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Effect of gamma irradiation on the color, structure and morphology of nickel-doped polyvinyl alcohol films: Alternative use as dosimeter or irradiation indicator

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ABSTRACT

Nickel-doped poly vinyl alcohol (PVA) films were developed for potential application in industrial sectors like radiation processing. We report in this paper the results of an experimental investigation of ^{60}Co source γ-radiation effect on colorimetric, structural and morphological properties of PVA films doped with 0.5% Ni^{2+} ions (PVA/Ni^{2+}). The PVA/Ni^{2+} films were irradiated by different gamma-radiation doses varying from 5 to 100 kGy. Color modification of films were studied using L^*, a^* and b^* color space measurements as function of the γ-dose and post-irradiation time. The visual change in all samples was verified by microstructure analysis, Fourier transforms infrared (FTIR) spectroscopy, X-Rays diffraction (XRD) and scanning electron microscopy (SEM). The color space exhibited a linear dose response at a dose ranging from 5 to 50 kGy, and then it reached saturation for higher γ-doses. The calculated color changes (ΔE) show a linear dose response relationship from 9.90 to 115.02 in the dose range from 0 to 50 kGy. It showed also the activation of stable color centers. The variability of the color change did not exceed 3% during 80 h (h) post-irradiation. Furthermore, the microstructure analysis evidenced that the color modification due to the optical activation of nickel-oxide (NiO) color center were obtained by complexing Ni^{2+} ions in irradiated PVA films. The obtained results inspire the possibility to use PVA films for the control process in industrial radiation facilities in dose range 5–50 kGy.

1. Introduction

Nowadays, transition metal-doped polymers are being considered as versatile materials in many scientific applications leading to industrial technological advancements [1,2]. Such applications appear to be highly serviceable in many fields such as electronic devices, electromagnetic interference shielding, solar cells, energy storage batteries and thick film electrode materials [3–5]. The transition metal-doped polymer gives the opportunity to improve their physical, mechanical, optical and electrical properties. Indeed, the addition of transition metal in polymer matrix has considerable effects in structure that may introduce new electronic levels into electronic band structure. Moreover, it can affect dramatically the optical, thermal, and electrical properties of a polymer matrix [6–8].

Due to their good stability, easy process ability and its wide variety of applications, as well as interesting optical, electrical and mechanical properties, Nickel-doped PVA films have attracted the interest of many researchers [9,10]. PVA polymer, a nontoxic synthetic polymer which can be considered amorphous or semi-crystalline, is soluble in water. It has a potential use for thin film preparation for organic solar cells [11]. Several approaches have been employed to change the structural, optical, electrical and thermomechanical properties of PVA films [9–12]. The doping combined with γ-irradiation processing is an interesting challenge, allowing producing polymer-metal compounds [4,13]. This method has opened a new gateway to improve the performance of materials in many potential applications like optical devices,

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biomedical science, coating materials and sensors [14,15]. The effect of γ-irradiation on the structure and optical properties of polymer films have received much attention in recent research due to their increasing application in radiation processing. The interaction between γ-irradiation and polymer films can induce 'permanent' and 'annealable color centers', corresponding to a stable alteration of the molecular structure and chemical reaction between radical species, respectively [16–18].

Although previous work has been conducted to reveal the structural and optical change of doped polymer under γ-irradiation, research on PVA/Ni^{2+} films was limited. Gamma-irradiation of pure PVA causes chemical defects such as production of radical species, hydrogen evolution, molecular changes, scissions and crosslinking. Furthermore, reactions between the radical species and oxygen lead to the formation of carbonyl and unsaturated carbonyl compounds. These compounds may cause the observed yellow color of irradiated pure PVA film.

Moreover, doping ions acts as recombination centers for radical species. Consequently, color change of the film can be observed. It is necessary to block these sites by controlling the monomer concentration and the mass ratio of metal introduced in the film. The stability of the color may be suitable for the development of a promising candidate γ-radiation sensing material.

The aim of this work is to explore the suitability PVA/Ni^{2+} films as a candidate for the process control in industrial irradiation. Given its industrial benefits, PVA/Ni^{2+} might be used as color indicator and introduced into the measurements of radiation dose. We describe experiments carried out to investigate the effects of γ-irradiation at various doses on colorimetric, structural and morphological properties of PVA/Ni^{2+} films. The color change was correlated with the absorbed dose. To the best of our knowledge, this is the first time that this type of materials has been explored as irradiation indicator and or radiation dosimeter.

2. Materials and methods

2.1. Materials

PVA powder hydrolyzed at 87–89% with molecular weight of 13,000–23,000 and dichloride nickel hexa-hydrate ($NiCl_2$ ($6H_2O$)) from Sigma- Aldrich were used to prepare PVA/Ni^{2+} films. Fifteen grams of PVA powder were dissolved in 100 ml of ultrapure water under stirring for four hours at 60 °C temperature. When the polymer was completely dissolved, it formed a clear viscous solution, then, $NiCl_2$ ($6H_2O$) was added on to nickel with a molar ratio of [PVA]/[Ni^{2+}] = 400. The mixture was stirred for about 30 min and was poured into cylindrical Petri dishes. The obtained films had 20 mm in diameter and one mm in thickness.

Irradiations were not performed under homogeneous oxidation conditions: oxidation occurs mainly on the film's surface because of the low diffusion rate of oxygen in the polymer and of the film's thickness.

To obtain films suitable for characterization, it was necessary to remove the aqueous solution by drying the mixture in Petri dishes at room temperature (20–25 °C) for 15 days, followed by heat treatment at 60 °C for four hours.

2.2. Irradiation facility

Irradiation of PVA/Ni^{2+} films was carried out at the Tunisian semi industrial ^{60}Co gamma irradiation facility at the dose rate of about 43 Gy/min [19]. The dose rate assessment was done using Fricke chemical standard dosimeters [20] and the traceability was established with alanine/EPR dosimetry system in terms of absorbed dose to water traceable to Aérial Secondary Standard Dosimetry Laboratory (SSDL), Strasbourg-France. The PVA/Ni^{2+} films were placed into a polystyrene in-plant calibration phantom obtained from Risø Laboratory in order to ensure electron equilibrium conditions [21,22]. The PVA/Ni^{2+} films were irradiated at room temperature and covering the dose range from 5 to 100 kGy.

2.3. Characterization techniques

In order to investigate the effect of γ-irradiation on color changes, the PVA/Ni^{2+} films were recorded 30 min after irradiation by using portable Konica Minolta colorimeters CR 300. The color space: L^*, a^*, b, was measured according to CIE 1976 [23], where L^* is a measure of lightness black- white, the coordinate a^* represents the relative amounts of red- green and the b^* coordinate expresses the relative amounts of yellow- blue. Both a^* and b^* coordinate values vary approximately in the range from −100 to 100. The lightness L^* increases in range from 0 to 100 [16,24,25]. It is important to note that the color space system distinguishes color because it is close to human eye perception.

The color difference ΔE between the two colors of film before and after irradiation can be written as follows [16,24]:

$$\Delta E = \sqrt{(L^*-L_0)^2 + (a^*-a_0)^2 + (b^*-b_0)^2} \quad (1)$$

where , $a_0$and $b_0$describes the color space values for un-irradiated PVA/Ni^{2+} films. The average threshold of color difference between two points is the value above which the human eye cannot differentiate them. Many thresholds were previously published in literature [24–26]. The most suitable value of ΔE for two colors ≤3.7 is considered imperceptible by the human eye [24].

The Fourier transform infrared (FTIR) spectroscopy is used to study the structural and chemical properties of un-irradiated and irradiated polymer films. It can also characterize the crystalliniy degree of films [27]. Here, due to the thickness and opacity of films, Attenuated Total Reflection (ATR-FTIR) Fourier Transform Infrared measurement was recorded by Vertex 70 infrared spectrometer from 4000 to 400 cm^{-1} at a spectral resolution of 2 cm^{-1} and 32 scans were averaged.

X-ray diffraction measurement were conducted by using Brucker D8 advance with CuKα (λ = 1.541 A° in the 2θ range 0–80). The obtained results were analyzed with X'PertHigh Score Plus program. The morphology of films was examined by scanning electron microscopy (SEM, JEOL JSM-6700) operating at low accelerating voltage of 5 kV to avoid the deterioration of samples.

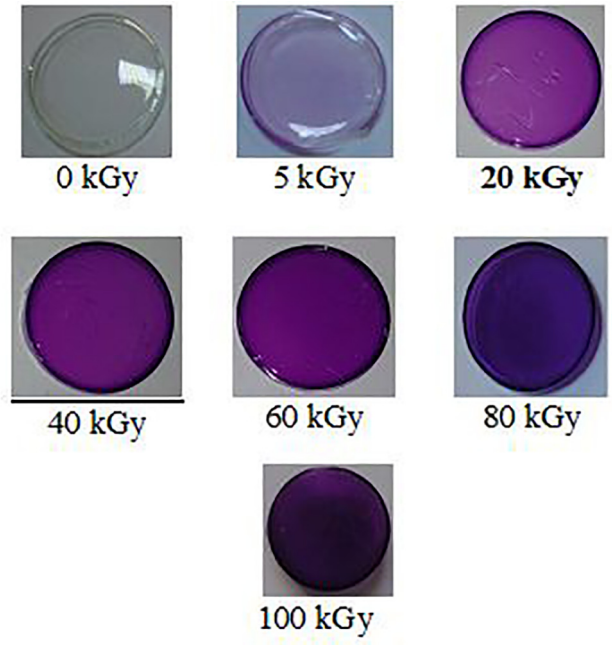

Fig. 1. Color change photos for PVA/Ni^{2+} films at different irradiation doses.