Sulfonated Polybutadiene Ionomer-Templated Nanocopper Composites

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ABSTRACT: New composites based on nanosize particles provide a promising route to the fabrication of novel materials for advanced technology applications in the 21st century. To prepare desired materials, it is important to control the composition and distribution of nanoclusters within the bulk or surface coating of nanostructured materials. To achieve this aim, we developed a novel method of preparing nanocopper–ionomer thermoplastic composite material with sulfonated *cis*-1,4-polybutadiene random ionomer as a matrix and a capping polymer in organic solvent. The effect of sonication on stabilized nanocopper colloid was studied. The self-assembled composite film was characterized by ultraviolet–visible spectroscopy, transmission electron microscopy, ^{1}H-NMR, and thermogravimetric analysis. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3180–3184, 2002

Key words: ionomers; nanocomposites; stabilization; colloids

INTRODUCTION

Nanostructured materials are now being investigated intensively because their physical properties are remarkably different from those of the bulk.[1] Many methods have been used to prepare nanostructured materials.[2,3] In the preparation of nanomaterials from the liquid phase, the solvent has an important role. The literature indicates that the dispersability of ultrafine metal particles depends on the nature of the solvent.[4] With thermal method, fine metal particles have been prepared in organic solvent.[5] If the organic solvents taken were of low dielectric constant, the particles aggregated due to weaker electrostatic stabilization associated with low polarity. So surfactants were taken for the effective dispersal of metal particles in low-polarity organic solvent. However, the surfactant stabilized metal particles lacked in film-forming ability and ready processability in the pilot scale as well as in batch-scale production. Therefore, there was a hunch of "forgiving"[1] material for advanced technology applications.

Particles in a polymer medium have received intense interest due to the better and ready processability of polymer films and possible future application in device structures.[6,7] In the solution phase, different methods with different stabilizing polymers, latex, and dendrimers have been used by those with different school of thought.[8−20] Thus, a variety of methods for the preparation and stabilization of metal colloids exists. The advantages and disadvantages of the methods are discussed in the literature.[1,11,13]

In this article, utilizing the concept of simple colloidal chemistry, we report on the preparation of self-assembled "smart" nanocopper thermoplastic ionomer composites and the observation of sonochemical disturbance on the morphology and stability of the nanocopper colloid in low-polar volatile organic media.

EXPERIMENTAL

Sulfonated *cis*-1,4-polybutadiene ionomer as a capping polymer was used in this work. Cupric acetate and the ultraviolet-grade solvents [tetrahydrofuran (THF), chloroform] were products of S. D. Fine Chemicals Ltd. (Mumbai, India). Sodium borohydride (extra pure), produced by Sisco Research Laboratory Pvt. Ltd. (Mumbai, India), was used as the reducing agent. These materials were used at their commercially available purity.

Absorption spectra were taken on Shimadzu spectrophotometer (model 3100 UV–VIS–NIR) with THF as a reference in the region from 190–700 nm with 10-mm path-length quartz cuvettes after baseline correction. The nanocopper–ionomer colloid materials were selectively imaged by transmission electron microscopy (TEM) with a Hitachi H-600 electron microscope at an operating voltage of 75 kV, without sonication, and after sonicating the stabilized colloidal
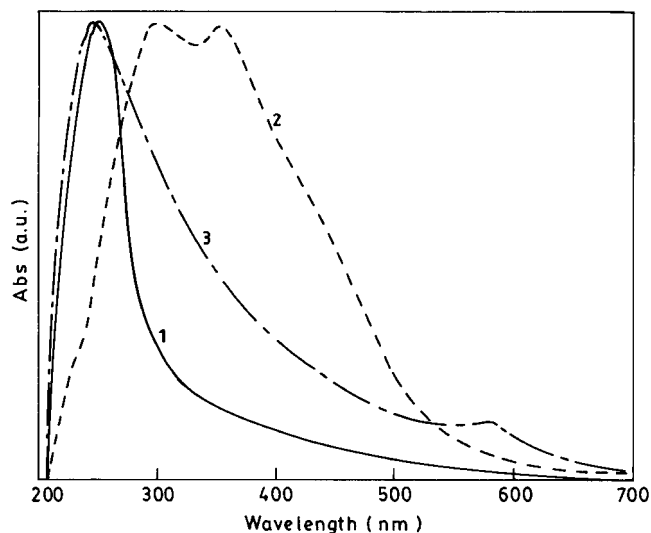
Figure 1 Absorption spectra in different regions for (1) the ionomer only, (2) the ionomer–Cu^{+2} interaction before reduction, and (3) the copper nanoparticles stabilized by the ionomer after borohydride reduction in THF.

solution for 0.5 h at ambient conditions. In both cases, we prepared the TEM samples by placing drops of the colloidal dispersion on a carbon-coated copper grid (200 mesh) with the help of a microsyringe. We allowed the excess solvent to evaporate at room temperature after soaking the grid onto a filter paper to remove solvent. Magnification of 50,000 was used. We determined particle sizes manually by processing from photographs. ^{1}H-NMR spectra were recorded on Bruker 400 MHz NMR spectrophotometer in CDCl$_3$ solvent. The same amount of nanocopper–ionomer composites was redispersed in the same amount of CDCl$_3$ with tetramethylsilane as an internal standard. Thermogravimetry (TG) of the ionomer and nanocopper–ionomer composite were analyzed on Shimadzu DT-40 in the presence of air, with identical thermal histories.

Preparation of nanocopper colloids

A transparent THF solution of the sulfonated *cis*-1,4-polybutadiene ionomer (0.10%)[21] and cupric acetate (10^{-5} M) in a mass ratio of polymer:metal = 10:1 was stirred at room temperature (30°C) for 0.5 h, to which a THF solution of freshly prepared NaBH$_4$ (10^{-4} M) was then added dropwise with vigorous stirring. A clear, yellowish brown solution resulted, apparently indicating the completion of the reduction within 5 min. No precipitate was visible, and the colloidal dispersion was stable for more than 15 days in ambient conditions in a stoppered vial without any special precautions. The entire procedure was reproducible. The ultraviolet–visible (UV–vis) spectra were obtained before and after the reduction.

Preparation of composite films

We prepared static cast films by allowing solutions in glass slides to evaporate slowly in a vacuum desiccator at room temperature for 2 days; the solutions were then kept under high vacuum for at least 24 h. The ionomer film was soft, transparent, and pale yellow, whereas the nanocopper embedded ionomer composite film appeared slightly brown, soft, and optically clear.

RESULTS AND DISCUSSIONS

UV–vis analysis

Figure 1 exhibits the absorption spectra (190–750 nm) of the nanocopper colloids in THF solution. Before reduction, the precursor Cu^{+2}-sulfonated ionomer showed a band at about 305 nm due to ligand-to-metal charge transfer (LMCT).[22] On reduction, the spectra displayed the appearance of a plasmon band of copper at 575 nm, which resembled earlier work.[23]

TEM micrograph analysis

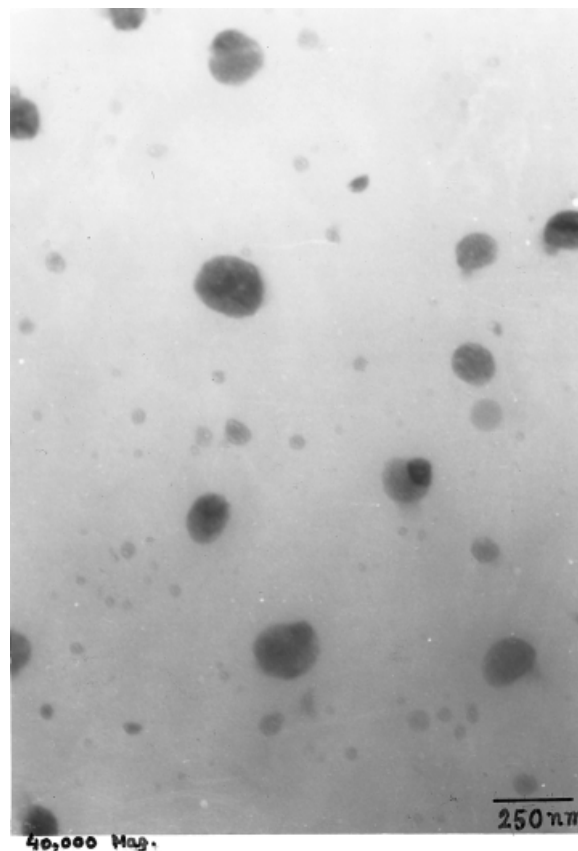Figure 2 exhibits the sulfonated polybutadiene ionomer microdomains formed in THF, and these may

Figure 2 TEM micrograph of sulfonated polybutadiene ionomer microdomain in THF.
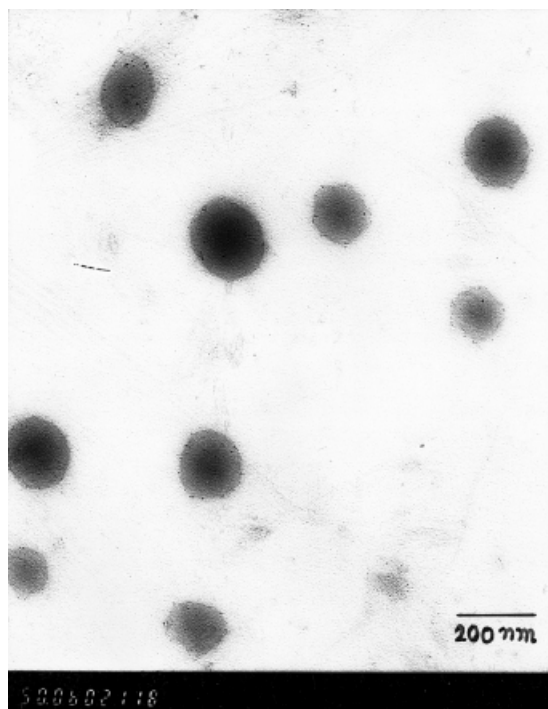
Figure 3 TEM micrograph of the slightly ellipsoidal nano-copper–ionomer composite particles before ultrasonication.

have acted as nanoreactor in the stabilization procedure.

The TEM (Fig. 3) shows that the nanocopper particles were mostly confined within slightly elliptical microdomains with a small percentage outside in the solvent. The elliptical domains had sharp circular coronal outlines, with a relatively darker core. Figure3 shows the TEM micrograph of the ellipsoidal nano-copper-sulfonated polybutadiene composite particles. The size of the ellipsoidal composite particles varied from 140 to 220 nm with respect to the major axis, and the minor axis varied from 120 to 180 nm. On ultrasonication, the shape of the composite particles self-assembled to a spherical shape (Fig. 4) due to elastic deformation by the viscoelastic matrix ionomer. The spherical copper nanocomposites prepared with ultrasonication had a minimum diameter of 60 nm and a maximum diameter of 180 nm (Fig. 4). Thus, the size and shape of the nanocopper composite was governed by the balance of the elastomeric capping polymer and the external force applied during particle growth or nucleation. Although the size and shape changed on ultrasonication during the formation of nanocomposites, the samples exhibited no change of color, and the color remained ruby (light reddish brown) in solution in both cases. On careful observation, Figure 3 shows the discrete nanoparticles dispersed on the matrix are of 5–10 nm in size, whereas discrete particles found adsorbed on the matrix ionomer microdomain after ultrasonication were 5–20 nm size (Fig. 4). Ultrasonication of viscoelastic ionomer matrix in this case led to

partial agglomeration of nanocopper particles followed by immobilization on the matrix ionomer because it is well known that copper nanoclusters tend to aggregate very quickly.[24] Although in both the cases, a fast reducing agent such as sodium borohydride was used; the ultrasonication assisted the quenching and rearrangement of composite particles. Therefore, the selection of the stabilizing polymer played a crucial role in controlling the features of the nanocomposites formed in the solution. The enhanced visibility of these spherical domains in the TEM micrograph was possibly due to the presence of enveloped metal nanoparticles with high electron densities. Without any additional characterization, it may not be opportune to draw any conclusion regarding the genre of these spherical domains. Nevertheless, microphase separations into spherical domains have been suggested as resembling the process of micelle formation for amphiphilic diblock copolymers in a selective solvent with a spherical core, surrounded by a corona of the soluble major components.[9] In both cases, copper nanoparticles were primarily encapsulated within sulfonate-functionalized microdomains (Fig. 2). It is clearly visible in the TEM micrograph that the domains were generally darker. Nanocopper that was generated in the solvent may have been adsorbed on the coronal part of these domains, and this again was shown by the TEM micrograph. Therefore, the formation of ordered clusters from spherical microdomains in sulfonated polybutadiene ionomer, nonethe-
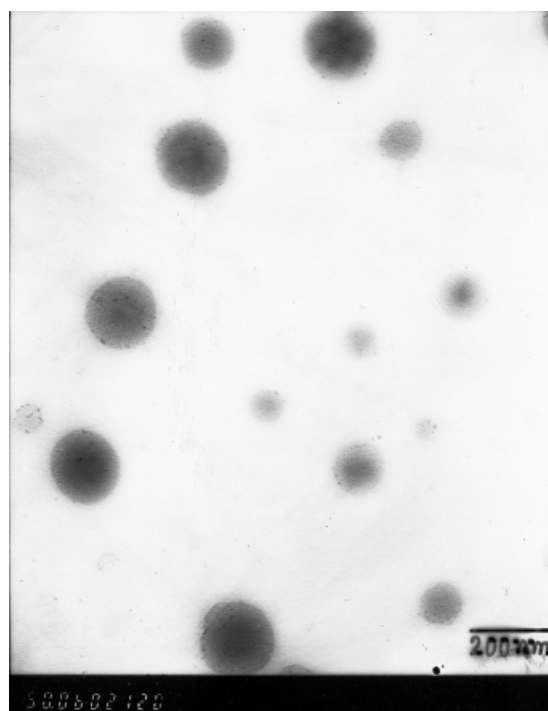

Figure 4 TEM micrograph of the almost spherical nano-copper–ionomer composite particles with 0.5-h ultrasonication in air.

less, in the light of the previous discussion, appeared to be a self-assembly process.

^{1}H-NMR analysis

Figure 5 exhibits the ^{1}H-NMR spectra of the nanocopper–ionomer composite redispersed in CDCl$_3$ solvent. The comparative ^{1}H-NMR spectrum in CDCl$_3$ revealed that the diagnostic signal due to the methine proton attached to the sulfonated carbon of the *cis*-1,4-polybutadiene ionomer, at δ 4.2 ppm had a high field shift at δ 4.9 ppm in the nanocopper-sulfonated polybutadiene composite redispersed in CDCl$_3$. Besides, the ionomer peak was sharper compared to the composite peak, the latter being relatively broad. The line broadening occurred due to discontinuity in the diamagnetic susceptibility of the copper-sulfonated hydrocarbon interface and the residual dipolar interactions in the layer occurred due to spatial constraints and confirmed that the sulfonated polybutadiene hydrocarbon moiety was indeed bound to the nanocopper surface.[25] Such "adsorptive" attachment of sulfonate ions might also indicate the possibility of vesicular conformation, likely to be adopted by the matrix polymer units, around the nanocopper particulates in the process of attaining electrosteric stabilization.

TG studies

Figure 6 displays the thermogram pattern of the nanocopper–ionomer composite and the sulfonated *cis*-1,4-polybutadiene ionomer. The weight loss by the composite around 260°C may have been due to the rupture of the bonds between the nanocopper particles and the
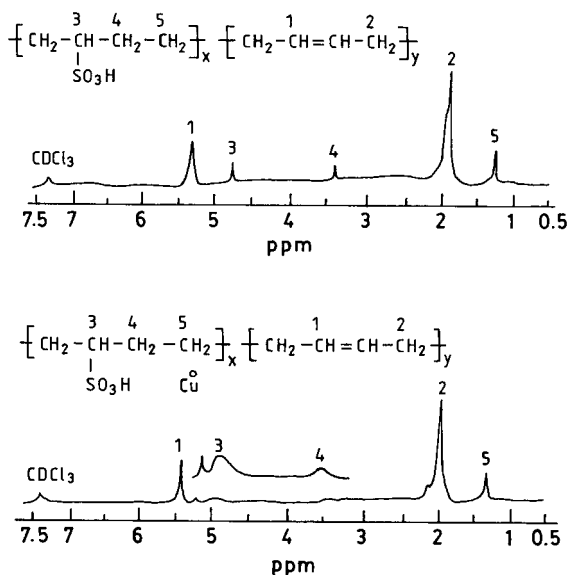
Figure 5 ^{1}H-NMR spectrum of sulfonated polybutadiene ionomer in CDCl$_3$ and stabilized nanocopper–ionomer composite film redispersed in CDCl$_3$.
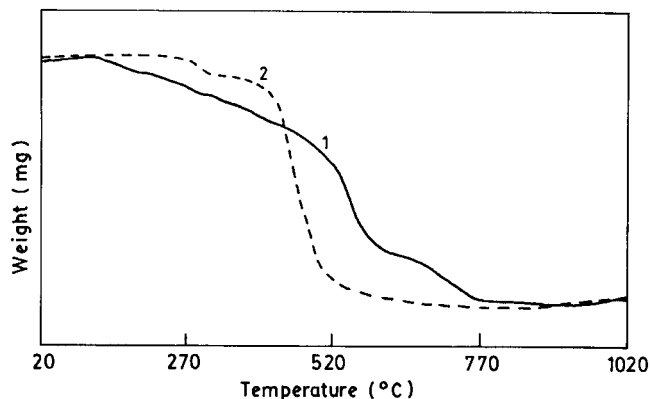
Figure 6 TG spectrum of (1) the nanocopper–ionomer composite film and (2) the ionomer film prepared under identical thermal histories.

ionomer microdomains.[26] The overall thermal stability of the nanocopper–ionomer composite also indicated improvement over the ionomer itself because the composite started degrading at 260°C, whereas the ionomer showed the onset of decomposition at 110°C.

CONCLUSIONS

The generation of stable nanocopper particulates in organic solvents in the presence of moderately sulfonated polybutadiene ionomer dispersions by the reduction of the precursor Cu^{+2} bonded to the sulfonate moieties of the polymer presents a novel and attractive pathway in the technology of the fabrication of nanocopper–ionomer composite films. This method might be one of the most promising methods for preparing solid polymer composite materials, which are expected to be useful as a photosensitive advanced materials such as plastic automobile windshields or display screens used in the vicinity of night-vision devices. Sonication helped to changed the morphology of the composite particles from ellipsoidal to spherical mostly, but no dendritic, fractal (with core), or fractal (without center) shapes were noticed.

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