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OBSERVATION OF UV-VIS ABSORPTION PROPERTIES OF SOME PVA MEMBRANES WITH SILVER NANOPARTICLES

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ABSTRACT. The UV-vis absorption properties of polyvinyl alcohol (PVA) membranes containing 0.04 ml silver nanoparticles were investigated by UV-vis spectroscopy. The samples were investigated in initial state and after UV and gamma exposure. Some modification appears in the spectra of samples containing AgNPs after gamma irradiation. This behaviour indicates modifications induced in the local structure of the polymeric membranes.

Keywords: *Poly (vinyl alcohol), AgNPs, gamma irradiation, UV-vis spectroscopy*

INTRODUCTION

Poly (vinyl alcohol) (PVA) is a water-soluble polymer widely used in industry because of its high capability to form aqueous membranes and gels [1, 2]. Owing to hydroxyl groups present in each unit, PVA is characterized by strong hydrophilic and hydrogen bonding character; thus, it forms hydrogels applied in medicine and pharmacy [3, 4, 5]. The first polymeric matrices doped with nanoparticles were obtained by Koon and coworkers in 1984 [6, 7]. The metal nanoparticles doped in polymer have many applications, such as optical filters, magnetic and optical data storage [8].

The aim of our study is the investigation of the properties of PVA doped with AgNPs, after UV and gamma irradiation. To monitor the effect of doping on the optical properties, the UV-vis spectra were recorded for samples in initial state and after exposure.

RESULTS AND DISCUSSION

The main effect of UV irradiation of materials is the excitation of electronic orbital or modification of vibration state of molecular bonds. At high doses ionization, scission of molecules or conformational changes can appear, which can induce modification of the absorbance spectrum in the UV-vis domain. These effects can be observed in systems containing only a single component, but also for doped system containing many components, i.e.

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binary systems formed by polymers doped with different nanoparticles. For such systems the spectrum contains the absorption characteristics of both components. To observe this behaviour we compared the absorption spectrum of pure polymeric matrix with the spectrum of doped membrane before UV irradiation. The pure polymer is characterised by a single absorption band centred at 275 nm, (Figure 1, curve A). As reported in literature this band may be assigned to a $\pi \rightarrow \pi^*$ transition. This transition was related to the carbonyl groups (C=O) associated with ethylene unsaturated bond (C=C) of the type – $(CH=CH_2)$ CO-. The existence of carbonyl functionalities is probably due to oxidation during manufacturing and processing [9, 10]. This band appears also in the spectrum of the doped membrane, but its amplitude is greater. A supplementary band, centred at 450 nm, appears in this spectrum. As reported in literature, this band is assigned to the plasmonic resonance frequency of silver nanoparticles [11].

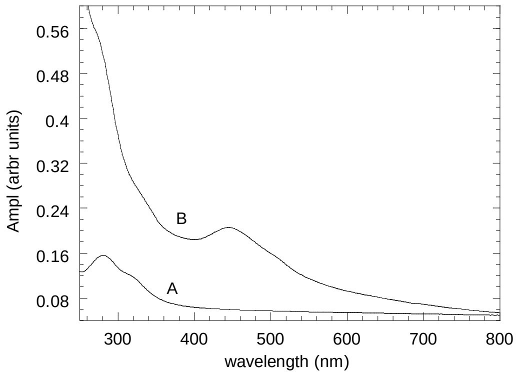

Figure 1. The UV-vis absorption spectra for the non doped and doped PVA membrane before irradiation. A). non doped sample; B). doped sample

The doped membranes were exposed to UV radiationat 254 nm for different time intervals and the absorption spectra were recorded. The main characteristics of the spectrum - the absorption bands at 275 and 450 nm - appear in all spectra but some differences can be observed depending on the dose of radiation. The absorption peaks at 450 nm were blue shifted as the time of UV irradiation increases, (Figure 2). After 4 hours of irradiation the absorption peak shifts to 432 nm. Blue shift means increasing of plasmonic resonance frequency, an effect which can be correlated with the existence of reduced size silver nanoparticles [11]. Some mechanisms can be suggested. UV irradiation facilitates the rearrangement of local chains and the migration of isolated Ag^+ ions existing in the system. By a self assembled mechanism such ions can give rise to new nanoparticles with different size compared to those existing initially in the system. Other possible mechanism is the scission of conglomeration nanoparticles, effect induced also by the rearrangement of local polymeric chains under UV exposure. The intensities of the peaks increase with increasing the time of UV irradiation (1.1 a.u for 1 hour UV irradiation, 1.7 a.u for 2 hours UV irradiation, 2.1 a.u for 3 hours UV irradiation and 2.3 a.u for 4 hours UV irradiation) [12]. This behaviour indicates the increase of the proportion of the absorbents domains in the system by scission of conglomeration of nanoparticle or apparition of supplementary nanoparticle by self assembled mechanism.

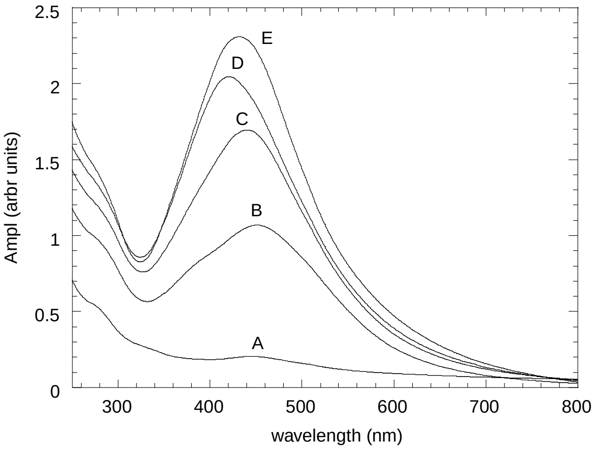

Figure 2 UV-vis absorption spectra for the doped sample before and after different time intervals of UV irradiation. A). before irradiation; B). after 1 hour irradiation; C). after 2 hours irradiation; D). after 3 hours irradiation; E). after 4 hours irradiation

Gamma irradiation produces the same effects as UV irradiation, except that processes requiring high energy, ionization or molecular breaking bonds, are more probable. Figure 3 shows the UV-vis spectrum of doped membrane before irradiation and the spectra for different gamma doses (729 Gy, 1478 Gy and 2217 Gy) [14]. For the unirradiated sample, the nearly zero absorption in the wavelength range 300-800 nm is followed by a continuous increase in the absorption in the wavelength range 200-300 nm. A very small absorption peak appears at 450 nm. When AgNPs is embedded in PVA membrane, the optical properties are the result of the electronic transition of the two materials. The absorbance in the domain 200-300 nm is characteristic to polymeric support, whereas the peak at 450 nm is assigned as plasmonic resonance band of the silver nanoparticles [13]. After gamma irradiation, the amplitude of absorption spectra increases. The amplitude of the 450 nm peaks is increasing from1.5 a.u at 739 Gy to 3.3 a.u at 1478 Gy and 4.6 a.u for the radiation dose at 2217 Gy).

The important enhancement in absorption is in agreement with the colour change of PVA samples, which varies from transparent for the unirradiated membrane to yellowish brown for the membrane irradiated with the highest irradiation dose (2217 Gy). This band is assigned as plasmonic resonance frequency of silver nanoparticles and it is associated to the striking colors of the samples [12]. As the radiation dose increased the plasmonic band is shifted from 450 to 432 nm. The plasmonic peak gets narrower and sharper and also increases in the intensity with increasing radiation dose from 0 Gy to 2217 Gy. As in the case of UV irradiation, we suggest as explanation the apparition of spontaneous silver nanoparticles or scission of conglomeration of such systems. The spontaneous formation of silver nanoparticles can be attributed to the direct redox between PVA and Ag^+ stimulated by the gamma irradiation. However, the amplitude of the absorption peak is greater in the case of gamma-irradiated samples, compared with the UV-irradiated samples, which suggests a greater probability of apparition of spontaneous silver nanoparticles or scission of agglomerations of nanoparticle under gamma irradiation.

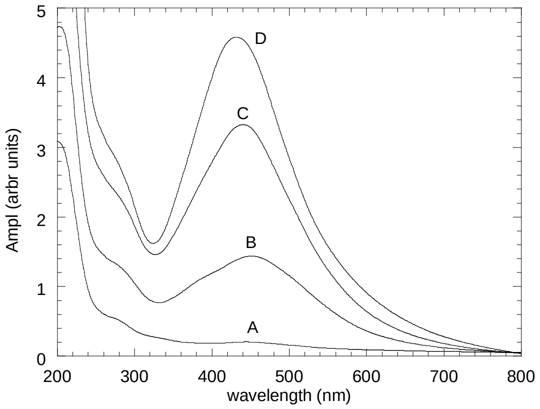

Figure 3 The UV-vis absorption spectra for doped samples irradiated at different gamma doses. A). before irradiation; B). after 739 Gy; C). after 1478 Gy; D). after 2217 Gy

CONCLUSIONS

The effect of UV radiation and gamma irradiation on the properties of PVA with AgNPs was observed by UV-vis spectroscopy. Compared with the spectrum of pure polymer, a supplementary absorption peak appears at 450 nm, attributed at AgNPs. The amplitude of the 450 nm absorption peak of doped membranes is increasing continuously with the time of UV exposure. A similar behaviour was observed after gamma irradiation, but the absorption effect is enhanced. This behaviour is associated with the spontaneous formation of silver nanoparticles or scission of agglomeration of such systems.

EXPERIMENTAL SECTION

The aqueous PVA membrane had a polymer concentrations 20% in initial state, to which 0,04 ml AgNPs was added. The PVA was obtained by mixing the polymer with distilled water at 55^0 C for 3 hours, until a homogeneous dispersion was obtained. A 10-mL volume of 1.0 mM silver nitrate was added dropwise (about 1 drop/second) to 30 mL of 2.0 mM sodium borohydride solution that had been chilled in an ice bath. The mixture was stirred vigorously on a magnetic stirrer. The solution turned light yellow after the addition of 2 mL of silver nitrate and a brighter yellow when all of the silver nitrate had been added. The entire addition took about three minutes, after which the stirring was stopped and the stir bar removed. These samples were analyzed in their original state and after UV and gamma exposure. UV irradiation was achieved with a VL 215 G lamp at 254 nm and 76 mW/cm^2. The gamma exposure was performed using a ^{60}Co source for different time intervals corresponding to 739 Gy and 2217 Gy. The UV-vis spectra were measured with a Jasco V-670 system with scan speed 200 nm/min, UV-vis bandwidth 2 nm, and NIR bandwidth 8 nm.

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