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# Novel in situ synthesis of copper oxide nanoparticles in epoxy network: kinetics, composite mechanical and dielectric properties

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# **Abstract**

>Mechanical properties of polymer composites with dispersed nanoparticles (CDNP) depend on interaction between the nanoparticles and the polymer matrix. Strength of polymer composites significantly decreases when there is no interaction between dispersed nanoparticles and the polymer. This limits the application of functional polymer composites with dispersed nanoparticles. In this study, CDNP based on ED-20 epoxy resin with dispersed copper oxide nanoparticles was obtained.These nanoparticles were synthesized in epoxy resin before curing: the nanoparticles were obtained by decomposition of copper hydroxide by heating its solution in ED-20 resin.The kinetics of copper oxide nanoparticles formation in CDNP samples were studied using two independent methods: electron microscopy and dielectric spectroscopy.The results of these studies demonstrate that complete decomposition of copper hydroxide to polycrystalline copper oxide nanoparticles in a solution of copper hydroxide in epoxy resin occurs after 10 hours at 90оС. Nanoparticles were needle-shaped: the average length was 310 nm, the width was 80 nm.Copper oxide nanoparticles volume fraction in the samples after their exposure to high temperature for more than 10 hours was 0.28%. It was demonstrated that mechanical properties of epoxy-based polymer composite increased when the size of copper oxide nanoparticles decreased. After the complete transition of copper hydroxide into copper oxide nanoparticles, a significant increase in mechanical properties was observed. Flexural modulus increased from 3.4±0.2GPa(for the samples without nanoparticles) to 5.5±0.6GPa, the ultimate strength increased accordingly from 53.3±4 N/mm2 to 85±5 N/mm2. A two-fold decrease in ultimate strain should be noted: 1.5±0.1% compared to ED-20 epoxy resin-based polymer without nanoparticles.

## Keywords

polymer composite, dispersed nanoparticles, copper hydroxide, copper oxide, epoxy resin

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# Novel In Situ Synthesis of Copper Oxide Nanoparticles in Epoxy Network: Kinetics, Composite Mechanical and Dielectric Properties

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#### Abstract

Mechanical properties of polymer composites with dispersed nanoparticles (CDNP) depend on interaction between the nanoparticles and the polymer matrix. Strength of polymer composites significantly decreases when there is no interaction between dispersed nanoparticles and the polymer. This limits the application of functional polymer composites with dispersed nanoparticles. It is possible to increase the interaction of dispersed particles with the polymer by synthesizing the nanoparticles directly in one of the components of the epoxy resin before it is cured. In this study, CDNP based on ED-20 epoxy resin with dispersed copper oxide nanoparticles was obtained. These nanoparticles were synthesized in epoxy resin before curing: the nanoparticles were obtained by decomposition of copper hydroxide by heating its solution in ED-20 resin. The kinetics of copper oxide nanoparticles formation in CDNP samples were studied using two independent methods: electron microscopy and dielectric spectroscopy. The results of these studies demonstrate that complete decomposition of copper hydroxide to polycrystalline copper oxide nanoparticles in a solution of copper hydroxide in epoxy resin occurs after 10 h at 90  $\degree$ C. Nanoparticles were needle-shaped: the average length was 310 nm, the width was 80 nm. Copper oxide nanoparticles volume fraction in the samples after their exposure to high temperature for more than 10 h was 0.28%. It was demonstrated that mechanical properties of epoxy-based polymer composite increased when the size of copper oxide nanoparticles decreased. After the complete transition of copper hydroxide into copper oxide nanoparticles, a significant increase in mechanical properties was observed. Flexural modulus increased from 3.4  $\pm$  0.2 GPa (for the samples without nanoparticles) to 5.5  $\pm$  0.6 GPa, the ultimate strength increased accordingly from 53.3  $\pm$  4 N/mm<sup>2</sup> to 85  $\pm$  5 N/mm<sup>2</sup>. A two-fold decrease in ultimate strain should be noted:  $1.5 \pm 0.1\%$  compared to ED-20 epoxy resin-based polymer without nanoparticles.

Keywords: Polymer composite, Dispersed nanoparticles, Copper hydroxide, Copper oxide, Epoxy resin

#### 1. Introduction

hen producing functional polymer composites with dispersed nanoparticles, one of the main tasks is to ensure the required mechanical properties of the final material apart from providing required functional properties, like electrical conductivity, biocidal effect, radio absorption  $[1–5]$  $[1–5]$  $[1–5]$ . Properties of the compounds, their

composition, structure and interfacial interaction define the mechanical properties of these materials [\[6](#page-9-1)], while the properties of dispersed nanoparticles define the functional ones. The reason behind a decrease in the mechanical properties of polymer composites with dispersed nanoparticles (CDNP) is the lack of interfacial interaction between dispersed nanoparticles and polymer matrix  $[7-9]$  $[7-9]$  $[7-9]$ . This leads to the formation of pores around the nanoparticles

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 $[10-12]$  $[10-12]$  $[10-12]$  and agglomeration. These defects not only affect the mechanical properties of CDNP but also lead to a decrease in their reproducibility [\[13](#page-9-4)]. There are two groups of methods used to increase the adhesion of dispersed nanoparticles to the polymer matrix.

- (i) The first group includes methods for modification of the nanoparticle surface  $[14-16]$  $[14-16]$  $[14-16]$  $[14-16]$  $[14-16]$ . Nanoparticle surface modification leads to an increase in its surface energy, which enhances the interaction with the polymer matrix and reduces agglomeration [\[13](#page-9-4)]. Modification of the surfaces of dispersed nanoparticles  $[16-18]$  $[16-18]$  $[16-18]$  does not solve all the issues. This method allows decreasing the number of agglomerates in CDNP under certain conditions, however, it is not possible to exclude them completely [[13\]](#page-9-4). An increase in surface energy may facilitate nanoparticles agglomeration prior to their introduction into polymer matrix [\[19](#page-10-0)], which is not taken into account in most studies. It should be noted that residual stresses in the polymer matrix in proximity of dispersed nanoparticles may appear [\[20](#page-10-1)].
- (ii) The second group includes methods for in situ synthesis of nanoparticles in the polymer matrix  $[21-24]$  $[21-24]$  $[21-24]$  $[21-24]$  $[21-24]$ . Nanoparticles are formed directly in the polymer matrix by adding compounds and initiating chemical reactions. In study [\[24](#page-10-3)], silver nanoparticles were formed in polylactide, and antimicrobial filaments were created. Silver nanoparticles were obtained by chemical decomposition of silver salt during polylactide extrusion. One of the disadvantages of the method is the formation of by-products of nanoparticles synthesis in the polymer. This leads to a significant decrease in the mechanical properties of a polymer composite. So, when synthesizing metal oxide nanoparticles in the polymer matrix in situ, metal salts may be produced [\[25](#page-10-4)] that decrease the strength properties of the material [[26\]](#page-10-5).

It is possible to avoid by-products during in situ synthesis of nanoparticles in epoxy polymers when producing metal oxide nanoparticles from metal hydroxides by heating [[27,](#page-10-6)[28\]](#page-10-7). Water is produced in the process of metal oxides formation, and this water may be removed from the epoxy resin before it is cured. This approach to in situ synthesis of nanoparticles in epoxy network eliminates formation of by-products in the composition and may significantly improve its mechanical properties. This provides the possibility of expanding the area of practical application of such composites. Thus, article [[8\]](#page-9-7) substantiates the outlook on the application of copper oxide nanoparticles to create composites with both biocidal and improved mechanical properties. Interfacial interaction between nanoparticles and the polymer defines the mechanical properties of the composite and the preservation of these mechanical properties after the composite is exposed to microbial destructors. In study [[29](#page-10-8)], a polymer composite was synthesized where the biocidal effect was provided by zinc oxide particles. A decrease in the strength of such polymer composite compared to an unfilled polymer was established. The reason behind it was poor adhesion of nanoparticles to the matrix polymer. An increase in interfacial interaction by in situ synthesis of nanoparticles in the polymer matrix is a promising approach to preservation of mechanical properties of a composite after exposure to microbial destructors.

Despite numerous studies aimed at in situ synthesis of nanoparticles in the polymer, there are no studies of such method for obtaining copper oxide (CuO) nanoparticles in the epoxy resin accompanied by a study of kinetics, mechanical and dielectric properties of polymer composites with these nanoparticles.

The aim of this study is to create a new ED-20 epoxy-based polymer composite with copper oxide nanoparticles synthesized in situ, to examine kinetics of the nanoparticles formation and mechanical and dielectric properties of the polymer composite.

First, copper hydroxide  $(Cu(OH)_2)$  powder was obtained from copper sulfate  $(CuSO<sub>4</sub>)$  and sodium hydroxide (NaOH) solution that was added to ED-20 epoxy resin. After that, ED-20 epoxy resin samples with copper oxide (CuO) nanoparticles were prepared by exposure to the temperature of 90  $^{\circ}$ C. Then, polymer composite samples with copper oxide nanoparticles in the polymer network were obtained. Kinetics of copper oxide nanoparticles formation and mechanical and dielectric properties of the samples were studied. Thus, the evidence was obtained that the proposed approach to obtaining a composite with nanoparticles in an epoxy network ensured improved mechanical properties. It opens up new horizons for practical application of epoxy resin-based composites filled with nanoparticles as polymers with biocidal properties.

#### 2. Methods and materials

#### 2.1. Materials

For in situ synthesis of copper oxide (CuO) nanoparticles in epoxy resin, copper hydroxide

 $(Cu(OH<sub>2</sub>)$  was used. It was preliminary synthesized from copper sulfate 20%-solution (CAS 7758-98-7) and sodium hydroxide (CAS 1310-73-2). A polymer composite was based on ED-20 epoxy resin (GOST 10587-84) with the addition of Polyethylenepolyamine hardener (TU 2413-010-75678843-2012, LTD 10587-84) with the addition of Foryet<br>amine hardener (TU 2413-010-75678843<br>Holding Company "FEM", Dzerzhinsk).

#### 2.2. A method for producing copper oxide nanoparticles in ED-20 epoxy resin

There were several stages in the process of producing copper oxide nanoparticles in ED-20 epoxy resin before it was cured. In the first stage, copper hydroxide was obtained from a solution of copper sulfate and sodium hydroxide [\[30](#page-10-9)]:

#### $CuSO_4 + NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$

For that purpose, 20%-solution of sodium hydroxide was gradually added to 20%-solution of copper sulfate under continuous stirring; the temperature of both solutions was  $23 \pm 2$  °C. Sodium hydroxide solution was added at the rate of 60 drops/minute to achieve homogeneity of the components when stirring in the round-bottom flask; average volume of one drop was  $0.05 \pm 0.01$  ml. The resulting blue precipitate was washed in distilled water to remove sodium sulfate. Copper hydroxide precipitate was separated through filter paper with  $(2\div 3) \pm 0.2$  µm pores using a Buchner funnel and a Bunsen flask. It was necessary to obtain copper hydroxide because when it interacts with carbon dioxide in the air, copper carbonates are formed, and they have a higher decomposition temperature [\[31](#page-10-10)[,32](#page-10-11)] than copper hydroxide. It should be noted that additional components in the polymer matrix, including copper carbonates, may affect its mechanical properties. That is why copper hydroxide was synthesized and mixed with epoxy resin right away, to exclude the presence of copper carbonates in the polymer composition in this study. This fact also defined the size of filter paper pores for both highquality and fast filtering: the filtering time did not exceed  $15 \pm 2$  min.

In the second stage, a mixture of ED-20 epoxy resin and copper oxide precipitate was produced following the proportion: 3 g of precipitate per 100 g of epoxy resin. The mixture was produced by adding the precipitate to ED-20 epoxy resin under continuous stirring until complete homogenization, which was controlled visually. The obtained mixture was degassed in a vacuum cabinet during  $10 \pm 1$  min under  $0.2 \pm 0.05$  bar to exclude any interaction of carbon dioxide in the air with copper hydroxide and a transition of the latter into the copper carbonate. After that, a half of the mixture obtained was additionally

homogenized using ultrasonic homogenizer (UZDN-2T, Russia, 10 W power) at 20 kHz during  $60 \pm 10$  s. These parameters of ultrasonic homogenizer excluded heating of mixtures to the temperatures exceeding 50 $\degree$ C, when the formation of copper oxide nanoparticles from copper hydroxide started [\[28\]](#page-10-7). After homogenization, both batches (halves) were placed in  $50 \pm 2$  g glasses each.

In the third stage, both batches in the glasses were exposed to the temperature of 90  $\pm$  1 °C and the pressure of  $0.2 \pm 0.05$  bar (excluding the samples of an initial mixture that was not heated). Sampling required for the production of CDNP samples was carried out every 2 h for 14 h, starting from the second hour of exposure. Thus, a reaction of copper hydroxide transition into copper oxide was initiated [\[28\]](#page-10-7), simultaneously dehydrating the epoxy resin solution:

$$
Cu(OH)2 \xrightarrow{90^{\circ}C} CuO + H2O
$$
 (1)

Generally, eight samples of each type of ED-20 epoxy resin solution were obtained before and after ultrasonic homogenization of the initial solution. A change in epoxy resin solution color was observed: from blue-green (initial mixture) to brown-black (a sample after 14-h exposure to temperature). In order to avoid production of copper carbonates after sampling, each sample was vacuum treated and stored at a low temperature of  $-5 \pm 0.5$  °C before curing. Thus, the optimal parameters of copper oxide nanoparticles formation in the epoxy network were selected based on the time of samples exposure to the temperature of  $90 \pm 1$  °C with the following analysis of nanoparticles sizes and mechanical properties of the polymer composite samples.

It should be noted that ED-20 epoxy resin degradation temperature is  $150\div180\text{ °C}$  [[33](#page-10-12),[34\]](#page-10-13). So, exposure of the samples to the temperature of 90  $\pm$  1 °C did not lead to epoxy resin degradation and formation of carbon particles in it. The technique used for samples preparation excluded the presence of foreign particles apart from copper oxide (CuO) ones.

Thus, when producing the samples [\(Table 1\)](#page-5-0), the time of exposure to high temperature for copper hydroxide solution in epoxy resin was varied. A change in color of the samples indicated a change in copper oxide nanoparticles concentration due to a reduction in copper hydroxide volume.

#### 2.3. A method for obtaining samples of a polymer composition of cured ED-20 epoxy resin with copper oxide nanoparticles

The samples of CDNP were obtained by curing respective samples of epoxy resin solutions using

Samples, produced without ultrasonic homogenization	ED-20 resin solution exposure to 90 $\pm$ 1 °C, hours	Samples, produced with ultrasonic homogenization	ED-20 resin solution exposure to 90 $\pm$ 1 °C, hours
Sample 1-0		Sample 2-0	
Sample 1-1		Sample 2-1	
Sample 1-2		Sample 2-2	
Sample 1-3		Sample 2-3	
Sample 1-4		Sample 2-4	
Sample 1-5	10	Sample 2-5	10
Sample 1-6	12	Sample 2-6	12
Sample 1-7	14	Sample 2-7	14

<span id="page-5-0"></span>Table 1. Classification of CDNP samples.

Polyethylenepolyamine hardener (TU 2413-010- 75678843-2012, LTD Holding Company "FEM", Dzerzhinsk) at a ratio of 10:1. The samples were cured in fluoroplastic mold after mixing appropriate solutions of ED-20 epoxy resin with Polyethylenepolyamine hardener; the dimensions of the CDNP samples were  $100 \times 20 \times 3$  mm. The classification of CDNP samples is provided in [Table 1](#page-5-0).

To obtain reliable results, 10 samples of each type were produced. After an experimental study of the properties of the samples, statistical processing of the results was carried out. The average values of mechanical and dielectric properties of the samples and their standard deviations are indicated in the graphs.

#### 2.4. Methods for studying the structure, physical, and mechanical properties of the samples

The kinetics of copper oxide nanoparticles growth were studied using two independent methods: scanning electron microscopy and dielectric spectroscopy [\[35](#page-10-14),[36\]](#page-10-15). Scanning electron microscopy was performed in KAI-Nanotech center using Carl Zeiss AURIGA Cross Beam microscope with Inca X-Max 80 mm<sup>2</sup> detector. To study the samples using scanning microscope, cross sections of samples (by thickness) were prepared using Ultra microtome system 2128 ultra-tome, USA; their thickness was  $\sim$ 10  $\mu$ m. These sections were placed on a conducting silicone surface, the accelerating voltage was ~10 kV. The average size of copper oxide dispersed nanoparticle was determined after processing the images obtained by using an electron microscope and the methods given in Refs. [\[8](#page-9-7),[37\]](#page-10-16). The images were processed in ImageJ software; the number of nanoparticles  $(N_0)$  was at least 1.000.

Dielectric measurements were performed using Novocontrol BDS-80 system. A combination of Alpha Analyzer and HVB4000 was used: Alpha Analyzer was used to generate a test signal and analyze the response; HVB4000 was used to amplify the test signal. A measuring cell was a capacitor: a

part of the studied sample was placed between two electrodes, located on its opposite surfaces. Electrodes of the measuring cell were М316 stainless steel discs, 10 mm in diameter. The surfaces of the electrodes were polished with GOI paste with a grain size of  $1-7$  µm to a mirror finish. Measurements were carried out at a constant temperature of 24  $\degree$ C, temperature maintenance accuracy was  $\pm$ 0.5 °C (Quatro Cryosystem cryostat was used). The amplitude of the probing oscillation was 100 V; relative error in dielectric constant measurement was 1%.

The mechanical properties, such as modulus of flexibility, ultimate strain and strength, were tested under GOST 11262-80 using a universal desktop testing machine Shimadzu AG-X 50 kN. The testing parameters were as follows: bending loading rate  $-$ 1 mm/min, ambient temperature was set at 23  $\pm$  2 °C. Lieb hardness measurements (GOST R 8.969 $-2019$ ) of samples were carried out using a desktop hardness tester TEMP-4 (Tehnotest LLC) at an ambient temperature of  $23 \pm 2$  °C.

#### 3. Results and discussion

3.1. Kinetics of dispersed copper oxide nanoparticles formation and CDNP samples structure

Analysis of images ([Fig. 1\)](#page-6-0) of dispersed nanoparticles obtained from the sections of samples [\(Table 1\)](#page-5-0) shows that the shape of the resulting nanoparticles can be described by equivalent ellipses [\[37](#page-10-16),[38](#page-10-17)] ([Fig. 1](#page-6-0)A).

When thermal methods are used for copper oxide nanoparticles formation, it is possible to obtain polycrystalline nanoparticles only [[27\]](#page-10-6). As the time of ED-20 epoxy resin exposure to high temperature grows, typical nanoparticle sizes (ellipses axes  $-$ [Fig. 1](#page-6-0)a) get reduced. Statistical analysis of micrographs of Type I samples [\(Fig. 1](#page-6-0)B and D) and Type II samples ([Fig. 1](#page-6-0)A and C) ([Table 1](#page-5-0)) at the same scale of electron microscope amplification shows an

<span id="page-6-0"></span>

Fig. 1. Typical micrographs of copper oxide nanoparticles in CDNP samples:  $A -$  Sample 2-1;  $B -$  Sample 1-1;  $C -$  Sample 2-5;  $D -$ Sample  $1-5$ .

increase in the copper oxide nanoparticles concentration with the increase of the time of their exposure to the temperature of  $90 \pm 1$  °C. Micrographs show that, as a result of reaction (1), needle-shaped polycrystalline structures appear [\[26](#page-10-5)]. Copper oxide nanoparticles were studied using SEM and were characterized in detail in Ref. [\[39](#page-10-18)].

Curves demonstrating dependence of sizes of the nanoparticles obtained without ultrasonic homogenization and depicted by ellipses with minor and major axes are presented in [Fig. 2.](#page-6-1)

Due to the fact that copper oxide nanoparticles have nano sizes, high interfacial interaction between the nanoparticles and epoxy resin should be expected [\[40](#page-10-19)]. This is indirectly confirmed by an absence of significant agglomerates in the samples, especially after ultrasonic treatment, and pores around the nanoparticles [\(Fig. 1](#page-6-0)). This should lead to an increase in the strength of the samples compared to a polymer without nanoparticles.

The kinetics of the new phase formation (dispersed copper oxide nanoparticles) were studied by the dielectric spectroscopy. This method was used because the dielectric constant of copper hydroxide  $(30 \div 40)$  is significantly different from the dielectric constant of copper oxide, which equals 9.77  $\div$  10.3 [[41\]](#page-10-20). That is why dielectric constant ( $\varepsilon$ ) and dielectric loss tangent (tg $(\delta)$ ) of the composition should decrease [[42,](#page-10-21)[43](#page-10-22)] as the concentration of copper hydroxide decreases turning into copper oxide when exposed to high temperature. It was confirmed by the results of dielectric constant measurement for the Type II samples [\(Table 1\)](#page-5-0) at zero frequency ([Fig. 3\)](#page-7-0). It should be noted that the curves ([Fig. 3\)](#page-7-0) for Type I and Type II samples

<span id="page-6-1"></span>

Fig. 2. Curves demonstrating dependence of sizes of the nanoparticles on the time (t) of epoxy resin exposure to high temperature.

<span id="page-7-0"></span>

Fig. 3. Dielectric properties of CDNP samples with respect to time (t) of epoxy resin exposure to high temperature:  $A$  – real part of dielectric constant vs t;  $B -$  dielectric loss tangent vs t.

coincide, taking measurement error in account. Dielectric spectra of the samples were measured immediately after keeping them in a vacuum cabinet at a reduced pressure of  $\sim 0.2 \pm 0.05$  bar to remove air moisture from the samples.

 $Re(\varepsilon)$  and tg( $\delta$ ) virtually remained the same, starting from 10 h of ED-20 epoxy resin exposure to high temperature (90  $\pm$  1 °C). Apparently, this was due to the complete decomposition of copper hydroxide in the resin to copper oxide. Thus, it is possible to assume that in Type I and Type II samples, starting from numbers  $1-5$  and  $2-5$ , respectively, there were only copper oxide nanoparticles in the polymer composition. So, it was possible to determine the volume fraction of these parts using the Bruggemann equation [[44](#page-10-23)[,45](#page-10-24)]:

$$
\frac{\varepsilon_f - \varepsilon_{eff}}{\varepsilon_{eff}^{1/3}} = \frac{(1 - \Phi)(\varepsilon_f - \varepsilon_m)}{\varepsilon_m^{1/3}}\tag{2}
$$

Here  $\varepsilon_f$ ,  $\varepsilon_{eff}$ ,  $\varepsilon_m$  are dielectric constants of the polymer composition, filler and polymer matrix, respectively;  $\Psi$  – is filler volume fraction. Thus, the volume fraction of dispersed copper oxide nanoparticles in Type I and Type II samples, starting from numbers  $1-5$  and  $2-5$ , was 0.28%. Considering the fact that from 3 g of copper hydroxide one can get approximately 1.8 g of CuO nanoparticles (see 1) with the average density of 6.31  $g/cm<sup>3</sup>$ , while the density of ED-20 epoxy resin is  $1.2$  g/cm<sup>3</sup>, the maximum volume fraction of these nanoparticles was ~0.3%. Calculated volume fraction of copper oxide nanoparticles based on the results of dielectric spectra measurements indicates an insignificant presence of sodium sulfate (apparently) in the samples. It should be expected that a small volume fraction of this salt will not lead to a significant drop in the mechanical properties of the composition.

#### 3.2. Mechanical properties of CDNP samples

Elasticity modulus  $(E)$  curves of CDNP samples presented in [Fig. 4](#page-7-1) confirm previously made assumptions about the effect that copper oxide nanoparticles have on the mechanical properties of CDNP.

Flexural modulus grows with the time of epoxy resin exposure to high temperature because the amount of copper hydroxide is reduced as it turns into copper oxide. Elasticity modulus of Type I samples is slightly lower than the value for Type II samples. Apparently, this is due to the use of ultrasonic homogenization of the samples. As it is known [\[46](#page-10-25)], dispersion of nanoparticles helps to reduce the number of agglomerates and to increase mechanical properties of polymer composites [[13\]](#page-9-4).

<span id="page-7-1"></span>

Fig. 4. Flexural modulus with respect to time of epoxy resin exposure to high temperature.

This behavior is also observed for the strength of the samples presented in [Fig. 5](#page-8-0).

An increase in ultimate strength [\(Fig. 5](#page-8-0)A) with a simultaneous decrease in the ultimate strain of the samples ([Fig. 5B](#page-8-0)) may be explained by the growth of

<span id="page-8-0"></span>

Fig. 5. The strength properties of CDNP samples over time (t) of epoxy resin exposure to high temperature:  $A -$ ultimate strength;  $B -$ ultimate strain; C – Leeb hardness,  $HL_0 = 788$ .

dispersed copper oxide nanoparticles concentration and their sizes getting reduced at the same time. In [Fig. 5](#page-8-0), the following designations are used:  $1$ curves corresponding to samples 1-;  $2 - curves$ corresponding to samples 2- ([Table 1](#page-5-0)).

Dispersed nanoparticles that interacted with the polymer network formed additional cross-links and thus helped to increase stiffness of the polymer network and decrease ultimate strain. This also led to an increase in Leeb hardness [\(Fig. 5](#page-8-0)C) and brittleness of the samples [[47\]](#page-10-26) which was observed in the experiments.

After the complete transition of copper hydroxide into copper oxide nanoparticles, a significant increase in the mechanical properties of the samples was observed, even in the possible presence of agglomerates: flexural modulus increased from  $3.4 \pm 0.2$  GPa in the samples without nanoparticles [\[8](#page-9-7)] to  $5.5 \pm 0.6$  GPa, ultimate strength increased from 53.3  $\pm$  4 N/mm<sup>2</sup> [\[8](#page-9-7)] to 85  $\pm$  5 N/mm<sup>2</sup>. There was an approximately two-fold decrease to  $1.5 \pm 0.1\%$  in ultimate strain  $(\Delta)$  compared to ED-20 epoxy resin without dispersed nanoparticles.

The ultimate strength of the samples experienced a 1.2-fold increase compared to the similar samples that contained polylactide-encapsulated copper oxide nanoparticles [\[8](#page-9-7)] with the same nanoparticles concentration of 0.28%. The article [\[8](#page-9-7)] demonstrates that encapsulation of the nanoparticles increases their interaction with polymer matrix and mechanical properties, as a result. The best ultimate strength values of the samples obtained in this work indirectly demonstrate better interaction of dispersed nanoparticles with the polymer matrix. Enhanced interfacial interaction of copper oxide nanoparticles with epoxy network and the quality of dispersion significantly define the mechanical properties of the composition. It opens up new horizons for the application of epoxy-based composites with nanoparticles as polymers with biocidal effect. Such biocidal polymer composite has better mechanical properties compared to similar composites [[8\]](#page-9-7). A study of biocidal properties of a new epoxy-based composite with copper oxide (CuO) nanoparticles will be presented in a separate article.

#### 4. Conclusion

The article studies a process for producing ED-20 epoxy resin-based polymer composites with dispersed nanoparticles when copper oxide nanoparticles are formed directly in the epoxy resin before it is cured. These dispersed nanoparticles are formed by decomposition of copper hydroxide to copper oxide under heating. The results of dielectric

spectroscopy as well as an increase in the mechanical properties of CDNP under consideration compared to the samples without dispersed nanoparticles indirectly indicate the fact that concentration of sodium sulfate in the samples is negligible. Copper hydroxide completely turns into copper oxide in the form of predominantly nanoparticles of a polycrystalline needle-shaped structure after 10-h exposure of copper hydroxide solution in epoxy resin to a temperature of 90  $\pm$  1 °C and a pressure of  $0.2 \pm 0.05$  bar. The modulus of elasticity and ultimate strength undergo a significant increase after the complete transition of copper hydroxide into copper oxide polycrystals, whereas the ultimate strain of CDNP decreases. This is because of the interfacial interaction between emerging nanoparticles and the polymer network. As a result, nanoparticles create additional cross-links in the polymer network, which is a reason behind a change in the mechanical properties. We believe that it is possible to adjust the mechanical properties of a composition by changing copper hydroxide concentration in epoxy resin. This will lead to a change in the number of additionally emerging cross-links in the polymer network because of a change in the number of nanoparticles. Enhanced interfacial interaction of copper oxide nanoparticles with epoxy network and the quality of dispersion significantly define the mechanical properties of the composition. Thus, a new ED-20 epoxy based composite with copper oxide nanoparticles synthesized in situ has improved strength properties. It may be promising as a biocidal polymer with improved strength when developing structural elements exposed to bio-corrosion.

#### Conflicts of interest

No conflict of interest among authors.

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