WATER DISPERSIONS OF SILVER NANOPARTICLES STABILIZED BY VINYLETHERS - MALEIC ANHYDRIDE ALTERNATING COPOLYMERS

D. DONESCU, R. SOMOGHI[*], C. L. NISTOR, M. GHIUREA, R. IANCHIS, C. PETCU, C. ILIE SPATARU, V. PURCAR
National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM,
202 Splaiul Independentei, 060021, Bucharest, Romania

Alternating copolymers of vinyl butyl ether (VBE) and triethylene glycol methyl-vinylether (VEO$_3$) with maleic anhydride were synthesized by solution polymerization. These polymers act as polyethers in water and the hydrophilic behaviour of maleic anhydride copolymers influence the stabilization of silver nanoparticles (silver NPs). The interactions between polymeric matrix and inorganic nanofiller decrease the chains mobility and favour the increase of the thermal stability shown by the TGA measurements. DLS analyses and SEM images confirms that shape and size of the particles depend on the content of the alternating copolymer.

1. Introduction

Metal-polymer nanocomposites have become an interesting domain for the past decades because of their enhanced mechanical properties compared with pure polymers [1]. When the filler used for synthesis are silver nanoparticles, the final material can find applications in catalyze, optics, electronics, quantum dots, bactericide materials.

There are numerous attempts to obtain Ag^0 nanodispersion in polymer aqueous solution due to the colloidal stability of macromolecular compounds but also due to the Ag$^+\rightarrow$ Ag^0 transformation which occurs very easily in water. Non-ionic water-polymers such as polyethers [2,3], polyvinylpyrrolidone [2-4], polyvinyl alcohol [5-7], poly (N-isopropyl acrylamide) [8], have been successfully used to stabilize Ag^0 nanoparticles (silver NPs). Depending on the silver NPs structure and synthesis, these polymers can act as nucleating, capping and stabilizing agents [8].

The proposed mechanism for silver NPs stabilization by polyvinyl pyrrolidone chains, suggests the possibility of polymer chain interaction with one or more metal particles[2]. Experimentally, it was shown that AgNPs shape and dimensions are affected by the polymer/metal ratio [2].

Compared with non ionic polymers, polyelectrolytes have the specific capacity to extend through dilution, consequently the conformation of the chains modifies [9]. Unlike non ionic polymers which present AgNP interaction through nonbonding electrons [2,5,7,8], polyelectrolytes could possess even stronger interactions with AgNPs. The ionizable groups as sulphate [10-13], carboxyl [2,14-22], amino [12,13,23], amide [17,18], thiol [24] are able to form silver (Ag$^+$) salts and metal-complex bonds after reducing to Ag^0.

Particularly interesting is that polyelectrolyte gels can be efficient nanoreactors for fixing AgNP [16-18, 25]. The polyelectrolyte layers deposited through layer by layer process by anionic and cationic polyelectrolytes may be efficient as well for Ag^0 retention [12,13,21]. These studies

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[*] Corresponding author: ralucasomoghi@yahoo.com

confirmed the possibility to obtain Ag^0NPs in the presence of polyelectrolytes with carboxyl groups [2, 14-22], some with pronounced germicidal effects [17, 18]. The base compounds, even in esther form, have the capacity to stabilize silver ions [3] which leads to very stable dispersions of metal particles. A previous study confirmed that two alternating copolymers of maleic anhydride had the capacity to stabilize the silver nanoparticle in base medium [26].

Present study evidence the hydrophilic behaviour of maleic anhydride comonomers which play a key role in the silver nanoparticles stabilization. The comonomers from the already mentioned paper [26] had different structures (sodium salt of styrene sulphonate and vinyl acetate). In order to avoid these structural differences and to define the stability domain for the colloidal dispersions, present study compares the alternating copolymers of maleic anhydride (MA) with two vinyl ethers: vinyl butyl ether (VBE) and vinyl ether triethylene glycol (VEO_3). The difference between these copolymers is shown by the synthesis of $AgNO_3$ with various concentrations of stabilizer and metal precursor. The changes of metal nanoparticles average size, the spectral properties of hybrid solutions (UV-VIS), Zeta potential, the thermal stability, the spectral properties evidenced the influence of the inorganic partner on the polyelectrolytes, in solid phase but also in aqueous solution.

2. Experimental

2.1 Materials and methods

Vinyl butyl ether, triethylene glycol methyl-vinylether (Merk) and maleic anhydride (Fluka) were purified through distillation and sublimation. Azoisobutyronitryl (AIBN) was purified through crystallization. Acetone (Chimopar) was purified via vacuum distillation. Silver nitrate and sodium borohydride (Fluka) were used without further treatment.

Alternating copolymers of maleic anhydride with VBE and VEO_3 were synthesized through radical copolymerization in solution. Quantities of 1g MA and 1.02g VBE (1.94g VEO_3, respectively) equimolecular mixtures, 0.06g initiator azoisobutyronitryl and 7ml dioxane, are mixed in a flask. The flask is sealed and the polymerization process occurs for 24 hours at 65°C. The resulted products are glassy crystalline solids and the conversions were gravimetrically established.

Silver particles were synthesized in aqueous solutions of copolymers neutralized with NaOH at pH=7. The copolymers were used as aqueous solutions of 10, 1, 0.1 % concentrations. The metal nanoparticles synthesis was realized in a flask through magnetically stirring (350 rot/min). 60g polymer aqueous solutions were mixed with different quantities of $AgNO_3$ dissolved in 10 ml water (Tab.1) and heated for 3 hours at 65^0C. After heating, the mixture was left overnight at room temperature. Then, different quantities of $NaBH_4$ dissolved in 10ml water were poured slowly and stirred. For example: 0.104g $NaBH_4$ was added over 0.1168g $AgNO_3$, quantity able to assure the complete transformation of silver salt in metal silver. Experimental recipes are mentioned in Table 1.

2.2 Measurements

Viscosity of the polymers aqueous solutions was measured with an Ubbelhode Viscosimeter at 25 ^{0}C. The mean average size of the particles and the Zeta Potentials were measured on a Zetasizer Nano ZS, ZEN 3600 (Malvern Int. Ltd.). UV spectra were recorded on an UV Nicolet 500 instrument. FTIR spectra for the samples resulted after water evaporation was measured with an FTIR-Tensor 30 BRUCKER instrument. Thermogravimetric analyses were accomplished with a Du Pont 2000 instrument on a heating velocity of 20^oC/min in air. Scanning electron microscopy images were obtained on a FEI Quanta 800 instrument.

3. Results and discussion

The polyelectrolyte behaviour of the synthesized alternating copolymers was confirmed by viscometric analyzes. As the concentration was lower the specific viscosity increased due to the chains lengths extension [9] as observed in Fig.1. These copolymers acted completely different as nonionic polymers solubilized in water.
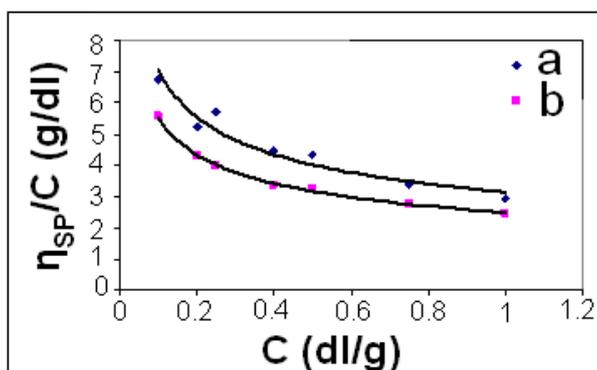
Fig. 1. Specific viscosities as a function of the polyelectrolytes concentration
(a – VEO₃-MA; b – VBE-MA)

The experimental conditions are mentioned in Tab.1. As our previous results [26], the most hydrophilic copolymer, VEO_3-MA, assured the stability of silver NPs dispersions synthesized with the maximum concentration of $AgNO_3$ precursor.

Table 1. The composition of the reaction mixtures (65 ^{o}C, 1 h, 80 ml), the average sizes (D_{med}) and the zeta potentials of the samples

| Copolymer type (g) | AgNO3 (g) | | | | | | | | |
| | 0.0584 | | | 0.1168 | | | 0.584 | | |
VBE-MA	Sample no.	Dmed. (nm)	Zeta Potential (mV)	No. sample	Dmed. (nm)	Zeta Potential (mV)	Sample no.	Dmed. (nm)	Zeta Potential (mV)
6	**1**	83	-54.5	**4**	94	-63	**7**	214	-58
0.6	**2**	89	-60	**5**	58	-54	**8**	110	-49
0.06	**3**	54	-49	**6**	35	-50	**9**	61	-42
VEO₃-MA									
6	**10**	197	-54	**13**	114	-46	**16**	130	-45.9
0.6	**11**	240	-53.7	**14**	32	-51	**17**	52	-49
0.06	**12**	100	-54	**15**	52	-52	**18**	44	-36
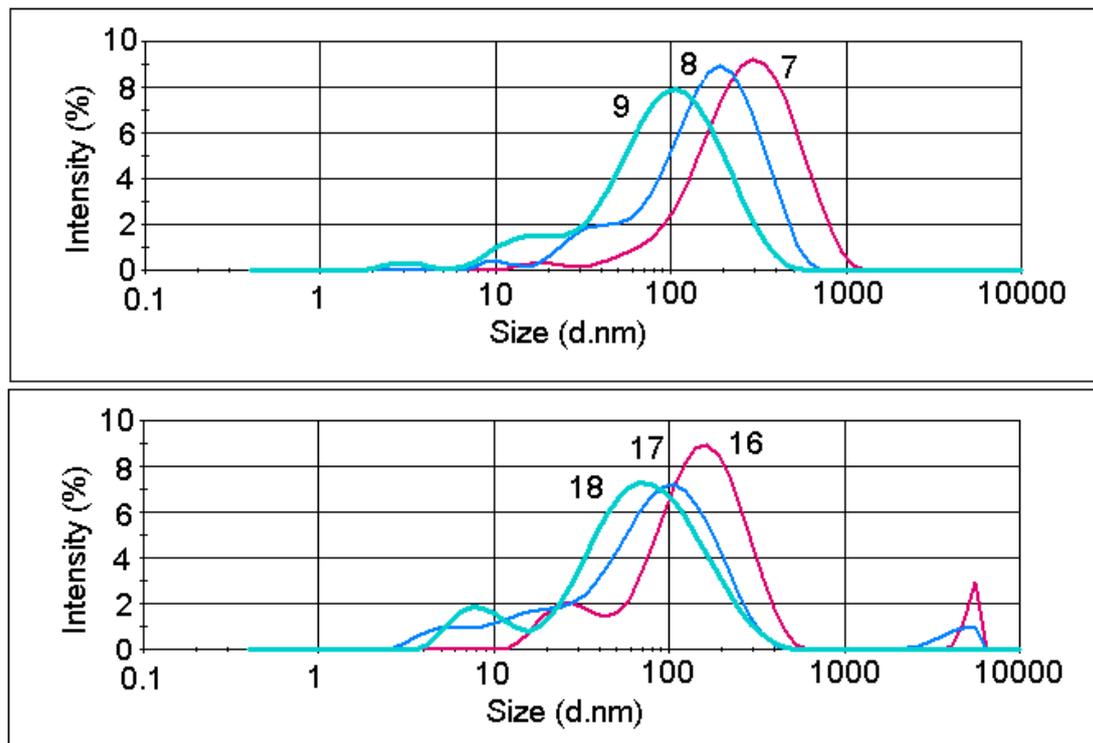
Fig. 2. Size distribution by intensity for the particles synthesized at three concentrations for both polyelectrolytes at the maximum concentration of AgNO$_3$ precursor (7, 8, 9 –VBE-MA samples; 16, 17, 18 – VEO$_3$-MA samples)

When AgNO$_3$ concentration was increased, higher average sizes were obtained. This phenomenon was explained by the formation of a larger quantity of silver NPs which nucleate in a limited number of centres. The soluble polymer in water is a nucleating, capping and stabilizing agent [8].

The synthesis of silver NPs in polymers aqueous solutions lead to the formation of new nanoparticles with macromolecular chain able to stabilize one or more metal particles. The silver NPs tend to agglomerate as the polymer has less extended conformations at higher concentrations [9]. TEM studies of silver particles in poly (N-isopropylacrylamide) solutions confirmed the agglomeration phenomena [8].

As observed from Table 1, VEO$_3$-MA copolymer, which is the most hydrophilic, presented particles of unusual high dimensions at low concentrations of AgNO$_3$. These increased average sizes can be explained by the low stabilization of the metal particles formed while reducing with NaBH$_4$.

It is well known that organic acids forms silver salts in the presence of metal salts [27]. It is also often referred the strong interaction between polyelectrolytes with carboxyl groups and Ag$^+$ ions and afterwards with silver NPs [15-22]. Copolymers of maleic anhydride saponified in water form silver salts due to the presence of two carboxyl groups at one structural unit [3]. The final salts are less soluble in water (the initial transparent mixture became opaque) and forms new particles with a better stabilization [18-20].

The increase of AgNO$_3$ concentration leads to the increase of the stabilizers concentration for the new formed particles, and from this reason these particles aggregates. The stabilizers formed in situ have a similar effect as the association of hydrophobically modified polyelectrolytes through hydrophobic demixing [28]. The similarity is also sustained by the opposite behaviour of VBE-MA copolymer with hydrophobic side groups. Similar experimental data [26] on copolymers with a higher hydrophilic character - alternating copolymers of maleic anhydride with sodium styrene sulphonate, were obtained. Also, a published study described the synthesis of silver NPs, when condensation products of sulphonate naphthalene with formaldehyde, were used as stabilizers. The authors, Sodi, Goia and Matijevic, explained the low stabilization of the particles

at small concentrations of AgNO$_3$, through the formation of the sulphonic groups' complex with silver ions. The concentration of the complex can affect the particles protection [10]. Zeta potentials measurements of the synthesized particles (as in Tab.1) also sustain these remarks (Fig.3). In good agreement with previously published data all particles have a negative Zeta potential [10, 11]. The majority of the samples that had an increased AgNO$_3$ concentration had also lower Zeta potential value. This negative Zeta potential can be explained by the formation of the silver salts, possibly incomplete transformed, or by the carboxyl groups involved in stabilizing a high quantity of silver NPs.
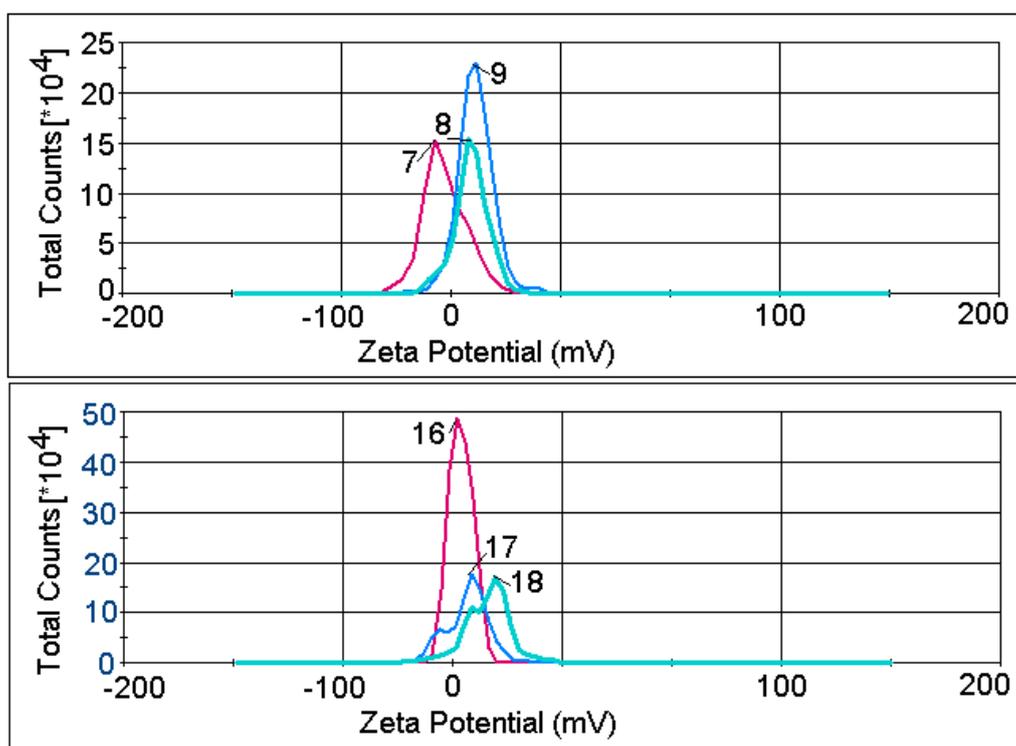
Fig. 3. Zeta potential values of the particles synthesized at three concentrations for both polyelectrolytes at the maximum concentration of AgNO$_3$ precursor (7, 8, 9 –VBE-MA samples; 16, 17, 18 – VEO3-MA samples)

Additional information's about Ag^0 NPs obtained in the presence of water soluble polymers were collected from UV spectra [5, 8, 10-23]. The superficial electrons of silver NPs determine the plasmon adsorption band around 400 nm. Plasmon resonance adsorptions [29] are affected by dielectric function of metal and polymer, particle size and shape distribution, the interface between particles and surrounding medium. A small number of systems were described having the wavelength at the maximum absorbance increasing the plasmon adsorption band together with the increase of Ag^0 particles diameters [5, 7, 10].

Figure 4 presents the change of $\lambda_{maximum}$ from plasmon resonance band obtained by UV analyses. UV spectra had a maximum value of adsorption around 400 nm for all dispersions, confirming the nanometer sized particles obtained by DLS analyses (Figure 2).

No significant change was observed for the hydrophilic copolymers VEO$_3$-MA (Fig.4a). Most dispersion exhibited a slight decrease of $\lambda_{maximum}$ with the increase of AgNO$_3$ concentration. Systematic decrease of the maximum with the increase of initial AgNO$_3$ concentration was remarked also for VBE-MA copolymer (Fig. 4b). The maximum decreasing tendency can be related with the increase of the polymers concentration in water. Similar results were observed for the alternating copolymers maleic anhydride – vinyl acetate [26].
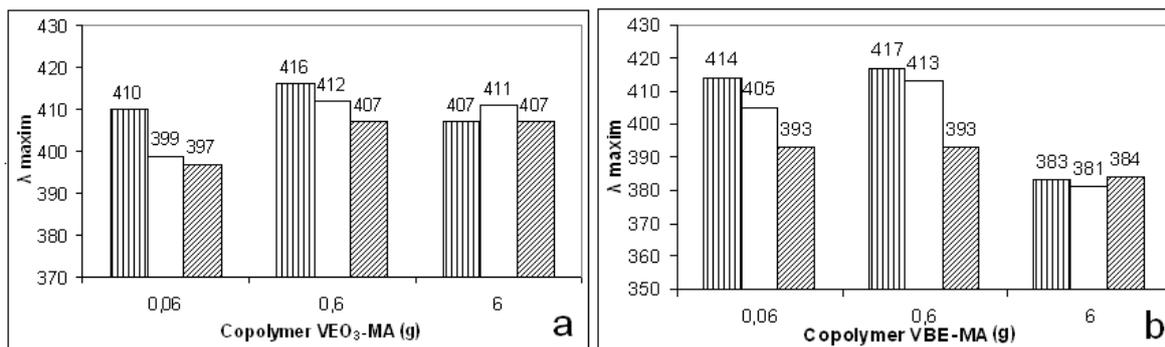
*Fig. 4. Variation of plasmon adsorption band for aqueous dispersions of Ag^0
nanoparticles determined by UV analyses.*

The increase of the particles average sizes couldn't be the reason of these changes, it would conflict DLS analyses, but the modification of the the particles surface neighbour with polymers could be a suitable explanation. This variation is possible for maleic anhydride copolymers with comonomers whose substituents can lead to associations through hydrophobic demixing.

In solid phase, the polymeric chains strongly interact with silver NPs, after water evaporation. TGA analyzes (Fig.5) showed Ag^o hybrids with an increased thermal stability compared with pure copolymers. The maximum decomposing temperature (the temperature at which the maximum weight loss is registered) increased at higher concentrations of silver NPs. Similar results have been obtained also for different maleic anhydride copolymers [26].
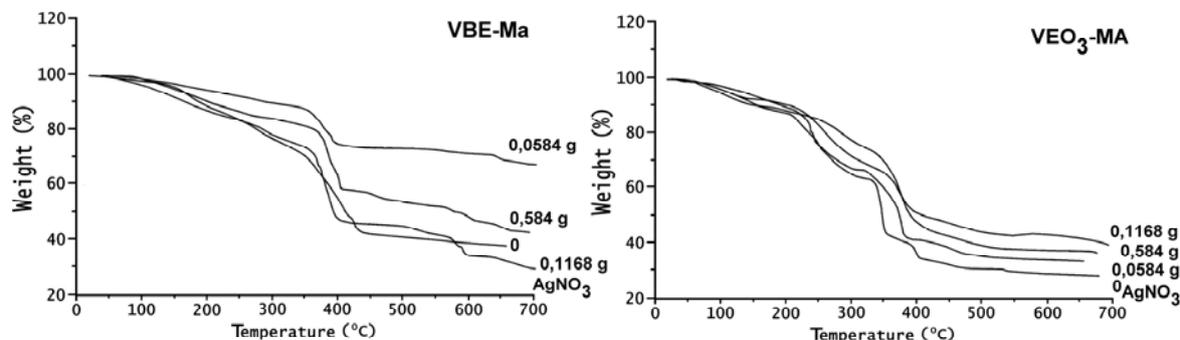
Fig. 5. TGA curves for solid hybrids of copolymers-silver NPs obtained at different AgNP concentrations

As showed before, thermal stability of polymers increases in the presence of silver NPs [5, 30, 31]. The interactions between polymeric matrix and inorganic nanofiller decrease the chains mobility and favour the increase of the thermal stability[5].

After water evaporation, the samples were analyzed by X-Ray diffraction. Similar to other alternating copolymers of MA, XRD diffractograms proved the behaviour of cubic crystalline systems for Ag^o particles [26]. Figure 6 presents the XRD pattern obtained for sample 14. The results were in good agreement with the previous published data [32-34]. The copolymer VBE-MA which has an increased hydrophobic character determined the shift of Ag^o crystallite to higher values than VEO_3-MA. At maximum quantity of $AgNO_3$ (Table1), the following values of cubic crystallite sides were obtained:
- VBE-MA copolymer: 17.3 nm (sample 13), 13.5 nm (sample 14)
- VEO_3-MA copolymer: 3 nm (sample 16), 4 nm (sample 17)
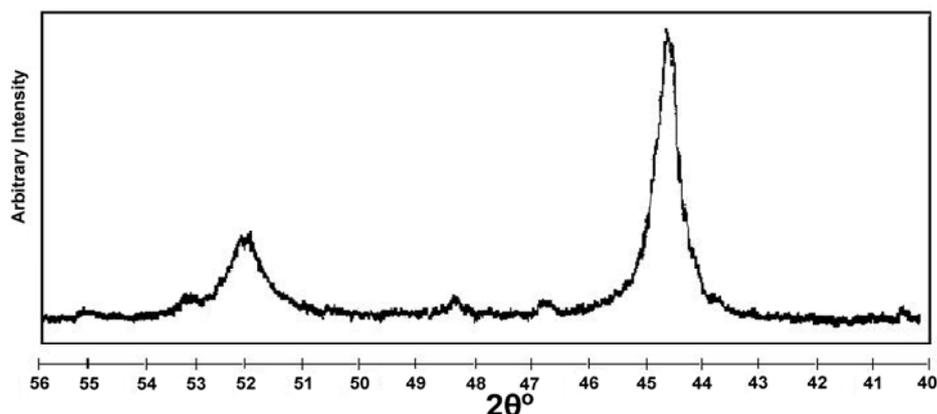
Fig. 6. XRD diagrams of sample 14 (Tab. 1: 0.6 g VBE - MA copolymer, 0.584 g AgNO$_3$)

As observed from XRD, the particles sizes difference between the two copolymers in solid phase correspond to DLS information's measured in aqueous dispersions (Fig.2). DLS evidenced particles greater than the particles measured by XRD. This fact indicates that the particles dispersed in aqueous medium are agglomerations of smaller crystallites. The hydrophobic separation of VBE-MA copolymers leads to the formation of lower amount of nucleating, crystallization and stabilization centres.
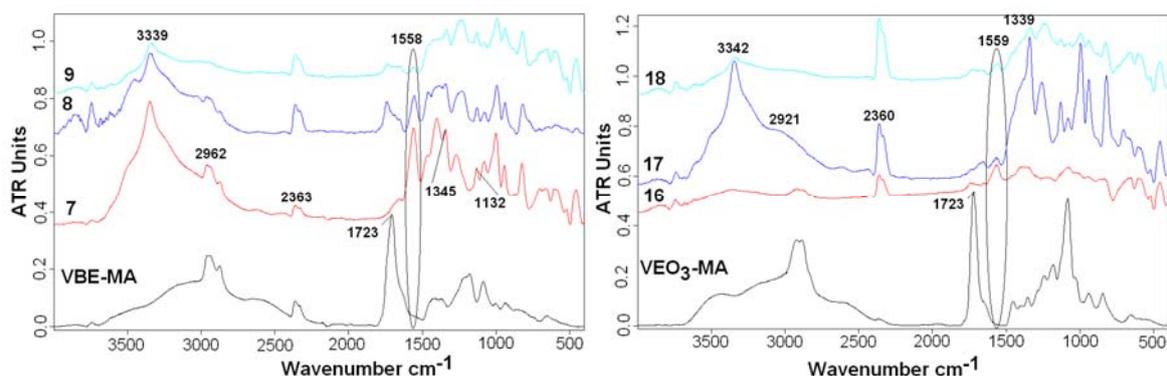
Fig. 7. FTIR spectra of AgNP with different concentrations of copolymer VBE-MA and VEO$_3$-MA.

FTIR spectra of the solid samples contains strong absorption bands related to vibrations of the associated OH from the carboxylic acid (3350cm^{-1}, broad) groups and a weak band at 1734cm^{-1} [n(C=O)] (Fig. 7). The disappearance of the strong peak at 1723cm^{-1} in FTIR spectra of the samples containing Ag nanoparticles can be due to the metal – ligand bond formation.

The peaks at 1855cm^{-1} and 1780cm^{-1} assigned to the MA residues disappeared from the polymer spectra, indicating that the copolymerization reaction has been complete.

The results confirmed the existence of strong metal-ligand bond between the metal ions and carboxyl oxygen in carboxylate salt, for both copolymers of MA: VBE-MA and VEO$_3$-MA (C=O absorption at 1559cm^{-1}). For VEO$_3$-MA copolymer, even though the samples were not measured quantitatively, the decrease of the peak intensity with the decrease of the polymer concentration was observed. On the other hand, strong peaks at 1129 and 1340cm^{-1} can be attributed also to the C=O stretching band of the carboxylic group COOH and the asymmetric and symmetric stretching bands of the carboxylate group COO$^-$.

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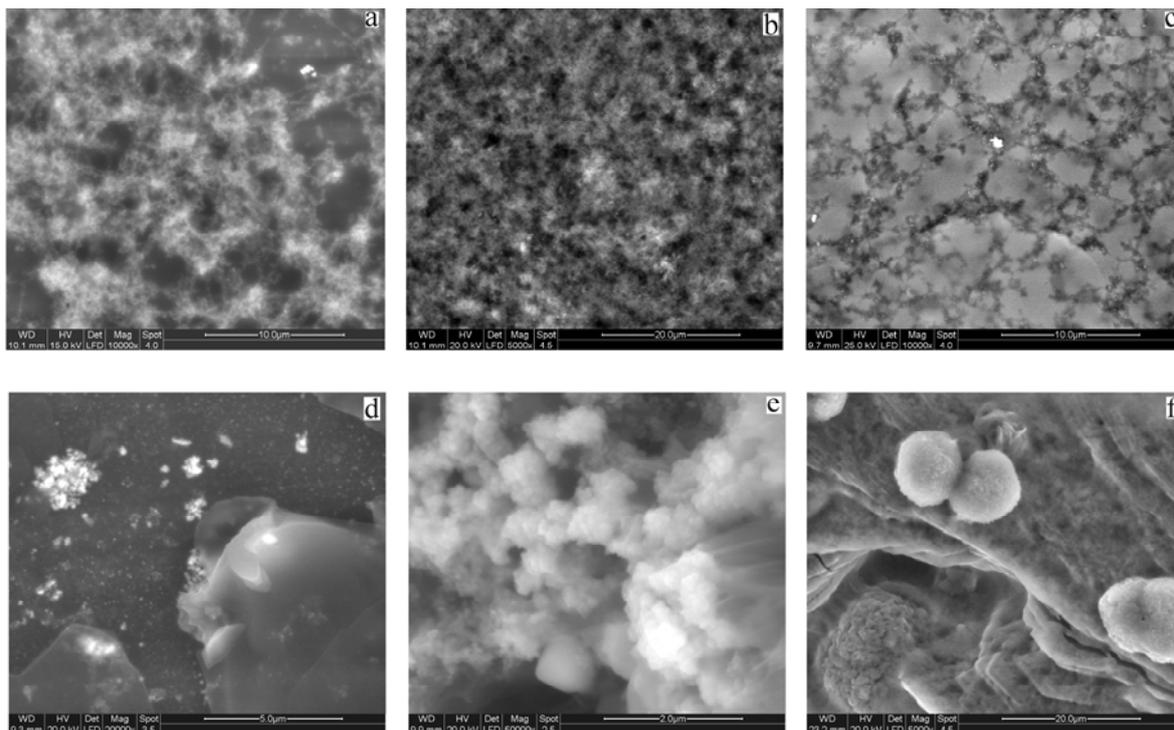
Fig. 8. SEM images of alternating copolymers of MA (MA-VBE: a- sample 3, b- sample 6, c-sample 8; MA-VEO₃: d– sample 12, e- sample 15, f- sample 16) with different concentrations of Ag°

SEM images of the hybrids composites showed that the shape and the size of the particles significantly depend on the content of the alternating copolymer. In the case of MA-VEO$_3$/Ag nanocomposites the formation of dispersed particles was observed. This phenomenon was more pronounced for the sample containing the highest quantity of copolymer and silver (Fig. 8f). The decrease of Ag content in the MA-VEO$_3$/Ag (sample 6) provided the agglomeration of the Ag particles contrary to sample 12 were Ag particles were better dispersed in the copolymer matrix.

In the case of copolymer MA-VBE/Ag nanocomposites, the formation of agglomerated nanoparticles, with Ag particles dispersed in the copolymer matrix, was observed. The sample with the highest quantity of copolymer and silver forms a microporous film, at micrometer range.

4. Conclusions

AgNO$_3$ concentration influenced stabilizers concentration for the new formed particles, leading to silver nanoparticles aggregations. This phenomenon was confirmed by X-Ray diffraction analyses, which evidenced characteristics of cubic crystalline systems for Ag° particles. TGA analyzes showed an increased thermal stability for Ag° hybrids compared with pure copolymers. The results confirmed the existence of strong metal-ligand bond between metal ions and carboxyl oxygen in carboxylate salt (C=O absorption at 1559cm^{-1}) for both copolymers of MA: VBE-MA and VEO$_3$-MA.

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