Original articles

Dispersed copper (I) oxide particles encapsulated by polylactide

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Abstract

One of the approaches for the production of polymer composite materials with a biocidal effect is based on the use of dispersed particles of some metal oxides as a filler (for example, copper oxide or zinc oxide). Such an approach allows not only providing a biocidal effect, but also increasing such mechanical characteristics as the modulus of elasticity, hardness, and abrasion resistance. The mechanical characteristics of such polymer composite materials can be controlled by formation of a sheath (for example, from polylactide) of a given thickness on the surfaces of dispersed particles. Polylactide is a biodegradable polymer, widely used as coating material for particles with biocidal properties. The parameters of the methods for forming a polylactide sheath are determined by the sheath's thickness and the sheath's adhesion to the particle surface. The purpose of the study was to determine the parameters of the polymer sheath's formation on the surfaces of dispersed submicron copper oxide (I) particles during coacervation of polylactide from the solution.

The encapsulation of copper (I) oxide particles was carried out by the coacervation process in a solution. Polylactide was displaced from the solution in benzene by hexane in the presence of copper (I) oxide particles. It was shown that a sheath thickness of about 250 nm can be obtained by using the polylactide sheath formation method. The recommended parameters of the polylactide sheath formation method were determined: solution temperature of 35÷38 °C, hexane volume not more than 30±2 ml. The sheath had weak adhesion to particle surfaces: adhesion was determined by the roughness of the particle surface.

The mechanical characteristics of the epoxy resin ED-20 polymer composition filled with the encapsulated particles were considered in the study. The increase in the mechanical properties of the polymer composition with encapsulated particles in comparison with the samples of polymer composition with non-encapsulated particles was revealed. That can indicate the increased adhesion of encapsulated particles to such polymer matrix.

Keywords: Encapsulation, Dispersed particles of copper (I) oxide, Polylactide

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1. Introduction

One of the main factors hindering the widespread use of polymer composite materials in tropical climates is their insufficiently high resistance to the simultaneous action of such external factors as high temperature, humidity, intense solar and UV radiation, and the destructive effect of microorganisms [1–4]. Thus, in [5, 6] a monotonous decrease in the mechanical characteristics of natural fibre reinforced polymer composites with was noted as a result of moisture absorption and hygrometric ageing of the composite. It was shown in [7] that the use of glass fibre reinforced epoxy composites as insulators, although promising, is limited by the destruction of this material caused by simultaneous exposure to air moisture, temperature, and high voltage. This causes the appearance and increase of cracks, starting from the surface of the material, which, in turn, leads to a decrease in its performance. Moreover, it was noted that one of the main reasons for the destruction of the composite is the destruction at the interface between the filler and the polymer matrix. The destructive effect of microorganisms is predominant for a number of polymeric materials, including polymer compositions based on epoxy resins or polyethylene [8, 9].

A promising approach to reducing the degradation rate of polymer composite materials is the use of dispersed functional fillers. Thus, in [10], the results of a comparative analysis of several approaches to increasing the resistance of cycloaliphatic epoxy resin coatings were presented and the expediency of using finely dispersed fillers in the composition was substantiated. The use of highly dispersed functional fillers with a biocidal effect, for example, silver or copper oxide particles, allows not only to increase the resistance of the polymer composite to biodegradation [11], but also to improve some of its mechanical characteristics, including hardness, modulus of elasticity, and increase resistance to abrasion [12–16]. The possibility of controlling of the mechanical characteristics of such polymer composites by creating and changing the thickness of the polymer sheath on the surfaces of the filler particles is known [12, 13].

Polylactide (PLA) is widely used as a polymer sheath material for particles with biocidal properties. For example, particles encapsulated by PLA were obtained for the production of temperature sensors [17, 18], for targeted delivery of ferrimagnetic particles in the treatment of oncological diseases [19] or targeted delivery of drugs after PLA degradation [20], for the protection of polymer composites based on epoxy resins [21, 22] from some fungi species.

The creation of a PLA sheath on particle surfaces is a non-trivial task. For example, when forming a PLA sheath by the polymerization of lactide on the surfaces of dispersed particles [21], the question of determining the mechanical properties of the sheath remains open. This is due to the complexity of determining the parameters of the formed polymer (molecular weight, modulus of elasticity, etc.), which are necessary for assessing the mechanical properties of the composite. In addition, the acids present in the solution during the formation of the sheath contribute to the destruction of certain types of particles. Thus, when copper oxide particles interact with acids, copper salts are formed. The use of evaporation methods, evaporator emulsification, or coacervation processes overcome this disadvantage. The mechanical properties of the sheath in this case will be close to the mechanical properties of the original PLA polymer. However, the issues of sheath adhesion to particle surfaces and the determination of the possible range of changes in the sheath thickness remain open. These issues can only be resolved experimentally: by selecting the parameters of the technological process for the formation of such a sheath [20].

The purpose of this study was to determine the parameters of the formation of the polymer sheath on the surfaces of copper oxide (I) dispersed particles during the coacervation of polylactide from a solution.

2. Experimental

2.1. Formation of a polylactide sheath on the surfaces of copper (I) oxide particles

A polylactide polymer sheath (manufactured by Natural Works LLC grade PLA 4043D) was prepared on dispersed copper(I) oxide particles (TU 6-09-765-76 analytical grade). The formation of this polymer sheath was carried out on the surfaces of dispersed Cu_2O particles in a dispersed

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medium using a coacervation in a PLA solution. For this, a PLA solution in benzene (GOST 5955-75 chemically pure reagent) was prepared: a weighed portion of PLA of 0.75±0.05 g was dissolved in 60±2 ml of benzene during heating to (40±1) ℃ and slow mixing on a heated magnetic stirrer (Ekros, model ES-6120) for 5–6 hours. After the PLA was dissolved in benzene, a viscous transparent solution was obtained. The homogenization of dispersed copper (I) oxide particles (m_{Cu2O}) 1±0.05 g was carried out in 27±2 ml of benzene using an ultrasonic bath (Daihan WUC-A01H, power 50 W) for 60±10 s. After homogenization solution of PLA in benzene was added into the resulting suspension with constant mixing at a temperature of 40±1 ℃ to the desired concentration (C_{PLA}) PLA, which was changed during the experiments. The coacervation process was initiated by the addition of a displacement solvent to the obtained solution. Hexane (TU 2631-158-44493179-13 chemically pure reagent) with a volume of 15±0.5 ml was used as a displacing solvent, adding it to the solution through a dropping funnel at a rate of ω_{hex}. After the introduction of the displacement solvent, the resulting solution was stirred for 20 min. The encapsulated particles were filtered off using multilayer filter paper followed by washing in hexane.

2.2. Research methods

The thickness of the PLA sheath on the surfaces of dispersed particles of copper (I) oxide (Cu_2O) was determined based on the difference in the sizes of encapsulated and non-encapsulated particles. The sheath thickness was estimated by statistical image processing (Fig. 1) using the ImageJ software environment [23]. Images of particles, both encapsulated (Fig. 1) and not encapsulated, were obtained by scanning electron microscopy (SEM) using Carl Zeiss AURIGA Cross Beam electron microscope with an EDV Inca X-Max 80 mm². The study of the adhesion of the PLA sheath to dispersed particles was carried out using the turbidimetric method [24, 25] by analysing the deposition curves of dispersed particles in a solution. The evaluation of the adhesion of the PLA sheath to the polymer matrix was carried out by studying the mechanical characteristics of samples of

polymer composite material based on epoxy resin ED-20. Sample preparation was carried out according to the procedure described in [26]. Martens hardness was measured on a Shimadzu DUH-211S ultramicro tester according to ISO 14577-1 using a Berkovich indenter (triangular indenter with a 115° apex angle). Twenty five independent measurements were carried out in different areas of the test sample with subsequent averaging of the obtained values [12]. The measurement of the modulus of elasticity and maximum deformation was carried out in accordance with GOST 11262-80 using Shimadzu AG-X 50 kN universal desktop testing machine for physical and mechanical testing of various materials. Test parameters: bending loading rate – 7mm/min; ambient temperature – 23±2 ℃.

3. Results and discussion

Typical micrographs of encapsulated Cu_2O particles at different resolutions of the Carl Zeiss AURIGA Cross Beam electron microscope are shown in Fig.1. The encapsulated particles shown in Fig. 1 were obtained under the following conditions: $m_{Cu2O} = 1 \pm 0.05$ g, $C_{PLA} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $\omega_{hex} = 15 \pm 1$ drops/min, hexane volume V 15±0.5 ml, solution mixing time was 20 min. Statistics were performed based on at least 3 microphotographs; a sample of 800–1200 particles was used. Examples of statistical processing of microscopic studies are shown in Fig. 2, where the envelopes of the histograms of distribution of the size of the initial and encapsulated (Fig. 1) Cu_2O particles can be seen. The following designations were used in Fig. 2: N is the number of particles with a certain size, N_0 is the number of particles corresponding to the maximum in the distribution. The size distribution of the number of encapsulated particles (Fig. 2b) is shown for particles obtained under the following conditions: $m_{Cu2O} = 1 \pm 0.05$ g, $C_{PLA} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $\omega_{hex} = 27 \pm 2$ drops/min, hexane volume V 27±1 ml, solution mixing time 20 min. For original and encapsulated particles N_0 was ~500±20.

The thickness of the polymer sheath on the surfaces of dispersed particles during its formation using the coacervation process is determined by the collision frequency (ν) of dispersed particles with PLA molecules displaced

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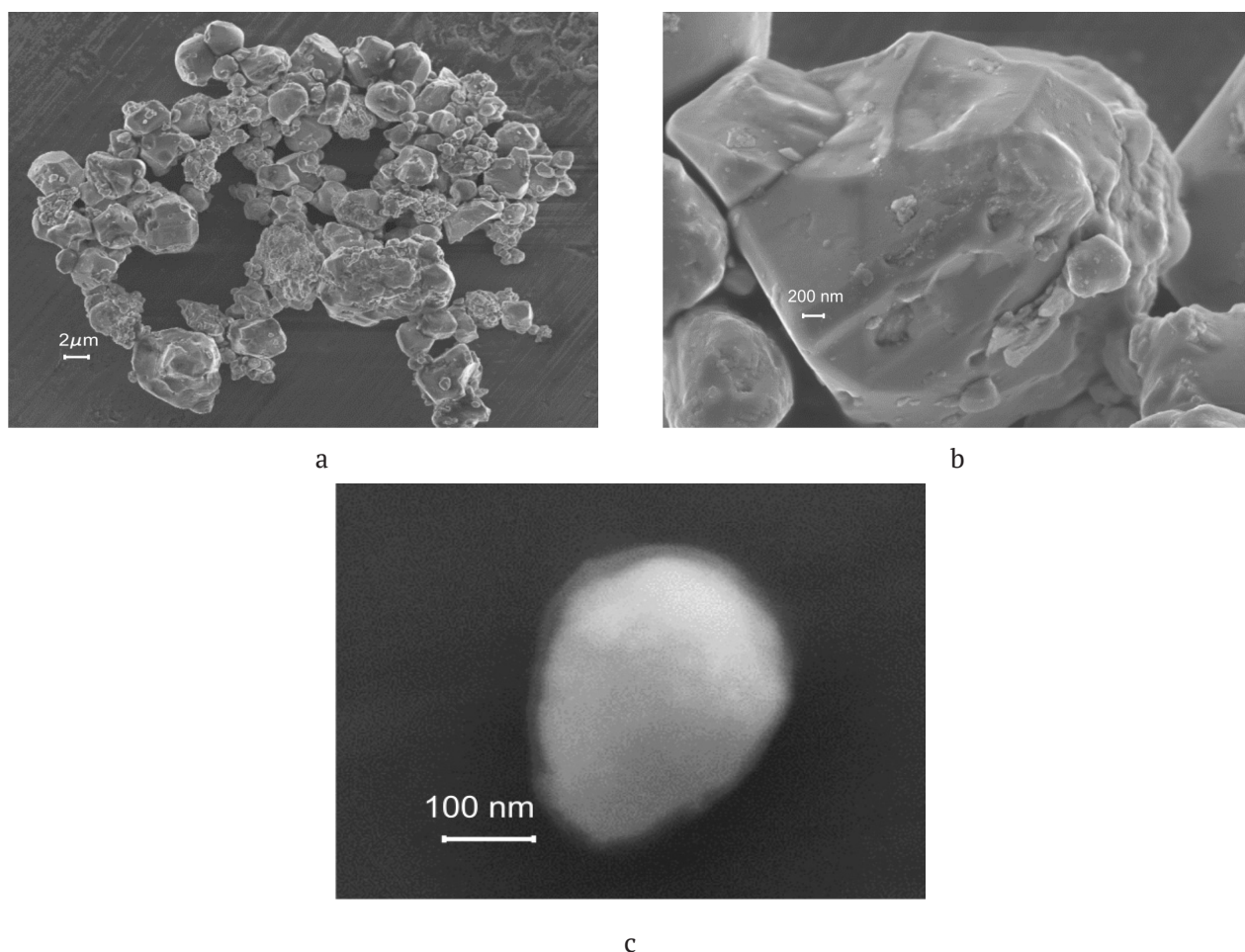

a

b

c

Fig. 1. Typical photomicrographs of encapsulated particles taken at various resolutions. Encapsulated particles were obtained under the following conditions: $m_{Cu2O} = 1 \pm 0.05\,\text{g}$, $C_{PLA} = (4.5 \pm 0.1) \cdot 10^{-4}\,\text{g}$ per 100 ml of benzene, $\omega_{hex} = 15 \pm 1$ drops/min, solution mixing time 20 min, hexane volume 15±0.5 ml
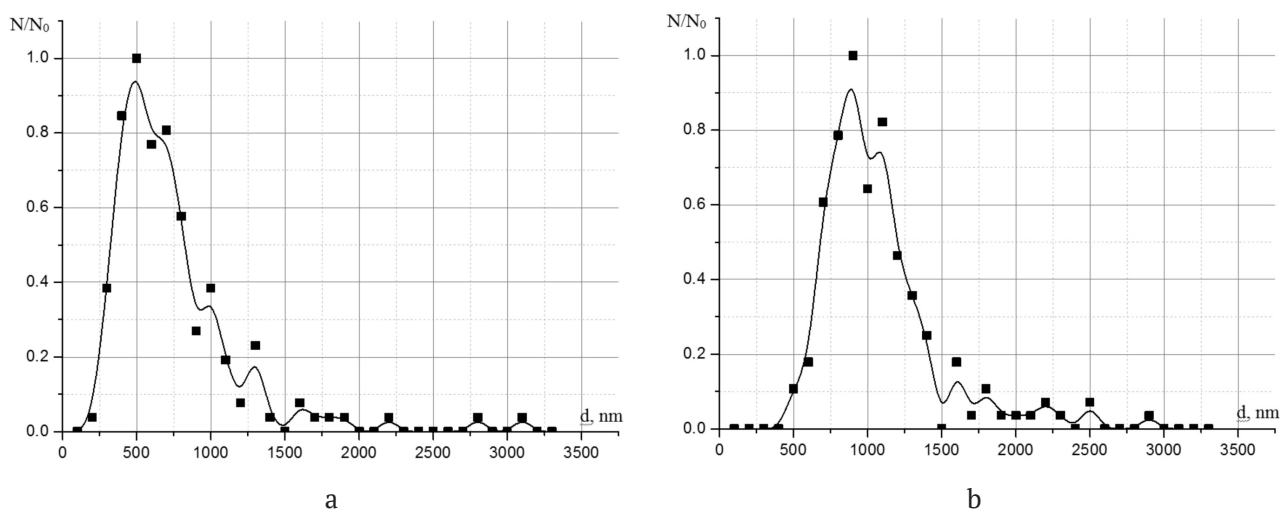

a

b

Fig. 2. Particle size distribution: a – initial particles; b – encapsulated copper (I) oxide particles, N – number of particles with a certain size, N_0 – number of particles corresponding to the maximum in the distribution

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from solution with benzene, as well as by the cross section (σ) of inelastic collisions [12, 27]. For testing the technological modes of PLA sheath formation, the following parameters were considered: mixing time (t) of the suspension of dispersed Cu_2O particles with PLA solution during coacervation; the ratio of the volume of the PLA solution in benzene to the volume of the displacing solvent (hexane); temperature of the solution during the formation of the PLA sheath. Three series of experiments for the investigation of the influence of each of these parameters on the thickness of the PLA polymer sheath were carried out in the study.

In the first series of experiments, we changed the time (t) of mixing the PLA solution with dispersed particles with the uniform addition of the displacing solvent: $C_{\text{PLA}} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $m_{\text{Cu2O}} = 1 \pm 0.05$ g, $\omega_{\text{hex}} = 15 \pm 1$ drops/min, $T = 40 \pm 2$ °C. The mixing time varied from 20 to 110 min. The dependence of the average thickness ($2h$) of PLA sheath vs. time t is shown in Fig. 3.

Reduction of the growth rate ($\upsilon = \Delta h / \Delta t$) of the sheath thickness was probably due to a decrease in the number of PLA molecules with time (respectively, the collision frequency υ decreased) displaced from the solution by hexane due to their deposition on the surface of dispersed particles. The control in the reduction of the growth rate υ is

possible by changing the number of PLA molecules displaced from the PLA solution by changing the amount of hexane added to the solution.

In the second series of experiments for the study of the change of the volumes of the PLA solution in benzene to the volume of the displacing solvent (hexane), we changed the volume of hexane added to the solution and achieved a change in the concentration of PLA molecules: $C_{\text{PLA}} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $m_{\text{Cu2O}} = 1 \pm 0.05$ g, $\omega_{\text{hex}} = 27 \pm 2$ drops/min, $T = 40 \pm 2$ °C, hexane volume V was changed in the range of $(5 \div 27) \pm 1$ ml. The dependence of the average thickness ($2h$) of PLA sheaths on hexane volume V is shown in Fig. 4.

It should be noted that in the case when the volume of hexane added to the solution exceeds 30 ± 2 ml, the rate of the coacervation process increased sharply. In experiments, the formation of agglomerates of encapsulated particles, which precipitated, was observed. The use of agglomerated particles as a filler of disperse-reinforced polymeric materials does not allow obtaining reproducible mechanical properties of composites [28, 29]. This imposes a limitation on both the maximum volume of hexane added to the solution ($V < 30$ ml) and sheath thickness ($2h < 500$ nm), which can be obtained on dispersed filler particles by varying this parameter during encapsulation using this method.
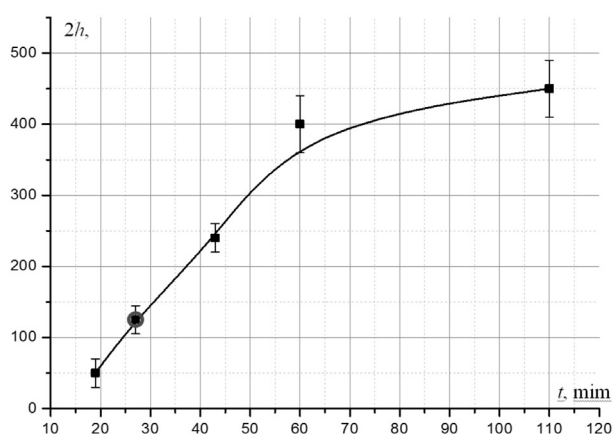

Fig. 3. The dependence of polylactide sheath average thickness on the mixing time of the solution. Encapsulated particles were obtained under the following conditions: $m_{\text{Cu2O}} = 1 \pm 0.05$ g, $C_{\text{PLA}} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $\omega_{\text{hex}} = 15 \pm 1$ drops/min, $T = 40 \pm 2$ °C, hexane volume 15 ± 0.5 ml, solution mixing time was changed from 20 to 110 min
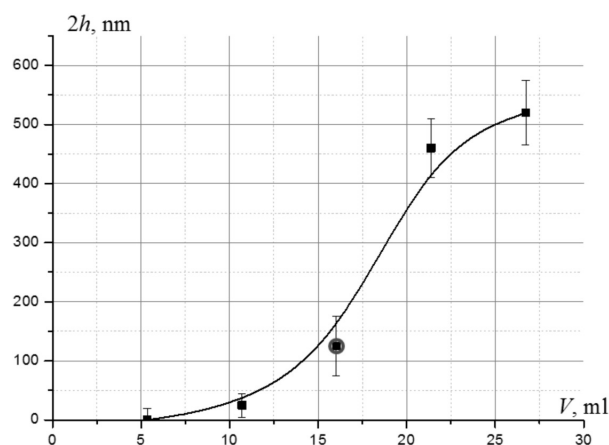
Fig. 4. The dependence of polylactide sheath average thickness on the volume of hexane added to the solution. Encapsulated particles were obtained under the following conditions: $m_{\text{Cu2O}} = 1 \pm 0.05$ g, $C_{\text{PLA}} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $\omega_{\text{hex}} = 27 \pm 2$ drops/min, $T = 40 \pm 2$ °C, hexane volume V was changed in the range $(5 \div 27) \pm 1$ ml, solution mixing time was 20 min

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In the third series of experiments, we studied the effect of changing the temperature of the PLA solution in benzene during the formation of a sheath on the particle surfaces. These experiments were carried out under the following conditions: $C_{PLA} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $m_{Cu2O} = 1 \pm 0.05$ g, $\omega_{hex} = 27 \pm 2$ drops/min, hexane volume V 15±1 ml, the temperature of the solution during sheath formation was changed within [25÷45]±2 ℃. The upper temperature limit was limited by the temperature of PLA softening (~50 ℃) [30]. At such a temperature of the solution, the probability of agglomeration of encapsulated particles due to their adhesion during collisions is high [31]. The dependence of the average value of the thickness (2h) of PLA sheath on the temperature of the solution is shown in Fig. 5.

The presence of an extremum of the curve in Fig. 5 can be explained by the fact that the solubility of PLA in benzene increases with increasing temperature starting from ~35 ℃. Due to this, the amount of PLA displaced by hexane from the solution decreases and, as a result, the thickness of the polymer sheath decreases. The increase of the sheath thickness with a change in temperature from 25 ℃ to 35 ℃ is associated with an increase in collision frequency (ν) of dispersed particles with PLA molecules displaced from the
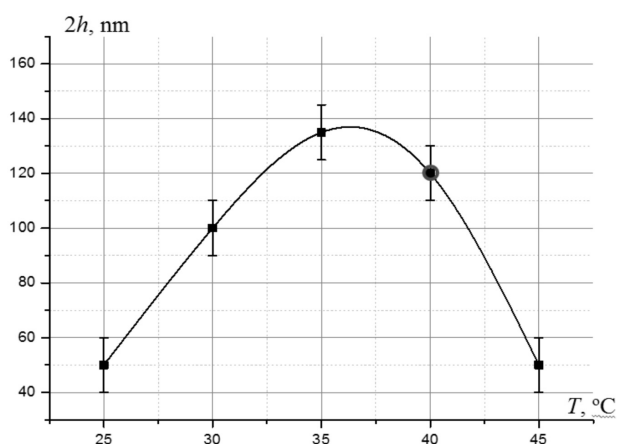

Fig. 5. The dependence of the average thickness of the polylactide sheath on the solution temperature. Encapsulated particles were obtained under the following conditions: $m_{Cu2O} = 1 \pm 0.05$ g, $C_{PLA} = (4.5 \pm 0.1) \cdot 10^{-4}$ g per 100 ml of benzene, $\omega_{hex} = 27 \pm 2$ drops/min, hexane volume V was 15±0.5 ml, the temperature of the solution during the formation of the sheath was changed in the range (25÷45)±2 ℃, solution mixing time was 20 min

solution with benzene. Thus, the temperature ~35 ℃ is the most appropriate in terms of achieving the maximum thickness of the sheath. Points on the graphs (Figs. 3-5), marked with a circle, indicate the results obtained under the same conditions of the encapsulation process. The high correlation of the sheath thickness for these conditions indicates a good reproducibility of the encapsulation process. It should be noted that the change in the PLA weight in the range of (2.25÷4.5)·10⁻⁴ g per 100 ml of benzene, as well as the weight of dispersed Cu₂O particles added to the solution in the range of (0.2÷2) g did not actually affect the thickness h of PLA sheaths under the considered conditions of the formation. Thus, the main parameters that allow to control the thickness h, are: the mixing time of the PLA solution after the addition of the displacement solvent, the ratio of the volumes of PLA solution in benzene to the volume of the displacement solvent (hexane), and the temperature of the solution during mixing.

The mechanical characteristics of a polymer reinforced with encapsulated dispersed particles are affected, among other things, by the adhesion of the polymer sheath both to dispersed particles and to the polymer matrix [12, 13]. The study of the adhesion of the PLA sheath to dispersed particles was carried out by the turbidimetric method [25, 24] by analysing the deposition curves of dispersed particles in solution (Fig. 6). The dotted lines in Fig. 6 show the equilibrium levels of optical density (D): 0.232 corresponds to curve 4; 0.135 corresponds to curve 3. Equilibrium level of optical density is the experimental value of the optical density at t = 15000 s. Sedimentation studies were carried out for the types of dispersed particles presented in Table 1.

The particle sedimentation curve (1) confirms the uneven size distribution function of the initial particles (Fig. 2a). It should be noted that, without preliminary ultrasonic treatment, significant agglomeration of the initial particles was observed. Therefore, such treatment is necessary for the encapsulation. Sedimentation curve 2 confirms the formation of PLA sheaths on the particle surfaces. The formation of a polymer sheath leads to a smoothing of the particle size distribution function (Fig. 2b), which, probably was caused by the equalization of the particle shape due to the sheath formed on their surfaces.

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Table 1. Description of sedimented particles

Curve number	Description of particle type	The solution in which sedimentation was performed	Treatment of particles in the solution before the experiment
1	Initial copper oxide (I) particles	PLA solution in a mixture of benzene and hexane in a ratio corresponding to the encapsulation process	Ultrasonic treatment (power of 50 W) for 60±10 s. Mixing with a magnetic stirrer for 10 min.
2	Copper (I) oxide particles encapsulated by PLA: $h \sim 125$ nm	PLA solution in a mixture of benzene and hexane in a ratio corresponding to the encapsulation process	Mixing with a magnetic stirrer for 10 min.
3	Copper (I) oxide particles encapsulated by PLA: $h \sim 125$ nm	PLA solution in a mixture of benzene and hexane in a ratio corresponding to the encapsulation process	Ultrasonic treatment of the solution of particles (power of 50 W, treatment time of 10 min) for the removal of the sheath from the particle surfaces
4	Капсулированные ПЛА частицы оксида меди (I): $h \sim 125$ nm	Benzene	Mixing with a magnetic stirrer (12 h) followed by ultrasonic treatment (50 W, treatment time of 5 min) for the removal of the sheath from the particle surfaces

The sheath thickness on the surfaces of copper (I) oxide particles was not the same. The polymer sheath was formed on the surface of all initial particles with equal probability: the deposition curve *2* for the entire time interval was below the deposition curve *1*.

The shape of sedimentation curves *3* and *4* indicates that after treatment with ultrasound and treatment in a solvent, for PLA, the sheath comes off the surface of the particles. Thus, curve *3* was characterized by a significant decrease in the size of the deposited particles and an increase in the equilibrium level (indicated by the dotted line in Fig. 6) of the optical density (*D*). An increase in the equilibrium level of optical density indicates that after ultrasonic treatment, the PLA sheath is destroyed, and its parts with the density significantly lower than the density of dispersed particles, led to an additional increase in the equilibrium level of the optical density of the solution. This determined the difference in the shape of the sedimentation curves *1* and *3*. The shape of the sedimentation curve *4* indicates the complete dissolution of the PLA sheath. In this case, there was an increase in the viscosity of the liquid phase of the solution (taken into account in Fig. 6) and an increase in the sedimentation time of the dispersed particles. The increase in the viscosity of the liquid phase of the solution was taken into account according to the procedure

described in [32].

The obtained results show that the considered method of encapsulation of dispersed particles allows to ensure with equal probability the formation of a polymer sheath on copper (I) oxide particles of all sizes. In this case, the thickness (*h*) of the polymer sheath was uneven on each of the particles. The uneven thickness *h* was probably determined by the habit of the initial
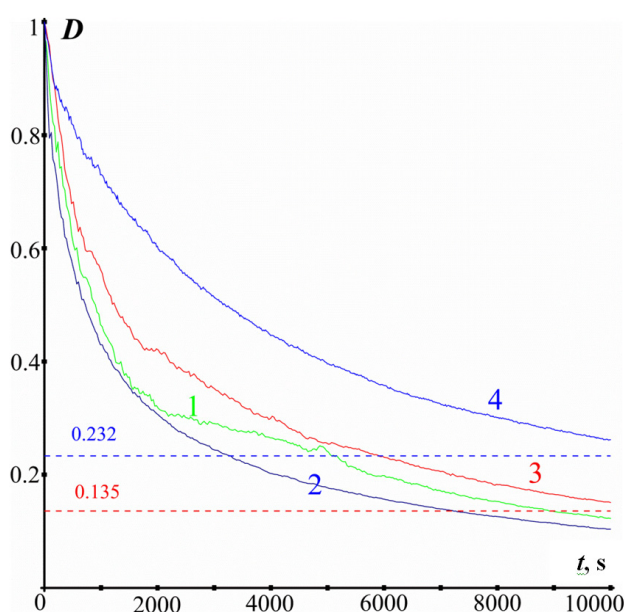

Fig. 6. Change in the optical density of solutions over time in photometric measurements. An explanation for the curve numbers are given in Table 1

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particles. The adhesion of the PLA sheath to the surface of the copper (I) oxide particles is weak and is determined by the surface roughness of the copper (I) oxide particles.

The study of the adhesion of the PLA sheath to the polymer matrix was carried out by comparing the mechanical characteristics of polymer composites based on epoxy resin ED-20 filled with encapsulated and non-encapsulated particles. Mechanical characteristics were studied for the following three samples: Sample 1 was without a filler, sample 2 was filled with non-encapsulated copper (I) oxide particles, sample 3 was filled with encapsulated copper (I) oxide particles. The concentration of particles in samples 2 and 3 was ~0.92±0.02 wt %. The sheath thickness on the surfaces of the encapsulated particles was ~25 ± 5 nm. The mechanical characteristics (Martens hardness HMs, N/mm^2; maximum stress σ, N/mm^2; ultimate strain ε, %) of the samples are presented in Table 2. Ten samples of each type were used in the experiment. The obtained values of mechanical characteristics were averaged. The error of the measured values of the mechanical characteristics was not higher than 15%.

Table 2. Values of the mechanical characteristics of the samples

Sample type	HMs, N/mm^2	σ, N/mm^2	ε, %
Sample 1	83.03	73.92	1.53
Sample 2	118.5	80.5	1.43
Sample 3	158.6	86.5	1.01

An increase in the average hardness and maximum stress values, and a decrease in maximum deformation for sample 3 was associated with a decrease in the mobility of matrix polymer macromolecules. This is possible with an increase in the adhesion of encapsulated particles to the matrix polymer, in contrast to unencapsulated particles [12, 13]. It should be noted that the thickness of the sheath significantly affects the mechanical properties of the composite polymer material. For the choice of the thickness of the polylactide sheath, in this case, we were guided by the results obtained in [12].

4. Conclusions

The considered method of forming a polylactide sheath on the surfaces of copper (I)

oxide particles, based on initiating the process of polylactide coacervation from a solution, allows obtaining a sheath with a thickness not higher than ~250 nm. The reason for this limitation is, in our opinion, the following factors: the process of agglomeration and subsequent sedimentation of aggregates with an increase in the concentration of the displacing solvent (hexane) by more than 30% by volume; a decrease in the number of PLA molecules in a solution after the addition of a displacing solvent during mixing. It should be noted that there is an extremum in the dependence of the sheath thickness on the temperature of the solution, observed at T = 35÷38 °C. The PLA sheath has weak adhesion to the surfaces of copper (I) oxide particles and is determined by the roughness of the surfaces of dispersed particles. An increase in the mechanical characteristics of samples of a polymer composition based on epoxy resin ED-20 filled with encapsulated particles compared to samples filled with initial particles indicates an increase in the adhesion of encapsulated particles to such a polymer matrix. Thus, the use of dispersed copper (I) oxide particles encapsulated by polylactide as a filler for epoxy resin ED-20 can not only provide increased resistance to biodegradation of such composites [33, 34], but also improves their mechanical characteristics.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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