

Effect of surfactant type on the particle dispersion in Ag/polystyrene nanocomposite prepared by microemulsion method

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Abstract

In this research work silver/polystyrene nanocomposite has been prepared using polymerization of w/o microemulsion system with two various types of surfactants. In order to investigate effect of surfactant-polymer interaction on the quality of final nanocomposite product, AOT as anionic surfactant and tween 80 as non-ionic surfactant, isobuthanol as co-surfactant and styrene monomer as oil phase were used to prepare microemulsion systems. Surface tension of the microemulsions was measured as a criterion for the reaction media properties. The microemulsion systems were polymerized by benzoyl peroxide initiator following formation of Ag nanoparticles in the fluid medium. The UV-vis absorption analysis has been used to trace the growth process in the microemulsion system. Scanning electron microscopy (SEM) was used to determine the morphology, particle size and dispersion of the Ag in the synthesized nanocomposites. The idea established in current work can potentially be used to synthesis uniform and morphologically well-defined nanocomposites by microemulsion method.

Keywords: Nanocomposites, Polystyrene, Ag nanoparticles, Microemulsion, Surface tension

1. Introduction

Polymer nanocomposites are materials in which nanoparticles (mostly inorganic nanoparticles) dispersed in an organic polymer matrix to improve the chemical, physical and mechanical properties of the polymer. Uniform distribution of particles in a polymer matrix can markedly improve these properties compared to the pure polymers [1,2]. Methods in which the particles are first synthesized and subsequently isolated and mixed with the polymer, often lead to products with reduced transparency because agglomeration of the filler particles. In-situ polymerization in microemulsion systems for synthesis of a nanocomposite has been developed to overcome agglomeration of particles [3-6]. Polymerization of a monomer in microemulsion systems was carried out for the first time by Gan and Chew [7]. Microemulsion is macroscopically homogeneous, optically isotropic, transparent, and thermodynamically stable, one-phase system containing of two or more immiscible liquids constituents that stabilized by an amphiphile with affinity for both the water and oil phases [8]. The microemulsions may be classified in the form of either microstructured dispersion (water-in-oil and oil-in-water, marked as W/O and O/W, respectively) or bicontinuous (BC) structure. In the case of the BC microemulsion, both the oil and aqueous pseudo phases are continuous so-called sponge phase structures. Different types of microemulsions can be used for different applications, because they form soft templates or nanoreactors with controllable size. In our previous research studies, the microemulsion systems, as restricted nanoreactors, have been used for different applications such as synthesis of nanoparticles [9], nano catalysts [10] and nanocomposites [11-21]. Recently a valuable review paper on microemulsion method for fabrication of polymer-based nanocomposite has been published [22]. The review paper focused on the research area of the microemulsion synthetic route for polymer nanocomposite preparation over the past two decades.

In a typical synthetic process using a ME system, at the first step a stable nanocolloid system, containing nanoparticles as suspension phase and a monomer as continuous phase, prepared by reduction of a metal precursor. In the second step, the entire oil phase is polymerized at a certain condition to obtain desired polymer nanocomposite. Thus, in this procedure the continuous monomer oil phase is converted into a solid block of the polymer with well dispersed nanoparticles into the polymer network. In this method, after reduction of metal precursors in microemulsion droplets and producing stable nanocolloid, the entire oil phase, which is monomer, is polymerized. Thus, continuous oil phase is converted into a solid block of the polymer with a low degree of inorganic particle agglomeration.

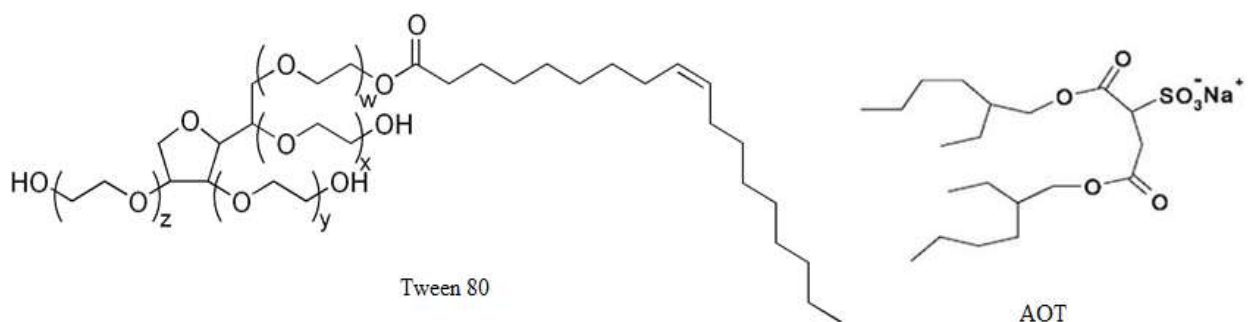


AOT as anionic surfactant and tween 80 as non-ionic surfactant, isobutanol as co-surfactant and styrene monomer as oil phase were used to prepare microemulsion systems. Surface tension of the microemulsion systems was measured as a criterion for the reaction media properties. The UV-vis spectroscopy was used to silver colloid formation and scanning electron microscopy (SEM) used to determine the morphology, dispersion and particle size of the Ag in the synthesized nanocomposites.

2. Materials and methods

2.1. Materials

The anionic surfactant Bis (2-ethylhexyl) sulfosuccinate sodium salt (AOT) was purchased from Acros Company and used without further purification. The non-ionic surfactant of tween 80, methyl methacrylate and styrene monomers (>99%) and benzoyl peroxide (BPO) were obtained from Merck. The molecular structures of anionic surfactant of AOT and non-ionic surfactant of tween 80 have been shown in Scheme 1. The styrene monomer was distilled under reduced pressure before using in polymerization reaction. All other reagents including silver nitrate ($\text{Ag}(\text{NO}_3)$), as source of metal, and hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), as reducing agent, were also obtained from Merck. All aqueous solutions were prepared with deionized water.



Scheme 1. Molecular structures of anionic surfactant of AOT and non-ionic surfactant of tween 80.

2.2. Surface tension measurement

Surface tension measurement of microemulsions was carried out using a force tensiometer (Sigma 702, KSV) at 25 °C that accurately measures surface tensions by use of platinum Du Noüy ring with convenient control keyboard operations and displayed resolution of ± 0.01 mN/m. The platinum ring was thoroughly cleaned and flame-dried before each measurement. Before each experiment, calibration was done by use of Sigma 702 calibration tools. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed ± 0.05 mN/m. Temperature control was done via its water-jacket vessel holder that was mounted on the motorized sample stage.

2.3. Preparation of stable colloidal Ag nanoparticles in W/O microemulsion

First of all, thermodynamic stability of W/O microemulsion systems of styrene/AOT/water and styrene/tween 80/isobutanol/water was investigated at different W ($W = [\text{H}_2\text{O}]/[\text{surfactant}]$). From this study the pseudo-binary phase diagrams and relationship between W and temperature can be readily seen. In none transparent region an surfactant/water phase separates from an oil-rich phase, while in transparent region the microemulsion system is thermodynamically stable. It is observed that for $W = 5$, the microemulsion systems are stable even at 60 °C. This observation is important because the polymerization process should be carried out at 60 °C.

Solutions of AOT or tween 80/isobutanol in styrene with concentration of 0.1 M were prepared and certain amount of aqueous AgNO_3 solution (0.01M) by fixing the mole ratio of water to surfactant ($W = 5$) added to the surfactant solution to form W/O microemulsion systems. The mixtures were stirred via constant speed for 1h at room temperature and then hydrazine as reducing agent was added dropwise to reduce silver ions to metal. After reducing silver ions the resulting colloid solution of Ag instantaneously became light yellow color. The Uv-vis spectroscopy was used to monitor the formation of the Ag nanoparticles by using Perkin Elmer lambda 15.

2.4. Preparation of Ag/PS nanocomposites

The polymerization process was carried out in an oven at 60 °C by adding benzoyl peroxide as the initiator. It should be noted that the prepared silver nanocolloid systems are thermodynamically stable at this temperature. The

amount of initiator was 0.2 % of the total weight of the styrene monomer. The reaction time of the polymerization was about 12 hours.

2.5. Characterization of Ag/PS nanocomposites

Scanning electron microscopy method was carried out to determine the morphology and particle size of the dispersed Ag nanoparticles in the prepared samples of Ag/PS nanocomposites. For this purpose, KYKY-EM 3200 Digital scanning electron microscope was used. SEM images were obtained on samples coated with a thin layer of gold, to a depth of approximately 20 nm, under vacuum.

3. Results and discussion

3.1. Surface tension results

Surface tensions of the water-in-oil microemulsion systems containing styrene/AOT/water and styrene/tween 80/isobutanol/water, with $W = 5$ were measured and reported in Table 1. As can be seen from data in Table 1, surface tension of the microemulsion system produced by anionic surfactant is more than that one which prepared by non-ionic surfactant. The reason for this phenomenon can be related to the interaction of the styrene monomer and different surfactants, which determine the power of the surfactant type to reduce surface tension. It means that styrene/AOT system creates more rigid micelle and then decreasing the k_{ex} (the rate constant of micellar exchange [23-26]). Obviously, this behaviour can influence the final particle size of the synthesized Ag nanoparticles in microemulsion droplets as well as distribution of the nanoparticles in the fabricated nanocomposite.

Table 1. Surface tension of the microemulsion systems and Ag particle size synthesized in different microemulsions

	W/O microemulsion system	
	Styrene/AOT	Styrene/Tween-80/isobutanol
Surface tension (mN/m)	32.7	31.0
Average particle size (nm)	21-36	38-74

3.2.Characterization of Ag colloid system and prepared nanocomposites

In order to confirm the formation of silver nanoparticles in water-in-styrene microemulsion system, UV-visible spectroscopy method was employed. A typical UV-visible result in Fig. 1, shows the characteristic surface plasma resonance of the colloidal silver nanoparticles, appeared at about 430 nm [20].

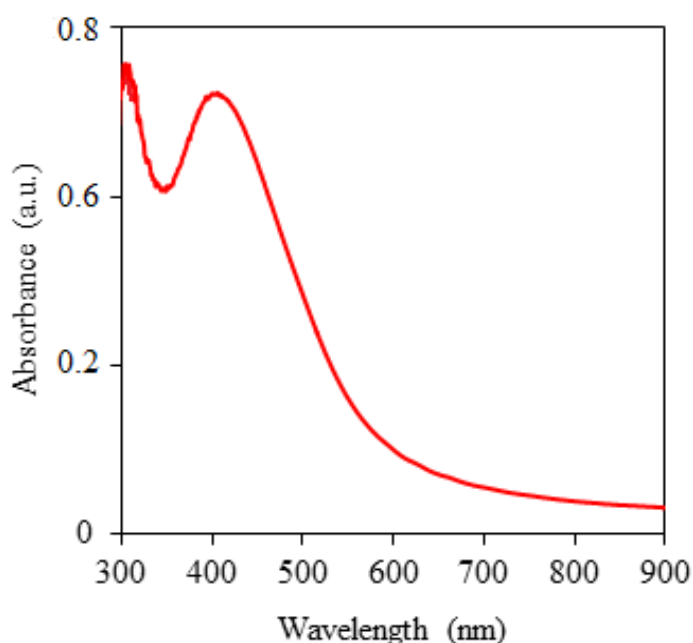


Fig. 1. UV- visible absorption spectra of the silver nanoparticles in water-in-styrene microemulsion system.

The results of SEM images of Ag/PS nanocomposites synthesised in microemulsion systems containing ionic surfactant of AOT and non-ionic surfactant of tween 80 are shown in Figs. 2 and 3, respectively. As can be seen the silver nanoparticles are dispersed almost in all over the matrix nanocomposite (polystyrene). The silver nanoparticle size in the microemulsion system containing AOT surfactant was obtained in the range of 21 to 36 nm, while the silver nanoparticle size in the microemulsion system containing tween-80/isobutanol is in the range of 38 to 74 nm. There is another interesting result that distribution of the nanoparticles in nanocomposites prepared with different surfactants is completely different. As can be seen in SEM images, the Ag nanoparticles are dispersed in the polymer matrix monotonically when AOT surfactant has been used.

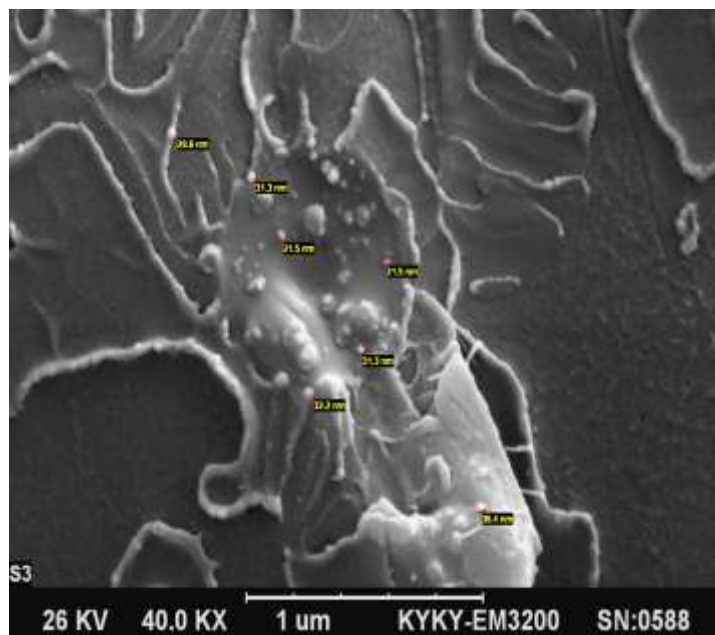


Fig. 2. SEM image of Ag/PS nanocomposite synthesised in microemulsion system containing ionic surfactant of AOT.

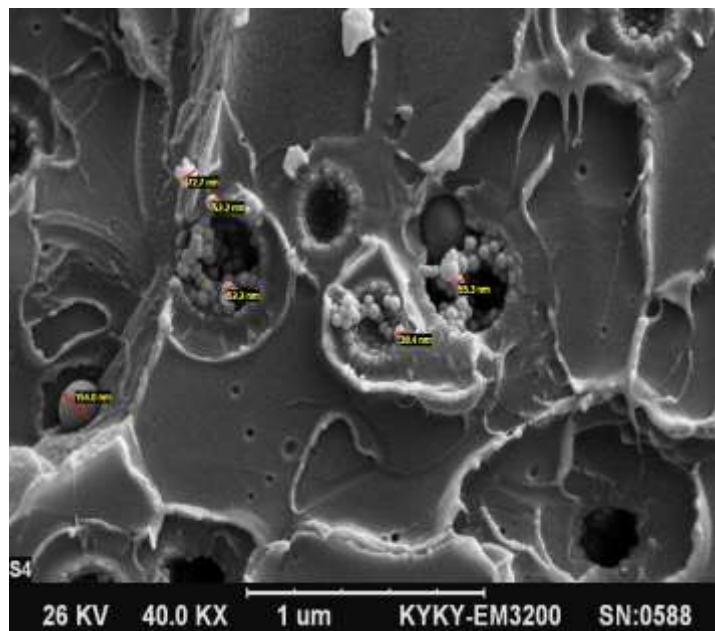


Fig. 3. SEM image of Ag/PS nanocomposite synthesised in microemulsion system containing non-ionic surfactant of tween 80.

On the other hand, in nanocomposite prepared by tween-80 surfactant the Ag nanoparticles are appeared as distinct islands. The locally distribution of the particles in polymer matrix containing tween-80 surfactant may be related to exchange rate of silver ions as well as Ag nuclei between microemulsion droplets. Obviously, the dynamic exchange process of the reactants in different microemulsion droplets plays an important role in controlling the particle size and distribution [27]. The mechanism of the nanoparticles formation and grown in the microemulsion systems is shown schematically in Fig. 4. After collisions between droplets silver ions and reducing agent interchanged and Ag nuclei is produced. The metallic nanoparticles growth finally occurred to produce final stabilized Ag nanoparticles.

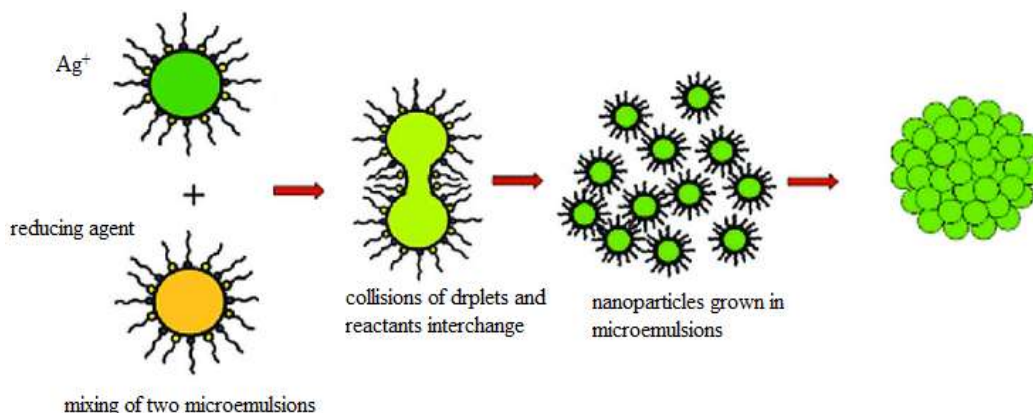


Fig. 4. Schematic showing various steps of the nucleation and grown of the Ag nanoparticles in microemulsion systems.

The results confirm that interface layer of W/O microemulsion droplets for system containing tween-80 surfactant should be softer than the layer containing AOT surfactant. This conclusion is compatible with surface tension results for two different surfactants which appeared in Table 1, so nonionic surfactant shows lower surface tension and then softer droplets than ionic surfactant. We posit here that boundary layer formed by nonionic surfactant favors exchange process of the Ag crystal nuclei in the growing step, whereas the ionic surfactant tend to favor fewer exchange rate. Then Ag particles size in microemulsion with nonionic surfactant is larger than nanoparticles obtained in ionic surfactant. This special character for microemulsion droplets in nonionic surfactants also leads to Ag particles growing together and then obtaining a non-uniform distribution.

4. Conclusion

In order to study the effect of the surfactant type on the final product of a nanocomposite prepared by microemulsion method, stabilized colloidal silver nanoparticles were synthesized in reverse microemulsion systems (W/O), containing AOT or Tween 80 as the surfactants and styrene monomer as the continuous phase. Ag/PS nanocomposite films were prepared by polymerization of the prepared colloidal systems. As an interesting result, SEM images confirmed that the silver nanoparticles were embedded and dispersed differently in the polystyrene matrix when different surfactants were used. The dispersion of nanoparticles in the nanocomposite product which prepared in Tween-80/styrene microemulsion system is as locally or island form with size particles between 38-74 nm. Inversely, for the nanocomposite produced in AOT/styrene microemulsion system a good dispersion with size particles between 21-36 nm for the Ag nanoparticles can be seen. This behavior related to interface layer of W/O microemulsion droplets which can be described by surface tension of the microemulsion systems. It is concluded that dispersion of metal particles in a nanocomposite can be highly affected by the surfactant type in microemulsion method.

Conflicts of Interest

The author declares no conflict of interest.

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