

Filled Polymers with High Nanoparticles Concentration—Synthesis and Properties

Julia E. Burunkova,¹ Igor Yu Denisyuk,¹ Todd R. Williams^{2*}

¹*Saint-Petersburg State University of Information Technology, Mechanics and Optics, Kronverskii 49, Saint-Petersburg 197101, Russia*

²*Display and Graphics Business Laboratory, 3M Corp., 3M Center Building 235-1WS-46, St. Paul, Minnesota 55144*

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ABSTRACT: High refractive index optical compositions based on polymer matrices filled with high concentrations of ZnS nanoparticles were developed. These materials have good optical properties and processability like usual polymers, and they are suitable for factory scale use. At 25 vol % ZnS nanoparticles concentration an increase in refractive index up to 0.25 in 150 μm transparent film was obtained. A process was developed for formation of polymeric compositions consisting of polymer filled with high

concentrations of inorganic crystalline nanoparticles. Effects connected to high concentration of nanoparticles in the polymer were discussed. Optical properties of these materials were investigated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1857–1866, 2010

Key words: nanocrystal; refractive index; filled polymer; UV-curable nanocomposite; nanocomposite structure; nanoparticle

INTRODUCTION

Presently, the homogeneous optical media such as optical glasses, monocrystals, and polymer materials are widely used. Each of these media has a specific set of properties; for example, the polymer materials allow producing flexible and transparent films, and they are inexpensive. The technology of their treatment is very simple and suitable for some applications. However, the refractive index of polymers typically does not exceed the value of 1.6. On the other hand, many inorganic monocrystals (e.g., ZnS or CdS) have a high refractive index. The absorption spectra of these crystals demonstrate broad bands and sharp absorption edges, but the technology of making devices from monocrystals is complex, and so these are expensive.

The possibility of combining the different properties of polymers and monocrystals into a single material should be rather useful. It is impossible to solve this problem by traditional ways because the properties reflect the internal structures of these different materials.

The method of nanostructuring provides the possibility of combining the properties of polymers and

crystals. The resulting nanocomposite is the mechanical mixture of inorganic semiconductor nanoparticles distributed uniformly in the polymer matrix. Under the condition of uniform distribution of nanoparticles and if the size of such nanocrystals is small (2–5 nm), they do not distort an incident light wave, and the light scattering is low. On the other hand, the small distance between nanocrystals provides an essential change of optical properties, for example, an increase in refractive index (RI). So at a rather high concentration of nanocrystals with small size, the nanocomposite becomes effectively a homogeneous medium, having increased RI with low scattering. The set of properties of this mixture is determined by both components, namely polymer and nanocrystals, and by the ratio of concentrations of them.

Currently, there are a lot of references regarding the synthesis, testing and applications of nanocrystals. There are only a few research activities on nanocomposites with high transparency, good optical quality, processability like polymers, and a refractive index increased significantly (more than 0.05) in comparison with the pure matrix material.^{1–3} In fact, nanocomposite material should have following properties for film with thickness of 100 μm : scattering not more than 2–4%, absence of heterogeneity, absence of visual color, processability similar to usual polymer: UV curing, molding, refractive index increased up to 0.1 in comparison with polymer matrix. The problem of obtaining nanocomposites having good optical and mechanical properties, like typical thermoplastic or UV-

*Now retired.

Correspondence to: I. Y. Denisyuk (denisiuk@mail.ifmo.ru).

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curable polymers, and high nanoparticle concentration at the same time, with no limitation on thickness of the film, has not been solved. As optical materials they should be transparent, colorless and possess a high RI ($RI \geq 1.7$). Turbidity of the composite in a thick layer should be close to that of the polymer matrix. Mechanical properties should permit the making of optical elements and/or coatings using current industrial methods suitable for polymer materials. The material should be processable in any form: coating, layer up to some hundreds of microns, and bulk. The material should be stable during processing, and its properties should not depend on layer thickness. Recent publications reported investigation of nanocomposite films prepared by spin coating and containing TiO_2 or ZnS , but their technologies are too difficult and not suitable for thick film preparation, and the light scattering of these materials is quite large even in 1–10 micron films.^{4–8}

In all the works cited above, the nanocomposite materials obtained had quite large turbidity that forced the use of thin films with thicknesses not more than some microns.

There is a well-known method to develop nanocomposite films by spin coating and drying of solutions containing both polymer and nanocrystals. This method is easy and has been used in different investigations.³ However, this method has a fundamental defect that does not allow the preparation of solid thick films of some hundreds of micrometers thickness at high nanocrystals concentration. At high concentration of unmodified nanoparticles in a polymer matrix, there are large interactions between them similar to interactions between microscopic particles in well-known filled polymers. As a result two processes occur:

1. If the polymer matrix is a liquid, nanoparticles tend to be coagulated. As a result, there is formed a nonuniform distribution of particles in the matrix, and the composite becomes cloudy. So, unlike a usual composition from two organic substances that can be prepared by simple mechanical mixing, upon mixing of nanoparticles with polymer, motion occurs of nanoparticles one to another and coagulation results. The use of dispersants or other surfactants is normally used to prevent this coagulation.
2. If one designs strong interactions between nanoparticles and the polymer matrix to avoid coagulation (for example use of surface active polymers with active groups), the drying of solvent will produce mechanical stresses, the modulus of the system will increase, and the coating (if it is not thin) will crack. The follow-

ing is a reasonable explanation of the source of such stresses.

Polymer chains can be some microns long, so a single chain having many active groups can make chemical links to the surfaces of many nanoparticles. At the same time, each nanoparticle with a diameter of 2–3 nm can make links to different polymer chains. As a result a cross-linked polymer is obtained. Upon drying the polymer chains will shrink, while at the same time the volume of nanoparticles will not change. As a result in the material will appear inner stress. For example, at 10% nanoparticles concentration in poly(vinylpyridine), which acts as its own “surfactant,” inner stress in the material will result in turbidity of the material after drying according to our results published previously.^{9,10} Similar results were obtained with polymers filled by carbon nanotubes.¹¹ Presumably, the major cause of turbidity is the formation of micro cracks during shrinkage. However, the same material having even a small quantity of residual solvent will retain its transparency (stresses do not appear when solvent is present). These processes were discussed in our previous reports.^{9,10}

This process is similar to the well-known result of polymer filled with inorganic microscopic particles. Because of the smaller size of nanoparticles in comparison with microparticles at the same weight % concentration, the number of nanoparticles will be more in comparison to number of microparticles in the same degree as each nanoparticle volume is smaller.¹² As the number of nanoparticles increases, the average distance between particles decreases. As a result of smaller distances between nanoparticles, the process of material hardening takes part at smaller nanoparticles concentration. This concept is similar to the more familiar one of molecular weight between crosslinks in thermoset polymers.

So, there is a contradiction: to avoid nanoparticles coagulation there is a need to increase interaction between them and the polymer matrix; but at the same time those interactions with polymer will result in hardening of the composites.

In most past work, this contradiction has been avoided by the use of very fast drying of material during its spin coating.¹³ In that work, the dangerous stage of particle–particle interactions was passed quickly and the composites kept their transparency. For example, if a layer is prepared by spin coating, the process of solid coating preparation occupies only some part of a second. However, this method is not suitable for preparing thick nanocomposite layers and bulk nanocomposites. Thick nanocomposites films can be prepared only without the use of a fugitive solvent. Suitable processes include hot molding of thermoplastic materials and radiation curing.

To solve the problem of producing bulk nanocomposites, we have investigated methods of preparing composites with high nanoparticles concentration, which methods have resulted in formation of new optical nanocomposite material classes with the following properties: colorless, with high RI, low light scattering, and suitable for extruding or for coating into thin films. The preferred method is based on the use of organic shell material strongly linked to the nanoparticles' surface and at the same time having only a small interaction with the polymeric matrix to avoid undesirable mechanical stress in the composite. In other words, we prepare nanoparticles covered by organic shell floating in "inert" polymeric matrix having small interaction with the shell. Separate methods were developed in this way to use either thermoplastic or UV-curable polymers as the matrix.

EXPERIMENTAL

Differential scanning calorimetry was conducted using a Netzsch DSC200 instrument. All scans were performed on samples weighing 10–20 mg, in aluminum pans heated at 10°C/min under nitrogen atmosphere. An empty pan was used as reference. When more than one scan was done on a sample, the sample was not moved while the furnace was cooled after the previous scan. Transmission electron microscopy was performed on cryomicrotomed samples held on a carbon grid with Formvar varnish. A Jeol Model microscope was used with magnifications of 15 and 30K. X-ray diffraction data were collected in the form of a survey scan by use of a Philips vertical diffractometer, copper K_{α} radiation, and proportional detector registry of the scattered radiation. X-ray generator settings of 45 kV and 35 mA were employed. Refractive index (RI) was measured using an Abbe refractometer with bromobenzene as coupling liquid for solid samples. As nanoparticles are small and do not distort light wavefront, so for calculation of refractive index of nanocomposites were used simple equation same as equations used for mixture of liquids (sum of RI and percentage products of components). Very likely that possible mistakes were not high. A complicated theory of refractive index calculation in disperse materials there is not applicable as nanocomposite is not disperse. UV-Vis spectroscopy was performed on a Perkin-Elmer UV-Vis Spectrophotometer, model 555 with 189–900 nm wavelength range. All synthesis experiments were accomplished at room temperature (+20°C) in air without special inert atmosphere. All concentration were indicate in volumetric percents as it is more important for refractive index measurement. As ZnS have density of 4.090 g/cm³, volumetric percent can be converting in weight percent by simple

mathematical equation. Polymers and monomers material have density near to 1.0 and its concentration in volumetric percents near to weight percents.

Nanoparticle preparation

ZnS nanoparticles were prepared according to the procedure described in our patent¹⁴.

Solution (1) containing H₂S in isopropanol (IPA) was prepared by passing a stream of fine bubbles of the H₂S gas through the IPA for 24 h, after which time it was assumed that the solution was saturated. A zinc acetate solution of known concentration was titrated with the H₂S solution until lead acetate paper indicated the presence of excess H₂S. From this titration was determined the volume of the H₂S solution having 0.00083 mole of H₂S. To prepare solutions for the following examples, this determined volume was multiplied by 10 and then IPA was added to make a total volume of 50 mL.

A solution was prepared by dissolving 2.0 g of zinc acetate dihydrate (0.0091 mole) and 0.06 g of 2-phenoxybenzoic acid in 40 mL of dimethylformamide (DMF). This was poured into 50 mL of the H₂S solution (1) described above, containing 0.0083 mole of H₂S in IPA (10 mole % excess of zinc over H₂S), with strong stirring agitation. To the resulting mixture was added with stirring 100 mL of water. The resulting mixture was allowed to stand at ambient conditions. A precipitate was formed over a day and was separated by centrifugation and washed with water and IPA. After drying overnight in a vacuum desiccator, a small amount of the solid was dissolved in DMF using ultrasonic agitation. This solution was examined using UV-Vis spectroscopy, and a shoulder on the absorption curve occurred at 290 nm, corresponding to an average particle size of 3.0 nm. Particle sizes were determined by exciton absorption maximum shift value. Our results are consistent with an earlier report on ZnS nanoparticle size.¹⁵

Nanocomposite preparation—Thermoplastic matrix

Experiment 1

A solution of 0.5 g polycarbonate Z (Iupilon[®] Z-200 from Mitsubishi Gas Chemical, CAS # 25,134-45-6) in 30 mL DMF without nanocrystals was poured into 500 mL water for the sedimentation. Within several minutes, large sediment flakes were deposited. This result means that there was rather little content of sedimentation centers in solution and every center caught a great volume of polymer.

Experiment 2

A colloidal solution of CdS nanoparticles (covered by the shell of 3-Phenylpropionic acid prepared by

TABLE I
Shell Materials

No	Name
1	3-Phenylpropionic acid
2	3-Phenylbutyric acid
3	5-Phenylvaleric acid
4	1-Naphthylacetic acid

method described previously) in DMF with polycarbonate Z dissolved in it was prepared. (Polycarbonate Z - 0.5 g; DMF - 30 mL; CdS/Polycarbonate ratio was 20 wt %). This solution was poured into 500 mL water for sedimentation. A fine precipitate formed over several hours, indicating many sedimentation centers.

High refractive index thermoplastic transparent nanocomposites based on ZnS nanoparticles in polycarbonate were prepared according to the procedure described in our patent¹⁶:

A solution was prepared by dissolving 1 g of zinc acetate, 0.05 g of 2-phenoxybenzoic acid (or equivalent quantity of other carboxylic acid from the Table I), and 0.5 g of Polycarbonate Z (Iupilon[®] Z-200 from Mitsubishi Gas Chemical, CAS # 25,134-45-6) with 0.25 g of plasticizer poly (phenylene oxide) (Fluka, Polyphenyl ether (6 rings) OS-138, product number 81,336, CAS # 56,378-65-5) in 30 mL of dimethylformamide. Another solution was prepared by dissolving 100 mL of isopropanol saturated with H₂S in 300 mL water. The zinc acetate solution was poured into the H₂S solution under intensive stirring with the use of a magnet rotation mixer. The mixture became turbid immediately and a white sediment deposited from the solution.

If complete sedimentation did not occur after several hours, a drop of ammonia was added. After complete sedimentation (several hours), the sediment was separated from water by decantation and centrifugation, and it was dried at 50°C in air. A dry powder was formed. A transparent film was fabricated from this powder by hot rolling at 180°C between counter-rotating cylinders turning at 5 cm/sec. Was used usual device for hot rolling polymer processing. The nanoparticles were present at 2; 5; 9 volume %, relative to the weight of the nanocomposite. After many experiments nanoparticles concentration of 10 and 12 vol % were obtained. These nanocomposites were transparent, and their refractive indices were higher according to the increase of nanoparticles concentration.

Nanocomposite preparation—Thermoset matrix

This process of nanocomposite preparation is based on replacement of residual solvent from nanopar-

ticles surface by polymerizable carboxylic acid with subsequent polymerization.

ZnS nanoparticles with the shell of 5-Phenylvaleric acid (Table I, No 3) were dispersed in toluene and heated for 10 h at 80°C. This operation is needed to remove water from the nanoparticles surface. After the nanoparticles powder was dried in air at 80°C during 10 min, it was put into CEA. Ultrasonic dispersion for about 30–40 min in apparatus was done. The disperser had ultrasonic power about 70 Watt delivered to a 3 mm diameter horn end. The ultrasonic frequency was 27 kHz. Firstly, at dispersion CEA became turbid because of dispersion of ZnS nanoparticles conglomerates. Upon continued dispersion the colloidal solution ZnS–CEA became more and more clear, as each nanoparticle became covered by an equal shell of CEA. Finally, the solution with ZnS nanoparticles became a transparent liquid. At the same time, the solution became more and more viscous during dispersion. After dispersion, the ZnS–CEA colloidal solution is stable and kept good transparency for at least 1 year at room temperature. It is possible to add inert acrylate monomer (PEA) to the colloidal solution without the nanoparticles settling out. Note that the viscosity of this composition is many times higher than the pure CEA. Dimethoxy phenyl acetophenone (0.1 wt %) was dissolved in the solution, which was coated between unprimed polyester sheets to a film thickness of 100 μm and irradiated with UV light (365 nm, 5 mW/cm²) at room temperature for 10 min. The result was a solid, barely hazy film.

DISCUSSION

Nanocomposites were composed from three classes of material: nanoparticles or nanocrystals, organic shell, and polymeric matrix.

ZnS was chosen as the nanocrystalline material, because it is colorless with a high RI. The concentration of nanocrystals in the composite was studied up to 10–20% by volume, and the particle size (1.5–20 nm) was expected to ensure low light scattering by the nanocomposite.

There are well-known different methods of inorganic nanoparticles preparation.^{17,18} They are based on chemical reaction in liquid with precipitation of colloidal solution. For obtaining small sized nanocrystals, one needs to choose suitable surfactant or shell material.¹⁹ In this work was used a precipitation method consisting of chemical reaction between hydrogen sulfide and acetate of metal (Zn or Cd) in a water/alcohol solution in the presence of organic surfactant similar to the method described in previous work.^{9,10} The presence of water was needed to increase dissolution of metal acetate. In many published works thiols or phosphines were used as

TABLE II
UV-curable Monomers

Name	Abbreviation	RI
2-Carboxyethyl acrylate	CEA	1.4570
2-Phenoxyethyl acrylate	PEA	1.5180

surfactant, but these materials are toxic and not preferred for factory use.^{3,20} In this work, aromatic carboxylic acids were chosen as surfactants, because carboxylic acids are not toxic, and a synthesis method was desired which would be suitable for factory scale production. Also, the aromatic groups were expected to give some degree of compatibility with polymers with aromatic groups. Such polymers already start with relatively high RI, making the task of reaching RI of 1.7 somewhat easier. Table I shows the shell acids used in this work.

The shell material has two functions. First, the shell should stop nanoparticles from growing beyond a definite size during synthesis to obtain monodisperse size distribution. Second, molecular structure of shell material as surface active substance provides the compatibilization of nanoparticles with aromatic polymer matrix to prevent coagulation.

Nanoparticles sizes do not depend on the shell material type, but the properties of the nanocomposite change according to the nature of the shell material. The best results were obtained with shell material # 3. The use of shell # 1 or # 2 resulted in two–three times higher turbidity of the nanocomposite. The use of shell # 4 gave low turbidity, but the resulting thermoplastic nanocomposite was much more brittle and fragile, compared with using shell #3.

Two types of polymer matrix were studied: thermoplastic and UV-curable polymers. As a thermoplastic polymer matrix was used Polycarbonate Z - (Mitsubishi Gas Chemical Company, Inc., product name: Iupilon Z-200, CAS number 25,134-45-6). The UV-curable monomers and an oligomer investigated in this project are shown in Table II.

We used CEA as the preferred UV-curable matrix material for nanocomposite preparation. It appeared that up to 70% of CEA could be replaced by PEA with improvement of the mechanical properties of cured nanocomposite and no obvious change in optical properties.

We propose the following explanation of the observations during the nanocomposite synthesis procedures described above.

Thermoplastic

During the nanocomposite synthesis two processes take part simultaneously: (1) chemical reaction between zinc acetate and H₂S in solution, with for-

mation of a colloidal solution of ZnS nanocrystals covered by carboxylic acid shell; and (2) coating of each ZnS nanoparticle by polycarbonate as a result of interaction between two hydrophobic substances (aromatic carboxylic acid shell on nanoparticle surface and aromatic polycarbonate) in the water. As a result all nanoparticles will be covered by approximately equal polymer layers and these particles form sediment in the bottom of the reaction vessel.

The nanocomposite in the sediment consists of numerous spheres pressed against each other. Each particle consists of at least one ZnS nanoparticle in the center, covered by polymer. As the diameters of the spheres are approximately equal, distances between their ZnS cores in the pressed material are approximately equal also. Certainly, this uniform nanocomposite material can be processed by hot molding, but dissolution of the material will result in separation of the homogenous material into separate phases of polymer and nanoparticles.

Thermoset nanocomposite

We assume the stability of the solution is caused by covering of each ZnS nanoparticle by a shell of polymerizable acid—CEA. Further, it is possible to dissolve this material in a suitable organic solvent. Finally, after drying of the solvent, the material once again keeps its homogeneity and transparency. The composition is stable in the unpolymerized liquid. Certainly, it should be possible to obtain this same type of stable solution by the use of an unpolymerizable carboxylic acid, such as propionic acid. But such a nanocomposite cannot be directly polymerized to a solid and was not studied here.

Nature of the shell and its interactions with nanoparticle surface and matrix

It is interesting to speculate on the nature of the bonding between the carboxylic acid shell material and the ZnS nanoparticles. If there is a compound of some kind formed, there certainly is very little of this substance, and as it is bonded to nanoparticles, it will be difficult to isolate it. A complete study of this material is beyond the scope of the present study. However, a couple of observations were made which shed a little light on the topic.

First, a previously unknown effect was observed: In this work, nanoparticles were usually synthesized by addition of surfactant material to Zn acetate solution before reaction with H₂S solution. Nanoparticles prepared by this method were well dispersed in CEA. If nanoparticles were synthesized without surfactant and then it was added after the reaction, similar nanoparticles were obtained, which were soluble in DMF, but which could not be dissolved in CEA.

These observations are interpreted as indicating that the freshly-prepared ZnS surface is very active and bonds strongly (the details of which bonding are unknown at present) to whatever acid groups are present. Water is presumably also bound, but its relative binding strength is not known. When shell acid is present during nanoparticle synthesis, it competes with acetic acid (from the original Zn acetate salt) for the surface binding sites. But there is also a competition between acid bound to the surface and acid dissolved in the large amount of solvent. Recall that the H₂S is added as a solution in ethanol/water. The typical shell acids (Table I) are not soluble in this solvent, but they are soluble in the DMF used to dissolve the zinc salt. Thus, it is reasonable to assume that, during the reaction and solvent change, the majority of released acetic acid is dissolved and diluted in the large excess of ethanol/water, whereas the shell acid precipitates onto the nanoparticle surface, where it competes with water for surface binding sites. If there is no added shell acid, then the low concentration of acetic acid competes with water for those binding sites.

When there is shell acid bound to the surface, the particles are soluble in CEA, especially after removing much of the surface water through the process of heating in toluene. However, if the shell acid is added after the particles have been synthesized, it apparently cannot displace the water and acetic acid already occupying surface binding sites. While the resulting particles can be largely dried by heating in toluene, they apparently are not stabilized and compatibilized enough to be soluble in CEA.

Second, X-ray scattering from the nanoparticles (Fig. 1) shows that they largely retain the sphalerite crystal structure. This is interpreted as indicating that the shell material binds only to the surface of nanocrystals and does not disrupt the native ZnS crystal structure.

Thermoplastic polymer filled by nanoparticles—Synthesis and behaviors

A method was sought to prepare thermoplastic nanocomposites, which would allow the use of inert polymer filled by nanoparticles covered by shell material. The use of solvent was impossible because of coagulation of nanoparticles during drying, as discussed above in the Introduction. Thus, the chosen method would arrange nanoparticles in solid material uniformly and then allow thermoplastic processing to obtain homogenous material.

Imagine a mass of equal spheres, each of which consists of one central nanocrystal coated with polymer. If these spheres are placed into some volume, they will pack there rather uniformly, and the distance between them will be essentially uniform. As

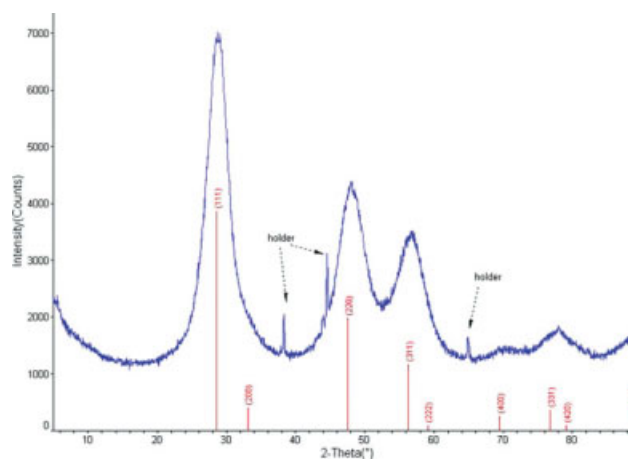


Figure 1 X-ray measurement of ZnS nanoparticles. Red curve is the signal from the nanocrystals. The vertical blue lines are a typical pattern from a large sphalerite crystal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

this material is heated slowly, deformation of spheres will be observed and the distance between their centers will decrease. Material thus prepared is still uniform. It resembles the polymer, and it can be transformed into a film by the hot forge-rolling. This route has no limit of concentration.

Nevertheless, in this case there are some restrictions connected with the change of flow properties as the nanocrystals concentration changes. If the thickness of particle coating decreases, the interaction between spheres increases, resulting in the increase of melt viscosity. It is a general effect in polymer filled by particles. However, this effect is expected to occur at high nanoparticles concentration, typically more than 20 vol %, and it should not prevent the preparation of thin films. How, then, can this route be realized practically and allow preparation of polymer spheres containing nanocrystals at the center?

We developed a rather simple and effective procedure. It is based on the following effect that was found: In an organic colloidal solution containing hydrophobic polymer and hydrophobic-coated nanoparticles, the polymer is deposited onto the surface of nanoparticles. As a result, the combined sedimentation of nanocomposite, containing the polymer with nanoparticles dispersed in it, has been observed upon addition of water.

If a hydrophobic polymer solution is poured into water, the polymer coagulation is observed. Any small particle in solution can be the center of coagulation (similar to the center of crystallization). Thus every nanocrystal will be coated by polymer layer and will form sediment. The polymer coating on nanocrystals will be nearly equal for every particle due to the uniform distribution of nanocrystals in

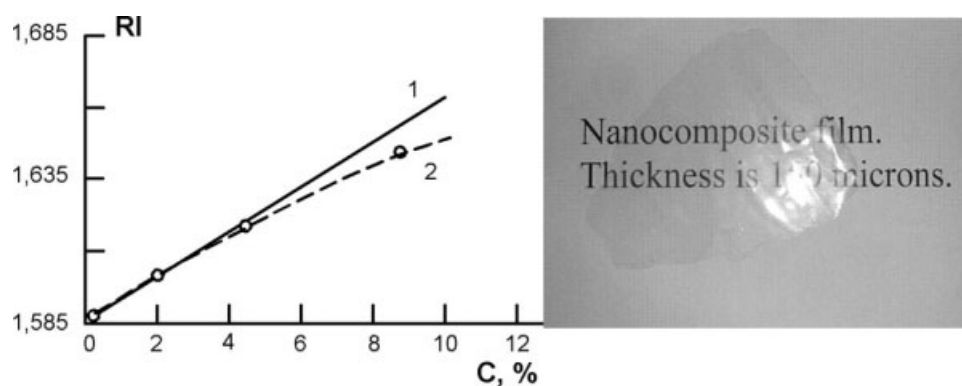


Figure 2 Dependence of RI of ZnS-polycarbonate nanocomposite on concentration C of inserted nanocrystals. a. Left: theory (solid curve); experiment (dashed curve, dots). b. Right: view of transparent nanocomposite film.

the original colloidal solution. Therefore, the nanocrystals are distributed uniformly in sediment. Then it is necessary to treat the prepared sediment with the aim of water elimination create the nanocomposite layer.

Let us consider the results of both the experiments that support the statement about formation of the fine coated particles under sedimentation. Refer to Experiments 1 and 2 in the Experimental Section, Nanocomposite preparation- thermoplastic matrix.

In Experiment 2, a nearly transparent colloidal yellow solution was formed with deposition of sediment occurring during several hours. The resulting sediment was yellow-colored and the supernatant solution was colorless. That means that there are many centers of crystallization in solution and every nanocrystal is coated by polymer. Such particles are the nanocrystals coated by two layers: at first by 3-Phenylpropionic acid and then by polymer. As the solution at all sedimentation stages was transparent with a slow rate of sedimentation, we can conclude that the particles were very small. The uniform deposition of them gives approximately the same thickness of coating for every nanocrystal. Higher CdS concentration in the initial solution resulted in an increase in deposition time. This observation is consistent with a decrease in deposited particles size. Then the solid prepared by polymer sedimentation was dried and it was hot-rolled at 120°C to form a transparent film about 150 microns thick.

The calculated and experimental refractive index values for various composites are shown in Figure 2. Calculations have been carried out proposing that the refractive index of a nanocomposite is the mean value of nanocrystals and matrix indices on a volume basis.

As it is shown in Figure 2 right, even at 9 vol % nanoparticles concentration, the nanocomposite film sample is clear and colorless. The sample is placed on the piece of paper with printed text that can be seen through the sample. Properties of this nano-

composite film are as follows: Shell: 1-Naphthylacetic acid; Volume content of nanocrystals: 9%; Thickness 50 μm ; Light scattering: 12%; Refractive index of nanocomposite $n_D = 1.635$. This transparency of the film is a result of homogeneous inside structure of nanocomposite. In Figure 3, the transmission electron microscopy photo of cut nanocomposite is shown. As can be seen the nanocrystals were distributed in the layer rather uniformly; there is no coagulation. However, they may form some loose structure that could explain an observed increase in melt viscosity at the increase of nanocrystals content.

To achieve hot molding processing of nanocomposite film we added 50 wt % of plasticizer (poly(phenylene oxide - 6 monomers per chain)). In spite of the large amount of plasticizer and low glass transition temperature of the composition (T_g of pure polymer is 220°C, while T_g of plasticized composite is about 12°C) (Fig. 4), the resulting nanocomposite

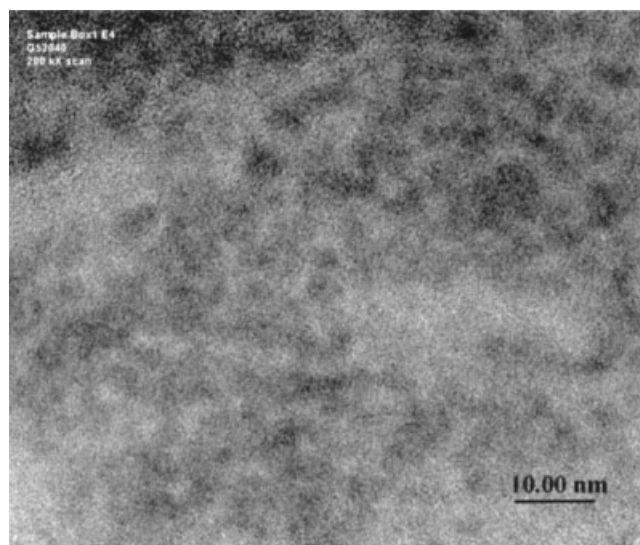


Figure 3 TEM photo of cut ZnS nanocomposite with high nanoparticle concentration (13 vol %).

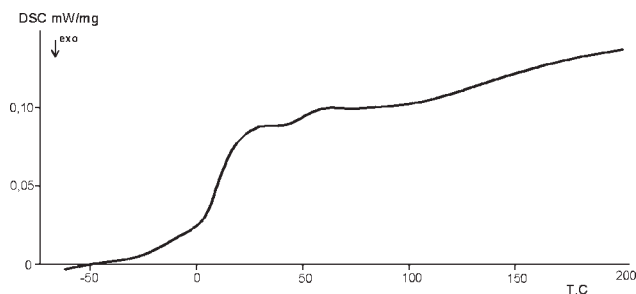


Figure 4 DSC of plasticized nanocomposite (50% of plasticizer, 12 vol % of ZnS nanoparticles). Glass transition: onset: 2.7°C; midpt: 11.1°C; inflpt: 12.9°C; endpt: 19.4°C.

material has higher melt viscosity than the pure polymer.

In this material, the nanoparticles concentration was limited by the inability to hot mold the nanocomposite even at 120°C. When the nanoparticles concentration was increased up to 12 vol %, the plasticized thermoplastic material lost flow properties completely. This behavior is similar to that of the polymer filled by carbon micro and nano sized particles at a concentration of more than 10 vol %.²¹ Our observations are consistent with significant interaction between the shell/nanoparticle and polymer matrix, as discussed earlier. Thus, it appears that in this example either the goal of having low interaction between shell and matrix was not accomplished or the shell material did not sufficiently shield the nanoparticles from direct interaction with the matrix.

Maximal parameters obtained with thermoplastic nanocomposites are in Table III. Higher concentrations of nanoparticles were precluded due to impossibility of thermal processing of the nanocomposite.

UV-curable polymer filled by nanoparticles— Synthesis and behavior

Because the nanoparticles concentration in thermoplastic material was limited by flow behaviors of the material, a possible method to obtain higher concentrations is to use as a matrix liquid monomers and then to UV cure the mixture to a solid nanocomposite.

TABLE III
Properties of Nanocomposite with Maximum
Nanoparticle Concentration

Maximum nanoparticle concentration obtained	16 vol %
Maximum concentration permitting hot pressing	10–12 vol %
RI of nanocomposite	1.635
RI of pure polymer	1.585
Haze of 100 μm film of 12% nanocomposite	4%

Our work has involved nanoparticles stabilization primarily by steric barriers. So, each nanoparticle should be covered by quite a thick shell linked with the surface of the nanoparticle. In the work discussed earlier, the thickness was accomplished by having a multi-atom chain connecting the acid group and aromatic group of the shell molecule.

Although there are hundreds of acrylic monomers available from many suppliers, there are very few commercially available UV-curable monomers with (for example) an acid group at one end and a vinyl group at the other and low viscosity at room temperature. Based on these requirements one suitable substance has been chosen: 2-carboxyethyl acrylate (Table II, CEA). This substance has an acrylic group for curing and can be used as shell material because of the acid group. This molecule has only a short distance between the groups, and only a relatively thin shell would be expected before polymerization. As discussed earlier, perhaps even a butyl or pentyl chain in the shell does not provide enough thickness to avoid matrix crosslinking at high nanoparticles concentration in a thermoplastic matrix. Certainly, we would expect additional monomer units from the matrix to add to the shell monomers during the UV curing reaction.

It was found that the speed of ZnS nanoparticles dispersion depends on processing them in toluene. Without processing in toluene, dispersion is possible, but very slow. Speed of dispersion increases also upon increase of time or temperature of processing in toluene. A possible explanation is the following: a lot of water is at the surface of nanoparticles. During processing in hot toluene water is removed as an azeotrope. Dispersion of nanoparticles is possible only as CEA becomes linked to ZnS surface, occupied previously by the water. So, removing of water will result in acceleration of

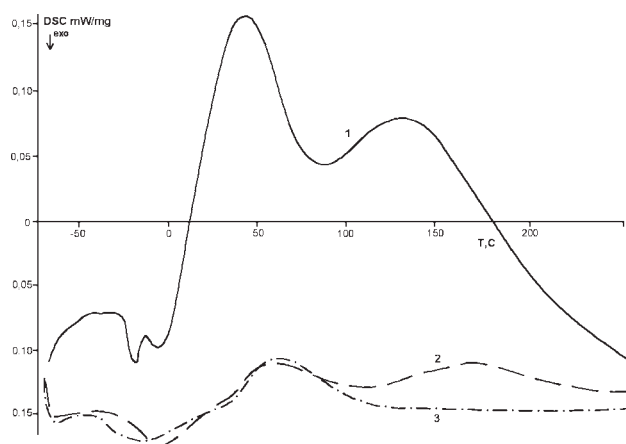


Figure 5 DSC scan of nanoparticles powder. First scan—1; second scan—2; third scan—3. Mass lost after first scan is 18%.

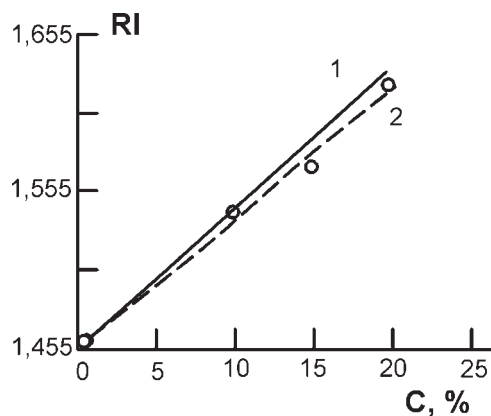


Figure 6 Dependence of ZnS-CEA nanocomposite RI on nanoparticles concentration, theory (solid curve); experiment (dashed curve, dots).

nanoparticles dispersion. In any case, the process of nanoparticles dispersion is very slow, since it is determined by chemical linking of CEA to nanoparticles surface.

DSC investigation was made and confirms this idea. Repeated DSC scans of nanoparticles powder dried in air at 80°C during 2 days are shown in Fig. 5.

The endothermic peak at about 50°C is due to loss of alcohol solvent remaining from the nanoparticle synthesis. The peak at about 140°C is due to loss of chemically linked water from the surface. This DSC scan shows that nanoparticles have about 18 wt % of water on the surface initially. This water is connected to the surface strongly and can be removed rapidly only by heating up to about 250°C. Note the large reduction of heat lost (due to change in water evaporation) between the first and second scans. The treatment in boiling toluene is another, slower way to remove this water.

The slow speed of the dispersion step of ZnS into CEA has the following possible explanation: Ultrasonic dispersion is a process of consecutive detachment of each nanoparticle from a conglomerate. The detachment of a particle begins with the joining of CEA acid groups to the surface of a nanoparticle. If the process is a step-wise consecutive detachment progressing over the surface of a nanoparticle, it is expected to be slow. The action of ultrasound acts to speed up this process. After dissolution of ZnS into CEA, a shell of CEA is formed at the surface of each nanoparticle. As the result ZnS-CEA nanocomposite dispersion (or solution) is stable for a long time.

After preparation of clear nanocomposite solution, a photoinitiator was added, and the liquid was cured as a film between polyester films with UV light. The nanocomposite layer was covered by polyester film to avoid inhibition of curing by oxygen. The resulting solid film is transparent and colorless, but more fragile in comparison with pure CEA film.

In our experiments, we have made compositions of ZnS-CEA with different ZnS concentrations by the same method described above. Maximal ZnS volumetric concentration in the compositions was 20 vol %. The RI of the resulting UV cured film was 1.61, compared with an RI of 1.45 for the pure CEA film. Thus, the RI increase is 0.16.

Dependence of RI of these nanocomposites on nanoparticles concentration is shown in Figure 6. Again, the theoretical RI was calculated based on volumetric averaging of RI of the components.

Maximal nanoparticles concentration in these compositions was limited by viscosity increase up to the point of a non-flowing composition before curing. An explanation is the following: for ultrasonic dispersion the liquid should be not too viscous, or the liquid will not oscillate in response to the oscillation of ultrasonic horn end. During ultrasonic dispersion, the dissolution of the ZnS nanoparticles is more and more slowed down as the quantity of dissolved ZnS increases. Presumably, this is because the viscosity of the solution increases greatly upon increase of ZnS concentration. As the result, the dispersion process will essentially stop at some ZnS concentration. This concentration is the practical maximum.

To obtain an even higher ZnS nanoparticles concentration in nanocomposite (25%), preparation method was modified to the viscous composition was added some quantity of dichloromethane as a solvent. At prolongation of ultrasonic dispersion all nanoparticles were dissolved. Then the dichloromethane was removed by heating up to 80°C at atmospheric pressure, and there was formed an almost

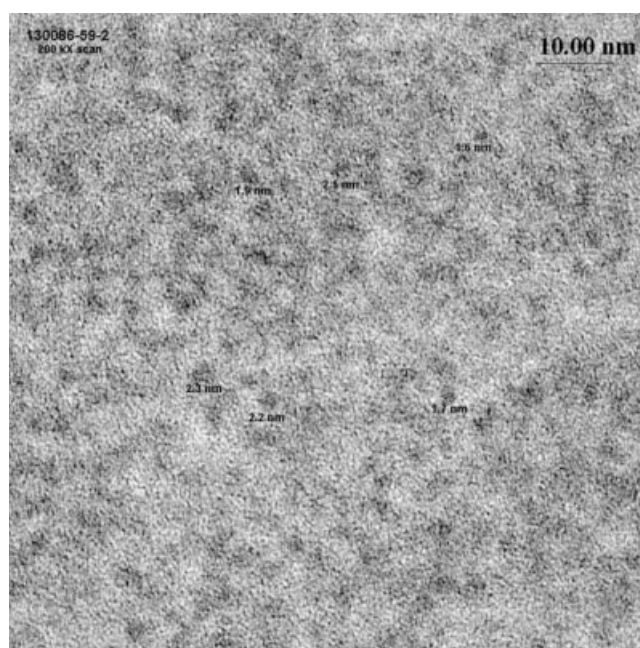


Figure 7 TEM photo of nanocomposite (nanoparticles concentration is 20 vol %).

solid uncured nanocomposite that could flow only under applied pressure. Nevertheless, UV curing of this composite resulted in a transparent film formation with extremely high RI = 1.7 (increasing of RI = 0.25 in comparison to CEA without nanoparticles). Curing conditions were the same as in previous cases. This RI value is tantalizingly close to, although still short of, the target of 1.7, indicating a good possibility of reaching the target in future work.

If a UV-curable matrix monomer with RI = 1.65 were used in this same procedure with 25% of ZnS nanoparticles, it might be possible to obtain a nanocomposite material with extremely high RI = 1.85–1.9.

All our experiments have shown a significant increase of ZnS–CEA nanocomposite viscosity as the nanoparticle concentration increased. On the other hand, cured nanocomposite films retained transparency even at the highest nanoparticle concentration. Certainly, these effects are connected with the internal structure of the nanocomposite and the interaction between nanoparticles without coagulation.

For the thermoplastic composites one can explain the increase in melt viscosity by invoking virtual interaction involving single polymer chains being attached to multiple nanoparticles simultaneously. However, for the monomeric CEA composites before curing, no such explanation seems reasonable. The CEA chain is short and has only one coordinating group per chain. A possible explanation is nanoparticle–nanoparticle interaction at the small separation distance afforded by short CEA chains, similar to that between carbon nanoparticles observed in previously cited work.²¹

The following TEM photo (Fig. 6) shows inside structure of nanocomposite. The photo was made of a thin slice of nanocomposite cured immediately after preparation. The nanoparticles concentration was 20 vol %. Note that the distribution of particles is almost uniform, which explains the transparency. Size of particles is varied between 1.6 and 2.5 nm, so nanoparticles are monodisperse. The turbidity of nanocomposite films having 5 and 25 vol % of nanoparticles were nearly equal (about 2% for 100 μm thickness). Scatter of data was 1–2% so it is not possible to show correlation between scattering and nanoparticles concentration in this range. The highly concentrated monomeric nanocomposite materials in uncured liquid state were stable for some years (2002–2008) and did not tend to coagulate or increase in viscosity.

CONCLUSION

This work has shown that it is possible to prepare nanocomposites of semiconductor (high RI) nanoparticles in both thermoplastic and thermoset commer-

cially available polymeric matrices. In all these experiments, an increase of nanoparticles concentration was accompanied by a dramatic increase in viscosity, which limited the maximum concentration of nanoparticles obtainable. At the same time, there was not an increase in turbidity of the nanocomposites. TEM photos of nanocomposites showed well-dispersed nanoparticles without coagulation (Figs. 3 and 7). Increases of RI up to 0.25 were obtained for nanocomposites, compared with native matrix polymers. The goal of RI of 1.7 for a nanocomposite with polymeric physical properties was obtained.

At the same time increasing of viscosity, absence of high turbidity show presence of some processes of nanoparticles interaction in polymer resulting of its self-organization. Study of these processes will be the aim for the future work.

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