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Calculating the composition of dispersion-filled polymer composite materials of various structures

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Objectives. *The aim is to calculate the composition of dispersion-filled polymer composite materials with different fillers and structures and to highlight differences in the expression of said composition in mass and volume units.*
Methods. *The paper presents the calculation of compositions in mass and volume units for various types of structures comprising dispersion-filled polymer composite materials according to their classification: diluted, low-filled, medium-filled, and highly-filled systems.*
Results. *For calculations, we used fillers with densities ranging from 0.00129 g/cm^3 (air) to 22.0 g/cm^3 (osmium) and polymer matrices with densities between 0.8 g/cm^3 and 1.5 g/cm^3, which represent almost all known fillers and polymer matrices used to create dispersion-filled polymer composite materials. The general dependences of the filler content on the ratio of the filler density to the density of the polymer matrix for dispersion-filled polymer composite materials with different types of dispersed structures are presented. It is shown that to describe structures comprising different types of dispersion-filled polymer composite materials (diluted, low-filled, medium-filled, and highly-filled) it is necessary to use only the volume ratios of components in the calculations. Compositions presented in mass units do not describe the construction of dispersion-filled polymer composite material structures because using the same composition in volume units, different ratios of components can be obtained for different fillers.*
Conclusions. *The dependences of the properties of dispersion-filled polymer composite materials should be represented in the coordinates of the property–content of the dispersed phase only in volume units (vol % or vol. fract.) because the structure determines the properties. Compositions presented in mass units are necessary for receiving batches upon receipt of dispersion-filled polymer composite materials. Formulas are given for calculating and converting dispersion-filled polymer composite material compositions from bulk to mass units, and vice versa.*

Keywords: *polymers, fillers, dispersion-filled polymer composite materials, structure, properties.*

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Расчет составов дисперсных наполненных полимерных композиционных материалов с разной структурой

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Цели. *Цель работы – предоставить расчеты по составам дисперсно-наполненных полимерных композиционных материалов (ДНПКМ) с разными наполнителями и структурами, а также показать существенные различия при выражении состава в массовых и объемных единицах.*

Методы. *В работе приведены расчеты составов в массовых и объемных единицах для различных видов структур дисперсно-наполненных полимерных композиционных материалов согласно их классификации: разбавленные, низконаполненные, средненаполненные и высоконаполненные системы.*

Результаты. *Для расчетов использованы наполнители с плотностью от 0.00129 (воздух) до 22.0 г/см^3 (осмий) и полимерные матрицы с плотностью от 0.8 до 1.5 г/см^3, которые охватывают практически все известные наполнители и полимерные матрицы, используемые для создания ДНПКМ. Представлены обобщенные зависимости содержания наполнителей от отношения плотности наполнителя к плотности полимерной матрицы для ДНПКМ с разными видами дисперсной структуры. Показано, что для описания разных видов структур ДНПКМ – разбавленные, низконаполненные, средненаполненные и высоконаполненные – необходимо в расчетах использовать только объемные соотношения компонентов. Составы, представленные в массовых единицах, не описывают построение структур ДНПКМ, так как при одном составе в объемных единицах можно получить для разных наполнителей разное соотношение компонентов.*

Выводы. *Зависимости свойств ДНПКМ следует представлять в координатах свойство–содержание дисперсной фазы только в объемных единицах (об. % или об. д.), так как структура определяет свойства. Составы, представленные в массовых единицах, необходимы для получения навесок при получении ДНПКМ. Приведены формулы для расчета и перевода составов ДНПКМ из объемных в массовые единицы и наоборот.*

Ключевые слова: *полимеры, наполнители, дисперсно-наполненные полимерные композиционные материалы, структура, свойства.*

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Determining the content of initial components in dispersion-filled polymer composite materials (DFPCM) with different structures and the design and calculation of such compositions is generally performed in mass units (mass fract. or mass %) [1–5]. Mass units indicate the presence of initial components in DFPCM (alongside weighed portions) but do not reflect the construction of various types of dispersed structures. These structures are divided into diluted (DS), low-filled (LFS), medium-filled (MFS), and highly-filled (HFS) systems [6]. Analysis of scientific and technical literature showed that when discussing the structure and properties of DFPCM, data and the dependence of properties based on the content of the dispersed phase were provided primarily in units of mass.

Research on polymer materials highlights that material structure determines their properties. However, the structure of DFPCM and their parameters can be described only in volume units (vol. fract. or vol %) because when using mass units, the density ratio of the initial components in the dispersed system must be taken into account. Therefore, in the case of DFPCM, at a constant volume fraction (φ_f, vol. fract.), e.g., 0.16 vol. fract. of the dispersed phase of the filler with different particle densities (from 0.00129 to 22.0 g/cm^3), the mass fraction will vary from 0.0007 to 0.96 at the constant density of the polymer matrix [7].

Calculation of fillers in this work was performed using density ranging from 0.00129 (air) to 22.0 g/cm^3 (osmium); this included the range for all known fillers for polymer

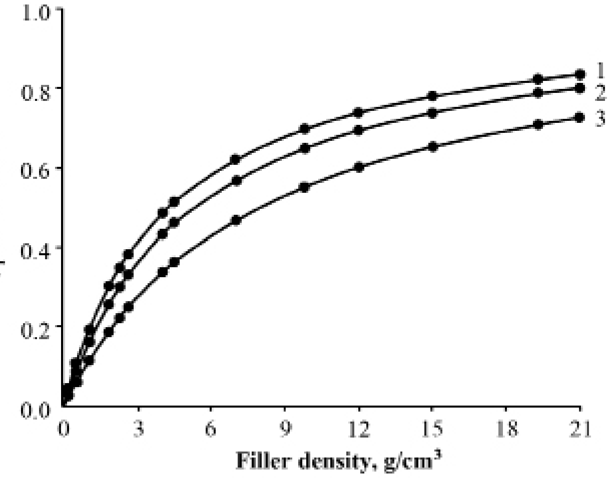

Fig. 1. Dependence of filler content φ_f in mass fractions (mass fract.) in DFPCM with a polymer matrix density ρ_p = 0.8 g/cm³ (1), ρ_p = 1.0 g/cm³ (2), ρ_p = 1.5 g/cm³ (3) at constant volumetric content φ_f = 0.16 vol. fract. on the density of filler.

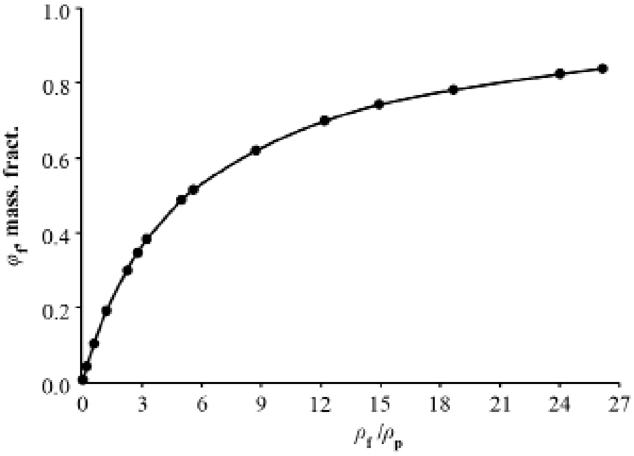

Fig. 2. Dependence of filler content φ_f in mass fractions (mass fract.) in a DFPCM on the density ratio of the filler to the polymer matrix at constant volumetric content φ_f = 0.16 vol. fract.

composite materials. Figure 1 shows the dependences of the content of the dispersed phase in DFPCM expressed in mass fractions, at different densities of the polymer matrix (0.8–1.5 g/cm³), as well as a constant filler content at 0.16 vol. fract. of filler density.

The presented data show that at constant structural parameters (φ_f = 0.16 vol. fract.), the composition of DFPCM expressed in mass units (mass fract.) was determined by the true density of the filler and the matrix and varied from 0.0007 to 0.96 mass fract.

In a generalized form, the graphs in Fig. 1 can be shown in different coordinates where the *X*-axis displays the ratio of densities (filler to polymer matrix). When doing so, the curve does not change according to the density of the polymer matrix. To determine the content of the dispersed phase in mass units at a constant volume fraction (0.16 vol. fract.), density ratio ρ_f / ρ_p should be calculated first for a specific DFPCM (Fig. 2).

This example convincingly shows that the structural parameters of DFPCM can be correctly expressed only in volume units (vol. fract. or vol %). In this case, they were not dependent on the density of the dispersed filler or the polymer matrix, which allowed us to compare the results for filled systems with different fillers and matrices. Thus, when designing DFPCM compositions with a set of specified properties and when representing dependences, data should only be provided in volume units (vol. fract. or vol %) as shown in [7].

Recalculation of DFPCM composition from mass unit ($\varphi_{\text{mass,f}}$) to volume unit ($\varphi_{\text{v,f}}$), and vice versa, can be done for a two-phase system (filler + polymer matrix) by employing the following equations [6]:

$$\varphi_{\text{v,f}} = \frac{\left(\frac{\rho_\text{p}}{\rho_\text{f}}\right)}{\left(\frac{1}{\varphi_{\text{mass,f}}}\right) + \left(\frac{\rho_\text{p}}{\rho_\text{f}}\right) - 1}, \text{ vol. fract.} \qquad (1)$$

$$\varphi_{\text{mass,f}} = \frac{\varphi_{\text{v,f}}}{\varphi_{\text{v,f}}\left(1 - \frac{\rho_\text{p}}{\rho_\text{f}}\right) + \frac{\rho_\text{p}}{\rho_\text{f}}}, \text{ mass fract.} \qquad (2)$$

The content of the dispersed filler is selected according to the classification of dispersed systems, based on the structural principle [6], lattice parameters (coordination number *Z* and packing density coefficient k_p), and the generalized structural parameter θ—the proportion of the polymer matrix for the formation of interlayers between dispersed particles.

The structural classification of DFPCM allows them to be divided into DS, LFS, MFS, and HFS types. Generalized parameter θ serves as the basis for the classification of all DFPCM based on the structural principle: DS: *diluted systems* – $1.0 \geq \theta \geq 0.90$ vol. fract.; LFS: *low-filled systems* – $0.90 \geq \theta \geq 0.75$ vol. fract.; MFS: *medium-filled systems* – $0.75 \geq \theta \geq 0.20$ vol. fract; MFS-1 − $0.75 \geq \theta \geq 0.45$ vol. fract. (up to yield stress); MFS-2 − $0.45 \geq \theta \geq 0.20$ vol. fract. (after yield stress); HFS: *highly-filled systems* – $0.20 \geq \theta \geq 0.0$ vol. fract.

When the maximum dispersed filler packing (φ_m) is known and filler content varies, the generalized structural parameter θ can be found using the following formula [6]:

$$\theta = \frac{\left(\varphi_{\mathrm{m}} - f^3\varphi_{\mathrm{v,f}}\right)}{\varphi_{\mathrm{m}}}, \qquad (3)$$

где $\varphi_{\mathrm{v,f}}$ is the volumetric content of dispersed filler and $f^3 = \left(1 + \frac{2\delta}{d}\right)$ is the coefficient that takes into account the ratio of the thickness of the boundary layer (δ) to diameter (d) of the dispersed particle.

When the boundary layer thickness δ in a DFPCM ranges from 50 to 500 nm and for dispersed particles with a diameter of more than 10 µm, a simplified formula can be used to calculate filler content [6]:

$$\theta = \frac{\left(\varphi_{\mathrm{m}} - \varphi_{\mathrm{v,f}}\right)}{\varphi_{\mathrm{m}}}. \qquad (4)$$

When the generalized structural parameter θ is found, the dispersed filler content and the composition of the polymer can be determined for each type of DFPCM—DS, LFS, MFS, or HFS. The calculations below serve as an example for the content of dispersed filler in volume units at a value of $\varphi_{\mathrm{m}} = 0.64$ for various dispersed systems according to their classification: DS: 0.076 vol. fract.; LFS: 0.16 vol. fract.; MFS-1: 0.255 vol. fract.; MFS-2: 0.34 vol. fract.; HFS: 0.52 and 0.64 vol. fract.

For DFPCM of different structures, it is possible to construct generalized dependences for the dispersed filler content in mass units at different constant values of the filler content in volume units. This will help to determine the construction of dispersions of various types of structures—DS, LFS, MFS, and HFS. Figure 3 shows the dependences of $\varphi_{\mathrm{mass,f}}$ in DFPCM at constant values of $\varphi_{\mathrm{v,f}}$, which are characteristic of different types of structures, on the density ratio of the filler to the polymer matrix.

For dispersed fillers with different φ_{m} values, the content of the filler in volume units ($\varphi_{\mathrm{v,f}}$) was determined by formulas (1) and (2) for different types of DFPCM structures (DS, LFS, MFS, and HFS); then, $\varphi_{\mathrm{mass,f}}$ was found at a constant $\varphi_{\mathrm{v,f}}$ (Fig. 3). The data noted in Fig. 3—based on calculations of the DFPCM compositions in mass and volume units—include almost all known polymer matrices and fillers.

Data on DFPCM properties presented in mass units are true only for a specific polymer matrix and dispersed filler. They are not related to the structure of the composite material and do not allow for comparing dispersed systems with one another. Thus, to design the structure—DS, LFS, MFS, and HFS—the composition of DFPCM should be calculated, and the feature–filler content functions should be considered using only volume units.

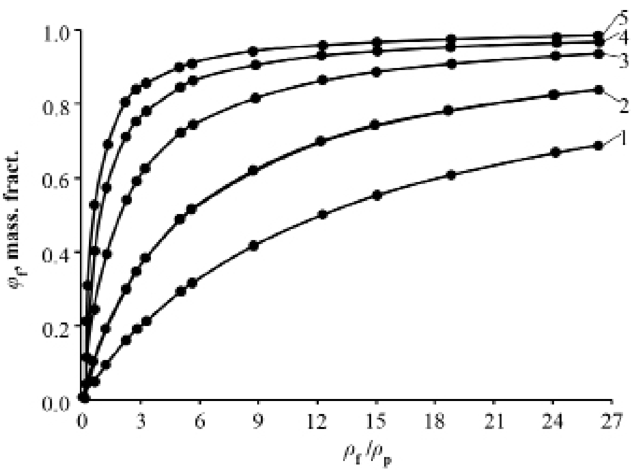

Fig. 3. Dependence of filler content $\varphi_{\mathrm{mass,f}}$ in mass fractions (mass fract.) in DFPCM on density ratio $\rho_{\mathrm{f}}/\rho_{\mathrm{p}}$ at constant volumetric content $\varphi_{\mathrm{v,f}}$:
1 – **DS**, 0.076 vol. fract. (θ = 0.90 vol. fract.);
2 – **LFS**, 0.16 vol. fract. (θ = 0.75 vol. fract.);
3 – **MFS**, 0.255 vol. fract. (θ = 0.60 vol. fract.);
4 – **HFS**, 0.52 vol. fract. (θ = 0.20 vol. fract.);
5 – **HFS**, 0.64 vol. fract. (θ = 0.0 vol. fract.).

The results presented herein enable a purposeful calculation of the DFPCM composition of different types of structures, determining the content of dispersed filler in both volume and mass units for almost all polymer matrices and fillers and correctly describing the composition–property dependences in the volume ratios of components.

CONCLUSIONS

This paper presented calculations for the composition of various types of DFPCM structures according to their classification in mass and volume units. Additionally, the necessity for using only volumetric ratios of components in calculations to describe different types of DFPCM structures was underscored because in doing so, different compositions can be compared, since the obtained structural parameters will not depend on the densities of components. Rather, the specific structure will determine the properties. Accordingly, the dependences of DFPCM properties must be represented in the property–dispersed phase content coordinates only in volume units (vol % or vol. fract.).

The authors declare no conflicts of interest.

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