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Preparation and characterization of selected types of inorganic nanomaterials

Annotation of the dissertation thesis
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1. INTRODUCTION

The term „nanotechnology“ represents the technical field that deal with the preparation and use of materials at the nanometer scale, which have applications in the real-scale world. Nanotechnologies involve the production and application of the physical, chemical and biological systems with atomic dimensions to sub-micron, but the integration of the resulting nanostructures into larger units. New materials are obtained with completely unique properties useful in various fields of human activities (e.g. electronics, health, engineering, building, car industry, military industry, environment, chemical and textile industries, etc.).

Nanomaterials should meet the following conditions:

- they have at least one dimension of its internal structure in the size interval 1-100 nm
- their properties are based on the physical or chemical characteristics of the matter at the level of atoms and molecules, which are unusual compared to the same material or system with larger dimensions
- they can be combined to form a larger structure having the similar properties in macro-scale

Classification of nanomaterials by geometric dimension:

- 0D - nanoelements, nanoparticles
- 1D - nanotubes, nanofibers
- 2D - nanolayers, nanoplates
- 3D - a combination of the above materials into larger units

Currently, much attention is paid to the preparation and study of the properties of different types of nanoparticles for various applications, and it is also very important to deal with the characterization of such systems.

2. AIMS

In this work the various methods of particle size distribution measurement were evaluated and compared. The selected types of commercial nanomaterials were measured: Silica Ludox and sodium montmorillonite.

The second aim of the work was the synthesis and characterization of zinc oxide nanoparticle designed for the application in water-based and solvent-based polymer systems as an additive and subsequent evaluation of their performance characteristics after curing.

The various kinds of ZnO nanoparticles were prepared for the three application environments with different hydrophobicity (water, alkyd and polyacrylate systems). Nanoparticles for the particular environment were prepared using different techniques; the basic idea, however, was the same for all types. ZnO nanoparticles were prepared from water-soluble salts and the appropriate base. The surface of ZnO nanoparticles was modified by molecular tailors designed to achieve full compatibility with the selected polymeric system. The surface was modified in-situ or by post-synthesis technique. The special modifiers were attached to the surface of the nanoparticles by means of physical or chemical bonding. The relation between size and concentration of the ZnO nanoparticles, type of modification and properties of the nanofilled polymer systems were investigated.

The first type of hydrophilic ZnO nanoparticles was synthesized and used in two paint composite systems: a ZnO water-based acrylic system and a ZnO water-based polyurethane system. Two other hydrophobic ZnO nanoparticles were developed for two solvent-based systems: an acrylate copolymer and an alkyd.

The composite systems were then analyzed. The analysis showed great improvements in mechanical properties and UV aging resistance. Those improvements could be achieved only with an excellent compatibility between the particles and the polymeric systems.

3. THEORY

Nano zinc oxide is, in terms of application possibilities, one of the most promising metal oxide in nanoform. It has several interesting features: N-type semiconductivity [1,2], exceptional piezoelectricity [3-5] and UV absorption. The most common applications of ZnO in powder form are photocatalysts [6,7] and UV absorbers [8,9]. As a UV filter, ZnO has much better performance than TiO₂ [10,11], and is transparent in the visible range. Nano ZnO is also known for its antimicrobial properties, which are enhanced in nanoform due to increased specific surface area. These properties are essential for various industrial applications, including medicine, construction, furniture, packaging etc.

The most commonly used methods for 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 synthesis [26,27]. Various modifications have been implemented to the basic precipitation method, including mainly the addition of different types of organic surfactants, which enables control of particle size, shape and aspect ratio of components.

Currently there doesn't exist any comprehensive theory, which would be able to predict the properties of the nano-structured polymers directly from information about the binder and nanoparticles. Availability of valid data required for reliable prediction is limited. For these reasons, the relations between size, shape, type of modification and the desired polymeric nanocomposite properties have to be found and verified experimentally.

4. APPLIED PROCEDURES

4.1 Particle size and shape measurements

Various methods were used to measure shape and particle size distribution, e.g. transmission electron microscopy (TEM), atomic force microscopy (AFM), acoustic spectrometry, methods based on the light scattering and X-ray disc centrifuge system.

4.2 Preparation of hydrophilic ZnO

Nano ZnO was prepared via precipitation of $\text{Zn}(\text{CH}_3\text{COO})_2$ by NaOH in aqueous phase, with the addition of a stabilizer to avoid aggregation and 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 water-based suspensions. Disperbyk 190 is in the form of solution and causes steric stabilization of particles. Disperbyk-2010 is in the form of a structured emulsion and causes both steric and electrostatic stabilization of the particles. Each stabilizer was used at different concentration for preparation of a set of five samples of ZnO (Table 1).

Typically, 250 ml of 2,4 mol/l NaOH aqueous solution with a selected amount of the respective stabilizer (Table 1), and 250 ml of 1,2 mol/l $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution with the same amount of the same stabilizer were prepared. The NaOH solution was then transferred into a separate burette and slowly dripped during 2,5 hours under vigorous stirring at 1000 rpm into the solution of $\text{Zn}(\text{CH}_3\text{COO})_2$ at room temperature. The resulting thick white suspension was then treated with an ultrasonic probe (equipment UP400S – probe H22), initially three times with 25 pulses at 100 % power, and then three times at an interval of 1 minute for 1 minute using 100 % power. The sample was manually mixed with a glass bar between each ultrasonic treatment. The final product was poured into a glass bottle and stored.

Table 1: The amount of stabilizers used for preparation of ZnO samples

Stabilizer		Stabilizer concentration (wt. %)
Disperbyk-190	Disperbyk-2010	
ZnO D-190-/3	ZnO D-2010-1/3	1,21
ZnO D-190-1/2	ZnO D-2010-1/2	1,81
ZnO D-190-1	ZnO D-2010-1	3,54
ZnO D-190-2	ZnO D-2010-2	6,84
ZnO D-190-3	ZnO D-2010-3	9,92

It was necessary to purify the suspensions from by-products in order to prevent its destabilization. Therefore the suspensions were centrifuged four times at 20 000 rpm and room temperature in a Sorvall Evolution RC centrifuge, and washed with distilled water.

4.2.1 Preparation of ZnO water-based acrylic composite

Purified aqueous suspension of ZnO D-2010 3 was concentrated to 15 wt. % using centrifugation. The suspension was further dispersed by ultrasounds in the commercial acrylic dispersion Axilat 967. Axilat 967 is an anionic aqueous dispersion of acrylate copolymer, supplied by Momentive Speciality Chemicals, Netherlands. Two composite systems were prepared with concentrations of 0,74 and 1,44 wt. % of dry matter.

4.2.2 Preparation of ZnO water-based polyurethane composite

Purified aqueous suspension of ZnO D-2010 3 was concentrated to 15 wt. % using centrifugation. It was further dispersed by ultrasounds in the commercial polyurethane dispersion U6150, supplied by Alberdingk Boley, USA.

4.3 Preparation of hydrophobic ZnO

Nano ZnO was prepared via precipitation of $\text{Zn}(\text{CH}_3\text{COO})_2$ by NaOH in a water/toluene emulsion. The emulsions were stabilized with one of the two following methacrylate copolymers: 30S and 31S (Synpo, Czech Republic). 30S is a methacrylate copolymer based on dimethylaminoethyl methacrylate and butyl methacrylate and 31S is a methacrylate copolymer based on dimethylaminoethyl methacrylate, butyl methacrylate and hydroxyethyl methacrylate. A surfactant block copolymer, containing a sulfate group allowing chemical bonding to the ZnO surface, and hydroxyl groups allowing reaction with the acrylate matrix, was added. Four ZnO samples were prepared with each copolymer containing different amount of hydroxyl groups. In a typical synthesis, two emulsions were prepared: the first (emulsion 1) contains 272 ml toluene, 2 g of the selected copolymer (30S or 31S), 10 ml of a 1,2 mol/l $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution and 2 g of the surfactant copolymer. The second (emulsion 2) contains 272 ml toluene, 2 g of the same copolymer, and 10 ml of a 2,4 mol/l NaOH aqueous solution. Each of the two emulsions was stirred 1 hour at 1000 rpm, followed by sonication using an ultrasonic probe at 70 W power for 2 minutes. Then both emulsions were mixed together, stirred for 1 hour at a speed of 1000 rpm, and sonicated at 70 W for 2 minutes.

The obtained suspensions were very stable, and it was impossible to separate the particles by using the centrifuge at maximum speed. Nanofiltration was utilized as an alternative to purify the suspensions. The filter assembly Nalgene DS320 with a membrane was used under constant stirring of the suspension in order to avoid colmatation of the membrane and vacuum in order to compensate the osmotic pressure. Clean toluene was added during the filtration to keep the suspension diluted and avoid aggregation of the nano-ZnO.

4.3.1 Preparation of ZnO solvent-based polyacrylate composite

The prepared nanoparticles were dispersed by ultrasonication (Hilscher UP 400S) into the solvent-based acrylic binder containing hydroxyl groups. Four samples were prepared (AKR-1,2,3,4) with 5 wt. % concentration of nanoparticles in dry matter. The systems were cured by hexamethylene diisocyanate (Desmodur[®] H). The curing conditions were 24 h at 25 °C and 5 h at 50 °C.

4.3.2 Preparation of ZnO solvent-based alkyd composite

Purified nanoparticles were dispersed into the chosen alkyd using ultrasound. Two samples were prepared (ALK1 with 30S additive and ALK2 with 31S additive) with 5 wt. % concentration of nanoparticles in dry matter of the dispersion.

4.4 AFM

Dimension Icon microscope (Bruker, USA) was used for AFM (atomic force microscopy) analysis. Samples for AFM analysis were prepared by application of respective nanoparticle dispersion on the surface of mica platelets and subsequent drying. Adhesion map and modulus map was measured. The modulus map allows to differentiate ZnO nanoparticles from the polymer matrix due to differences in modulus. In this case, the ZnO has higher modulus and is shown brighter, while the polymer particles with a lower modulus appear darker. The adhesion follows the same principle as previous, but this time, the ZnO has a lower adhesion with the AFM measuring tip and appears darker, as opposed to the polymeric particles which have a higher adhesion and appear lighter.

4.5 Dynamic light scattering method

System 90 Plus/BI-MAS (Brookhaven Instruments Corporation, USA) is designed to measure particle size in diluted dispersions. All samples were measured in a plastic cuvette

(dimensions 1x1 cm). When measurement was necessary, each sample diluted with distilled water. All measurements were performed at 90°.

4.6 *Sedimentation in a centrifugal field (XDC)*

BI-XDC device (Brookhaven Instruments Corporation, USA) is used for measuring the particle size distribution in the centrifugal field by XDC method.

The small amount of pure solvent was charged to disk of the device and at intervals of 10 seconds was measured and the stored signal value corresponding to 0 % concentration of the dispersion, i.e. the state in which there are no particles. The solvent was removed from the disk drive and dried. Subsequently, it was charged with 20 ml of the sample and the corresponding signal value was measured. During the measurement, the sample was stirred in order to maintain it homogeneous. The obtained signal corresponds to a concentration of 100 %. After these calibration measurements stirring was switched off, switched on, the motor apparatus and the speed of the disk were set at a selected fixed value. After completion of the measurement, both the distribution and the cumulative curve can be seen on the computer monitor.

4.7 *DMA*

DMA (dynamic mechanical analysis) of neat Axilat 967 binder (acrylic dispersion, Momentive Speciality Chemicals, Netherlands) and binder filled with ZnO nanoparticles (concentration 0,71 and 1,44 %) was performed on the device ARES (TA Instruments, USA). The measurement was performed in torsion, heating rate 3 °C/min in the temperature range from -50 to 25 °C and at a frequency of 1 Hz. The measurement was carried out according to standard EN ISO 6721.

4.8 *Tensile measurement*

Tensile properties of the systems were measured according to standard ASTM D 1708 on the device Adamel LHOMARGY DY 36 (SMS-Labo, France). The loading speed was 100 mm/min.

4.9 *Mechanical tests - hardness, bending strength, and impact resistance testing*

The three tests are standard for laquers evaluation and were carried out following the standards ČSN ISO 1522, ČSN ISO 1519 and ČSN ISO 6272 respectively. The tests were performed on films of nanocomposite prepared using a ruler with a 300 µm gap.

4.10 Analysis in a QUV panel

The samples of alkyd system unfilled and filled with hydrophobic ZnO nanoparticles were tested in a QUV panel. The measurements were performed according to standard EN 927-6 Paints and varnishes - Coating materials and coating systems for exterior wood - Part 6: Exposure of wood coatings to artificial weathering using fluorescent UV lamps and water. The lamps were set at 340 nm. The measurement was performed in weekly cycles and conditions were as follows:

Day 1: 24 hours without irradiation, temperature 50 °C, the condensation of 95 %

2 to 7 Day: alternation of 2,5 hours exposure and 30 min sprinkling water

5. RESULTS

5.1 Measurement of particle size distribution

Two types of nanoparticles were selected to compare various methods used to measure particle size distribution: spherical silica and plate-like montmorillonite.

5.1.1 Silica Ludox 10% (Grace)

Material properties:

- 10% aqueous dispersion of nanosilica
- without special stabilization
- spherical shape

Table 2: Mean values of particle sizes measured by various methods:

Method	Particle size
acoustic spectrometry	30 nm
methods based on the light scattering	25 nm
XDC	18 nm
AFM	23 – 28 nm
particle size specified by the producer	28 ± 5 nm

Practically all methods provided results close to declared data.

5.1.2 Sodium montmorillonite Cloisite Na⁺ (BYK-Gardner)

Material properties:

- montmorillonite clay dispersed in distilled water
- plate-shaped particles

Table 3: Mean values of particle sizes measured by various methods:

Method	Particle size
acoustic spectrometry	22 - 35 nm
methods based on the light scattering	190 nm
XDC	10 nm
AFM	plates 120 – 250 nm, aggregates 400 nm
TEM	plates 30 - 200 nm

In the case of plate-shaped particles only AFM or TEM are suitable to give accurate information about their size and shape.

5.2 ZnO hydrophilic

5.2.1 ZnO nanoparticles for water-based acrylate system

The morphology of the neat Axilat 967 and the nano-ZnO modified system were assessed by AFM. Spherical particles ranging from 370 to 400 nm interconnected in small groups were identified for both systems (Figure 1 and 2).

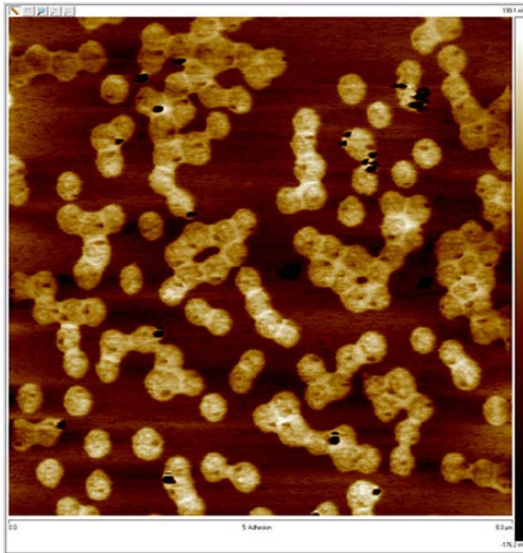


Figure 1: Adhesion map of the neat Axilat 967 dispersion. Scan size 8 μm .

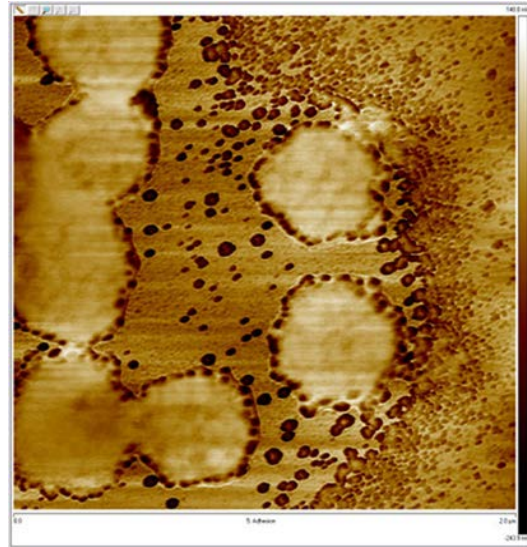


Figure 2: Adhesion map of Axilat D967/ZnO D-2010 3 composite. Scan size 2 μm .

Additionally, there are ZnO nanoparticles (10-50 nm in diameter) on the surface of the polymer particles in the composite. Such pattern resemble to raspberries, and may have undesirable effects on the mechanical properties since ZnO nanoparticles on the surface of the polymer particles can 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 (Figure 3, Table 4). The nanofilled polyacrylate samples had higher shear modulus in the glassy area at relatively low concentration of filling. An increase of the elasticity modulus is usually the sign of a good dispersion quality.

Table 4: The resulting values of the DMA analysis

Sample	G' (-50) (MPa)	G' (25) (MPa)	Tg (tan(δ)) ($^{\circ}\text{C}$)
Axilat 967	1330	76,8	-13
Axilat 967 + 1,44 % ZnO	2014	73,1	-15
Axilat 967 + 0,71 % ZnO	2011	57,0	-15

It was found that the addition of nanoparticles had also a positive effect on tensile properties (Figure 4). The addition of the nanoparticles significantly increases the work to break (2 times) and toughness (1,5 times), compared with the unmodified system. On the basis of tensile and mechanical tests, it can be concluded that "raspberry" effect is not reflected negatively on the compactness of the system.

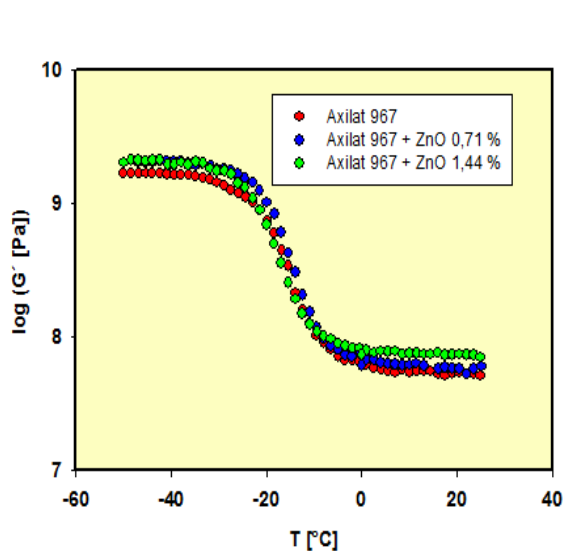


Figure 3: Temperature dependence of the real shear modulus and loss tangent for the indicated samples

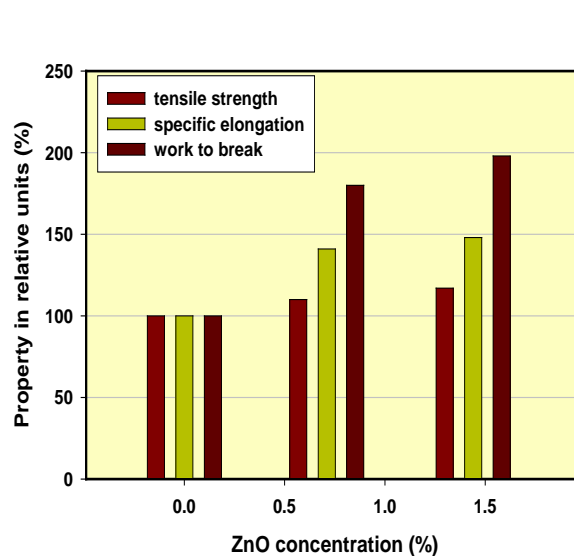


Figure 4: Comparison of tensile properties of filled samples with the original system

The obtained results of the prepared films which were measured after 21 days are summarized in Table 5.

Table 5: The resulting values of the film properties

Sample	Hardness 21D (%)	Bending strength 21D (mm)	Impact resistance 21D (mm)
Axilat 967	2,42	< 3	100/100
Axilat 967 + 1,44 % ZnO	2,17	< 3	100/100
Axilat 967 + 0,71 % ZnO	2,17	< 3	100/100

The hardness, bending strength and impact resistance are in a good agreement with the results of tensile tests. High values of specific elongation at break (Figure 4) gave the premise for outstanding results in bending strength and impact resistance (Table 5). Low hardness value (Table 5) is in good agreement with the low elasticity modulus (Table 4).

5.2.2 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), we observe that the mean values of particle size are both around 40 nm (Figure 5).

The ZnO-U6150 composite dispersion was analyzed by AFM. The results for polyurethane dispersion which were modified by nanoparticles ZnO D-2010 are presented in Figure 6.

The modulus maps allow to distinguish the soft particles of polyurethane dispersion which appear darker and hard ZnO nanoparticles which appear brighter (Figure 5). The AFM scans show no significant aggregation of ZnO nanoparticles in the polyurethane dispersion. Conversely, it is possible to observe similar behavior as the acrylic dispersions in which the polymer particles are "coated" with homogeneously mixed nanoparticles ZnO.

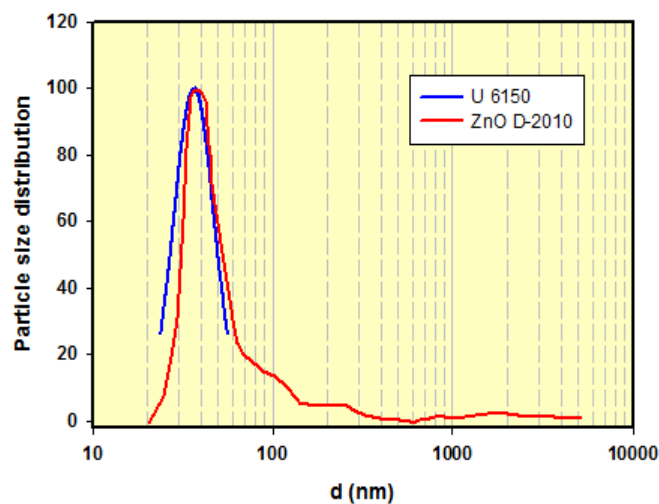


Figure 5: Distribution curve for the sample U 6150 and ZnO D-2010

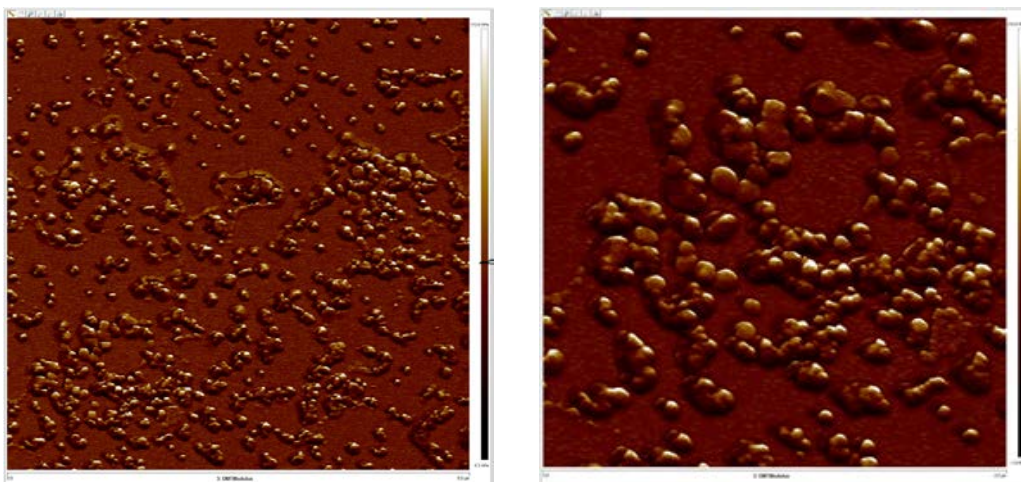


Figure 6: AFM modulus map of the polyurethane dispersion U 6150 with nano ZnO D-2010. Scan size 5 μm on the left and 2 μm on the right.

Tensile measurement and glass transition temperature were measured by penetration method on the composite film (Figure 7).

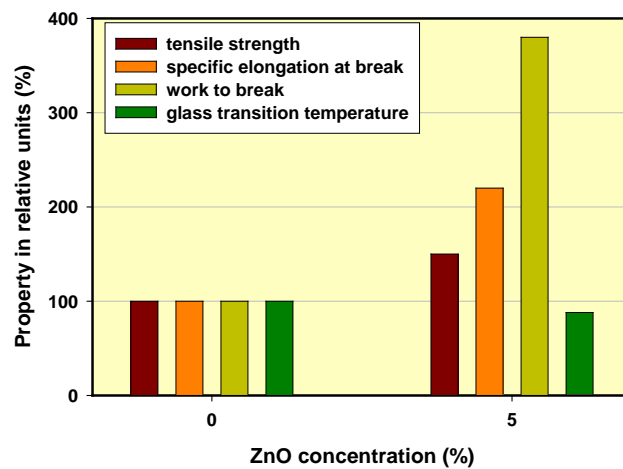


Figure 7: Comparison of the tensile properties and the glass transition temperature of the filled sample with the original system

Addition of 5 % of ZnO nanoparticles in the polyurethane dispersion had a positive effect on the tensile properties. Especially, a significant increase in elongation at break and work to break was observed. The described increase was accompanied by a slight decrease of glass transition temperature (about 4 °C). It may be due to the effect of the modifying component.

5.3 ZnO hydrophobic

5.3.1 ZnO nanoparticles for alkyd system

After purification, the particles were characterized using AFM (Figure 8). Figure 8 shows mainly aggregates up to 400 nm. The aggregates are composed of primary particles of a laminar shape, with a thickness ranging from 20 to 30 nm, and a width ranging from 80 to 150 nm. Due to the extensive aggregation, the particle size distribution was not evaluated.

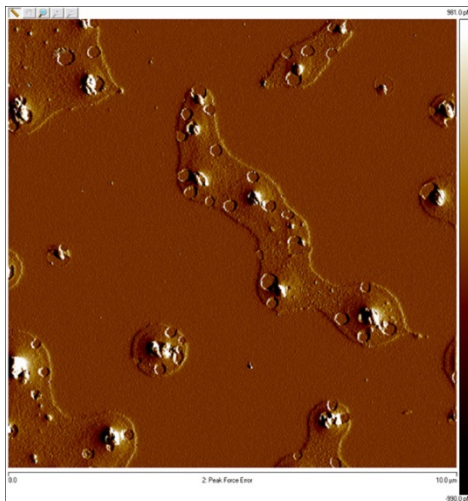


Figure 8: Peak Force Error map of purified ZnO sample. Scan 10 μm .

The suitability of the modification to the selected alkyd was evaluated on the basis of one-month stability of the prepared dispersions. The appearance of the dispersions after one month's storage is shown in Figure 9. From this figure it is clear that the dispersion of nanoparticles ALK1 is much more stable than the dispersion ALK2. In the dispersion ALK2 agglomeration of particles occurred, and consequently their sedimentation. The quality of the dispersion of the modified nanoparticles ALK1 was studied using XDC (Figure 10) and AFM (Figure 11).

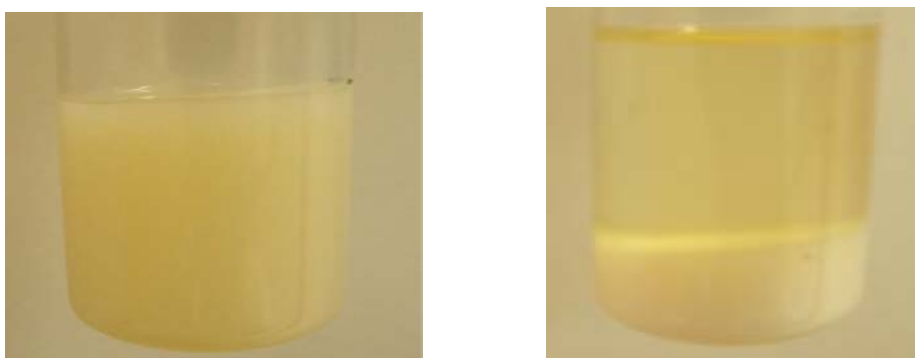


Figure 9: Appearance of the dispersion ALK1 (left) and ALK2 (right) after one month

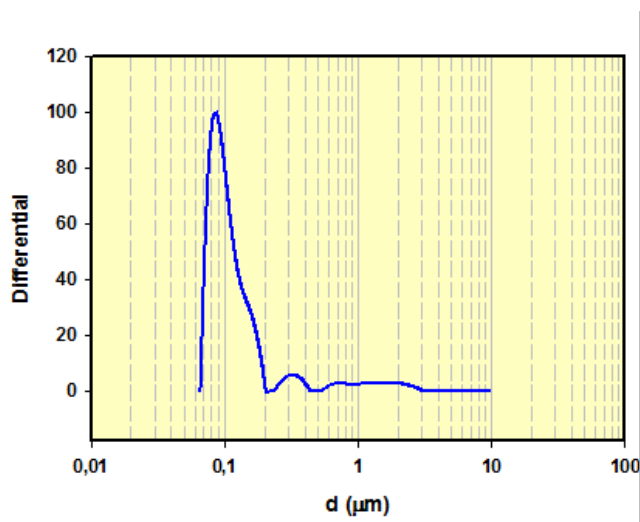


Figure 10: The particle size distribution of the ZnO nanoparticles for sample ALK1

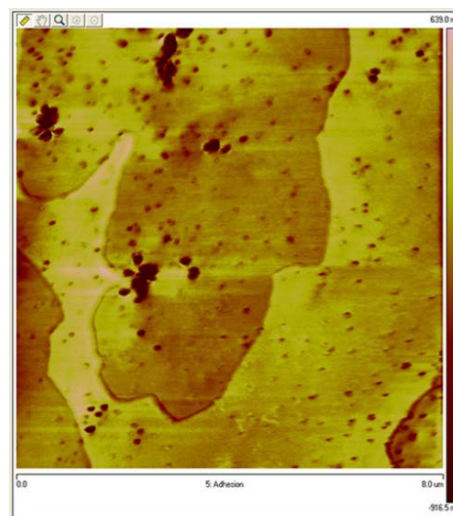


Figure 11: Adhesion map of sample ALK1. Scan 8 μm .

Cured free films of filled and unfilled alkyd were compared by DMA. Figure 12 compares the temperature dependence of the real tensile moduli of both systems. The addition of ZnO nanoparticles increased tensile modulus both in the glassy state (18%) and the rubbery region. Taking into account that ZnO nanoparticles were used in low aspect ratio, such result can be considered as a very significant increase. The significant increase in modulus in the glassy state indicates a very good dispersion of the nanoparticles. A very interesting observation is the shift of the glass transition region to a temperature 10 $^{\circ}\text{C}$ higher.

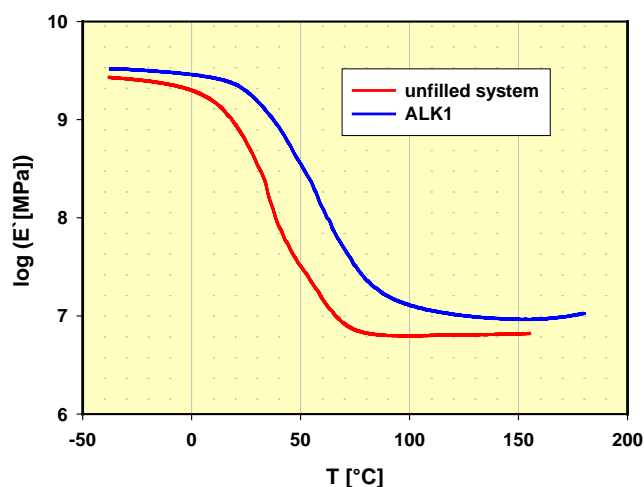


Figure 12: Temperature dependence of the real tensile modulus of filled and unfilled alkyd system

The resistance of alkyd system to aging under UV irradiation was tested in a QUV panel. For this study the tensile properties and Tg of neat and ZnO-filled systems were measured for different exposition times (Figures 13 and 14). The strain at break and the work to break are lowered with increasing exposure time to UV for both systems. However the ZnO filled system shows slower decay than the neat system, and has higher values at any exposure time. For example, the work to break after 500 hours of exposure is three times higher for the nanofilled system, than for the neat system. The tensile strength and glass transition temperature of both samples increase after exposure that may be due to further double bonds cross-linking. However the strength decreases after 200 hours for the neat system, and 800 hours for the ZnO filled system. The neat system lost its mechanical properties after 600 hours of exposure and could not be tested anymore, explaining the missing data. The measurements clearly show the increased resistance of the alkyd film to UV radiation when modified by ZnO nanoparticles.

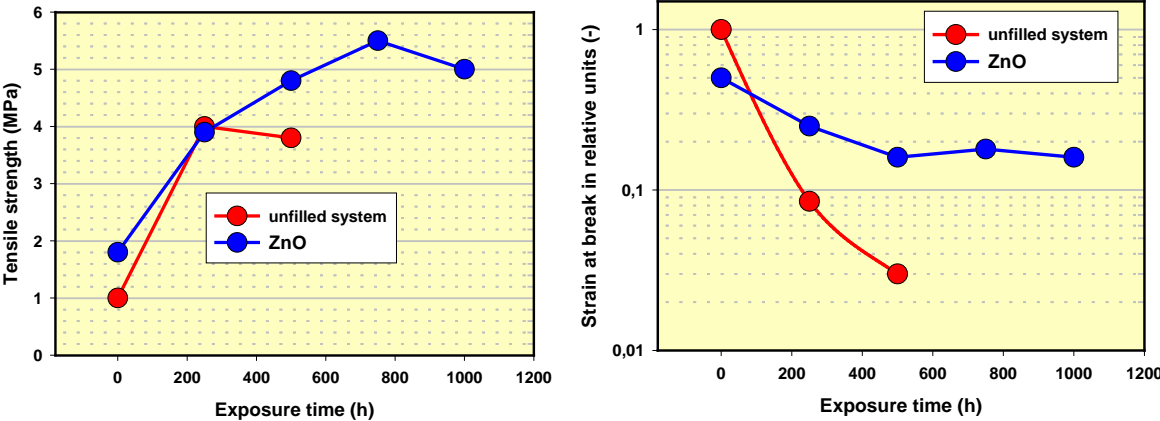


Figure 13: Effect of exposure in the QUV panel on the tensile strength and strain at break

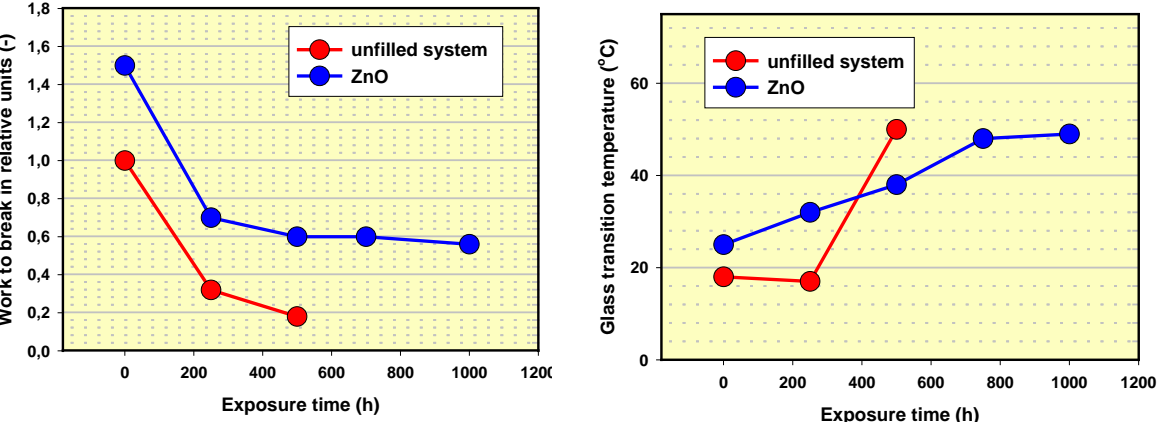


Figure 14: Effect of exposure in the QUV panel on work to break and the glass transition temperature

5.3.2 ZnO nanoparticles for solvent polyacrylate system

The prepared dispersions were stable without aggregation and subsequent sedimentation after two month storage (Figure 15).



Figure 15: Appearance of the dispersion AKR-4 after two months storage

Prepared ZnO nanoparticles were analyzed using AFM. ZnO nanoparticles have the character of laminar with dimensions in the range 50-180 nm (Figure 16).

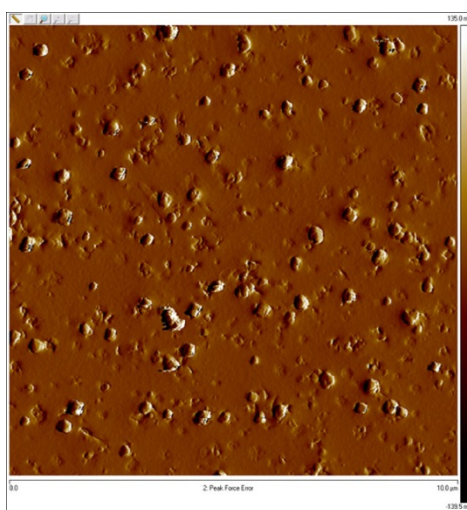


Figure 16: Peak Force Error map of purified sample of dispersion AKR-3

To assess the quality of dispersion in the final polymer, cured polymers have been cut using an ultramicrotome under cryogenic conditions, and scanned by AFM (Figure 17).

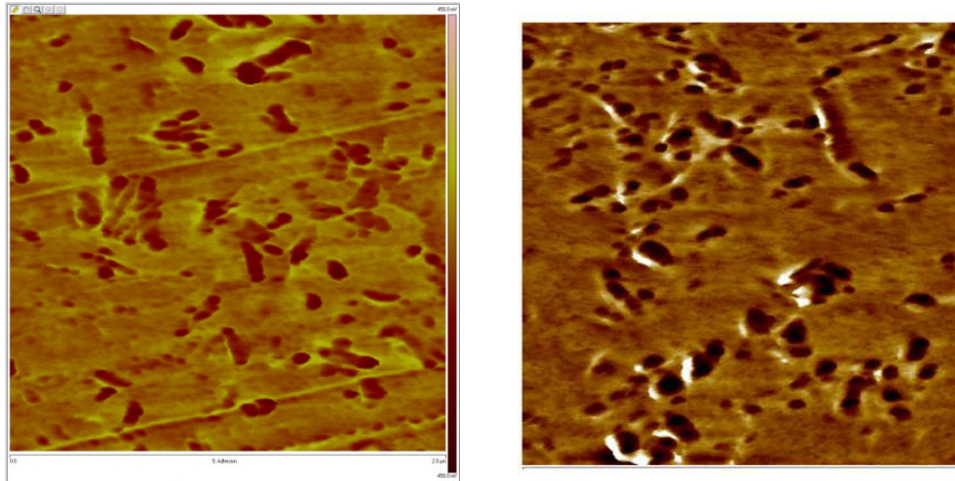


Figure 17: Use of AFM for evaluating the quality of dispersion of nano ZnO in the cured polyacrylate system. Scan size 2 μm .

The effect of hydroxyl group concentration on surface of the ZnO nanoparticles on the composite mechanical properties was studied and compared to the neat system. Figure 18 displays the temperature dependence of the real shear modulus for filled and unfilled systems.

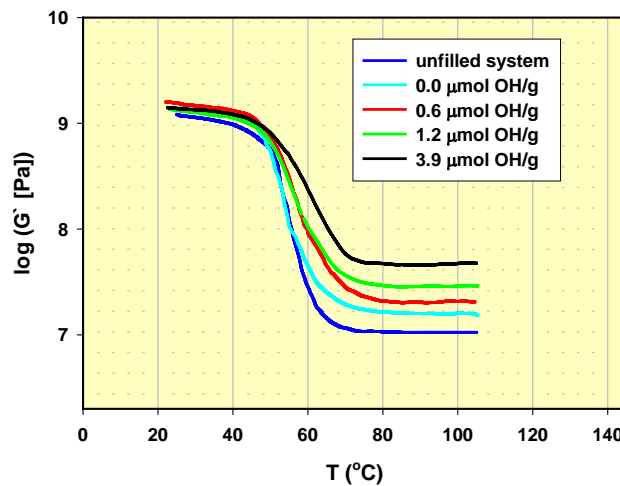


Figure 18: The temperature dependence of the real shear modulus of neat polyacrylate system and systems with differently modified nano ZnO

The thermal transition position of the main areas are practically the same. All nanofilled systems have practically the same shear modulus in the glassy state. Significantly higher values of shear modulus of nanofilled systems compared to the unfilled system confirms the good dispersion of the nanofiller in the polymeric binder. In rubber state, the modulus increases significantly with a higher concentration of hydroxyl groups on the surface of the nanoparticles (Figure 19).

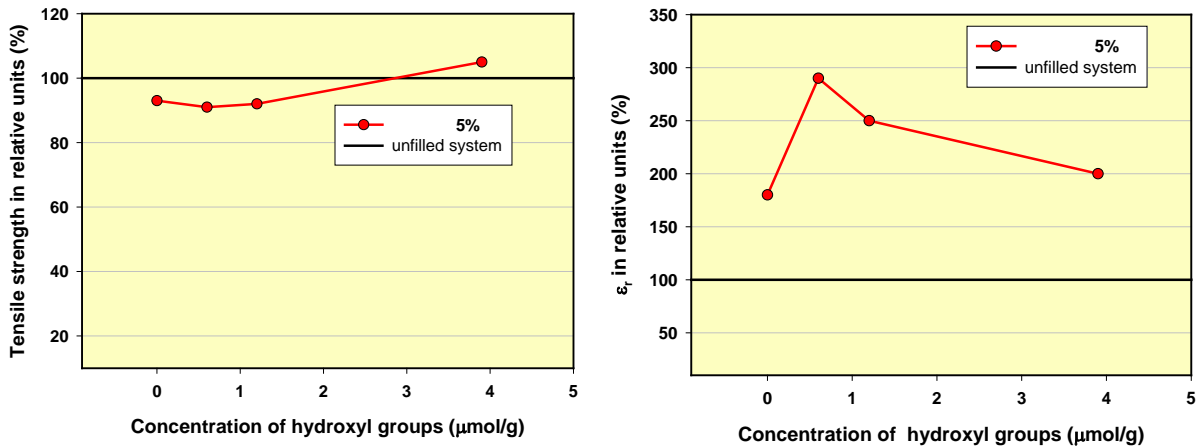


Figure 19: Effect of hydroxyls concentration on the tensile strength and elongation at break

The addition of the nanoparticles slightly reduced the tensile strength for low concentration of OH groups (Figure 19). On the other hand it increased drastically the value of specific elongation at break ϵ_r . The dependence of specific elongation at break shows a maximum for a concentration of 0,6 $\mu\text{mol/g}$ of OH groups. Practically the same tensile strength and significant increase in specific elongation at break indicates that there was a significant increase in toughness due to the addition of modified ZnO nanoparticles. These conclusions are confirmed by Figure 20, where dependence of work to break on the concentration of hydroxyl groups is presented. Logically, this dependence has a maximum which is similar to specific elongation at break.

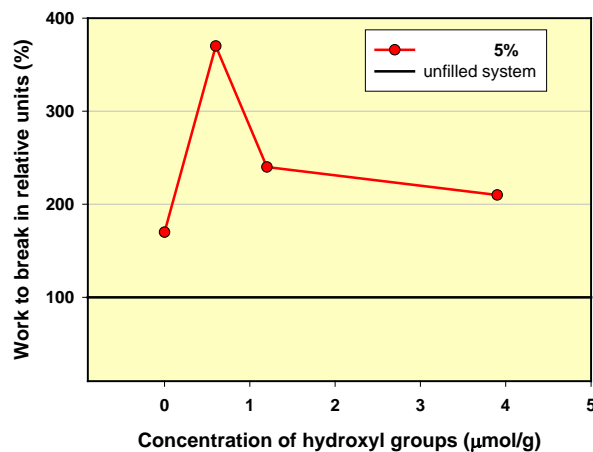


Figure 20: Dependence of work to break on the concentration of hydroxyl groups

6. CONCLUSION

Performed experiments proved that methods used to measure particle size distribution based on the light scattering require very diluted sample dispersions. These conditions of measurement can unfavorably affect the particle size distribution due to agglomeration of the particles. For these reasons methods working with concentrated suspensions, without a great dilution, are more suitable to obtain correct results for such colloidal systems, for example acoustic spectrometry and X-ray disc centrifuge system. Results achieved by means of these two methods were in a good coincidence with those from AFM and TEM. To get information on the shape of particles TEM and AFM methods were used.

The test results for the various environments in which the nano ZnO was applied can be summarized as follows:

Water-based systems

Nanoparticles of ZnO were prepared using the commercial types of surfactants Disperbyk-2010 and Disperbyk-190. 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. It was found that ZnO nanoparticles were homogeneously dispersed and the tensile properties of both systems significantly improved. The main disadvantage of this solution is that the surfactant is adsorbed only on the nanoparticle surface and therefore may be removed during dilution or washing. Particles with a reduced concentration of surfactant on the surface tend to agglomerate, which was experimentally confirmed. Furthermore, the surfactant may diffuse in the polymer during its lifetime, leading to unwanted plasticization.

Alkyd system

ZnO nanoparticles were prepared using a water/toluene emulsion, washed, and undergone surface modification in two steps. In the first step, the first component was chemically bound to the surface of ZnO. Next, the second component was also bound by a chemical bond, which defined the final surface properties. Using these modified ZnO nanoparticles it was possible to prepare stable dispersions in alkyd system. In this case, the addition of the modified nanoparticles led to a reduction of elongation at break of the cured system; however, an increase in tensile strength and modulus in the glassy state, indicating a good dispersion of particles of ZnO in the system, was observed. It was also observed an increase in glass

transition temperature. This phenomenon can be explained by reaction of the carboxyl groups of the binder system with the nanoparticle surface, which was confirmed by infrared spectroscopy. Extra practical importance has the finding that the addition of nano ZnO increases the resistance of alkyd system against the effects of ultraviolet radiation.

Acrylate system

Modified ZnO nanoparticles for solvent acrylate systems were prepared by one-step procedure. In surface treatment, acrylate copolymers with reactive groups for reaction with the surface of the ZnO nanoparticles and the group for the crosslinking reaction with the polymer binder and isocyanates were used. The nanoparticles were prepared with different concentrations of functional groups suitable for crosslinking reactions. Nanoparticle dispersion in acrylate solvent system was stable over time. The concentration of functional groups for crosslinking reaction had a major effect on the tensile properties of the cured system. The optimal concentration of the functional groups leading to a maximum value of work to break and elongation at break was found. Compared to unfilled systems, the addition of nano ZnO has increased the specific elongation in three times and work to break – in four times. The addition of the nanoparticles almost did not effect the glass transition temperature.

The exceptional properties of ZnO in nanoform can potentially benefit a wide range of polymers. Therefore, it is necessary to design the synthesis conditions and surface modification, tailored to each polymeric system. Based on our experience, we were able to prepare three different ZnO nanoparticle, that were successfully dispersed in four polymeric systems. All the composites showed great improvements in terms of mechanical properties, as well as UV aging resistance. This is only an example of many potential applications of nano-ZnO in polymer industry.

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