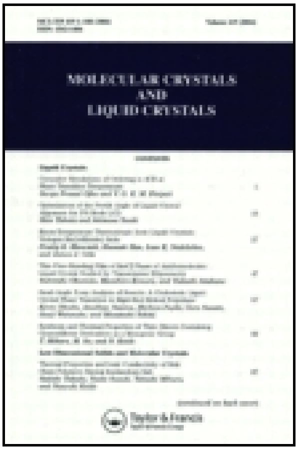

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Oriented Nanocomposites of Ultrahigh-Molecular-Weight Polyethylene and Gold

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Oriented Nanocomposites of Ultrahigh-Molecular-Weight Polyethylene and Gold

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Polymer nanocomposites were prepared by mixing ultrahigh-molecular-weight polyethylene and gold colloids coated with a self-assembled monolayer of dode-canethiol. Subsequently, these materials were oriented by solid state drawing which induced the formation of uniaxially oriented arrays of gold particles. As a result of the orientation of the gold arrays, the VIS-NIR spectra of the drawn composites strongly depended in polarized light on the angle between polarization direction and the orientation axis of the particle arrays, with shifts in the absorption maxima up to ca. 100 nm. It is assumed that these color shifts originated from the small dimensions of the dispersed metal phase in combination with their uniaxial orientation.

Keywords: nanocomposites; gold; polyethylene; dichroism; uniaxial orientation

INTRODUCTION

Nanocomposites consisting of a polymer matrix containing well dispersed inorganic particles with dimensions below 50 nm have found increasing attention in this decade. In such materials, light scattering is highly reduced.[1,2] For example, optically clear films have been prepared with polymers containing colloidal-size semiconductors;[3,4] such films absorb but do not significantly scatter light. Nanocomposites which are fully transparent in the whole visible wavelength range have also been described.[5,6] Other nanocomposites of polymers and inorganic particles show quantum size effects,[7] nonlinear optical properties[8,9] and ultralow or ultrahigh refractive indices.[10,11]

The studies performed so far were focussed in the preparation of nanocomposites with randomly dispersed particles. However, in old and widely forgotten reports[12-18] the reduction of metal salts in oriented fibers and films containing elongated hollow spaces was described. As a result, materials with anisotropic metal objects were obtained. These objects obviously caused in polarized light different colors depending on the angle between the polarization direction of the incident light and the orientation axis of the metal objects. However, all these nanocomposites contained residual metal salts and reaction byproducts which may affect the optical properties, and the fraction of reduced metal ions and their distribution in the polymer matrix was not known.

The following investigations deal with a new route for the preparation of nanocomposites with anisotropic optical properties. Ultrahigh-molecular-weight polyethylene (UHMW-PE) was mixed in hot solution with surface-coated gold particles. Gold particles surrounded with a monolayer of dodecanethiol can be isolated, purified and redispersed in organic solvents. [19] Hence, the incorporation of byproducts stemming from the reduction of the metal ions is prevented. Orientation of the gold particles was induced by solid state drawing of the nanocomposites. Hereby, the use of UHMW-PE allows particularly high draw ratios.

EXPERIMENTAL

Materials

The polyethylene grade used was Hostalen Gur 412 ($M_w = 4 \cdot 10^6$; Hoechst). Hydrogen tetrachloroaurate, dodecanethiol, tetraoctylammonium bromide, toluene, and *p*-xylene were purchased from Aldrich.

Synthesis of Surface-Modified Gold Particles

An aqueous solution of hydrogen tetrachloroaurate (30 ml, 30 mmol/l) was mixed with a solution of tetraoctylammonium bromide (phase transfer agent) in toluene (80 ml, 50 mmol/l). The two-phase mixture was vigorously stirred until the tetrachloroaurate was transferred completely into the organic layer. Then, dodecanethiol (170 mg) was added to the organic phase. An aqueous solution of sodium borohydride (25 ml, 0.4 mol/l) was slowly added under vigorous stirring. After stirring for 3 h, the organic phase was separated, evaporated to a residue of ca. 10 ml in a rotary evaporator, and mixed with 400 ml ethanol to remove the excess dodecanethiol. The mixture was kept for 24 h at −18 °C whereupon a dark brown precipitate formed which was filtered and washed with ethanol. The precipitate was dried under vacuum for several hours.[19]

Preparation of Gold-PE Nanocomposites

Depending on the gold-PE ratio indicated in the text, 10 or 20 mg gold particles were dissolved in 40 g *p*-xylene. After addition of the UHMW-PE (0.5 g), the solution was degassed under vacuum for 15 min, in order to prevent air bubbles during the following reaction stages. The solution was heated under manual stirring to 130°C in order to dissolve the PE. Manual stirring was performed to avoid coagulation of PE particles. After the PE was dissolved, the solution was kept at 130°C for the times indicated in the text. Thereafter the solution was poured into a petri dish and the xylene was evaporated at room temperature under a constant air flow for 48 h.

Solid State Drawing

Gold-polyethylene films were oriented by drawing on a hot stage at 90°C to a draw ratio of 15. Higher draw ratios were obtained with a second drawing at 120°C. The draw ratio (D.R.) was determined by measuring the displacement of ink marks.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC thermograms were determined with a Netzsch DSC200 differential scanning calorimeter. The measurements were recorded at heating and cooling rates of 10

°C/min. TGA measurements were carried out under a constant air flow (150 ml/min) with a heating rate of 5 °C/min, using a Netzsch TGA209.

Transmission Electron Microscopy (TEM)

Specimens for examination with TEM were obtained by evaporation of one or two drops of a toluene solution containing the nanoparticles on carbon films supported on standard copper grids, or by embedding nanocomposites in epoxy resin followed by cutting on a Reichert Ultracut Microtome with a diamond knife. The oriented nanocomposites were sectioned parallel to the draw direction. The electron micrographs were taken on a Philips EM 301 with an acceleration voltage of 80 kV.

VIS-NIR Spectra

VIS-NIR spectra were recorded on a Perkin Elmer Lambda 900 instrument equipped with a polarizer. The absorption spectra of the nanocomposites were determined with the nanocomposites embedded in paraffin oil and placed between two glass slides. In the reference beam, two glass slides with a paraffin oil layer were present. The paraffin oil was applied to reduce the surface light scattering.

RESULTS AND DISCUSSION

Surface modified nanometer-sized gold particles were prepared according to the literature[19] in a two phase system containing water, toluene and a phase transfer reagent (tetraoctylammonium bromide). Tetrachloroaurate was reduced with sodium borohydride in presence of a surface stabilizing agent (dodecanethiol) which formed self-assembled monolayers at the surface of the gold particles. The isolated gold colloids were dark brown and had a waxy texture. TEM photographs of the nanoparticles (Figure 1) revealed average diameters of 2.2 nm and a standard deviation of 0.5 nm.

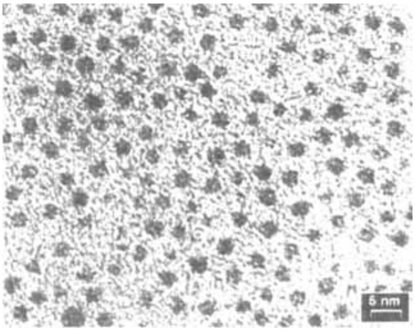

FIGURE 1. TEM image of dodecanethiol-coated gold particles.

DSC thermograms of the gold particles showed a pronounced endotherm transition at 38°C, which probably originated from the melting of the self-assembled organic monolayer adsorbed on the gold particles. Thermogravimetric analysis indicated that the gold particles were stable in the solid state up to approximately 150°C. In the temperature range of 280-900 °C, the residual mass remained constant at 71 % w/w. We assume that this mass consisted of elemental gold. From the analysis of gold and sulfur with X-ray fluorescence spectroscopy, the content of gold was calculated to 74 % w/w and that of dodecanethiol to 25 % w/w. The isolated gold particles redissolved in a number of organic solvents, such as chloroform, decaline, ethanol, pentane, tetrahydrofuran, toluene, trichloroethane, and *p*-xylene.

The nanometer-sized gold particles were dissolved together with UHMW- PE in *p*-xylene at 130°C. Upon heating for 300 min, the color of the mixture changed from brown to blue. Nanocomposites with 2 or 4 % w/w gold were obtained after evaporation of the xylene. The behavior of the materials with 2 and 4 % w/w gold was very similar, and we refer in the following only to the samples with 2 % w/w gold. Analogous to the color in solution, the nanocomposites that emerged from a solution that had been preheated for 20 min appeared brown and those preannealed for 300 min blue, as reflected by the VIS spectra in Figure 2. We assume that the heating procedure leaded to a partial desorption of the dodeready long ago that such agglomerations induce a bathochromic shift.[20] Agglomerates could indeed be observed in samples that had been preannealed for 300 min (Figure 3). The cross section of those agglomerates corresponded up to ca. 10000 primary particles. In the brown samples (20 min preannealing), a noteworthy agglomeration was not observed. An increase in the diameter of the primary gold particles would also cause a shift of the absorption maximum to higher wavelengths.[21,22] The TEM images did not allow an unambiguous decision if the size of the primary particles had changed during the heat treatment.

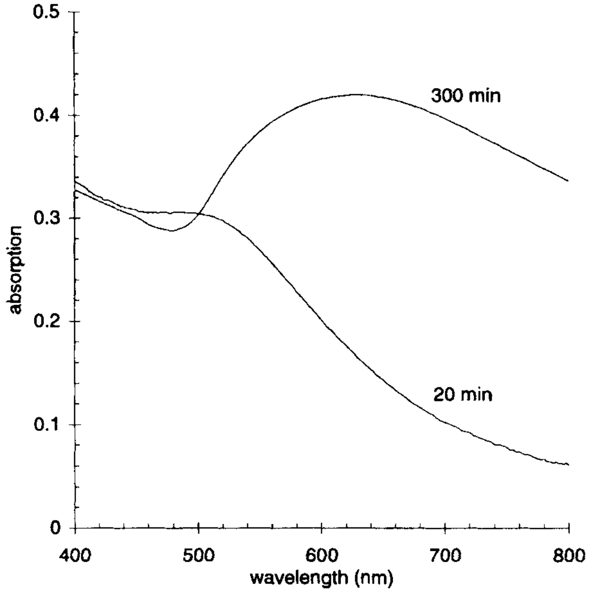

FIGURE 2. VIS spectra of undrawn UHMW-PE nanocomposites (2.0 % w/w gold) preannealed for various periods in *p*-xylene at 130 °C.

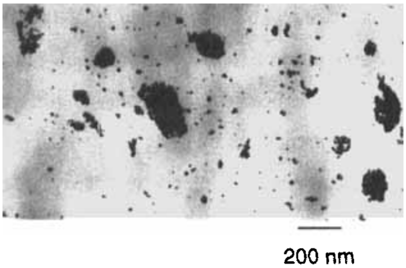

FIGURE 3. TEM image of an undrawn UHMW-PE nanocomposite (2.0 % w/w gold, 300 min preheating in *p*-xylene).

Gold-polyethylene films were oriented by drawing the materials at 90-120 °C to a ratio (D.R.) between typically 10 and 45. Samples with draw ratios of 60 were occasionally also prepared. The drawing procedure induced the formation of arrays of particles in the drawing direction (Figure 4). The thickness of the arrays as observed in TEM images corresponded typically to 10-20 primary particle diameters, and aspect ratios between 10 and 30 were frequently found. The tensile deformation of the spheric agglomerates in the isotropic films probably plays a major role in the formation of the linear arrays.

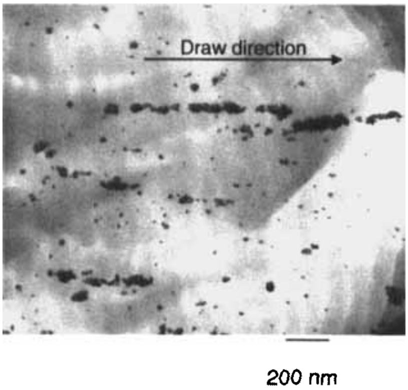

FIGURE 4. TEM image of a drawn UHMW-PE nanocomposite (2.0 % w/w

The stretched materials that had been preheated at 130 °C for 180-1320 min showed a strong anisotropic absorption of polarized light. This effect was hardly detectable with samples that had been subjected only to 20 min preheating. In the former samples, the color shifted from red to blue when the polarization axis of the incident light was oriented perpendicular or respectively parallel to the orientation axis of the particle arrays. An example of a resulting VIS-NIR spectrum with polarized light is shown in Figure 5. It is clearly evident that the absorption maximum depends at the angle between the polarization direction of the incident light and the orientation axis of the particle arrays (φ). In the NIR region, the absorption at φ=0° was much stronger than that at φ=90°. At 630 nm, an isosbestic point was observed (Figure 6), indicating that the dependence of the light absorption on φ can be described empirically with two extinction coefficients at each wavelength, e.g. with one for φ=0° and one for φ=90°.

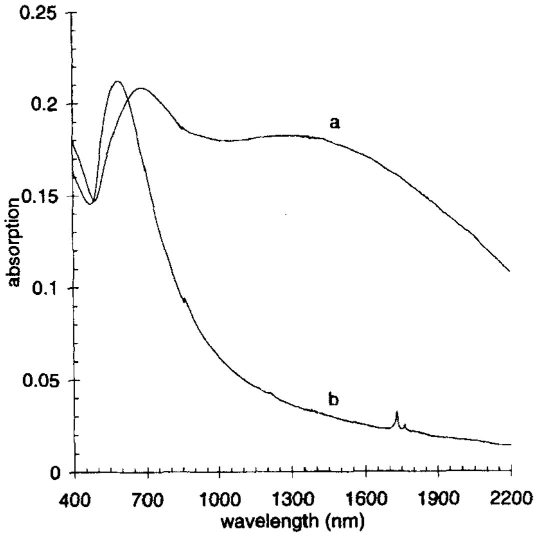

FIGURE 5. Polarized VIS-NIR spectra of a drawn UHMW-PE nanocomposite (2.0 % w/w gold, 300 min preheating in *p*-xylene, D.R.= 45) for φ=0° (a) and φ=90° (b).

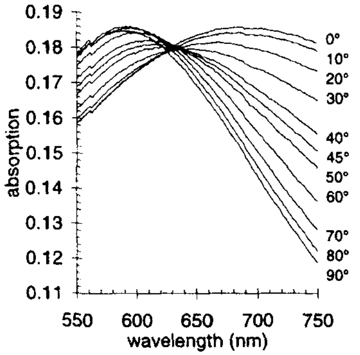

FIGURE 6. Polarized UV-VIS spectrum of a drawn UHMW-PE nanocomposite (2.0 % w/w gold, 300 min preheating in *p*-xylene, D.R.= 45). Measurements were performed at different φ.

In the samples with preheating times between 180 and 1320 min, the polarization effects were pronounced already with draw ratios of 10, but some increase in the differences of the absorption maxima at φ=0° and φ=90° ($\Delta\lambda_{max}$) may appear at higher draw ratios (an example is shown in Figure 7). It seems that the spheric aggregates present in the nanocomposites before drawing are deformed already in the early stages of the stretching process. With 300 min preheating, a $\Delta\lambda_{max}$ of 45 nm was obtained for a D.R. of 10 and a $\Delta\lambda_{max}$ of 100 nm for a D.R. of 45. The corresponding values for 1320 min preheating were 55 and 75 nm and those for 180 min preheating 40 and 45 nm.

It is evident that a dichroism as observed here is caused by the uniaxially oriented metal objects. The primary metal particles could be in touch with each other since probably a part of the thiol layer desorbed during the heat pretreatment in solution. However, the forces between the individual particles are not very strong as they can obviously be deformed in spheric aggregates by tensile deformation, indicating that the adhesion between the particles is limited. For example, a single spheric polycrystalline gold particle is not expected to be deformed under the shear forces acting during the drawing procedure.

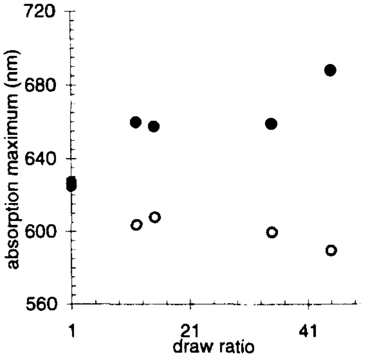

FIGURE 7. Absorption maxima of an UHMW-PE nanocomposite (2.0 % w/w gold, 300 min preheating in *p*-xylene) in polarized light as a function of the draw ratio. Filled circles: φ=0°, open circles: φ=90°.

The optical properties of the nanocomposites with the particle arrays are probably similar to those of analogous materials with elongated primary particles since anisotropic light absorption was also observed with nanometer-sized metal wire-type structures.[23-27] These materials also exhibit shifts in the absorption maximum if the angle between the polarization direction of the light and the orientation of the elongated metal particles is changed.

CONCLUSIONS

Anisotropic metallic structures can be generated in an UHMW-PE matrix by solid state drawing of isotropic nanocomposites containing spherical gold aggregates with weak forces between the primary particles. The anisotropic structures are already formed at moderate draw ratios. The oriented nanocomposites absorb polarized light anisotropically, i.e. the VIS-NIR spectra obtained with polarization parallel to the draw direction differ from the spectra with polarization perpendicular to the draw direction. These effects are caused by the anisotropic arrangement of the dispersed metallic objects.

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