PREPARATION OF ZINC OXIDE NANOPARTICLES FOR POLYMERIC SYSTEMS

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The aim of the work was the synthesis of zinc oxide nanoparticles incorporated into water-based polymer systems together with assessment of their effect on the mechanical properties of the prepared nanocomposites. ZnO nanoparticles were prepared by basic precipitation of zinc salts in water. To ensure perfect compatibility with the polymeric systems and to control the particle size, the ZnO nanoparticle surface was modified by polymeric surfactants tailored for this purpose. ZnO particles were physically bonded to the water-based system via electrostatic interactions. All the composites have shown improved mechanical properties compared to the unmodified systems depending on the ZnO concentration in the water-based system.

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Introduction

Nano zinc oxide is, in terms of application possibilities, one of the most promising metal oxides in the nanoform. It has several interesting features: N-type semiconductivity [1,2], exceptional piezoelectricity [3-5], and capability of UV absorption. The most common applications of ZnO in powdered form are as photocatalysts [6,7] and UV absorbers [8,9]. As an UV filter, ZnO has much better performance than TiO_2 [10,11], being transparent in the visible region. Nano ZnO is also known for its antimicrobial properties that are enhanced in the nanoform due to the increased specific surface area. These properties are essential for various industrial applications, including medicine, construction industry, furniture manufacturing, packaging technologies, etc.

The most commonly used methods of preparation of ZnO *via* wet chemistry include: chemical (reactive) precipitation or co-precipitation [12,13], synthesis in microemulsions or reverse micelles [14,15], hydrothermal [16,17] or solvothermal synthesis [18,19], sol-gel process [20,21], microwave-assisted synthesis [22,23], supercritical hydrothermal fluid processing [24,25], and sonochemical production [26,27]. Various modifications have been implemented to the basic precipitation method, including the addition of different types of organic surfactants enabling to control the particle size, the shape and aspect ratio. ZnO nanocomposites can be prepared by incorporating ZnO in various polymeric systems, either in thermoset or thermoplastic arrangement [29-33].

The aim of the work was to synthesize and characterize the zinc oxide nanoparticles for water-based polymer systems with the subsequent evaluation of their performance after curing. For these purposes, a method of the chemical precipitation of nano ZnO was chsen; sodium hydroxide and zinc acetate being used as the raw materials. Prepared ZnO nanoparticles had to be compatible with final media; therefore, the surface modification was carried out. Hydrophilic ZnO nanoparticles were synthesised and used in two-paint composite arrangements: as (i) a ZnO water-based acrylic and (ii) a ZnO water-based polyurethane system.

Experimental

The following materials were used in this work: $Zn(CH_3COO)_2 \cdot 2H_2O$ p.a. (Penta, the Czech Republic), NaOH p.a. (Penta, the Czech Republic), Axilat 967 – anionic aqueous dispersion of acrylate copolymer (Momentive Speciality Chemicals, The Netherlands), U 6150 – aqueous polyurethane dispersion (Alberdingk Boley, USA), Stabilizer Disperbyk-190 – solution of a highly molecular weight block copolymer (BYK-Chemie GnbH, Germany), and Stabilizer Disperbyk-2010 – aqueous emulsion of a structured acrylate copolymer (BYK-Chemie GmbH, Germany).

Preparation of Hydrophilic ZnO

Nano ZnO was prepared by precipitating $Zn(CH_3COO)_2$ with NaOH in aqueous phase, with the addition of a stabilizer in order to avoid aggregation and to reduce the particle size. Two types of stabilizers were chosen: Disperbyk-190 and Disperbyk-2010 (BYK-Chemie GmbH, Germany). They consist of high molecular weight block copolymers, intended to improve wettability and dispersion of the water-based suspensions. Disperbyk 190 was applied in the form of solution enabling steric stabilization of particles; Disperbyk-2010 in the form of a structured emulsion for both steric and electrostatic stabilization of the particles. Each stabilizer was used at a different concentration representing a set of five samples of ZnO (Table I).

Table I   The amount of stabilizers used for preparation of ZnO samples

Stabilizer		Amount of stabilizer g	Stabilizer concentration wt %
Disperbyk-190	Disperbyk-2010		
ZnO D-190-1/3	ZnO D-2010-1/3	3.375	1.21
ZnO D-190-1/2	ZnO D-2010-1/2	5.063	1.81
ZnO D-190-1	ZnO D-2010-1	10.125	3.54
ZnO D-190-2	ZnO D-2010-2	20.25	6.84
ZnO D-190-3	ZnO D-2010-3	30.375	9.92

Typically, 250 ml 2.4 mol l^{-1} NaOH aqueous solution was prepared with a selected amount of the respective stabilizer (Table I), whereas 250 ml 1.2 mol l^{-1} $Zn(CH_3COO)_2$ aqueous solution contained the same amount of the same stabilizer. The NaOH solution was then transferred into a separatory funnel and slowly dripped during 2.5 hours under vigorous stirring at 1000 rpm into the solution of $Zn(CH_3COO)_2$ at room temperature. Afterwards, the resulting thick white suspension was treated with an ultrasonic probe (equipment UP400S – probe H22), initially three times with 25 pulses at 100 % intensity; then, three times for 1 min., again, at full power. Between each ultrasonic treatment, the sample was manually mixed with a glass bar. The final product was placed into a glass bottle and stored.

It was necessary to purify the suspensions from by-products to prevent their destabilization and, therefore, the suspensions were centrifuged four times at 20 000 rpm at room temperature in a centrifuge (Sorvall Evolution RC, Thermo Scientific, USA), and rinsed with distilled water.

Preparation of ZnO Water-Based Acrylic Composite

Purified aqueous suspension of ZnO D-2010 3 was concentrated into 15 wt. % using centrifugation. The suspension was further dispersed by sonication in an acrylic dispersion — commercially available Axilat 967 (anionic aqueous dispersion of acrylate copolymer; Momentive Speciality Chemicals, The Netherlands). Two composite systems were prepared with concentration set to 0.74 and 1.44 wt. % of dry matter.

Preparation of ZnO Water-Based Polyurethane System

Purified aquous suspension of ZnO D-2010 3 was made 15 wt % in concentration using centrifugation and further dispersed by sonication in a polyurethane dispersion (product U6150; Alberdingk Boley, USA).

Measurements

- Atomic Force Microscopy (AFM)

For the respective analysis, dimension icon microscope (Bruker, USA) was used. Samples for AFM imaging were prepared by applying the corresponding nanoparticle dispersion upon the surface of mica platelets and subsequently dried. Adhesion and modulus maps were measured. The former one allowed to differentiate ZnO nanoparticles from the polymer matrix due to the differences in modulus. In this case, the ZnO has a higher modulus and appears brighter, while the polymer particles with a lower modulus are darker. The adhesion follows the same principle as the previous approach but, in this case, the ZnO has a lower adhesion with the AFM measuring tip giving rise to a darker tone, as opposed to the polymeric particles which have a higher adhesion and appear lighter.

- Dynamic Mechanical Analysis (DMA)

DMA of neat Axilat 967 binder (an acrylic dispersion; Momentive Speciality Chemicals, Netherlands) and a binder filled with ZnO nanoparticles (at a concentration of 0.71 and 1.44 %) was performed on the device ARES (TA Instruments, USA), by selecting the torsion mode, heating rate at 3 °C min^{-1} in a temperature interval from –50 to 25 °C and with frequency of 1 Hz. The whole measurement was carried out according to standard EN ISO 6721.

- Tensile Measurements

Tensile properties of the systems were measured according to the standard ASTM D 1708 on the device Adamel (model LHOMARGY DY 3; SMS-Labo, France). The loading speed was 100 mm min^{-1}, temperature 23 °C and humidity 52 %.

- Mechanical Tests — Hardness, Bending Strength, and Impact Resistance Testing

The three tests as a standard for lacquers evaluation were carried out following the standards ČSN ISO 1522, ČSN ISO 1519, and ČSN ISO 6272, respectively; the measurements as such being performed with the films of nanocomposite prepared using a ruler with a 300 µm gap.

- Thermogravimetric Analysis

TG was performed on a thermogravimetric analyzer (model Q 500; TA Instruments, USA); the measurements being carried out with powdered samples in the form of platinum pans, and with a heating rate of 10 °C min^{-1} set from a room temperature up to 1000 °C in atmosphere of air and nitrogen. TGA was used for characterization of the modified zinc oxide nanoparticles designed for the solvent-based polyacrylate system. Different methods were sought for determining the distribution and concentration of hydroxyl groups on the surface of ZnO nanoparticles.

Results and Discussion

Based on the particle size distribution of the prepared ZnO, dispersion ZnO D-2010 3 with the highest concentration of stabilizer (9.92 wt. %) was selected for application tests in water-borne systems. The efficiency of the purification was assessed by TGA measurements of washed and unwashed suspensions (see Fig. 1).

It has been found that sodium acetate is the major impurity, becoming undetectable after washing, which is particularly clear from the derivative of the mass loss (ZnO does not loss any mass under 1000 °C). The curves for sodium acetate and the ZnO before washing have matched the peak positions. The latter exhibiting peaks at totally different positions that, more likely, have corresponded to a degradation of modifier at the surface.

A knowledge of this parameter allowed us to optimize the surface modification of nanoparticles in terms of crucial properties. Several methods — e.g. titration method and infrared spectroscopy — were tested to determine the content of hydroxyl groups on the surface of the prepared ZnO nanoparticles. TGA analysis was evaluated as the most efficient method for indirect determination of the hydroxyl groups concentration, when the respectrive weight loss was found to

correspond to the amount of modifying components adsorbed on the surface of nanoparticles.
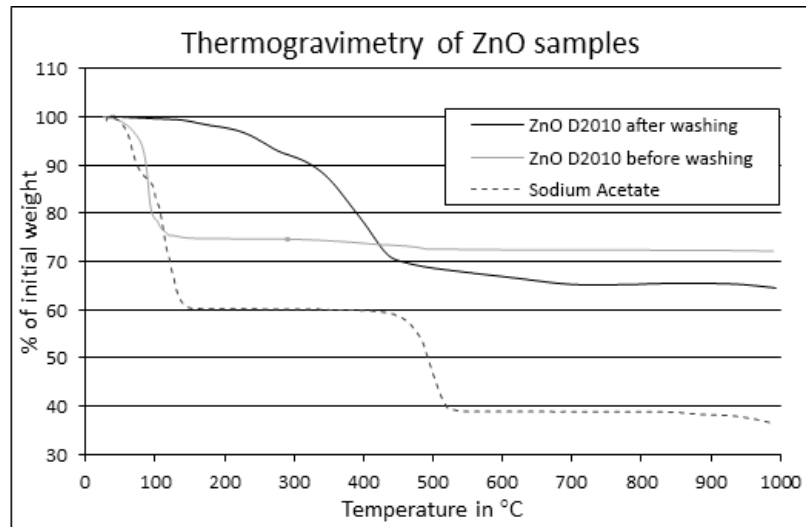

Fig. 1   Thermogravimetric analysis of ZnO D-2010 3 samples before and after washing and the initial sodium acetate

ZnO Nanoparticles Water-Based Acrylate System

The morphology of the initial Axilat 967 dispersion and the nano-ZnO modified system were assessed by AFM, when spherical particles ranging from 370 to 400 nm interconnected in aggregated into small groups for both systems could be identified (Figs 2 and 3).
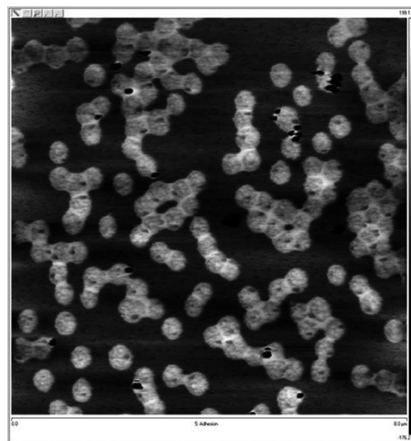

Fig. 2   Adhesion map of the neat Axilat 967 dispersion. Scan size 8 μm

Additionally, in the composite, there were ZnO nanoparticles of about 10 to 50 nm in diameter on the surface of the polymer particles. Such pattern has resembled raspberries, and might have undesirable effect on the mechanical

properties since ZnO nanoparticles on the surface of the polymer particles could prevent the creation of a compact film.

DMA measurements showed that the addition of the nanoparticles did not influence the glass transition temperature of the polymer system (Fig. 4, Table II). The nanofilled polyacrylate samples had a higher shear modulus in the glassy area at relatively low concentration of filling. An increase of the elasticity modulus is usually a sign of good dispersion quality.
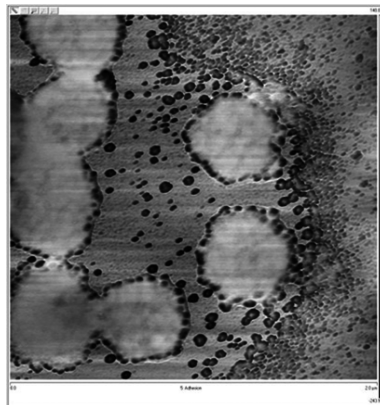

Fig. 3   Adhesion map of Axilat 967/ZnO D-2010 3 composite. Scan size 2 μm
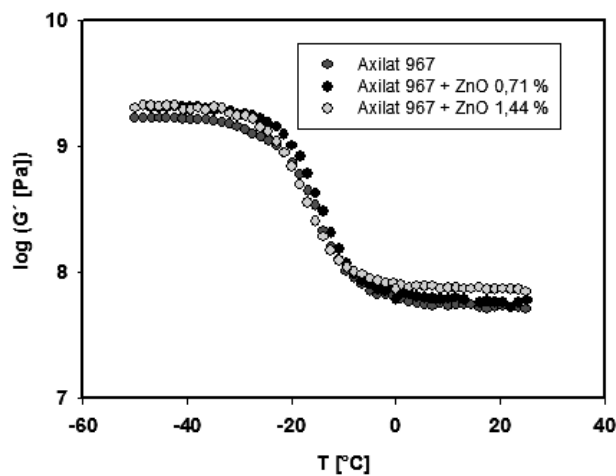

Fig. 4   Temperature dependence of the real shear modulus and loss tangent for the indicated samples

Table II   The resulting values of the DMA analysis

Sample	G' (−50) MPa	G' (25) MPa	T_g (tan(δ)) °C
Axilant 967	1330	76.8	−13
Axilant 967 + 1.44 % ZnO	2014	73.1	−15
Axilant 967 + 0.71 % ZnO	2011	57.0	−15

Also, it was found out that the addition of nanoparticles had had a positive effect on the tensile properties (Fig. 5). The addition of the nanoparticles significantly increased (two times) the work to break and (by a half) the toughness, compared with the unmodified system. Based on tensile and mechanical tests, it can be concluded that "raspberry" effect has not been reflected negatively in the compactness of the system.
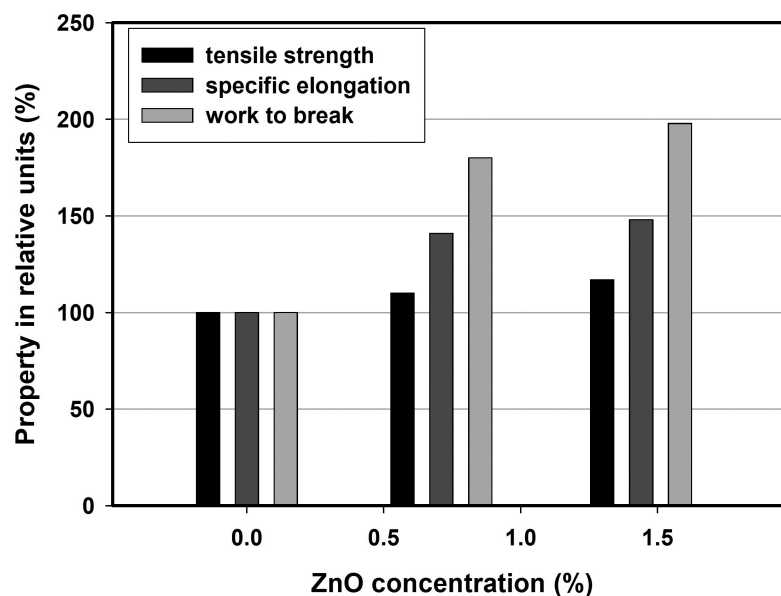

Fig. 5 Comparison of tensile properties of filled samples with the original system

Table III   The resulting values of the film properties

Sample	Hardness 21D %	Bending strength 21D mm	Impact resistance 21D mm
Axilant 967	2.42	< 3	100 / 100
Axilant 967 + 1.44 % ZnO	2.17	< 3	100 / 100
Axilant 967 + 0.71 % ZnO	2.17	< 3	100 / 100

The hardness, bending strength, and impact resistance have agreed well with the results of the tensile tests. Low hardness value (Table III) were in good agreement with the low elasticity modulus (Table II), whereas high values of specific elongation at the break (Fig. 5) gave some promise for the outstanding results in bending strength and impact resistance (Table III).

The properties of the films measured after 21 days are summarized in Table III.

ZnO Nanoparticles Water-Based Polyurethane System

The particle size distribution of the neat dispersion U6150 and the ZnO particles were measured using a dynamic light scattering method. By comparing the distribution curves of both dispersions U 6150 and ZnO D-2010, it has been observed that the mean values of particle size are both around 40 nm (Fig. 6). The ZnO-U6150 composite dispersion was analyzed by AFM and the resultant AFM modulus maps of the polyurethane dispersion (modified by dispersion of nanoparticles ZnO D-2010) are shown in Fig. 7.
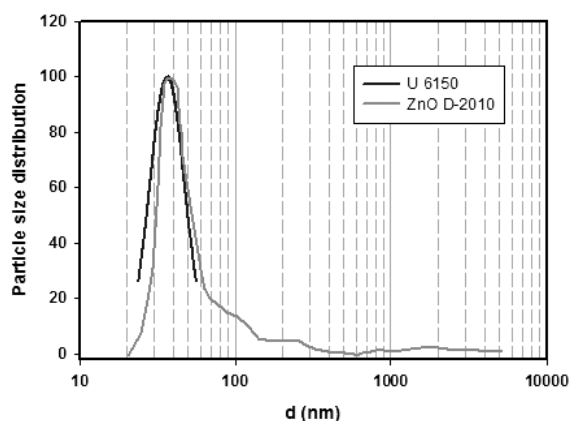

Fig. 6 Distribution curve for the sample U 6150 and ZnO D-2010
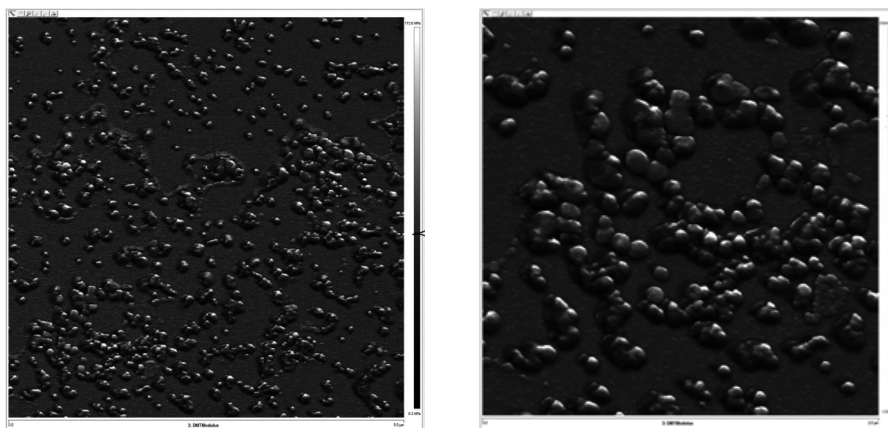

Fig. 7 AFM modulus map of the polyurethane dispersion U 6150 with nano ZnO D-2010, scan size 5 μm on the left, and 2 μm on the right

The modulus maps have allowed us to distinguish the soft particles of polyurethane dispersion that appeared darker than a configuration of hard ZnO nanoparticles coloured brighter (Fig. 6). The AFM scans also show no significant aggregation of ZnO nanoparticles in the polyurethane dispersion. Conversely, one could notice a behavior similar to the acrylic dispersions, in which the polymer particles were "coated" with homogeneously mixed nanoparticles of ZnO.

Finally, tensile measurement and glass transition temperature of the composite film were analysed by penetration method (Fig. 8).
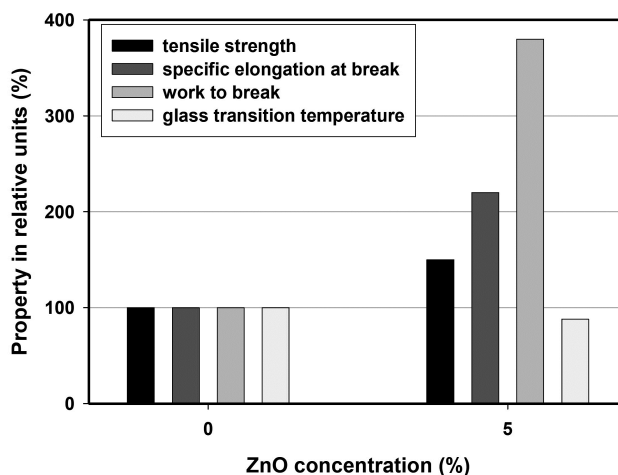

Fig. 8 Comparison of the tensile properties and the glass transition temperature of the filled sample with the original system

As seen, addition of 5 % of ZnO nanoparticles in the polyurethane dispersion had a positive effect on the tensile properties; especially, with respect to a significant increase in elongation at the break. The described increase was accompanied by a slight decrease of the glass transition temperature (of about 4 °C), which may be explained by the effect of the modifying component.

Conclusion

Nanoparticles of ZnO were prepared using the commercial types of surfactants *Disperbyk-2010* and *Disperbyk-190* for water-based systems. The best results were obtained using *Disperbyk-2010* at a concentration of 9.92 % for the ZnO synthesis. The prepared ZnO nanoparticles were incorporated to acrylate and polyurethane dispersions.The test results for the various polymeric systems in which the nano ZnO has been applied can be summarized as follows.

It has been found out that ZnO nanoparticles is being homogeneously dispersed and significantly improves the tensile properties of both systems. The main disadvantage of this solution is that the surfactant is only adsorbed on the nanoparticle surface and, therefore, it may be removed during dilution or washing. The particles with a reduced concentration of surfactant on the surface tend to agglomerate, which has also been confirmed experimentally. Furthermore, the surfactant may diffuse in the polymer during its lifetime, leading to unwanted plasticization.

The exceptional properties of ZnO in the nanoform can potentially benefit to a wide range of polymers. For this purpose, it is necessary to design the proper

conditions of synthesis and the surface modification should be tailored individually to each polymeric system. Based on our experience, we were able to prepare the different ZnO nanoparticles and with successful dispersion into the water-based polyacrylate systems. All the composites have shown great improvements in terms of mechanical properties. The results of the presented work are a very good example showing great potential for the effective applicability of ZnO in manufacturing of various kinds of polymeric nanocomposites.

Acknowledgement

References

[1]   Look D.C.: Mater. Sci. Eng. B **80**, 383 (2001).
[2]   Carcia P.F., McLean R.S., Reilly M.H.: Appl. Phys. Lett. **88**, 123509 (2006).
[3]   Wang Q.J., Pflügl Ch., Andress W.F., Ham D., Capasso F., Yamanishi M.: J. Vac. Sci. Technol. B **26**, 1848 (2008).
[4]   Pang H., Garcia-Gancedo L., Fu Y.Q., Porro S., Gu Y., Luo J.K., Zu X., Placido F., Wilson J.I.B., Flewitt A.J., Milne W.I.: Phys. Status Solidi A **210**, 1575 (2013).
[5]   Jagadish C., Pearton S.: *Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties and Applications*, Elsevier Ltd., Oxford, 2006.
[6]   Ekambaram S.: J. Alloys Compd. **390**, L4 (2005).
[7]   Johnson J.A., Heidenreich J.J., Mantz R.A., Baker P.M., Donley M.S.: Prog. Org. Coat. **47**, 432 (2003).
[8]   Goh E.G., Xu X., McCormick P.G.: Scr. Mater. **78-79**, 49 (2014).
[9]   Joni I.M., Purwanto A., Iskandar F., Hazata M., Okuyama K.: Chem. Eng. J. **155**, 433 (2009).
[10] Pinnell S.R., Fairhurst D., Gillies R., Mitchnick M., Kollias N.: Dermatologic Surgery **26**, 309 (2000).
[11] Barnes R.J., Molina R., Xu J., Dobson P., Thompson I.P.: J. Nanopart. Res. **15**, 1432 (2013).
[12] Kolodiejczak-Radzimska A., Jesionowski T., Krysztafkiewicz A.: Physicochem. Probl. Miner. Process. **44**, 93 (2010).
[13] Lanje A.S., Sharma S.J., Ningthoujam R.S., Ahn J.S., Pode R.B.: Adv. Powder Technol. **24**, 331 (2013).
[14] Hirat T., Asada Y.: J. Colloid Interface Sci. **284**, 184 (2005).
[15] Li X., He G., Xiao G., Liu H., Wang M.: J. Colloid Interface Sci. **333**, 465

(2009).

[16] Ni Y., Wei X., Hong J., Ye Y.: Mater. Sci. Eng. B **121**, 42 (2005).

[17] Demyanets L.N., Li L.E., Uvarova T.G.: J. Mater. Sci. **41**, 1439 (2006).

[18] Wang Ch., Shen E., Wang E., Gao L., Kang Z., Tian Ch., Lan Y., Zhang Ch.: Mater. Lett. **59**, 2867 (2005).

[19] Chen S., Li L., Chen X., Xue Z., Hong J., You X.: J. Cryst. Growth **252**, 184 (2003).

[20] Ristic M., Music S., Ivanda M., Popovic S.: J. Alloys Compd. **397**, L1 (2005).

[21] Lee K., Saipolbahri Z.A., Guan B.H., Soleimani H.: Am. J. Appl. Sci. **11**, 959 (2014).

[22] Schneider J.J., Hoffmann R.C., Engstler J., Klyszcz A., Erdem E., Jakes P., Eichel R., Pitta-Bauermann L., Bill J.: Chem. Mater. **22**, 2203 (2010).

[23] Hu X.L., Zhu Y.J., Wang S.W.: Mater. Chem. Phys. **88**, 421 (2004).

[24] Sue K., Murata K., Kimura K., Arai K.: Green Chem. **5**, 659 (2003).

[25] Viswanathan R., Gupta R.B.: J. Supercrit. Fluids 27, **187** (2003).

[26] Alammar T., Mudring A.V.: ChemSusChem **4**, 1796 (2011).

[27] Banerjee P., Chakrabarti S., Maitra S., Dutta B.K.: Ultrason. Sonochem. **19**, 85 (2012).

[28] Espitia P.J.P., Soares N.F.F., Teófilo R.F., Coimbra J.S., Vitor D.M., Batista R.A.,Ferreira S.O., de Andreade N.J., Medeiros E.A.A.: Carbohydr. Polym. **94**, 199 (2013).

[29] Anitha, S., Brabu, B., et al.: Carbohydr. Polym. **87**, 1065 (2012).

[30] Ahangar E.G., Abbaspour-Fard M. H., Shahtahmassebi N., Khojastehpour M., Maddahi P.: J. Food Process. Preserv. **39**, 1442 (2015).

[31] Nenna G., De Girolamo Del Mauro A., Massera E., Bruno A., Fasolino T., Minarini C.: J. Nanomater. **2012**, 7 (2012).

[32] Hemalatha K. S., Sriprakash G., Ambika Prasad M.V.N., Damle R., Rukmani K.: J. Appl. Phys. **118**, 154103 (2015).

[33] Rýznarová B., Zelenka J., Lednický F., Baldrian J.: J. Appl. Polym. Sci. **109**, 1492 (2008).