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UV ABSORPTION PROPERTIES OF DOPED PVA TiO_2 MEMBRANES

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ABSTRACT. The effect of UV exposure on PVA membranes doped with TiO_2 was observed by UV-vis and Raman spectroscopy. After several hours of moderate UV exposure, the absorption coefficient of non doped membranes is modified. The absorption property of PVA was enhanced by addition of TiO_2.

Keywords: *PVA, UV-vis Raman spectroscopy,* TiO_2

INTRODUCTION

Poly vinyl alcohol (PVA) is one of the most popular polymers with applications in different domains of activity, beginning with the industry, and finishing with the medicine [1, 2, 3]. In medicine it is used as matrix for drug controlled release, in making artificial blood vessels, or contact lenses [4, 5]. During these applications, especially in the skin care, the polymeric matrix may be deliberately or accidentally exposed to UV radiation. Such high energy radiation can have destructive effects on the microscopic structure of the polymer. The interest is to maintain unaffected, as long as possible, the properties of the polymeric matrix against the aggressive actions. PVA provides only a weak protection against UV radiation at 291 nm. Usually the protection against this radiation is enhanced by adding TiO_2, which is well tolerated by the biological tissues at small concentration [6, 7]. The aim of our work was to observe the behaviour of this polymeric matrix submitted to UV exposure, and the possibility to enhance the UV absorption property by addition of TiO_2. The investigations were done by methods sensitive on molecular scale, Raman and UV-vis spectroscopy.

RESULTS AND DISCUSSION

We observed the absorption property as a function of UV time exposure. In Figure 1 are presented the absorption spectra for the membrane with polymeric concentration 20% in initial state and after 4 hours of UV irradiation.

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The spectrum of the non irradiated sample is broad, showing an important absorption in the domain 250-350 nm, (Figure 1 curve B). The maximum absorption peak appears at 281 nm and its amplitude is $A_{0\ 20}$=0.156 a.u. The width of the spectrum suggests a large distribution of the energetic states of absorbent molecules, determined by rotation and vibration of molecules.

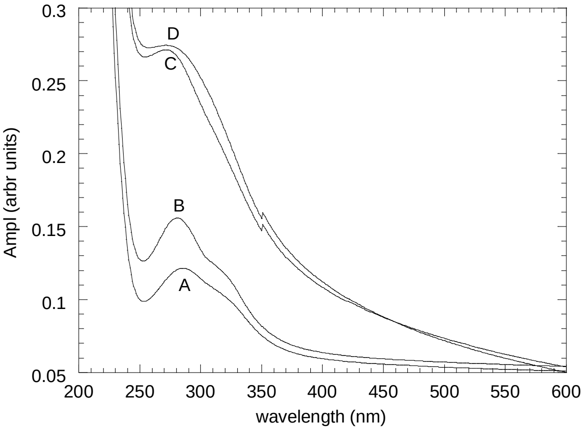

Figure 1 The UV-vis absorption spectra of doped and non doped membranes: Curve A the non doped membrane after 4 hours UV irradiation; Curve B the non doped membrane before irradiation; Curve C membrane with 10% TiO_2 before irradiation; Curve D membrane with 10% TiO_2 after 4 hours UV irradiation.

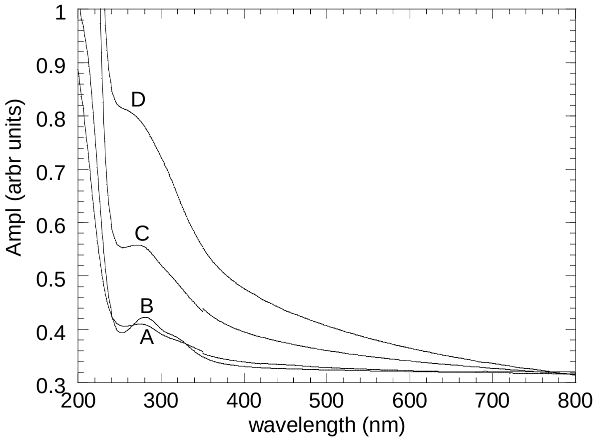

Figure 2 The UV-vis absorption spectra for the non doped membrane and membranes with different content of TiO_2, before irradiation. Curve A, the non doped membrane; Curve B, with 1% TiO_2; Curve C, with 10% TiO_2; Curve D, with 20% TiO_2

When the time of exposure increases, the amplitude of the peak decreases continuously. After 4 hours of irradiation its amplitude is $A_{4\ 20}$=0.12

a.u., (Figure 1 curve A). The intense UV irradiation facilitates the apparition of local order, even formation of crystalline domains in polymeric materials, and the polymeric network became more rigid [8].These modification of the molecular order are responsible for the modification of the absorption spectrum after irradiation.

Enhancement of the UV absorption property can be obtained by addition of different inert compounds to the polymeric matrix. We selected TiO_2 because it is known as one of the substances characterized by very good absorbance in the UV domain and also for its compatibility with biological tissues [9]. We observed the absorption properties of polymeric membranes doped with different concentrations of TiO_2 in initial state and after different time intervals of UV irradiation. At 1% concentration the absorption spectrum is very little modified. As the concentration of TiO_2 increases, the absorption peak is observed at the same wavelength but its amplitude increases continuously, being few times greater than that of the non doped membrane, (Figure 2). This behaviour shows clearly the enhancement of absorption properties after addition of TiO_2 [10].

The doped membranes were subsequently irradiated for different time intervals with UV radiation and, the absorption spectra were recorded again. For all the concentrations of TiO_2 the amplitude and the shape of absorption spectra are very little modified after irradiation, (Figure 1 curves C and D). This behaviour is contrary to those of non doped membranes, where the absorption is reduced after irradiation. The doped membranes appear to be more stable under UV irradiation compared with the non doped ones.

In the next stage of our work we were interested to observe the existence of possible interaction between the polymeric matrix and the TiO_2, and possible modifications on the molecular structure of doped and non doped membranes after UV exposure. For this aim we compared the Raman spectra of non doped and doped membranes before and after UV irradiation, (Figure 3). The spectrum of non doped membrane before irradiation contains well defined vibration bands in the domain 1200-1600 cm^{-1}, (Figure 3 curve D). The most intense bands are assigned as follows: 1290 cm^{-1} – CH wagging, 1365 cm^{-1} – CH- bending and OH – bending; 1414 cm^{-1}– CH_2 bending. These bands appear also in the spectrum of the doped membrane, before irradiation, at the same wave number. Supplementary bands appear at 400 cm^{-1}, 514 cm^{-1} and 638 cm^{-1} for the samples containing TiO_2. As reported in literature, in the domain 200-800 cm^{-1} TiO_2 exhibits three vibration bands at 400, 514 and 638 cm^{-1} [11]. The apparition of vibrational bands of PVA and TiO_2 at the same wave number before and after doping suggests no interaction between the polymeric matrix and the TiO_2, and that the chemical structure of both components remains unchanged after doping.

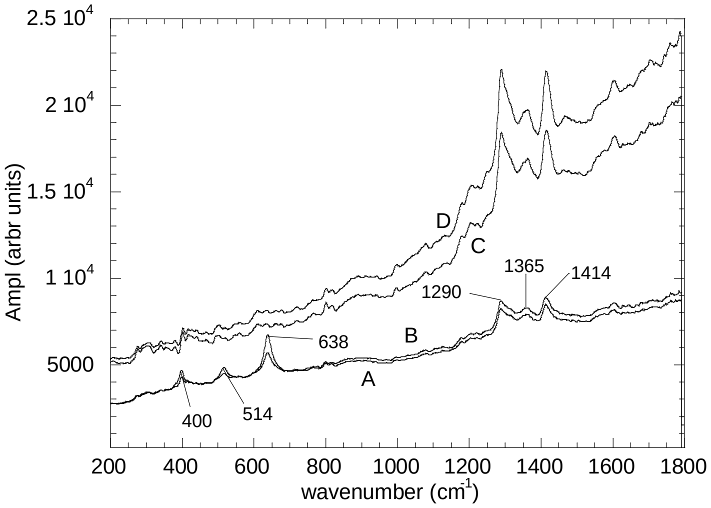

Figure 3 The Raman spectra of doped and non doped membranes. Curve A, membrane with 20% TiO_2 before irradiation; Curve B, membrane with 20% TiO_2 after 4 hours irradiation UV; Curve C, non doped membrane after 4 hours irradiation UV; Curve D, non doped membrane before irradiation

The same analysis was done after UV irradiation. The spectra of doped membranes are very similar before and after irradiation without modifications, (Figure 3 curves A and B). The spectra of non doped membranes show some differences in the domain 1200-1600 cm^{-1} before and after irradiation. The vibrational bands appear at the same wavelength in both spectra, but the amplitude of irradiated one is reduced, (Figure 3 curve C). This behaviour indicates no modifications on the chemical structure of components after UV irradiation.

CONCLUSIONS

The effect of UV radiation on the properties of PVA was observed by UV-vis and Raman spectroscopy. The amplitude of the absorption peak of PVA diminishes continuously with the time of UV exposure. This effect suggests an effect of crystallization induced by iradiation. The absorption property of PVA is enhanced by addition of TiO_2. The absorption coefficient increases with the concentration of dopant. The absorption properties of doped membranes are very little affected by UV irradiation. This fact demonstrates the stabilization effect of TiO_2 on the absorption property. Raman analysis of doped and non doped membranes indicates no modification of chemical structure after UV exposure.

EXPERIMENTAL SECTION

A PVA membrane with polymeric concentrations of 20% was employed, in initial state and after addition of TiO_2. The membrane was obtained by mixing the polymer with distilled water, at constant temperature 25^0 C, during several hours, until a homogeneous dispersion of polymer was obtained. Then the gel was displayed on a glass plate and kept 24 hours in dark, at room temperature, until the water evaporates. To obtain doped samples, the TiO_2 was introduced in the polymeric gel in concentration 1%, 10% and 20%, mixed many hours, and then dried on open air [12]. These samples were analyzed in their original state and after UV irradiation at different intervals of time. The UV irradiation was performed with an VL 215 G lamp, at 254 nm and 76 mW/cm^2 intensity. For all the samples 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. The Raman investigations were performed with R 3000 CN systems, with excitation power 150 mW at wavelength λ= 785 nm.

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