

Research Article

Self-Organization of ZnO Nanoparticles on UV-Curable Acrylate Nanocomposites

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Our work focused on synthesis and investigation of nanoparticles role in structuring of homogenous nanocomposite based on ZnO nanoparticles in UV-curable monomers mixture. Due to strong interaction between nanoparticles surface and polymerizable carboxylic acid, nanoparticles were distributed homogeneously, and density of nanocomposite increased also in comparison with pure polymer matrix. Light scattering, plasticity, and water sorption non-monotonically depends on the concentration of nanoparticles concentration. UV-curable active matrix polymerization on the surface of ZnO nanoparticles was investigated using IR spectroscopy. The set of structural modifications of polymeric nanocomposites were observed by ASM, light scattering, Brinell hardness, and water sorption. Suggestions that the nanoparticles in the polymerization process play the role of photocatalysts and provide structuring effect on the nanocomposite were discussed.

1. Introduction

Nanocomposites based on metal nanoparticles and their oxides into a polymer matrix are intensively developing fields of physics and chemistry of nanosized state. Structural organization of such nanosized particles is an important problem, and without solving it, it will be difficult to make nanocomposite material suitable for practical application. The need to improve the stability of nanocomposites is attracting attention to new ways to control their morphology, structural organization, and architecture [1]. Investigation of self-regulating systems in which synthesis of the polymer matrix and the growth of nanoparticles take place simultaneously can be the best solution to the problem of stabilization of nanoparticles polymers and their structural organization. In other words, the aim is to develop methods for creating nanocomposites with architecture “microcapsulated nanoparticles in a polymer shell” formed *in situ*. This is done by generating a polymerized matrix of cluster dispersions, thereby limiting the growth of nanoparticles. There are many ways to do this: polymerization of vinyl monomers in the intensive mechanical dispersing of metals (initiators are freshly formed metal surface), the introduction

of organometallic compounds to the polymerizing system, which decompose at temperatures close to the temperature of polymerization, γ -coirradiation of the precursor and the monomer at room temperature, polymerization of metal containing monomers, and so forth [1–3].

Nanostructured ZnO has attracted intensive research efforts for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, photocatalysis, photoprotecting, piezoelectric devices, chemical sensors, and spin electronics [4, 5]. Based on these remarkable physical properties and the motivation of device miniaturization, large effort has been focused on the synthesis, characterization, and device application of ZnO nanomaterials [6, 7]. In order to change the surface physicochemical properties of ZnO nanomaterials for the special applications, the methods such as chemical adsorption or grafting and physical wrapping were widely used [8].

There are different synthesis methods for ZnO nanopowder preparation [9–13]. Li et al. [9] and Vaezi and Sadrezaad [10] performed some studies in the field of ZnO nanopowder preparation via precipitation routes. They used a zinc salt and varied the pH and some other parameters. Chu et al. [11] used zinc acetate, citric acid, and ammonia

and succeeded in obtaining its ZnO nano particles. Westin et al. [12] and Pillai et al. [13] used a sol-gel method to produce ZnO nanoparticles and applied the prepared powder to a varistor application and observed very high electrical properties.

In spite of the diversity of researches, there are few papers on the optical grade nanomaterials in which a high concentration of nanoparticles is combined with good optical properties.

The difficulty of these task consists in that a high concentration of structuring additives is usually accompanied by significant light scattering on them or by fluctuations in their concentration.

This work is a continuation of our research in the field of nanostructuring of polymers for optical purposes [14–16] and the last work on SiO₂-based nanocomposite investigation [17]. Nanocomposites were prepared by UV curing of acrylic monomers in the presence of nanoparticles embedded in a curable matrix. Morphology of the material depends on nature and concentration of nanoparticles strongly.

The aim of the work is to study the structural changes of UV-curable polymeric ZnO nanocomposites and the main factors that determine their properties, such as mechanical characteristics, sorption and optical properties. Our work shows that addition of nanoparticles strongly interacting with polymer matrix will not result in worsening its homogeneity in contrary to filled polymers.

It has been found that ZnO nanoparticles are actively involved in the process of UV curing. Introduction in the polymerizable composition of ZnO nanoparticles leads to the formation of transparent and less scattering nanocomposite with good processability.

2. Experimental

Chemicals. We used monomers 2-Carboxyethyl acrylate (2Carb, Aldrich No. 552348), Bisphenol A glycerolate (BisA, Aldrich No. 41,116-7). For structuring nanomodification we used ZnO nanoparticles with a size of 20 nm (Russian local supplier).

Polymer films (thickness from 12 to 100 microns) were obtained from the previously prepared solutions containing monomer, nanoparticles, and its UV curing. The drop of solution is trapped between two polyester films to prevent inhibitory effects of oxygen. All experiments were accomplished at room temperature in air without special inert atmosphere. UV curing was made by a mercury lamp (100 W) used at the mercury line at 365 nm.

Transmission spectra of the films were measured on a spectrophotometer Perkin-Elmer 555 UV-Vis. For the IR spectra we used Fourier IR spectrometer FSM 1201 Manufacturer Company “Monitoring.” Samples were prepared by pressing pellets with KBr.

Refractive index is measured on an Abbe refractometer in accordance with the recommendations of the European standard ASTM D542.

In this paper we study sorption of water vapor by gravimetric method.

Hardness is measured by Brinell hardness method with “Bulat-T1” device.

Light scattering is measured by the photometric sphere method in accordance with the recommendations of the European standard ASTM D1003.

Investigation of the surface profile of samples was made with an atomic force microscope Ntegra used in contact mode.

3. Results

We find some effects at mixing of nanoparticles with monomers mixture. At ZnO introduction in the composition of the monomer BisA/2Carb (30/70) above a concentration of 8 wt.% the viscosity of solutions increases greatly. At higher concentrations (14 wt.% and higher) viscosity of the solution continues to grow and the mixture becomes solid at room temperature.

Transparent nanocomposites were obtained up to 14 wt.% of ZnO nanoparticles with formation of transparent film after UV curing. More than 14 wt.% of ZnO particles addition to the monomer mixture resulted in turbid films. The system becomes heterogeneous.

The films are transparent in the visible and UV spectral region. A significant decrease in optical transmission is observed at high concentrations of ZnO (more than 14 wt.%).

The calculated (1) and experimental (2) values of the refractive index nanocompositions are shown in Figure 1(a). For the theoretical calculation of the refractive index, Maxwell-Garnett’s model of effective medium has been used [18]:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_2}{\varepsilon_{\text{eff}} + 2\varepsilon_2} = f_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}, \quad (1)$$

Where ε_1 is the permittivity of the medium, ε_2 is the permittivity of inclusions, ε_{eff} is the permittivity of the composite medium, $f_1 = (1/V)\sum_i V_i$ is the volumetric filling factor, (V_i is the volume of i th particle, V is the volume of the composite environment).

This model is applicable when the volume filling factor: $f_1 \leq 1/3$, that is, fraction of inclusions is small. The experimentally obtained values for the film samples are higher than theoretically calculated. This effect can be explained by the following: according our recent results, there is interaction between nanoparticles and polymer matrix. Model of Maxwell-Garnett is applicable in the case when nanoparticles are distributed in any matrix. As a result of interaction between nanoparticles and polymer matrix this model condition is not accomplished. [19]. Refractive index of composition with maximum ZnO concentration (14 wt.%) is increased by 0.045 compared with the polymer without nanoparticles.

Figure 1((b), curve 3) shows that at increasing ZnO concentration, scattering of nanocomposite decreases, but near 4 wt.% there is a maximum of scattering. We think that near this concentration takes place a reorganization of polymer inner structure from polymeric structure with

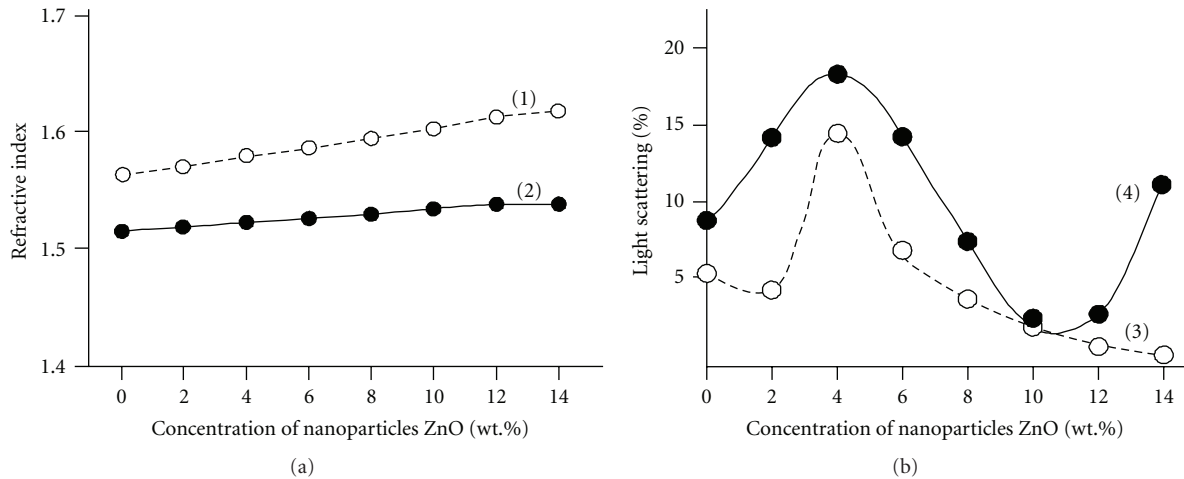


FIGURE 1: Refractive index (a): experimental RI (1) and calculation RI (2), light scattering (b): before (3) and after (4) water sorption of the composition BisA/2Carb (30/70) versus ZnO nanoparticles concentrations.

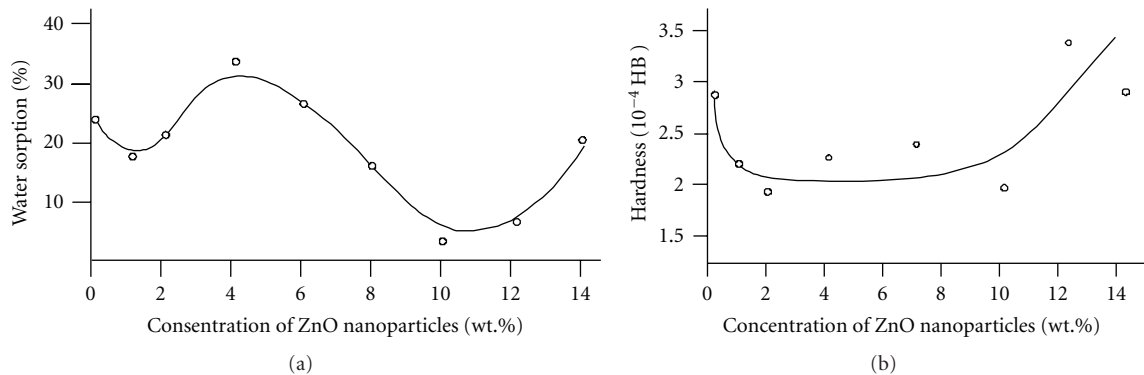


FIGURE 2: Sorption of water (a) and hardness (b) of composite BisA/2Carb (30/70) versus concentrations of ZnO.

inclusion of nanoparticles to self-organized nanocomposite structure (see Figure 3).

When the concentration of ZnO is more than 14 wt.%, light scattering is independent of the concentration of nanoparticles. ZnO amount is sufficient for uniform distribution in volume, and homogeneous polymer composites are formed. In this structure, the light scattering decreases compared to pure polymer, approximately twice.

The water sorption experiments were conducted to study changes in the internal volume of the polymer as a result of effect of free volume filling by ZnO nanoparticles (Figure 1 (b), curve 4)).

Water sorption properties of nanocomposite have strong dependence on nanoparticles concentration (Figure 2(a)). There is a sorption maximum near 4% (reorganization of polymer inner structure). At higher nanoparticles concentration (12 wt. % ZnO) water sorption increases, perhaps as a result of disordering of the nanocomposite.

For pure polymer value, water sorption is 23%. The introduction of 10 wt.% nanoparticles achieved reduction in water sorption by 5 times compared with the pure composition.

The hardness investigation of films is an indirect way to study the effect of ZnO on the structural change of nanocomposites (Figure 2(b)).

At the introduction of ZnO up to 10 wt.% the hardness of the films decreases. Further, the hardness of the film increases and reaches the one of pure polymer.

The changes of the polymer nanocomposite properties (water sorption, light scattering, hardness) confirmed that nanoparticles influence on the polymer structure by means of possible interactions of ZnO with active groups of the polymer [20].

The investigation of the surface relief of the nanocomposites made by atomic force microscopy is shown in Figure 3.

As can be seen from Figure 3, there are essential changes in the composition structure as compared with the original by introduction at 4 wt.% ZnO nanoparticles. The formation of separate polymer regions of structured ZnO was observed clearly. The grain uniform structure are observed throughout the material when ZnO concentration achieves 10 wt.%. Apparently, formation of this structure is due to the ability of nanoparticles to create weak bonds with the active groups

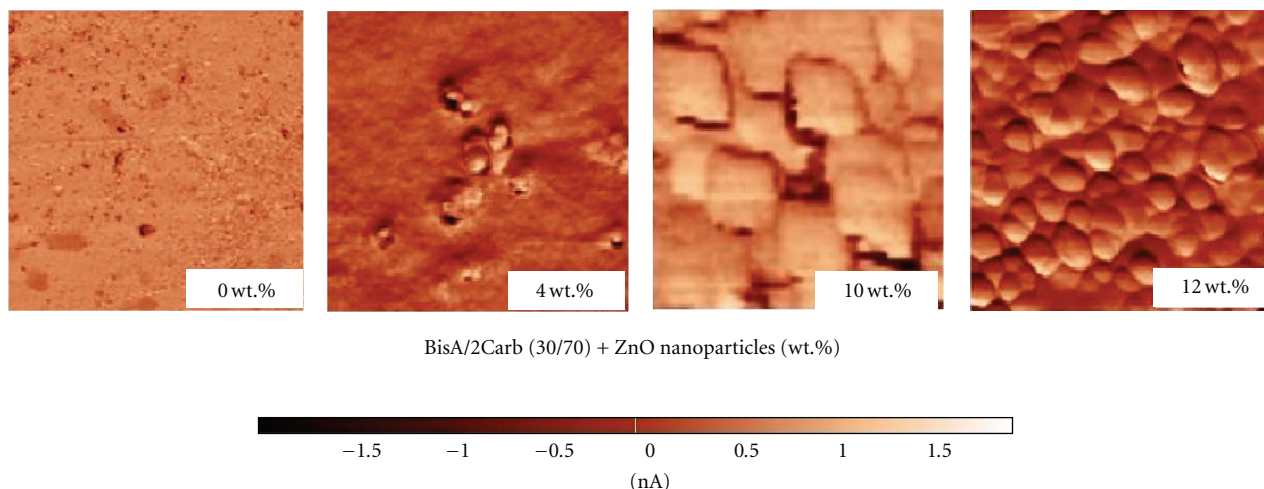


FIGURE 3: Relief of polymer films with the introduction of 0 wt.% (a), 4 wt.% (b), 8 wt.% (c), 12 wt.% (d) ZnO nanoparticles (AFM). The size of photos 5×5 mkm.

of the monomer molecules and to work as centers of polymerization.

When the ZnO concentration is more than 10 wt.%, free polymer phase disappears and all available polymers form spheres on nanoparticles surface.

At low concentrations of nanoparticles, modified polymer areas are not enough and composites are heterogeneous. Heterogeneous structures are reflected in their properties. With increasing ZnO concentration, size and number of hybrid fields are growing, thus it is conditioned by forming of a completely different structure of the material.

The formation of submicron spheres around each nanoparticle is the cause of formation of quasi-homogeneous materials, in which light scattering does not exceed the pure polymer. Indeed (Figure 3), submicron spheres formed around each nanoparticle possess almost identical diameters. This fact can be explained by identical growth rates of these spheres. The result is structure consisting of sphere particles located in the self-organized quasilattice. Eventually, the above-named effects lead to a homogeneous distribution of nanoparticles and the formation of a homogeneous environment.

Determination of possibility and mechanism of polymerization on surface of ZnO nanoparticles were investigated by mean of FTIR nanocomposite spectra (Figure 4). FTIR spectra of monomers mixture BisA/2Car (30/70) may be seen as peaks at 1737, 1410 and 1188, 1050 cm^{-1} . The first peak corresponds to valency vibration of carboxylic group, next three—to combination of flat deformation vibration of hydroxide group and valency vibration of C-O links in carboxylic acids [21].

At preparation of nanocomposite FTIR spectra change essentially, peak 1720 cm^{-1} (C-O group) keep and peak $1410\text{--}1450 \text{ cm}^{-1}$ (valency vibration of carboxylate anion) will intensify. It is important to notice that the peak at 500 cm^{-1} corresponds to Zn-O vibration. A peaks appears between $1620\text{--}1550 \text{ cm}^{-1}$. This area is typical of asymmetric valency vibration of carboxylic anion. According to informa-

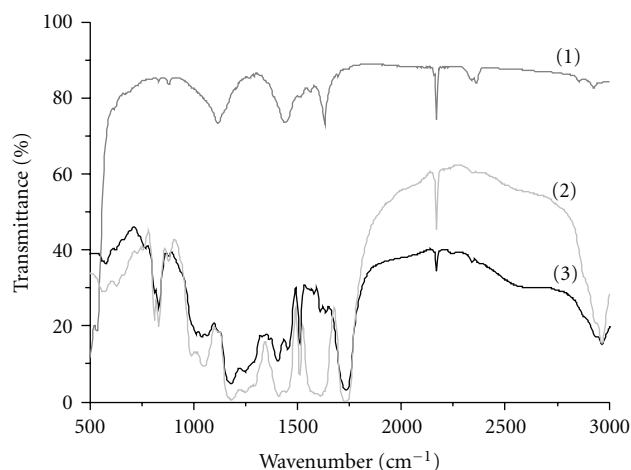


FIGURE 4: FTIR spectra: nanoparticles ZnO (1), composition 2Carb/BisA (70/30) + 12 wt.% ZnO (2), and pure 2Carb/BisA (70/30) (3).

tion of works [22–25] interaction of inorganic nanoparticles ZnO and carbonyl group results in change in IR spectra, as metal atoms can be connected to carbonyl oxygen by electron pair transfer. The increase of peak intensity O-H at 1550 cm^{-1} can be a result of formation of a complex between the polymer and nanoparticle.

Next, in nanocomposite peaks appearing at $1640\text{--}1650 \text{ cm}^{-1}$, they are typical for C=C valency vibration in $\text{CH}_2=\text{CHR}$, and peak 990 cm^{-1} is typical for C-H deformation vibration in $\text{CH}_2=\text{CHR}$. $\text{CH}_2=\text{CHR}$ groups can photopolymerize on ZnO surface, acting as photoinitiator. Principal scheme of described process is shown in Figure 5.

4. Discussion on Obtained Results

Our results show that ZnO nanoparticles can be involved in UV polymerization process with formation of bonds

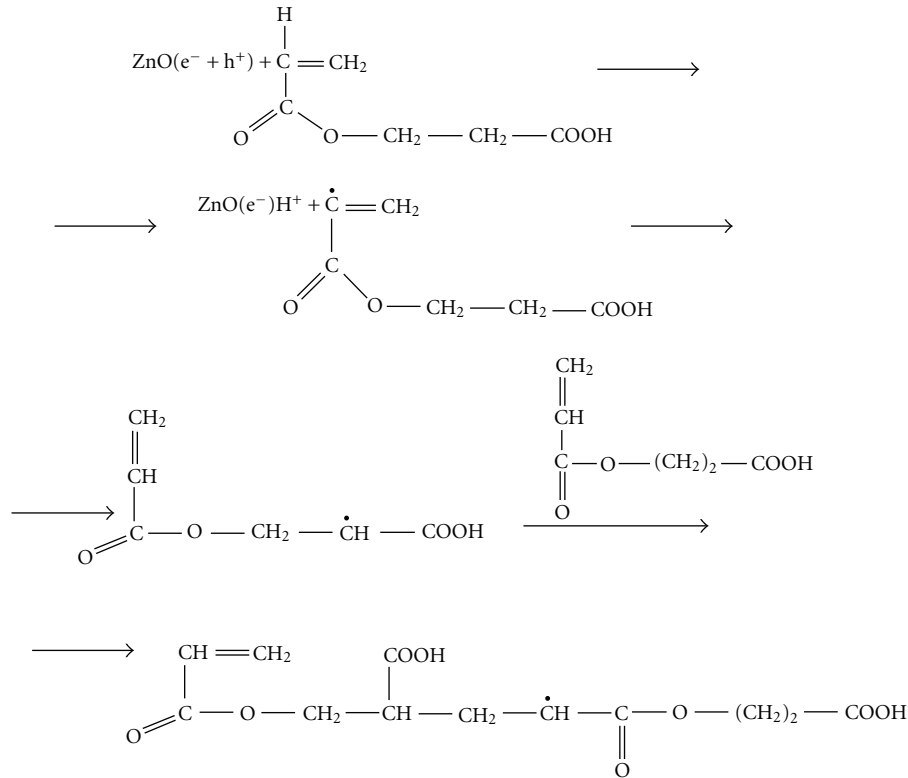


FIGURE 5: Scheme of photocatalysis process.

between nanoparticle surfaces and polymers. Thus, the ZnO nanoparticles act as centers of formation of a new polymer phase—the nanocomposite, other than with the pure polymer properties.

According to FTIR spectra of ZnO nanocomposites we assume that nanoparticles act as photocatalysts in polymerization and became as a centers of polymerization as a result of interaction with carboxylic group of one of the composition monomers. Our hypotheses are proved by formation of micron size spheres in nanocomposite around each nanoparticle (Figure 3). Nanosized semiconductor clusters have the potential of photooxidation and photocatalysis through the combined effects of photoelectrons production at UV light absorption and high surface area in which electron-transfer-induced polymerization takes place. According to results of the work in [26], during the photocatalytic process, the illumination of a semiconductor photocatalyst with ultraviolet (UV) radiation activates the catalyst, establishing a redox environment in the aqueous solution. Semiconductors act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. So, light absorption by semiconductor nanoparticles will result in photocatalytic process in its surface including photopolymerization processes. The work in [27] shows possibility of this process of methyl methacrylate photopolymerization initiation by TiO_2 nanoparticles. In our experiments we obtain similar

process that is proved by FTIR and atomic force microscopy results (formation of equal spheres around each nanoparticle as a center of polymerization and chemical bonding between nanoparticles surface and polymer).

Formation of spheres around each nanoparticles as a result of photopolymerization on its surface results in transformation of polymer structure: at augmentation of nanoparticles concentration all proprieties of composition have sudden extremums at the same values of nanoparticles concentration. Characteristic points are 4 and 10 wt%. According AFM photos between 2 and 4 wt% of nanoparticles, new phase of polymer generated on nanoparticles surface will occupy mostly part of nanocomposite volume. It results in structuring of material, light scattering, and water sorption will decrease. At nanoparticles concentration more than 10 wt %, all volume of polymers will be involved in formation of new phase; perhaps next increasing of nanoparticles concentration will result in competition between nanoparticles as the center of polymerization resulted in missequencing of material. AFM photo shows that structures consisting of micro spheres occupy all volume, and light scattering and water sorption increase. Above-listed effects are proved by missequencing of nanocomposite.

Certainly these suggestions are our hypothesis only. Future investigation of nanocomposite with active nanoparticles is needed to understand the causes of these strange effects of composite reorganization.

5. Conclusion

The sorption of water vapor, Brinell hardness, optical transmission, refractive index, and light scattering of film polymer ZnO nanocomposites were studied.

Composites are transparent in the visible spectrum at high concentrations of ZnO nanoparticles (14 wt.%). With the introduction of 14 wt.% ZnO the refractive index composite increases to 0.045. With the introduction of 10 wt.% ZnO the sorption decreases five times. Hardness, until a maximum concentration of nanoparticles 12 wt.% ZnO, does not exceed the hardness of the pure polymer, while light scattering is not increased.

Nonmonotonic changes in the properties, the AFM data, and the IR spectra demonstrate the ability of nanoparticles to act as centers of polymerization and to form a granular structure in the nanocomposite.

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