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ScienceDirect
European Polymer Journal 42 (2006) 3180–3189
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

# Synthesis of metal/polymer nanocomposite by UV-radiation curing

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Received 10 May 2006; received in revised form 21 July 2006; accepted 16 August 2006

## Abstract

Nanocomposite polymers containing bismuth nanoparticles (2 wt%) have been obtained by photopolymerization of acrylic resins. The bismuth nanoparticles have been synthesized by reduction of $BiCl_3$ with *t*-BuONa activated sodium hydride. In situ *t*-BuONa stabilization protects the metallic particles against aggregation. Transmission electron microscopy (TEM) analysis has shown that the bismuth nanoparticles are well dispersed in the acrylic resin. The curing process was followed quantitatively by infrared spectroscopy through the decrease upon UV exposure of the IR bands characteristic of the functional groups. The bismuth nanoparticles were found to have no detrimental effect on the photopolymerization kinetics. Dynamic mechanical analysis (DMA) has shown that the viscoelastic properties of the nanocomposite photopolymer are significantly modified in comparison with corresponding UV-cured polymer. The addition of metal nanoparticles was found to greatly reduce the gloss of UV-cured coatings.

*Keywords:* UV curing; Nanocomposites; Bismuth; Acrylates; Polymer

## 1. Introduction

Nanoparticles of semiconductors and metals have been extensively studied in recent years due to their novel properties which are greatly different from those of their bulk substances [1–6]. Research on metal/polymer nanocomposites has attracted growing interest because these materials offer new performance by combining properties from both the inorganic and the polymer components [7,8]. The nanoparticles exhibit unique properties which differ from their bulk materials, owing to the quantum size effects and the large number of unsaturated surface atoms. The polymeric matrix provides additional qualities, such as the processability, solubility or thermal stability of the systems. In this way, nanocomposite materials possessing novel catalytic, conductive, magnetic or optical properties can be obtained.

Various methods can be used to produce metal nanoparticles within a polymeric matrix [7–9]. Most of them are based on in situ reactions, that is, the particles are generated from the respective metal precursors in the presence of the matrix polymer.

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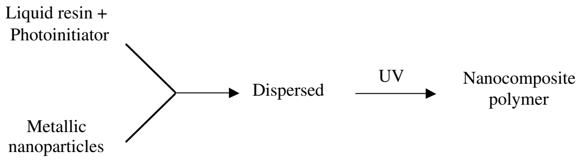
doi:10.1016/j.eurpolymj.2006.08.016

Different procedure for the synthesis range from chemical reduction, photoreduction and thermal decomposition, to vapor deposition methods and sputtering [1,2,4,10]. Several basic routes can be employed. In the case of dispersions, the solution of the metal precursor and the polymer are combined, and the reduction is subsequently performed in solution. Another method is by deposition, where the metal precursor and the polymer are first sprayed onto a substrate, and the reduction to the metal colloids is then performed. The last method is the immersion, where the solid polymeric material is placed into a solution containing the metal precursor. The selection of the polymeric matrix is crucial for the optimization of the systems. Frequently, the polymers are not only employed as protective coatings but also as the dispersing and stabilizing media for the metal nanoparticles. In many cases, the polymers that surround the metal nanoparticles can also exert direct influence on the particles and materials properties. Up to now several types of stabilizing and protective agents for metal nanoparticles have been thoroughly investigated [11,12].

We have recently reported a simple scenario of reduction and complexation between bismuth nanoparticles and *t*-BuONa [13]. The technique used to synthesize Bi(0) nanoparticles takes advantage of the weak coordinating properties of *t*-BuONa which acts as a stabilizer and avoids aggregation of the particles generated in the course of the reduction. Bismuth nanoparticles are very attractive for research in nanotechnology because of their appealing features. Indeed, the semi-metal bismuth is an interesting material for electronic applications because of its highly anisotropic electronic behavior, low conduction band, high electron mobility and its potential to induce a semiconductor transition with decreasing crystallite size.

It was recently demonstrated that clay–polymer nanocomposites can be rapidly produced at ambient temperature by photoinitiated crosslinking polymerization of multifunctional monomers and oligomers [14–18]. As well as nanocomposite polymers containing silica nanoparticle [19,20]. The objective of this work was to apply the UV-curing technology for the fabrication of nanocomposite materials containing Bi nanoparticles within a polymer matrix. Besides its environment-friendly aspect (no emission of volatile organic compounds, low energy consumption), this technology offers a number of advantages, namely, ultrafast curing, ambient temperature operation, spatial and temporal control of the process, and wide range of mechanical properties of the highly crosslinked polymer formed [21–23]. The basic principle of this in situ curing process can be represented schematically as follows:



We present here the first report on the synthesis of metal/polymer nanocomposites by UV-radiation curing of multifunctional acrylate monomers containing bismuth nanoparticles. Special attention has been paid to both the dispersion of the metal nanoparticle in different monomers and oligomers and the photopolymerization kinetics, as well as to the optical and viscoelastic properties of the UV-cured nanocomposites.

## 2. Experimental

*tert*-Butyl alcohol (*t*-BuOH), bismuth chloride ($BiCl_3$) and sodium hydride (65 wt%) in mineral oil were obtained from Aldrich. The *t*-BuOH was distilled on sodium.

The following compounds were used for the formulation of the UV-curable resin:

- polyethylene glycol 400 diacrylate (PEG400DA) and polyethylene glycol 600 diacrylate (PEG600DA) from Sartomer,
- tetrahydrofurfuryl methacrylate (THFMA) from Sartomer,
- aliphatique urethane acrylate from Sartomer,
- hydroxyphenylketone (Darocur 1173) from Ciba Specially Chemicals, as photoinitiator.

The bismuth nanoparticles, synthesized by reduction of $BiCl_3$ with *t*-BuONa activated sodium hydride, were dispersed into the liquid UV-curable resin and stirring for 1 h at ambient temperature. The nanoparticles were introduced in the formulations at a concentration of 1 wt%. The photopolymerization was monitored in situ by real-time Fourier transformed infrared spectroscopy (RT-FTIR), a technique commonly used to study the ultrafast curing of acrylic resins [24]. The liquid resin was applied onto a $BaF_2$ crystal by means of a calibrated wire-wound applicator. The thickness