In-situ Synthesis of Nano Silver Particles Used in Obtaining of Antimicrobial Film-Forming Materials

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In this paper are presented the results of experimental research regarding the preparation and characterization of Ag-nanoparticles. As a solution, it was chosen the chemical synthesis (in situ) of Ag-nanoparticles, which involves dissolving and reducing of some metal salts in a polymer matrix. As silver precursor was used $AgNO_3$ which was reduced by sodium borohydride in the presence of acrylic polymers. Stabilization of Ag nanoparticles was accomplished with acrylic styrene polymers, avoiding the use of additional protective agents. The structure, morphology and size of Ag nano particles were characterized by the X-ray diffraction and Zetasizer, while the ability to release Ag^+ ions in an aqueous solution of polymer was demonstrated by the electrical conductivity.

Keywords: silver nanoparticles, silver ion removal, in-situ

Silver nano particles generally vary from 1 atom to 100 nm. Nano-Ag offers a special attention, because it is a continuous release reservoir of silver ions [1,2]. Ag-nanoparticles can be obtained by different chemical procedures and these are most often used due to their simplicity, low costs and ability to produce large quantities of materials [3-5]. The size of nano-particles influences their antimicrobial activity. So it was found that Ag-nanoparticles with sizes below 10 nm have a weaker antibacterial activity than those between 40-60 nm widths of which have the best antibacterial effect [6,7].

The purpose of this study is to obtain Ag-nanoparticles stable in time that can be used in formulating antimicrobial coating materials. *In situ* synthesis was chosen for obtaining silver-nanoparticles; as a precursor of Ag was used a salt (silver nitrate), which was reduced with sodium borohydride in the presence of acrylic polymer, Acronal 290 D as protective agents. The molar ratio between $AgNO_3$/polymer was /10:6 and $AgNO_3$ was of 0.005 M. The solvent used was a mixture of water/propylene glycol in a 1:1 ratio. The resulted silver-nanoparticles were analyzed, by the X-ray diffraction, and their size was determined using Zetasizer. The ability to remove Ag ions in aqueous solution has been demonstrated by electrical conductivity.

Experimental part

Materials and methods

All the chemical substances were of analytical grade: $AgNO_3$ supplied by Sigma- Aldrich 99%, acrylic polymer Acronym 290 D (BASF), propylene glycol (OLTCHIM), sodium borohydride (Sigma-Aldrich, >98.5%), and ammonia (OCI AGRO Netherlands).

Vibrational spectra were recorded using a Shimadzu 8400 spectrometer in the wave numbers range of 400 – 4000 cm^{-1}.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. The samples were scanned in the Bragg angle 2θ range of 10 – 800, with a sampling interval of 0.02.

The nano Zetasizer- size distribution measurements uses a process called Dynamic Light-Scatteing – DLS. DLS measures the Brownian motion and correlates it with the particle size.

The Electrical Conductivity - Conductivity Cond 330. Electrical conductivity depends on the ion concentration, the nature of ions, temperature and the viscosity of the solution.

Synthesis of silver nanoparticles

Ag nanoparticles were obtained in two steps:
- Step I – synthesis of silver-nanoparticles
- Step II - Seed and feed grown particles

Step I

The synthesized silver nanoparticles in a batch reaction were done by reducing silver precursor ($AgNO_3$) with sodium borohydride ($NaBH_4$) in the presence of acrylic polymers (Acronal 290 D), serving as capping agents. The molar ratio between the species was $AgNO_3$/polymer in 10:4 and the concentration of $AgNO_3$ was of 0.005 M. A mixture of water/ propylene glycol (1:1) was used as a solvent.

The synthesis took place at room temperature, at 20-23°C and *p*H 8-9. The *p*H correction was made with ammonia (24.5% solution). How to obtain Ag nanoparticles is shown in figure 1.

Step II

Ag^+ ions released in the solution, reduce the larger crystallites and facilitate the increasing size of silver particles. This leads to a higher reaction time and great polydispersability.

The Ag ions reduction reaction is:

$$Ag^+ + e^- \rightarrow Ag \quad E°reduction = 0.8V \qquad (1)$$

Sodium borohydride acts as a reduction agent:

$$BH_4^- + H_2O \rightarrow B(OH)_3 + 7\,H^+ + 8e^- \quad E°oxidation = -0.481V \qquad (2)$$

Growth of silver nanoparticles

$$\overset{+}{Ag} + \overset{-}{BH_4} + H_2O \longrightarrow \overset{o}{Ag} + \overset{+}{BH_3} + \overset{-}{OH} \qquad (3)$$

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Experiment NPAg	Molar ratio $AgNO_3$ / acrylic polymer	$NaBH_4$ ml
1	10:1	50
2	10:3	60
3	10:4	65
4	10:5	70
5	8:5	60

Table 1
SAMPLES OF AG NANOPARTICLES MARKED AS **NP-AG** 1- **NP-5AG**

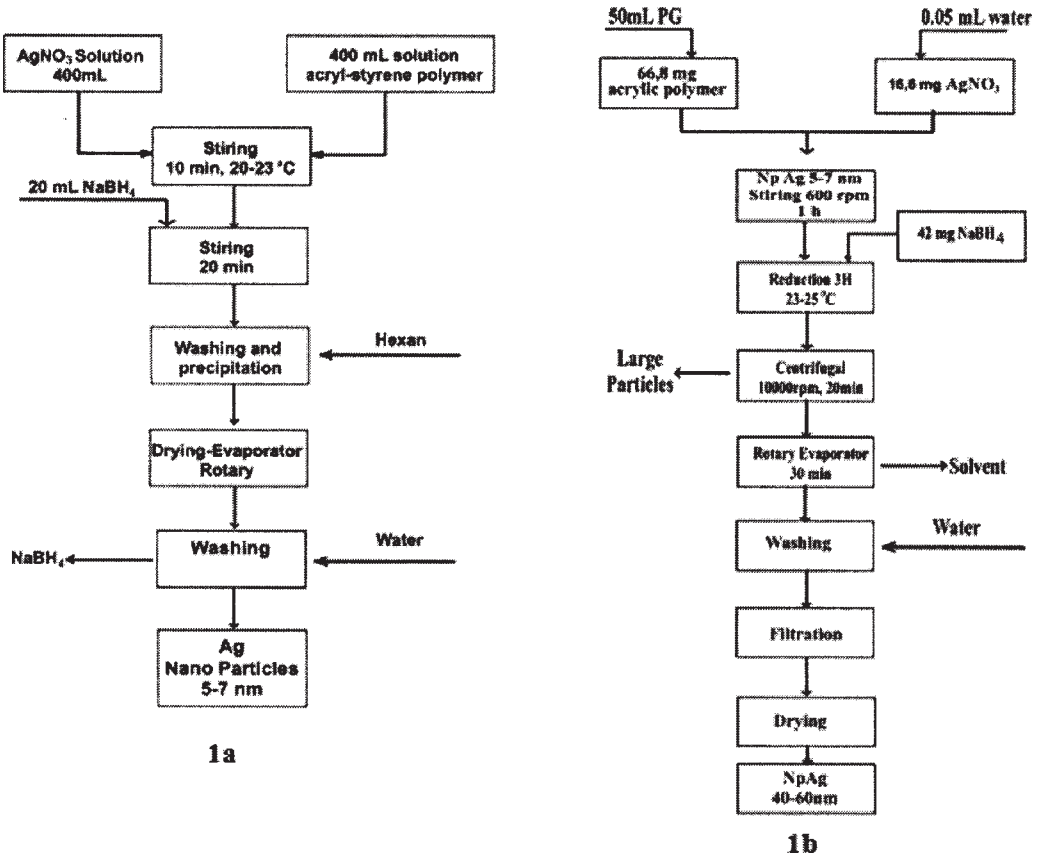

Fig. 1 - (1a) Synthesis of Ag-nanoparticles - step I; (1b) - Seed and feed growth of Ag-nanoparticles -step II

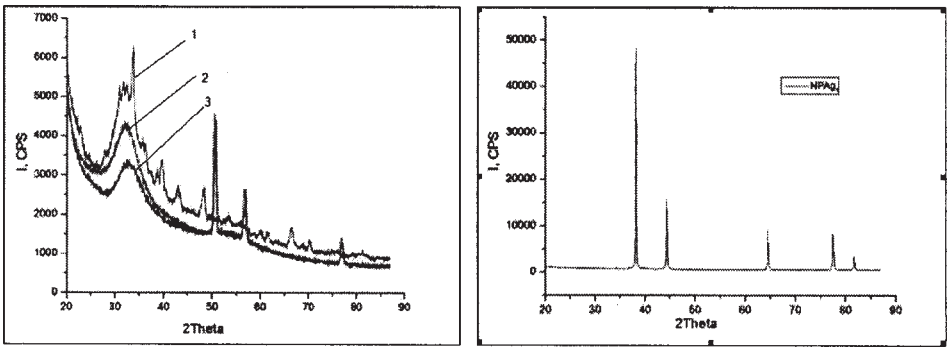

Fig. 2.- X-ray diffraction pattern of Ag nano particles: curve 1- NPAg 4;curve 2-NPAg 3; curve 3- NPAg 2

Experimental diffraction angle [2θ in degrees] -200 plane	Standard diffraction angle [2θ in degrees]
44.3	44.3

Table 2
EXPERIMENTAL AND STANDARD DIFFRACTION ANGLES OF AG SPECIMEN

Redox reaction was observed immediately after mixing and the mixture changed the aspect from clear to pale yellow, which indicated the formation of small sized silver nanoparticles.

Five experiments were done varying the molar ratio of $AgNO_3$/polymer and the quantity of reduction agents (table 1).

Results and discussions

XRD measurements

The structure of nano-silver obtained in the described way was analyzed by XRD spectroscopy.

The XRD study confirms the formation of silver nanoparticles. Table 2 shows the experimentally obtained

Diffraction plane	2θ	cosθ	Br	D=Kλ/(Br cosθ) [nm]
111	38.12	0.945163	0.00327537	44.27
200	44.3	0.926181	0.00327354	45.21
220	64.45	0.845922	0.00268861	60.26
311	77.4	0.780376	0.00270172	65.01
222	81.54	0.757277	0.00399137	45.35

Table 3
THE SIZE OF AG NANO PARTICLE

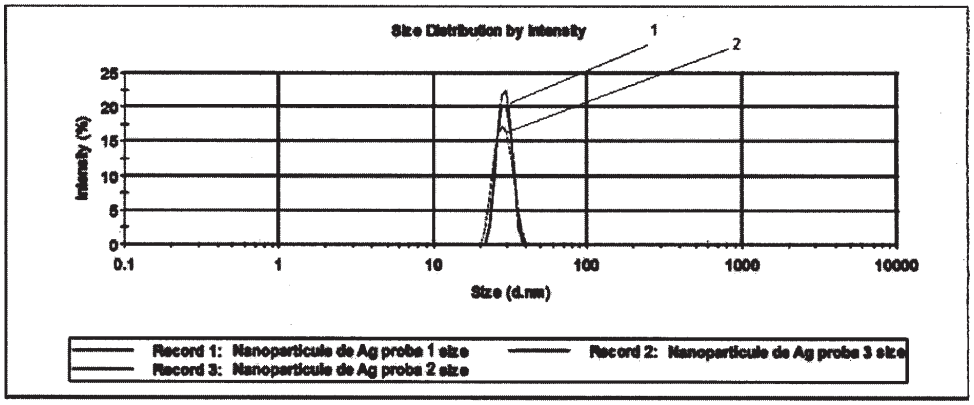

Fig. 3. Ag nanoparticle size distribution– curve 1- sample NP Ag 1, NP Ag ; curve 2- sample NP Ag 3

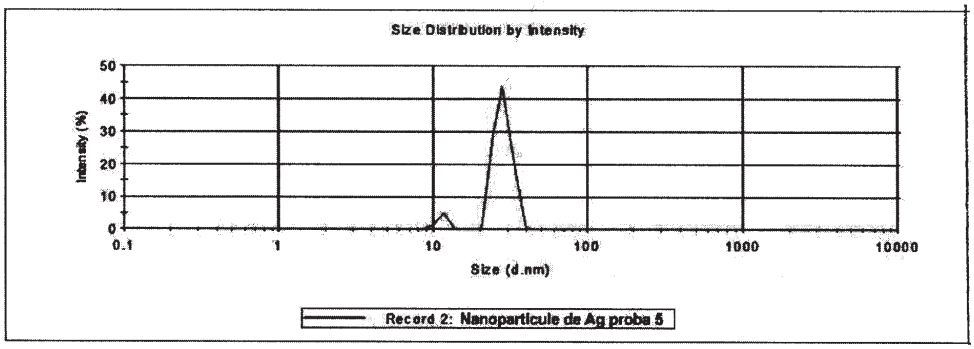

Fig. 4. Ag nanoparticle size distribution– sample NP Ag 5

Sample	Temperature °C	Salinity	Mineralization degree	Electrical Conductivity (μS/cm)
NP Ag 1	22.6	3.5	□2000	6.44
NP Ag 2	22.5	3.45	□2000	6.22
NP Ag 3	22.6	3.5	□2000	6.35
NP Ag 4	22.6	3.45	□2000	6.32
NP Ag 5	22.6	3.45	□2000	6..23
Acronal 290 D	22	1.3	□2000	2.7

Table 4
ELECTRICAL CONDUCTIVITY

X-ray diffraction angle and the standard diffraction angle [5] of Ag specimen.

The Ag nano-particle size was calculated with the Debye-Scherrer formula [6] and the results are shown in the table 3.

$$t=K\lambda/(Br\ \cos\theta)$$

where:

- Br is the Bragg angle
- 2θ - is the diffraction angle
- λ – is wave length of X-Ray (0.1541 nm).

A narrow distribution between 44-65 nm was obtained for Ag nanoparticles obtained by this procedure.

Particle size distribution measurements

Nanoparticle size was checked and controlled using Nano Zetasizer process called DLS (Dynamic Light Scatteing). The figures 3 and 4 present graphically the particle size distribution based on the scattered light intensity fluctuations and their number, for a colloidal solution of Ag-nano without tensiocativ agent. Measurements of particle size distributions were made on the ultrasonic sample for 3 h. The three successive measurements on the same sample prove that the sample is relatively stable, but with a slight decrease of sedimentation proven in the time loss of the average diameter. From studying the correlation curves it is also observed a slight tendency to form conglomerates.

It can be observed that most particles (for samples NP Ag 1, NP Ag 2, NP Ag 3 have a distribution of particles between 40-60 nm, which correspond to its purpose (measurements confirmed also the XRD results). Note that for sample NP Ag 5, smaller particles of 10-20 nm appear, which correspond to the hypothesis that $AgNO_3$ is in a quantity too small.

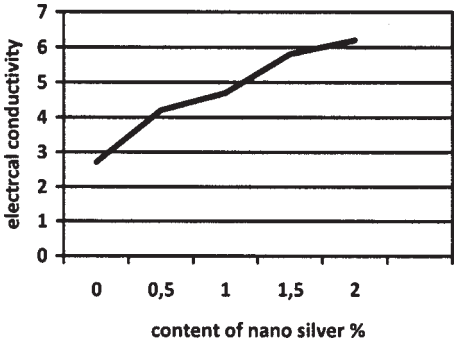

Fig. 5. Variation of electrical conductivity with different contents of nano silver

Measuring the electrical conductivity

The ability to release Ag ions in a polymer aqueous solution was demonstrated by measuring the electrical conductivity with the help of Conductivity Cond 330 according to ISO 7888-1983. Electrical conductivity depends on the ion concentration and their nature, temperature and solution viscosity. The results are shown in the table 4.

It can be seen that, by introducing the Ag nanoparticles in acrylic polymer, its conductivity increases because of the high ionic conductivity of Ag ions. As the nano Ag content is higher so the conductivity of the polymer solution increases, corresponding to the hypothesis of controlled releases of Ag ions in aqueous solution of polymer (fig. 5).

Conclusions

Ag-nanoparticles stable in time were obtained, which can be used in formulating antimicrobial coating materials.

It was chosen, as a method for obtaining silver nanoparticles, *in-situ* synthesis using $AgNO_3$ as Ag-precursor, which was reduced by the sodium borohydride in the presence of acrylic polymer (Acronal 290 D) as a protective agent. Molar ratio between $AgNO_3$/polymer was of /10:6 and 0.005 M $AgNO_3$ concentration. The solvent used was a mixture of water/propylene glycol in 1:1 ratio. So we obtained nano silver particles disposed in acrylic polymer with size distribution between 40-60nm, results highlighted by XRD measurements and Zetasaizer. The ability to remove Ag ions in aqueous solution of acrylic polymer was demonstrated by the electrical conductivity.

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