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Silver Nanoparticles Capped with Poly[(maleic anhydride)-*co*-(vinyl acetate)]

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ABSTRACT

Anhydride containing functional co-polymer, Poly[(maleic anhydride)-*co*-(vinyl acetate)] (pMAVAc) was synthesized by free radical polymerization reaction presence of methyl ethyl ketone (MEK) media with benzoyl peroxide radical initiation at 80 ◦C. Surface modification of pMAVAc was carried out with silver to obtain size specific silver nanocomposites by well-known chemical-reduction approach. Structural characterizations of the samples were performed spectroscopic measurement and surface morphology identification using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and Scanning Electron Microscopy (SEM), respectively. Results obtained from the ATR-FTIR analysis, detection of the characteristic spectrum data of the co-polymer composition in pMAVAc-AgNPs nanocomposite is proof that the co-polymer structure remains unchanged after treatment. The size and morphological properties of the silver nanoparticles were compatible with the characteristic nanomaterial structure and their average size was found to be 35 nm. In addition, as expected, MAVA-AgNPs nanocomposite, the detection of 79.73% Ag by mass is evidence of the high silver content in the material, and it was concluded that the co-polymer was successfully coated with silver. In recent years, considering the increasing importance of biocompatible nanomaterials in drug delivery systems and in pharmaceutical industry, the synthesized nanocomposites are thought to be a useful drug carrier system with potential antibacterial activity.

Keywords: Maleic anhydride-vinyl acetate copolymer, Surface modification, Silver nanoparticle, FTIR, SEM.

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Introduction

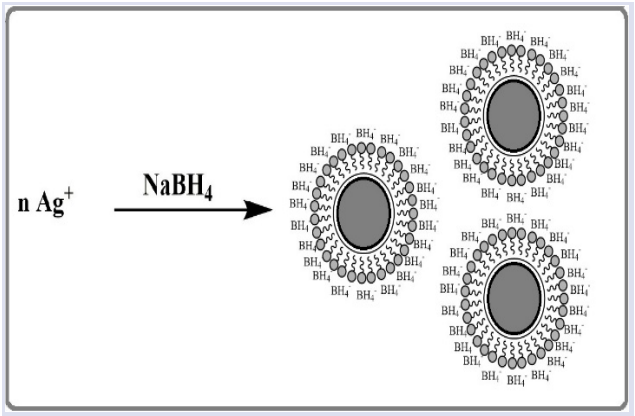
The production and applications of polymers have attracted great interest in both academic and industrial research fields in the last twenty years due to their high potential to produce useful materials with desired properties [1]. Functional polymers have been designed specifically, as for example solubilizing agents, surface modification, nanoparticles, macromolecules as drug carriers, medical devices as diagnostic/imaging agents and implants etc. Functional polymers generally design for the purpose of biomedical applications, such as prostheses, dental filling materials, contact lenses, and pharmaceutical formulations as drugs, drug or enzyme conjugates, and gene delivery systems with having many biological activities [2].

Maleic anhydride (MA) containing materials, anhydride or acid form, indispensable tools that widely used for copolymer design for biomedical applications, especially in health research area to diagnosis and treatment of the diseases [3]. Polymer-drug conjugates were first introduced to research area by Helmut Ringsdorf in 1975. The model basically is based on synthetic covalent bond interaction between the pharmaceutically active substances and a polymer backbone [4]. On the other hand, the unique surface modification capability of maleic anhydride makes it possible to design different materials, drug carrier tools because of its unique functionalization capacity, for biomedical applications. These carriers can be easily produced by free radical chain polymerization as non-toxic, non-immunogenic, and biodegradable property under mild conditions with biological activities [5]. They are synthetically produced as targeted functional biomaterials using many types of reactions. Water solubility property makes them attractive for rational polymer-drug fabrication and controlled drug delivery systems.

MA, $C_4H_2O_3$, is a well-known functional monomer with electron acceptor property, which can undergo chemically versatile structural modification through its reactive anhydride moiety with nucleophiles. The functionality of the anhydride moiety allows the production of polymer-based pharmaceutical systems with the desired capacity thanks to special reactions, especially for the design of biocompatible drug carriers. Synthetic modification of polymer surfaces for various applications is an interesting research area, especially in developing new formulations and producing useful materials. Large amounts of anhydride moieties located along the alternating co-polymer backbone tend to react specifically with polar groups, -OH and $–NH_2$, easily [6]. One of the interesting studies on the surface properties of Poly(4-styrenesulfonic acid-*co*-maleic acid) (SMA) is SMA coated with silver nanoparticles (AgNPs) designed to have potential antibacterial activity [7]. Chemical reduction method used for co-polymer coated AgNPs preparation includes silver nanoparticles starting with the reduction of

a silver salt (silver nitrate, $AgNO_3$) with a reducing agent (sodium borohydride, $NaBH_4$) in the presence of colloidal stabilizer (1) [8,9].

$$AgNO_3+NaBH_4 \longrightarrow Ag+½H_2+½B_2H_6+NaNO_3 \quad (1)$$



Scheme 1. Schematic representation of the repulsive forces separating Ag nanoparticles with the adsorbed borohydride layer [10].

Nanosilver-based materials plays a major role in nanotechnology and is widely used in nano-medicine. There are many factors linked to potential action and cytotoxicity of silver nanoparticles such as particle size, exposure dose, coating materials, and aggregation behaviour of the particles [11]. Coating is a remarkable method to enhance the advantages of nanoparticle-containing material, which can increase the stability of AgNPs and reduce their aggregation. One of the most striking roles of the coating is to minimize the potential cytotoxic effect of silver nanoparticle against living cells. Moreover, the function of the coating is highly dependent on the properties of the coating agents [12].

The coating process can be explained as the dispersion and bonding of nano-sized silver particles on the surface of the copolymer. Silver nanocomposite based on carboxymethyl cellulose exhibits antibacterial, antifungal, and anticancer activities [13], Poly(vinyl alcohol (PVA) and poly(*N*-vinyl 2-pyrrolidone (PVP) [14] cause angiogenesis via the production of an angiogenic factor [15], chitosan coating can act as a photothermal agents against human non-small lung cancer cells [16], a suture coating led to high anti-inflammatory activity in the intestinal anastomosis during early healing in mice [17]. Furthermore, polysulfone (PS) [18], polyethersulfone (PES) [19], polyvinylidene fluoride (PVDF) [20], cellulose acetate (CA) [21] is widely used other well-known polymers to obtain polymer-coated silver nanoparticles. For example, a recent study showed that the addition of PVA-AgNP ((poly(vinyl alcohol) doped by AgNPs) composites, prepared by spin coating and electrospinning and dip coating techniques, to the non-toxic and colourless polymer leads to a remarkable change in the optical and antibiofilm capacities of the polymer [22]. In another study, it was observed that by incorporating AgNPs into the PES polymer matrix, the antibacterial properties [23] and thermal stability [24] of the polymer composite were significantly improved. As for the animal models, healing has been observed in injured tissues, especially by triggering new collagen synthesis. Thus, modified-AgNPs with oligonucleotides accelerated wound healing without any adverse effects [25]. On the other hand, techniques using PVP-coated silver nanoparticles as colour indicators can be listed as biosensing, environmental protection, food control and medical diagnosis [26]. The coating of all these materials is intended to improve the properties of the surface, especially in terms of reducing initial toxicity and increasing stability.

In this study, pMAVAc, AgNPs, and pMAVAc-AgNPs were synthesized and characterized for size and morphology by SEM analysis. ATR-FTIR spectroscopy was also carried out for the enlightening of the copolymer composition. pMAVAc composed of equal proportions of maleic anhydride and vinyl acetate monomers that it was radically synthesized and using as a capping agent through its anhydride group. Surface modification of pMAVAc was performed with silver to obtain size specific silver nanocomposites by chemical-reduction approach. pMAVAc selected as a capping agent because our previous studies was also confirmed that pMAVAc have almost no cytotoxicity on cultured cell lines and it has been a suitable carrier for drugs or pharmaceutically active molecules such as noradrenaline and doxorubicin [27,28]. Since the synthesized Ag-nanocomposite is thought to potentially have antibacterial effects on Gram-positive and Gram-negative bacteria, it is planned to be investigated in our future studies.

Materials and Methods

Materials

Chemicals and reagents of analytical purity were used as follows: Maleic anhydride (MA, with anhydrous benzene recrystallization method), methyl ethyl ketone (MEK), and radical initiator benzoyl peroxide (BPO) were purchased from Merck. Absolute ethyl alcohol (95% purity) was supplied by Carlo-Erba. Vinyl acetate (VA), petroleum ether, and ethyl acetate, and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich. The reducing agent (sodium borohydride, $NaBH_4$) was obtained from Merck.

Instrument

The ATR-FTIR spectra of all samples were recorded on a FTIR spectrophotometer (Bruker Mode: Tensor II) at 400–4000 cm^{-1}. Morphological characteristics (shape and size) of silver nanoparticles were determined by scanning electron microscope (SEM) equipped with Energy Dispersive X-Ray spectroscopy (EDX) at 30 keV (TESCAN MIRA3 XMU). The polymer and copolymer silver nanoparticle composite was coated with 5 nm gold at 10 keV and visualized with the SE detector.

Synthesis of pMAVAc Capping Agent

Alternating based maleic anhydride-vinyl acetate *co*-polymer (Scheme 2) was synthesized using the *in situ* charge transfer complex (CTC) radical polymerization method by free-radical polymerization in MEK for initiated with benzoyl peroxide (BPO) 24h at 80 °C (Table 1). An overnight ethyl acetate purification method and vacuum filtration system (at 50 °C, for 24 h) were used for co-polymer and liquid phase removing, respectively [27].

Preparation of Silver Nanoparticles

AgNPs Sample

AgNPs were prepared according to chemical-reduction method (Table 1) [7,8]. Briefly, 10 mM silver nitrate salt solution was prepared by adding 84.9 mg of $AgNO_3$ salt to 50 mL distilled water. The reducing solution was obtained by adding 18.915 mg of $NaBH_4$ (10 mM) to same volume of the distilled water (50 mL). Solvents mixed well and shaken for 10 min to obtain a greenish brown solution and then allowed to further incubation for 3h at 250 rpm at room temperature in dark conditions for the formation of new silver nanoparticles. As a result, it was observed that a black particle precipitated to the bottom and a very transparent liquid formed on it. The precipitate was carefully separated from the liquid and left to dry for 1 day in a cold environment and further solvent evaporation was also performed in a vacuum oven at 50 °C for 24h. Particles in the form of black powder (AgNPs) were formed stored in a vacuum desiccator until further use.

pMAVAc-AgNPs Sample

The chemical reduction method was used in the preparation of pMAVAc-AgNPs as described above for the preparation of AgNPs (Table 1) [7,8]. Briefly, same volume (50 mL) of the 10 mM $AgNO_3$ salt and 1 mM pMAVAc solution were mixed, then 50 mL solution of 10 mM $NaBH_4$ was rapidly poured into the co-polymer-$AgNO_3$ mixture in one step to reduce all of the silver ions. According to our previous study, the concentration of the copolymer solution was calculated using the average molecular weight (M_w), which was measured as 398.00 Da by size exclusion chromatography (SEC) [27]. The reaction was terminated after 3h incubation at 250 rpm, under room temperature in dark conditions until the mixture became a dark brown solution. The final solution was washed several times with ethyl alcohol, left in the cold for half an hour to allow the particles to become apparent and centrifuged at 14000 rpm for 15 min. Then, nanoparticles dried in a vacuum oven at 50 °C for 24h. Particles in the form of shiny silver powder (pMAVAc-AgNPs) were formed stored in a vacuum desiccator until further use.

Water Solubility of the Samples

Water-soluble polymers are widely used clinically for surface modification of biomaterials. Solubility is a mandatory property for biocompatibility in order to target biomedical applications. Considering the importance of this criterion, water solubility test was also performed for silver nanoparticles. Samples were incubated in ultrapure water (1 g/mL) for 1 h at 25 °C. Solubility in water was checked after one hour by centrifugation of the solution at 6000 rpm with mechanical stirring.

Table 1. Reaction conditions and mixing ratios for the synthesized AgNPs and the MAVA/AgNPs.

Sample code	Monomers/Components (mM)	Solvent (mL)	Initiator (g)	Temperature (°C)	Time (h)
MAVA	MA : VA (1:1)	MEK (5)	BPO (0.025)	80	24
AgNPs	$AgNO_3$ and $NaBH_4$	d.water (50)	-	25	3
MAVA-AgNPs	MAVA : AgNPs (1:1)	d.water (50)	-	25	3

**BPO: Benzoyl peroxide; MEK: Methyl ethyl ketone*

Results and Discussions

The chemical structure and morphological properties of the copolymer and the modification product were elucidated by ATR-FTIR spectroscopic method and SEM analysis, respectively.

FTIR Analysis

Characteristic spectral region of non-conjugated AgNPs recorded at 400–3900 cm^{-1} (Fig. 1a). Typically BH_4^- bending modes observed around at 1993 cm^{-1} and B–H stretching modes detected at 2116 cm^{-1} and 2329 cm^{-1} [29,30]. According to the selection rules, for a tetrahedral system (BH_4^- ion) only two different IR active modes exist; one bending and one stretching mode. The additional bands generally appeared approximately around at 2300 cm^{-1} as 2329 cm^{-1} [29].

Characteristic maleic anhydride functionality containing IR spectrum for poly(MA-*alt*-VA) was obtained (Fig. 1b). Briefly, capping polymeric agent had the characteristic anhydride group at 1857, and 1781 cm^{-1}, belongs to symmetric and asymmetric carbonyl (-C=O) characteristic vibrations of MA-anhydride as expected, respectively [31]. Characteristic vibration modes recorded at 1026 and 934 cm^{-1} attributed to the C–O–C fragment on MA moiety. Stretching modes of $-CH_3$ and $-CH_2$ groups on VA were detected at 1374 and 1432 cm^{-1}, respectively [32]. In addition, $-COCH_3$ stretching modes on VA

appeared around at 1095 cm^{-1} and 1216 cm^{-1} was assigned to the ester groups (CO–O–C) on VA [33]. FTIR results confirmed the pMAVAc copolymer structure [31,32].

The FTIR spectrum of the modification product pMAVAc-AgNPs is shown in Figure 1c as compared to both pure AgNPs and capping agent-pMAVAc. Characteristic vibrations of the anhydride ring belongs to capping agent poly(MA-*alt*-VAc) were appeared in pMAVAc-AgNPs spectrum. In addition the IR spectrum of the modification product consists of two parts, including the characteristic peaks of both capped AgNPs and capping agent pMAVAc. Briefly, on the left side of the spectrum characteristic peaks observed at 2116 cm^{-1} frequencies arising from BH_4^- following the electron capture by BH_4 radical [30] and 2663 cm^{-1} attributed to vibrational frequencies BH_4 [30], 2329 cm^{-1} bending mode of BH_4 [34], and 1993 cm^{-1} assigned to BH_4^- bending modes [40]. On the other hand, on the left side of the spectrum characteristic anhydride asymmetric carbonyl (C=O) vibrations observed at 1788 cm^{-1} [31]. Finally, the antisymmetric and symmetric stretching vibrations of the C-O-C bond in MA detected around at 1166 cm^{-1} and 886 cm^{-1}, respectively [35,36].The remaining frequency observed at 3665 cm^{-1} assigned to hydrophilic groups according to the O–H stretching vibrations, ensuring good water solubility [37].

This result revealed that silver nanoparticles successfully capped with pMAVAc copolymer. These findings obviously demonstrated that a new nanoparticle structure formed following the surface functionality.

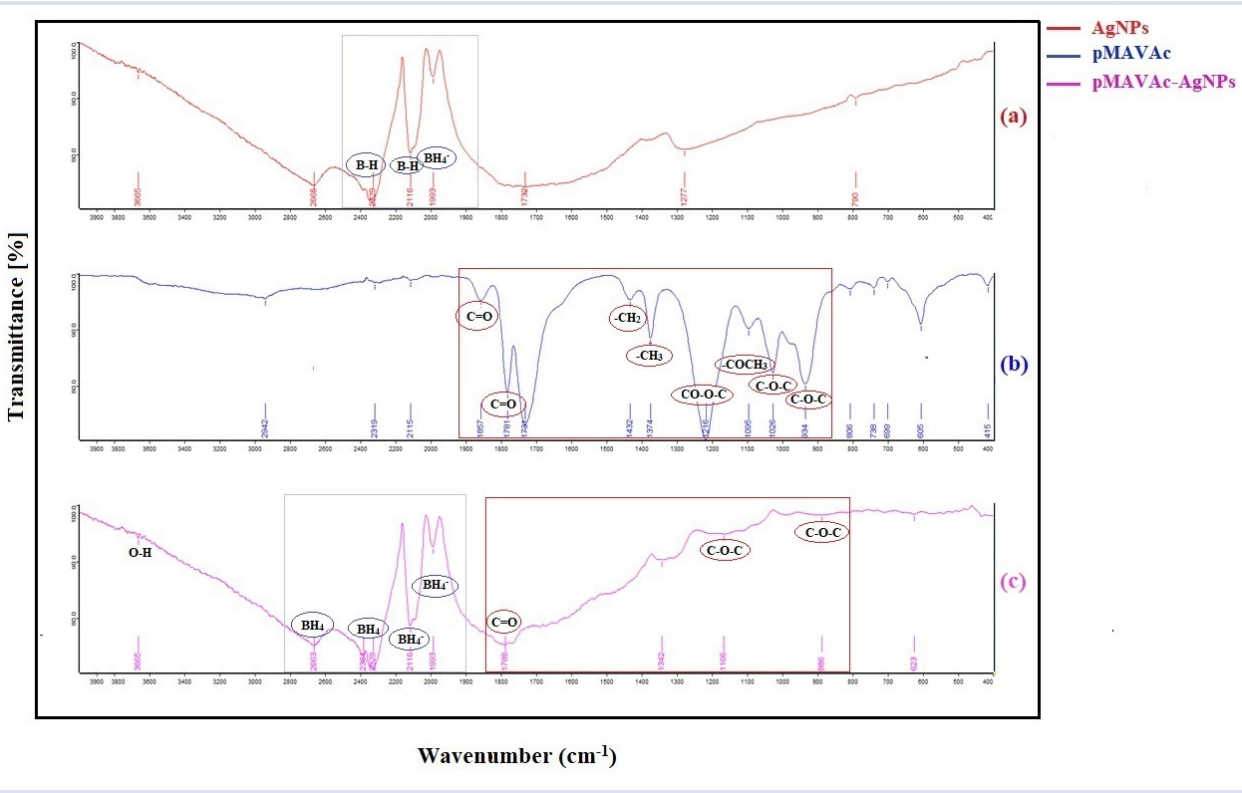


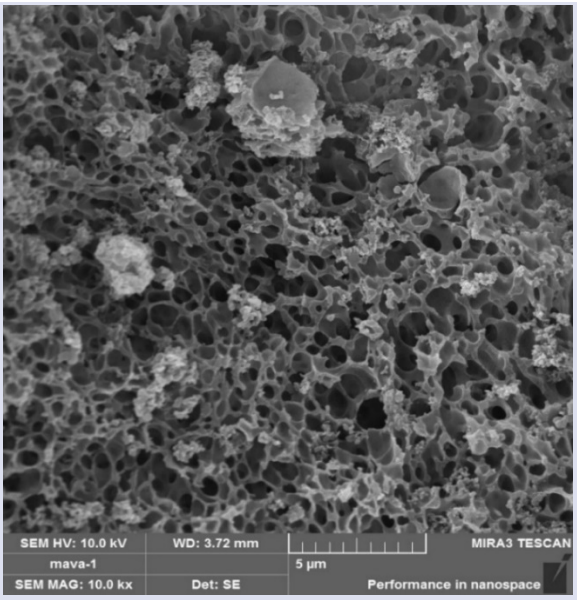
Figure 1. FTIR spectra of the copolymer and the modification product. (a) AgNPs, (b) pMAVAc, and (c) pMAVAc/AgNPs.

SEM Analysis

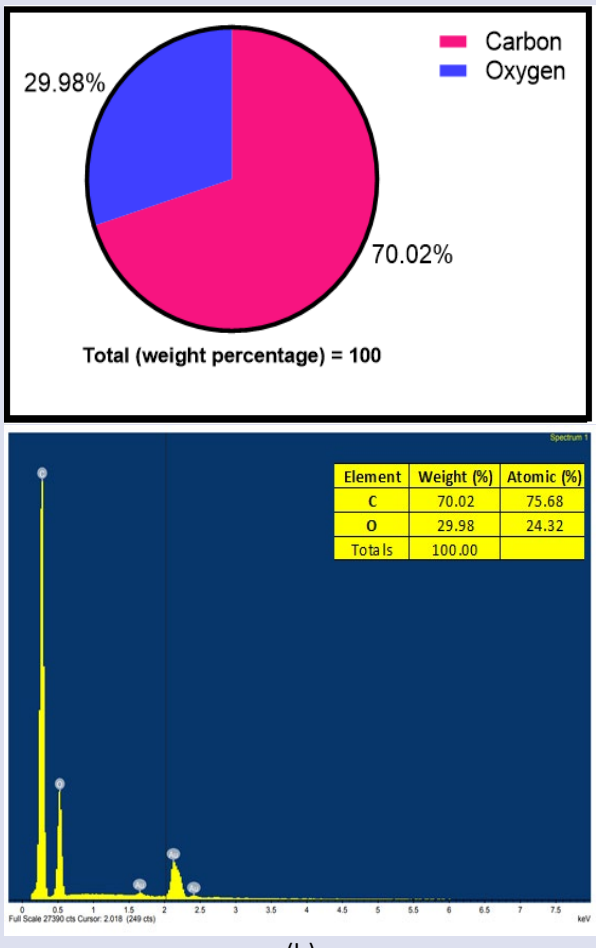
Scanning electron microscopy (SEM) was employed to enlighten of the main characteristics of the copolymer and synthesized silver nanoparticles such as size, shape and surface morphologies. Energy dispersive spectrometry (EDX) analysis was also performed to confirm the presence of elemental silver. SEM images of copolymer and copolymer-silver nanoparticle taken at 5µm 10.0 KX given in Fig. 2a and Fig. 3a. The size and morphological properties of the copolymer uncoated silver nanoparticle are also given in Fig. 4. As can be seen, the size and morphological properties of uncoated silver particles are compatible with the characteristic nanomaterial structure because of its spherical in shape with narrow size distribution. Their sizes range from 12 nm to 70 nm, with an average size of 35 nm [38].

Morphological characteristics of silver nanoparticles were determined by scanning electron microscope (SEM) equipped with EDX at 30 keV. Figure 2b and 3b show EDX analyses of MAVA copolymer and MAVA-AgNPs nanocomposite. Elemental analysis results were also recorded for reduced silver nanoparticles. Since the copolymer used as the coating agent has only carbon (C) and oxygen (O) atoms in the main chain, the presence of carbon and oxygen was observed, while in the silver-containing nanocomposite, only C, O and Ag elements were determined as % composition, as expected. In the spectrum, the presence of high levels of O and C elements in the structure of the MAVA copolymer and high amount of Ag elements in the silver surface modified copolymer (MAVA-AgNPs) the most important evidence of the inclusion of silver elements in the copolymer structure.

Quantitatively, the weight percent of atoms for the pMAVAc copolymer was determined as 70.02% C and 75.68% O atoms (atomic percentage; % 29.98 C and % 24.32 O), while 7% C, 13.26% O and 79.73% Ag atoms (atomic percentage; % 27.14 C, % 38.52 O, and % 34.35 Ag) were determined for the modification product pMAVAc-AgNPs, as expected [38].



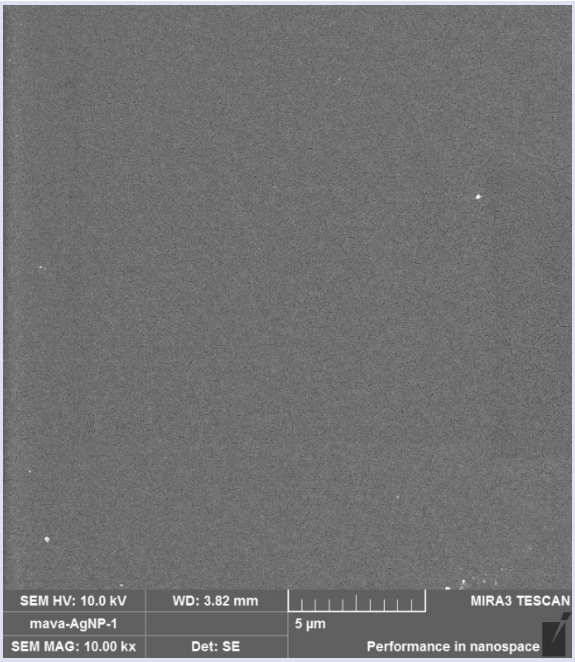
(a)



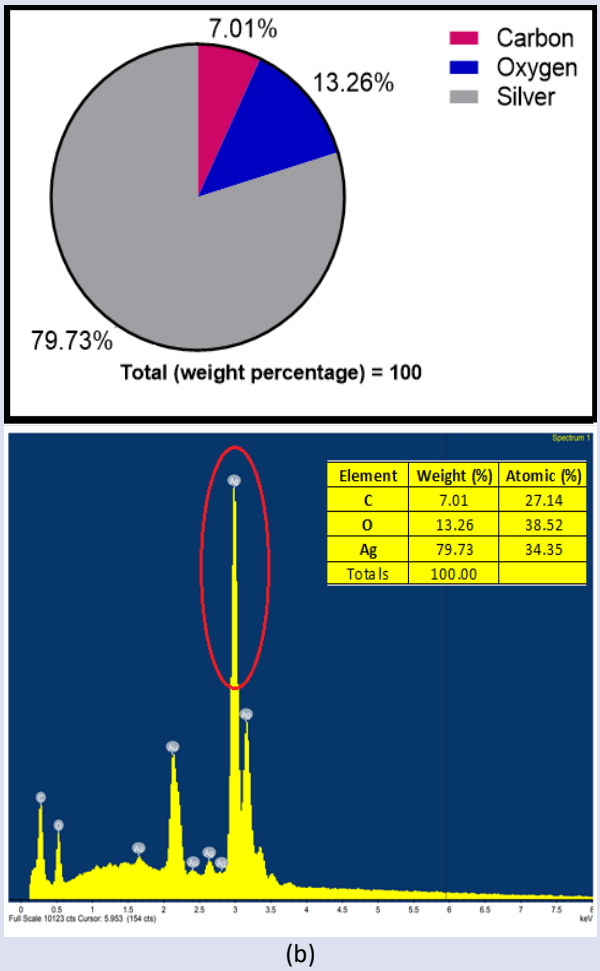
(b)

Figure 2. a) SEM image (5µm, 10.0 KX magnification) and b) EDX spectrum of pMAVAc copolymer.

It can be obviously concluded that silver nanoparticles reduced by pMAVAc copolymer have the weight percentage of silver atoms as 79.73%.



(a)



(b)

Figure 3. a) SEM image (5µm, 10.0 KX magnification) and b) EDX spectrum of pMAVAc-AgNPs.

In the light of the spectroscopic and morphological findings obtained, it was concluded that the surface of the copolymer was successfully coated with silver nanoparticles.

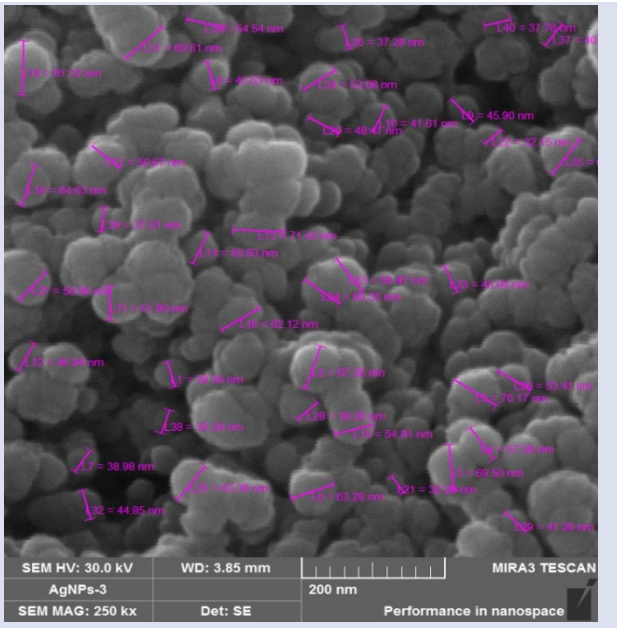


Figure 4. SEM image of AgNPs (200 nm, 250 KX magnification).

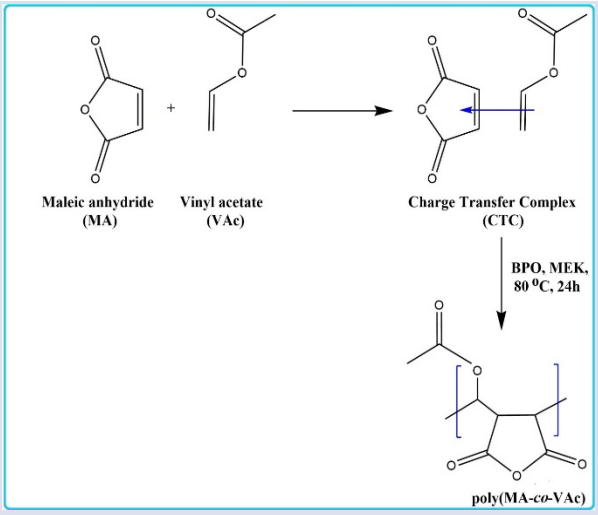
Water Solubility of the Samples

According to "like dissolves like" rules polar/ionic solvents dissolve polar/ionic compounds, nonpolar solvents dissolve nonpolar compounds. The water solubility test clearly showed that the newly designed pMAVAc-AgNPs nanocomposite is highly soluble in water. As supported by the FTIR results of the functional groups of the copolymer and nanocomposite, its *polyanionic character* provides high water solubility.

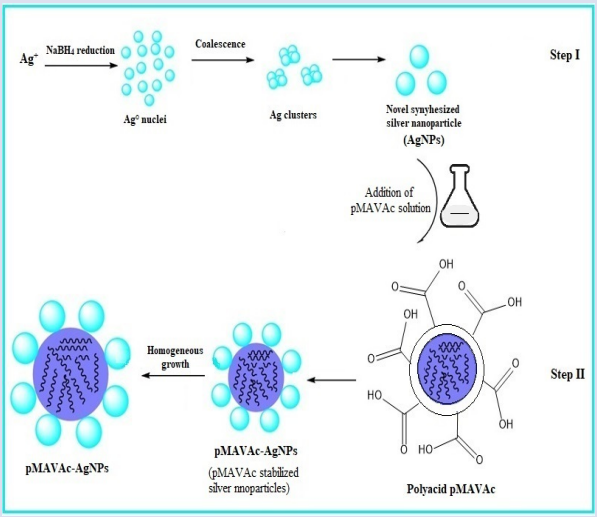
Proposed Reaction Mechanisms for Copolymer and Silver Nanoparticle

Spectroscopic analysis results, FTIR, clearly showed that the mechanism of synthesis reaction for MA containing copolymer is compatible with radical initiated free-radical polymerization and AgNPs nanoparticles capping with this copolymer according to chemical-reduction method (Scheme 2 and 3) [28].

The physical appearances of the synthesized copolymer, silver nanoparticle and the modified product copolymer-silver nanoparticle (after drying and purification) coated with the copolymer are given in Figure 5.



Scheme 2. Schematic illustration of the preparation of maleic anhydride-vinyl acetate (pMAVAc) copolymer.



Scheme 3. Schematic illustration of the preparation of silver nanoparticles and its surface modification.

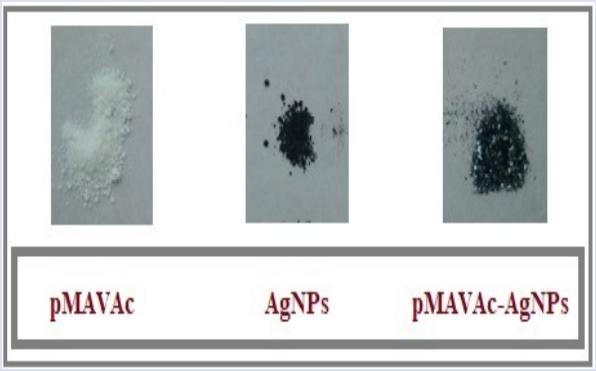


Figure 5. Physical appearance of the prepared copolymer, silver nanoparticle and surface modified silver nanoparticle.

Conclusions

Polymer-based nanocarriers are known as the most versatile biomaterials useful for controlled drug delivery systems. AgNPs are widely used in the many diverse research areas such as cosmetics, food, electronics, optics and also medical purposes as biosensors and drug delivery systems. Current therapeutic applications of AgNPs, especially in healthcare, are closely related to their size, shape and surface coating properties. The chemical-reduction methods used in this study for anhydride containing functional co-polymer, pMAVAc, *via* surface coating process to obtain size specific silver nanocomposites. The characteristic spherical shape and size-specific properties of the designed silver nanoparticles were confirmed by the current literature data, which they gained by surface coating process.

Spectroscopic and surface morphology analyses were used for the samples to structure characterization by ATR-FTIR and SEM, respectively. Detection of the ATR-FTIR spectrum revealed that the characteristic copolymer composition in the pMAVAc-AgNPs nanocomposite remained unchanged after surface modification. The size, shape and morphology of the silver nanoparticles were compatible with the characteristic nanocomposite structure and their average size was found to be 35 nm. The detection of 79.73% Ag atoms as a weight percent for the pMAVAc-AgNPs nanocomposite is proof of the high silver content in the material, as well as the successful silver coating of the copolymer surface. Water solubility and biocompatibility of polymers used as coating materials are very important parameters for the design of size-specific and also stable silver nanocomposites [39]. In this study, used functional co-polymer, pMAVAc with average molecular weight (Mw) 398.00 Da, convenient capping agent for the design of novel silver nanoparticle because of its promising properties, such as water solubility, biocompatibility and non-cytotoxicity etc [27]. According to our previous studies, it was also proposed as a very suitable and stable drug-carrier to be synthesized copolymer-drug conjugates [28].

In addition, polymers with functional groups such as ester, thiol and thioether used as capping agents are suitable surface ligands for design and synthesizing nanoparticles (NPs) with reproducibility and high yield stable properties [40]. Therefore, the selected pMAVAc with a vinyl ester monomer such as vinyl acetate, thanks to its ester functional group, allowed the successful production of nano-scale, water-soluble and stable pMAVAc-AgNPs nanomaterial with high silver content by capping process. As stated before, water solubility is a mandatory property for biocompatibility for biomedical applications. The polyanionic nature of the pMAVAc-AgNPs nanocomposite gives the material the advantage of high solubility in water. In recent years, as researchers have focused on biocompatible nanomaterials in drug delivery systems and the pharmaceutical industry, the synthesized nano-sized composite could be a useful drug delivery system with potential antibacterial activity, and also an easy, short-term and inexpensive way to produce new coated materials.

As a result, it has been shown that pMAVAc tends to yield smaller and narrowly dispersed silver nanoparticles with desirable properties in various applications. It is suggested that the synthesized nano-sized composite can be developed for next-generation drug delivery systems for antibacterial treatment and detailed bioactivity studies can be made.

Conflicts of interest

There are no conflicts of interest in this work.

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