



Characterization of silver/polystyrene nanocomposites prepared by *in situ* bulk radical polymerization



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ABSTRACT

Nanocomposites (NCs) with different content of silver nanoparticles (Ag NPs) embedded in polystyrene (PS) matrix were prepared by *in situ* bulk radical polymerization. The nearly monodisperse Ag NPs protected with oleylamine were synthesized *via* organic solvo-thermal method and further used as a filler. The as-prepared spherical Ag NPs with diameter of 7.0 ± 1.5 nm were well dispersed in the PS matrix. The structural properties of the resulting Ag/PS NCs were characterized by transmission electron microscope (TEM) and Fourier transform infrared (FTIR) spectroscopy, while optical properties were characterized using optical absorption measurements. The gel permeation chromatography (GPC) measurements showed that the presence of Ag NPs stabilized with oleylamine has no influence on the molecular weight and polydispersity of the PS matrix. The influence of silver content on the thermal properties of Ag/PS NCs was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that resistance of PS to thermal degradation was improved upon incorporation of Ag NPs. The Ag/PS NCs have lower glass transition temperatures than neat PS because loosely packed oleylamine molecules at the interface caused the increase of free volume and chain segments mobility near the surface of Ag NPs.

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1. Introduction

The adequate choice of polymer nanocomposite components, as well as size, shape and content of the nanofiller can lead to the significant improvement of thermal, mechanical, optical, electric, magnetic, barrier flammability, processing and other properties of the polymer matrix [1–8]. The possibility to design and modify nanoparticle-filled polymers in various manners enabled their widespread application in different areas. That is the main reason for the continuous increase of the importance of polymer NCs over the past twenty years. The properties of polymer NCs strongly depend on the synthetic procedure, type of the polymer matrix, the state of the particle dispersion in polymer matrix and specifications of the used nanofillers, such as type, size, shape and concentration. The intensity and nature of the interaction between polymer and NPs is also important factor which significantly

affects the desired properties of the polymer NCs. The appropriate modification of the NPs surface can facilitate the interfacial interactions between the polymer matrix and particles and prevent their aggregation, which is the main problem in polymer nanotechnology [9].

Silver NPs are probably the most studied and best established systems due to their size and shape dependent optical properties [10–12]. Their antimicrobial activity is well known and widely used in various medical and biochemical devices and products [13–18]. It has been shown that Ag NPs keep this specific performance after embedding in polymer matrix, especially against microorganisms such as *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and *Salmonella* [5,14,19,20]. Additional driving force for the continuous interest in Ag/polymer NCs is the improvement of thermal and optical properties of the polymer matrix [1,3,6–8,19,21] and possible application of silver based NCs as optical materials [22], in the production of films and coatings for food packaging [23], in surface-enhanced Raman scattering, fluorescence control, optical biosensing [24], etc.

In order to obtain desired properties of Ag/polymer NCs it is essential to control the particle size, to achieve good dispersion of particles within the polymer at the level of individual particles and to maintain their uniform distribution in polymer matrix. This is

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quite difficult considering that generally all NPs have tendency to aggregate due to their high surface energy. Aggregation involves rearrangement of particles and results in the enhancement of inter-particle adhesion forces. The usual purpose of the surface treatment of particles is to decrease their free surface energy in order to hinder their interactions using long hydrocarbon chains. The literature data show that beside adequate surface modification of the Ag NPs, the application of PS as polymer matrix efficiently support stabilization of Ag NPs [25].

Numerous attempts have been made to distribute Ag NPs in a PS matrix using quite different methods. One simple approach is the use of blending technique to homogenize the previously prepared particles into the polymer. This method was recently reported by Chatterjee [26], Lim [27], Zeng [28] and Vodnik [25]. The second method involves the *in situ* synthesis of Ag NPs in the polymer matrix, using photochemical [29] or gamma radiation [30] synthesis. The third approach consists of polymerizing the matrix around the Ag NPs and can be performed *via in situ* emulsion polymerization [31,32] or dispersion polymerization [33] of the styrene in the presence of Ag NPs. Despite the great amount of recent work dealing with different NC systems, it is still difficult to find a consistent tendency for the resistance of the obtained NCs material to thermal degradation mainly due to their different preparative history.

The motivation for this work originates from a need to further understand the influence of Ag NPs on the optical and thermal properties of polymer. The present paper represents the continuation of our study on the interaction between Ag NPs and PS matrix that governs the properties of polymer [7,8,21,25]. Namely, in order to achieve homogeneous distribution of Ag NPs in the PS matrix, the *in situ* bulk radical polymerization of styrene was performed in the presence of monodisperse surface modified Ag NPs. For this purpose, a simple colloidal method for preparation of Ag NPs in organic solvent was developed. PS was selected as the polymer matrix based on its optical transparency and high chemical resistance. In this manner homogeneous distribution of Ag NPs in PS matrix was obtained. The influence of the presence of Ag NPs and their concentration on resistance of the material to thermal degradation and optical properties of PS matrix was investigated in details using UV–vis spectroscopy, FTIR and GPC, as well as DSC and TG analysis performed in argon and air atmosphere.

2. Experimental

2.1. Chemicals

Silver nitrate, chloroform and oleylamine were supplied by Merck. Styrene and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Fluka. Styrene was purified from stabilizer by washing with 5% aqueous NaOH, followed by repeated washing with distilled water to remove excess of alkali. After that, styrene was dried with calcium chloride by keeping it overnight, filtered and finally vacuum distilled. AIBN was recrystallized from methanol. All other chemicals were of analytical grade, purchased from Aldrich and used as received.

2.2. Synthesis of Ag organo-sol

Nearly monodisperse Ag NPs were prepared using a simple one-pot method. In a typical experiment, a solution containing 50 mg of $\text{Ag}(\text{NO}_3)_3$ in 1 mL of oleylamine was injected into a hot chloroform (50 mL) and refluxed with stirring for 19 h at 80 °C (first stage), followed by the aging and ripening at 60 °C for 5 h (second stage). After cooling to the room temperature, 50 mL of methanol was added into the solution and the Ag NPs were separated by

centrifugation (8000 rpm, 10 min). This process was repeated three times in order to remove the remaining residues. The final precipitate was dried under an argon flow and then redispersed in 20 mL of chloroform to give a yellow-brownish dispersion stable for weeks. The concentration of Ag in organo-sol, determined by ICP-AES, was estimated to be 0.185 mg/mL. The hydrophobic Ag NPs can be readily resuspended in a variety of other non-polar solvents.

2.3. Synthesis of Ag/PS NCs

The Ag/PS NCs were obtained by *in situ* bulk radical polymerization of styrene in the presence of different amount of surface modified Ag NPs (0.1, 0.2 and 0.5 wt.%, labeled Ag(1)/PS, Ag(2)/PS and Ag(3)/PS, respectively). The concentration of the initiator (AIBN) was 0.025 M. The polymerization was performed in a glass tube, in dark, at 60 °C for 5 h. Before sealing, the dispersions were purged with nitrogen for 30 min to remove oxygen. The synthesized Ag/PS NCs were precipitated in methanol, filtered and dried under vacuum at 40 °C to constant weight. The polymerization of styrene without Ag NPs was performed on the same manner.

2.4. Characterization

The content of the Ag NPs in the composites was determined using inductively coupled plasma atomic emission (ICP-AES) measurements (Perkin-Elmer 6500 Spectrometer).

The UV–vis absorption spectra of the Ag NPs dispersed in chloroform, as well as Ag/PS NC films were recorded on a Thermo Evolution 600 spectrophotometer.

Transmission electron microscope (TEM) JEOL-1200EX was used to determine the size distribution of Ag NPs and microstructural characterization of the Ag/PS NCs. For that purpose Ag/PS NCs were embedded in an epoxy resin (Epofix, Electron Microscopy Sciences) and cured overnight at 40 °C. Samples were then microtomed to a thickness of around 70 nm, using a Leica Ultracut UCT-ultramicrotome and Diatome diamond knife at room temperature. Finally, microtomed sections were floated on water and placed on copper grids.

Fourier transform infrared (FTIR) spectra of the neat PS and Ag/PS NCs were obtained using a Thermo Nicolet Corporation Model 380 Fourier transform IR Spectrophotometer in attenuated total reflection mode.

The molecular weights characteristics of the pure PS and PS extracted from Ag/PS NCs were determined by gel permeation chromatography (GPC). Measurements were conducted on a Spectra-Physics chromatograph equipped with Rheodyne universal injector and Spectra-Physics differential refractive index detector. The separation was done across a set of two gel columns (MZGPC columns) with porosities of 1000 Å. Tetrahydrofuran (THF) was used as eluent at a nominal flow rate of 1 cm³/min. The quantity of injected polymer was 100 µL and the measurements were carried out at 25 °C. A polystyrene calibration curve, constructed with narrow molecular weight distribution polystyrene standards, was applied. For the GPC measurements, the Ag NPs present in the NCs were separated by making a solution in THF and centrifuging at 8000 rpm for 10 min. The PS solution was removed, and the precipitate was re-dispersed in new portion of THF and centrifuged again. This process was repeated a few times, until the methanol remained clear after adding to obtained PS solution, which represents the proof that the PS is fully separated from Ag NPs.

Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 200 instrument in the temperature range from 50 to 150 °C under nitrogen atmosphere at a heating rate of 20 °C min⁻¹.

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