Polystyrene Molecular Weight Determination of Submicron Particles Shell

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Abstract

The method of determination of the molecular weight of the polystyrene, which is formed as the shell on the surfaces of submicron aluminum oxide particles is considered in the paper. This method is based on the sedimentation of submicron particles, covered by polymer molecules, in a solvent for polystyrene. It is shown that the average polystyrene molecular weight is 39500±11250 amu, when the polymer shells on the surfaces of submicron particles (Al2O3) are formed by the vapor-phase method.

Keywords

photo sedimentation, molecular weight, polymer shell, encapsulated nanoparticles, polystyrene, aluminum oxide

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1. Introduction

The expansion of application areas of dispersion-reinforced polymer composite materials (DRPCM) requires materials with predetermined properties. One of the approaches to the creation of DRPCM with required properties is based on mathematical modeling of their mechanical characteristics. Basing on the results of the mathematical modeling the recommendations for choosing a specific type of polymer matrix and filler particles are proposed. When formalizing mathematical models of polymer mechanics, the mechanical properties of the polymer matrix, dispersed particles, and also the interfacial layer, formed at the particle-polymer interface, are taken into account [1,2]. As a result of interaction of the particles and the polymer an interfacial layer is formed, making the main contribution to the modification of mechanical characteristics of the initial polymer, especially at a low volume concentration of particles. It is shown that the sharp gradient of mechanical properties in the interfacial layer (at the particle-polymer borderline) leads to a decrease in the maximum deformation and ultimate strength of DRPCM [3,4].

Currently, there are two main approaches to formalizing the mathematical model of the mechanical characteristics of the interfacial layer. The first of them is the macroscopic approach, which is based on using the traditional apparatus of polymer mechanics [1,2]. The second one is the microscopic approach, which is based on the apparatus of molecular dynamics [5−7]. Both approaches have their own fundamental limitations. A feature of the macroscopic approach to modeling the mechanical properties of DRPCM is the complexity of using macroscopic parameters (such as elastic modulus, Poisson's ratio, etc.) due to the small characteristic size of the interfacial layer ($\sim 1 \div 100$ nm), because this cannot be justified with physical points of view. On the other hand, the microscopic approach allows operating only with a limited number of polymer molecules within the framework of mathematical models of molecular dynamics. It also complicates the formalization of the interfacial layer model on the particle-polymer borderline.

It should be noted that the traditional macroscopic approach, firstly, is convenient when the developed apparatus of polymer mechanics is used; secondly, it is justified also for practical usage, taking into account the scatter of the mechanical properties of polymer

composites due to technological tolerances to the formation of these materials [8,9]. At the same time, the task of determining the numerical estimates of the mechanical characteristics of the interfacial layer remains open. Thus, a macroscopic approach to modeling the mechanical properties of DRPCM is discussed in detail in Ref. [10], taking into account the interfacial layer. But when numerical calculations are performed the interfacial layer is neglected, taking into account its small size in comparison with the computing cell size.

The mechanical characteristics of the interphase layer can be estimated by solving the inverse task by comparing the results of mathematical modeling with experimental results. There is a way to increase the reliability of the results of calculating the mechanical characteristics of the interphase layer by taking into account a priori information about these characteristics. For example, when using polymer-encapsulated DRPCM filler particles [11,12], a priori information on the mechanical characteristics of the polymer shell constituting the particle-polymer interfacial layer can be determined by the awareness of the molecular weight of the polymer of shell [13,14].

Measuring methods of molecular weight in a wide range (from 102 to 107 amu) are well studied [17−20]. In most cases, the implementation of these methods usually requires the examined polymer fractionation in solutions. It also requires a priory information on solution concentration, etc. It is difficult to satisfy all these requirements when the molecular weight of a polymer shell, formed on the surfaces of submicron particles, is evaluated, in particular, when the technology [12] is used. This is due, at least, to the following factors: a small thickness of the shell (10−100 nm, [12]), a small amount of the shell polymer substance; the complexity of separating submicron particles from the polymer in a solution.

The goal of this work is to estimate the molecular weight of the polymer of the shell on the surface of submicron particles of the DRPCM filler.

2. Experimental part

Determination of the molecular weight of the polymer in the shell on the surfaces of submicron filler particles was carried out experimentally. The submicron Al_2O_3 particles (a mixture of δ and θ, size range 40−190 nm, manufactured by "Plasmotherm", product

number: PL1344281) with a polystyrene shell on their surfaces were examined. The polystyrene shell was produced by the vapor phase method implemented in multiphase gas flows [12].

The method of molecular weight of polystyrene estimating is based on the difference of the sedimentation of particles with different sizes and masses (polystyrene molecules and submicron particles) in the solution. The analysis of the difference allows determining the average molecular weight.

The solution of submicron aluminum oxide particles encapsulated by polystyrene in ethyl acetate, which is a solvent of polystyrene, was prepared. After that, the solution was kept within 10 min in the ultrasonic bath with the power ~50 W for preliminary homogenization of the solution. The determination of the average value of the molecular weight of polystyrene was carried out by the sedimentation time constant comparison of examined polymer molecules (τ) with sedimentation time constant of molecules with known molecular weight (τ_0), where the sedimentation time constant (τ) characterizes the time during the optical density D of the solution decreases by a factor of e (Euler's number).

The photometric measurement method of the optical density D of the solution was used to measure the sedimentation time constants (τ and τ_0). The designed photometer worked in a pulse mode with central wavelength equaled to 470 nm; the length of the cuvette was 45 mm. The experimental setup scheme is shown in Fig. 1.

The optical density D of the solution was determined by the relation:

$$D = \lg(I_0 / I_M), \tag{1}$$

where I_M and I_0 are the output currents of the photodiode 9 when the light beam passes through the solvent 5 with and without the examined particles, respectively.
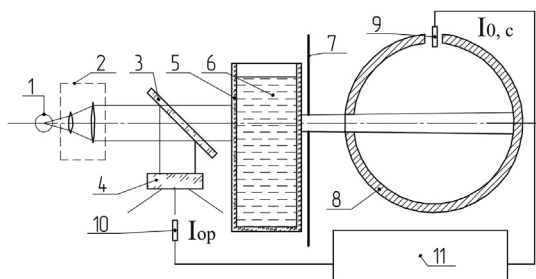

Fig. 1. The experimental setup scheme: 1 − LED; 2 − lens; 3 − light-dividing plate; 4 − diffuse-scattering plate; 5 − cuvette; 6 − solution; 7 − diaphragm; 8 − photometric sphere; 9 − signal, 10 − reference photodiode; 11 − digital oscilloscope ASK-4174.

The output current of the photodiode 9 was normalized at the output current of the reference photodiode 10 to exclude the fluctuation of the light source intensity on measurement results.

It should be noted that the duration of the process of sedimentation of polymer molecules under the gravity force only can reach several dozen hours. At the same time, the temperature drift of the zero-point of the most common spectrophotometers ("KFK-3.5", "Unico 2100", and "Apel PD303", for example) can reach 0.004 per hour, thus limiting their usage in long-time experiments. The pulsed mode of the photometer with the reference channel allows reducing the temperature drift of zero-point down to 0.00012 per hour, thus giving opportunity to carry out long-time experiments [15].

The aqueous solution of a polyelectrolyte with a known and narrow distributed molecular weight was prepared for the photo sedimentation experiment. The aqueous solution of a cationic surfactant was added to the solution to compensate the charge of the polyelectrolyte macromolecules, providing the sedimentation of the macromolecules only under the gravity force. The distribution of the molecular weight remained narrow because the molecular weight of polyelectrolyte molecules was chosen significantly (more than one order of magnitude) larger, than the molecular weight of the surfactant molecules [16].

The water passed through the "Milli Q" purification system (18.20 MΩ cm) was used as a solvent and dispersion medium for the sample preparation. Aqueous dispersions of the polymer−colloidal complex (PCC) were obtained by adding dropwise a 0.05 mol/L aqueous solution of surfactant (cetyltrimethylammonium bromide, purity ≥ 99%, manufactured by "Sigma") to a solution of 0.05 mol/L polyelectrolyte (sodium salt of polyacrylic acid, purity 95%, manufactured by "Sigma") with a molar weights of 5100 g/mol (PAK-5.1); 240,000 g/mol (PAK-240); sodium polystyrene sulfonate (purity 95%, manufacturer Sigma) with a molar weight of 70,000 g/mol (PSS-70) with constant stirring on a magnetic stirrer (300 rpm at 25 °C) until the stable opalescence appeared [17,18]. The zeta-potential was measured for PAC 5.1 (30.9 mV), PSS-70 (0.06 mV), and PAK-240 (76.3 mV) on a "Zetasizer Nano" analyzer ("Malvern"). The values, obtained for PAC 5.1 and PAK 240, indicate the presence of the charge on the molecules of the polymer−colloidal complex. On the one hand, the presence of a charge prevents the agglomeration of molecules [19], on the other hand, the low concentration of the polymer-colloidal complexes does not affect

the sedimentation rate in the observation region (upper area of the cuvette) [20]. The sedimentation time constants (τ and τ_0) in general case depend on several solution parameters, the main of them are: molecular weight M and concentration C of sedimented particles, viscosity η and density ρ of the solvent [21,22]. The dependence of the sedimentation time constant on concentration can be neglected at low concentrations (less than 1–2%) because this dependence is weakened with the concentration decreasing [21]. It makes it possible to exclude one of the solution parameters, namely the concentration, during analyzing the measurement results. The concentration of polymer molecules washed off by the solvent from the surface of submicron particles was not known also. The preliminary experiments were carried out to determine the measurement conditions under which the simplification of the molecular weight estimation was possible. The optical density of solutions, according to the Beer-Lambert-Bouguer law, is proportional to the concentration of absorbing particles. In analogy with [21], the conditions of solution preparation with an initial optical density at which the sedimentation rate did not depend on the concentration of macromolecules in the solution were determined in this work. The typical dependence of the characteristic sedimentation time τ on optical density for PSS with a molecular weight of 70,000 amu is shown in Fig. 2.

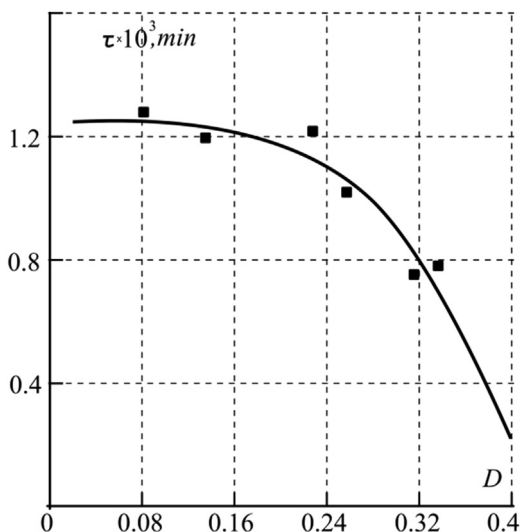The influence of the polymer concentration on the sedimentation time constant at the optical density below 0.16–0.18, can be neglected. Due to this fact, all measurements were carried out at the initial value (before the sedimentation starting) of the optical density not exceeding 0.17.

The calibration dependence for determining the molecular weight of the shell polystyrene was obtained from the results of measuring the sedimentation time constant of polymer molecules in the prepared PAC samples with different molecular weights of the polyelectrolyte: PAK 5.1 (Sample 1), PSS 70 (Sample 2), and PAK 240 (Sample 3). This dependence is shown in Fig. 3.

It is necessary to take into account the different values of the viscosity of water and ethyl acetate when the calibration characteristic is used. The viscosity changing was taken into account using the correction factor K_P [23]:

$$K_P = \eta_W / \eta_S, \qquad (2)$$

where η_w is the dynamic viscosity of water; η_p is the dynamic viscosity of the used solvent. The time constant of the sedimentation of polystyrene molecules in solution τ_{vw}, which is used to estimate the molecular weight from the calibration dependence, is determined by the formula:

$$\tau_{vw} = K_P \tau, \qquad (3)$$

where τ is the sedimentation time constant of polystyrene molecules in ethyl acetate, measured in the experiment.

Fig. 2. Dependence of the sedimentation time constant for PCC PSS with a molecular weight of 70,000 amu on the optical density of the solution.
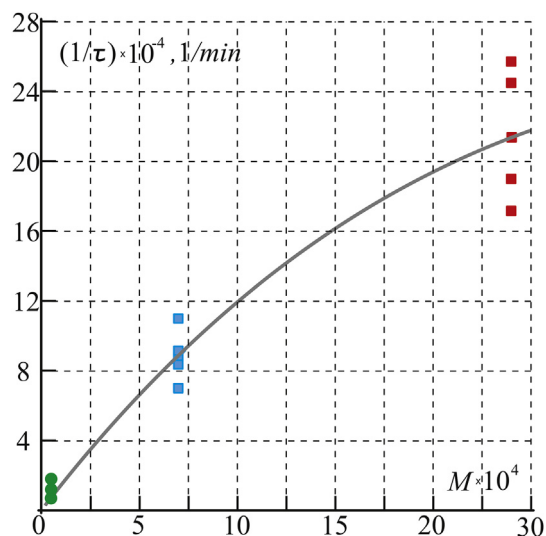

Fig. 3. The calibration dependence of the sedimentation rate on the molecular weight for the: ● – PAK-5.1 (green marker); ■ – PSS-70 (cyan marker); ■ – PAK-240 (red marker).

3. Results and discussion

Typical photos of submicron particles are shown in Fig. 4: the initial particles of aluminum oxide Al_2O_3 (Fig. 4,a and b), the particles of aluminum oxide encapsulated with polystyrene (Fig. 4,c and d), the particles of aluminum oxide after the dissolution of a part of the polystyrene shell (Fig. 4,e and f).

The particle size estimation was carried out by statistical processing of the particles photos in the "ImageJ" software. The samples of 800−1200 particles were used for carrying out statistics using at least three photos. The results of statistical processing of microscopic analysis are shown in Fig. 5, which shows the particle size distribution. The shift of the curve maxima was used to determine the change in the particle
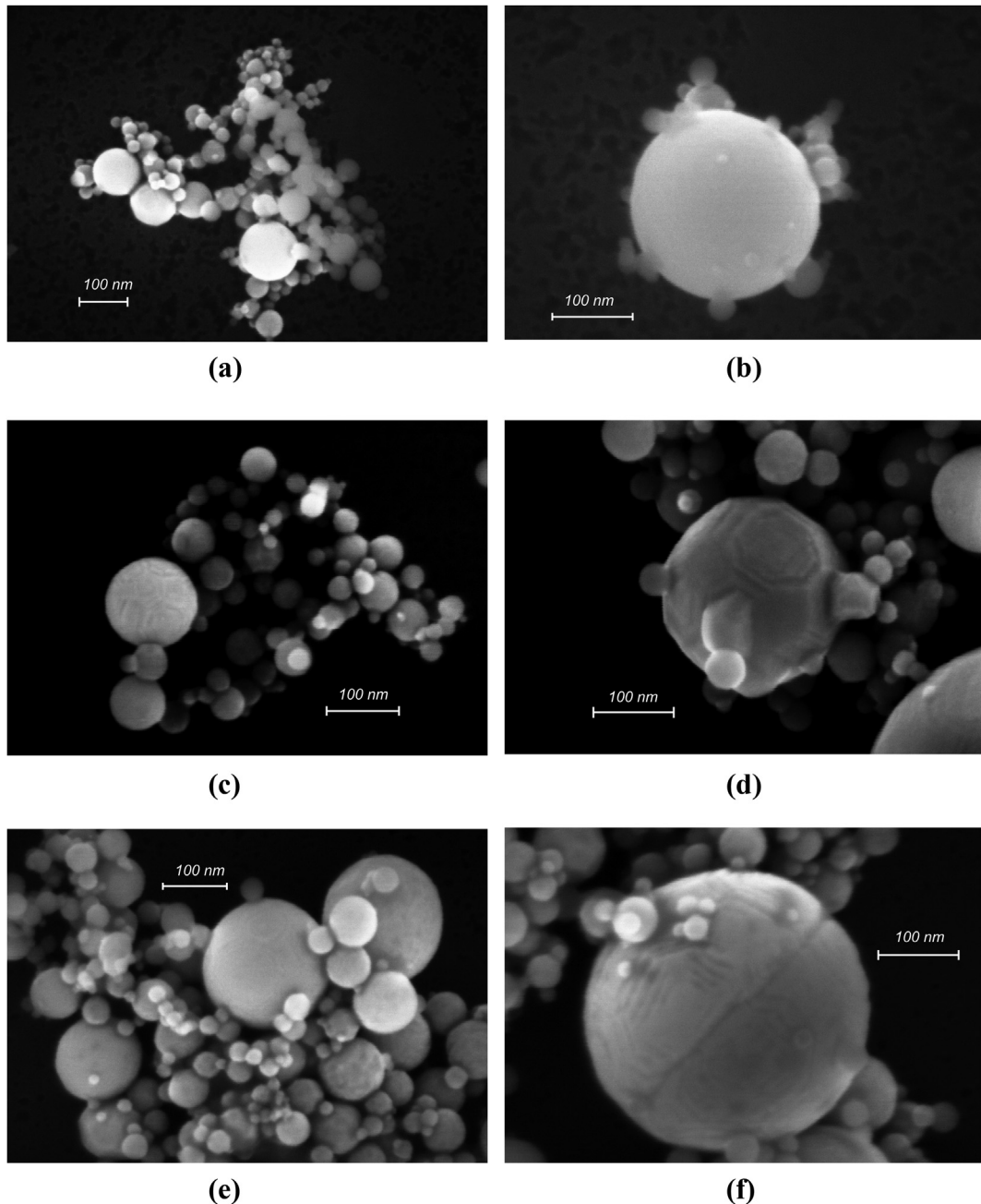

(a)   (b)

(c)   (d)

(e)   (f)

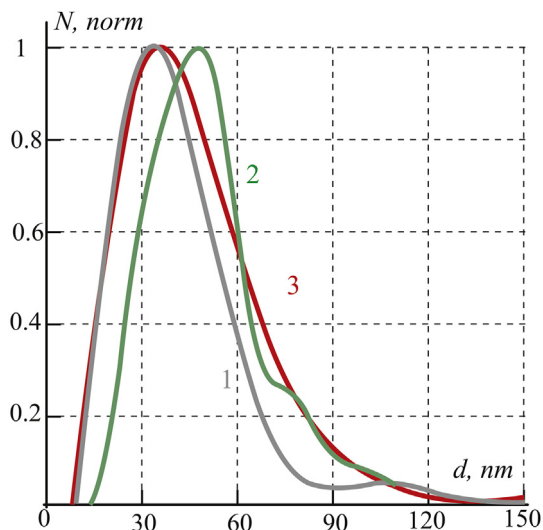Fig. 4. Scanning electron microscopy images of Al_2O_3 particles.

Fig. 5. Particle size distribution histograms: green line – particles of aluminum oxide; blue line – particles encapsulated by polystyrene; red line – particles after the dissolution of a part of the polymer shell.

Fig. 6. Sedimentation curve of aluminum oxide particles with remains of the polystyrene shell and polymer molecules in an ethyl acetate solution.

sizes after the formation of a polymer shell on their surfaces.

The results show that after obtaining the solution of encapsulated aluminum oxide particles in ethyl acetate, the polymer shell partially dissolves, since the average shell thickness decreases from 8.5 to 2.4 nm. Therefore, there must be a dispersion in the mass of Al_2O_3 particles with the remains of the polymer shell. Thus, the initial region of the sedimentation curve is determined by the co-sedimentation of Al_2O_3 particles with remains of the polymer shell on their surfaces, polymer molecules, and their agglomerates, and the final region is determined by the sedimentation of only polystyrene molecules [24]. This allows using the sedimentation method to determine the polystyrene molecular weight. The shell on the surfaces of submicron aluminum oxide particles was controlled by scanning electron microscopy "Carl Zeiss Auriga Cross-Beam" with subsequent statistical processing of the resulting image.

A typical sedimentation curve of the particles ensemble (aluminum oxide with remains of the polystyrene shell and polymer molecules) in the ethyl acetate solution is shown in Fig. 6, where the changing of the optical density of the solution is shown in the figure by the red line; the changing of derivative of optical density on time is shown by the blue line. The changing of the optical density on time characterizes the decreasing of the concentration of particles in the volume.
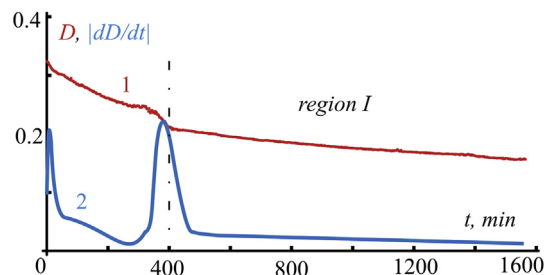
The first peak of derivative of optical density on time, most likely, corresponds to the sedimentation of heavy particles (aluminum oxide) with the remains of the polystyrene shell on their surfaces; the second peak corresponds to the sedimentation of agglomerates of polystyrene molecules [25]. The time constant, corresponding to the region-I on the sedimentation curve 1, measured as a result of experiments on the sedimentation of dispersed polystyrene molecules in ethyl acetate, is 928 ± 225 min. The time constant (τ_{vw}) calculated according to equation (3) taking into account the solvent ethyl acetate ($K_P = 2.066$, (2)) is 1918 ± 465 min. Thus, the average molecular weight of polystyrene molecules in solution is estimated at $39,500 \pm 11,250$ amu.

4. Conclusions

The proposed method allows estimating the polymer molecular weight values only qualitatively. This assumption is based on good repeatability of the results with the standard deviation less than 1 % when the experiments are repeated with preliminary homogenization of the colloidal solution in an ultrasonic bath for 30 s with a power of 10 W. In addition, the zeta-potential was measured for PAC 5.1 (30.9 mV), PSS-70 (0.06 mV), and PAK-240 (76.3 mV) on a "Zetasizer Nano" analyzer ("Malvern"). The obtained values for PAC 5.1 and PAK 240 indicate the presence of the charge on the molecule surfaces of the polymer−colloidal complex. On the one hand, the presence of a charge prevents the molecules agglomeration [19], on the other hand, the low concentration of the polymer-colloidal complexes does not affect the sedimentation rate in the observation region, located in the upper area of the cuvette [26]. It should be noted that the estimation of the value of the polymer molecular weight of the shell, formed on the surfaces of

submicron particles, allows limiting the range of a solution of the inverse task of polymer mechanics and, as a consequence, to increase its adequacy [27].

The conditions of technology of shell, forming on the surface of the submicron particles of aluminum oxide using the vapor-phase method [28], provide a low molecular weight of polystyrene ~39,500 amu, and, accordingly, low mechanical characteristics of the polystyrene shell, in comparison with the threshold mechanical characteristics of most polymeric materials used as DRPCM matrices. In this regard, a significant increase of the tensile strength of composites using submicron particles encapsulated by this method is possible only at small thicknesses (up to 5−15 nm) of the polystyrene shell, which is confirmed by the results of relevant studies, for example [12].

Conflicts of interest

No conflict of interest among authors.

Acknowledgements

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