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Influence of the structural arrangement of particulate-filled polymer composites on their thermal expansion and elasticity

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It is showing that the mutual arrangement of composition elements, as there combination are affected to the thermal expansion and elasticity of dispersed-filled polymer composite materials. This made it possible to substantiate the difference in the results of theoretical models and experiments of that characteristic. It is showing that using the empirical coefficients into the mixture model can take into account the mutual arrangement of the elements of the composition.

Keywords: polymer composites, particulate fillers, coefficient of linear thermal expansion, voids, rule-of-mixtures model.

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Various models (e.g., [1–3]) used to calculate the coefficient of linear thermal expansion (CLTE) of particulate-filled polymer composite materials (PPCMs) reveal a monotonic variation (in most cases, a decrease) of CLTE with increasing concentration of filler particles. However, the experimental dependences of CLTE on particle concentration have a minimum. This minimum is present regardless of the type of filler particles or the type of polymer matrix [4,5]. No unified approach to explaining this discrepancy between experimental and theoretical data has been proposed in literature.

In our view, when the concentration dependence of CLTE is analyzed, one needs to take into account not only the composition elements themselves (polymer, filler particles, agglomerates, voids) and their characteristics, but also the relative positions of these elements. For example, voids surrounding dispersed particles and their agglomerates exert a significant influence on the composition characteristics by, e.g., reducing its elasticity and strength [1]. It is fair to assume that not only the presence of certain elements in a composition, but also the structural features (mutual arrangement of elements) influence the nature of the concentration dependence of CLTE and elasticity of a PPCM.

The aim of the present study is to clarify the influence of the relative positions of elements of a polymer composition on the concentration dependences of CLTE and elastic modulus (Young's modulus).

PPCM samples consisting of polymethyl methacrylate (PMMA) (SP-1, TU 2216-055-55856863-2009, AO EKSTRUDER) and aluminum oxide Al_2O_3 powder [6] were synthesized in two stages. At the first stage, an ultrasonic bath (Daihan WUC-A01H, 50 W) was used to mix filler particles and beaded PMMA in an aqueous suspension with subsequent evaporation of water. Different mass fractions of filler particles in the mixture were set in these experiments (Table 1). The mass fraction was determined by weighing the polymer mixture with particles on a scale with an accuracy of 10^{-4} g. At the second stage, PPCM samples in the form of plates $120 \times 20 \times 3$ mm in size were fabricated (with a manufacturing error no greater than 1 %). These PPCM plates were obtained by hot pressing in a furnace at a temperature of $210 \pm 5\,^\circ$C with a holding time of 30 min.

The relative positions of composition elements were determined by scanning electron microscopy (SEM) using an AURIGA CrossBeam complex with an Inca X-Max 80 mm^2 energy-dispersive spectrometer. The sizes of agglomerates and their volume fraction were investigated using an Axio Imager.Z2m optical microscope (Carl Zeiss, Germany) with subsequent statistical analysis of the obtained images in the ImageJ software package [7]. The samples were scanned depthward, and the number of agglomerates in each layer was analyzed. The number of layers was 25, and three test areas were examined in each sample. The total scanning volume was approximately 1/3 of the volume of each sample. Having determined the equivalent diameters and the number of agglomerates, we calculated their volume fraction (assuming that these agglomerates were distributed uniformly in the samples). The coefficient of linear thermal expansion and the Young's modulus were measured experimentally and compared with the values calculated using the rule-of-mixtures model. The Young's modulus was determined in accordance with GOST 4648–2014 using a Shimadzu AG-X 50 kN testing machine. The sample loading rate in tensile tests was 0.1 mm/min with an error no greater than 10 %.

Table 1. Results of experimental and theoretical (rule-of-mixtures model) studies of sample characteristics (SD — standard deviation)

Sample designation	Mass fraction of filler in the sample	CLTE α_Σ, 10^{-5} 1/°C	SD of CLTE, 10^{-5}	CLTE α (rule-of-mixtures model 10^{-5} 1/°C	Volume fraction of agglomerates γ_2	Elastic modulus E, MPa	Density of samples in the experiment ρ_{exp} g/cm^3	Density of samples according to the mixed model ρ_{calc}, g/cm^3
Sample 0	0	6.282	0.393	6.282	–	1357	1.23	1.23
Sample 5	0.025	6.06	0.671	6.143	0.024	1247	1.22	1.25
Sample 4	0.05	5.91	0.356	6.004	0.056	1199	1.2	1.27
Sample 3	0.107	4.386	0.267	5.69	0.190	930	1.25	1.33
Sample 2	0.197	5.416	0.677	5.19	0.192	1085	1.3	1.45
Sample 1	0.39	4.91	0.318	4.06	0.179	1064	1.42	1.61

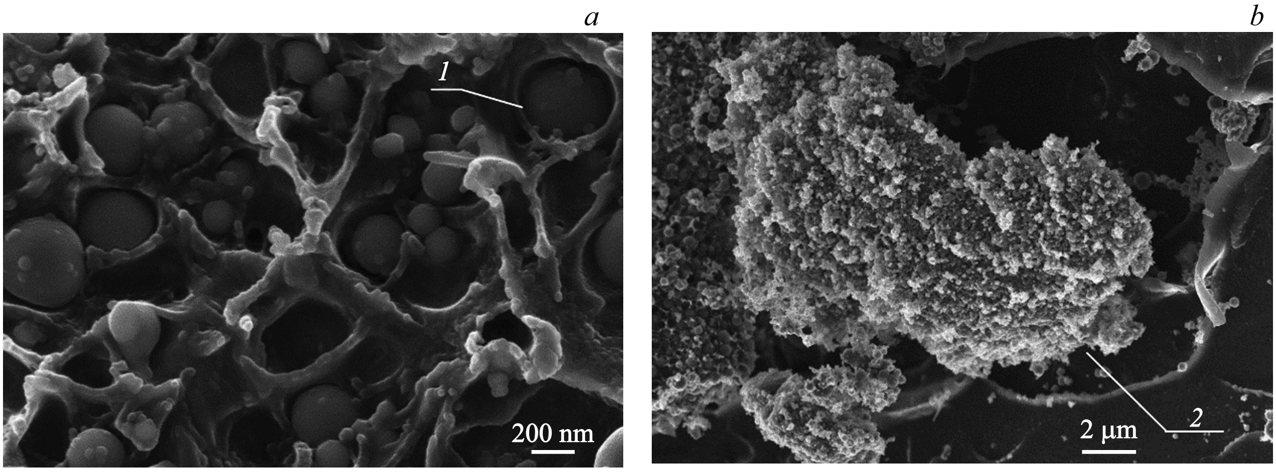

Figure 1. SEM images of the microstructure of the composite (sample 1). *1* — Particle in a void; *2* — agglomerate in a void.

Example images with different resolutions of an agglomerate of aluminum oxide particles in sample 1 are shown in Fig. 1.

These images reveal the presence of voids both along the perimeter of the agglomerate (Fig. 1, *b*) and along the perimeters of most of the aluminum oxide particles forming this agglomerate (Fig. 1, *a*). The results of measuring the density of samples and their comparison with the calculated values (Table 1) confirm that voids visible in the SEM image are not of a random nature.

The density (ρ_{calc}) of samples was calculated using a rule-of-mixtures model taking into account the volume fractions of particles and the polymer matrix (the following values of component densities were used: $\rho_{\mathrm{PMMA}} = 1.19\,\mathrm{g/cm^3}$, $\rho_{\mathrm{Al_2O_3}} = 3.99\,\mathrm{g/cm^3}$). The comparison of experimental and calculated densities revealed a monotonic decrease in density (Table 1), which is apparently attributable to the formation of voids.

The mass fraction of filler particles was determined by weighing the polymer mixture with particles on a scale with an accuracy of 10^{-4} g. The volume fraction of filler particles was determined in accordance with the following formula:

$$\gamma_3 = \frac{\rho_{exp}}{\rho_{\mathrm{Al_2O_3}}} \frac{m_{part}}{m_{exp}}, \qquad (1)$$

where ρ_{exp} is the density of experimental samples (determined experimentally), m_{exp} is the sample mass (determined experimentally), and m_{part} is the mass of filler particles in the sample (determined experimentally).

The results provided by the rule-of-mixtures model are satisfactory neither qualitatively nor quantitively (Fig. 2): $E_0 = 1357\,\mathrm{MPa}$, $\alpha_0 = 6.282 \cdot 10^{-5}\,1/°\mathrm{C}$ (Table 1).

In our view, the reason for the discrepancy between theory and experiment is that the rule-of-mixtures model does not take into account the structural features of the composite material: the mutual arrangement of dispersed particles and their agglomerates in voids. In accordance with this hypothesis, the positioning of particles in a void suppresses their influence on the composite deformation due to „screening“ of the transfer of deformation from the polymer matrix to filler particles. Electron microscope images reveal that a certain fraction of dispersed particles are embedded in the polymer matrix and are in direct

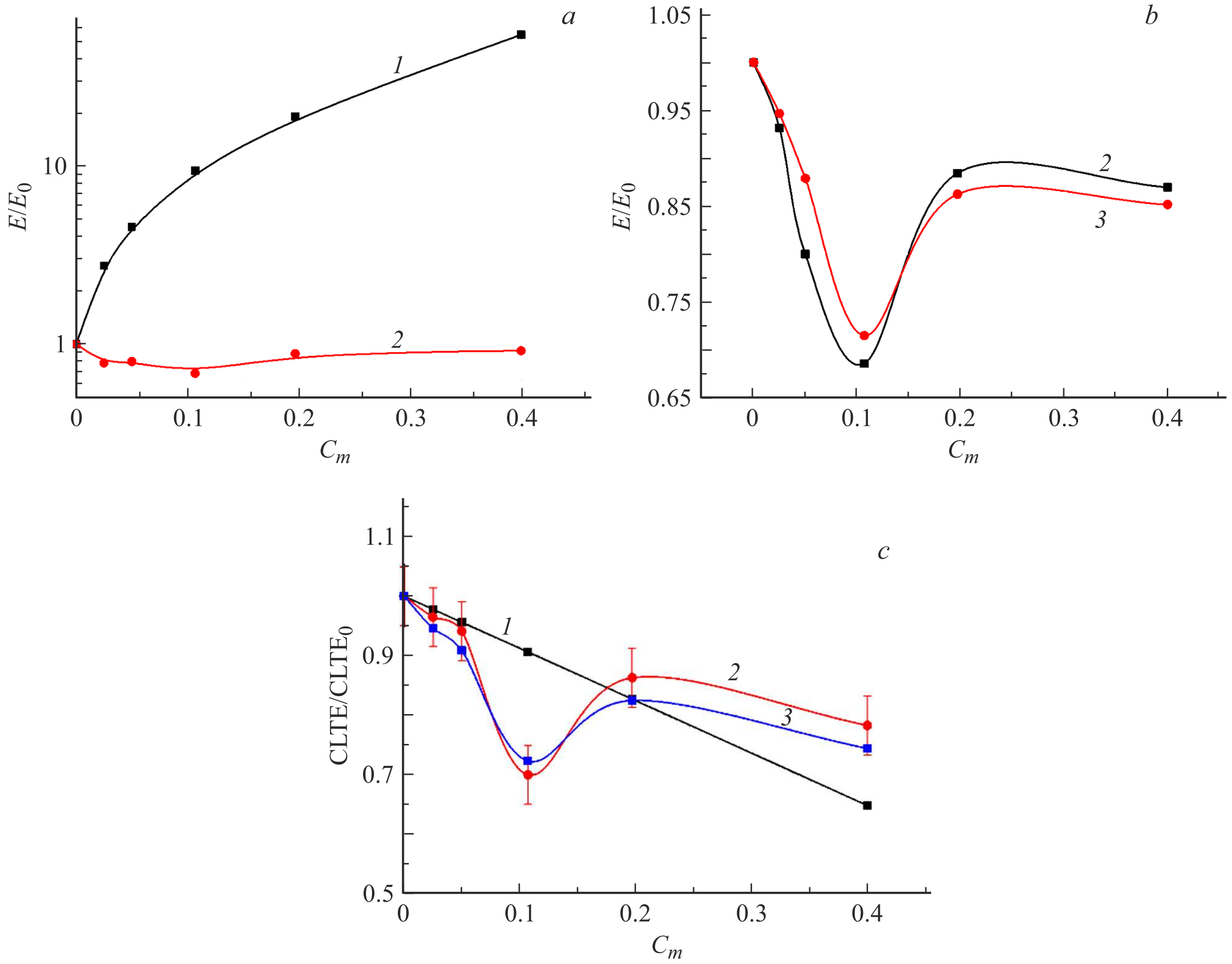

Figure 2. Experimental and theoretical (rule-of-mixtures model) dependences on the filler mass fraction. *a*, *b* — Young's modulus; *c* — CLTE. *1* — Rule-of-mixtures model, *2* — experiment, and *3* — rule-of-mixtures model with empirical coefficients.

contact with it. This mutual arrangement of elements of the composition contributes to an increase in Young's modulus and a reduction in CLTE of the composite. It was emphasized in literature [8,9] that as-prepared polymer composites inevitably contain a certain amount of pores, which have a negative effect on their properties. It should also be noted that agglomerates exert a significant influence on the mechanical and strength properties of PPCMs [10,11]. This is attributable to a reduction in effective cross-section of samples and to the emergence of local stress-strain states in the boundary region of such defects [12,13].

To take into account the relative positions of elements of the composition, we introduce coefficients k_i into the rule-of-mixtures model that is used to analyze the concentration dependences of CLTE and Young's modulus:

$$\alpha_\Sigma = \gamma_0\alpha_0 + k_1\gamma_1\alpha_1 + k_2\gamma_2\alpha_2 + k_3\gamma_3\alpha_3,$$

$$E_\Sigma = \gamma_0 E_0 + k_1\gamma_1 E_1 + k_2\gamma_2 E_2 + k_3\gamma_3 E_3, \qquad (2)$$

where α_i is the CLTE of the ith composition element, E_i is the Young's modulus of the ith composition element, and γ_i is the volume fraction of the ith composition element; $i = 1$, $i = 2$, and $i = 3$ correspond to voids, agglomerates, and dispersed particles, respectively. The results of measurements of the sample density allowed us to estimate the volume fraction of voids (γ_1) (Fig. 3) based

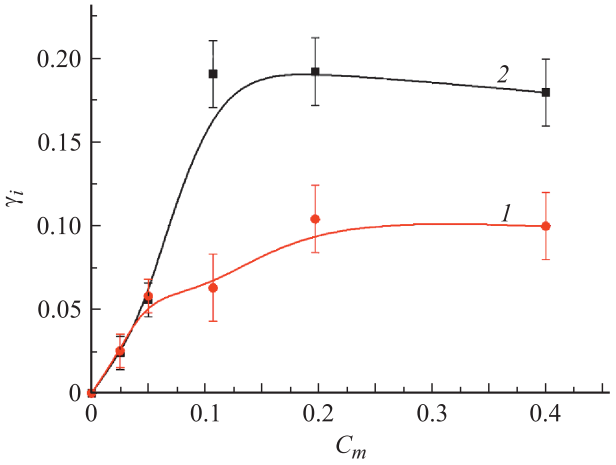

Figure 3. Dependences of the volume fraction of voids (*1*) and agglomerates of dispersed particles (*2*) on the filler mass fraction.

Table 2. Data and calculation results for refined rule-of-mixtures model (1)

Sample designation	k_1	$k_2 \cdot 10^{-4}$	$k_3 \cdot 10^{-4}$	CLTE (rule-of-mixtures model (1)), $10^{-5}\,1/^\circ$C	SD of CLTE, $10^{-5}\,1/^\circ$C	Elastic modulus E (rule-of-mixtures model (1)), GPa	SD of E, MPa
Sample 0	0	0	0	6.28	0	1.357	0
Sample 5	0.005	5	5	4.67	0.24	1.104	130
Sample 4	0.01	5	5	5.17	0.24	1.115	30
Sample 3	0.01	10	10	4.53	0.15	0.969	40
Sample 2	0.1	20	60	5.54	0.37	1.192	10
Sample 1	0.1	20	100	5.94	0.12	1.284	40

on the measured volume fraction of agglomerates and the calculated volume fraction of dispersed aluminum oxide particles:

$$\gamma_1 \approx 1 - \frac{m_{calc}}{m_{exp}} \frac{\rho_{exp}}{\rho_{calc}}, \tag{3}$$

where m_{calc} and m_{exp} are the sample mass calculated based on density ρ_{calc} and the sample mass determined experimentally, respectively, and ρ_{exp} is the density of experimental samples.

It is evident that the volume fractions of agglomerates and voids are correlated (Fig. 3). It should be noted that poor wetting of filler particles by the matrix polymer is one of the reasons contributing to agglomeration and the formation of voids around the particles [14,15].

The empirical coefficients (Table 2) introduce the relative positioning of elements of the composition into analysis and reflect the proportion of elements of the composition embedded in the polymer matrix: k_2 is a coefficient correcting for the fraction of agglomerates that are embedded in the polymer matrix and are in direct contact with it, while k_3 is a coefficient correcting for the fraction of dispersed particles that are embedded in the polymer matrix and are in direct contact with it. The following values were used in calculations: $\alpha_0 = 6.282 \cdot 10^{-5}\,1/^\circ$C, $\alpha_1 = 122.6 \cdot 10^{-5}\,1/^\circ$C, $\alpha_3 = 7.26 \cdot 10^{-6}\,1/^\circ$C, $\alpha_2 \sim \alpha_3$, $E_1 = 0$ GPa, $E_3 = 304$ GPa, and $E_2 \sim E_3$ [16].

The monotonic growth of empirical coefficients k_i with increasing filler concentration in the PPCM illustrates an increase in proportion of the corresponding elements of the composition that are embedded in the polymer matrix and interact with it. It is evident that the determination of coefficients k_i in this case should be considered as a solution to the inverse problem, which requires additional research to verify the uniqueness of it.

The obtained results confirm the proposed hypothesis, which states that the thermal expansion and elasticity of PPCMs are influenced not only by composition elements, but also by the material structure (relative positions of these elements). The positioning of particles and particle agglomerates in voids suppresses their influence on the composite deformation due to „screening" of the transfer of deformation from the polymer matrix to filler particles (and vice versa) via the deformable low-modulus void volume. The presence of a minimum in the concentration dependences of CLTE and Young's modulus of the PPCM may be regarded as a result of competition of two processes: reduction (due to an increase in void fraction and a decrease in polymer fraction in the composition) and growth (due to an increasing fraction of filler particles getting embedded in the polymer matrix) of the values of these quantities. The introduction of empirical coefficients allows one to take into account the relative positions of composition elements in the rule-of-mixtures model. The determination of these coefficients requires additional studies into the PPCM structure, which are needed to reduce the ambiguity of the solution of the corresponding inverse problem.

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Conflict of interest

The authors declare that they have no conflict of interest.

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