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OPTICAL AND ELECTRONIC PROPERTIES OF METAL DOPED POLYMERS FOR INTEGRATED OPTICS

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The electronic mechanism responsible for the optical behavior of the mixed Fe and Sn doped polymers were studied in comparison with the correspondent single doped (Fe or Sn) ones. Optical absorption as well as ^{57}Fe and ^{119}Sn Mössbauer measurements were performed on different UV exposed films. The new data provided the role of each element from the pair on the involved electronic mechanism induced by irradiation.

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1. Introduction

The doped polymers may present useful applications in integrated optics or in real time holography. In order to tailor materials with improved properties within the doped polymer class, it is necessary to understand and control the electronic mechanisms involved in the optical behavior. The present work reports on the electronic transfer phenomena appearing in pair mixed valence metal doped polymers under the UV exposure. The electron delocalisation processes and the metal local configurations obtained by Mössbauer spectroscopy are corroborated with optical data provided by optical absorption measurements.

2. Experimental

In order to understand better the acceptor/donor processes between the doping metal and polymer matrix and also to increase the material sensitivity, different elements or pairs of elements were doped in various polymeric matrices. Two elements, Fe and Sn, and their equatomic combination have been used as doping metals of PVA (Polyvinyl alcohol), PMMA (Polymethylmethacrylate), PS (Polystyrene), PAA (Poly acrylicacid) polymers. The inorganic salts were added in the solution of polymers previously dissolved in water (PVA, PAA) or suitable organic solvents (PMMA, PS). Thick polymer films (tenths of microns) were prepared for Mössbauer measurements by gravity deposition from solution on glass supports, whereas much thinner films (a few μm) were prepared by spin coating for optical absorption measurements. The films were exposed to UV light (λ < 400 nm, P = 25 mW/cm^2) in subsequent steps, up to 600 s. The absorption spectra

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were recorded using a standard SHIMADZU UV-VIS Spectrometer. ^{57}Fe and ^{119}Sn Mössbauer spectra were obtained in a conventional set-up with symmetrical waveform.

3. Results and discussion

In our previous papers it was proved that for the iron doped polyvinyl alcohol (PVA:Fe) the optical parameters are strongly related to the modifications of the Fe valence state under the UV exposure [1-3]. Both the refractive index and the absorption coefficient are changing due to a local electron transfer from the PVA matrix to the Fe^{3+} ions. The Mössbauer spectra show the coexistence of Fe^{3+} and Fe^{2+} species, the later increasing in relative content with the UV exposure energy. The absorption coefficient is related to electronic charge redistribution around the Fe^{2+} configurations, whereas the refractive index is strongly influenced by the the Fe^{2+}/Fe^{3+} ratio. In polymers containing only Fe doping element, the acceptor–donor mechanism (each Fe ion receives an electron from the polymer matrix) is different compared to the Sn doping case, were an opposite behavior (each Sn ion transfers two electrons to the polymer matrix) was observed [4]. The transfer is more efficient in polymer matrix containing residual water. In spite of an expected higher sensitivity for the Sn doped polymers compared with the Fe case, the relatively smooth changes in the absorption spectra under the UV exposure have been related to the difficulty to stabilize higher amounts of Sn^{2+} in the initial state.

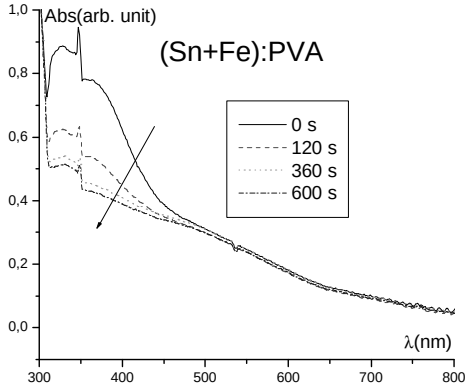


Fig. 1. Optical absorption spectra taken on a doped PVA:(Fe+Sn) sample after different UV exposures.

Hetero-doping elements, as the (Fe+Sn) pair, should manifest in a polymer a mechanism induced by the simultaneous presence of the two different doping metals having multiple valence states in the matrix. The absorption spectra of an hetero-doped PVA:(Fe+Sn) polymer versus different exposures are presented in Fig. 1. The absorption coefficient is decreasing in the UV range (below 450 nm), in agreement with either an $Fe^{3+} \rightarrow Fe^{2+}$ [2] or an $Sn^{2+} \rightarrow Sn^{4+}$ [4] transformation. However, these changes are less significant than in PVA:Fe doped polymers [1,2], but more significant than in PVA:Sn systems. From a glimpse to Fig. 1 and Fig. 2 one can see that the optical changes are relatively more effective in PVA that in PAA doped polymers, namely in polymers containing more residual water. It is worth mentioning that in doped polymers without residual water, the optical changes are even less pronounced. In order to elucidate the electronic mechanisms induced by the UV exposure on the hetero-doped PVA:(Fe+Sn) polymers, both ^{57}Fe and ^{119}Sn Mössbauer experiments were performed on different exposed samples.

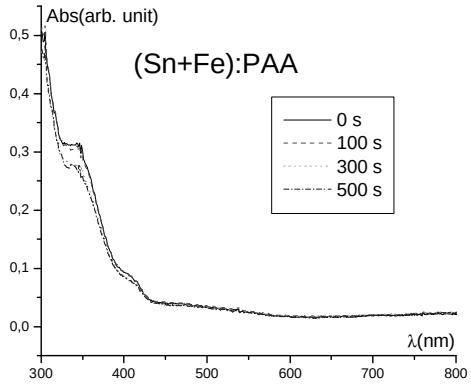


Fig. 2. Optical absorption spectra taken on a doped PAA:(Fe+Sn) sample after different UV exposures.

The ^{57}Fe Mössbauer spectra put in evidence three Fe positions. The central doublet with low isomer shift (IS = 0.18 mm/s) and quadrupolle splitting (QS = 0.3(1) mm/s) belongs to a Fe^{3+} position, whereas the two doublets with much higher IS and QS (IS_1 = 1.1(1) mm/s, QS_1 = 2.1(1) mm/s and IS_2 = 1.1(1) mm/s, QS_2 = 3.1(1)) were assigned to two Fe^{2+} positions with different distortions. Fig. 3 shows that the total number of the Fe^{2+} ions remains unchanged vs. the exposure energy as resulted from the almost constant relative area of the Mössbauer patterns of these species and, consequently, can not be related to the variation of the absorption coefficient in the UV range.

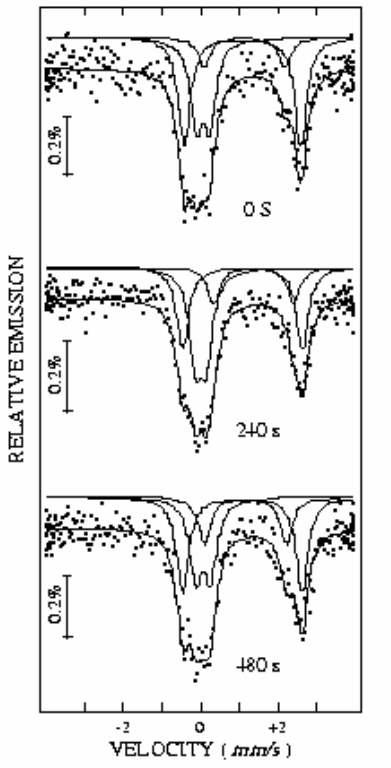


Fig. 3. ^{57}Fe Mössbauer spectra taken on a hetero-doped PVA:(Fe+Sn) sample after different UV exposures.

The ^{119}Sn Mössbauer spectra show also 3 different Sn positions. The central doublets with low IS (IS_1= 0.2(1) mm/s and IS_2=0.3(1) mm/s) were assigned to two Sn^{4+} with different distortions, whereas the doublet with high IS (IS = 3.2(1) mm/s) belongs to an Sn^{2+} phase (Fig. 4). After an exposure of about 300 s, the Sn^{2+} species transforms almost completely into Sn^{4+}.

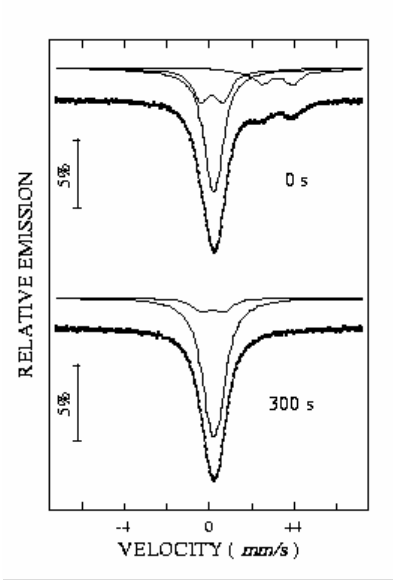


Fig. 4. ^{119}Sn Mössbauer spectra taken on a hetero-doped PVA:(Fe+Sn) sample after different UV exposures.

The variation of the relative content of the active Sn^{2+} and Fe^{3+} species in hetero-doped PVA:(Fe+Sn) polymers vs. the exposure time, are shown in Fig. 5. In the same figure there are also presented the variations of the two species in the homeo-doped PVA:Sn and PVA:Fe polymers, respectively, as previously mentioned in [4]. It can be seen that in the PVA:Fe polymer, the initial dominant Fe^{3+} species changes its relative content with more than 35% after an exposure time of 8 min, whereas in the hetero-doped polymer the relative content of these species, already in minority in the unexposed sample, remains almost constant under the UV exposure. On the contrary, the Sn^{2+} relative content, decreases more drastically in the hetero-doped polymer (about 15 %), compared with a much smaller decrease (4%) in the homeo Sn doped polymer. It is worth noticing that the decrease of the absorption coefficient in the UV range is related to the transformation of the initially present Sn^{2+} and Fe^{3+} active species. Therefore, the actual results show that the active ions responsible for the variation of the absorption coefficient under the UV exposure in hetero-doped PVA:(Fe+Sn) polymers are mainly the Sn^{2+} ones.

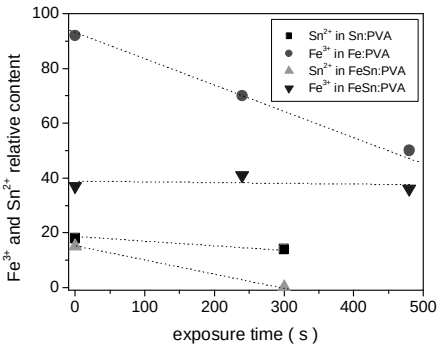


Fig. 5. The variation of the relative content of Sn^{2+} and Fe^{3+} species vs. the exposure time in hetero-doped PVA: (Fe+Sn) and the corresponding homeo-doped polymers.

4. Conclusions

The electronic mechanism influencing the optical absorption coefficient under the UV exposure in hetero-doped PVA:(Fe+Sn) polymers consists mainly in the valence change of the initial Sn^{2+} ions. The presence of the Fe ions (mainly as Fe^{2+}) facilitates the decrease of the local electronic charge in the matrix around the Sn ions, providing an easy electron transfer process $Sn^{2+} \rightarrow Sn^{4+}$ compared to the case of the homeo Sn doped polymer. Therefore, the electronic transfer in this case is completed by the mutual presence of two types of ions and the resulted hetero-doped material gives rise to improved and attractive performances, compared with the homeo-doped ones. Polymer composites containing pair doping elements and improved properties will be further developed for other applications.

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