{0}}{0.6023 \times 10^{24} \rho_{\text{np}} abhw_{\text{pol}}} \right]^{-1},$$
(8)

where *a*, *b*, and *h* are the length, width, and thickness of a nanoparticle respectively.

Given that nanoparticles are short segments of a fiber, Eqn (7) becomes

$$T_{gj} = \left(\sum_{i} \Delta V_{i}\right) \left[\left(\sum_{i} a_{i} \Delta V_{i} + \sum_{j} b_{j}\right) - b_{j} \frac{n_{\text{pg}} m_{\text{np}}^{\Sigma} M_{0}}{0.6023 \times 10^{24} \rho_{\text{np}} \pi R_{\text{np}}^{2} l_{\text{np}} w_{\text{pol}}} \right]^{-1},$$
(9)

where R_{np} is the fiber radius and l_{np} is its length.

Let us consider the dependences of the flow temperature on the polymer chemical structure and concentration, nanoparticle size and concentration, and chemical structure and concentration of the functional groups on the surface of nanoparticles. The polymer flow temperature is described by the following equation [6, 7]:

$$\frac{T_{\rm g}}{T_{\rm f}} = 1 + \frac{1}{26} \ln \frac{B}{\left(M/M_{\rm s}\right)^{3/2} \left\{ \left[\left(2.4M/M_{\rm s}\right)^{1/2} - 1 \right]^3 + 1/3 \right\}}$$
(10)

where B = 0.5, M is the polymer molecular mass, and M_s is the molecular mass of the mechanical segment of a macromolecule, i.e., a molecular mass at which the glass transition temperature becomes independent of M.

The value of M_s is calculated using the following equation [6, 7]:

$$N_{\rm s} = \frac{M_{\rm s}}{M_0} = 0.24 T_{\rm g,0} \left[N_{\rm A} \left(\sum_i \Delta V_i \right) \right]^{1/3}, \tag{11}$$

where N_s is the number of repeating units within the mechanical segment, M_0 is the molecular mass of a repeating unit, N_A is the Avogadro number, $\sum_i \Delta V_i$ is the van der Waals volume of a repeating unit, and $T_{g,0}$ is the glass transition temperature of the initial polymer containing no nanoparticles.

Substituting (11) into Eqn (10) yields in the general case

$$\frac{T_{\rm g}}{T_{\rm f}} = 1 + \frac{1}{26} \ln \left(B \left[\frac{M}{0.24M_0 T_{\rm g,0} \left(N_{\rm A} \sum_i \Delta V_i \right)^{1/3}} \right]^{-3/2} \times \left\{ \left[\left(\frac{10M}{0.24M_0 T_{\rm g,0} \left(N_{\rm A} \sum_i \Delta V_i \right)^{1/3}} \right)^{1/2} - 1 \right]^3 + \frac{1}{3} \right\}^{-1} \right\}.$$
 (12)

For example, consider the calculation of the dependence of the glass transition temperature on all parameters of the system in which the matrix polymer is represented by polyvinyl chloride (PVC).

The calculation procedure is as follows. All parameters listed in Table 2 are fixed except one, which serves as the argument. The dependence of glass transition temperature $T_{\rm g}$ on this unfixed parameter is calculated. First of all, glass transition temperature $T_{\rm g,0}$ and flow temperature $T_{\rm f}$ for the starting polymer must be calculated using the aforementioned Cascade program. For example, if M = 30,000, $T_{\rm g,0} = 341$ K, $T_{\rm f} = 384$ K.

The values of T_g/T_f for PVC are presented in Table 3. Substituting the parameters presented in Tables 1 and 2 into

Table 2. Parameters of the linear polymer-nanoparticle system.

n _{pg}	$ ho_{ m np}, ho_{ m mp}, ho_{ m cm^{-3}}$	R _{np} , nm	M_0	$\begin{array}{c}\sum_{i}\Delta V_{i},\\ \mathring{A}^{3}\end{array}$	w _{pol} , g	w _{np} , g	$\frac{\sum_i a_i \Delta V_i + \sum_j b_j}{\operatorname{\AA}^3 \mathbf{K}^{-1}},$
10^{4}	0.74	5.0	62.5	48.9	0.95	0.05	0.1434

Table 3. Values of $T_{g,0}$, T_f and $T_{g,0}/T_f$ for PVC at various molecular masses M.

M	$T_{\rm g,0},{ m K}$	$T_{\rm f},{ m K}$	$T_{ m g}/T_{ m f}$
10,000	327.2	327.2	1.0
20,000	341.2	360.5	0.946
30,000	341.2	384.3	0.888
40,000	341.2	402.7	0.847
50,000	341.2	417.8	0.817
60,000	341.2	430.8	0.792

(6) yields formulas for the description of the flow temperature at different parameters of nanoparticles and polymer molecular mass.

The dependence of $T_{\rm f}$ on the number of surface polar groups (M = 30,000) looks like

$$T_{\rm f} = \frac{55.07}{0.1434 - 0.07758 \times 10^{-5} n_{\rm pg}} \,. \tag{13}$$

The dependence of $T_{\rm f}$ on the nanoparticle weight $w_{\rm np}$ (M = 30,000) is expressed as

$$T_{\rm f} = \frac{55.07}{0.1434 - 0.1474 w_{\rm np}/(1 - w_{\rm np})},$$
 (14)

and the dependence of $T_{\rm f}$ on the nanoparticle radius $R_{\rm np}$ at M = 30,000 as

$$T_{\rm f} = \frac{55.07}{0.1434 - 969.8/R_{\rm np}^3} \,. \tag{15}$$

The dependences calculated with the use of relations (13)–(15) are presented in Figs 2–4. Evidently, the flow temperature increases significantly as the number of polar groups on the spherical nanoparticle surface and polymer molecular mass increase. However, $T_{\rm f}$ decreases with growing nanoparticle radius.

These results should be taken into consideration in the development of a nanoparticle-polymer mixing technology in a melt at high temperature.



Figure 2. Flow temperature versus the number of polar groups at the surface of a spherical nanoparticle. I - M = 10,000; 2 - M = 20,000; 3 - M = 30,000; 4 - M = 40,000; 5 - M = 50,000; 6 - M = 60,000 [11].



Figure 3. $T_{\rm f}$ versus spherical nanoparticle mass $m_{\rm np}$. I - M = 10,000; 2 - M = 20,000; 3 - M = 30,000; 4 - M = 40,000; 5 - M = 50,000; 6 - M = 60,000 [11].



Figure 4. $T_{\rm f}$ versus spherical nanoparticle radius $R_{\rm np}$. I - M = 10,000; 2 - M = 20,000; 3 - M = 30,000; 4 - M = 40,000; 5 - M = 50,000; 6 - M = 60,000 [11].

4. Influence of chemical structure and degree of crystallinity on heat conductivity of polymers

One of the recent calculation schemes for the quantitative analysis of the thermal properties of polymers is designed to estimate heat conductivity based on their chemical structure and degree of crystallinity [17]. A detailed theoretical approach to solving the heat conductivity problem is presented in general terms in monographs [18, 19]. For amorphous dielectric polymers, the thermal conductivity mechanism and temperature dependence are related to the main kinetic equation

$$\lambda = \frac{1}{3}\rho C_V \langle c \rangle \langle l \rangle , \qquad (16)$$

where λ is the thermal conductivity, C_V is the heat capacity, $\langle c \rangle$ is the mean phonon propagation speed, and $\langle l \rangle$ is the mean phonon free path.

Since the polymer heat capacity at temperature T_g shows a positive jump, the thermal conductivity must likewise undergo a step-wise rise in accordance with (16). However, such a behavior of temperature dependence of thermal conductivity is almost never observed in polymer glasses (polymethyl methacrylate exemplifies a material best explored in this respect). It was suggested in [20] that an energy transfer at temperatures near T_g occurs due to interand intramolecular interactions. Such a mechanism is characteristic of the thermal conductivity of fluids. Since amorphous polymers are considered to be fluids in terms of the phase state, Ref. [17] describes their heat conductivity by the Vargaftik equation [21] for organic liquids,

$$\lambda = A \, \frac{C_p \rho^{4/3}}{M^{1/3}} \,, \tag{17}$$

where C_p is the heat capacity at constant pressure, M is the molecular mass of the fluid, and A is a constant.

For polymers, Eqn (17) needs to be converted bearing in mind that even the use of molecular mass M_0 of a repeating unit is fraught with uncertainty, as exemplified by polyamides. Polyamide-6 has the following chemical structure:

$$-NH-(CH_2)_5-CO-.$$

The molecular mass of the repeating unit in polyamide-6 equals 113. The chemical structure of polyamide-6,6 is

$$-CO - (CH_2)_4 - CO - NH - (CH_2)_6 - NH -$$

The molecular mass of its repeating unit is equal to 226.

Substituting these masses into Eqn (17) yields different thermal capacities, whereas their measured values are equal. Therefore, Ref. [17] reduces the molecular mass of the polymer repeating unit M_0 to a single atom, i.e., M_0 is divided by the number of atoms *m* in the repeating unit. In this case, Eqn (17) takes the form

$$\lambda = A \, \frac{C_p \rho^{4/3}}{\left(M_0/m\right)^{1/3}} \,. \tag{18}$$

Quantity A depending on the polymer chemical structure is expressed as [17]

$$A = \frac{\sum_{i} a_{i} + \sum_{j} b_{j}}{N_{\mathrm{A}} \sum_{i} \Delta V_{i}} \,, \tag{19}$$

where a_i are atomic constants characteristic of each atom, b_j are constants for the polar groups responsible for dipole– dipole interaction or hydrogen bond formation, and ΔV_i is the van der Waals volume of the *i*th atom.

The best variant of the calculation scheme taking into account different types of intermolecular interaction, degree of crystallinity, and positions of atoms in the main or side chains has been proposed in [17] based on the following manipulations:

(1) differentiation of atoms localized in the main and side chains of a polymer. Atomic constants a_i for the atoms in the main chain are marked by index m and those for the side-chain atoms by s (Table 4);

(2) taking account of the influence of dipole–dipole interactions, aromatic cycles, and double bonds in the main chain on the thermal conductivity by introducing b_j parameters. The influence of double bonds proved insignificant. At the same time, the possibility of heat conductivity increases for polymers containing identical

Table 4. Atomic constants and parameters describing specific intermolecular interactions.

Atom and type of intermolecular interaction	Conventional symbols	Numerical values
Carbon in the main chain Carbon in the side chain Hydrogen in the side chain Oxygen in the side chain Oxygen in the side chain Oxygen in the side chain Nitrogen in the side chain Nitrogen in the side chain Nitrogen in the side chain Chlorine Fluorine Silicon Sulphur	$a_{C, m}$ $a_{C, s}$ $a_{H, m}$ $a_{H, s}$ $a_{O, m}$ $a_{O, s}$ $a_{N, m}$ $a_{N, s}$ a_{Cl} a_{F} a_{Si} a_{S}	1.99 1.699 -0.205 -0.017 3.706 -1.693 8.88 1.108 1.548 0.114 2.016 15.226
Polymers containing (thermal conductivity)–CH ₂ – or –CF ₂ – Dipole-dipole interaction Aromatic ring (backbone)	b_CH ₂ -(-CF ₂ -) b _{dd} b _{ar.cycle}	3.504 4.83 -2.755
Double bolid	U_{\pm}	0.934

Polymer	$ ho, \ { m g} \ { m cm}^{-3}$	$C_p,$ J (g grad) ⁻¹	M_0	т	$\sum_i \Delta V_i$, Å ³	$\lambda_{calc}, \ W (m K)^{-1}$	$\lambda_{exp}, \ W (m K)^{-1}$
$Nylon-6 \\ -C - (CH_2)_5 - NH - \\ U \\ O$	1.169	1.49	113	19	116	0.245	0.24
Nylon-6,6 	1.159	1.50	226	38	232	0.244	0.24
Polycarbonate $-O \longrightarrow C \longrightarrow C \longrightarrow O \longrightarrow C \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow $	1.265	1.19	254	33	239	0.198	0.20
Polyethylene terephtalate $-(CH_2)_2-O-C-O-C-O-C-O-C-O-C-O-C-O-C-O-C-O-C-O-$	1.378	1.15	192	22	166	0.25	0.15 0.24
Polytetrafluorethylene $-CF_2-CF_2-$	2.121	1.02	100	6	54.9	0.261	0.25
Polyvinylchloride (flexible) -CH2CH- Cl	1.517	1.08	62.5	6	48.9	0.191	0.17 0.21
Polybutadiene CH2CH==CHCH2	0.973	2.03	54.1	10	64.2	0.222	0.22
Polyethylene —CH ₂ —CH ₂ —	0.955	2.19	28.1	6	34.1	0.40	0.33 0.42
Polypropylene CH_3 $-CH_2$ -CH	0.964	2.16	42.1	9	51.2	0.199	0.12 0.20
Polystyrene CH2CH-	1.07	1.30	104	16	110	0.155	0.16
$\begin{array}{c} Cellulose\\ CH_2 - OH\\ CH - OH\\ CH - CH\\ CH - CH\\ CH - CH\\ OH OH\end{array}$	1.464	1.36	162	21	132	0.186	0.071 0.13 0.17
Polyacrylonitrile $-CH_2$ — CH_1 C=N	1.168	1.22	53.1	7	54.0	0.259	0.26
Polymethylmethacrylate -CH ₂ -C- C-O-CH ₃ O	1.17	1.38	100	15	96.4	0.156	0.16 0.167 0.17 0.19 0.20 0.21 0.23
Polyvinyl acetate -CH2-CH- O-C-CH3 O	1.23	1.32	86.1	12	79.4	0.154	0.159

Table 5. Polymer chemical structure, parameters needed for the calculation, and experimental and theoretical data on thermal conductivity λ .

groups of atoms only in the main chain; such polymers are inevitably crystallized, which requires the introduction of a special parameter $b_{-CH_2-(-CF_2-)}$ (see Table 4). Such polymers include polyethylene $-CH_2-CH_2-$ and polytetrafluorethylene $-CF_2-CF_2-$.

Results of calculations for certain polymers are presented in Table 5.

It should be borne in mind that experimental values of heat conductivity may sometimes differ for the same polymer.

The correlation diagram in Fig. 5 shows theoretical and measured values of thermal conductivity.

Equation (18), together with (19), allows us to estimate the influence of temperature and the degree of crystallinity on thermal conductivity. The dependence of thermal conductivity ity on the degree of crystallinity is estimated using the following relations [22, 23]:

$$\lambda = \alpha_{\rm cr} \lambda_{\rm cr} + (1 - \alpha_{\rm cr}) \lambda_{\rm a} , \qquad (20)$$



Figure 5. Correlation diagram for the set of amorphous and partly crystallized polymers listed in Table 5 [17].



Figure 6. Dependence of thermal conductivity on the degree of crystallinity for polyethylene [17].

$$\lambda = \frac{2\lambda_{\rm a} + \lambda_{\rm cr} + 2\alpha_{\rm cr}(\lambda_{\rm cr} - \lambda_{\rm a})}{2\lambda_{\rm a} + \lambda_{\rm cr} - \alpha_{\rm cr}(\lambda_{\rm cr} - \lambda_{\rm a})} \lambda_{\rm a} , \qquad (21)$$

where α_{cr} is the degree of crystallinity, λ_{cr} is the thermal conductivity of the crystallized sample, λ_a is the thermal conductivity of the amorphous sample.

 λ_a and λ_{cr} are calculated using formula (18) and density values for amorphous and totally crystallized samples. The dependence of thermal conductivity on the degree of crystallinity calculated by formula (18) for polyethylene is shown in Fig. 6. Dependences of thermal conductivity on the degree of crystallinity obtained with the use of formulas (20) and (21) are very similar.

Thus, the calculation scheme proposed in [17] allows sufficiently accurate estimation of polymer thermal conductivity based on the polymer chemical structure. It should be remembered that the measurement of thermal conductivity encounters difficulties, and literature publications report different experimental values of λ for one and the same polymer. Moreover, the calculation scheme allows thermal conductivity to be estimated as a function of the degree of crystallinity and temperature.

5. Calculation scheme for estimating the boiling point of polymer-solvent mixtures

A calculation scheme for estimating the boiling point of polymer-solvent mixtures has been developed in recent years [24]. It finds application in the ebullioscopic method for



Figure 7. Dependence of the boiling point of a polystyrene solution in toluene T_1 on polystyrene mole fraction $\alpha_{m,p}$ [24].

determining polymer molecular masses. The authors of Ref. [24] analyzed the Hildebrand solubility parameter, latent heat of evaporation, solvent boiling point, etc. Ref. [24] also deals with calculation methods for estimating temperature dependences of these parameters and reports on a theoretical analysis of boiling temperature variations in the solution at different concentrations of a polymer introduced into the solvent. The enthalpy of solvent vaporization at the boiling temperature of the solution is expressed through the temperature-dependent Hildebrand solubility parameter. In this way, an expression relating the boiling point of a polymer solution to the mole and weight fractions of the dissolved polymer was obtained that allows predicting the ebullioscopy constant and estimating the polymer molecular mass. The resulting formula for the calculation of the boiling point of a solution has the form [24]

$$T_1 = T_0 \left\{ 1 + \frac{RT_0 \ln \left[A/(1+A) \right]}{V\delta^2 + R(298 - T_0)} \right\}^{-1},$$
(22)

where $A = (M_p/M_s)(1/\alpha_{w,p} - 1)$, T_0 is the boiling point of the solvent, T_1 is the boiling point of the solution, δ is the solubility parameter (Hildebrand parameter), R is the universal gas constant, V is the fluid mole volume, M_p and M_s are the polymer and solvent molecular masses, respectively, and $\alpha_{w,p}$ is the polymer weight fraction.

Figure 7 exemplifies the dependence of the solution boiling point T_1 on the polystyrene mole fraction $\alpha_{m,p}$. The solvent is toluene. Parameters needed for the calculation are presented in Table 6.

Table 6. Parameters needed to calculate the boiling point of polystyrene solution in toluene.

$V, \mathrm{cm}^3 \mathrm{mol}^{-1}$	δ , (J cm ⁻³) ^{0.5}	T_0, \mathbf{K}
106	18.1	383.8

The proposed calculation scheme for the qualitative estimation of the boiling point of polymer solutions in an organic solvent [24] allows calculations based on the chemical structure of the polymer and the solvent; it do not require preliminary experiments and therefore possesses predictive power.

6. Water absorption and water permeability of polymers and copolymers

This section describes the calculation scheme recently developed to predict the water permeability of polymers [25–27]. A relation is proposed for calculating the activation energy of the permeation process. The calculation is based on the use of a set of atomic constants describing the contributions of each atom and polar group to the energy, summarized to estimate the total energy taking account of the polymer chemical structure, degree of crystallinity, temperature, and free (void) volume. The method is computerized. The program permits solving both the direct problem of estimating polymer parameters from the chemical structure of the repeating unit and the inverse problem of searching for polymer structures with a given permeability range.

The study of the effect of water on polymer properties attracts the persistent interest of researchers. Versatile chemical and physical processes in polymer materials result from the prolonged contact of water with different polymer materials. Water permeation through polymers leads to deterioration of their physical and mechanical properties owing to crack formation, partial degradation, etc. For this reason, elucidation of the relationship between permeability and such characteristics as the Hildebrand solubility parameter, cohesive energy, and free volume remains a topical problem. Let us consider some general aspects of water permeability through polymers.

Water permeation through polymer membranes was shown to depend on salt concentration. This problem is related to the deficit of pure fresh water in many areas of the globe [28, 29] and therefore the necessity of water desalination [30]. A series of recent papers designed to study the barrier properties of polysulfone membranes at different NaCl levels is reported in Refs [31–34]. Their results may be of use for designing membranes for water desalination [35, 36].

The authors of Ref. [37] undertook a comparative analysis of water diffusion coefficients and selectivity depending on the water-to-salt ratio for membranes based on cross-linked polyamide, polyimide, cellulose acetate, sulfonated poly(arylene ether sulfone), etc. Reference [38] is devoted to the protection of organic light-emitting diodes and other optoelectronic materials exposed to direct contact with surrounding moisture. Such protection is a serious challenge for the developers of flexible displays and other flexible electronic devices. The authors of [39] studied the permeability of water vapor through polymer films based on PVC, blends of PVC with perchlorovinyl, copolymer of vinyl chloride with vinyl acetate and vinyl chloride with ethylene. The study revealed a nonlinear dependence of water permeability on film thickness. The nonlinear dependence of water permeation through a membrane based on vulcanized rubber on the membrane thickness is described using an equation proposed in [40] based on the results of theoretical research [41, 42].

6.1 Influence of polymer chemical structure

The possibility of predicting polymer or copolymer permeability from their chemical structure is discussed in [25–27]. The authors of these works attempted to develop a calculation scheme and its computerization for the accurate estimation of permeation through polymer membranes from the chemical structure of polymer matrices and the degree of polymer crystallinity. Let us analyze the calculation scheme. The basic equation describing polymer permeability *P* has the form

$$P = P_0 \exp\left(-\frac{\Delta E}{RT}\right),\tag{23}$$

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

In accordance with the principles of designing calculation schemes for predicting polymer parameters [43], ΔE is described by the relation [25–27]

$$\Delta E = \frac{\sum_{i} \Delta E_{i}^{**}}{N_{\rm A} \sum_{i} \Delta V_{i}},\tag{24}$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit, $\sum_i \Delta E_i^{**}$ is the activation energy of the permeation process multiplied by the van der Waals volume of the repeating unit (the sum of van der Waals volumes of each atom or specific polar group responsible for dipole–dipole interaction and hydrogen bond formation).

Then,

$$\ln P = \ln P_0 - \frac{\sum_i \Delta E_i^{**}}{N_{\rm A} R T \sum_i \Delta V_i} \,. \tag{25}$$

Minor transformations yield

$$\frac{\sum_{i} \Delta E_{i}^{**}}{RT} - \left(N_{\rm A} \sum_{i} \Delta V_{i}\right) \ln P_{0} = -\left(N_{\rm A} \sum_{i} \Delta V_{i}\right) \ln P.$$
(26)

Equation (26) was used in Ref. [27] to derive a redundant system of equations using permeability values for the so-called polymer standards with well-known permeability [44–75]. The solution of this system of equations yielded a set of atomic constants and a number of parameters characterizing the energy of strong intermolecular interactions for selected individual groups (Table 7). $\ln P_0 = 3.002$, where P_0 is expressed in barrers.

A correlation diagram for 40 polymers is presented in Fig. 8, demonstrating excellent agreement between theory and experiment.

 Table 7. Atomic constants and parameters describing specific intermolecular interactions.

Atom and type of intermolecular interaction	Symbol	$\Delta E_i^{**}/(RT_{298})$	$\Delta E_i^{**},$ kJ mol ⁻¹
Carbon	$\Delta E_{ m C}^{**}$	42.75	105.85
Hydrogen	$\Delta E_{ m H}^{**}$	-36.65	-90.75
Oxygen	$\Delta E_{\mathrm{O}}^{**}$	-8.20	-20.3
Hydrogen bond for	$\Delta E_{\rm NHCO}^{**}$	-385.2	-953.7
-NHCO- group			
Double bond	$\Delta E_{=}^{**}$	-182.8	-452.6
Chlorine	ΔE_{C1}^{**}	44.1	109.2
Fluorine	$\Delta E_{\mathrm{F}}^{**}$	-60.1	-148.8
Hydrogen bond	$\Delta E_{\rm h}^{**}$	-28.3	-70.1
Aliphatic ring (skeleton)	ΔE_{alc}^{**}	-234.5	-580.6
Dipole-dipole interaction	$\Delta E_{\rm dd}^{**}$	-109.8	-271.9
Aromatic ring (skeleton)	$\Delta E_{\rm ar.c.m}^{**}$	-203	-502.6
in the main chain	,		
Nitrogen	$\Delta E_{ m N}^{**}$	29.8	73.8
Silicon	$\Delta E_{\rm Si}^{**}$	-156.9	-388.5
Sulphur	$\Delta E_{\rm S}^{**}$	-621	-1538
Aromatic ring (skeleton)	$\Delta E_{\rm ar.c.s}^{**}$	-326.3	-808
in the side chain			







The temperature dependence of permeability P is a function of the sign of $\sum_i \Delta E_i^{**}$. Given that $\sum_i \Delta E_i^{**}$ is positive, P increases with temperature; P decreases as temperature grows if the value is negative. For example, for polyvinylidene chloride (PVDC),

$$\sum_{i} \Delta E_{i}^{**} = 2\Delta E_{C}^{**} + 2\Delta E_{H}^{**} + 2\Delta E_{Cl}^{**}$$

= 2 × 105.85 - 2 × 90.75 + 2 × 109.2
= 248.6 kJ mol⁻¹, N_A $\sum \Delta V_{i}$ = 38.4 Å³.

Hence,

$$P = \exp\left(3.002 - \frac{248.6 \times 10^3}{8.31T \times 38.4}\right) = \exp\left(3.002 - \frac{779}{T}\right) (27)$$

The temperature dependence of water permeability for PVDC is shown in Fig. 9, demonstrating its rise with temperature.

6.2 Influence of the degree of crystallinity on water permeability

It is well known that ideal crystals lack permeability. The permeability of partially crystalline polymers is calculated as

$$P = (1 - \alpha_{\rm d.cr}) P_0 \exp\left(-\frac{\Delta E}{RT}\right), \qquad (28)$$

where $\alpha_{d.cr}$ is the degree of crystallinity. For example, the following equation holds for polyacrylonitrile (PAN):

$$P = (1 - \alpha_{\rm d.cr}) \exp\left(3.002 + \frac{566}{T}\right).$$
 (29)



Figure 10. Dependence of PAN permeability on the degree of crystallinity at different temperatures: *I* — 290 K, *2* — 300 K, *3* — 310 K, *4* — 320 K, *5* — 330 K [26].

Dependences of water permeability on $\alpha_{d,cr}$ at different temperatures are shown in Fig. 10. Naturally, it decreases as the degree of crystallinity increases.

6.3 Influence of free volume

The influence of the free volume on permeability is discussed in Refs [25–27]. The following definition of a free volume is used as the most suitable for the case in question. The free volume is the difference between the polymeric body volume at a given temperature and the volume of the ideal crystal obtained for a polymer of the same chemical structure. This definition originates from the fact that no penetrant molecule can enter an ideal crystal without destroying it. Such a molar free volume is described by the relation

$$\Delta V = \frac{N_{\rm A} \sum_{i} \Delta V_{i}}{k_{\rm am}} - \frac{N_{\rm A} \sum_{i} \Delta V_{i}}{k_{\rm cr}}$$
$$= N_{\rm A} \sum_{i} \Delta V_{i} \left(\frac{1}{k_{\rm am}} - \frac{1}{k_{\rm cr}}\right), \tag{30}$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the polymer repeating unit, and k_{am} and k_{cr} are molecular packing coefficients for amorphous polymer and ideal crystal, respectively.

The value of $k_{\rm am}$ can be estimated using the Cascade computer program. Values of $k_{\rm cr}$ for ideal crystals can be borrowed from monographs [4, 6, 7]. For polymers whose ideal crystals have yet to be explored, the mean $k_{\rm cr}$ value can be assumed to equal 0.74 (as a rough estimation).

Specific free volume Δv is described by the relation

$$\Delta v = \frac{N_{\rm A} \sum_{i} \Delta V_{i}}{M_{0} k_{\rm am}} - \frac{N_{\rm A} \sum_{i} \Delta V_{i}}{M_{0} k_{\rm cr}}$$
$$= \frac{N_{\rm A} \sum_{i} \Delta V_{i}}{M_{0}} \left(\frac{1}{k_{\rm am}} - \frac{1}{k_{\rm cr}}\right), \tag{31}$$

where M_0 is the molecular mass of the polymer repeating unit.

It should be emphasized that the free volume being described is only partly permeable to penetrant molecules. The size of the pores must be roughly twice that of the penetrant molecules. The size of the free volume element ensuring penetration can be determined from the void size distribution curve. It is necessary to increase the known diameter of penetrant molecules nearly twofold and find the required free volume from the integral distribution curve. The authors of Refs [25-27] used the Schulz distribution,

$$q(l_{\rm v}) = \frac{\alpha^{z+2}}{\Gamma(z+2)} l_{\rm v}^{z+1} \exp\left(-\alpha l_{\rm v}\right),\tag{32}$$

where l_v is the current void size, $\alpha = 1/l_{av}$, l_{av} is the mean void size, and z = 0, 1, 2, 3, $\Gamma(z + 2)$ is the gamma function.

In the specific case of z = 0, the distribution has the form

$$q(l_{v}) = \alpha^{2} l_{v} \exp\left(-\alpha l_{v}\right).$$
(33)

Formula (33) presents the differential distribution function. The integral distribution function has the form

$$Q(l_{v}) = 1 - \exp(-\alpha l_{v}) - \alpha l_{v} \exp(-\alpha l_{v}).$$
(34)

The void distribution depends on l_{av} .

As an example, let us consider the case of polyethylene terephthalate (PETP). Calculations using the Cascade computer program yielded the following parameters at room temperature: molecular packing coefficient k = 0.680, $V = 146.7 \text{ cm}^3 \text{ mol}^{-1}$, $\rho = 1.31 \text{ g} \text{ cm}^{-3}$, $v = 0.758 \text{ cm}^3 \text{ g}^{-1}$. The van der Waals volume of water: $\sum_i \Delta V_i = 17.3 \text{ Å}^3$. The spherical molecule diameter: D = 3.2 Å. The differential distribution function at $l_{av} = 10 \text{ Å}$ is presented in Fig. 11, and the integral distribution function in Fig. 12.

The free volume available for penetration depends on the degree of crystallinity and void size distribution type. The value of the degree of crystallinity is known to be given by the



Figure 11. Differential distribution function at $l_{av} = 10 \text{ Å}$ [77].



formula

$$\chi_{\rm d.cr} = \frac{\rho_{\rm cr}}{\rho} \frac{\rho - \rho_{\rm am}}{\rho_{\rm cr} - \rho_{\rm am}} , \qquad (35)$$

where $\rho_{\rm am}$ is the density of an absolutely amorphous polymer, ρ is the density of the polymer of interest, and $\rho_{\rm cr}$ is the ideal crystal density.

The formula for the description of the degree of crystallinity in terms of molecular packing coefficient k is derived using the equation [4, 6–7]

$$v = \frac{1}{\rho} = \frac{N_{\rm A} \sum_i \Delta V_i}{kM_0} \,, \tag{36}$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit and M_0 is the molecular mass of this unit. The use of formulas (35) and (36) yields

$$\alpha_{\rm d.cr} = \frac{k_{\rm cr}}{k} \frac{k - k_{\rm am}}{k_{\rm cr} - k_{\rm am}} , \qquad (37)$$

where k, k_{am} , and k_{cr} are the molecular packing coefficients of the polymer being analyzed, the absolutely amorphous polymer, and the ideal crystal, respectively.

The use of formula (37) permits us to express the dependence of permeability P on the degree of crystallinity as

$$P = \left(1 - \frac{k_{\rm cr}}{k} \frac{k - k_{\rm am}}{k_{\rm cr} - k_{\rm am}}\right) P_{\rm am} \,. \tag{38}$$

The free volume fraction (FVF) is usually calculated using the Bondi formula [76],

$$FVF = \frac{v - 1.3v_w}{v} , \qquad (39)$$

where v is the specific volume and v_w is the specific van der Waals volume, or the formula

$$FVF = \frac{V - 1.3V_w}{V}, \qquad (40)$$

where V is the molar volume and V_w is the molar van der Waals volume.

Factor 1.3 in (39) and (40) is an empirical parameter. Its physical sense is defined in [27–27]. Taking account of (30) leads to

$$1.3V_{\rm w} = \frac{N_{\rm A}\sum_i \Delta V_i}{k_{\rm cr}} \,. \tag{41}$$

Thus, $1.3 = 1/k_{cr}$, which means that the molecular packing coefficient for a perfect crystal is $k_{cr} = 0.769$, in accordance with Bondi's formula. The value of k_{cr} actually depends on the polymer structure and the type of the crystallographic elementary cell [4, 6–8]. For the purpose of a rough estimation, $k_{cr} = 0.74$. In this case, the formula for the free volume calculation has the form

$$FVF = 1 - \frac{k}{k_{cr}}.$$
(42)

For more accurate calculations, experimental k_{cr} values should be used along with the value calculated based on experimental density.

The use of the aforementioned parameters for PETP in accordance with Eqn (39) yields $\Delta v = 0.0947 \text{ cm}^3 \text{ g}^{-1}$. This is the free volume only partly accessible to penetrant molecules. To calculate the free volume fully accessible to these molecules, one has to estimate the part of free volume in which the size of the voids $\geq 2l_p$, where l_p is the size of a

penetrant molecule. This procedure is performed using the integral distribution function (see Fig. 12).

To recall, the part of the free volume accessible to penetrant molecules depends on the mean void size l_{av} . If $l_{av} = 5 \text{ Å}$ and the size of water molecules is 3.2 Å, the part of the available volume can be found using the integral distribution function shown in Fig. 12 by taking the part of the curve starting from $l_v = 6.4 \text{ Å}$ up to the end. In the case under discussion, this part is roughly equal to 0.6.

The resulting expression describing the dependence of the water permeability of a polymer material on the degree of its crystallinity, temperature, and free volume has the form [25–27]

$$P = \left[1 - \exp\left(-\alpha x\right) - \alpha x \exp\left(-\alpha x\right)\right] \\ \times \left(1 - \frac{k_{\rm cr}}{k} \frac{k - k_{\rm am}}{k_{\rm cr} - k_{\rm am}}\right) \exp\left(\ln P_0 - \frac{\sum_i \Delta E_i^{**}}{N_{\rm A} RT \sum_i \Delta V_i}\right),$$
(43)

where $x = l_v$. Equation (43) does not require an obligatory assignment of molecular packing coefficients or the free volume fraction for each polymer. These quantities are determined using the Cascade program for individual polymers, depending on their chemical structure, degree of crystallinity, and temperature. They can also be given each polymer and used to estimate the dependence of permeability on these parameters.

6.4 Computerization of the assessment of polymer water permeability

The authors of [25–27] developed a computer program allowing the calculation of the water permeability of polymers whose chemical structure is written on the screen. The program is integrated as a special option into the Cascade computer program as an intrinsic component. This option allows the chemical structure of a polymer repeating unit or a repeating part of the polymer network to be written on the display and the necessary calculation to be performed automatically. For this purpose, Table 7, containing atomic constants and specific intermolecular interactions, is introduced into the database. The remaining parameters (van der Waals volumes) are computed with the use of the Cascade program. The following relation is used to calculate the permeability of two-component copolymers [25–27]:

$$\ln P_{0} = \frac{\alpha_{\mathrm{m, p, l}} \left[\left(\sum_{i} \Delta E_{i}^{**} \right)_{\mathrm{p, l}} - \left(\sum_{i} \Delta E_{i}^{**} \right)_{\mathrm{p, 2}} \right] + \left(\sum_{i} \Delta E_{i}^{**} \right)_{\mathrm{p, 2}}}{N_{\mathrm{A}} \left\{ \alpha_{\mathrm{m, p, l}} \left[\left(\sum_{i} \Delta V_{i} \right)_{\mathrm{p, l}} - \left(\sum_{i} \Delta V_{i} \right)_{\mathrm{p, 2}} \right] + \left(\sum_{i} \Delta V_{i} \right)_{\mathrm{p, 2}} \right\}},$$
(44)

where $(\sum_i \Delta E_i^{**})_{p,1}$ and $(\sum_i \Delta E_i^{**})_{p,2}$ are magnitudes of intermolecular interaction between the repeating units of polymers 1 and 2, respectively, and $(\sum_i \Delta V_i)_{p,1}$ and $(\sum_i \Delta V_i)_{p,2}$ are van der Waals volumes of polymers 1 and 2, respectively, $\alpha_{m,p,1}$ is the mole fraction of polymer 1.

Formula (44) can be used to calculate the permeability of a copolymer or compatible two-component polymer mixture.

6.5 Computer synthesis of polymers with predetermined water permeability

A computer program for searching structures with a desired water permeability, the range of which is loaded into the computer, has been developed in [25–27]. The solution of this problem is based on the selection of combinations of the so-called smallest basic fragments forming the structure of polymer repeating units. These basic fragments are input into the computer memory. The smaller the size of the basic fragments used to construct a repeating unit of the polymer, the greater the number of variants that can be obtained due to the large variety of combinations of fragments in the repeating unit.

In Refs [25–27], computer synthesis of a polymer with assigned properties was performed using the smallest fragments that can not be further 'cut' or divided. Examples of basic fragments presented in Table 8 are chosen so that they have all the fourteen end-groups and, accordingly, the same number of labels. All in all, Refs [25–27] introduce 111 basic pieces.

Expression (25) was used to calculate $\sum_i \Delta E_i^{**}$ values. To indicate the probability for the smallest fragments stored in computer memory coming into contact with one another, each end of the part was assigned a certain label. In the case under consideration, the fragments have only 14 different repeating groups and, accordingly, 14 labels (see Table 8). The fragments can take part in 'chemical interactions' with each other in accordance with the matrix input into the computer memory.

Table 8. Examples of the chemical structure of basic parts, van der Waals volumes, and intermolecular interaction energy

Fragment number	Chemical structure of fragment and neighbouring atoms	Length of the bond to neighboring atoms, Å		Labels		van der Waals volume, Å ³	$-\sum_{kJ}\Delta E_i^{**},$ kJ mol ⁻¹
		Left	Right	Left	Right		
1	2	3	4	5	6	7	8
1	ССH ₂ С	1.48; 1.54	1.48; 1.54	1	1	17.1	75.65
2	C····-CH-···C CH ₃	1.48; 1.54	1.48; 1.54	2	2	34.2	151.3
3	СС ОСН ₃	1.48; 1.54	1.48; 1.54	2	2	43.65	175.6
4	C····-C Cl	1.48; 1.54	1.48; 1.54	2	2	31.85	147.6
5	$C \cdots - CCl_2 - \cdots C$	1.48; 1.54	1.48; 1.54	2	2	46.85	-324.25
6	СС	1.48; 1.54	1.48; 1.54	2	2	92.6	611.55

1	2	3	4	5	6	7	8
7	C CF ₂ C	1.48; 1.54	1.48; 1.54	1	1	27.5	191.75
8	с — с—…с 0	1.48; 1.54	1.48; 1.54	2	2	18.6	186.35
9	c	1.48	1.48	3	3	75.6	230.5
10	сс	1.48	1.48	3	3	75.6	230.5
11	CCH2O	1.54	1.50	1	4	20.2	75.65
12	C	1.48	1.37	3	5	78.8	230.5
13	0	1.37	1.37	5	5	82.1	230.5
14	СОС	1.50	1.50	8	8	3.4	20.3
15	СС	1.37	1.50	9	8	2.7	20.3
16	СОС	1.37	1.37	9	9	2.1	20.3
17	CCC II O	1.54	1.50	2	8	25.1	206.65
18	$C - CH_2 - N$	1.54	1.37	1	6	18.6	75.65
19	CN	1.48	1.37	3	6	77.4	230.5
20	CNHCC U O	1.37	1.48; 1.54	11	2	28.4	885.1
21	SC	1.76	1.48	7	3	76.8	230.5
22	CSC	1.76	1.76	12	12	16.5	1538
23	$\begin{array}{c} CH_3\\ O\cdots - \begin{array}{c} Si \\ i \\ CH_3\end{array} \\ \end{array} \\ O \end{array} \\ O $	1.64	1.64	13	13	71.6	721.3
24	SiSi	1.64	1.64	10	10	0.5	20.3
25	O ^{HOMe} HOH HOH HOH	1.50	1.50	4	4	147.6	1150.8
26	ССН=С	1.54	1.34	2	14	15.1	437.5
27	C····-C CH ₃	1.34	1.50	14	2	32.2	513.15

Table 8 (continued)

Let us consider as an example the results of computer synthesis of polyurethanes with assigned water permeability. For this purpose, we introduce a permeability range of 0-400 barrers (1 barrer = 10^{-10} cm³ (STP) cm (cm² s cm Hg)⁻¹ (STP—standard temperature and pressure). Then, if the number of basic fragments in a polymer repeating unit equals six, the electronic synthesis results in a few tens of thousands structures providing water permeability in the range from 0 to 400 barrers.

Here is a detailed diagram of one of the structures obtained in a computer-aided study:



This structure contains six basic fragments (BF). The data from Table 8 allow the $\sum_i \Delta E_i^{**}$ and $\sum_i \Delta V_i$ values to be calculated:

$$\sum_{i} \Delta E_{i}^{**} = 2BF(\text{No. 1}) + BF(\text{No. 34}) + BF(\text{No. 36}) + 2BF(\text{No. 98}) = 1690 \text{ kJ mol}^{-1}.$$
$$\sum_{i} \Delta V_{i} = 381 \text{ Å}^{3}.$$

Here, the basic fragment numbers correspond to their numbers in [15–27].

Calculations using (25) give $P \approx 400$ barrers. For comparison, PA-6 also contains six basic fragments: 4BF(No. 1), BF(No. 32), BF(No. 36). The calculation by formula (25) yields $P \approx 29,000$ barrers.

In conclusion, to significantly reduce polyamide water permeability, chlorine-containing components need to be introduced into its structure (naturally, this is only one of the possible approaches).

7. Calculation scheme for estimating water permeability of nanocomposites

This section describes the calculation scheme developed in [77, 78] for predicting the permeability of polymer nanocomposites, taking into account the chemical structure of surface nanoparticles, their concentration in the composite, the concentration of polar functional groups on the surface of nanoparticles, and their shape and size. It is shown below that nanoparticle concentration and the number of polar groups on their surface have the most pronounced influence on permeability. An analysis of the influence of anisometric nanoparticle size distribution and orientation on permeability is performed. The calculation technique is computerized and integrated into the Cascade program as a special option allowing the calculation and prediction of nanocomposite permeability after the input of the chemical structure and assigned parameters of nanoparticles into the computer memory.

Control over nanocomposite permeability has been a focus of attention of researchers for decades, with special reference to the nanocomposites containing extended flat nanoparticles responsible for the 'winding' path of fluid molecules that results in a significant decrease in the diffusion rate and permeability.

Thus, e.g., the permeability of a number of polylactic acid (PLA)-based nanocomposites containing up to 6 mass % of layered montmorillonite silicate (nanoclay) [79] was investigated. It was shown that the measured permeability values decreased with increasing nanoclay content to 5 mass % as predicted by the Nielsen model [80].

A review of gas permeability of nanocomposites is presented in [81]. Reference [82] describes a geometric model predicting effective diffusion through composite membranes that contain impermeable anisotropic domains, depending on their volume proportion and orientation. Predictions of this model are compared with experimental findings. References [83–92] discuss models that describe composites containing layered fillers in the polymer matrix. Experimentally observed properties of nanocomposites containing nanoclay particles are described in [89–92].

References [85, 87, 93], devoted to the development and verification of the theory underlying the prediction of barrier membrane properties, are the most relevant to the subject of the present section. Special attention is given to the prediction of permeability changes in response to variations in the concentration and the aspect ratio of the planar particles used to fill composite materials. It is shown in [87] that the permeability of polymer films with parallelpacked impermeable particles of the filler can be two or three orders of magnitude lower than that of same-size films containing no filler. However, if the planar particles of the filler exhibit size distribution, the decrease in permeability can result from a compromise between the shorter diffusion paths in any region containing fine particles and the particle concentration. The theoretical and experimental data suggest that the diffusion resistance of films containing 3 vol% of flat particles is 20% higher than that of films containing 6 vol % of such particles.

A geometrical model for predicting efficient diffusion through nanocomposites, depending on the polymer nanoclay volume proportion and orientation as well as on its interaction with the polymer matrix, is proposed in [92]. Good agreement between the predications of the model and the results of numerical simulation is documented. As far as the existing theoretical models are concerned, the authors believe that the proposed model more adequately describes diffusion in conventional nanocomposites. This model ceases to work when inorganic lamellas agglomerate into clusters.

A series of studies [94-98] deals with methods for the preparation of layered nanocomposites and their barrier properties. Reference [94] describes nanocomposites based on PA-12 and montmorillonite (the experimental data are used below to verify the adequacy of the proposed calculation scheme). Morphological and barrier properties of PA and montmorillonite-based nanocomposites were studied in [96]. An increase in the montmorillonite content up to 18 mass % resulted in a 24% decrease in CO₂ permeability. Reference [97] reports the preparation of a poly(ε-caprolactone)-layered silicate nanocomposite. Thick films of the nanocomposite exhibited a considerable reduction in permeability for water vapor. The permeability was shown to be linearly dependent on silicate content. For example, the permeability of a nanocomposite containing 4.8 vol % of silicate proved to be reduced 10-fold compared with that of pure $poly(\varepsilon$ -caprolactone). The authors of Ref. [98] propose a method for nanocomposite production based on the use of epoxy resin containing montmorillonite nanoparticles.

The most detailed analysis of gas permeation through nanocomposites is reported in [99], which contains a large number of literature references and considers 19 variants of models taking account of nanocomposite morphology and polymer-filler interaction. These studies are devoted to gas permeability, but analogous models are suitable for the interpretation of experimental results obtained in water permeability studies.

All the above models and the respective equations make use of such parameters as the outer diameter, diffusion coefficient, nanoparticle length, molecular mass, shape factor, diameter-to-length ratio of fibrous fillers, volume fraction or filling, orientation angle, and thickness of a polymer layer. The models allow predicting the barrier properties of nanocomposites.

However, the prediction does not apply to the chemical structure of matrix polymers or the concentration of functional groups on this surface. Therefore, the authors of [77, 78] propose a calculation scheme allowing the water permeability of nanocomposites to be predicted based on the chemical structure of the matrix polymer and modifying agents introduced to improve the compatibility of nanoparticles with the matrix. For this purpose, a simplified variant of the calculation scheme is proposed that permits determining the water permeability of matrix polymers and copolymers, taking into consideration their chemical structure and the component ratio. This scheme is used to analyze the water permeability of nanocomposites with regard to nanoparticle size, shape, concentration, and orientation in the polymer matrix.

In sum, the calculation scheme proposed in [77, 78] provides a comprehensive solution to the problem of predicting the nanocomposite permeability based on the development of calculation schemes for estimating the permeability of matrix polymers or copolymers and analyzing the influence of nanoparticle size, shape, and concentration, taking into account chemical modification of their surface.

It is well known that hard particles introduced into amorphous polymers are not involved in transport processes. Therefore,

$$P = P_0^* (1 - \alpha_{\rm d,f}), \qquad (45)$$

where *P* is the permeability of the composite consisting of a polymer and nanoparticles, P_0^* is the permeability of the initial polymer, and $\alpha_{d,f}$ is the nanoparticle volume fraction.

Various chemical groups on the surface of each nanoparticle affect permeability, which justifies representing each nanocomposite as a mixture of the initial polymer (free of nanoparticles) and chemical groups localized on their surfaces.

Let us consider, following [77, 78], the influence of localized chemical groups on nanocomposite permeability, taking account of the following factors:

(a) polymer chemical structure;

(b) polymer concentration;

(c) chemical structure of the nanoparticle surface;

(d) nanoparticle concentration in the composite and concentration of functional groups on the nanoparticle surface;

(e) nanoparticle size and shape.

The number of chemical groups β localized on the nanoparticle surface per repeating unit can be estimated as follows. The number of nanoparticles n_{np} in 1 g of the nanocomposite is

$$n_{\rm np} = \frac{m_{\rm np}^{\Sigma}}{m_{\rm np}} = \frac{m_{\rm np}^{\Sigma}}{\rho_{\rm np} v_{\rm np}} , \qquad (46)$$

where m_{np}^{Σ} is the total mass of nanoparticles in the nanocomposite, m_{np} is the mass of a single nanoparticle, ρ_{np} is the nanoparticle density, and v_{np} is its volume.

The number of chemical groups N_{cg} in all nanoparticles of the nanocomposite is expressed as

$$N_{\rm cg} = \frac{n_{\rm cg} m_{\rm np}^2}{\rho_{\rm np} v_{\rm np}} \,, \tag{47}$$

where n_{cg} is the number of polar groups on the surface of a single nanoparticle.

The total number of repeating units N_{ru} in the system of interest is

$$N_{\rm ru} = 0.6023 \times 10^{24} \frac{m_{\rm pol}}{M_0} \,, \tag{48}$$

where m_{pol} is the polymer mass and M_0 is the mass of a repeating fragment.

Then, the number of chemical groups per repeating unit of a linear polymer or repeating part of a polymer network is calculated as

$$\beta = \frac{n_{\rm cg} m_{\rm np}^{\Sigma} M_0}{0.6023 \times 10^{24} \rho_{\rm np} v_{\rm np} m_{\rm pol}} \,. \tag{49}$$

The values of P_0^* (water permeability of a polymer free from nanoparticles) are calculated using the Cascade program.

Here are a few examples of calculations. First of all, the possible range of the polymer content in the nanocomposite needs to be estimated (it depends on both the polymer chemical structure and the parameters of the nanoparticles). Evidently,

$$\alpha_{\mathrm{m,p}} = \frac{1}{1+\beta} , \quad \alpha_{\mathrm{m,cg}} = \frac{\beta}{1+\beta} , \quad (50)$$

where $\alpha_{m,p}$ is the polymer molar fraction and $\alpha_{m,cg}$ is the molar fraction of chemical groups.

Substituting β from (49) into (50) yields

$$\alpha_{\rm m,p} = \frac{1}{1 + n_{\rm pg} m_{\rm np}^{\Sigma} M_0 / (0.6023 \times 10^{24} \rho_{\rm np} v_{\rm np} m_{\rm pol})} \,. \tag{51}$$

In the presence of planar nanoparticles shaped as tablets, Eqn (51) converts into

$$a_{\rm m,p} = \frac{1}{1 + n_{\rm pg} m_{\rm np}^{\Sigma} M_0 / (0.6023 \times 10^{24} \rho_{\rm np} \pi R_{\rm np}^2 h_{\rm np} m_{\rm pol})} , \quad (52)$$

where R_{np} and h_{np} are the nanoparticle radius and thickness, respectively.

For flat nanoparticles in the form of a parallelepiped, the following equation holds:

$$\alpha_{\rm m,p} = \frac{1}{1 + n_{\rm pg} m_{\rm np}^{\Sigma} M_0 / (0.6023 \times 10^{24} \rho_{\rm np} ab h_{\rm np} m_{\rm pol})} , \qquad (53)$$

where a, b, and h_{np} are nanoparticle length, width, and thickness, respectively.

For fiber-shaped nanoparticles, the molar fraction is defined by the relation

$$\alpha_{\rm m,p} = \frac{1}{1 + n_{\rm pg} m_{\rm np}^{\Sigma} M_0 / (0.6023 \times 10^{24} \rho_{\rm np} \pi R_{\rm np}^2 l_{\rm np} m_{\rm pol})} , \quad (54)$$

where R_{np} and l_{np} are the fiber radius and length, respectively.

Let us calculate, e.g., the permeability of polylactonic acid-based nanocomposites containing SiO₂ groups. To recall, if the nanoparticle volume is expressed in Å³, the factor 10²⁴ in relation (51) is omitted. For this polymer, $M_0 = 72.1$. The following parameters for the polymer and nanoparticles are chosen: $n_{pg} = 5000$, $m_{np}^{\Sigma} = 0.05$ g, $\rho_{np} =$ 1.45 g cm⁻³, $m_{pol} = 0.95$ g, $R_{np} = 6$ nm, $h_{np} = 2$ nm. Every time, one of these parameters is used as an argument, while the others are left unaltered. Under these conditions, the dependences of the polymer molar proportion on all the parameters were obtained (Figs 13–16).



Figure 13. Polymer molar fraction $\alpha_{m,p}$ versus the number of chemical groups per nanoparticle [77].



Figure 14. Polymer molar fraction $\alpha_{m,p}$ versus nanoparticle mass m_{np} in 1 g of composite [78].



Figure 15. Polymer molar fraction $\alpha_{m, p}$ versus nanoparticle radius R_{np} [77].





We use a simplified equation [25–27] to estimate permeability P_0^* :

$$\ln P_0^* = \frac{\left(\sum_i \Delta E_i^{**}\right)}{N_{\rm A} \sum_i \Delta V_i},\tag{55}$$

where $(\sum_i \Delta E_i^{**})$ is the reduced intermolecular interaction energy and $\sum_i \Delta V_i$ is the van der Waals volume of a repeating unit.

Constructing a (55)-based redundant system of equations in Refs [25–27] made it possible to determine atomic constant values and a small number of increments for dipole–dipole interactions, hydrogen bonds, and aromatic rings (Table 9).

The increment value of the hydrogen bond energy for the –NHCO–amide group is introduced separately.

For nanocomposites in which the surface of nanoparticles is modified by groups of a certain chemical structure, the

 Table 9. Atomic constants and increments taking account of specific interactions.

Atom and type of intermolecular interaction	Symbol	$\Delta E_i^{**},$ kJ mol ⁻¹
Carbon	$\Delta E_{\rm C}^{**}$	-27.85
Hydrogen	$\Delta E_{\rm H}^{**}$	44.84
Oxygen	ΔE_{Ω}^{**}	19.5
Nitrogen	$\Delta E_{\rm N}^{**}$	-19.5
Silicon	ΔE_{Si}^{**}	194
Chlorine	ΔE_{C1}^{**}	-9.5
Fluorine	$\Delta E_{\mathrm{F}}^{**}$	77.3
Sulphur	$\Delta E_{\rm S}^{**}$	637
Hydrogen bond for	$\Delta E_{\rm NHCO}^{**}$	353
-NHCO-group		
Double bond	$\Delta E_{=}^{**}$	190
Hydrogen bond	$\Delta E_{ m h}^{**}$	30.5
Aromatic ring (skeleton)	$\Delta E_{\rm ar.c.m}^{**}$	219
in the main chain	,	
Aromatic ring (skeleton)	$\Delta E_{ m ar.c.s}^{**}$	123
in the side chain	,	
Aliphatic ring (skeleton)	$\Delta E_{\rm alc}^{**}$	239
Dipole-dipole interaction	$\Delta E_{ m dd}^{**}$	122

following relation holds:

$$\ln P_0^* = \left(1 + \frac{n_{\rm pg}m_{\rm np}^{\Sigma}M_0}{0.6023 \times 10^{24}\rho_{\rm np}v_{\rm np}m_{\rm pol}}\right)^{-1} \left[\left(\sum_i \Delta E_i^{**}\right)_{\rm p} - \left(\sum_i \Delta E_i^{**}\right)_{\rm cg}\right] + \left(\sum_i \Delta E_i^{**}\right)_{\rm cg} \times \left[N_{\rm A}\left\{\left(1 + \frac{n_{\rm pg}m_{\rm np}^{\Sigma}M_0}{0.6023 \times 10^{24}\rho_{\rm np}v_{\rm np}m_{\rm pol}}\right)^{-1} \times \left[\left(\sum_i \Delta V_i\right)_{\rm p} - \left(\sum_i \Delta V_i\right)_{\rm cg}\right] + \left(\sum_i \Delta V_i\right)_{\rm cg}\right]^{-1},$$
(56)

where $(\sum_i \Delta E_i^{**})_p$ and $(\sum_i \Delta E_i^{**})_{cg}$ are the reduced energies of intermolecular interaction for the repeating unit and the chemical group localized on the nanoparticle surface, respectively, and $(\sum_i \Delta V_i)_p$ and $(\sum_i \Delta V_i)_{cg}$ are the van der Waals volumes of the repeating unit and the chemical group localized on the nanoparticle surface, respectively.

Equation (56) relates water permeability to the parameters of nanocomposites, such as the polymer chemical structure and concentration, the chemical structure of the nanoparticle surface in a composite, and the concentration of functional groups on the nanoparticle surface, as well as the nanoparticle size.

Let us calculate, e.g., the permeability of nanocomposites containing chemical groups on the surface of SiO₂-based nanoparticles:



For the starting polymer, $P_0^* = 938$ barrers and $(\sum_i \Delta V_i)_p = 62.3 \text{ Å}^3$ as determined using a modified version of the Cascade program. $(\sum_i \Delta E_i^{**})_{cg} = 5\Delta E_C^{**} + 11\Delta E_H^{**} + 3\Delta E_O^{**} + \Delta E_{Si}^{**} + \Delta E_d^{**} = 728.5 \text{ kJ mole}^{-1}, (\sum_i \Delta V_i)_{cg} = 136.75 \text{ Å}^3$. The use of these parameters yields the formula for calculating the dependence of nanocomposite water permeability on the



Figure 17. Dependence of P_0^* on $\alpha_{m,p}$.

polymer mole fraction:

$$\ln P_0^* = \frac{728 - 472\alpha_{\rm m,\,p}}{82 - 44.8\alpha_{\rm m,\,p}} \,. \tag{57}$$

The dependence of P_0^* on $\alpha_{m,p}$ is illustrated in Fig. 17.

Using relations (50) and (52)–(54) the dependences of P_0^* on all parameters of nanoparticles can be obtained. For example, the dependence of P_0^* on the nanoparticle radius is shown in Fig. 18.

If nanoparticles are shaped like planar parallelepipeds, the polymer mole fraction is described by the relation

$$\alpha_{\rm m, p} = \frac{1}{1 + n_{\rm pg} m_{\rm np}^{\Sigma} M_0 / (\rho_{\rm np} ab h_{\rm np} m_{\rm pol} \, 0.6023 \times 10^{24})} \,, \quad (58)$$

where a, b, and h_{np} are the nanoparticle length, width, and thickness, respectively.

Using the above procedure, it is easy to calculate the permeability of nanocomposites with the surface modified by various introduced chemical groups.

Let us consider the influence of filler element orientation (the order parameter) on permeability. In the case of a uniform nanoparticle distribution in a composite volume of 1 cm^3 , the number of nanoparticles

$$N = \frac{V}{v} , \qquad (59)$$

where V is the total volume of the nanoparticles and v is the volume of a single nanoparticle.

If the particles are shaped like parallelepipeds, the volume of a single nanoparticle is expressed as

$$v = abc, (60)$$



Figure 18. Dependence of water permeability on nanoparticle radius R_{np} .

where a, b, and c are the length, width, and height, respectively.

The volume fraction of nanoparticles in a 1-cm³ nanocomposite is $\Phi = V$. Then, the number of nanoparticles

$$N = \frac{V \,[\text{cm}^{3}]}{abc \,[\text{nm}^{3}]} = \frac{10^{21} V}{abc} \,. \tag{61}$$

The number of nanoparticles located on a straight line (considering the cubic volume)

$$n = \sqrt[3]{N} = \frac{10^7 \sqrt[3]{V}}{\sqrt[3]{abc}} \,. \tag{62}$$

The distance between nanoparticle centers is

$$l_0 = \frac{1 \text{ cm}}{n} = \frac{\sqrt[3]{abc}}{\sqrt[3]{V}} = \sqrt[3]{\frac{abc}{\Phi}}.$$
(63)

It follows from formula (63) that the inter-particle distance grows with increasing a, b, and c.

Let us analyze the influence of the nanoparticle volume on the distance between the neighboring nanoparticles. Bearing in mind that v = abc, we get from Eqn (63)

$$l_0 = \sqrt[3]{\frac{v}{\Phi}}.$$
(64)

Now let us consider the influence of nanoparticle orientation on the free distance Δl accessible to penetration by water molecules. Figure 19 illustrates the packing of nanoparticles at an orientation angle α . Evidently, the free space available for penetration by the molecules of a low molecular weight fluid is minimal at $\alpha = 0$ and maximal when $\alpha = 90^{\circ}$. If $\alpha = 90^{\circ}$, $\Delta l = l_0 - c$. This equality holds if the inter-particle distance in the vertical plane is greater than $l_0 - c$. In other words, the free space Δl accessible to penetration of the molecules of a fluid can be calculated using the formula

$$\Delta l = l_0 - a\cos\alpha - c\sin\alpha. \tag{65}$$

The free linear space Δl available for penetration depends on the penetration path. If this process occurs in accordance with the scheme presented in Fig. 20a, then $\Delta l_1 = l_0 - a$ (case I). The most accessible pathway for nanoparticle permeation is realized when penetrant molecules pass between nanoparticles, as shown in Fig. 20b. In this case,



Figure 19. Uniform distribution of planar nanoparticles (side view); α – angle of rotation [77].



Figure 20. (a) Uniform distribution of planar nanoparticles (side view) [77]. (b) Uniform distribution of planar nanoparticles (top view) [77].



Figure 21. Free linear space Δl versus nanoparticle volume fraction for cases I (*1*) and II (*2*) [78].

the free linear space accessible to permeation is defined as $\Delta l_2 = l_0 - b$ (case II). The dependences of Δl on the nanoparticle volume proportion for cases I and II are shown in Fig. 21.

Let us consider the influence of the random size distribution of the space available for water penetration on the water permeability of nanocomposites. In this case, the integral Δl distribution function is described by the relation

$$F(\Delta l) = 1 - \exp\left(-\frac{\Delta l}{\Delta l_{\rm av}}\right),\tag{66}$$

where Δl is the linear space accessible to penetration by water molecules, and Δl_{av} is the mean linear space size.

Dependences of $F(\Delta l)$ at different Δl_{av} are presented in Fig. 22.

It follows that Δl depends on the mean distance Δl_{av} between neighboring nanoparticles. In case II, the mean distance between the neighboring nanoparticles is greater than in case I. This accounts for the shape of the $F(\Delta l)$ dependences shown in Fig. 22b.

To calculate the fraction of distances α_{pen} accessible to penetration of water molecules, one should take into account that the diameter of a molecule is D = 3.2 Å. Therefore, α_{pen} is calculated by the formula

$$\alpha_{\text{pen}} = 1 - F(\Delta l) = \exp\left(-\frac{0.64}{\Delta l_{\text{av}}}\right).$$
(67)



Figure 22. (a) Dependences of *F* on Δl at different Δl_{av} values (case I). Curve numbers indicate Δl_{av} values [77]. (b) Dependences of *F* on Δl at different Δl_{av} values (case II). Curve numbers indicate Δl_{av} values in Angstrom units [77].

The dependences of α_{pen} on Δl_{av} are presented in Fig. 23, showing that the fraction of distances accessible to penetration by water molecules increases with Δl_{av} .

The problem becomes more complicated in the case of the distribution by rotation angles α . Let us consider the Poisson distribution

$$P(k) = \frac{\lambda^k \exp\left(-\lambda\right)}{k!}, \qquad (68)$$

where $k = 1, 2, ..., n, \lambda$ is the expected mean value.

The dependences of P(k) on $\alpha = 10k$ are presented in Fig. 24. Obviously, their maximum becomes shifted with respect to the angle of rotation as λ increases.

Let us calculate $\Sigma P(k)\Delta l$. The dependences $P(k)\Delta l$ on $\alpha = 10k$ are shown in Fig. 25 and the dependences $\Sigma P(k)\Delta l$ on λ in Fig. 26. To calculate the membrane region accessible to penetration by water molecules at the orientation angle $\alpha = 0$, it is necessary first of all to find the nanoparticle region corresponding to case I (Fig. 20a). The area of nanoparticles $S_{np} = n^2 ab$, where *n* is their number along a straight line. The use of formula (62), bearing in mind that $V = \Phi$, leads to

$$S_{\rm np} = \frac{10^{14}ab}{\frac{3}{2}\sqrt{abc/\Phi}} = \frac{\sqrt[3]{ab}}{\frac{3}{2}\sqrt{c/\Phi}} \quad [\rm cm^2] \,. \tag{69}$$

The area of the part of the region occupied by all nanoparticles in the membrane plane is S_{np} , because the entire membrane area is 1 cm². The area between neighboring nanoparticles is estimated as $\Delta l_{av}b$ in case I (Fig. 20a) and as $\Delta l_{av}a$ in case II (Fig. 20b). The area of the region inaccessible

α





Figure 24. Dependences of P(k) on α . Curve numbers indicate dimensionless values λ [27].







Figure 26. Dependences of $\sum P(k)\Delta l$ on λ at a = 40 nm, b = 4 nm, $l_0 = 54.3$ nm [27].

to water molecules in case I is expressed as

$$S_{\rm I} = \sqrt[3/2]{\frac{\Phi}{abc}} \Delta l_{\rm av, I} b(1 - \alpha_{\rm pen})$$
$$= \sqrt[3/2]{\frac{\Phi}{abc}} \Delta l_{\rm av, I} b \left[1 - \exp\left(-\frac{0.64}{\Delta l_{\rm av, I}}\right) \right].$$
(70)

The analogous quantity for case II is

$$S_{\rm II} = \sqrt[3/2]{\frac{\Phi}{abc}} \Delta l_{\rm av, II} a (1 - \alpha_{\rm pen})$$
$$= \sqrt[3/2]{\frac{\Phi}{abc}} \Delta l_{\rm av, II} a \left[1 - \exp\left(\frac{-0.64}{\Delta l_{\rm av, II}}\right) \right], \tag{71}$$

where $\Delta l_{\text{av, I}} = \sqrt[3]{abc/\Phi} - a$, and $\Delta l_{\text{av, II}} = \sqrt[3]{abc/\Phi} - b$.

Thus, the total proportion of the region inaccessible to permeation by water molecules is described as

$$\begin{aligned} \varepsilon_{\rm impen} &= \frac{\sqrt[3]{ab}}{\sqrt[3]{2/c/\Phi}} + \sqrt[3/2]{\frac{\Phi}{abc}} \left\{ \Delta l_{\rm av,\,I} \, b \left[1 - \exp\left(-\frac{0.64}{\Delta l_{\rm av,\,I}} \right) \right] \right. \\ &+ \Delta l_{\rm av,\,II} \, a \left[1 - \exp\left(-\frac{0.64}{\Delta l_{\rm av,\,II}} \right) \right] \right\}. \end{aligned}$$
(72)

An experimental verification was performed in Refs [77, 78] as follows. Expression (56) was modified by reducing it to the form describing the dependence of permeability on the molar fraction of chemical groups $\alpha_{m,cg}$ chemically bound to the nanoparticle surface:

$$\ln P_0^* = \frac{\alpha_{\rm m, cg} \left[\left(\sum_i \Delta E_i^{**} \right)_{\rm cg} - \left(\sum_i \Delta E_i^{**} \right)_{\rm p} \right] + \left(\sum_i \Delta E_i^{**} \right)_{\rm p}}{N_{\rm A} \left\{ \alpha_{\rm m, cg} \left[\left(\sum_i \Delta V_i \right)_{\rm cg} - \left(\sum_i \Delta V_i \right)_{\rm p} \right] + \left(\sum_i \Delta V_i \right)_{\rm p} \right\}} .$$
(73)

Let us make use of the experimental data on the permeability of PA-12 based on nanocomposites and montmorillonite nanoparticles with the surfaces modified by groups [97]:

$$CH_2-CH_2-OH$$

$$|$$

$$T-N^*-CH_3$$

$$|$$

$$CH_2-CH_2-OH$$
Modifier.

Structures	$P_0^*,$ barrer	$\sum_{\substack{i \\ A^3}} \Delta V_i,$	M_0	$ ho, \ { m g}{ m cm}^{-3}$	$\left(\sum_{i} \Delta E_{i}^{**}\right)$, barrer Å ³
PA-12	2940	218	197	1/02	1049
Modifier $C_n = 18$	563	434	389	0/980	1655
Modifier $C_n = 16$	578	400	361	0/980	1531
Modifier $C_n = 14$	597	366	332	0/981	1409
Modifier blend	569	420	378	0/980	1605

Table 10. Physical parameters of PA-12 and the modifier.

Here, T denotes the residues of aliphatic fatty acids with the number C_n of carbon atoms edual to 18 (65%), 16 (30%), and 14 (5%). The physical parameters needed for the calculation are listed in Table 10. They are derived with the use of the Cascade program.

The formula for converting molar fractions $\alpha_{m,\,2}$ into volume fractions \varPhi is

$$\alpha_{\rm m,2} = \frac{1}{1 + (M_1/M_2)(\rho_2/\rho_1)(1/\Phi - 1)} \,. \tag{74}$$

Substituting parameter values from Table 10 into formula (74) yields

$$\alpha_{\rm m, cg} = \frac{1}{0.422 + 0.578/\Phi} \,. \tag{75}$$

It then follows from (73) that

$$\ln P_0^* = \frac{606 + 999\Phi}{75.9 + 177.3\Phi} \,. \tag{76}$$

The mean length of nanoparticles in Ref. [97] is a = 41 nm, and their width and thickness are b = c = 3 nm. Substituting these data into (72) yields the dependence of the volume fraction inaccessible to water penetration:

$$\begin{aligned} \alpha_{\rm impen} &= 2.391 \ {}^{3/2} \sqrt{\Phi} + 0.058 \ {}^{3/2} \sqrt{\Phi} \left(\frac{7.17}{\sqrt[3]{\Phi}} - 41 \right) \\ &\times \left(1 - \exp \frac{-0.64 \sqrt[3]{\Phi}}{7.17 - 41 \sqrt[3]{\Phi}} \right) + 0.797 \ {}^{3/2} \sqrt{\Phi} \\ &\times \left(\frac{7.17}{\sqrt[3]{\Phi}} - 3 \right) \left(1 - \exp \frac{-0.64 \sqrt[3]{\Phi}}{7.17 - 3 \sqrt[3]{\Phi}} \right). \end{aligned}$$
(77)

The total relative nanocomposite permeability is given by the formula

$$\frac{P}{P_0^*} = 2.391 \, {}^{3/2}\sqrt{\Phi} + 0.058 \, {}^{3/2}\sqrt{\Phi} \left(\frac{7.17}{\sqrt[3]{\Phi}} - 41\right) \\ \times \left[1 - \exp\left(-\frac{0.64\sqrt[3]{\Phi}}{7.17 - 41\sqrt[3]{\Phi}}\right)\right] + 0.797 \, {}^{3/2}\sqrt{\Phi} \\ \times \left(\frac{7.17}{\sqrt[3]{\Phi}} - 3\right) \left[1 - \exp\left(-\frac{0.64\sqrt[3]{\Phi}}{7.17 - 3\sqrt[3]{\Phi}}\right)\right] \\ + \frac{1}{2940} \exp\left(\frac{606 + 999\Phi}{75.9 + 177.3\Phi}\right).$$
(78)

The dependence of relative nanocomposite permeability deduced from formula (78) is illustrated in Fig. 27, which also shows experimental data on relative permeability (squares), borrowed from [97]. Evidently, experimental and



Figure 27. Dependence of the relative permeability of a nanocomposite on the volume fraction of nanoparticles Φ [77].

theoretical results are in good agreement for all volume proportions of nanoparticles except $\Phi = 0.04$ (probably due to a reduction in the degree of crystallinity in the presence of large amounts of the modifier).

Thus, the calculation scheme proposed in [77, 78] allows predicting the permeability of polymer nanocomposites containing planar nanoparticles of various shapes at different concentrations for small molecules (e.g., water). In the case of rectangular particles, special attention is given to anisometric ones that imitate particles of nanoclay and other planar fillers.

It is shown that permeability mainly depends on the concentration and length of nanoparticles, as well as their orientation in a polymer matrix. The proposed calculation scheme takes account of all these factors. The main thing is that the scheme takes into consideration the chemical structure of the matrix polymer and modifying agents introduced to improve the compatibility between the matrix and nanoparticles. For this purpose, an original simplified version of the calculation scheme is proposed that permits the permeability of matrix polymers and copolymers to be calculated taking into account their chemical structure and component ratio. Its experimental verification revealed good agreement between experimental and theoretical data on concentration-related variation in relative permeability.

8. Analysis of the influence of chemical structure and concentration of the components of polymer-solvent mixtures on the yield strength and viscosity

In this section we analyze the calculation scheme for estimating the yield strength and viscosity of systems containing a polymer and a solvent (plasticizer), taking account of their chemical structure, the intermolecular interaction between the polymer and the solvent, the van der Waals volume, and the molecular mass of repeating units in the polymer and solvent molecules, as well as the solvent concentration.

The rheological properties of polymer solutions are of importance both theoretically and for applications, because a number of polymer processing operations imply the use of such solutions. Certain polymer materials, e.g., polyvinyl chloride, find application mainly in a plasticized form. Therefore, problems related to the development of calculation schemes for predicting polymer properties, such as the yield strength and viscosity, remain in the focus of attention. Reference [98] reports an attempt to develop and computerize a calculation scheme allowing prediction of the aforementioned properties.

8.1 Yield strength

The term 'yield strength' is applied to characterize the glassy state of polymers. Therefore, it is first of all necessary to determine the range of solvent (or plasticizer) concentrations necessary to maintain the glassy state of a plasticized polymer.

As an example, let us consider a polymethyl metacrylate (PMMA), dibutyl phthalate (DBP), system. Results of calculations indicate that the introduction of a DBP weight fraction of 0.23 into the PMMA causes a rubbery state of the system at room temperature, because the glass transition temperature at such a DBP concentration is $T_g = 293$ K.

The next calculation step is the determination of the yield point $\sigma_{el,T}$ at a given temperature and at the temperature of the glassy state close to the polymer's T_g which can be implemented by using the simplified expression [3] in the form

$$\sigma_{\text{el},T} = 0.028E_T,\tag{79}$$

where E_T is Young's modulus of a glassy polymer at temperature *T* calculated by the formula

$$E_T = 2(1 + v_T)G_T = 3(1 - 2v_T)B_T, \qquad (80)$$

where G_T is the shear modulus of a glassy polymer at temperature T,

$$G_T = \frac{3(1-2\nu_T)}{2(1+\nu_T)} B_T,$$
(81)

and B_T is the bulk modulus depending on T,

$$B_T = 8.23333 E_{\rm coh} \left[\frac{5(V_{\rm M,0})^4}{(V_{\rm M,T})^5} - \frac{3(V_{\rm M,0})^2}{(V_{\rm M,T})^3} \right],\tag{82}$$

where $V_{M,0}$ is the mole volume at absolute zero temperature, $V_{M,T}$ is the mole volume at temperature T, E_{coh} is the cohesive energy per mole (that can be calculated using the Cascade program), and v_T is the *T*-dependent Poisson's ratio (in the glassy state):

$$v_T = v_0 + \frac{50T}{T_g} \left\{ 0.00163 + \exp\left[0.459(T - T_g - 13)\right] \right\}, \quad (83)$$

$$v_0 = v_{298 \text{ K}} - \frac{14900}{T_g} \left\{ 0.00163 + \exp\left[0.459(285 - T_g)\right] \right\}, (84)$$

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

where $V_{\rm w}$ is the van der Waals volume and $I_{\rm m}$ is the length of the repeating unit in a fully extended polymer conformation.

Estimate shows that the yield strength is 63 MPa at $T = 40^{\circ}$ and 10.6 MPa at $T = 75^{\circ}$ C (near the glass transition temperature). According to the principle expounded in [5–7], the yield strength can be deduced from the equation

$$\sigma_{\rm el} = \frac{\left(1 - \alpha_{\rm m,s}\right) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} + \alpha_{\rm m,s} \left(\sum_{i} \Delta V_{i}\right)_{\rm s}}{\left(1 - \alpha_{\rm m,s}\right) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} / \sigma_{\rm el,p} + \alpha_{\rm m,s} \left(\sum_{i} \Delta V_{i}\right)_{\rm s} / \sigma_{\rm el,s}},$$
(85)

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

Because the yield strength is measured in the glassy state of a system (the polymer-solvent system in the present case), relation (85) holds only within a fixed range of solvent concentrations and has to be reduced to the following form:

$$\sigma_{\rm el} = \frac{(1 - \alpha_{\rm m,s+p}) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} + \alpha_{\rm m,s+p} \left(\sum_{i} \Delta V_{i}\right)_{\rm s+p}}{(1 - \alpha_{\rm m,s+p}) \left(\sum_{i} \Delta V_{i}\right)_{\rm p} / \sigma_{\rm el,p} + \alpha_{\rm m,s+p} \left(\sum_{i} \Delta V_{i}\right)_{\rm s+p} / \sigma_{\rm el,s+p}},$$
(86)

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 said mixture regarded as critical (if the solvent concentration exceeds a critical value, the mixture transits to a rubbery state), and $\sigma_{el,s+p}$ is the yield strength for the polymer-solvent system with the critical solvent concentration).

In the case of interest, the critical mass fraction of the solvent is 0.23 and its molar concentration $\alpha_m = 0.097$.

The following formula holds within a $\alpha_{m,s+p}$ range from 0 to 1:

$$\left(\sum_{i} \Delta V_{i}\right)_{s+p} = (1 - 0.097) \left(\sum_{i} \Delta V_{i}\right)_{p} + 0.097 \left(\sum_{i} \Delta V_{i}\right)_{s} = 114.2 \text{ Å}^{3}.$$
 (87)

In accordance with (86) and taking into account all calculated physical parameters,

$$\sigma_{\rm el} = \frac{96.4 + 183.5\alpha_{\rm m,s}}{1.547 + 48.3\alpha_{\rm m,s}} \,. \tag{88}$$

Eqn (88) holds within the solvent molar fraction range $\alpha_{m,s}$ from 0 to 0.097. The dependence of the yield strength on the solvent (plasticizer) molar fraction is shown in Fig. 28.

If σ_{el} given by formula (88) needs to be expressed via the solvent mass fraction, then

$$\sigma_{\rm el} = \frac{96.4 + 183.5/[1 + (M_{\rm s}/M_{\rm p})(1/\alpha_{\rm w,s} - 1)]}{1.547 + 48.3/[1 + (M_{\rm s}/M_{\rm p})(1/\alpha_{\rm w,s} - 1)]} \,. \tag{89}$$

Relation (89) holds for the PMMA-DBP system in question within the $\alpha_{w,s}$ range from 0 to 0.23. Since, in the example under consideration, $M_s = 278$ and $M_p = 100$, we get the relation

$$\sigma_{\rm el} = \frac{96.4 + 183.5/(2.78/\alpha_{\rm w,s} - 1.78)}{1.547 + 48.3/(2.78/\alpha_{\rm w,s} - 1.78)} \,. \tag{90}$$

The dependence of the yield strength on the solvent mass fraction is presented in Fig. 29. Such dependences can be obtained for any temperature interval of the glassy state for polymer-solvent (plasticizer) systems.



Figure 28. Yield strength versus DBP molar fraction. $T = 40 \degree C$ [98].



Figure 29. Yield strength versus DBP mass fraction. $T = 40 \,^{\circ}\text{C}$ [98].

In the case of PMMA and DBP, relation (86) transforms into

$$\sigma_{\rm el} = \frac{96.4 + 183.5\alpha_{\rm m,s}}{\left(\sum_{i} \Delta V_{i}\right)_{\rm p} / \sigma_{\rm el} + 48.3\alpha_{\rm m,s}} \,. \tag{91}$$

Expression (91) holds within the $\alpha_{m,s}$ range from 0 to 0.097. The σ_{el} value depends on temperature and can be calculated using the PDTools program based on the Bicerano method [3]. The values of yield strength for PMMA at different temperatures are listed in Table 11.

The use of these values permits the dependences of the yield strength on the DBP plasticizer level to be calculated. They are presented in Fig. 30. Temperature dependences of the yield strength are presented in Fig. 31.

The above considerations demonstrate the possibility of analyzing the influence of temperature and chemical structure of the components of a polymer-plasticizer mixture on the yield strength.

Table 11. Calculated values of the yield strength σ_{el} at different temperatures for PMMA.

Temperature, °C	$\sigma_{\rm el}, { m MPa}$
20	91.6
30	77.0
40	62.3
50	47.6
60	33.0
70	18.3



Figure 30. Yield strength versus, DBP molar fraction at $20 \degree C$ (curve *I*), $30 \degree C$ (2), $40 \degree C$ (3), $50 \degree C$ (4), $60 \degree$ (5) [98].



Figure 31. Temperature dependences of yield strength. Curve numbers indicate DBP plasticizer molar fraction [98].

8.2 Viscosity

According to Ref. [5] the dependence of viscosity on the solvent volume fraction is described by relation

$$\ln \frac{\eta}{B} = 4 \ln \rho + \left\{ \alpha_{\rm v, p} \left[0.025 + \Delta \alpha \left(T - T_{\rm g, p} \right) \right] + (1 - \alpha_{\rm v, p}) \left[0.025 + \alpha_{\rm s} (T - T_{\rm g, s}) \right] \right\}^{-1},$$
(92)

where *B* is a combined constant including molecular mass, ρ is polymer concentration, $\alpha_{v,p}$ is the polymer volume fraction, $\Delta \alpha$ is the difference between coefficients of linear thermal expansion at temperatures above and below the polymer glass transition temperature, $T_{g,p}$ is the polymer glass transition temperature, α_s is the thermal expansion coefficient of the solvent (plasticizer), and $T_{g,s}$ is the solvent glass transition temperature, $\Delta \alpha = \alpha_L - \alpha_G$, where α_L and α_G are coefficients of polymer linear thermal expansion in the rubbery and glassy states respectively.

The quantity ρ is defined as

$$\rho = \frac{m_{\rm p}}{v_{\rm p} + v_{\rm s}} = \frac{m_{\rm p}}{m_{\rm p}/\rho_{\rm p} + m_{\rm s}/\rho_{\rm s}} = \frac{1}{1/\rho_{\rm p} + m_{\rm s}/(\rho_{\rm s}m_{\rm p})} ,$$
(93)

where m_p is the polymer mass in the solution, m_s is the solvent mass, ρ_p is the polymer density, ρ_s is the solvent density, v_p is the polymer volume, and v_s is the solvent volume. The value ρ can be expressed via the polymer volume fraction as

$$\alpha_{\rm v,p} = \frac{v_{\rm p}}{v_{\rm p} + v_{\rm s}} = \frac{1}{1 + v_{\rm s}/v_{\rm p}} = \frac{1}{1 + m_{\rm s}\rho_{\rm p}/(\rho_{\rm s}m_{\rm p})} \,. \tag{94}$$

It follows from (94) that

$$\frac{m_{\rm s}}{m_{\rm p}} = \frac{(1/\alpha_{\rm v,p} - 1)\rho_{\rm s}}{\rho_{\rm p}} \,. \tag{95}$$

Substituting (95) into (94) yields

$$\rho = \rho_{\rm p} \alpha_{\rm v, \, p} \,. \tag{96}$$

Quantity *B* can be found from (92) if the viscosity of the initial polymer containing no solvent at a given temperature *T* is known. In such a case, $\alpha_{v,p} = 1$, and Eqn (92) converts into

$$\ln \frac{\eta}{B} = 4 \ln \rho_{\rm p} + \left[0.025 + \Delta \alpha \left(T - T_{\rm g, p} \right) \right]^{-1}.$$
 (97)

Viscosity η can be determined using the Bicerano equation [3]: in the $T_{\rm g} < T < 1.2T_{\rm g}$ range, the equation for calculating zero shear viscosity ($\eta_{\rm Cr, T}$) depending on *T* is used:

$$\log_{10} \frac{\eta_{\rm Cr, T}}{\eta_{\rm Cr, 1.2T_g}} = 26.32 \left(\frac{T_g}{T}\right)^2 - 11.11 \frac{T_g}{T} - 9.02.$$
(98)

For $T > 1.2T_g$, the relation

$$\log_{10} \frac{\eta_{\rm Cr, T}}{\eta_{\rm Cr, 1.2T_g}} = \frac{(T_g - T)E_{\eta}}{2.3RTT_g}$$
(99)

is used, where $\eta_{Cr, 1, 2T_g}$ is zero shear viscosity at $1.2T_g$ and E_η is the viscous flow activation energy [3].

The resulting equation for the calculation of viscosity depending on the polymer volume fraction has the form

$$\ln \frac{\eta}{B} = 4 \ln \rho_{\rm p} \alpha_{\rm v, p} + \left\{ \alpha_{\rm v, p} \left[0.025 + (\alpha_{\rm L} - \alpha_{\rm G})(T - T_{\rm g, p}) \right] + (1 - \alpha_{\rm v, p}) \left[0.025 + \alpha_{\rm s}(T - T_{\rm g, s}) \right] \right\}^{-1}.$$
 (100)

Parameters of the polymer $\rho_{\rm p}$, $T_{\rm g,p}$, $\alpha_{\rm L}$, $\alpha_{\rm G}$ are calculated using the Cascade program and viscosity η at a given temperature by the Bicerano method [3]. The value of $\alpha_{\rm s}$ is either found in experiment or assumed to be $\alpha_{\rm s} \approx 10^{-3} \text{ K}^{-1}$.

As an example, we shall analyze a polystyrene (PS)toluene system. Parameter *B* in Eqn (92) can be calculated by formula (97), provided that viscosity η_0 of the initial polymer is known. The results for the polystyrene-toluene system are presented in Fig. 32.

Thus, an analysis of the influence of temperature, chemical structure, and content of both components on the yield strength and viscosity can be performed for various



Figure 32. Temperature dependences of shear viscosity. Polymer volume fraction $\alpha_{v,p}$: curve I = 1.0; 2 = 0.95; 3 = 0.90 [98].

polymer–solvent systems. The computerized calculation procedure enables an analysis in an automatic mode after the choice of the chemical structure of both the polymer and the solvent. The dependences of glass transition temperature on the molar or weight concentration of the solvent make it possible to determine the temperature range in which a system exists in the glassy state and can be characterized by relations proposed in Ref. [98].

9. Calculation scheme for estimating dynamic viscosity, storage and loss moduli depending on temperature

It was shown [99, 100] that the polymer storage modulus at high frequencies is expressed as

$$G = \frac{\sum_{i} \Delta V_{i}}{\sum_{i} g_{i} \Delta V_{i} + \sum_{j} f_{j}}, \qquad (101)$$

where coefficients g_i characterize the mean contribution of each atom to $S_i/(\kappa_i l_i)$, $g_i = S_i/(\kappa_i l_i)$, f_i is a set of constants characterizing the influence of strong intermolecular interactions (dipole–dipole interactions, hydrogen bonds), S_i is the van der Waals surface area of the *i*-th atom through which the intermolecular interaction occurs, κ_i is the elasticity coefficient of the bond of the *i*-th atom, l_i is the characteristic bond size, and ΔV_i is the van der Waals volume of the *i*-th atom in the polymer repeating unit. The values of g_i and f_j reported in [99, 100] are presented in Table 12.

For a system of compatible polymers, relation (101) takes the form

$$G = \frac{\alpha_1(\sum_i \Delta V_i)_1 + \alpha_2(\sum_i \Delta V_i)_2}{\alpha_1(\sum_i g_i \Delta V_i + \sum_j f_j)_1 + \alpha_2(\sum_i g_i \Delta V_i + \sum_j f_j)_2}, \quad (102)$$

where α_1 and α_2 are the molar fractions of polymers 1 and 2, respectively, $(\sum_i g_i \Delta V_i + \sum_j f_j)_1$ and $(\sum_i g_i \Delta V_i + \sum_j f_j)_2$ are the sets of constants for polymers 1 and 2, respectively.

Bearing in mind that, in accordance with (101),

$$\sum_{i} g_i \Delta V_i + \sum_{j} f_j = \frac{\sum_i \Delta V_i}{G} \,,$$

Eqn (102) can be presented in the form

$$G = \frac{(\sum_{i} \Delta V_{i})_{1} + \alpha_{2} [(\sum_{i} \Delta V_{i})_{2} - (\sum_{i} \Delta V_{i})_{1}]}{(\sum_{i} \Delta V)_{1}/G_{1} + \alpha_{2} [(\sum_{i} \Delta V_{i})_{2}/G_{2} - (\sum_{i} \Delta V_{i})_{1}/G_{1}]},$$
(103)

where G_1 and G_2 and are the moduli of components 1 and 2, respectively.

Equation (103) allows describing the dependence of the G modulus on the mole concentration of polymer 2.

Table 12. g_i and f_j constants

Atom and type of intermolecular interaction	g_i and f_j constants					
Carbon Hydrogen Oxygen Double bond Dipole-dipole*	$g_{\rm C}, {\rm cm}^2 {\rm kg}^{-1} \\ g_{\rm H}, {\rm cm}^2 {\rm kg}^{-1} \\ g_{\rm O}, {\rm cm}^2 {\rm kg}^{-1} \\ f_{=}, {\rm \mathring{A}}^3 {\rm cm}^2 {\rm kg}^{-1} \\ f_{\rm dd}, {\rm \mathring{A}}^3 {\rm cm}^2 {\rm kg}^{-1}$	-1.277 4.376 116.95 30.925 84.472				
*Parameter f_{dd} for each branch of the main and side chains.						



Figure 33. Storage modulus versus PC weight fraction $\alpha_{w, PC}$ [99].

Here is an example of calculations. A mixture of fully compatible polymers consists of polystyrene and polycarbonate. The latter has the following chemical composition:



The use of parameters from Table 12 and the value of the van der Waals volume of the atoms from Ref. [5] for polystyrene (PS) yields

$$\left(\sum_{i} g_i \Delta V_i + \sum_{j} f_j\right)_{\rm PS} = -1.277(13.1 + 8.7 + 8.4 + 5 \times 12.7) + 4.376(8 \times 2.0) + 84.472 = 34.8.$$

The van der Waals volume of the PS repeating unit $(\sum_i \Delta V_i)_{\rm PS} = 110 \text{ Å}^3$. Therefore, the PS storage modulus $G_{\rm PS} = 3.15 \text{ kg cm}^{-2}$, its experimental value being $G_{\rm PS} = 3.16 \text{ kg cm}^{-2}$.

For polycarbonate (PC),

$$\left(\sum_{i} g_{i} \Delta V_{i} + \sum_{j} f_{j}\right)_{PC} = -1.277(4 \times 16.9 + 6 \times 8.4)$$

+ 2 × 11.6 + 4 × 12.7 + 4.5 + 2 × 12.7 + 19.0) + 4.376
× (22 × 2.0) + 116.95(2 × 2.7 + 5.95) + 84.472 = 1285.3.

The polycarbonate van der Waals volume $(\sum_i \Delta V_i)_{PC} = 305.3 \text{ Å}^3$. The calculated storage modulus for polycarbonate $G_{PC} = 0.24 \text{ kg cm}^{-2}$.

The dependence of the storage modulus on the polycarbonate weight fraction is shown in Fig. 33.

10. Influence of structure on refractive index and dielectric constant of polymer nanocomposites

References [100, 101] consider causes behind discrepancies between theoretical and experimental values of polymer dielectric constants. It is shown that the discrepancies are due either to the action of the remnants of the synthesis products or to the presence of solvent residues formed during film manufacture (plasticizing effect). They also can arise from the influence of nonlinearity on polymer polarization which is not taken into account in the classical Clausius– Mossotti function. The causes of discrepancies were elucidated in the framework of the calculation schemes discussed in the above publications; in addition, the influence of nanoparticles on refractive indices of certain polymeric nanocomposites was estimated.

At present, methods for the calculation of the physical properties of polymers are developed well enough to facilitate the solution of major problems of polymer physics. Results of such studies are reported in monographs [2–7]. They confirm that the main characteristics of polymers can be found by calculating with a $\leq 5\%$ margin of error in respect to experimental data. However, in certain cases, e.g., in the calculation of polymer dielectric constants ε , the error can be much higher than 5% (see [6, Ch IX], where the number of such polymers amounts to 23% of the total), because only their chemical structure was taken into consideration in ε calculations.

For real polymers, there are a great variety of factors influencing dielectric constant values, including a finite chain length (the influence of end-groups of various structures), inhomogeneous chain packing (electric field nonuniformity in the bulk, the Clausius–Mossotti function suggesting an isotropic homogeneous medium), and the presence of charge carriers due to natural ionization.

Let us dwell on the influence of the molecular mass. For example, let us calculate the refractive index and dielectric constant for polystyrenes having different molecular masses and end-groups of various structures (see [6, 7]). The results of n and ε calculations are presented in Table 13, taking into account the influence of the chain packing coefficient upon a change in molecular mass, from a monomer to a polymer, with the molecular mass at which the rubbery state develops.

It follows from Table 13 that the packing coefficient k significantly increases with growing molecular mass, which leads to a rise in the refractive index and dielectric constant. These processes occur when the molecular mass is smaller than the mechanical segment of the macromolecule (by mechanical segment is meant the molecular mass of a polymer, exceeding which leads to the appearance of the rubbery state). Polymers studied in Ref. [6] as a rule have a molecular mass higher than the mechanical segment.

A marked difference between theoretical ε_{calc} and measured ε_{exp} values can be due to several causes: (1) the presence of synthesis products in polar polymers, (2) the contribution of nonlinear terms to polarization of certain polymers, (3) the formation of micropores, (4) the presence of films containing solvents with the dielectric constant higher or lower than that in a pure sample. Considering these factors is paramount for the development of polymer materials finding application in electronics engineering and nonlinear optical devices.

Table 13. Refractive index n, dielectric constant e, and molecular packing coefficient k for polystyrene of different molecular masses M.

М	k	Molar refraction, cm ³ mol ⁻¹	Molar volume, cm ³ mol ⁻¹	$\begin{array}{c c} Molar & n \\ volume, \\ cm^3 mol^{-1} \end{array}$	
314	0.5970	93	314	1.5041	2.2623
939	0.5994	389	981	1.5092	2.2777
5000	0.6106	1660	5307	1.5380	2.3654
10,000	0.6229	3248	10,316	1.5423	2.3787
15,000	0.6358	4825	14,819	1.5647	2.4483
20,000	0.6487	6402	19,435	1.5728	2.4787
25,000	0.6617	7979	24,152	1.5748	2.4800
33,000	0.6823	10,473	30,615	1.6018	2.5658

Optical and dielectric properties of polymer materials can be modified by creating micropores and introducing into them multi-component nanoparticle systems (nanocomposites). However, solving this problem encounters difficulties arising from the necessity to stabilize the micropores. An unwanted collapse of the micropores can be prevented in two ways:

(1) the goal-oriented selection of a linear matrix polymer with such a chemical structure that would preclude its dissolution by nanoparticle destruction products formed under the effect of heating during its manufacture or operation;

(2) cross-linking of macromolecules of a linear polymer and suppressing diffusion of the low molecular weight products being formed.

An advantage of the chemical cross-linking procedure is that even if a cross-linked polymer shows thermodynamic compatibility with destruction products, it undergoes no more than swelling and a decrease in the pore size without any movement of molecules or the pore collapse observed in linear polymers. The entire scope of the above issues and problems is considered below.

10.1 Effect of the plasticizing action of the residual synthesis products and a solvent on polymer dielectric constant

The products of polymer synthesis reaction can be more or

less successfully removed when preparing polymer samples of interest for the measurement of dielectric constants. However, the removal of certain products encounters great difficulties. The solution to this problem is of primary importance for polymers used in microelectronics, because their plasticizing action essentially distorts the dielectric properties of the material. By the example of polymers [6] for which the calculation error exceeds 5%, let us estimate the contribution of these factors and try to identify them.

Consider the Lorentz–Lorentz (L–L) formula, the optical analog of the Clausius–Mossotti (C–M) formula:

$$\Phi_{\rm L-L} = \frac{n^2 - 1}{(n^2 + 2)\rho} = \frac{4\pi\beta}{3M} , \qquad (104)$$

where *n* is the polymer refractive index, ρ is the polymer density, and *M* is the molecular mass of the polymer repeating unit,

$$\beta = \sum_{i} \frac{e_i^2}{m_i(\omega_i^2 - \omega^2)}, \qquad (105)$$

$$\omega_i^2 = \frac{\kappa_i}{m_i} \,, \tag{106}$$

Table 14. Influence of moisture on the polymer dielectric constant.

where ω_i is the eigenfrequency of *i*th charge oscillations, e_i and m_i are the charge and mass of the *i*th particle, respectively, κ_i is the elasticity coefficient of the bond of the *i*th atom, and ω is the alternating field frequency.

Expression (104) for Φ_{L-L} converts into the Clausius– Mossotti equation for Φ_{C-M} at $\omega = 0$ (at $\omega \leq \omega_i$, to be precise). In this case, $\beta = \sum_i e_i^2/k_i$. To calculate the contribution of the elastic constituent to molecule polarizability β , the expression for the elasticity modulus of an amorphous polymer *E* can be expressed in accordance with [100, 101] as

$$\frac{1}{E} = \frac{\sum_{i} S_i \Delta V_i / (k_i l_i)}{\sum_{i} \Delta V_i} = \frac{\beta}{\alpha} , \qquad (107)$$

where α is a certain constant that can be calculated as $\alpha = (\sum_i e_i^2/k_i)(\sum_i \Delta V_i)/(\sum_i S_i \Delta V_i/(k_i l_i))$, ΔV_i is the van der Waals volume of the *i*-th atom in the repeating unit, S_i is the van der Waals surface area of the *i*-th atom through which the intermolecular interaction is transferred, and l_i is the characteristic bond size.

To analyze the influence of synthesis products, residual solvent, and nonlinearity, Φ_{C-M} is chosen in the form $\Phi_{C-M} = (\epsilon - 1)/(\epsilon + 2)$ and the right-hand side as $x = 4\pi\beta\rho/(3M)$, where

$$\beta = \frac{\alpha}{E} \,. \tag{108}$$

According to [102], $E \sim T_g$. Therefore, the plasticizing action of the reaction products and the solvent can be taken into account using the plastification function $Pl(W) = T_g(W)/T_{g0}$, where W is the mass fraction of residual synthesis products, $T_g(W)$ is the glass transition temperature of the plasticized polymer, and T_{g0} is the glass transition temperature of the plasticized polymer in the absence of synthesis products. Coming back to the initial expression, $\Phi_{C-M}(W)$ of the plasticized polymer can be written as

$$\frac{x(W)}{x(0)} = \mathrm{Pl}^{-1}(W) \,. \tag{109}$$

The Clausius–Mossotti function $\Phi_{C-M}(0)$ is usually found by calculation [3, 6, 7].

The use of Eqn (109) allows PI(W) to be calculated for polymers in which the discrepancy between theoretical and experimental ε values exceeds the accuracy of the calculation method. If $PI(W) \leq 1$, the discrepancy may arise from the presence of residual synthesis products. Usually, the calculated ε value for such polymers is lower than the measured one. If $PI(W) \ge 1$, the discrepancy is due to other factors considered below.

Tables 14 and 15 present experimental data for a number of polymers [6], the plastification of which by the

Polymer	$\Phi_{\mathrm{C-M}}(0)$	$\Phi_{\mathrm{C-M}}(W)$	€ _{C−M}	€ _{exp}	$\Delta \varepsilon$, %	$\operatorname{Pl}(W)$
Poly(1,4-butadiene)	0.297	0.335	2.27	2.51	-9.6	0.887
Poly[1,1 cyclohexane bis (4-phenyl) carbonate]	0.396	0.348	2.97	2.6	14.2 (-2.7)	1.14 (1)
Poly(N-vinyl) carbazole	0.360	0.388	2.69	2.90	-7.2	0.928
Poly[4,4'-isopropylidene diphenoxy di((4-phrenilene) sulphone]	0.391	0.421	2.93	3.18	-7.9	0.929
Poly[2,2'-(m-phenilene)-5,5'bis - benzimidazole]	0.364	0.434	2.72	3.30	-17.6	0.838

Polymer	x	€ _{calc}	€ _{exp}	Δε, %	x(W)	$\operatorname{Pl}(W)$
Poly(1,4-butadiene)	0.297	2.27	2.51	-9.6	0.335	0.887
Poly(n-butyl) met-acrylate	0.353	2.64	2.82	-6.4	0.377	0.935
Poly(N-vinyl) carbazole	0.360	2.69	2.90	-7.2	0.388	0.928
Poly[4,4'-isopropylidene diphenoxy di((4-phrenilene) sulphone]	0.391	2.93	3.18	-7.9	0.421	0.929
Poly(ether ether) ketone	0.4	3.00	3.20	-6.2	0.423	0.945
Poly(hexamethylene sebacamide)	0.446	3.60	3.8	-5.3	0.483	0.924
Poly[2,2'-(m-phenilene)-5,5'-bis benzimidazole]	0.364	2.72	3.30	-17.6	0.434	0.84
Poly(β-vinyl) naphthalene	0.314	2.37	2.51	5.6	0.335	0.938
Poly[1,1-ethane bis (4-phenyl) carbonate]	0.351	2.62	2.90	9.6	0.388	0.905
Poly-3,4-dichlorostyrene	0.351	2.62	2.94	7.5	0.393	0.894
* Names of polymers with dielectric constants containing contributions from both non-linearity and residual synthesis products are highlighted in bold.						

Table 15. Values of the plastification function Pl(W) for polymers^{*} having a negative error $\Delta \varepsilon$.

residual reaction products of synthesis markedly affects the accuracy of estimation of their dielectric constants. The high calculation error ε for poly[1,1-cyclohexane *bis* (4-phenyl) carbonate] with $Pl(W) \ge 1$ is due to the nonlinear polarization dependence of the Clausius–Mossotti function.

10.2 Influence of nonlinearity on the Clausius–Mossotti function

The following expression obtained by Jepsen [103] makes it possible to take into account the influence of temperature on the optical properties of nanocomposites:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = x - \frac{15x^3}{16} \,. \tag{110}$$

Table 16 presents the results obtained by estimating dielectric constants of polymers with a positive calculation error ($\Delta \varepsilon > 0$) taking into consideration expression (110).

Table 16. Values of dielectric constants ε_J for polymers^{*}, taking account of Jepsen's corrections^{**}.

Polymer	x	$\epsilon_{ m calc}$	€ _{exp}	Δε, %	£ј	$\Delta \varepsilon_1, \%$
Poly(4-methyl-1-pentane)	0.297	2.27	2.13	6.6	2.12	-0.5
Poly(vinyl cyclohexane)	0.315	2.38	2.25	5.8	2.2	-2.22
Poly(β -vinyl naphthalene)	0.355	2.65	2.51	5.6	2.37	-5.7
Poly[1,1-cyclohexane <i>bis</i> (4-phenyl) carbonate]	0.396	2.97	2.60	14.2	2.53	-2.7
Poly[1,1-ethane <i>bis</i> (4-phenyl) carbonate]	0.421	3.18	2.90	9.6	2.62	-9.56
Poly(3,4-dichlorostyrene)	0.419	3.16	2.94	7.5	2.62	-10.9

* If only the error sign changes when the linear term is taken into account in the cases of poly[1,1-ethane *bis* (4-phenyl) carbonate] and poly(β -vinyl naphthalene), it means that both polymers contain, in addition, either the products of synthesis or the solvent, the influence of which can be taken into consideration via the plastification function (see Table 14).

^{**} $\Delta \varepsilon_1$ is the discrepancy between experimental and theoretical values of dielectric constants found as described by Jepsen (taking account of the nonlinear terms).

The ε calculation error in the case of poly(4-methyl-1pentane) and poly(vinyl) cyclohexane decreased so as to meet the conditions of the calculation schemes, while the error for the remaining polymers only changed sign. This means that the ε calculation error for these compounds is markedly affected not only by nonlinearity but also by the plasticizing effect caused by residues of synthesis products (the names of these polymers in Table 15 are highlighted in bold type). In the case of poly(β -vinyl) naphthalene, $\varepsilon = 2.3$ (given that both the plasticizing effect and the nonlinearity are taken into consideration). This value for poly[1,1-ethane *bis* (4-phenyl) carbonate] and poly(3,4-dichlorostyrene) is $\varepsilon = 2.5$ and $\varepsilon = 2.52$, respectively.

It was shown that only three of the above polymers showed marked discrepancies between the results of predictions of dielectric constants related to their nonlinear properties (see Table 16). The effect of introducing SiO_2 on the polymer optical properties is exemplified by poly[1,1-cyclohexane *bis* (4-phenyl) carbonate]. It was estimated using the modified expression from [9]:

$$n_{\rm nc}^2 = n_{\rm pol}^2 + \xi \frac{3(n_{\rm np}^2 - n_{\rm pol}^2)n_{\rm pol}^2}{n_{\rm np}^2 + 2n_{\rm pol}^2} + \xi^2 \frac{(n_{\rm np}^2 - n_{\rm pol}^2)^2}{n_{\rm np}^2 + 2n_{\rm pol}^2}, \quad (111)$$

where $n_{\rm nc}$ is the nanocomposite refractive index, $n_{\rm pol}$ is the polymer refractive index, $n_{\rm np}$ is the nanoparticle refractive index, and ξ is the micropore volume proportion.

For the polymer of interest with $\xi = 0.3$, $n_{\rm pc} = 2.25$. In other words, the refractive index decreased by 13%. The assessment of polarization *x* from Eqn (110) suggests that it is practically unaltered by the introduction of SiO₂ nanoparticles, which, however, can significantly change the elastic properties of the nanocomposite [10–12]. Similar investigations can be carried out with ZnO ($n_{\rm np} = 1.96$) and ZnS ($n_{\rm np} = 2.2$) nanoparticles, widely used to design nanocomposites.

10.3 Influence of nanoparticle composition on the optical properties of nanocomposites

The authors of [100, 101] analyzed the influence of the macroporous structure on dielectric constants and refractive indices of polymers containing micropores, i.e., so-called nanofoams. Porous polymers are regarded as finely dis-

persed mixtures of two components, i.e., a polymer having the dielectric constant ε_{pol} and nanoparticles with the dielectric constant ε_{np} . When all the particles of the mixture are isotropic and the difference between the dielectric constants of the polymer and the nanoparticles is arbitrary, the dielectric constant ε_m of the material with a small pore volume fraction ξ can be determined with the use of the relation [13]

$$\varepsilon_{\rm m} = \varepsilon_{\rm pol} + \xi \frac{3(1 - \varepsilon_{\rm pol})\varepsilon_{\rm pol}}{1 + 2\varepsilon_{\rm pol}} \,. \tag{112}$$

For example, Eqn (112) gives $\varepsilon_{\rm m} = 2.55$ at $\varepsilon_{\rm pol} = 2.95$ and $\zeta = 0.16$.

To calculate ε_m in the case of a large pore volume fraction ξ , equation (112) was modified in Ref. [104]. The equation for ε_m allowing a description of the dependence of ε_m on ξ over the entire range of ξ variations (from 0 to 1) has the form

$$\varepsilon_{\rm m} = \varepsilon_{\rm pol} + \xi \frac{3(1 - \varepsilon_{\rm pol})\varepsilon_{\rm pol}}{1 + 2\varepsilon_{\rm pol}} + \xi^2 \frac{(1 - \varepsilon_{\rm pol})^2}{1 + 2\varepsilon_{\rm pol}} \,. \tag{113}$$

In general, if the dielectric constant of a material ε_{np} with a low pore volume fraction is other than unity, in Eqn (113) the unity should be replaced with ε_{np} :

$$\varepsilon_{\rm m} = \varepsilon_{\rm pol} + \xi \frac{3(\varepsilon_{\rm np} - \varepsilon_{\rm pol})\varepsilon_{\rm pol}}{\varepsilon_{\rm np} + 2\varepsilon_{\rm pol}} + \xi^2 \frac{(\varepsilon_{\rm np} - \varepsilon_{\rm pol})^2}{\varepsilon_{\rm np} + 2\varepsilon_{\rm pol}} \,. \tag{114}$$

Equation (114) allows estimating pore or nanoparticle concentration ξ responsible for dielectric constant variations for any nanocomposite.

To calculate the nanocomposite refractive index, the substitution $\varepsilon \rightarrow n^2$ is needed. It gives

$$n_{\rm m}^2 = n_{\rm pol}^2 + \xi \frac{3(n_{\rm np}^2 - n_{\rm pol}^2)n_{\rm pol}^2}{n_{\rm np}^2 + 2n_{\rm pol}^2} + \xi^2 \frac{(n_{\rm np}^2 - n_{\rm pol}^2)^2}{n_{\rm np}^2 + 2n_{\rm pol}^2} \,. \tag{115}$$

For example, if $n_{\text{pol}} = 1.52$ and $n_{\text{np}} = 1.45$, then $n_{\text{m}} = 1.506$ at $\xi = 0.20$.

Refractive indices of multi-component nanocomposites are calculated from the relation reported in [6]:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{k_{\rm av} \sum_{i=1}^{i=n} \alpha_i R_i}{N_{\rm A} \sum_{i=1}^{i=n} \alpha_i (\sum_j \Delta V_j)_i},$$
(116)

where α_i is the molar fraction of the *i*th component, R_i is the molar refraction of the *i*th component, $(\sum_j \Delta V_j)_i$ is the van der Waals volume of the *i*th component, and k_{av} is the averaged molecular packing coefficient.

The composite refractive index can be expressed via the refractive index of its components as [6]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\sum_{i=1}^{i=n} \alpha_i (n_i^2 - 1) / (n_i^2 + 2) (\sum_j \Delta V_j)_i}{\sum_{i=1}^{i=n} \alpha_i (\sum_j \Delta V_j)_i} , \qquad (117)$$

where n_i is the refractive index of the *i*th component, and α_i is the molar fraction of this component.

Here is an example of the calculation of the dependence of the refractive index of a cured epoxy resin-based nanocomposite containing SiO₂ nanoparticles on the resin molar fraction with the use of Eqn (117). The nanoparticle surface was treated with phenyltrimethoxysilane. For such a system, the refractive indices of cured epoxy resin, the nanoparticles, and a modifier are $n_1 = 1.52$, $n_2 = 1.45$, and $n_3 = 1.4734$, respec-



Figure 34. Nanocomposite refractive index *n* versus the anhydride-cured epoxy resin molar fraction [100].

tively. The van der Waals volumes of these components are $(\sum_i \Delta V_i)_1 = 41 \text{ Å}^3$, $(\sum_i \Delta V_i)_2 = 34 \text{ Å}^3$, $(\sum_i \Delta V_i)_3 = 194 \text{ Å}^3$. The dependence of the nanoparticle refractive index on the epoxy resin molar fraction is illustrated by Fig. 34, showing that the introduction of SiO₂ nanoparticles into the epoxy resin-based composite causes a slight change in the refractive index.

Dielectric constant ε of multicomponent nanocomposites is found from Eqn (117) by substituting $n^2 \rightarrow \varepsilon$:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\sum_{i=1}^{i=n} \alpha_i (\varepsilon_i^2 - 1) / (\varepsilon_i^2 + 2) (\sum_j \Delta V_j)_i}{\sum_{i=1}^{i=n} \alpha_i (\sum_j \Delta V_j)_i} , \qquad (118)$$

where ε_i is the dielectric constant of the *i*th component.

Let us estimate the dependence of air-filled micropores on the refractive index of cured epoxy resin-based nanocomposites using Eqn (117). The refractive index of air $n_{air} = 1$. Components molar fractions are expressed via volume fractions. The volume fraction of any gas is

$$\xi = \frac{v_{\text{gas}}}{v_{\text{gas}} + v_{\text{pol}}},\tag{119}$$

where v_{gas} is the gas volume and v_{pol} is the polymer volume. Eqn (119) can be presented in the form

$$\xi = \frac{22.4m_{\text{gas}}}{22.4m_{\text{gas}} + m_{\text{pol}}V_{\text{pol}}} = \frac{1}{1 + m_{\text{pol}}V_{\text{pol}}/(22.4m_{\text{gas}})},$$
(120)

where m_{gas} is the number of gas moles, m_{pol} is the number of polymer moles, V_{pol} is the polymer molar volume, $V_{\text{pol}} = \sum_i \Delta V_i / k_{\text{av}}$, $\sum_i \Delta V_i$ is the van der Waals volume of repeating units in the polymer network, k_{av} is the mean molecular packing coefficient in the polymer glassy state $k_{\text{av}} = 0.681$.

Gas molar fraction α_1 is expressed as

$$\alpha_1 = \frac{m_{\rm gas}}{m_{\rm gas} + m_{\rm pol}} = \frac{1}{1 + m_{\rm pol}/m_{\rm gas}} \,. \tag{121}$$

Substituting the expression for ξ into formula (121) yields

$$\alpha_1 = \frac{1}{1 + 22.4(1 - \xi)/(\xi V_{\text{pol}})} \,. \tag{122}$$

The use of Eqn (117) and parameters $n_{pol} = 1.52$ and $n_{gas} = 1$ leads to the final equation for the nanocomposite refractive



Figure 35. Dependences of refractive index on the void volume fraction at different n_v : 1.1 (1), 1.2 (2), 1.3 (3), 1.4 (4), 1.5 (5) [101].

index:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{0.304}{1 + \left[\xi/(1 - \xi)\right]^2 V_{\text{pol}}/22.4} \,.$$
(123)

Eqn (123) relates the refractive index to the microvoid volume fraction ξ in a nanocomposite. The dependences of *n* on ξ of air-containing voids calculated by Eqns (115) and (123) are shown in Fig. 34. They are similar within the limits of measurement accuracy.

The voids may be filled with other gases, besides air. The dependences of n on ξ are calculated based on Eqn (115) containing different values of the refractive index n_v for a given gas instead of n_{np} . Results of the calculations are presented in Fig. 35. They suggest that the refractive index for nanofoams varies within a broad range.

Let us analyze the influence of structural defects on the dielectric constant. Disturbances of the ideal chemical structure of polymers include chain branching during synthesis or under the effect of thermal factors during sampling for dielectric measurements as exemplified by isoprene (IP) chain branching. The chemical structure of branched IP is frequently presented as



Calculations of dielectric constants ε for linear PI copolymers and branched PI were performed using formula (118). The dependence of ε on the molar fraction of the branched structure is shown in Fig. 36. The number of branches being low (up to 10 mol %), the dielectric constant ε increases but insignificantly (0.4%), and its changes fall within the range of usual discrepancies between theory and experiment. The rise occurs at a greater rate as the number of branches reaches 40 mol %, while the discrepancy amounts to 3.5%. A further growth of ε slows down as the degree of branching continues to increase. Naturally, variations in the chemical structure of the main chain and its branches result in the alteration of the above discrepancies, especially if the branches contain polar groups involved in dipole–dipole interactions and hydrogen bond formation. However, the changes are insignificant if the



Figure 36. Dielectric constant ε versus molar fraction of the polyisoprene branched structure [101].

number of branches is small: they remain within calculation accuracy bounds. They also may be due to other causes.

10.4 Influence of temperature

on the optical properties of nanocomposites

Equations (115) and (116) allow determining quite accurately the refractive indices of polymers and homogeneous composites depending on their chemical structure. To further improve the precision of estimations, the temperature dependence of refractive indices needs to be taken into consideration, which is calculated using the formulas [6]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{Rk_g}{\left[1 + \alpha_G(T - T_g)\right]N_A \sum_i \Delta V_i}, \quad T < T_g, \quad (124)$$

$$\frac{n^2 - 1}{n^2 + 2} = \frac{Rk_g}{\left[1 + \alpha_L (T - T_g)\right] N_A \sum_i \Delta V_i}, \quad T > T_g, \quad (125)$$

where $\alpha_{\rm G}$ and $\alpha_{\rm L}$ are polymer thermal expansion coefficients in the glassy and rubbery states respectively, $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit, and $k_{\rm g}$ is the molecular packing coefficient at glass transition temperature $T_{\rm g}$.

Figure 37 shows an example of temperature dependences of the refractive index for poly(3,4-dichlorostyrene), PS, a polyarylate of terephthalic acid, and phenolphthalein. The refractive index n regularly decreases with increasing temperature. For poly(3,4-dichlorostyrene) in the glassy state, the



Figure 37. Temperature dependences of the refractive index for polymers: I - poly(3,4-dichlorostyrene), 2 - PS, 3 - polyarylate of terephthalic acid and phenolphthalein [101].

decrease is estimated at 4%, for PS at 3.5%, and for polyarylate at 4%. This suggests that the influence of temperature in the glassy state is not too strong and does not exceed the difference between theory and experiment. The reduction in the refractive index for poly(3,4-dichlorostyrene), PS, and polyarylate in the rubbery state is equivalent to 5.3%, 5.0%, and 3.3%, respectively, meaning that the rubbery state is just as well characterized by small changes in the refractive index. A comparison of refractive indices over the entire temperature range shows that the change for PS amounts to 8.5%, for poly(3,4-dichlorostyrene) to 8.0%, and for polyarylate to 7.4%. In other words, the measurement of the refractive index of a polymer having a low enough glass transition temperature is fraught with error if it is carried out at room temperature. For the glassy state, the error is insignificant, because the glass transition temperature of all the above polymers exceeds room temperature. This implies that the difference between calculated and measured values of the refractive index and dielectric constant can not be attributed to the influence of temperature.

Substituting dependences (124) and (125) for homogeneous multicomponent composites into Eqn (116) yields

$$\frac{n^2 - 1}{n^2 + 2} = \frac{k_g \sum_{i=1}^{i=n} \alpha_i R_i}{\left[1 + \alpha_G (T - T_g)\right] N_A \sum_{i=1}^{i=n} \alpha_i (\sum_j \Delta V_j)_i},$$

 $T < T_g,$ (126)

$$\frac{n^{2}-1}{n^{2}+2} = \frac{k_{g} \sum_{i=1}^{i=n} \alpha_{i} R_{i}}{\left[1 + \alpha_{L} (T - T_{g})\right] N_{A} \sum_{i=1}^{i=n} \alpha_{i} (\sum_{j} \Delta V_{j})_{i}},$$

$$T > T_{g}.$$
(127)

Strictly speaking, the temperature dependences (126) and (127) thus obtained are valid in the microwave and IR ranges when dipole polarizability α_{dip} can be assumed zero (as for nonpolar dielectrics with $p_0 = 0$) and the Langevin–Debye formula converts into the Clausius–Mossotti formula; similarly, in the visible and UV ranges (where even ions fall behind the field and $\alpha_{ion} = 0$), the Langevin–Debye formula transforms into the Lorentz–Lorentz formula.

In a lower frequency range, formulas (126) and (127) need to be supplemented by correction for the temperature dependence in accordance with the Langevin–Debye relation when molar refraction R_i is expressed as $R_i \sim a_{0i} + p_{0i}^2/(3k_BT)$, where a_{0i} is the polarizability of polymer structural elements, p_{0i} is the dipole moment of polar groups of polymer repeating units, and k_B is the Boltzmann constant.

To conclude, the approach proposed in [100, 101] permits us to elucidate the causes of deviation from the error of the method for the calculation of the polymer dielectric constant and to take into account the influence of such factors as plasticizing by remnants of synthesis products and the solvent, nonlinear polarization, and multicomponent micropore composition. Analysis of calculated data shows that for all polymers characterized by a high negative error of ε estimation (over 5%) the discrepancy of experimental data from the theory is due to the plasticizing effect of the solvent and synthesis products. In the case of large positive errors of ε , there are two possible causes of the deviation, namely, plastification (then Pl(W) < 1) or deviation from linear model. Only for three of 13 such polymers, with a margin of error for the estimation of ε larger than 5%, is the deviation related to nonlinearity, the selection criterion being the Pl(W) > 1 condition. In the remaining 10 polymers, the deviation is due to the plasticizing action of residual synthesis products and solvent.

The three distinguished polymers are of independent significance for nonlinear optics [105]. In the framework of the approaches developed earlier, the targeted search for such materials [106–108] and their subsequent application in various optoelectronic and acousto-electronic devices can be realized. Since the class of polymers with nonlinear optical characteristics is already known, expression (110) should be used for calculations, while the influence of residual synthesis products and solvents on ε is estimated from the mean value of the plastification function $\langle Pl(W) \rangle = 0.913$ found based on the data from Table 14.

To sum up, the approaches proposed in [100, 101] make it possible to elucidate the influence of nanosize voids and nanoparticles introduced in a polymer material on the refractive index and dielectric constant of nanofoams and nanocomposites. Producing materials with low dielectric constants is of importance from a practical perspective. Their optical and dielectric properties depend on the chemical structure of polymer matrices and the structure and mode of treatment of nanoparticle surfaces. These properties of composites having a microporous structure (nanofoams) depend on the chemical composition of the gases filling the micropores.

11. Conclusion

The past few years have witnessed a sustained interest in the creation of new and modification of the available calculation schemes allowing the quantitative estimation of such physical properties of polymer systems as glass transition and flow temperature, thermal conductivity, water permeability, refractive index, dielectric constant, yield strength, viscosity, and boiling point of polymer-solvent mixtures. Much attention was paid to the characteristics of nanocomposites and polymer mixtures. The proposed calculation schemes take account of the chemical structure of matrix polymers and polar groups grafted to the surface of nanoparticles. Also considered are nanoparticle concentration, shape, size, and orientation distribution.

Good agreement between theory and experiment is documented for many polymers. The causes of previously reported discrepancies are analyzed, and ways to improve the quality of calculations are outlined. The computerization of calculations promoted not only their automatic performance but also computer-assisted synthesis of polymers with predetermined properties. Taken together, these achievements are likely to make easier the work of chemists and technologists developing new polymers, mixtures and nanocomposites thereof.

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