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Formation and dissolution of silver nanoparticles

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The emulsion polymerization of styrene (St), butyl acrylate (BuA) and methyl methacrylate (MMA), in the presence of sodium dodecylsulfate (SDS) and nonylphenol ethoxylate with 25 moles of ethylene oxide ($NPEO_{25}$) was realized. The silver particles were obtained from reaction between $AgNO_3$ and $NaBH_4$ during the radical polymerization. This phenomenon takes place prevalently when $NPEO_{25}$ is introduced for stabilization. The copolymerization of vinyltriethoxysilane (VTES) with monomers used, assures covalent bonds between silica generated by sol-gel process and polymers obtained by radical polymerization. This covalent bonding determines the increase of thermal stability of the obtained hybrids.

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1. Introduction

The special interest for metallic nanoparticles [1] permitted the initiation of studies to show the possibility to obtaining some polymeric nanocomposites which can contain these types of particles [2, 3].

For the silver nanoparticles, the components of monomers, which are soluble in water, like poly glycols [4], polyvinylpyrollidone [2, 5-9], acrylic acid [2], polyvinyl alcohol [9, 10], coordinated the Ag^+ ions and stabilized the Ag^0 nanoparticles just formed. The polyglycols and polyvinyl alcohol can play a reducing role in reaction of forming the metallic nanoparticles [4, 6, 10].

The polar polymers swelled in water, like polyvinyl acetate (PVAc), are efficient supports in preparation of silver nanoparticles [11, 12]. Due to the existing water in polymeric support and the complexing groups, Ag^+ salts are dispersed under chelates foams, but after the metallic particles precipitation, these are efficiently stabilized [11, 12]. PVAc dispersed in water as latexes [13] or suspensions [14] constitute also a support for Ag^0 nanoparticles.

The surfaces of some polymers as polymethylmethacrylate (PMMA) [15], polyethylene phtalate (PEP) [16], butyl acrylate copolymer (BuA) with glycidyl methacrylate –iminodiacetic acid [17], styrene copolymer with 4,4'-isopropylidendiphenol bismethacrylate [18], can be efficient supports for Ag^0 particles generation due to the possibility of Ag^+ ions coordination with polar groups. The role of these phenomenon is very well put in evidence by demonstrating the rate reduction for forming the Ag^0 nanoparticles on PEP, comparing with poly(2ethyl-2 oxazoline) support [16]. Metallic ions are much better preservation in polymeric matrix due to the formation of Ag^+ chelates more stable with PEP by coordination with phthalic groups [16]. Ag^+ ions have the complexing capacity with monomers as acrylonitrile [19], natrium acrylate [20], the last having also the capacity of generating the Ag^0 metallic particles by aqueous solutions refluxing of $AgNO_3$.

The polymeric systems obtained in dispersed medium as suspension [14], dispersion [21] and emulsion [13, 22-25], were also studied in the view of Ag^0 nanoparticles fixation on formed particles. The studied polymers were polyvinyl acetate (PVAc) [13, 14], polystyrene (PSt) [21, 22] and polymethacrylate (PMMA) [23-25]. Like in previous cases for a good coordination of Ag^+ and a good stabilization of Ag^0 nanoparticles, were used complexant comonomers as macromers of poly(N-isopropylacrylamide) [21], natrium styrene sulfonate [22], methacrylic acid [25].

For simplification of these very complex systems, it were elaborated the studies in which the same reactant can initiate the radical polymerization and generated the Ag^0 nanoparticles, for example azoizobutironytril [21] or sodium borohydrure [23].

Due to the interest presented by the nanocomposite systems which contain (alongside polymer and Ag^0 nanoparticles) another inorganic component, for example silica [18, 24], in this paper we presented the possibility to obtaining latexes of PSt, PBuA and PMMA. As silica generator was used vinyltriethoxysilane (VTES), which can copolymerize with used comonomers [26] and 3-(trimethoxysilyl)-1-propanethiol (HSTMS) [27] and can have an important effect in Ag^0 nanoparticles stabilization.

Sodium dodecylsulfate (SDS) [2, 4] and nonylphenol ethoxylate [29], reactants used in Ag^0

particles stabilization in aqueous medium, were used as surfactants.

2. Experimental section

2.1. Materials

Styrenes (St), butyl acrylate (BuA) and methyl methacrylate (MMA), commercially products, were purified by vacuum distillation. Others monomers were used as such. Vinyltriethoxysilane (VTES) (Merck-Schuchardt), 3-(trimethoxysilyl)-1-propanethiol (HSTMS) (Aldrich), sodium dodecylsulfate (SDS) (Merck-Schuchardt) and nonylphenol ethoxylate with 25 moles of ethyleneoxide ($NPEO_{25}$), commercial products, were utilized without supplementary purifications. The ethoxylation degree for $NPEO_{25}$ was estimated by RMN. The concentration of nonylphenol ethoxylate is higher two orders magnitude than the critical micellar concentration. The initiator, ammonium persulfate (APS) (Loba-Chemie) was utilized also, without purification.

2.2. Procedures

In a vessel with three neck, supplied with refrigerant and thermometer, were introduced under magnetic stirring (350 rot./min.) distilled water (20 ml) and surfactant (1g). After surfactant dissolution is added under stirring the monomer (4 ml), in which the VTES (0.4 ml) was dissolved, and HSTMS (0.2 ml). At this stage, it is added a solution of $AgNO_3$ (0.0584 g) in water (30 ml). After homogenization, it is added drop by drop a solution of $NaBH_4$ in water (30 ml). Depending of reactants type used the mixture composition is showed in Table 1. The mixture is heated at 65°C and the initiator (0.2 g) being added. After cooling, the obtained latexes are transferred, a part of them in glass vials, and another part in polyethylene dishes to be dried at room temperature (25°C).

Table 1. Composition of reaction mixtures.

Reactants	Variants Studied								
Name	Quantity (g)	V+S	V+S -Ag	V+S -B	V	S	X	B	O
Water	80	+	+	+	+	+	+	+	+
Surfactant	1.0	+	+	+	+	+	+	+	+
Monomer	4.0	+	+	+	+	+	+	+	-
Ammonium persulfate (APS)	0.2	+	+	+	+	+	+	+	+
Vinyltriethoxysilane (VTES)	0.4	+	+	+	+	-	-	-	+
3-(trimethoxysilyl)-1-propanethiol (HSTMS)	0.2	+	+	+	-	+	-	-	+
Silver Nitrate ($AgNO_3$)	0.0584	+	-	+	+	+	+	-	+
Sodium borohydrure ($NaBH_4$)	0.052	+	+	-	+	+	+	-	+

2.3. Method

The conversions were estimated by gravimetric analysis. The thermal analyses (TGA) were realized with a Du Pont 2000 instrument with heat rate of 20°C/min. The particles sizes and Zeta potential were analyzed by dynamic light scattering (DLS) (Nano-ZS from Malvern). FT-IR spectra were measured with Fourier transforms infrared spectrophotometer (Tensor 37 from Bruker) using potassium bromide (KBr)-based pellets prepared by mixing KBr powder with powder samples. The UV-VIS spectra were measured with an UV-VIS spectrophotometer (Nicolet Evolution 500 from Thermo Electron Corporation) directly on latexes. Diluted hybrid latexes were deposed on conductor stage. After drying, these samples were visualized by scanning electron microscopy (SEM) (FEI QUANTA 200), using low vacuum working mode and 15 kV accelerating voltage.

3. Results and discussion

The experimental work includes three principal processes: radical polymerization and monomers copolymerization with VTES, the process of Ag^0 production by $AgNO_3$ and $NaBH_4$ reaction [23], the sol-gel process of VTES, HSTMS in the water presence for generation of substituted silica.

The experiments which contain all the reactants mentioned in Table 1 (V+ S) got as final results different products as function of surfactant type. The syntheses which were performed in the presence of SDS permitted the obtaining of some colored, stable latexes. The UV-VIS spectra show absorptions at ~400 nm, which are characteristic for Ag^0 nanoparticles ((Fig. 1 (a)).The increase of λ_{max} is a proof of nanoparticles agglomeration and of increasing of formed aggregates sizes [4-7, 17, 29]. The maximum size of particles was obtained in the absence of polymers (O), case in which the particles are probable stabilized only by modified silica in the sol-gel process. The presence of HSTMS assures highly interaction between latexes functionalized with thio groups and silver nanoparticles [27]. In case of polymers, the latexes medium sizes increased with increasing of their polarity (PSt < PBuA < PMMA) (Figure 1_b) [30]. The increase of λ_{max} in concordance with increasing of medium size of latex particles is a proof of the fact that the particles contain Ag^0 aggregates, which modify their spectral properties as function of polarity and polymeric matrix size.

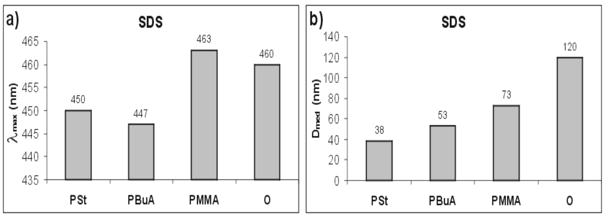

Fig.1. Modification of maximum wavelength for UV-VIS absorption (a) and of medium sizes (b) for latexes PSt, PBuA, PMMA and those obtained without monomers (O) (V+S-Table 1).

The obtaining of composite latexes in the presence of $NPEO_{25}$ puts in evidence some phenomenon not mentioned yet. After emulsification of monomers and of silane derivatives, colored Ag^0 particles are formed by addition of $NaBH_4$ over the mixture which containing $AgNO_3$. Once the radical polymerization starts in the presence of APS at 65°C, the colored latexes are changed in majority, at their milky-white aspect of blank latexes (B, Table 1). These were synthesized without $AgNO_3$ and silane coupling agents. The cause of these modifications is due to the oxidation of Ag^0 particles by APS [24].

To demonstrate the effect of APS in dissolution of Ag particles, was performed a supplementary experiment. Over discoloured latexes, without UV-VIS absorption, it was added a supplementary amount of $NaBH_4$ at room temperature and under stirring. Immediately is noticed the typical color of Ag^0 nanoparticles.

The difference observed between SDS and $NPEO_{25}$ could be due to the ability of first surfactant, with sulfate groups, to stabilize by Ag particles complexation [1].

To follow the formation and stabilization process of Ag^0 particles were realized other experiments: using just VTES (V, Table 1), using only HSTMS (S, Table 1), the synthesis with V + S without $AgNO_3$ (V+S-Ag, Table 1) or without $NaBH_4$ (V+S-B, Table 1), synthesis without silane derivates (X, Table 1), without monomers (O), synthesis of pure latexes (B, Table 1).

The various tested compositions do not present an important influence. The majority of final hybrid latexes, which are colored due to the Ag^0 particles, are obtained with SDS.

The modification of the medium size of latex particles and of the Zeta potential for the three used monomers are represented in Fig. 2(a), (b) and (c) and in Fig. 3 (a), (b) and (c) respectively.

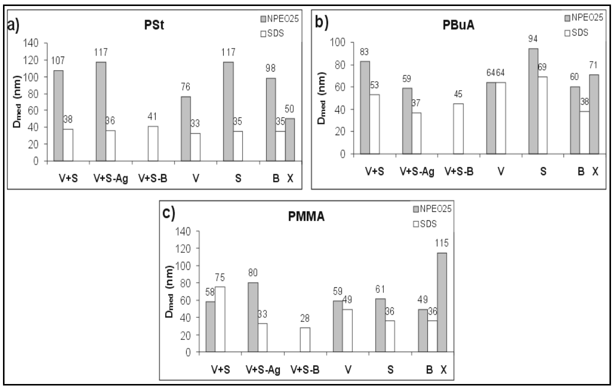

Fig. 2 . Changing the medium sizes of latex particles as function of reactants nature (Table 1: □SDS, ■ $NPEO_{25}$) and the obtained polymer type ((a) PSt, (b) PBuA, (c) PMMA).

A first conclusion, which can be formulated by comparing the data included in Figures 2 and 3, is that the sizes of latex particles obtained with $NPEO_{25}$ are bigger than those with SDS. This result demonstrates that the nonionic surfactant have a reduced ability to stabilize the latexes. Due to a better ability of stabilization, SDS is efficient in stabilizing against oxidation with APS [24]. The Zeta potential for stabilized particles with anionic surfactant, SDS, is higher than the nonionic surfactant, $NPEO_{25}$. It is another proof of a better stabilization of latexes obtained with SDS.

Comparing Zeta potential values for latexes without inorganic compound and Ag precursor ($AgNO_3$ + $NaBH_4$) (B, Table1) with those obtained only in absence of VTES and HSTMS (X, Table 1) is noticed that the last composition produces a smaller value to this parameter.

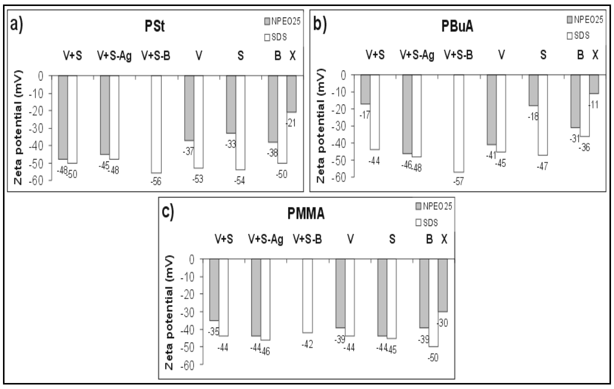

Fig. 3. Zeta potential variation as function of reactants nature (Table 1: □SDS, ■ $NPEO_{25}$) for particles of latexes as: (a) PSt, (b) PBuA, (c) PMMA.

Reaction between APS and Ag^0 particles reduce the possibility of forming of some terminal sulfate groups which can affect Zeta potential. In all discussed cases above mentioned the conversions are almost total.

For latexes syntheses only with HSTMS and without $AgNO_3$, the conversions are much more reduced. This fact is explicable by chain transfer of thio group. If for latexes obtained in these conditions, it is added $AgNO_3$ and

$NaBH_4$, are obtained colored latexes. Due to the existence of nonpolymerized monomer, the swollen latexes have the sizes much bigger than those presented in Figure 2 ($NPEO_{25}$): 158 nm (PSt), 159 nm (PBuA), 552 nm (PMMA). This type of latexes remained colored, so they have Ag nonmodified particles, but they have a reduced stability in time.

A concern element is the mode in which the hydrophobic groups of silica, generated from VTES and HSTMS, affects the thermal stability of the composites. For this objective, it was studied the thermal decomposition of some hybrids obtained in the presence of both partners (V+S) with and without addition of $AgNO_3$, or hybrids obtained only with VTES or only with HSTMS. Figure 4 show the modification of temperature in which the thermal decomposition rate is maximum (T_{max}) comparative with that of blank latex (B, Table 1). For the three utilized polymers, the T_{max} value varies in the order PSt > PBuA > PMMA (see Figure 4_a, 4_b and 4_c). Comparing the results for each polymer, it is observed that the polymers obtained in absence of VTES (S, B, Table 1) have a decomposition temperature smaller than the other three analyzed compositions. The T_{max} value higher in case of VTES presence demonstrates that the silica network is covalently bonded with the polymer by its copolymerization [26] and sol-gel process with HSTMS [27]. The increasing of T_{max} is credible because was verified for the all tree polymers categories. By this covalent bonding, silica could have a protective roll in reacting with the oxygen in conditions of heating the material.

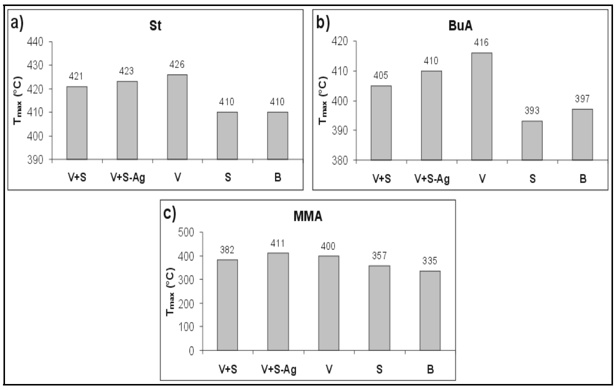

Fig. 4. Hybrids composition influence over the thermal decomposition temperature with maximum rate (T_{max}) (composition as in Table 1, ((a) St, (b) BuA, (c) MMA).

Fig. 5 show the FTIR spectra of different reaction mixtures with PMMA. The characteristic bands for ≡Si-CH=CH_2 group from VTES were observed in the 2953-2998 cm^{-1} interval, at 1274 cm^{-1} and at 988 cm^{-1}, respectively (C-H, out-of-plane deformation vibration). These bands can not be found in spectra of reaction mixture to contain just HSTMS or PMMA, which is a proof that the polymerization of the double bond from VTES didn't occurred total. The bonds observed between 1000 and 1200 cm^{-1} confirm the existence of adsorption maxim specific for Si-O-Si silicates, stretching vibration. For Si-O, bending vibration, a bond at 964 cm^{-1} was observed. The characteristic band for Si-CH_3 group at 810 cm^{-1} (CH_2, rocking vibration) was showed.

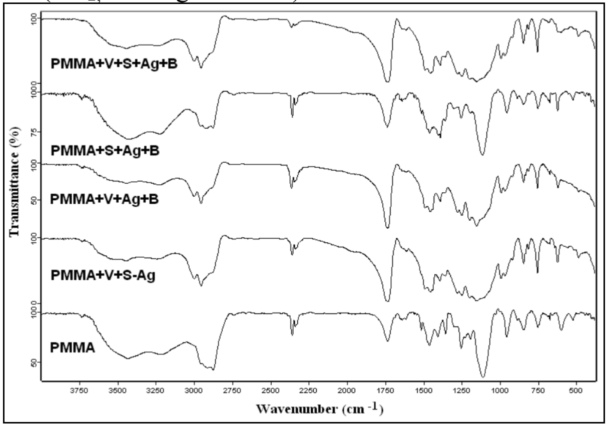

Fig. 5. FT-IR spectra of different reaction mixtures with PMMA.

The SEM images of some hybrid latexes are presented in Fig. 6. Generally are observable agglomerations of particles. These particles are much better contoured for PSt (Figures 6_I (V+S) and 6_{II} (V+S-Ag)), due to glass transition temperature higher, than for PBuA (Figures 6_{III} (V+S) and 6_{IV} (V+S-Ag)).

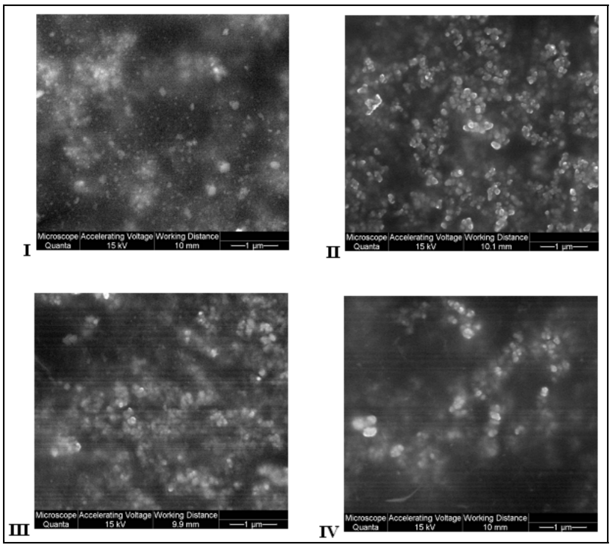

Fig. 6. SEM imagines for some hybrid latexes obtained in presence of PSt (I (V+S), II (V+S-Ag)), PBuA (III (V+S), IV (V+S-Ag) (conditions as in Table 1).

4. Conclusions

The composites of PSt, PBuA, PMMA- functionalized silica-Ag0 particles were obtained by emulsion polymerization in the presence of SDS, complexation surfactant. The silica network was obtained by sol-gel process of VTES and HSTMS. If emulsion polymerization takes place in the presence of Ag^0 nanoparticles, these could be dissolute in aqueous medium due to the reaction with the initiator, APS. The composites particles have a smaller sizes and Zeta potential higher if they were synthesized with SDS comparative with $NPEO_{25}$. The thermal stability of the composites, in which the silica network is covalently bonded with the polymer, is maxim. This type of covalent bond is ensured by the copolymerization with vinyl groups from VTES.

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