Novel epoxy-based biocidal composite material filled with polylactide-capsulated copper (I) oxide particles

Maxim Danilaev
Kazan National Research Technical University named after A.N. Tupolev-KAI, 10, K. Marx str., 420011, Kazan, Rus-sian Federation, danilaev@mail.ru

Safaa.M.R.H. Hussein
University of Karbala, Karbala, 56001, Iraq,

Elena Bobina
Kazan National Research Technical University named after A.N. Tupolev-KAI, 10, K. Marx str., 420011, Kazan, Rus-sian Federation

Sergey Karandashov
Kazan National Research Technical University named after A.N. Tupolev-KAI, 10, K. Marx str., 420011, Kazan, Rus-sian Federation,

Vladimir Kuklin
Kazan National Research Technical University named after A.N. Tupolev-KAI, 10, K. Marx str., 420011, Kazan, Rus-sian Federation,

See next page for additional authors

Follow this and additional works at: https://kijoms.uokerbala.edu.iq/home

Recommended Citation

Novel epoxy-based biocidal composite material filled with polylactide-capsulated copper (I) oxide particles

Abstract

To maintain performance of polymer composite materials (PCM) in tropical climate, it is necessary and relevant to deal with biodegradation among other factors. Increasing strength and improvement of biodegradation resistance of polymer composites simultaneously is a critical practical challenge. State-of-the-art methods of polymer composites production do not provide a possibility to address both issues at the same time. In this study, it is the first time when a method to increase strength of ED-20 epoxy-based polymer composite and improve its biodegradation resistance simultaneously is applied. In this study, the authors applied for the first time polylactide-capsulated copper oxide particles to improve biocidal and mechanical performance of ED-20 epoxy-based polymer composite. It was established that composite filled with capsulated particles has better resistance to micromycete-induced damage compared to the one filled with non-capsulated particles. Reduction of surface area affected by micromycetes isolated from samples exposed to tropical conditions was demonstrated for the composite that contained capsulated particles. The paper highlights that prevalence of Aspergillus niger is based on the high productivity of organic acids. It was found that elasticity moduli of polymer composite samples do not have significant differences. The average elasticity modulus of PCM samples was 3.4 ± 0.2 GPa before and after exposure to tropical conditions. Apparently, the thing that elasticity modulus remained the same after exposure to tropical conditions was due to the fact that only surface of the sample was subject to destruc-tion. The samples with non-capsulated particles experienced 20% decrease in ultimate strength after exposure to tropi-cal conditions while the samples with capsulated particles experienced only 10% decrease, so the material with capsu-lated particles was stronger. The fact that the elastic moduli of samples with capsulated particles remain the same after exposure to the microbial destructors indicates improved resistance of new PCM to biodegradation and confirms prom-ising practical application of the created material. Thus, this article is the first one to demonstrate that application of polylactide-capsulated copper oxide particles in combination with ED-20 epoxy-based polymer provides a possibility to obtain a new composite with improved biocidal effect

Keywords

biodegradation, polymer composite, encapsulated, submicron particles.

Creative Commons License

Authors

Maxim Danilaev, Safaa.M.R.H. Hussein, Elena Bobina, Sergey Karandashov, Vladimir Kuklin, Mikhail Klabu-kov, Hong Quan Le, Ekaterina Mironskaya, Galina Yakovleva, and Olga Ilinskaya

RESEARCH PAPER

Novel Epoxy-based Biocidal Composite Material Filled with Polylactide-capsulated Copper (I) Oxide Particles

Maxim Danilaev [a,*], Safaa.M.R.H. Hussein [b], Elena Bobina [a], Sergey Karandashov [a], Vladimir Kuklin [a,c], Mikhail Klabukov [a], Hong Q. Le [d], Ekaterina Mironskaya [c], Galina Yakovleva [c], Olga Ilinskaya [c]

[a] Kazan National Research Technical University Named After A.N. Tupolev-KAI, 10, K. Marx str., 420011, Kazan, Russian Federation
[b] University of Karbala, Karbala, 56001, Iraq
[c] Kazan Federal University, 18, Kremlevskaya st., 420008, Kazan, Russian Federation
[d] Coastal Branch of the Joint Vietnam - Russia Tropical Science and Technology Research Center, 30, Nha Trang, Khanh Hoa, Viet Nam

Abstract

To maintain performance of polymer composite materials (PCM) in tropical climate, it is necessary and relevant to deal with biodegradation among other factors. Increasing strength and improvement of biodegradation resistance of polymer composites simultaneously is a critical practical challenge. State-of-the-art methods of polymer composites production do not provide a possibility to address both issues at the same time. In this study, it is the first time when a method to increase strength of ED-20 epoxy-based polymer composite and improve its biodegradation resistance simultaneously is applied. In this study, the authors applied for the first time polylactide-capsulated copper oxide particles to improve biocidal and mechanical performance of ED-20 epoxy-based polymer composite. It was established that composite filled with capsulated particles has better resistance to micromycete-induced damage compared to the one filled with non-capsulated particles. Reduction of surface area affected by micromycetes isolated from samples exposed to tropical conditions was demonstrated for the composite that contained capsulated particles. The paper highlights that prevalence of *Aspergillus niger* is based on the high productivity of organic acids. It was found that elasticity moduli of polymer composite samples do not have significant differences. The average elasticity modulus of PCM samples was 3.4 ± 0.2 GPa before and after exposure to tropical conditions. Apparently, the thing that elasticity modulus remained the same after exposure to tropical conditions was due to the fact that only surface of the sample was subject to destruction. The samples with non-capsulated particles experienced 20% decrease in ultimate strength after exposure to tropical conditions while the samples with capsulated particles experienced only 10% decrease, so the material with capsulated particles was stronger. The fact that the elastic moduli of samples with capsulated particles remain the same after exposure to the microbial destructors indicates improved resistance of new PCM to biodegradation and confirms promising practical application of the created material. Thus, this article is the first one to demonstrate that application of polylactide-capsulated copper oxide particles in combination with ED-20 epoxy-based polymer provides a possibility to obtain a new composite with improved biocidal effect.

Keywords: Biodegradation, Polymer composite, Capsulated, Submicron particles

1. Introduction

Application of polymer composite materials (PCM) components in extreme climates requires their service life to be increased. Biodegradation is one of the factors that contributes to the decrease of the service life. Microbial destructors cause damage to the material by using it as a food source and producing aggressive metabolites [1—3]. An ability of the microorganisms to

produce organic acids and hydrolytic enzymes leads to modification of structural and functional performance of various materials and may cause the "sick building syndrome" [4—7]. Biodegradation of PCM surface leads to microcracks, cavities, increase in surface roughness [8], and destruction of chemical bonds between polymer molecules in the near-surface area under the action of organic acids released by microbial destructors [9].

Although biodegradation of polymer materials has been well studied [9—13], there is still a challenge to ensure targeted biocidal effect of epoxy and polyester resins, for example, and mechanical performance, including strength, simultaneously. A particular feature of the ongoing studies of PCM biodamage is that they are intrinsically applied ones dealing with biocidal effect. Works [14—17] demonstrate results of biodegradation by typical microorganisms and study the methods used to protect polymers. These and other articles do not provide any analysis of a possibility to keep and, moreover, modify mechanical performance of PCM and simultaneously secure their biodegradation resistance.

The main disadvantages of existing approaches to improve biodegradation resistance of polymer composites should be noted.

(i) Application of antimicrobial additives (chlorine compounds, aldehydes, zinc, tin, copper salts, etc.) in protective coatings [18,19] or in composites [17]. The main limitation of this approach is related to the modification of the physics and performance of polymer composites [20] and release of toxic agents that have adverse effects on environment and humans [21—23]. It is possible to keep mechanical properties of such polymer composites only if using nanoparticles [24].

(ii) Application of distributed particles (e.g., silver, silver nitrate, copper oxide, mercury chromate, etc.) that are toxic for the microorganisms in polymer composites [25,26]. This approach has a limitation related to poor adhesion of some particles to matrix polymer. For example, the authors of article [27] synthesized a PCM that demonstrated a biocidal effect due to zinc oxide particles. And there was a decrease in strength of such PCM compared to the polymer without the particles due to poor adhesion of particles to matrix polymer.

However, in some cases application of nanoparticles provides a possibility to improve mechanical performance of polymer materials [28,29]. Encapsulating nanoparticles in polymer increases their adhesion to polymer matrix and thus improves mechanical performance of a composition [30,31]. Biodegradable polymers, for example, polylactide [32], as capsulating material for distributed particles may not only improve mechanical performance of PCM, but also be a food source for the microorganisms, providing access to toxic particles [33]. Enzymes and organic acids that microorganisms synthesize when they interact with capsulating material promote the release of distributed particles, such as copper (I) oxide, and formation of ions that are about three times more toxic than the nanoparticles themselves [34,35]. This is a local process that takes place in the areas where polymer composite is affected by the microorganisms and leads to the destruction of the latter. Thus, application of biocidal distributed particles capsulated with a biodegradable polymer, e.g., copper oxide particles, makes it possible to improve biodegradation resistance of polymer composites and their performance.

The aim of this study is to create a new polymer composite based on ED-20 epoxy resin and filled with polylactide-capsulated copper oxide particles and to examine biocidal and mechanical performance of this composite compared to the composite filled with non-capsulated particles.

First, polylactide-capsulated copper oxide particles with specified capsulating thickness were obtained, and a small weight fraction of these particles was introduced into ED-20 epoxy resin-based polymer composite. Then, the authors studied biodegradation resistance of the polymer composite samples in the laboratory. Finally, certain changes in mechanical performance and structure of the samples caused by the microorganisms were described. Thus, the evidence was obtained that filling polymer composites with capsulated copper oxide (Cu_2O) particles had the potential to improve performance and biodegradation resistance of polymer composites.

2. Materials and methods

2.1. Obtaining polylactide-capsulated Cu_2O distributed particles

Cu_2O distributed particles were capsulated by polylactide (PLA 4043D by Natural Works LLC) by initiating its coacervation from benzene solution, gradually adding hexane [36].

Polylactide (PLA) benzene solution was prepared in 200 ml round-bottom flask. PLA particles with the mass of 0.75 ± 0.05 g were dissolved in 50 ± 1 g of benzene by stirring using magnetic stirrer during

6 h ($\pm$10 min) at 35 $\pm$ 2 $^{\circ}$C. The capsulating was applied on Cu_2O particles with the average size of 500 nm (Fig. 1A). The following values were selected for experiments: the mass of displacing solvent (hexane) was 10 $\pm$ 1 g, the mass of copper oxide particles in suspension was 1 $\pm$ 0.1 g Cu_2O particles (1 $\pm$ 0.1 g) and benzene (25 $\pm$ 2 g) were placed in an ultrasonic cleaner (Daihan WUC-A01H, 50 W), dispersion took 1 $\pm$ 0.1 min. After homogenization, the suspension was placed into a 100 ml glass. Then, 50 $\pm$ 1 g of benzene with polylactide was introduced into the suspension while continuously stirring on a magnetic stirrer at 35 $\pm$ 2 $^{\circ}$C, and then hexane, a displacing solvent, was introduced using addition funnel at a rate of 7 $\pm$ 2 drops per minute. Coacervation — displacement of polylactide molecules from its benzene solution and the following precipitation on Cu_2O particles — was initiated as a result of displacing solvent introduction. After the entire amount of hexane (10 $\pm$ 1 g) was introduced, the suspension was being stirred for 10 $\pm$ 1 min and then filtered to obtain polylactide-capsulated Cu_2O particles (Fig. 1B). It should be noted that the following main factors have an effect on the thickness of polylactide coating on the surface of copper oxide particles: temperature of solution, hexane introduction rate, the time of particles exposure to the solution, particles and polylactide concentrations in the solution [37]. These parameters remained the same in this study, so the thickness of polylactide coating on the surface of copper oxide particles was the same for all samples.

2.2. Producing polymer composite samples

Polymer composite samples were produced by introduction of polylactide-capsulated Cu_2O particles and non-capsulated Cu_2O particles into the ED-20 resin. 200 ml glass was filled with ED-20 resin, and it was heated to 35 $\pm$ 2 $^{\circ}$C in a water bath. Cu_2O particles were introduced with continuous stirring. Even distribution of the particles in the epoxy resin was secured by the stirring rate of ~10 $\pm$ 1 rpm, particles introduction rate was 0.1 $\pm$ 0.05 g/min, stirring time was 30 $\pm$ 5 min. M4 hardener (ISO 7327:1994) was introduced into the suspension at a ratio of 1:6 to epoxy resin with continuous stirring, and then the stirring was being performed for 15 more minutes. After that, the suspension was placed into the cylindrical mold that had a net-shape of the samples (Ø9 $\pm$ 1 mm, 50 $\pm$ 2 mm high). The samples stayed in the mold for 24 $\pm$ 3 h until the epoxy was fully cured at ambient temperature of 18 $\div$ 25 $^{\circ}$C and humidity of 30 $\div$ 60%.

Biocidal and mechanical performance of polymer composite samples were studied for different concentrations of particles in the samples. Classification of the samples is presented in Table 1.

2.3. Isolation and identification of micromycetes from the surface of polymer composite samples

Polymer composite samples were kept for 6 months at the climatic testing stations of the joint Russian-Vietnamese Research and Technology Center. Mycological stands with the samples were located in a way to avoid sunlight. After exposure, the samples were delivered to the laboratory, where the identification of strains in the detected microbial fouling and analysis of changes in the mechanical and optical performance of the samples were carried out.

To do that, each sample was placed in a flask with 5 ml of sterile tap water and given a shake. 0.1 ml of suspension was applied on the surface of the broth
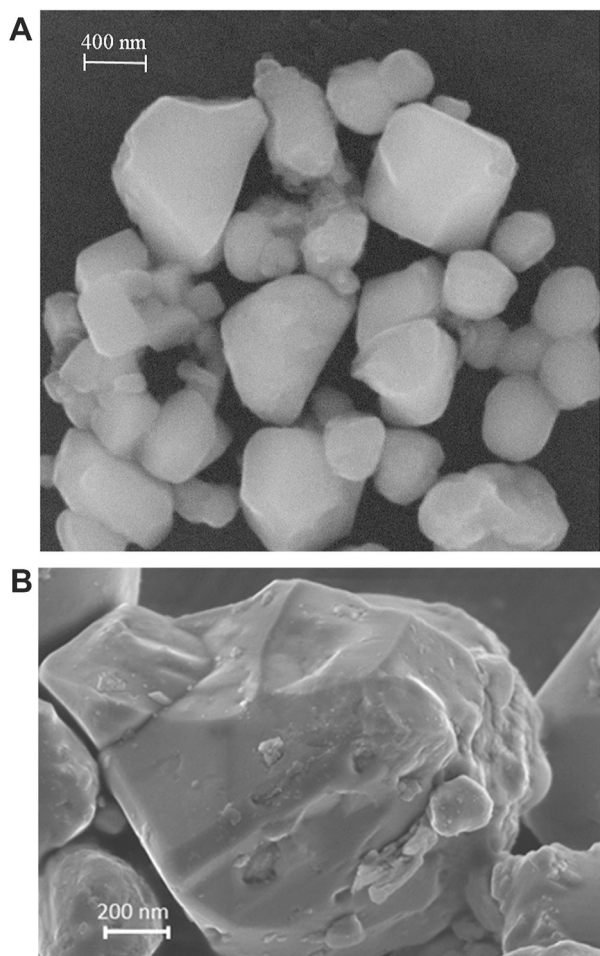

Fig. 1. Standard micrographs of Cu_2O particles: A — non-capsulated particles; B — capsulated particles.

Table 1. Samples used to study resistance to micromycetes.

Samples	Capsulated?	Mass fraction (C) of Cu_2O particles, %
Sample 0	–	0
Sample 1.1	–	0.05 ± 0.01
Sample 1.2	–	0.16 ± 0.02
Sample 1.3	–	0.33 ± 0.03
Sample 1.4	–	0.5 ± 0.05
Sample 1.5	–	0.67 ± 0.07
Sample 1.6	–	0.83 ± 0.09
Sample 1.7	–	1.1 ± 0.1
Sample 2.1	+	0.05 ± 0.01
Sample 2.2	+	0.16 ± 0.02
Sample 2.3	+	0.33 ± 0.03
Sample 2.4	+	0.5 ± 0.05
Sample 2.5	+	0.67 ± 0.07
Sample 2.6	+	0.83 ± 0.09
Sample 2.7	+	1.1 ± 0.1

in Petri dishes and evenly distributed over the entire diameter. Czapek's medium (g/l) was used: $NaNO_3$ − 2.0; KH_2PO_4 − 1.0; $MgSO_4 \times 7H_2O$ − 0.5; KCl − 0.5; $FeSO_4$ − 0.01; sucrose − 30.0; agar − 20.0. The dishes were incubated in a thermostat at 30°C for 7 days. The obtained micromycetes were identified based on morphology and cultural properties.

2.4. Polymer composite resistance to biodegradation

Polymer composite samples were sprinkled with sterile Czapek's medium and placed into sterile plastic containers. Testing was performed at 30°C and relative humidity exceeding 90%. To reach such humidity, a small amount of sterile distilled water was poured into the bottom of the chamber. The testing lasted for 28 days with an interim inspection after 7 days. The chamber was uncovered for 3−5 min every 7 days to ensure some air inflow.

The micromycetes fouling area of samples was calculated from photographs using the ImageJ program, version 1.53. The area of fouling was expressed as the ratio of affected areas (S1) to the affected area (S0) of the Sample 0. MicroMed microscope with FMA050 Touptek Photonics adapter with 0.1 μm resolution was used to obtain optical images of the samples.

2.5. Study of the structure and mechanical performance of the samples

Carl Zeiss AURIGA CrossBeam station with Inca X-Max 80 mm^2 SDD was used to study the structure of polymer composite samples as well as capsulated and non-capsulated Cu_2O particles. The experiment was carried out under the following conditions: vacuum − at least $1 \cdot 10^{-5}$ Pa, temperature − 23°C. All samples were fixed on sample holder using

conducting carbon adhesive tape (cat. № G3939, Agar Scientific, UK) for electron microscopy. Primary electron beam current was ~$10 \cdot 10^{-9}$ A, acceleration voltage was 5 kV. The thickness of polylactide capsulating on Cu_2O distributed particles was determined based on the size of capsulated and non-capsulated particles. The images (Fig. 1) were statistically processed in ImageJ software to determine the thickness of the capsulating. The number of particles for which statistical processing was carried out was approx. 800−1300. The average thickness (h) of polylactide capsulating on copper oxide particles was determined the following way:

$$h = (d_2 - d_1) / 2$$

Here, d_2 is the size of capsulated particles that corresponds to the maximum of distribution chart (Fig. 2B), d_1 is the size of non-capsulated particles that corresponds to the maximum of distribution chart (Fig. 2A).

Mechanical performance was studied on Shimadzu AG-X 50 kN testing machine with the
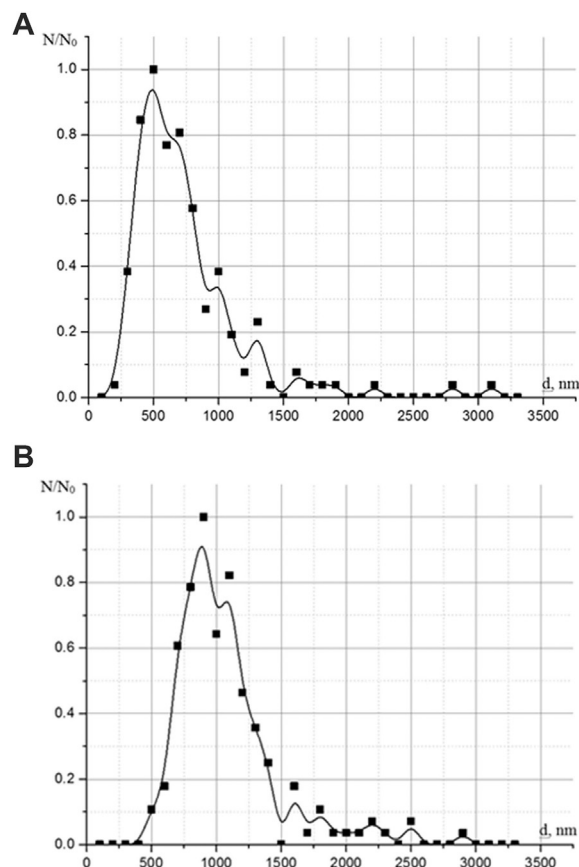

Fig. 2. Particles size distribution: A − non-capsulated particles; B − capsulated copper (I) oxide particles; N − the number of particles with a certain size, N_0 − the number of particles (~100) that corresponds to the maximum in the distribution.

following testing parameters: compression rate was 0.1 mm/min, ambient temperature was 23 ± 2 °C. Shimadzu Trapezium X software was used. Accuracy grade of the testing machine was 1%. The measurements were performed each 0.2 msec, which ensures the accuracy of compression diagrams.

3. Results

3.1. Characteristics of capsulated Cu_2O particles and their adhesion to matrix polymer

It is known that the temperature of solution, the volume of displacing solvent and solution stirring time define the thickness of the capsulating when it is being applied [38]. The conditions for capsulating application were constant, and calculated average thickness (h) of the capsulating was ~150 nm. Capsulated particles sample increase did not change distribution charts (Fig. 2).

With particles' size increase, polylactide capsulating thickness increased pro rata. In fact, the shape of distribution charts for capsulated and non-capsulated particles remained the same; the width of the charts (Fig. 2) at 0.5 for capsulated and non-capsulated particles was the same: ~500 nm. Surface roughness (dispersion component of the surface energy of the particles) determines adhesion of polylactide capsulating to the Cu_2O particles. The method used to introduce capsulated particles into polymer matrix secured the capsulating (Fig. 3).

The quality of adhesion of capsulated and non-capsulated Cu_2O particles to the matrix polymer was assessed by the wettability of these particles. Micrographs of the chips on the samples after compressive testing were analyzed to perform the assessment (Fig. 3). It is found that wettability of capsulated particles by matrix polymer is better compared to non-capsulated ones.

3.2. Isolating pure micromycetes culture from the surface of polymer composite samples and their initial identification

Four types of microscopic fungi were isolated from the surface of the samples incubated for 6 months in tropical conditions: *Aspergillus*, *Penicillium*, *Fusarium*, and *Alternaria*. The major part of micromycetes (81%) were *Aspergillus* and *Penicillium*. The rest 19% were *Fusarium* (10%) and *Alternaria* (9%). The most common fungus on the surface of the samples was *Aspergillus niger*. It should be noted that spores of all identified micromycetes were present on all the samples under study.
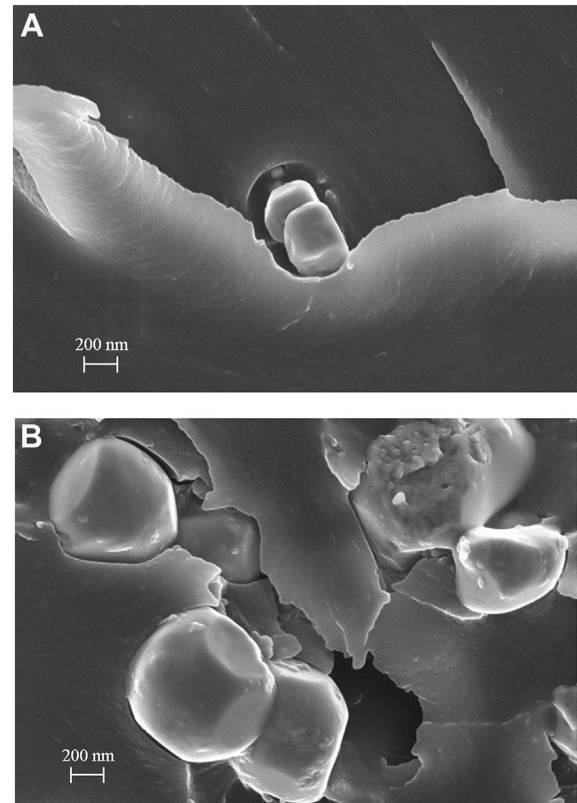
Fig. 3. Standard micrographs of chips on the samples containing copper oxide: A — non-capsulated; B— capsulated.

3.3. Micromycetes resistance of polymer composite samples

The effect of Cu_2O on micromycetes resistance of polymer composite samples was assessed by the rate of germination of micromycetes spores located on the surface of the samples. For this purpose, favorable conditions were created.

(i) optimum temperature and humidity;
(ii) the broth (sprinkling with Czapek's medium).
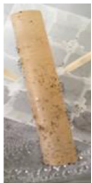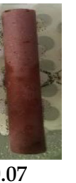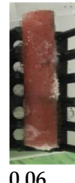
Mycelia and conidiophores of *A. niger*, both on the control samples (without Cu_2O particles) and on the samples with 0.05% and 0.16% of Cu_2O particles, were identified on the third day. The fouling area on the samples with capsulated particles was visually smaller. Starting from incubation day 7, intensive growth of *A. niger* on the samples without Cu_2O particles and samples with non-capsulated Cu_2O particles in the amount not exceeding 0.67% was highlighted. At higher Cu_2O content, the growth was insignificant. Introduction of capsulated particles into ED-20 resin resulted in the decrease of fouling area at 0.05−0.67% of Cu_2O and suppression of spore fouling at higher

content. On the samples with 0.05–0.33% Cu_2O content, *Aspergillus* и *Penicillium* growth was identified, apart from *A. niger*, regardless of the type of the particles introduced. However, following the further incubation *A. niger* suppressed their growth completely (Table 2). Rate is an average rate of fungi growth on the surface of the samples in a time period indicated in the first column of Table 2.

After 28 days, micromycetes fouling was washed off the samples. Microscopy demonstrated the presence of residual micromycetes hyphae on the surface of the samples with non-capsulated particles (Fig. 4A). The depth of decay did not exceed samples roughness (Ra): it was ~0.6 μm before exposure to tropical conditions and approx. 4.2 μm after the exposure (the samples with non-capsulated Cu_2O particles) and 3.25 μm (the samples with capsulated particles). Micromycetes affected area (S_1) decreased with increasing content (C) of the distributed particles in relation to the affected area ($S_0 \approx 10.35$ cm^2) of the Sample 0 (Fig. 4B). Here, this decrease was more significant for the samples filled with capsulated particles.

Table 2. An effect of Cu_2O particles on the growth of microscopic fungi on the surface of polymer composite samples.

Days	Cu_2O	Cu_2O content (%) in ED-20 samples							
		0	0.05	0.16	0.33	0.5	0.67	0.83	1.1
7	non-capsulated								
	Rate, cm^2/day		0.12	0.10	0.10	0.09	0.07	0.07	0.05
	capsulated								
	Rate, cm^2/day	0.09	0.08	0.06	0.06	0.04	0.03	0.03	0.02
21	non-capsulated								
	Rate, cm^2/day		0.32	0.25	0.25	0.24	0.18	0.17	0.14
	capsulated								
	Rate, cm^2/day	0.31	0.30	0.22	0.20	0.13	0.11	0.09	0.06
28	non-capsulated								
	Rate, cm^2/day		0.35	0.28	0.27	0.27	0.20	0.19	0.15
	capsulated								
	Rate, cm^2/day	0.36	0.35	0.26	0.24	0.15	0.13	0.11	0.08
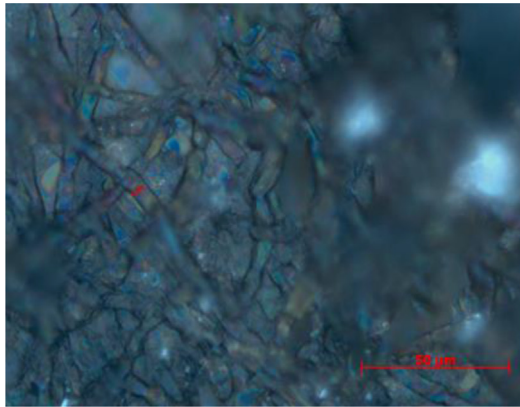
A
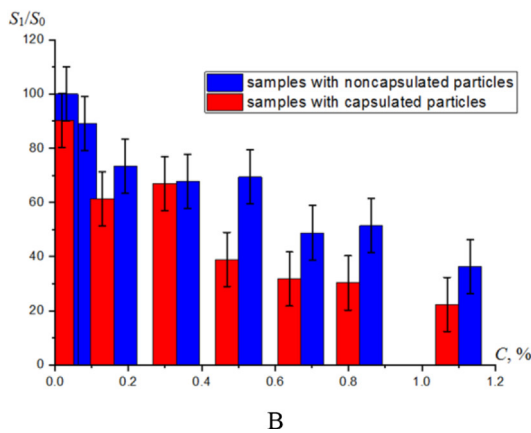
B

Fig. 4. Micromycetes attack: A − micromycetes hyphae on the surface of the samples with 1.1% non-capsulated Cu_2O particles after the fouling was washed off; B − relative micromycetes fouling area vs. Cu_2O particles content.

3.4. Mechanical performance of polymer composite samples

It was established that elasticity modulus (E_0) of polymer without any particles was ~3.4 ± 0.2 GPa. The dependence between $\alpha = E_2/E_1$ (a ratio between elasticity moduli of samples with capsulated (E_2) and non-capsulated (E_1) particles) and Cu_2O content is presented in Fig. 5.

It is found that elasticity moduli of the samples in Table 1 are defined only by the polymer and do not experience significant changes with a change in the concentration of capsulated and non-capsulated particles. It should be noted that after exposure to tropical conditions elasticity modulus remains the same taking into account measurement error. It happens due to the fact that micromycetes attack only the surface of the samples. However, exposure of the samples to microbial destructors may lead to changes in their strength. It was established that polylactide (capsulating material) has an effect on the strength of polymer composite samples. Ultimate relative strain ($\Delta\epsilon_0(0)$) of the polymer composite before and after biocorrosion testing was 2.8 ± 0.4% and 2.55 ± 0.3%, respectively. Ultimate strength ($\Delta\sigma(0)$) before and after testing was 53.3 ± 4 N/mm² and 45.5 ± 5 N/mm², respectively. Differences in strength of samples filled with capsulated and non-capsulated particles should be noted. Ultimate strength of the samples filled with capsulated particles is 1.4 times lower compared to the samples filled with non-capsulated particles,
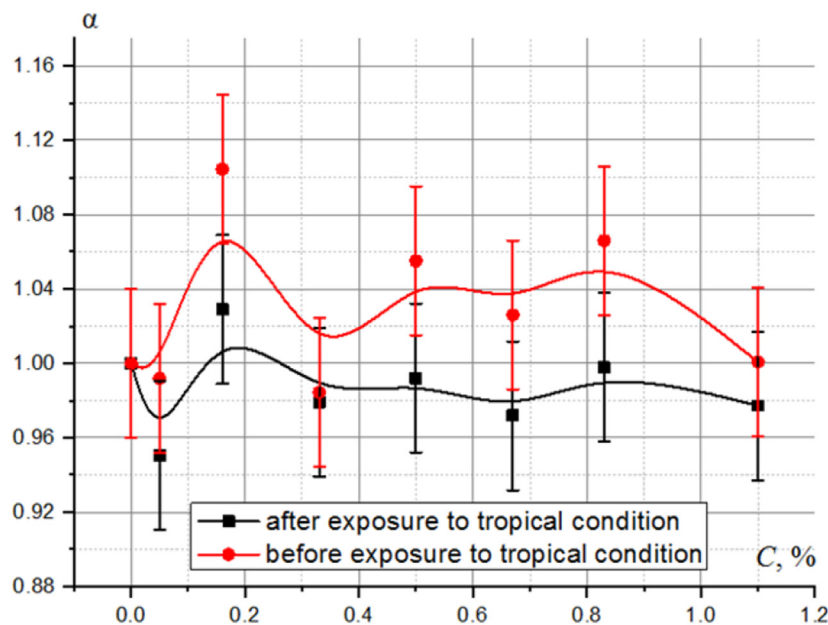
Fig. 5. α vs. particles content in the polymer composite. Measurement error did not exceed 10%.

and ultimate strain is 1.3 times higher (when particles content $C = 1\%$). It happens, because the capsulating has an effect on mechanical performance of the polymer composite [30,36]. Strength performance decreases after exposure to tropical conditions. Ultimate strength of the samples filled with capsulated particles demonstrates 10% decrease and ultimate strain — 15% decrease ($C = 1\%$). As for the samples with non-capsulated particles, the decrease is 20% and 15%, respectively ($C = 1\%$).

4. Discussion

4.1. Characterization of the obtained material

Characterization of the obtained new material with polylactide-capsulated Cu_2O particles included elasticity modulus, ultimate strength and ultimate

strain compared to the material filled with non-capsulated particles.

It was demonstrated earlier that if the matrix polymer and capsulating polymer had significantly different elasticity moduli, then elasticity moduli of polymer composites filled with non-capsulated and capsulated particles with polymer capsulating thickness exceeding 50 nm would be different as well [39]. In our study, elasticity moduli of matrix polymer based on ED-20 resin (~3.4 ± 0.2 GPa) and polylactide 2 ÷ 3 GPa [38], (Fig. 5) have close values. That is why elasticity moduli of polymer composite samples do not have significant differences. It is critical to note that elasticity moduli of the materials are the same before and after expose to tropical conditions (Fig. 5).

It was demonstrated earlier that surface decomposition of the samples by the microorganisms
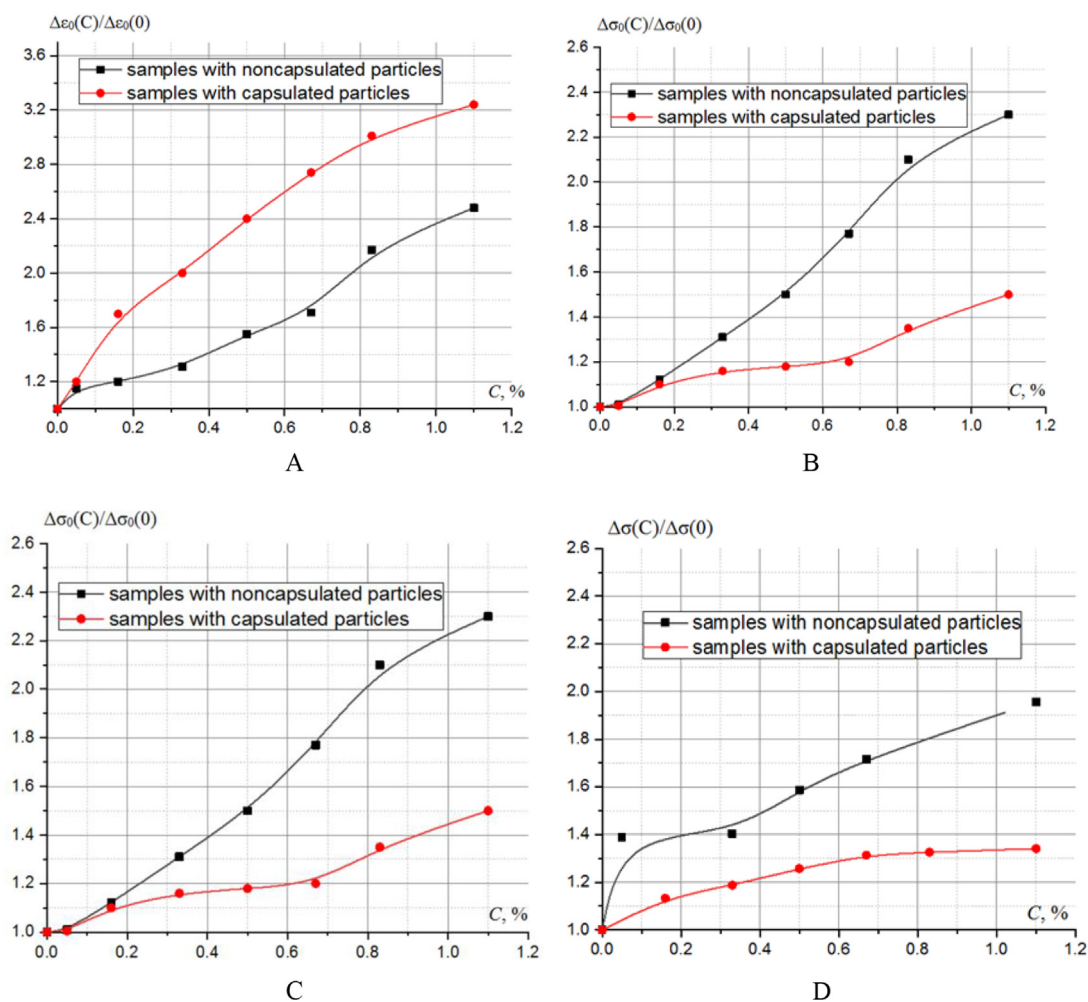
Fig. 6. Strength performance of the polymer composite based on non-capsulated and capsulated copper (I) oxide particles content: (A, B) − relative ultimate strain before and after exposure to tropical conditions, respectively; (C, D) − ultimate strength before and after exposure to tropical conditions, respectively. Measurement error did not exceed 10%.

affected the strength of the material [39]. As it was assumed, difference in mechanical performance of polymer composites filled with capsulated and non-capsulated particles appeared in their strength values (Fig. 6).

This difference in strength is caused by the polylactide capsulating [30,36]. Apparently, polylactide has better plasticity compared to ED-20 resin-based polymer which is reflected in increased relative ultimate strain of the samples (Fig. 6A and B) compared to the samples filled with non-capsulated particles.

Samples filled with capsulated particles have lower ultimate strength compared to samples filled with non-capsulated particles (Fig. 6C and D) because of two reasons.

(i) Polylactide has lower ultimate strength compared to matrix polymer [40,41].
(ii) Matrix polymer has higher stiffness near capsulated particles due to decrease in macromolecular mobility [30].

Increased interaction between particles and macromolecules of the polymer leads to enhanced wettability of capsulated particles (Fig. 3B) [30,42]. This interaction leads to limited mobility of macromolecules and, as a result, increases stiffness of polymer matrix near such particles.

It should be noted that the best wettability of capsulated particles with matrix polymer promotes decrease in the number of agglomerates [43]. Presence of agglomerates significantly affects mechanical performance of polymer composite, decreasing its strength [44]. Enhanced wettability of the particles with matrix polymer promotes the increase in resistance to the motion in epoxy resin when stirring. It decreases the frequency of non-elastic collisions between the particles and, consequently, decreases the number of agglomerates of such particles [45]. The authors did not determine agglomerates content in the samples, but they found that wettability of capsulated particles with matrix polymer is better compared to wettability of non-capsulated particles. This fact indirectly indicates the smaller number of agglomerates in the material with capsulated particles and its better mechanical performance.

4.2. The effect of micromycetes on the obtained material

Filling ED-20-resin based composite with distributed polylactide-capsulated Cu_2O particles provides a possibility to increase biodegradation resistance of polymer composites and simultaneously increase such strength characteristics as ultimate strain (Fig. 6A, B). Experimental studies demonstrated that the main factor that influenced mechanical performance of a composition was viscoelasticity of polymer capsulating. After exposure to microbial destructors that leads to an even insignificant fouling of the material surface, the strength of the samples decreases. It is known that degradation of polymer material in most cases is induced by defects on its surface [39]. More in-depth decay of samples filled with non-capsulated particles due to micromycetes attack is the reason for a greater decrease in the strength properties of these samples. A decrease in ultimate strength of the samples filled with non-capsulated particles after exposure to tropical conditions was 20%, and 10% for the samples filled with capsulated particles. That increases the strength of the material at the same ultimate strength decrease of ~15% (Fig. 6C and D). Unchanged elasticity modulus (Fig. 6) of the samples filled with capsulated particles and increase in their ultimate strain (Fig. 6 A, B) even after their exposure to microbial destructors indicates an increase in biodegradation resistance of the new polymer composite.

It was established that the area affected by micromycetes got reduced with an increase in distributed particles content (Fig. 4B). At the same time, this reduction was more significant for the samples with capsulated particles compared to the material with non-capsulated particles. Antimicrobial effect of copper is well-known. It is shown that toxicity of copper oxide nanoparticles is linked to production of reactive oxygen species and reactive nitrogen species and about three times less than that of the copper ion [34,44]. Copper oxide particles demonstrate antifungal activity [35]. Toxicity of copper oxide particles was mainly driven by copper ions released from particles. Copper ions release from nanoparticles is induced by acids [45]. In nature, Cu_2O is slowly oxidized to copper (II) hydroxide that reacts with organic acids produced by micromycetes and forms more toxic soluble salts, e.g., copper citrate. Cu^{2+} ion modulated production of organic acids by micromycetes and induced disturbances of the mycelium growth; at the same time, crystalline copper oxalate is accumulated in the mycelium of *Penicillium,* but not in *Aspergillus.* This interesting fact partly explains why *Aspergillus* fungi supersede *Penicillium* fungi that are more apt to the toxic effects of copper salts. *A. niger* isolated from the surface of materials exposed to tropical conditions produces an especially large number of organic salts [46], and that explains its final prevalence on the samples.

5. Conclusion

The study demonstrates that combination of polylactide-capsulated copper oxide particles with ED-20 epoxy-based polymer results in a new composite with enhanced biocidal effect. An approach to production of polymer composites with biocidal effect suggested in this paper may be applied for composite components operating in tropical conditions. It should be noted that after exposure of the samples to tropical conditions in The Tropical Center (T 1.12 program), among micromycetes obtained from samples, *A. niger* prevailed due to the fact that this fungus produced large amounts of organic acids. Biocidal efficiency of polylactide-capsulated particles in the samples is confirmed by the smaller damaged area in the samples filled with capsulated particles compared to the material filled with non-capsulated ones.

It should be noted that elasticity moduli of the samples do not depend on the type of the particles (capsulated or non-capsulated). Elasticity modulus of 3.4 ± 0.2 GPa did not change after exposure of the samples to the tropical conditions. The same elasticity moduli of the samples with capsulated and non-capsulated particles are explained by the close elasticity moduli values of ED-20 epoxy-based matrix polymer and coating polymer (polylactide). Apparently, the thing that elasticity modulus remained the same after exposure to tropical conditions was due to the fact that only surface of the sample was subject to destruction. Surface roughness after exposure to tropical conditions increased 7 times for the samples with non-capsulated particles (average damage depth was 4.2 µm) and 5.4 times for the samples with capsulated particles (average damage depth was 3.25 µm). Surface damage after exposure to tropical conditions led to a decrease in mechanical performance of the samples. The samples with non-capsulated particles experienced 20% decrease in ultimate strength after exposure to tropical conditions while the samples with capsulated particles experienced only 10% decrease, so the material with capsulated particles was stronger.

The fact that the elastic moduli of samples with capsulated particles remain the same after exposure to the microbial destructors indicates improved resistance of new PCM to biodegradation and confirms promising practical application of the created material. Thus, this article is the first one to demonstrate that application of polylactide-capsulated copper oxide particles in combination with ED-20 epoxy-based polymer provides a possibility to obtain a new composite with improved biocidal effect.

Conflicts of interest

No conflict of interest among authors.

References

[1] A. Omazic, G. Oreski, M. Halwachs, G.C. Eder, C. Hirschl, L. Neumaier, G. Pinter, M. Erceg, Relation between degradation of polymeric components in crystalline silicon PV module and climatic conditions: a literature review, Sol. Energy Mater. Sol. Cell. 192 (2019) 123−133, https://doi.org/10.1016/j.solmat.2018.12.027.

[2] D. Wu, D. Zhang, S. Liu, Z. Jin, T. Chowwanonthapunya, J. Gao, X. Li, Prediction of polycarbonate degradation in natural atmospheric environment of China based on BP-ANN model with screened environmental factors, Chem. Eng. J. 399 (2020) 1−11, https://doi.org/10.1016/j.cej.2020.125878.

[3] T. Pertin, G. Minatchy, M. Adoue, A. Flory, L. Romana, Investigation of nanoindentation as a fast characterization tool for polymer degradation study, Polym. Test. 81 (2020) 1−8, https://doi.org/10.1016/j.polymertesting.2019.106194.

[4] V.C. Castiglia, F. Kuhar, Deterioration of expanded polystyrene caused by Aureobasidium pullulans var. melanogenum, Rev. Argent. Microbiol. 47 (2015) 256−260, https://doi.org/10.1016/j.ram.2015.05.001.

[5] G. Yakovleva, E. Sagadeev, V. Stroganov, O. Kozlova, R. Okunev, O. Ilinskaya, Metabolic activity of micromycetes affecting urban concrete constructions, Sci. World J. 2018 (2018) 1−9, https://doi.org/10.1155/2018/8360287.

[6] O. Ilinskaya, A. Bayazitova, G. Yakovleva, Biocorrosion of materials and sick building syndrome, Microbiol. Aust. 39 (2018) 129−132, https://doi.org/10.1071/MA18040.

[7] B. Sahlberg, M. Gunnbjörnsdottir, A. Soon, R. Jogi, T. Gislason, G. Wieslander, C. Janson, D. Norback, Airborne molds and bacteria, microbial volatile organic compounds (MVOC), plasticizers and formaldehyde in dwellings in three North European cities in relation to sick building syndrome (SBS), Sci. Total Environ. 444 (2013) 433−440, https://doi.org/10.1016/j.scitotenv.2012.10.114.

[8] C.A. Woolnough, T. Charlton, L.H. Yee, M. Sarris, L.J.R. Foster, Surface changes in polyhydroxyalkanoate films during biodegradation and biofouling, Polym. Int. 57 (2008) 1042−1051, https://doi.org/10.1002/pi.2444.

[9] V.K. Plakunov, A.V. Gannesen, S.V. Mart'yanov, M.V. Zhurina, Biocorrosion of synthetic plastics: degradation mechanisms and methods of protection, Microbiology 89 (2020) 647−659, https://doi.org/10.1134/S0026261720060144.

[10] A. Amobonye, P. Bhagwat, S. Singh, S. Pillai, Plastic biodegradation: frontline microbes and their enzymes, Sci. Total Environ. 759 (2021) 143536−143555, https://doi.org/10.1016/j.scitotenv.2020.143536.

[11] N. Atanasova, S. Stoitsova, T. Paunova-Krasteva, M. Kambourova, Plastic degradation by extremophilic

bacteria, Int. J. Mol. Sci. 22 (2021) 1–19, https://doi.org/10.3390/ijms22115610.

[12] J. Guo, S. Yuan, W. Jiang, L. Lv, B. Liang, S.O. Pehkonen, Polymers for combating biocorrosion, Frontiers in Materials 5 (2018) 1–15, https://doi.org/10.3389/fmats.2018.00010.

[13] A.L. Leão, I. Cesarino, M.C. de Souza, O.A.T. Dias, M. Jawaid, Nano-biodegradation of plastic materials, in: R. Bhat, A. Kumar, T.A. Nguyen, S. Sharma, eds., Nanotechnology in Paper and Wood Engineering, Elsevier. 2022, pp. 175–195, https://doi.org/10.1016/B978-0-323-85835-9.00008-8.

[14] J.-D. Gu, Microbial colonization of polymeric materials for space applications and mechanisms of biodeterioration: a review, Int. Biodeterior. Biodegrad. 59 (2007) 170–179, https://doi.org/10.1016/j.ibiod.2006.08.010.

[15] S.K. Mohan, T. Srivastava, Microbial deterioration and degradation of polymeric materials, J. Biochem. Technol. 2 (2010) 210–215.

[16] V.F. Stroganov, D.A. Kukoleva, A.S. Akhmetshin, I.V. Stroganov, Biodeterioration of polymers and polymer composite materials, Polym. Sci. Ser. D. 2 (2009) 164–166, https://doi.org/10.1134/S1995421209030071.

[17] L.P. Wackett, S.L. Robinson, The ever-expanding limits of enzyme catalysis and biodegradation: polyaromatic, polychlorinated, polyfluorinated, and polymeric compounds, Biochem. J. 477 (2020) 2875–2891, https://doi.org/10.1042/BCJ20190720.

[18] A. Lambole, V.N. Lad, Promising soft coating material for protection of foldable substrates exposed to corrosive environment, J. Inorg. Organomet. Polym. 27 (2017) 1090–1099, https://doi.org/10.1007/s10904-017-0559-z.

[19] A. Mukherjee, M. Joshi, S.C. Misra, U.S. Ramesh, Antifouling paint schemes for green SHIPS, Ocean Eng. 173 (2019) 227–234, https://doi.org/10.1016/j.oceaneng.2018.12.057.

[20] A.V. Kurnoskin, Strength of metalliferous epoxy-chelate polymers, J. Macromol. Sci., Part A. 29 (1992) 483–498, https://doi.org/10.1080/10101329208052176.

[21] T. Lomonaco, E. Manco, A. Corti, J. La Nasa, S. Ghimenti, D. Biagini, F. Di Francesco, F. Modugno, A. Ceccarini, R. Fuoco, V. Castelvetro, Release of harmful volatile organic compounds (VOCs) from photo-degraded plastic debris: a neglected source of environmental pollution, J. Hazard Mater. 394 (2020) 1–9, https://doi.org/10.1016/j.jhazmat.2020.122596.

[22] G. Qin, Z. Niu, J. Yu, Z. Li, J. Ma, P. Xiang, Soil heavy metal pollution and food safety in China: effects, sources and removing technology, Chemosphere 267 (2021) 1–12, https://doi.org/10.1016/j.chemosphere.2020.129205.

[23] R. Bharti, R. Sharma, Effect of heavy metals: an overview, Mater. Today: Proc. 51 (2022) 880–885, https://doi.org/10.1016/j.matpr.2021.06.278.

[24] A.K. Thakur, S.A. Hashmi, Polymer matrix–filler interaction mechanism for modified ion transport and glass transition temperature in the polymer electrolyte composites, Solid State Ionics 181 (2010) 1270–1278, https://doi.org/10.1016/j.ssi.2010.06.055.

[25] P. Teper, A. Sotirova, V. Mitova, N. Oleszko-Torbus, A. Utrata-Wesołek, N. Koseva, A. Kowalczuk, B. Mendrek, Antimicrobial activity of hybrid nanomaterials based on star and linear polymers of N,N′-Dimethylaminoethyl methacrylate with in situ produced silver nanoparticles, Materials 13 (2020) 1–15, https://doi.org/10.3390/ma13133037.

[26] A. Kausar, A review of high performance polymer nanocomposites for packaging applications in electronics and food industries, J. Plast. Film Sheeting 36 (2020) 94–112, https://doi.org/10.1177/8756087919849459.

[27] Y. Wang, H. Hua, W. Li, R. Wang, X. Jiang, M. Zhu, Strong antibacterial dental resin composites containing cellulose nanocrystal/zinc oxide nanohybrids, J. Dent. 80 (2019) 23–29, https://doi.org/10.1016/j.jdent.2018.11.002.

[28] E. Çetkin, M.E. Demir, R.K. Ergün, The effect of different fillers, loads, and sliding distance on adhesive wear in woven e-glass fabric composites, Proc. IME E J. Process Mech. Eng. 237 (2023) 418–429, https://doi.org/10.1177/09544089221136808.

[29] R.K. Ergün, H. Adin, Investigation of effect of nanoparticle reinforcement woven composite materials on fatigue behaviors, Iran J Sci Technol Trans Mech Eng 47 (2022) 729–740, https://doi.org/10.1007/s40997-022-00543-8.

[30] A.A. Akhmadeev, E.A. Bogoslov, M.P. Danilaev, M.A. Klabukov, V.A. Kuklin, Influence of the thickness of a polymer shell applied to surfaces of submicron filler particles on the properties of polymer compositions, Mech. Compos. Mater. 56 (2020) 241–248, https://doi.org/10.1007/s11029-020-09876-4.

[31] O.Yu. Bogomolova, I.R. Biktagirova, M.P. Danilaev, M.A. Klabukov, Yu.E. Polsky, S. Pillai, A.A. Tsentsevitsky, Effect of adhesion between submicron filler particles and a polymeric matrix on the structure and mechanical properties of epoxy-resin-based compositions, Mech. Compos. Mater. 53 (2017) 117–122, https://doi.org/10.1007/s11029-017-9645-0.

[32] M.P. Danilaev, N.V. Dorogov, S.V. Drobyshev, S.A. Karandashov, M.A. Klabukov, V.A. Kuklin, Dispersed copper (I) oxide particles encapsulated by polylactide, Condensed Matter and Interphases 25 (2023) 27–37, https://doi.org/10.17308/kcmf.2023.25/10943.

[33] A.P. Gupta, V. Kumar, New emerging trends in synthetic biodegradable polymers – polylactide: A critique, Eur. Polym. J. 43 (2007) 4053–4074, https://doi.org/10.1016/j.eurpolymj.2007.06.045.

[34] A.V. Kadammattil, S.P. Sajankila, S. Prabhu, B.N. Rao, B.S.S. Rao, Systemic toxicity and teratogenicity of copper oxide nanoparticles and copper sulfate, J. Nanosci. Nanotechnol. 18 (2018) 2394–2404, https://doi.org/10.1166/jnn.2018.14542.

[35] S. Naz, A. Gul, M. Zia, R. Javed, Synthesis, biomedical applications, and toxicity of CuO nanoparticles, Appl. Microbiol. Biotechnol. 107 (2023) 1039–1061, https://doi.org/10.1007/s00253-023-12364-z.

[36] F. Ondreas, P. Lepcio, M. Zboncak, K. Zarybnicka, L.E. Govaert, J. Jancar, Effect of nanoparticle organization on molecular mobility and mechanical properties of polymer nanocomposites, Macromolecules 52 (2019) 6250–6259, https://doi.org/10.1021/acs.macromol.9b01197.

[37] M.P. Danilaev, S.A. Karandashov, A.G. Kiyamov, M.A. Klabukov, V.A. Kuklin, I.N. Sidorov, A.I. Enskaya, Formation and behavior of residual stresses in particulate-filled polymer composites with a partially crystalline structure, Phys. Mesomech. 25 (2022) 335–343, https://doi.org/10.1134/S1029959922040075.

[38] M. Murariu, A.L. Dechief, L. Bonnaud, Y. Paint, A. Gallos, G. Fontaine, S. Bourbigot, P. Dubois, The production and properties of polylactide composites filled with expanded graphite, Polym. Degrad. Stabil. 95 (2010) 889–900, https://doi.org/10.1016/j.polymdegradstab.2009.12.019.

[39] N.T. Evans, C.W. Irvin, D.L. Safranski, K. Gall, Impact of surface porosity and topography on the mechanical behavior of high strength biomedical polymers, J. Mech. Behav. Biomed. Mater. 59 (2016) 459–473, https://doi.org/10.1016/j.jmbbm.2016.02.033.

[40] S. Farah, D.G. Anderson, R. Langer, Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review, Adv. Drug Deliv. Rev. 107 (2016) 367–392, https://doi.org/10.1016/j.addr.2016.06.012.

[41] S. Savotchenko, E. Kovaleva, Mechanical properties of cured epoxy resin, Mod. Phys. Lett. B 35 (2021) 2150445–2150544, https://doi.org/10.1142/S0217984921504455.

[42] C.G. Robertson, C.J. Lin, M. Rackaitis, C.M. Roland, Influence of particle size and Polymer–Filler coupling on viscoelastic glass transition of particle-reinforced polymers, Macromolecules 41 (2008) 2727–2731, https://doi.org/10.1021/ma7022364.

[43] V. Kuklin, S. Karandashov, E. Bobina, S. Drobyshev, A. Smirnova, O. Morozov, M. Danilaev, Analysis of aluminum oxides submicron particle agglomeration in

polymethyl methacrylate composites, Int. J. Mol. Sci. 24 (2023) 1—9, https://doi.org/10.3390/ijms24032515.

[44] R.N.R. Anreddy, Copper oxide nanoparticles induces oxidative stress and liver toxicity in rats following oral exposure, Toxicol Rep 5 (2018) 903—904, https://doi.org/10.1016/j.toxrep.2018.08.022.

[45] J. Zhao, Y. Liu, B. Pan, G. Gao, Y. Liu, S. Liu, N. Liang, D. Zhou, M.G. Vijver, W.J.G.M. Peijnenburg, Tannic acid promotes ion release of copper oxide nanoparticles: impacts from solution pH change and complexation reactions, Water Res. 127 (2017) 59—67, https://doi.org/10.1016/j.watres.2017.10.006.

[46] M. Danilaev, G. Yakovleva, S. Karandashov, V. Kuklin, H.Q. Le, W. Kurdy, O. Ilinskaya, Polysiloxane coatings biodeterioration in nature and laboratory, Microorganisms 10 (2022) 1—13, https://doi.org/10.3390/microorganisms10081597.