

SPECTROSCOPIC INVESTIGATION OF SOME POLY (ACRYLIC ACID) GELS WITH EMBEDDED GOLD NANOPARTICLES

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ABSTRACT. Some physical properties of poly (acrylic acid) gels with embedded gold nanoparticles, (PAA-GNP), as prepared and after neutralization with triethanolamine, (TEA), were investigated by UV-VIS and fluorescence methods. The UV-VIS spectra of the PAA-GNP gels contain the characteristics absorption peaks of both PAA and GNP pure components, with modified intensities and positions. Excitation at 250 nm of pure PAA and pure GNP are followed by characteristic fluorescence transitions. The peaks of pure components appear in the fluorescence spectrum of the PAA-GNP gels with some modifications compared with the pure state. Some modifications of the UV-VIS and fluorescence spectra were observed after neutralization with TEA. The particularities of these spectra indicate some changes of the conformation of the polymeric matrices after the introduction of GNP and after neutralization.

Keywords: *poly (acrylic acid), gold nanoparticles, UV-VIS and fluorescence.*

INTRODUCTION

In the last decades the development of intelligent pharmaceutical has known a high interest due to the advantages offered by these systems compared to the traditional pharmaceutical products. These systems offer the possibility to transport the active substance only in the desired region of the living bodies, the possibility to release the drug with controlled rate, and the possibility to initiate the delivery at desired time [1, 2]. Usually such

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pharmaceuticals consist of two main parts, the host matrix and the medical drug or an inorganic compound with therapeutic effect. Many polymers were tested as host matrix, the poly (vinyl alcohol) (PVA), poly (ethylene oxide) (PEO), and most recently the poly (acrylic acid) (PAA). Inorganic compounds as TiO_2 or graphite were introduced in these matrices in order to obtain polymeric gels and membranes with enhanced absorption in the UV domain [3, 4]. The well known pharmaceutical, the clotrimazole, was introduced into PAA matrix to obtain gels with possible use in the treatment of skin diseases, [5]. Particularly attention is focused actually on the gold nanoparticles (GNP) which can attach on their surface different compounds with antimicrobial effect. The advantages of such systems are the good compatibility with the living tissues, the great chemical stability and the possibility to initiate the pharmaceutical effect, (the delivery of the active substance, fluorescence emission, or local heating), by external excitation of the system with a well defined radiation [6]. Usually IR or UV-VIS radiation is used for this purpose. But the irradiation of the polymeric matrix could have undesired effects on the structure and local conformation of the chains, with negative consequences on the mechanical properties and physical stability of the system. On the other side, the answer of GNP to external excitation depends on their shape and size and the connections established with the host matrix. The efficiency of the excitation of GNP depends on the absorption properties of the system.

The irradiation in the UV-VIS domain produces excitation of the electrons from a full bonding or non-bonding orbital into an empty anti-bonding orbital [7-9]. The incident photon is absorbed if its energy corresponds to the difference between the electronic levels involved in the transition. The absorption is proportional with the concentration of the absorber, [10]. In the PAA the most important absorption is determined mainly by the $\pi \rightarrow \pi^*$ transition of the carbonyl groups and it is observed around 207 nm, [11]. The absorption is modified after introduction of GNP and after neutralization. The investigation of the UV-VIS absorption of these systems deals with our work.

The UV excitation of PAA-GNP system can be followed by characteristic fluorescence emission. The absorption of the incident photon produces the excitation of the electron from the electronic fundamental level to an excited vibrational level of the next electronic level. The excited electron recovers its initial state by two mechanisms, non radiative transition between the vibrational levels of the excited electronic state and then radiative transition between the electronic levels. A part of the energy of the incident photon is lost by transfer to other vibrational modes of the molecule or by thermal conversion during the vibrational transitions, [12, 13]. From this reason the photon emitted

by fluorescence has small energy compared with the absorbed one. The fluorescence spectrum contains emission lines situated at higher wavelength than that of the excitation photon. Modification of the energetic levels of the molecule determined by chemical bonds established with other neighbors leads to modification of the fluorescence spectrum. This is a way to investigate the possible interaction between the GNP and PAA matrix, and represents other objective of our work.

We performed preliminary studies on the PAA gels with embedded GNP by UV-VIS and fluorescence methods. PAA is a hydrophilic polymer well accepted by the living tissues, but its acid character could have some times undesired effects on the living tissues. In addition, in aqueous gel, without any reinforcement of its local organization, this polymer is characterized by low mechanical resistance and low viscosity. Improvement of these properties can be obtained by neutralization with triethanolamine (TEA). Moreover, the neutralization eliminates the acid character of the gel and enhances its compatibility with the living tissues. For these reasons, a part of our study is dedicated to the investigation of neutralized PAA gels. Our goal is the obtainment of polymeric gels containing GNPs with enhanced absorption properties in the UV domain and specific fluorescence emission.

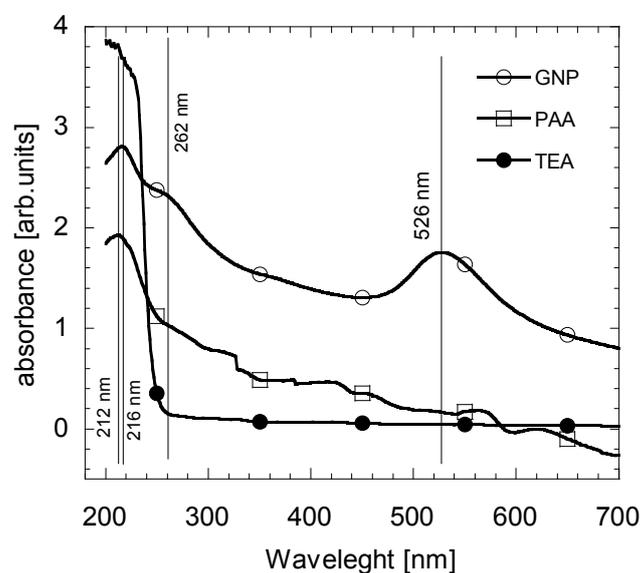


Figure 1. The UV-VIS absorption spectra of pure PAA, TEA and GNP

RESULTS AND DISCUSSION

In order to disclose the possible interactions between the polymer and GNP, the components were analyzed separately and then in combination in the gel. The pure PAA shows a maximum UV-VIS absorption at 212 nm, with the amplitude of 1.9 a.u., after that the absorbance decreases progressively in the domain 250-700 nm. The pure TEA has a maximum at 200 nm, with the amplitude of 3.86 a.u, and then the absorbance decreases sharply until 250 nm, and remains almost constant in the domain 250-700 nm (Figure 1). The spectra of pure GNP show an absorption peak at 216 nm with the amplitude of 3.8 a.u. and another one at 526 nm with the amplitude of 1.75 a.u. (Figure 1). The second peak is determined by the plasmonic resonance of the gold nanoparticles. A shoulder can be seen at 262 nm.

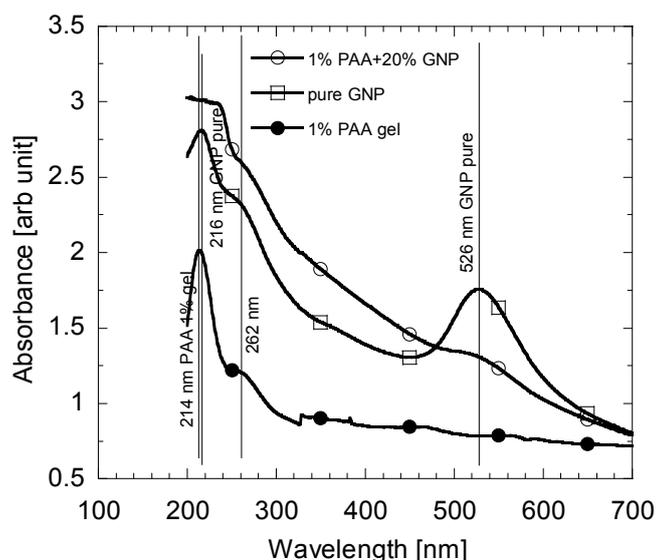


Figure 2. The UV-VIS absorption spectra of pure GNP, 1% PAA gel and 1% PAA gel with GNP

The spectrum of the aqueous gels, without GNP and TEA, contains the characteristic elements of pure PAA, but some differences appear. At 1% wt. PAA concentration the absorption peak of PAA gel without GNP shifts slowly from 212 to 214 nm (Figure 2).

This effect is determined by the perturbation of the hydrogen bonds established between the PAA monomers in the presence of water. This behavior was analyzed in previous paper [14]. The spectra of PAA gel with embedded GNP contain the characteristic peaks of both the components, pure PAA and pure GNP. We can see an intense peak in the domain 212-216 nm, a small one at 526 nm and a shoulder at 262 nm. However some differences appear between the pure components and the gels. The peak at 526 nm of GNP at has much small amplitude in the gel compared with the pure GNP. This decrease of the intensity is explained by the screening effect determined by the attachment of the polymeric chains to the surface of gold nanoparticles. A great fraction of GNPs are almost entirely covered by a thin layer of polymer. The incident radiation cannot penetrate the polymeric layer attached to the surface of the gold nanoparticles, (or penetrates it very few), and the GNPs cannot be excited by the radiation. The absorption of the radiation is determined mainly by the polymer. For this reason the absorption peak of the polymer at 212-216 nm can be clearly seen in the spectrum. Although this mechanism is dominant, some GNPs are not covered, or are partially covered by the polymeric layer, giving a small contribution to the spectrum, fact that explain the existence of the small peak at 526 nm and the shoulder at 262 nm.

After neutralization with TEA the absorption properties of samples change. First we analyzed the samples without GNP. For these gels the absorbance of the neutralized sample is greater than the absorbance of the aqueous gel, (almost two times greater for the neutralized sample) (Figure 3). This increase of the absorbance is determined by the presence of neutralizer in the system, which has absorption greater than the polymer. Other modification is the shift of the position of the absorption peak from 214 nm towards 200 nm (Figure 3). This shift is determined by the presence of TEA, for which the absorption peak appears at 200 nm. We can affirm that the neutralization enhances the absorbance of the gels [15]. For the samples with GNP, after neutralization, we can observe the attenuation of the shoulder at 526 nm. The shoulder at 262 nm almost disappears. That means that almost all the GNPs are covered by a thin layer of polymer and the incident radiation cannot excite these nanoparticles. The peak 212-216 nm becomes narrow and shifts towards 212 nm (Figure 3).

This shift is determined by the presence of the neutralizer in the samples. The UV-VIS investigations were completed by fluorescence measurements. We analyzed first the pure components. The spectrum of pure PAA excited at 250 nm shows two clear peaks, a sharp one with high amplitude at 465 nm, and a large one at 419 nm with smaller amplitude.

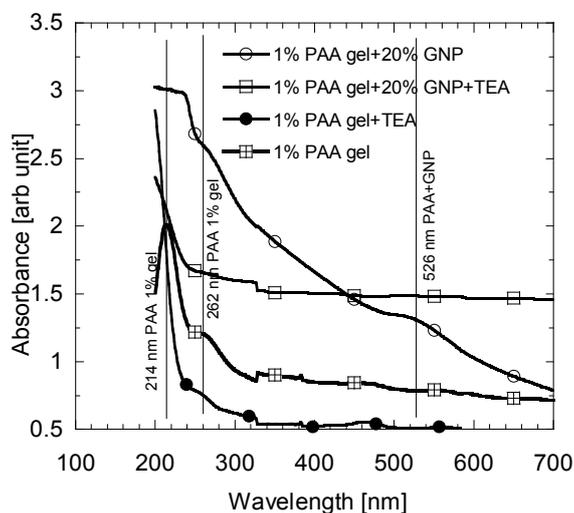


Figure 3. The UV-VIS spectra of PAA aqueous gel and PAA-GNP gel, before and after neutralization

A weak shoulder can be seen at 307 nm (Figure 4). These peaks are associated with three electronic transitions with different probabilities of apparition, the most probable corresponding to the lowest energy, (465 nm). The pure TEA shows a peak at 386 nm and the GNP shows a peak at 407 nm (Figure 4).

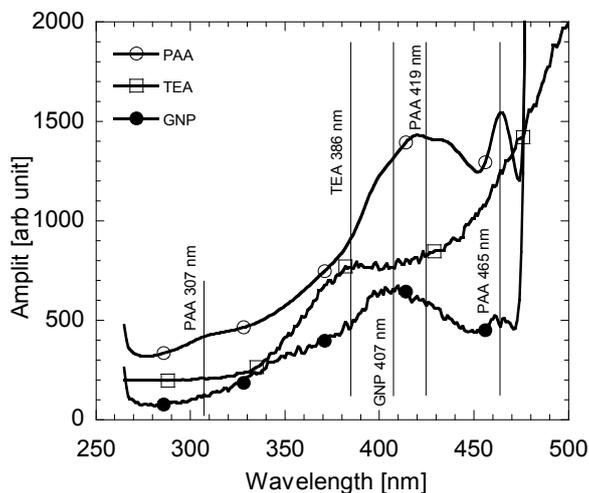


Figure 4. The fluorescence spectra of pure PAA, TEA and GNP excited at 250 nm

The spectrum of the 1% wt. PAA gel, without GNP, is almost similar to the spectrum of pure PAA, but some differences of the amplitude and position of the peaks can be seen. The first peak appears at 465 nm as in the case of pure PAA, but it has small amplitude. The second one appears at 412 nm, (instead 419 nm as for pure PAA), and its amplitude is greater than those of the first peak. The shoulder at 307 nm of pure PAA is now shifted at 321 nm (Figure 5). The gel excited at 250 nm shows three fluorescence transitions, as the pure PAA, but the most probable transition is situated at 412 nm, instead 465 nm for pure PAA. After the incorporation of GNP in the structure of the gel, we can observe the broadening between 400 and 420 nm of the peak initially centered at 419 nm in pure PAA and 412 nm in 1% wt. PAA gel. We can attribute this effect to the presence of GNPs, which gives its peak at 407 nm. The shift of the peak in the gel is determined by the superposition of the peaks of pure PAA and pure GNP. The peak at 465 nm remains at the same wavelength and

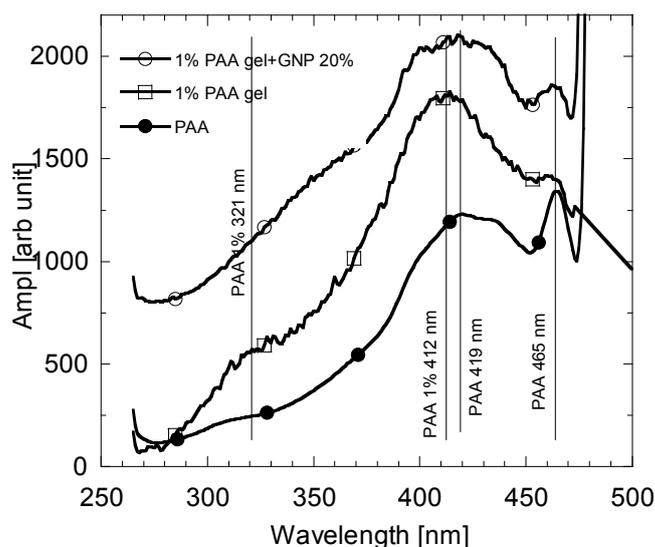


Figure 5. The fluorescence spectra of pure PAA, 1% PAA gel and 1% PAA-GNP gel, excited at 250 nm

the shoulder at 321 nm disappears. After neutralization no great differences appear. The peaks at 465 nm and 412 nm can be seen again without shift or important modification of the shape (Figure 6). However the amplitude of the peak 465 nm is greater for the neutralized sample. A small and broad shoulder

can be seen at 331 nm. This one can be associated to the shoulder at 321 nm observed in the spectrum of the gel without GNP. In the neutralization reaction new chemical bonds appear between the PAA monomers and TEA molecules. The electronic structure of these systems is modified, fact that give rise to modifications of the fluorescence spectra. These modifications are in concordance with the UV-VIS observations. The GNP do not react with TEA, fact that explains the relatively small modification of the fluorescence peaks assigned to these particles. On the other hand, the neutralization is followed by modification of the local conformation of the polymer, changes that can be seen by other experimental methods, including IR, Raman and viscosity measurements. Complete characterization of the effect of neutralization can be achieved by correlation of the data collected by different experimental techniques as indicated above.

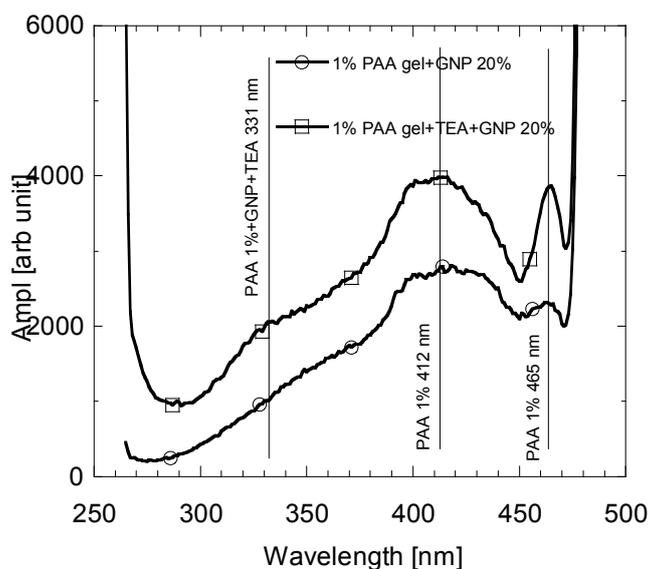


Figure 6. Comparison between the fluorescence spectra of the 1% PAA gels-GNP, before and after neutralization with TEA, excited at 250 nm

CONCLUSIONS

The introduction of GNP into the matrices of aqueous PAA gel, before neutralization, has as consequence the apparition of new absorption peaks in the UV-VIS spectra. After neutralization with TEA the UV-VIS absorption of PAA aqueous gels increases. This tendency is more pronounced in the

samples with GNP. This behavior is determined by the modification of local polymeric conformation after hydration of the polymer and after neutralization. The modification of some chemical bonds by neutralization is followed by the some modification of the electronic states of the molecules. This mechanism is confirmed by the modification of the fluorescence spectra before and after neutralization.

EXPERIMENTAL SECTION

The aqueous PAA was obtained by mixing the powder polymer, (molecular mass 104400 g/mol), with distilled water at room temperature until a homogeneous composition is obtained. The concentration of the polymer in the solutions was 1% wt. The aqueous gels were neutralized with TEA in the proportion 1.5/1 g/g TEA/PAA. At this ratio base/polymer the PH of gel is about 6.5-7.

The gold nanoparticles were prepared on basis of standard methods presented in literature, [16, 17]. We used 100 ml aqueous solution of 1 mM tetrachloroauric acid which was brought to its boiling point. Then we added 6 ml sodium citrate (1%) and the mixture was stirred at constant temperature for 15 minutes. After that the solution was left to cool down to room temperature. Sodium citrate is responsible for the reduction of Au ions from solution, with the formation of spherical nanoparticles [18]. Then the GNPs were introduced in the gel and the system was stirred 4 hours until a homogeneous dispersion of GNPs was obtained. The samples contain 1% wt polymer and 20% wt GNP. After that the composition was neutralized with TEA following the same procedure used for the neutralization of the gels without TEA. All the precursors, PAA, TEA, tetrachloroauric acid and sodium citrate were purchased from Aldrich and used without further purification.

The UV-VIS spectra were recorded with a Jasco V-670 system with scan speed 200 nm/min, UV-VIS bandwidth 2 nm, and NIR bandwidth 8 nm. The fluorescence investigation was done with Jasco SP6100 system.

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