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# Efficient dispersion of coated silver nanoparticles in the polymer matrix

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HIGHLIGHTS

- Nanosilver was modified for preventing agglomeration in organic media.
- Modified silver nanoparticles form a stable colloidal dispersion in a polymer matrix.
- High dispersibility of the nanoparticles can be achieved at high silver contents.
- The method can be used for preparation of nanosilver dispersions in polyacids.

GRAPHICAL ABSTRACT
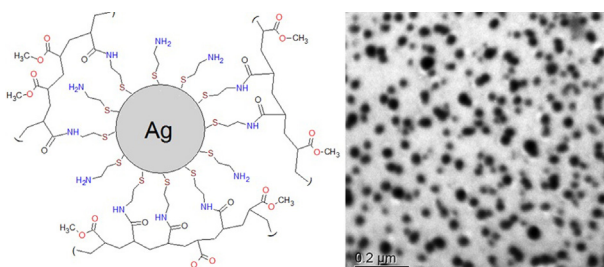
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ABSTRACT

Silver–polymer composite material containing highly dispersed silver nanoparticles (AgNPs) of 20–100 nm diameter can be obtained from bare nanosilver. The synthesis consists of three steps. The first step is modification of AgNPs by 2-aminoethanethiol. Second, polyacrylic acid is bonded to the silver 2-aminoethanethiolate by the carbodiimide method. Then esterification of the remaining carboxyl groups of the product by methanol results in formation of a stable colloidal dispersion of AgNPs in the polymer matrix. The method allows obtaining of nanocomposites with silver contents up to 1.4 wt%.

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1. Introduction

Silver–polymer nanocomposites attracted a great interest of scientists due to their unique combination of physical, chemical and biological properties. Their fields of applications include controlled drug delivery in medicine [1], modification of textiles [2], dental materials [3], implants [4], optical materials [5], sensors [6], food packing [7], etc. Numerous applications of silver–polymer nanocomposites are discussed in a review of Folarin et al. [8].

One of the most important features of these materials is their antimicrobial activity at very low toxicity for humans and plants [9–13]. In particular, Bechert et al. showed that slow release of silver from dispersion of AgNPs in poly(methyl acrylate) (PMA) inhibits growth of bacteria *S. aureus* [14]. It was confirmed that Ag+ ions are responsible for bactericidal activity of Ag/PMA. Thus, metal–polymer nanocomposites are widely used as biomaterials in tissue engineering [15].

Several reviews discuss synthesis of silver–polymer nanocomposites [16–18]. Materials of this type can be obtained using two main approaches. The first of them is in situ reduction of silver salts and controlled growth of metal nanoparticles in the presence of a polymer. Numerous publications reported synthesis of such nanocomposites (e.g., [19–21]). However, this method has a

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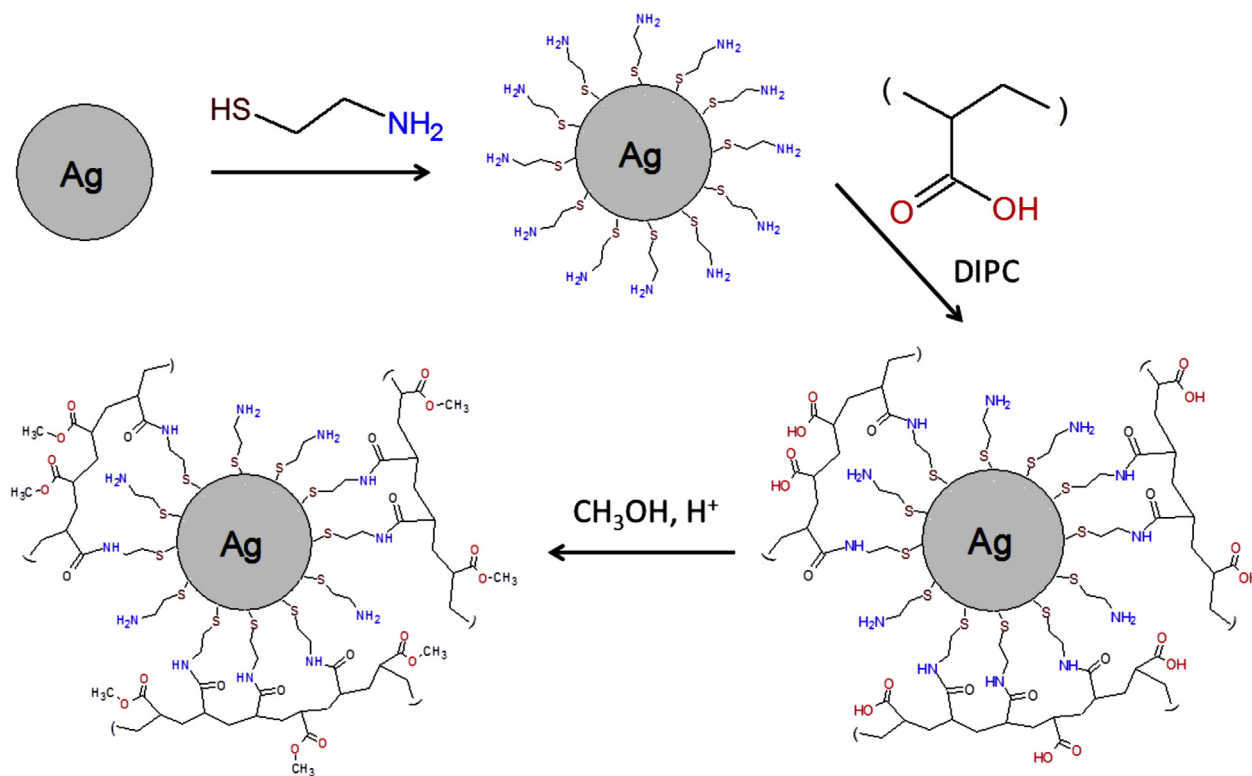 *E-mail address:* vasiliev@etsu.edu (A. Vasiliev).

Fig. 1. Scheme of Ag/PMA synthesis.

drawback due to difficulties in controlling nanoparticle morphology and size distribution.

The second approach is based on polymer grafting on the surface of already prepared nanosilver. The main problem impeding extensive implementation of this method is the tendency of AgNPs to agglomeration in organic media [22]. Bokern et al. [23] obtained highly dispersed AgNPs with mean diameter below 4 nm in polystyrene. Ishizu et al. [24] described an Ag/PMMA-block-PBA nanocomposite with nanoparticle sizes less than 3.6 nm. To present time no publications reported grafting of polymers on AgNPs of larger size (up to 100 nm).

Some other methods (e.g., matrix-assisted pulsed laser evaporation [25] or γ-irradiation [26]) were also developed but they did not find a wide application in the synthesis of silver–polymer nanocomposites.

Until present time, direct dispersion of non-coated nanosilver in a polymer allowed obtaining of nanocomposites with very low silver contents. Hsu et al. prepared Ag/polyurethane nanocomposite with only 30 ppm of silver [27]. In our past work it was shown that agglomeration of AgNPs can be significantly reduced by hydrophobization of nanoparticle surface by its thiolation with long-chain alkanethiols [28]. However, only 0.24% of AgNPs could be dispersed in polyacrylic acid (PAA). Even hydrophobic AgNPs agglomerated if their concentration in polymers exceeded this limit.

The objective of this work is the development of an efficient method of AgNPs modification enabling its easy dispersing in a polymer matrix.

2. Materials and methods

2.1. Materials

High purity, ultra-fine silver powder with particle sizes in the range of 20–100 nm was acquired from Ferro Corporation (South Plainfield, NJ). Prior to treatment, silver was washed with deionized water to remove surfactant. 2-Aminoethanethiol was purchased from TCI America (Portland, OR). Diisopropylcarbodiimide (DIPC), methanolic HCl and polyacrylic acid (PAA, M.W. = 1800) were purchased from Sigma–Aldrich (St. Louis, MO). All reagents were used as received.

2.2. Synthetic procedures

The synthesis of silver/poly(methyl acrylate) nanocomposite (Ag/PMA) was conducted in three steps (Fig. 1). On the first step, 2-aminoethanethiol was grafted on the silver surface. A 10 g sample of nanosilver was added to 15 mL of THF containing 2×10^{-3} mmol of 2-aminoethanethiol. The suspension was stirred for 1 h, filtered, washed by THF and dried on air overnight.

Ag/PAA material was obtained by a condensation of carboxyl groups of PAA with amino groups of the grafted 2-aminoethanethiol. Amino-modified AgNPs were dispersed in 20 mL of 10% solution of PAA in DMF using an Ultra-Turrax T25 disperser (IKA Works, Inc., Wilmington, NC). Then 0.05 g of DIPC was added dropwise. The solution was stirred for 3 h at room temperature, DMF was evaporated on a rotary evaporator, and the residue was washed by acetone and dried on air overnight.

Ag/PMA nanocomposite was prepared by acid-catalyzed esterification of remaining COOH groups of grafted PAA. Obtained Ag/PAA (1 g) was dispersed in 50 mL of methanolic HCl. Reaction mixture was refluxed for 30 min, the solvent was evaporated, and the residue was dried in vacuum at 110 °C for 2 h.

2.3. Characterization

Contents of silver in the samples were determined on a Shimadzu AA 6300 atomic absorption spectrophotometer (Kyoto, Japan) at λ = 328 nm. Before measurements, the samples were dissolved in concentrated HNO_3. FT-IR spectra were recorded on a Shimadzu Prestige-21 FT-IR spectrophotometer (Kyoto, Japan).