

DOI: 10.17725/rensit.2023.15.161

## Synthesis of polymer composite materials based on zinc oxide nanoparticles synthesized in a plasma discharge under the ultrasonic action

**Nikolay A. Bulychev**

Moscow Aviation Institute, <http://www.mai.ru/>  
Moscow 125993, Russian Federation

*E-mail: nbulychev@mail.ru*

**Yuri G. Mikhaylov**

National Research University of Electronic Technology, <http://www.miet.ru/>  
Zelenograd 124498, Moscow, Russian Federation

*E-mail: icc.miet@mail.ru*

*Received May 24, 2023, peer-reviewed May 31, 2023, accepted June 07, 2023*

**Abstract:** Zinc oxide nanoparticles were synthesized and samples of films of polymer composite materials on their basis were obtained and studied. Zinc oxide nanoparticles were synthesized in a plasma discharge under the action of ultrasonic cavitation. To create composites with a homogeneous distribution of nanoparticles, solution technology was used, and then melt compounding technology. Composite materials based on a copolymer of polyethylene and vinyl acetate and zinc oxide nanoparticles were obtained, and not sonicated and sonicated nanoparticles were used. The obtained samples of composite materials were studied by X-ray phase analysis, X-ray fluorescence analysis and scanning electron microscopy. It was shown that there are differences between the samples: in the case of nanoparticles without ultrasonic treatment, the particles are more strongly aggregated inside the composite material and their average size is visually larger than in the case of a sample with nanoparticles subjected to ultrasonic treatment.

**Key words:** nanoparticles, polymers, composite materials, zinc oxide

**PACS:** 61.46.+w

**Acknowledgments:** This work was supported by the Russian Science Foundation, project no. 23-19-00540.

**For citation:** Nikolay A. Bulychev, Yuri G. Mikhaylov. Obtaining polymer composite materials based on zinc oxide nanoparticles synthesized in a plasma discharge under the action of ultrasound. *RENSIT: Radioelectronics. Nanosystems. Information Technologies*, 2023, 15(2):161-168e. DOI: 10.17725/rensit.2023.15.161.

### CONTENTS

1. INTRODUCTION (161)
  2. MATERIALS AND METHODS (162)
  3. RESULTS AND DISCUSSION (163)
  4. CONCLUSION (166)
- REFERENCES (167)

### 1. INTRODUCTION

Currently, composite materials based on various classes of polymers reinforced with nanosized fillers of various compositions and geometries (in the form of spheres, fibers, planar two-dimensional structures, etc.) are actively used in various fields of

science and technology, representing a very competitive alternative to materials from metals and alloys. High specific mechanical characteristics make this class of materials extremely valuable when used as structural materials in industry (aerospace, automotive), as well as in a number of other areas [1–6].

When using nanoparticles based on metals and ceramics and organic polymers as a matrix as fillers, it is necessary to take into account the very weak adhesion of nanoparticles to the material of the polymer matrix, which is due to the chemical inertness of the nanoparticle surface. Obviously, in the absence of chemical interaction between the components of the composite material, a very low level of strength of the interfacial interaction at the nanoparticle-matrix interface will be achieved, and this will negatively affect the physical and mechanical characteristics of the entire resulting material [3, 4]. This effect is especially pronounced when studying films made of such a composite material, where strengthening due to impregnated inclusions is especially important. At present, to increase the strength of interfacial interaction between a polymer and fillers, various methods are used, among which chemical or physical modification of the surface of fillers [7], functionalization of the polymer matrix [8], plasma treatment [9], and in-situ polymerization of the polymer on the surface of the filler are distinguished. [10] etc. A common feature of all the above methods is the formation of reactive functional groups on the surface of the reinforcing particles, capable of forming strong chemical bonds with the matrix polymer. However, it should be taken into account that these methods and approaches

should be carried out taking into account the individual characteristics of each specific filler-polymer pair and provide the required level of interfacial interaction in the resulting composite [11–14].

When developing methods, technologies and equipment for obtaining functional and structural composite materials, as well as functional elements from filled polymers, it is also necessary to ensure the physicochemical and physicomechanical characteristics of the materials obtained, which is determined both by the properties of the dispersed filler and by the interaction of the filler and the matrix.

Therefore, in the framework of this work, zinc oxide nanoparticles were synthesized in a plasma discharge under the action of ultrasonic cavitation, and samples of films of polymer composite materials were obtained and studied on their basis.

## 2. MATERIALS AND METHODS

Zinc oxide nanoparticles were synthesized in a plasma discharge under the action of ultrasonic cavitation according to a previously developed procedure [15–17]. To create composites with a homogeneous distribution of nanoparticles, solution technology was used, and then melt compounding technology using heated laboratory mixing rolls. An ethylene-vinyl acetate copolymer was used as the polymer matrix. The content of vinyl acetate in the copolymer is 28%, the melt flow index is 25 g/10 min.

The copolymer was dissolved in chemically pure butyl acetate at 60°C with stirring with a magnetic stirrer. Powder of nanoparticles was poured into the resulting solution while stirring continued.

An IKA T18 Digital ULTRA TURRAX submersible high-speed disperser was used to break up particle agglomerates in the polymer solution for 10 min at a speed of 10,000 rpm. For ultrasonic treatment of nanoparticles before obtaining a sample, a Technosonic-1000 ultrasonic emitter was used at a frequency of 40 kHz and an intensity of 2 W/cm<sup>2</sup> for 2 min. After dispersion, the solutions were dried under draft. The dried samples were then subjected to rolling. Mixing rollers are designed for the preparation and processing of rubber, plastic mixtures with various parameters of technological processes. Before rolling, the crushed components were subjected to conditioning at a temperature of 50±5°C in an oven (Loip, Russia) for 3 hours.

To obtain a composite, the resulting dried concentrate was diluted with pure copolymer granules to a final filler concentration of 1% wt. Melt mixing was carried out on a UBL-6175-BL laboratory mixing roll (Dongguan BaoPin International Precision Instruments Co., Ltd., China). When compounding, the following technological parameters were used: 8 rpm and a gap between the rolls of 1 mm, the temperature regime of the rolls was 130°C and 150°C. Next, the films were pressed on a cellophane substrate using an RPA-12 laboratory hydraulic press (Biolent, Russia) at a temperature of 150°C and a pressure of 20 kgf/cm<sup>2</sup>.

The identification of the phase composition of the obtained samples was carried out on a Bruker D8 Advance setup operating in reflection mode using Cu-K $\alpha$  radiation (40 kV, 40 mA,  $\lambda = 1.54056 \text{ \AA}$ ). Qualitative determination of the metal in the obtained samples of materials by

X-ray fluorescence analysis was carried out on the analyzer Olympus Vanta (Japan) in the GeoChem mode with a 3-beam mode (scanning time: 45 s on each beam). Morphology was studied by scanning electron microscopy on a Carl Zeiss Supra 40-30-87 instrument.

### 3. RESULTS AND DISCUSSION

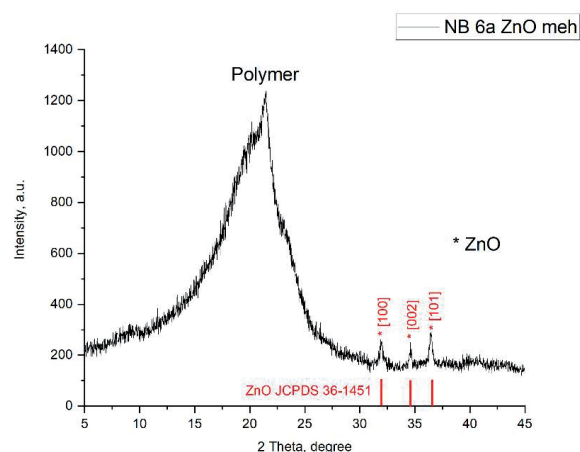
As was shown in previous studies, the combined impact on a liquid medium of pulsed or stationary electric fields and high-intensity ultrasonic vibrations above the cavitation threshold leads to the appearance of a special form of electric discharge in a cavitating liquid medium [15–17]. This type of discharge is still a little studied physical phenomenon, which has original electrical and optical characteristics. At the same time, as it was proved earlier, the use of ultrasonic cavitation makes it possible to solve the problem of preventing the agglomeration of synthesized nanoparticles after synthesis and activates their surface, creating additional active adsorption centers on it, which contributes to the effective interaction of such particles with organic polymers and makes it possible to create polymer composite materials with high operational properties [15-17].

Zinc metal electrodes were used as starting materials for the synthesis of nanoparticles. Synthesis was carried out in various liquid media: water, alcohols (ethanol, isopropanol). The nanometer size and high resistance of nanoparticles to aggregation made it possible to obtain relatively stable aqueous disperse systems (suspensions) of nanoparticles without the use of any stabilizing compounds [15–17].

This is explained by the fact that, firstly, ultrasonic action on a liquid-phase medium in the mode of developed cavitation changes the conditions of electrical breakdown between the discharge electrodes in the reaction chamber during the synthesis of nanoparticles due to the fact that cavitation bubbles in a liquid in an electric field are able to line up in chains, thus changing the medium from liquid-phase to vapor-liquid; while the discharge itself has a falling current-voltage characteristic similar to the current-voltage characteristic of an anomalous glow discharge. Optically, this is determined in the form of a more intense glow of the discharge. Secondly, intense ultrasonic cavitation during synthesis ensures efficient dispersion of particles formed [15–17]. In the case of association of nanoparticles, they were additionally ultrasonically dispersed in an aqueous medium for 1 min.

Typical discharge parameters during the synthesis of nanoparticles are: DC voltage 30–60 V, current strength 3–5 A [15–17]. These parameters were chosen, on the one hand, based on the need to ensure stable discharge burning, and, on the other hand, to create reproducible conditions for the synthesis of nanoparticles.

At the next stage of the work, studies were carried out on the introduction of zinc oxide nanoparticles synthesized in a plasma discharge into a polymer matrix to obtain polymer composite materials and study their physical and mechanical properties. At this stage, a copolymer of polyethylene and vinyl acetate was used as a matrix. Composite materials based on zinc oxide nanoparticles were obtained, and

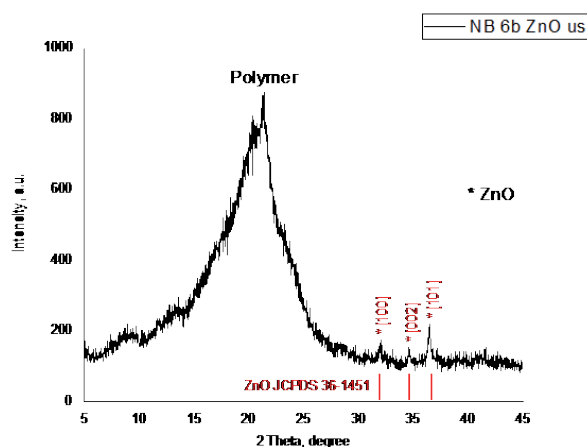


**Fig. 1.** Results of the X-ray phase analysis of a sample of a composite material based on nanoparticles without sonication.

nanoparticles not treated with ultrasound and treated with ultrasound were used.

Figures 1 and 2 present the data of studies of samples of polymer films based on a copolymer of polyethylene and vinyl acetate as a matrix and zinc oxide nanoparticles as a filler by X-ray phase analysis.

According to X-ray diffraction data, the sample contains at least two phases. A strongly broadened peak at  $2\theta = 22^\circ$



**Fig. 2.** Results of X-ray phase analysis of a composite material sample based on nanoparticles after sonication.

corresponds to the phase of a complex polymer. Also on the diffraction pattern there are peaks at  $2\theta$  values:  $31.29^\circ$ ,  $34.68^\circ$  and  $36.50^\circ$  corresponding to the zinc oxide phase (JCPDS # 36-1451, wurtzite structure).

According to X-ray phase analysis, the sample with nanoparticles after ultrasonic treatment also contains a complex polymer phase (a strongly broadened peak at  $2\theta = 21.2^\circ$ ) and peaks at  $2\theta$ :  $31.90^\circ$ ,  $34.61^\circ$  and  $36.52^\circ$ , corresponding to the oxide phase zinc (JCPDS # 36-1451, wurtzite structure). It should be noted a slight decrease in the intensity of the peak corresponding to the polymer in comparison with the data in Fig. 1, as well as a slight decrease in the intensity of the peaks corresponding to the zinc oxide phase. This may indicate an increase in the interaction of the nanoparticle surface with the polymer when ultrasound is used, as well as a decrease in the size of the filler nanoparticles themselves.

Figures 3 and 4 show the data of studies of samples of polymer films based on a

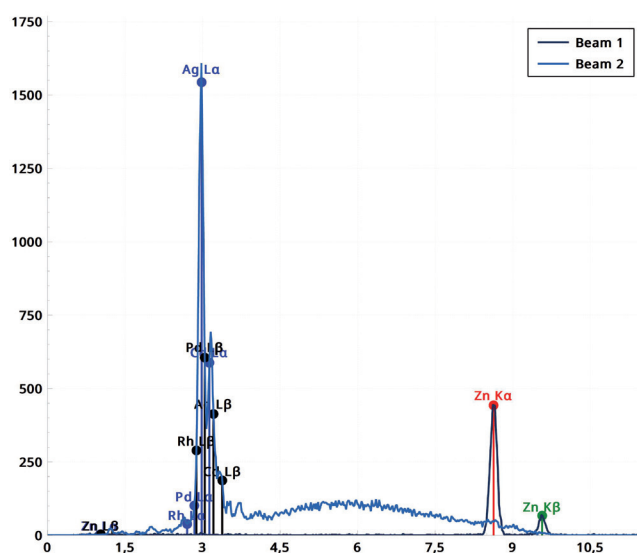


Fig. 3. Results of X-ray fluorescence analysis of a composite material sample based on nanoparticles without sonication.

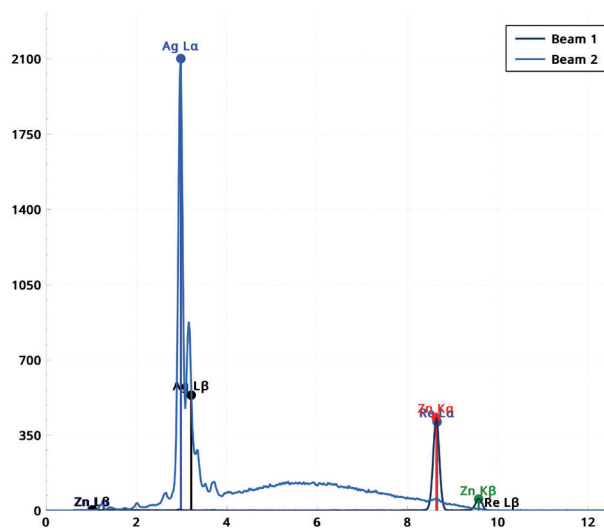


Fig. 4. Results of X-ray fluorescence analysis of a composite material sample based on nanoparticles after sonication.

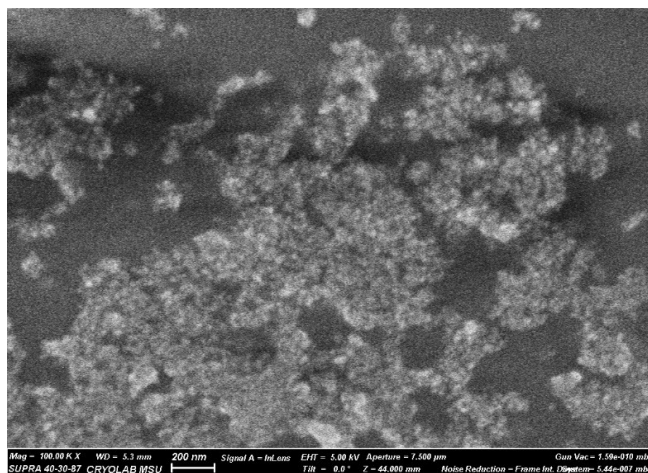
copolymer of polyethylene and vinyl acetate as a matrix and zinc oxide nanoparticles as a filler by X-ray fluorescence analysis.

According to the data of X-ray fluorescence analysis, the presence of zinc oxide nanoparticles was qualitatively confirmed in the sample.

X-ray fluorescence analysis also qualitatively confirmed the presence of zinc oxide in the film sample. In this case, the intensity of the peak increases in comparison with the sample obtained on the basis of nanoparticles without ultrasonic treatment.

Figures 5 and 6 show the data of studies of samples of polymer films based on a copolymer of polyethylene and vinyl acetate as a matrix and zinc oxide nanoparticles as a filler by scanning electron microscopy.

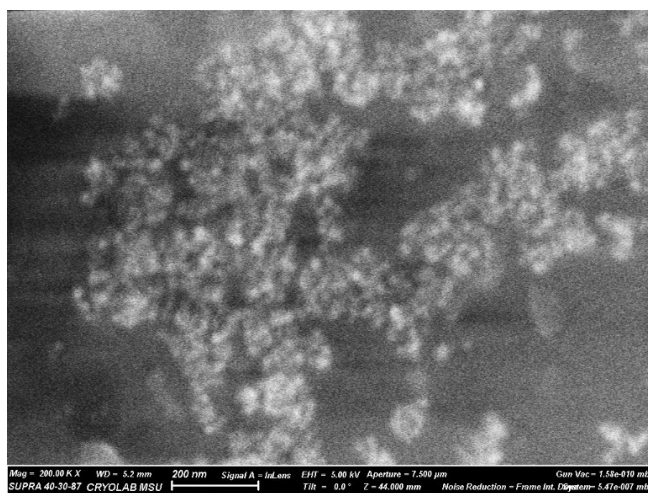
Scanning electron microscopy confirms that the zinc oxide nanoparticles are enclosed within the polymer film. In this case, there are differences between the samples: in the case of nanoparticles



**Fig. 5.** Results of a study by scanning electron microscopy of a sample of a composite material based on nanoparticles without sonication.

without ultrasonic treatment, the particles are more strongly aggregated inside the composite material and their average size is visually larger than in the case of a sample with nanoparticles subjected to ultrasonic treatment.

Thus, as a result of the studies carried out by the methods of physicochemical analysis, it was shown that the activation of the surface of particles using the methods of physical and physicochemical effects is an important factor that can significantly increase the efficiency of interaction



**Fig. 6.** Results of a study by scanning electron microscopy of a sample of a composite material based on nanoparticles after sonication.

between filler particles and the polymer matrix. Among the physical methods, first of all, the effect of intense ultrasound should be noted. The use of methods that would allow the synthesis of filler particles with an activated surface can give a great impetus to the production of composite materials with improved physical and mechanical characteristics [15–17].

#### 4. CONCLUSION

Composite materials in the form of films based on zinc oxide nanoparticles that were not sonicated and sonicated were obtained and studied. According to X-ray diffraction analysis, a sample with nanoparticles after ultrasonic treatment shows a slight decrease in the intensity of the peak corresponding to the polymer. This may indicate an increase in the interaction of the nanoparticle surface with the polymer when ultrasound is used, as well as a decrease in the size of the filler nanoparticles themselves. X-ray fluorescence analysis also qualitatively confirmed the presence of zinc oxide in the film sample. In this case, the intensity of the peak increases in comparison with the sample obtained on the basis of nanoparticles without ultrasonic treatment. Scanning electron microscopy confirms that the zinc oxide nanoparticles are enclosed within the polymer film. In this case, there are differences between the samples: in the case of nanoparticles without ultrasonic treatment, the particles are more strongly aggregated inside the composite material and their average size is visually larger than in the case of a sample with nanoparticles subjected to ultrasonic treatment.

## REFERENCES

1. Sai Krishna Samudrala C, Krishna Sai Radhi P, Murthy BS. Metal, ceramics and polymer nano-composites for various applications: A review. *Materials Today. Proceedings*, 2022, 56(3):1120-1128.
2. Nanda T, Singh, Shelly D, Mehta R. Advancements in multi-scale filler reinforced epoxy nanocomposites for improved impact strength: A review. *Critical Reviews in Solid State and Materials Sciences*, 2021, 46:281-329.
3. Pavlović VB, Pavlović VP. Polymer-ceramic nanocomposites and converging technologies. *Encyclopedia of Materials: Composites*, 2021, 2:134-144.
4. Khare V, Srivastava S, Kamle S, Kamath GM. Effect of Filler Functionalization on the Thermo-Mechanical behavior of Polypropylene Nanocomposites. *Procedia Structural Integrity*, 2019, 14:215-225.
5. Pukanszky B. Interfaces and interphases in multicomponent materials: past, present, future. *Eur. Polym. J.*, 2005, 41:645-662.
6. Sharma M, Gao S, Mader E, Sharma H, Wei LY, Bijwe J. Carbon surfaces and composite interphases. *Compos. Sci. Technol.*, 2014, 102:35-50.
7. Wen Z, Xu C, Qian X, Zhang Y, Wang X, Song S, Dai M, Zhang C. A two-step carbon fiber surface treatment and its effect on the interfacial properties of CF/EP composites: The electrochemical oxidation followed by grafting of silane coupling agent. *Appl. Surf. Sci.*, 2019, 486:546-554.
8. Salavagione HJ, Martinez G. Importance of covalent linkages in the preparation of effective reduced graphene oxide-poly(vinyl chloride) nanocomposites. *Macromolecules*, 2011, 44:2685-2692.
9. Lin J, Sun C, Min J, Wan H, Wang S. Effect of atmospheric pressure plasma treatment on surface physicochemical properties of carbon fiber reinforced polymer and its interfacial bonding strength with adhesive. *Composites Part B: Engineering*, 2020, 12:199-205.
10. Rafiee MA, Rafiee J, Srivastava I, Wang Z, Song H, Yu ZZ, Koratkar N. Fracture and fatigue in graphene nanocomposites. *Small*, 2010, 6:179-183.
11. Jeziorska R, Zielecka M, Gutarowska B, Zakowska Z. High density polyethylene composites filled with nanosilica containing immobilized nanosilver or nanocopper: thermal, mechanical, and bactericidal properties and morphology and interphase characterization. *Int. J. Polym. Sci.*, 2014, 10:1-13.
12. Pourbeyram S, Mohammadi S. Synthesis and characterization of highly stable and water dispersible hydrogel-copper nanocomposite. *J. Non-Crystalline Solids*, 2014, 402:58-63.
13. Xue B, Jiang Y, Li G. Preparation of Cu/Dickite/LLDPE nanocomposites and synergistic effect of exfoliated dickite and nano Cu in LLDPE matrix. *Polymer Composites*, 2013, 34(7):1061-1070.
14. Cárdenas G, Diaz J, Meléndrez MF, Cruzat C, García A. Colloidal Cu nanoparticles/chitosan composite film obtained by microwave heating for food package applications. *Polym. Bull.*, 2009, 62:511-524.
15. Bulychev NA. Preparation of Stable Suspensions of ZnO Nanoparticles with Ultrasonically Assisted

- Low-Temperature Plasma. *Nanosci. Techn.: An International J.*, 2021, 12(3):91-97.
16. Bulychev NA, Kolesnik SA. Reinforcement of Polymer Composite Materials by Titanium Dioxide Nanoparticles Synthesized in Plasma Discharge under Ultrasonic Cavitation. *IOP Conf. Proc.*, 2022, 2231:012012.
17. Bulychev NA. Study of Interaction of Surface-Active Polymers with ZnO Nanoparticles Synthesized in Ultrasonically Assisted Plasma Discharge. *Nanosci. Techn. An International J.*, 2022, 13(1):55-65.