Newest models and calculation schemes for quantitative analysis of physical properties of polymers

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Abstract. New models and calculation schemes have been developed for the quantitative analysis of a number of physical properties of polymers — 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 losses 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 effect of temperature, the composition of copolymers and homogeneous mixtures of polymers, the concentration of nanoparticles, their shape, size distribution, orientation angles, the structure of polar groups grafted to the surface of nanoparticles, the energy of intermolecular interactions are taken into account. All computational schemes are computerized and allow calculations to be carried out automatically after the introduction of the structure of a repeating unit of polymer unit into the computer, as well as the shape and size of nanofillers.

1 Introduction

In recent years, we have developed new and modified previous calculation schemes for the quantitative description of a number of physical properties of polymers. Among the properties are the glass transition temperature, the flow temperature of polymer nanocomposites, thermal conductivity, boiling point of polymer solutions, water absorption and water permeability of polymers and nanocomposites, the strength, viscosity, storage and losses moduli, refractive index and dielectric constant. All design schemes are based on the structure of linear and cross-linked polymers; their degree of crystallinity, free volume, temperature effect, composition of copolymers and homogeneous mixtures of polymers are taken into account. The concentration of nanoparticles, their shape, size distribution, orientation angles, the structure of polar groups grafted to the surface of the nanoparticles, the energy of intermolecular interactions are taken into account. Spherical nanoparticles, rectangular plates and nanofibers are considered. The calculation scheme for the refractive

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index and dielectric constant takes into account the influence of the plasticizing effect of the residues of the synthesis products and the solvent, nonlinearity on the Clausis-Mossoty function, the composition of nanoparticles, and temperature. All computational schemes are computerized and allow calculations to be carried out automatically after the introduction of the structure of a repeating unit of polymer into the computer, as well as the shape and size of nanofillers.

2 Methods

Used methods for constructing models and design schemes, published in [1-5]. To develop computational schemes, it is necessary to calculate the van der Waals volume of repeating units of polymers, as well as the energy of intermolecular interactions. In the calculations of the refractive index and dielectric constant, molar refraction and polarizability were calculated. In the work actively used a computer program "Cascade", developed in INEOS RAS.

3 Results

3.1. Glass transition temperature of polymers

In order to modify the calculation scheme [1-3] to estimate the glass transition temperature, we introduced atomic constants and energies of dipole – dipole interactions and hydrogen bonds for atoms and atomic groups located in the main and side chains. The equation used to describe the glass transition temperature of polymers T_g:

$$T_g = \frac{\left(\sum_i \Delta V_i \right)}{\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_{back.bone} + \left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_{sidegroup}} \,, \qquad (1)$$

where a_i are the atomic constants associated with the energy of weak dispersion interaction; b_j are the constants associated with the energy of the dipole-dipole interactions of b_d and hydrogen bonds b_h; $\left(\sum_i \Delta V_i \right)$ is the van der Waals volume of the repeating unit.

The correlation diagram containing over 50 polymers is shown in Figure 1; the correlation coefficient is 0.999.
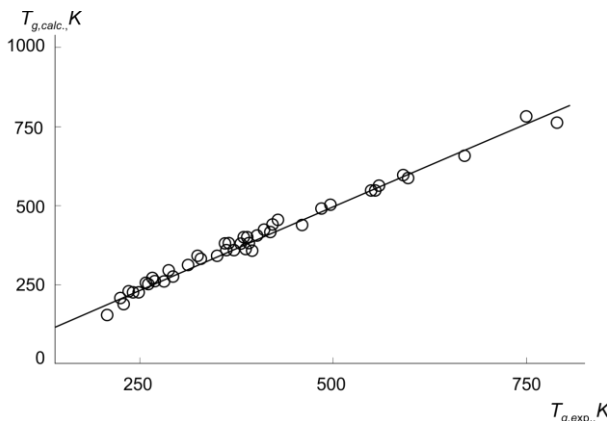
Fig. 1. Correlation diagram. $T_{g,exp.}$ and $T_{g,calc.}$ are the experimental and calculated values of glass transition temperature, respectively.

3.2 Flow temperature of polymer nanocomposites

Flow temperature T_f of polymer nanocomposites is calculated by the ratio, which includes the concentration and radius of the nanoparticles, the number of polar groups grafted on their surface, the density of the nanoparticles, the molecular weight of the polymer.

3.3 Thermal conductivity of polymers

This characteristic in this paper is calculated by the formula

$$\lambda = \frac{\sum_i a_i + \sum_j b_j}{N_A \sum_i \Delta V_i} \cdot \frac{m^{1/3} \cdot c_p \cdot \rho^{4/3}}{M_0^{1/3}},\qquad(2)$$

where a_i are the atomic constants characteristic of each atom; b_j are the constants for polar groups leading to dipole-dipole interaction or to hydrogen bonds; N_A is the Avogadro number, ΔV_i is the van der Waals volume of the i-th atom, m is the number of atoms in the repeating unit, c_p is the specific heat capacity, M_0 is the molecular mass of the repeating unit, ρ is the density.

The arrangement of atoms in the back bone and side chains, the degree of crystallinity are taken into account. The correlation diagram is shown in Figure 2.
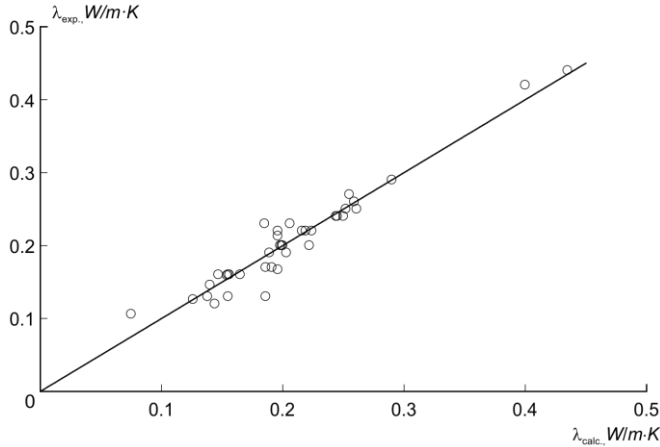
Fig. 2. Correlation diagram for the set of amorphous and semi-crystalline polymers

3.4 Calculation scheme for estimating the boiling point of a mixture of polymer and solvent.

This design scheme is important for the ebullioscopic method for determining the molecular masses of polymers. The enthalpy of evaporation of the solvent at the boiling point is expressed in terms of the Hildebrand solubility parameter, which, in turn, depends on the temperature. As a result, the ratio was obtained linking the boiling point of the polymer solution with the mole and weight fractions of the dissolved polymer:

$$T_1 = \frac{T_0}{1 + \dfrac{RT_0 \ln\left(1 - \dfrac{1}{1 + \dfrac{M_p}{M_s}\left(\dfrac{1}{\alpha_{w,p}} - 1\right)}\right)}{V\delta^2 + R(298 - T_0)}},\qquad(3)$$

where 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 molar liquid volume, M_p and M_s are the molecular masses of the polymer and solvent, respectively, $\alpha_{w,p}$ is the weight fraction of polymer.

The proposed calculation scheme for quantitative estimation of the boiling point of polymer solutions in an organic solvent allows calculations based on the chemical structure of the polymer and solvent, does not require preliminary experiments, and therefore has predictive power.

3.5 Water absorption and water permeability of polymers and copolymers

The correlation is proposed for calculating the activation energy of the permeability process, based on the set of atomic constants describing the contribution of each atom and polar groups to the energy of intermolecular interaction with water, which are summarized to estimate the total energy. The chemical structure of the polymer, the degree of crystallinity, temperature and free (empty) volume are taken into account.

$$\ln P = \ln P_0 - \frac{\sum_i \Delta E_i^{**}}{N_A RT \sum_i \Delta V_i}, \tag{4}$$

where P is the permeability, P_0 is the constant, $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit of polymer, $\sum_i \Delta E_i^{**}$ is the activation energy of the permeability process multiplied by the van der Waals volume of the repeating unit.

The method is computerized. The computer program allows to solve both the direct problem associated with the evaluation of the properties of polymers based on the chemical structure of the repeating unit, and the inverse problem, which consists in searching for such polymer structures that have a given permeability interval.

3.6 Design scheme for assessing the permeability of nanocomposites

The calculation scheme has been developed for predicting water permeability through polymer nanocomposites. The chemical structure of the polymer and its concentration, the chemical structure of the nanoparticle surface, the concentration of nanoparticles in the composite and the concentration of polar functional groups on the surface of the nanoparticles, the size and shape of nanoparticles are taken into account. The concentration of nanoparticles and the number of polar groups on their surface have the greatest effect on permeability. The influence of the size distribution of anisometric nanoparticles and their orientation on permeability is analyzed. The calculation method is computerized and included as the special option in the CASCADE computer program (INEOS RAS), which allows calculations and predictions of the permeability of nanocomposites after the chemical structure and the specified parameters of nanoparticles are introduced into the computer.

The permeability of the composite P, consisting of a polymer and nanoparticles, is described by the ratio

$$P = P_0^*\left(1 - \alpha_{d,f}\right), \tag{5}$$

where P_0^* is the permeability of the original polymer, $\alpha_{d,f}$ is the volume fraction of nanoparticles.

For nanocomposites, in which the surface of the nanoparticles is modified by chemical groups of a particular chemical structure, the following relationship applies:

$$\ln P_0^* = \frac{\dfrac{1}{1+\beta}\left[\left(\sum_i \Delta E_i^{**}\right)_p - \left(\sum_i \Delta E_i^{**}\right)_{cg}\right] + \left(\sum_i \Delta E_i^{**}\right)_{cg}}{N_A\left\{\dfrac{1}{1+\beta}\left[\left(\sum_i \Delta V_i\right)_p - \left(\sum_i \Delta V_i\right)_{cg}\right] + \left(\sum_i \Delta V_i\right)_{cg}\right\}}, \qquad (6)$$

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

The value of β is described by the formula

$$\beta = \frac{n_{cg} c_{np} M_0}{\rho_{np} v_{np} c_p 0.6022 \cdot 10^{24}}, \qquad (7)$$

where n_{cg} is the number of polar groups on the surface of one nanoparticle, c_{np} is the weight of nanoparticles in a nanocomposite, c_p is the weight of the polymer, ρ_{np} is the density of the nanoparticle, v_{np} is the volume of one nanoparticle.

3.7 Analysis of the influence of the chemical composition and concentration of the components of the polymer-solvent mixture on the strength and viscosity

The calculation scheme is proposed for estimating the strength σ_y and viscosity η of a system containing a polymer and a solvent (plasticizer). This scheme takes into account the chemical structure of the polymer and the solvent, the intermolecular interaction between the polymer and the solvent, the van der Waals volume and molecular weight of the repeating unit of the polymer and the solvent molecule, as well as the concentration of the solvent.

Since the value of strength is measured in the glassy state of the system (in our case, in the polymer + solvent system), the following relationship applies:

$$\sigma_y = \frac{(1 - \alpha_{m,s+p})\left(\sum_i \Delta V_i\right)_p + \alpha_{m,s+p}\left(\sum_i \Delta V_i\right)_{s+p}}{(1 - \alpha_{m,s+p})\dfrac{\left(\sum_i \Delta V_i\right)_p}{\sigma_{y,p}} + \alpha_{m,s+p}\dfrac{\left(\sum_i \Delta V_i\right)_{s+p}}{\sigma_{y,s+p}}}, \qquad (8)$$

where $\alpha_{m,s+p}$ is the mole fraction of the polymer + solvent mixture, $\left(\sum_i \Delta V_i\right)_{s+p}$ is van der Waals volume of the mixture mentioned above, which is critical (if the concentration of solvent exceeds the critical one, the mixture goes into a rubbery state); $\sigma_{y,s+p}$ is the strength for the "polymer + solvent" system, which has a critical solvent concentration.

The final equation for calculating the viscosity depending on the volume fraction of the polymer is

$$\ln\left(\frac{\eta}{B}\right) = 4\ln c_p \alpha_{v,p} + \left\{\alpha_{v,p}\left[0.025 + (\alpha_L - \alpha_G)(T - T_{g,p})\right] + (1 - \alpha_{v,p})\left[0.025 + \alpha_s(T - T_{g,s})\right]\right\}^{-1}, \quad (9)$$

where B is a combined constant, including molecular weight; c_p is the polymer concentration, $\alpha_{v,p}$ is the volume fraction of the polymer, T is the temperature, $T_{g,p}$ is the glass transition temperature of the polymer, α_s is the thermal expansion coefficient of the solvent (plasticizer), $T_{g,s}$ is the glass transition temperature of the solvent, α_L and α_G are the thermal expansion coefficients polymer in the rubbery and glassy state of the polymer, respectively.

This calculation scheme allows us to predict the dependence of the strength and viscosity of the "polymer + plasticizer" system.

3.8 The calculation scheme for estimating the dynamic viscosity, storage modulus and loss modulus depending on temperature

In [4], it was shown that the storage modulus of polymer at high frequencies is described by the following equation

$$G = \frac{\sum\limits_i \Delta V_i}{\sum\limits_i g_i \Delta V_i + \sum\limits_j f_j}, \quad (10)$$

where $g_i = \dfrac{S_i}{\kappa_i l_i}$; the g_i values characterize the average contribution of each atom to the

quantity $\dfrac{S_i}{\kappa_i l_i}$; f_i is the set of constants that characterize the effect of a strong intermolecular

interaction (dipole-dipole interaction, hydrogen bonds); S_i is the van der Waals surface of the i-th atom, through which the intermolecular interaction is transferred; κ_i is the coefficient of elasticity of the bond of the i-th atom; l_i is the characteristic bond size; ΔV_i is the van der Waals volume of the i-th atom included in the repeating unit of the polymer.

The values of g_i and f_j found in [5] are shown in table 1:

Table 1. The values of the constants g_i and f_j.

Atom or type of intermolecular interaction	Values g_i or f_j	
Carbon	g_C, cm^2/kg	-1.277
Hydrogen	g_H, cm^2/kg	4.376
Oxygen	g_O, cm^2/kg	116.95
Double bond	$f_{\neq}$, Å$^3\cdot$cm^2/kg	30.925
Dipole-dipole interaction*	f_d, Å$^3\cdot$cm^2/kg	84.472

* f_d parameter for each branch in the back bone or side chain.

4 Conclusions

Thus, the proposed and modified computational schemes make it possible to accurately evaluate various physical characteristics of polymers and polymeric materials based on their chemical structure, composition of mixtures and nanocomposites, and the nature of the orientation of nanoparticles. The influence of the structure of polar groups grafted onto the surface of nanoparticles and their size distribution are also taken into account. The design

schemes described in this article can provide substantial assistance in the development of new building polymeric materials.

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