

Preparation and Characterization of Polystyrene-Silver Nanocomposite Using Microemulsion Method and its Antibacterial Activity

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Abstract

Polymer nanocomposites containing metals have been used in a wide range of applications due to their versatility, and tunable characteristics including physical, chemical, biological and mechanical properties. In this research work polystyrene-silver nanocomposite has been produced using polymerization of a w/o microemulsion system. Styrene monomer was used as the oil or continuous phase of the microemulsion system and polymerized following formation of Ag nanoparticles in the fluid medium. The UV-vis absorption and dynamic light scattering methods have been used to trace the growth process and size distribution of the Ag nanoparticles in the microemulsion system. Scanning electron microscopy (SEM) was used to determine the morphology and particle size of the Ag particles in the synthesized nanocomposites.

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1. Introduction

The future progress in the field of science and technology will depend on the materials that are in nanoscale [1]. Nanocomposites are a new group of materials that the dimension of one or more phases is in nanometer scale. In polymer-metal

nanocomposites, metal particles are dispersed in the polymer matrix at the nanometer scale [2,3]. The polymer-metal nanocomposites are of general interest due to their multi usefulness, ease of preparation and possible for mass production, when compared to oxide/noble metal multi layers [4-6]. Silver

nanoparticles as a noble metal have comprehensive application such as, catalysis [7], antimicrobial [8], optical sensor [9], medical application [10], etc. Preparing nanocomposites can induce some useful mechanical, thermal, optical and biological properties. In order to obtain these properties, it is necessary to control size and size distribution of the metal particles embedded into the polymer matrix. In recent years several methods, such as sol-gel [11-13] and in-situ microemulsion methods [14, 15], have been developed to overcome agglomeration of nanoparticles [16-19]. Gan and Chew, introduced a method that nanocomposites can be synthesized by *in-situ* approach via an inverse microemulsion process [20, 21]. In this method, after reduction of precursors in the microemulsion droplets and producing stable nanocolloid, the entire oil phase (monomer) is polymerized. Thus, continues oil phase is converted into a solid block of the polymer with a low degree of inorganic particle agglomeration.

Diverse polymers have been used as a support that the silver nanoparticles incorporated into them, such as: polystyrene [22], polyvinyl pyrrolidone [23] and polytetrafluoro ethylene [24]. Kamrupiet *al.* successfully synthesized silver-polystyrene nanocomposite particles by using water in supercritical carbon dioxide medium [22]. They also investigated antimicrobial activity of the prepared nanocomposite. In continuing our research on metal-polymer nanocomposites based on microemulsion method [25], the target of this research is preparation of the silver-polystyrene nanocomposite with a good dispersion of silver nanoparticles. The microemulsion system containing AOT as ionic surfactant and pure styrene monomer as oil phase was used to synthesize Ag nanocolloid with high stability and narrow size distribution. The UV-vis absorption and dynamic light scattering methods have been used to characterize the colloid system. After that, continues oil phase was

polymerized by radical polymerization to obtain block of polystyrene with entrapped Ag nanoparticles inside the polymer matrix. The morphology and particle size of the Ag in the synthesized polystyrene/silver (PS/Ag) nanocomposite was determined by scanning electron microscope. The bacterial effect of the PS/Ag nanocomposite was also studied against *E. coli* bacteria.

2. Experimental procedure

2.1. Materials

Silver nitrate (Merck 99.9%) was used as the starting material for the silver nanoparticles, and sodium bore hydrate (Merck, 99%) as the reducing agent. Styrene monomer (>99%) and benzoyl peroxide was purchased from Merck. The styrene monomer was distilled to remove the inhibitors. Sodium bis (2-ethylhexyl) sulfosuccinate (AOT) was purchased from Acros Company and used without further purification.

2.2. Microemulsion phase diagram

The pseudo-binary phase diagrams can be depicted on w vs temperature plots (where $w = [\text{water}]/[\text{surfactant}]$) at fixed surfactant concentration. Microemulsion phase equilibrium was determined by visual inspection of samples made-up in 5 ml vials and thermostatted by a heater-cooler-circulator water bath accurate to ± 0.5 °C.

Samples were made-up with appropriate amount of styrene monomer and AOT and different water content. In all cases, the AOT concentration was kept constant at 0.20 mol dm^{-3} .

2.3. Preparation of colloidal suspension of silver nanoparticles

In a typical procedure, a microemulsion system with $w = 5$ was prepared by mixing aqueous solution of silver nitrate (0.2 M) and a solution of 0.2 M AOT/styrene. The same microemulsion system containing NaBH_4 was also prepared separately. The molar ratio of NaBH_4 to silver nitrate was held constant for all experiments at a value of 3. The microemulsion containing NaBH_4 was added into another microemulsion containing metal ion drop by drop, while the solution that containing metal ion was stirred. The resulting microemulsion mixture changed to a stable light yellow color, indicating the formation of Ag nanoparticles. The obtained stable nanocolloid system of Ag/styrene is ready for polymerization process. To confirm the formation of Ag nanoparticles and size distribution of the particles, UV-vis absorption and dynamic light scattering (DLS) techniques were applied to the colloid solution.

2.4. Fabrication of polystyrene-silver nanocomposite

In order to synthesis the PS/Ag nanocomposite, benzoyl peroxide was used as the initiator. Adequate amount of the initiator was added to the silver nanocolloid system to start polymerization process. The system was kept at 60 °C for 48 hours in an oven to obtain the desired nanocomposite. Fig. 1S of supporting material shows the photograph of the synthesized polystyrene and PS/Ag nanocomposite samples, which are ready for characterization. The surface

morphology and the average size of the Ag nanoparticles in the prepared nanocomposite were determined by scanning electron microscope (SEM).

3. Results and discussion

3.1. Phase behavior of the AOT/styrene microemulsion system

A composition-temperature phase diagram of the $\text{H}_2\text{O}/\text{AOT}/\text{styrene}$ system was constructed, at fixed AOT concentration (0.2 mol dm^{-3}). The resulted pseudo-binary phase diagram as a relation between w and temperature is shown in Fig.2. In this diagram the upper temperature phase limit, T_U , and the lower temperature phase boundary, T_L , are indicated. At temperatures above T_U , an AOT/water phase separates from an oil-rich phase. On the other hand, at low temperatures below T_L a water-rich phase co-exists with AOT. The one phase region in the phase diagram has been shown as ϕ_1 and two phase region shown as ϕ_2 . The results showed that for $w = 5$ the system are thermodynamically stable and transparent from 1 to 90°C. This observation is important because the polymerization process should be carried out at 60°C.

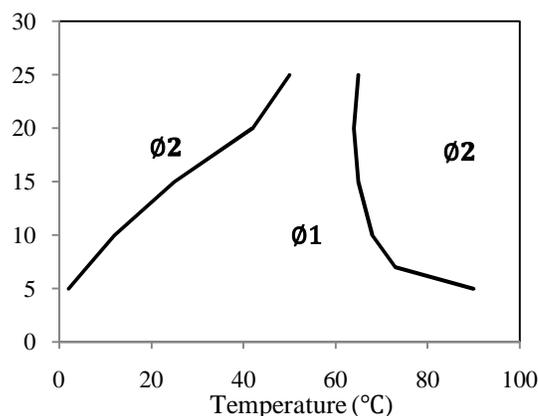


Fig.1.Phase behavior of the microemulsion system containing AOT as surfactant and styrene monomer as oil phase; the water-to-surfactant ratio, w , is plotted

against temperature at constant AOT concentration of 0.20 mol dm^{-3} .

3.2. UV-vis and DLS analysis of the silver nanocolloid system

Upon mixing of the two microemulsion systems, the resulting solution instantaneously became light yellow and the intensity of the coloration was increasing slowly with time, indicating the reduction of silver ions into its metal form. UV-vis measurement of silver nanocolloid has an absorption band centered at approximately 420 nm, as reported by Zhanget *al.* [26]. This characteristic absorption band is attributed to the surface plasmon excitation of silver particles. In this study, for the silver nanocolloid that was synthesized in the reverse microemulsion system, the UV-vis absorption band was observed at about 418 nm (Fig.2), which approves formation of silver nanoparticles.

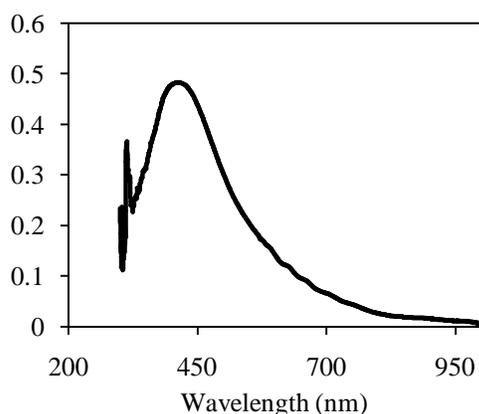


Fig.2. UV-vis absorption band for silver nanoparticles stabilized in reverse microemulsion system contain AOT as the surfactant and styrene as the oil phase.

The suspension silver nanoparticles size and size distribution was investigated by DLS technique. From DLS results the suspension silver nanoparticle size was obtained in the range of 3-10 nm, whereas the

nanoparticles with 5.6 nm in diameter have higher number and volume percent. Fig. S2 in the supporting information shows the size distribution measured using DLS technique, by number and volume percent.

3.3. SEM analysis of the polystyrene-silver nanocomposite

The surface morphology of the prepared PS/Ag nanocomposite was determined via results of SEM analysis. The results of SEM images show that the silver nanoparticles are dispersed almost in all of the matrix nanocomposite (polystyrene) and also, size range of the silver nanoparticles is in the range of 20-70 nm (Fig.3). However, in compare to DLS results for size of the silver nanoparticles in nanocolloid system (3-10 nm), it is large. This results verify that the some part of Ag nanoparticles aggregate during polymerization process. However, this scale aggregation is too low in compare to other methods. As can be seen in Fig.3, the silver particles have the same size in all samples is not affected by the Ag concentration.

3.4. Antibacterial activity

Fig. 4 shows the *in vitro* antibacterial activity results of PS/Ag nanocomposites with different concentrations of silver nanoparticles against the gram negative *E. coli*. The obtained results were showed that the prepared nanocomposites have uniformity and high antibacterial activity. Also, antibacterial effect of PS/Ag nanocomposites was increased via enhance of the silver nanoparticles concentration in the nanocomposite matrix. The average diameter zones of inhibition, as shown in Fig. 4 and reported in Table 1, confirms the results.

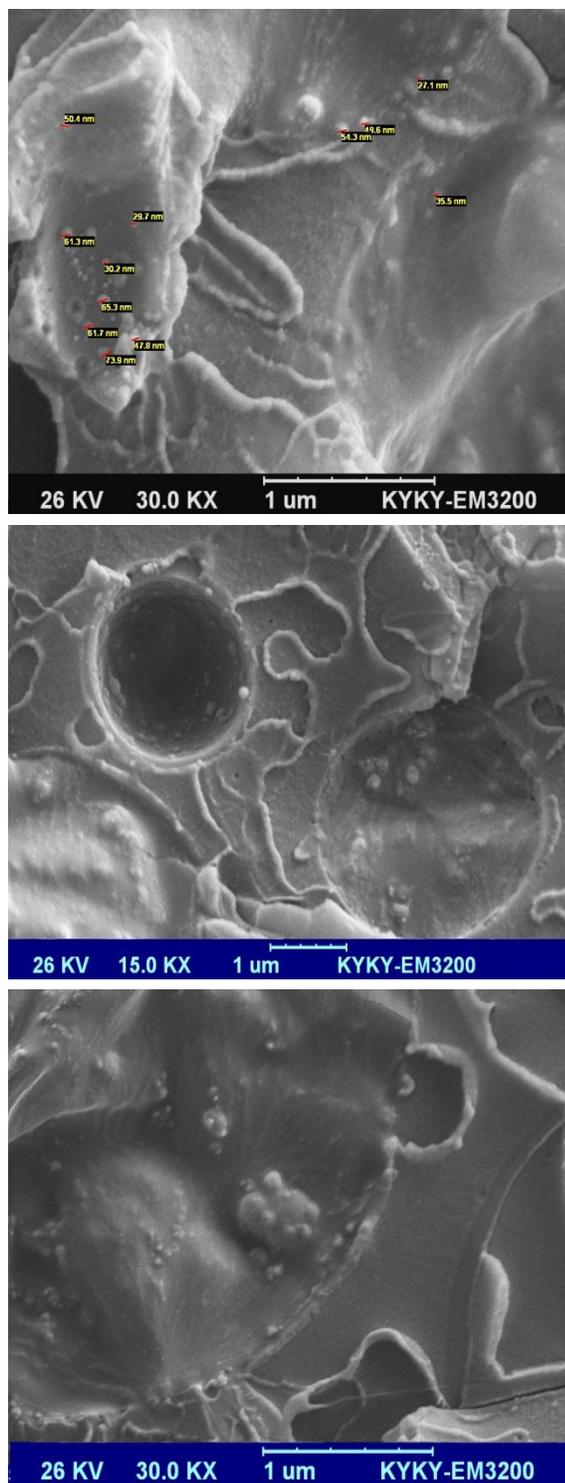


Fig. 3. SEM images of the PS/Ag nanocomposites for all samples with different Ag nanoparticles content (0.007-0.02 wt%).

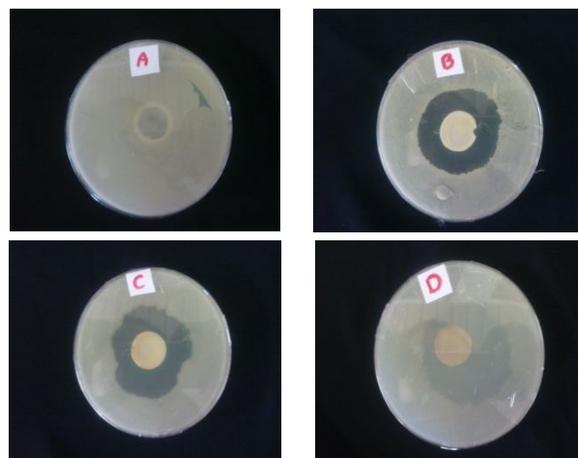


Fig. 4. *In vitro* antibacterial activity (zone of inhibition) of PS/Ag nanocomposites with different concentrations of Ag nanoparticles against *E. coli* by disc diffusion method. (A) blank sample, (B) 0.007 w%, (C) 0.013 w% and (D) 0.02 w%.

Table 1. Antibacterial activity results of PS/Ag nanocomposites by disc diffusion method.

Sample	Silver loading in nanocomposite (w%)	Average diameter of inhibition zone (cm)
Blank (A)	0.0	0.0
B	0.007	4.3
C	0.013	5.0
D	0.020	6.2

4. Conclusion

Stabilized colloidal silver nanoparticles were synthesized in reverse microemulsion system (w/o), containing AOT as the surfactant and styrene as the continuous phase. Mean diameters of the silver nanoparticles in the colloidal suspension was obtained in the range of 3–10 nm by DLS technique. PS/Ag nanocomposite film was prepared by in-situ polymerization of the prepared colloid system. SEM result was shown that the silver nanoparticles were embedded and dispersed in the

polystyrene matrix. The average size of the silver nanoparticles in the nanocomposite was determined about 10-20 nm. Antibacterial effect of the prepared nanocomposite film was tested on the *Escherichia coli*, as a very important application. The results confirmed the hypothesis of uniformity and high antibacterial activity of PS/Ag nanocomposite. The antibacterial effect was increased with enhancement of silver nanoparticle concentration in the nanocomposite film.

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