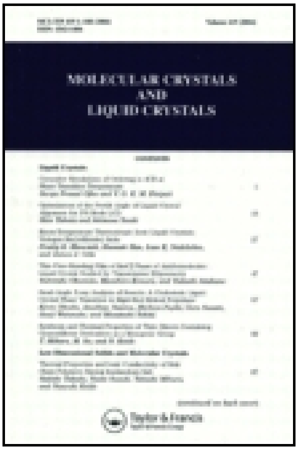

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Hybrid Optical Material with Nanoparticles at High Concentrations in UV-Curable Polymers - Technology and Properties

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Hybrid Optical Material with Nanoparticles at High Concentrations in UV-Curable Polymers – Technology and Properties

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Optical hybrid materials with comparable concentrations of inorganic nanoparticles and polymer matrix components are studied. Materials are homogeneous and have good optical properties and processability. Effects related to a high concentration of nanoparticles in the polymer are discussed. Optical and rheological properties of these materials are investigated.

Keywords: nanocomposites; nanostructure; optics; photopolymerization; refractive index

INTRODUCTION

Polymer–inorganic nanoparticle composite materials derived from several components have attracted the interest of a number of researchers due to their synergistic and hybrid properties. Being in a solution or bulk, these materials offer unique mechanical [1], electrical [2], optical [3], and thermal properties [4] that are induced by the physical presence of nanoparticles, the interaction of a polymer with nanoparticles, and the state of dispersion [5–7].

Microsized particles used as filling agents scatter light, thus reducing the light transmittance and optical clarity. The efficient nanoparticle dispersion combined with a good polymer-particle interfacial adhesion should eliminate the scattering and allow the

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exciting possibility to develop new transparent films and coatings. The possibility of combining the different properties 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.

If one prepares a material with nanoparticles and a polymer under the condition of a 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 should be low, even at high nanoparticle concentrations. A homogenous hybrid material is obtained. On the other hand, the small distance between nanocrystals provides a significant change in the composite's properties, for example, an increase in the refractive index (RI), increasing the viscosity, etc. However, the development of such a material would appear to require a significant investigation both in the physics of the interaction of nanoparticles at small distances and in the technology of synthesis of highly concentrated nanocomposites.

At the present time, there are many references regarding the synthesis, testing, and applications of nanocrystals. There are only a few research activities on nanocomposites with high transparency, good optical quality, and a refractive index significantly greater than that of the pure matrix material [8–10]. To this date, there has been no practical demonstration of the principle that one can obtain a significant increase in the RI of nanocomposites, while maintaining their transparency in spite of the presence of nanocrystals. The problem to obtain nanocomposites with good optical and mechanical properties like those of a typical thermoplastic or UV-cured polymer and, at the same time, with a high nanoparticle concentration has not been solved.

There is the well-known method to develop nanocomposite films by spin coating and drying a solution containing both a polymer and nanocrystals. This method is easy and has been used in different investigations [10]. However, this method has a fundamental defect that does not allow the preparation of solid thick films of some hundreds of micrometers in thickness at a high concentration of nanocrystals. At a high concentration of nanoparticles in the polymer matrix, there are large interactions between them similar to the 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 non-uniform distribution of particles in the matrix, and the composite becomes cloudy. So, unlike a solution from two organic substances that can be prepared by the simple

mechanical mixing, at the mixing of nanoparticles with a polymer, contact occurs between nanoparticles and coagulation results.

2. If one designs a solution with strong interactions between nanoparticles and the polymer matrix to avoid coagulation (for example, the use of surface active polymers with active groups), the drying of a solvent will produce mechanical tensions, and the coating (if it is not thin) will crack. These tensions probably arise from two major sources. Polymer chains can be quite 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 many different polymer chains. As a result, we obtain a cross-linked polymer. Upon drying, the solvent leaves from the polymer-rich regions which then shrink. At the same time, the volume of nanoparticles will not change. As a result, the inner tension will appear in the material.

For example, our work has shown that, after drying the solution in isopropyl of a nanocomposite consisting of 10% of ZnS nanoparticles and polyvinylpyridine, inner tensions will result in turbidity of the material. It is presumed that the major cause of turbidity is the formation of microcracks during shrinkage. However, the same material having even a small quantity of the residual solvent will keep its transparency (tensions do not appear). This process is similar to the well-known result on the hardening of a polymer filled with carbon nanotubes [11]. But, because of the smaller size of our 2 nanometer-sized nanoparticles, the number of nanoparticles will be significantly higher than the number of carbon nanotubes in the same degree, as each nanoparticle volume is smaller. 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 place at smaller concentrations of nanoparticles. This corresponds to a reduction in the molecular weight between crosslinks in an unfilled crosslinked polymer.

Thus, there is a conundrum: to avoid the coagulation of nanoparticles, an increase in the interaction between them and the polymer matrix is desirable, but, at the same time, those interactions with a polymer will result in the hardening of the composite.

One solution to this problem would be the formation of strong interactions between each nanoparticle and a spherical organic shell around it and then the cross-linking between the shells by a typical polymerization process. The result would be the formation of a material with equivalent distances between neighboring nanoparticles (at the centers of shell spheres), so the distribution of nanoparticles should be uniform. At the same time, the usual polymerization of shells would result in a minimum change in rheological properties before the crosslinking. However, at the present time, there are no published studies of the development of this approach to the construction of highly concentrated homogenous nanocomposite materials. This task is the aim of the present work.

Nanocrystals used in this work were of ZnS, because they have a high RI with relatively low density. The concentration of nanocrystals in the composite was studied up to 10–25% by volume, and their size (1.5–20 nm) ensured the low light scattering by the nanocomposite. ZnS nanocrystals were synthesized by an original method as described below.

In some experiments were used ZnO and SiO_2 nanocrystals purchased from Aldrich.

Method of ZnS nanocrystals preparation.

There are different well-known methods of inorganic nanoparticles preparation [12,13]. They are based on a chemical reaction in the liquid medium with precipitation of a colloidal solution. To obtain small-sized nanocrystals, one needs to choose a suitable surfactant or shell [14]. In this work, we used the precipitation method involving the chemical reaction between hydrogen sulfide and metal (Zn or Cd) acetate in a water/alcohol solution in the presence of an organic surfactant, similar to the method described in the previous works [15,16]. The presence of water was needed to increase the dissolution of metal acetate. Many studies have reported using thiols or phosphines as surfactants, but these materials are toxic and not preferred for the factory use [17]. In the present experiments, aromatic carboxylic acids were used as surfactants, because carboxylic acids are not toxic, and a synthesis method was desired which would be suitable for the factory-scale production.

The shell material has two functions. First, the shell should stop nanoparticles from growing beyond a definite size during the synthesis to obtain a monodisperse size distribution. Second, the molecular structure of the shell material as a surface active substance should provide the compatibilization of nanoparticles with the polymer matrix to prevent coagulation. The shell material used here was 5-phenylvaleric acid. The UV-curable monomer used in this project was 2-carboxyethyl acrylate having an acid group and a polymerizable vinyl group at opposite ends.

EXPERIMENTAL

All experiments were accomplished at room temperature in air without special inert atmosphere. UV curing was performed with a mercury lamp (100 W) with maximum emission at the 365-nm mercury line.

Preparation of ZnS Nanoparticles

ZnS nanoparticles were prepared according to the procedure described in a patent [Surface modified nanoparticle and method of preparing same; Publication number: WO2006102231; Publication date: 2006-09-28]:

Solution (1) containing H_2S in isopropanol (IPA) was prepared by passing a stream of fine bubbles of the H_2S gas through IPA for 24 h. After that time, it was assumed that the solution was saturated. A standard zinc acetate solution was titrated with the H_2S solution until lead acetate paper indicated the presence of excess H_2S. From this titration, we determined the volume of the H_2S solution having 0.00083 mole of H_2S (10 mole% excess of zinc over H_2S). In order 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 (0.00027 mole) of 5-phenylvaleric acid in 40 ml of DMF. This was poured into 50 ml of the H_2S solution (1) described above, containing 0.0083 mole of H_2S in IPA, with strong stirring agitation. To the resulting mixture, 100 ml of water was added with stirring. The resulting mixture was allowed to stand under ambient conditions. A precipitate was formed over a day and was separated by centrifugation and washed with water and IPA. After the drying in a vacuum desiccator overnight, 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 the exciton absorption maximum shift. These results are consistent with the earlier report on ZnS nanoparticle size [18].

Preparation of UV Cured Nanocomposite

ZnS nanoparticles with a shell of 5-phenylvaleric acid were prepared as above. The dried nanoparticles were put into toluene and heated for 10 h at 80°C. Nanoparticles/toluene weight ratio was 1/50. After filtering, the nanoparticle powder was dried in air at 80°C for 10 min, min, and then it was put into CEA. Ultrasonic dispersion for about 30–40 min in an open apparatus was done. The disperser had an ultrasonic power of about 70 W delivered from a 3-mm-diameter horn end. The ultrasonic frequency was 27 kHz. At first, the liquid CEA became turbid because of the dispersion of ZnS nanoparticle conglomerates.

Upon the continued dispersion, the colloidal solution ZnS – CEA became more and more clear. Finally, the solution with ZnS nanoparticles became a transparent liquid. At the same time, the solution became more and more viscous during the dispersion. After the dispersion, the ZnS – CEA solution kept good transparency for at least one year. Note that the viscosity of this composition is many times higher than that of pure CEA. The maximum concentration of ZnS nanoparticles in CEA was 20 vol.%. A noticeable increase of the viscosity took place at 5 vol.% ZnS nanoparticles.

After the preparation of a clear nanocomposite solution, dimethoxy phenyl acetophenone (0.1 wt.%) was added, a sandwich of this fluid between polyester films was made (the fluid was approximately 100 μm thick), and this sandwich was irradiated with a mercury lamp (5 mW/cm^2) for 10 min. After the polyester films were removed, the resulting solid film was transparent and colorless, but fragile in comparison with a pure CEA film.

DISCUSSION

The aim of this work was the development of homogenous materials with increased RI and minimal light scattering. The initial approach was to ensure that nanoparticles would be well distributed over the material – i.e., the distance between neighboring particles should be constant, and the nanoparticle–nanoparticle interactions should be minimized. Conceptually, the nanoparticles should be self-assembled into some lattice within the polymer matrix. This concept can be reached if each nanoparticle is placed at the center of a polymeric sphere chemically bonded to its surface. The material of the sphere should be compatible with the polymer matrix and polymerizable to form a uniform homogenous nanocomposite material.

The initial plan was to make nanocrystals covered by a thick polymerizable shell composed of surface active acrylic monomers, which would result in the formation of the structure described in introduction. Each nanocrystal should be covered by quite a thick shell linked with the surface of the nanocrystal. It was discovered that the best shell material for the preparation of nanoparticles was 5-phenylvaleric acid, having a multiatom chain connecting the acid group and the aromatic group. But then the problem remained that these shell molecules were not polymerizable.

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 one and with low viscosity at room temperature.

Based on these requirements, one suitable substance was chosen: 2-carboxyethyl acrylate (CEA). This substance has an acrylic group for curing and can be used as a 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. Another unpublished work executed at our laboratory showed that a thin shell formed during the synthesis of nanoparticles is not enough to avoid the coagulation at high nanoparticles concentrations in a thermoplastic matrix. Certainly, it was expected that additional monomer units would add to the shell monomers during the UV curing reaction.

It was found that the rate of ZnS dispersion is directly related to "pre-processing" nanoparticles in hot toluene. Without processing in toluene, the dispersion is possible, but it is very slow. The rate of dispersion increases also with the time or the temperature of the processing in toluene. A possible explanation is the following: a lot of water and alcohol is adsorbed on the surface of nanoparticles. We recall that a stoichiometric insufficiency of the shell acid was used in the nanoparticle synthesis, so probably not all surface sites were covered. During the processing in hot toluene, water and alcohol are removed and dissolved in the toluene. Yet, toluene does not bind well to the surface, leaving the surface accessible to CEA in the next synthetic step. The dispersion of nanoparticles is possible only as CEA becomes linked to the ZnS surface occupied previously by water. So, the removal of water will result in the acceleration of the dispersion of nanoparticles. In any case, the process of dispersion of nanoparticles is quite slow, since it is determined by the chemical linking of CEA to the surface of nanoparticles.

A DSC investigation was made and confirms this idea. Repeated DSC scans of a powder of nanoparticles dried in air at 80°C for two days (no exposure to hot toluene) are shown in Figure 1.

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

The slow rate of the dispersion step of toluene-dried 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

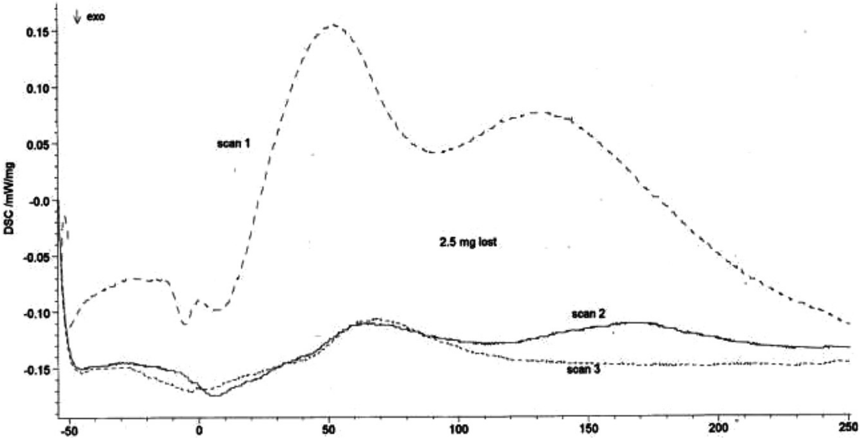

FIGURE 1 Repeated DSC scans of a powder of nanoparticles.

groups to the surface of a nanoparticle. The action of ultrasound only speeds up this process. If the process is a step-wise consecutive detachment progressing over the surface of a nanoparticle, it is expected to be slow. After the dissolution of ZnS into CEA, a stabilizing shell of CEA is formed at the surface of each nanoparticle. As a result, the ZnS – CEA nanocomposite dispersion (or solution) is stable for a long time.

Compositions of ZnS – CEA with different ZnS concentrations were made by the method described above. The maximum ZnS volumetric concentration in the compositions was 25%, but a slightly modified procedure was required for that sample. The dependence of RI on the concentration of nanoparticles is shown in Figure 2.

The maximum achievable concentration of nanoparticles was limited by increasing the viscosity up to the point of a non-flowing composition. An explanation is the following: for the ultrasonic dispersion, the liquid should be not too viscous, or the liquid will not oscillate vigorously in response to the oscillation of an ultrasonic horn end. During the ultrasonic dispersion, the viscosity of a solution increases greatly with the ZnS concentration. Therefore, the dissolution of ZnS nanoparticles is more and more slowed down as the amount of dissolved ZnS increases. Thus, the dispersion process will essentially stop at some ZnS concentration. This concentration is the practical maximum.

To obtain the maximum concentration of ZnS nanoparticles in the nanocomposite (25 vol.%), we added a small amount of dichloromethane as a solvent and a viscosity reducer to the viscous composition (still hazy from undispersed agglomerates). At the prolonged ultrasonic dispersion, all nanoparticles were dissolved. Then

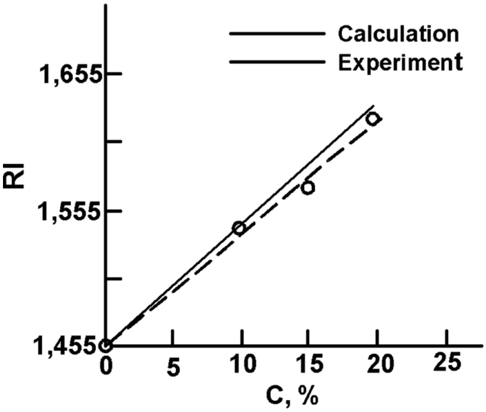

FIGURE 2 Dependence of the RI of the nanocomposite on the concentration of nanoparticles.

dichloromethane was removed by heating up to 80°C at atmospheric pressure, and there was formed an almost solid uncured nanocomposite that could flow only under applied pressure. Nevertheless, UV curing of this composite resulted in a transparent film formation. The RI of the resulting UV cured film was 1.65, compared with an RI of 1.45 for a pure CEA film. Thus, the RI increase is 0.20. Light scattering in a 100-µm-thick film of this nanocomposite was 2%, which is close to that of the pure cured polymer. A photo of this transparent nanocomposite film is shown in Figure 3.

All the experiments showed a significant increase of the ZnS – CEA nanocomposite viscosity as the nanoparticle concentration increased. On the other hand, the cured nanocomposite films retained transparency even at high nanoparticle concentrations. Certainly, these effects are related to the detailed structure of a nanocomposite and the interactions between nanoparticles without coagulation.

The external structure of cured nanocomposites was investigated by atomic force microscopy. In Figure 4, we show the photos made by an atomic-force microscope at different concentrations of nanoparticles in UV cured ZnS-CEA nanocomposites. In the photos is clearly visible the formation of small areas around each nanoparticle and the gradual filling of the entire nanocomposite area by it.

First, at 1.3 vol.% of nanoparticles, the relatively few nanoparticles protruding from the surface are surrounded by the polymer. When the concentration of these structures is increased, and they occupy all the volume at 2.6 vol.%, there is the minimal “free” polymer. At 4 vol.%, the entire polymer is involved in the formation of a structure, and each

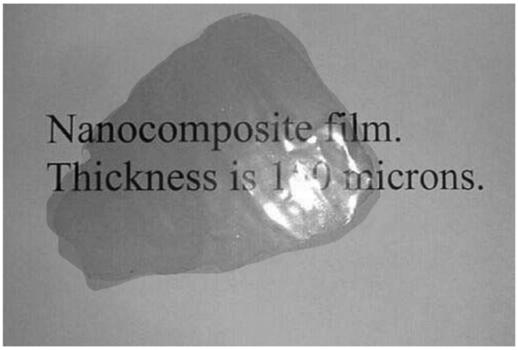

FIGURE 3 View of a transparent nanocomposite film of 150 μm in thickness.

structure element has decreased in size. At higher concentrations of nanoparticles, the material turns to a homogenous state with the absence of visible structured areas around nanoparticles. Consequently, there is formed a hybrid material consisting of nanoparticles each covered by a thick organic shell with constant thickness. There is formed a self-assembly of spheres with nearly constant diameters packed in a superlattice like a photonic crystal with uniform distribution and minimal interaction between nanoparticles as a result of the thick solid polymeric shell.

The following TEM photo (Fig. 5) shows the inside structure of a nanocomposite with a nanoparticle concentration of 20 vol.%. The

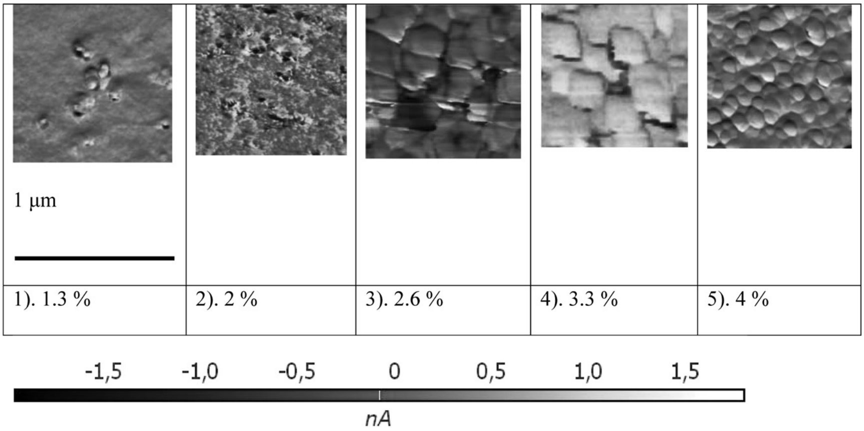

FIGURE 4 Photos made by an atomic force microscope. (below – the scale of heights in color). The size of each photo is 1 × 1 μm. Nanoparticles concentration is shown in vol.%.

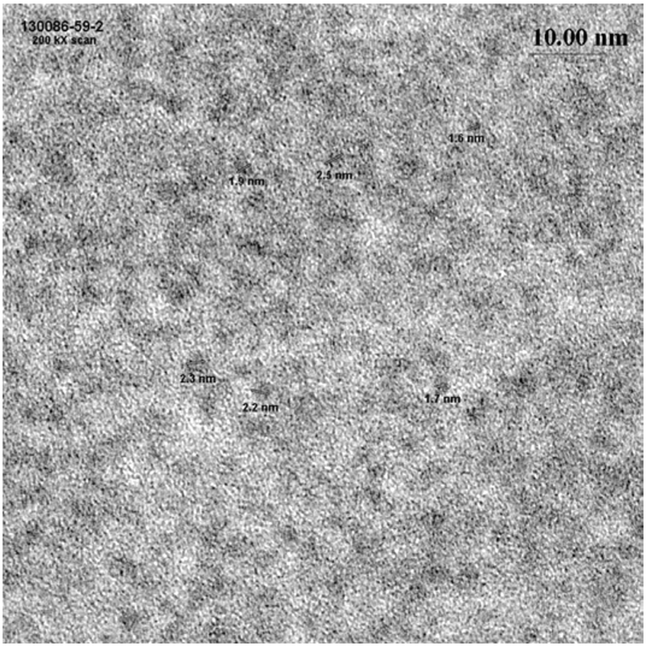

FIGURE 5 TEM photo of the UV cured ZnS-CEA nanocomposite (the concentration of nanoparticles is 20 vol.%).

photo was made of a nanocomposite cured immediately after the dispersion. Note that the distribution of particles is almost uniform, which explains the transparency. The sizes of particles vary between 1.6 and 2.5 nm, so the nanoparticles are nearly monodisperse.

CONCLUSION

We have prepared a set of materials with high refractive index which involve ZnS nanoparticles covered with organic shells and dispersed uniformly in a UV cured polymer matrix. Preferred shell and matrix molecules are linear with a carboxylic acid group to bind to the ZnS surface at one end and with an aromatic group or a polymerizable vinyl group at the other end. The presence of the shells resulted in minimal interactions between nanoparticles, providing a homogeneous structure. These materials display the increase in RI by up to 0.20 above RI of the native matrix with very little light scattering.

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