Effect of ion and electron beam irradiation on surface morphology and optical properties of PVA (Post-print)

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Date: 2023-06-18T00:00:00+00:00

Abstract

Polyvinyl alcohol (PVA) is a well-known friendly polymer for paper-making, textiles, and a variety of coatings, biomedical applications such as artificial pancreas, synthetic vitreous body, wound dressing, artificial skin, and cardiovascular device. In this paper, ion/electron beam is employed to get insight into the irradiation effect on surface morphology and optical properties of PVA polymer. UV-Vis spectra are recorded to investigate the effect of induced defects on the optical band gap and the formed carbon clusters size. Scanning electron microscopy (SEM) is used to relate and investigate surface morphology and optical properties of the target polymer with different doses (15, 30 and 60 min). Also, PVA polymer is subjected to theoretical studies by using semi-empirical PM7 quantum chemical method.

Full Text

Effect of Ion and Electron Beam Irradiation on Surface Morphology and Optical Properties of PVA

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Polyvinyl alcohol (PVA) is a well-known environmentally friendly polymer used in paper-making, textiles, and various coatings, as well as biomedical applications such as artificial pancreas, synthetic vitreous body, wound dressing, artificial skin, and cardiovascular devices. In this study, ion and electron beams are employed to investigate irradiation effects on the surface morphology and optical properties of PVA polymer. UV-Vis spectra are recorded to examine the effect of induced defects on the optical band gap and the size of formed carbon clusters. Scanning electron microscopy (SEM) is used to correlate and investigate the relationship between surface morphology and optical properties of the target polymer at different irradiation doses (15, 30, and 60 min). Additionally, PVA polymer is subjected to theoretical studies using the semi-empirical PM7 quantum chemical method.

Keywords: Electron/ion beams, Optical band gap, Polyvinyl alcohol (PVA), UV-Vis spectra

I. INTRODUCTION

Polymers have experienced rapid development during the last few decades because of their low cost, easy processability, low weight, high-quality surfaces, and straightforward fabrication of thick and thin samples. The most significant interest in polymers stems from their special physico-chemical properties, such as ion transport, electrochemical effects, photoactivity, catalytic behavior, and electronic junction effects.

Ion/electron beam bombardment of a solid target causes significant transformation to the structure and properties of the bombarded surface. When a beam of energetic particles enters a solid, several processes are initiated in the interaction area. A fraction of the particles are backscattered from the surface layers, while others are slowed down in the bulk. The collision induces secondary processes such as recoil and sputtering of constituent atoms, defect formation, electron excitation and emission, and photon emission. Thermal and radiation-induced diffusion contribute to various phenomena including mixing of constituent elements, phase transformation, amorphization, crystallization, track formation, and permanent damage.

Polyvinyl alcohol (PVA), an important polymer available in powder, fiber, and film forms, is a water-soluble polymer widely used as paper coating agents, adhesives, and films. PVA has been utilized in adhesives for automotive safety glass, textile sizing and finishing, paper sizing and coating, and as a binder for ceramics, foundry cases, nonwoven fabric, and various pigments. Additionally, PVA acts as an electron donor in the photoreduction process.

In this work, 4-mm thick sheet samples were prepared from aqueous solutions of different PVA concentrations (2 g, 4 g, 5 g, and 6 g). It was found that the

2 g and 4 g PVA sheets produced the best results. Consequently, the samples were exposed for 15, 30, or 60 min to N^+ ion or electron beams produced from a modified saddle field source. The irradiated samples were characterized by UV-Vis spectroscopy to determine the band gap energy and number of carbon atoms per conjugation length in PVA film, and by scanning electron microscopy (SEM) to examine surface morphology and optical properties.

II. METHODOLOGY

Different concentrations of polyvinyl alcohol (2 g, 4 g, 5 g, and 6 g) were dissolved in 100 mL distilled water, kept at 70°C for 6 h for complete dissolution, cast on a glass plate, and left to dry for 3 days. Several trials were performed from 2-6 g to obtain smooth, uniform, and homogeneous surfaces, and the sheet samples prepared from 2 g and 4 g PVA solution exhibited the best surface quality. The sample sheets were irradiated for 15 min, 30 min, and 60 min using a low-energy dual ion/electron beam source with nitrogen gas.

Molecular orbital calculations were performed using the semi-empirical PM7 method described in Refs. [15, 16]. Semi-empirical PM7 calculations have proven effective for predicting geometric properties and vibrational frequencies of transition metal and organometallic complexes. The modeling program was run on a microcomputer under the molecular orbital calculation package MOPAC2012. Figure 1 [Figure 1: see original paper] shows the geometrical structure of PVA and its numbering system.

A. Experimental Details

The experimental setup utilized for ion/electron beam treatment is a home-built system shown in Fig. 2 [Figure 2: see original paper] [19]. It consists of two copper anode rods surrounded by a cylindrical cathode. Inside the cylindrical cathode is a Perspex cylinder having two opposite holes of Φ5 mm for producing ion/electron beam current. PVA samples were placed on a Faraday cup at a distance of 1 cm from the cylindrical cathode.

The film samples were irradiated in a vacuum chamber at 10^{-5} mbar. The ion fluence (Φ, in ions/cm^2) was estimated by $\Phi = It/(qeA)$ [3, 20], where I is the ion beam current (A), t is the irradiation time (s), q is the charge state of the ion (q = 1 in the present study), e is the electron charge (1.6×10^{-19} C), and A is the beam spot area (cm^2).

III. RESULTS AND DISCUSSION

In this study, the system was evacuated to about 3×10^{-5} mbar to remove residual gases before nitrogen gas injection. The source apparatus was polished and washed with acetone. Polishing the electrodes removes irregular parts from their surfaces and contamination due to eroded materials from the discharge.

A. Operating Characteristics of the Dual Beam Source

Nitrogen ion and electron beams from the modified saddle field source were used to irradiate the PVA films. As shown in Table 2 , the PVA samples were irradiated by N^+ ions or electrons for 15 min, 30 min, or 60 min, at N^+ ion fluence of 2.81×10^{17}-1.12×10^{18} ion/cm^2, and electron fluence of 4.21×10^{17}-1.68×10^{18} electrons/cm^2.

TABLE 2. Irradiation parameters of PVA samples.

Samples	I (15 min)	II (30 min)	III (60 min)
Beam fluence (10^{17} ions/cm^2)			
N^+ ion	2.81	5.62	11.2
Electron	4.21	8.42	16.8

Operation characteristics of the ion/electron source were studied under different experimental conditions. Figure 3 Figure 3: see original paper shows the discharge characteristics using nitrogen gas, i.e., the relationships between discharge voltage and current at different gas pressures. The discharge current increases with discharge voltage, characteristic of abnormal glow discharge [21, 22]. Figure 3(b) shows the ion beam efficiency, i.e., the relationship between output ion beam current and discharge current at different nitrogen gas pressures. The ion beam current increases with discharge current and reaches its maximum value at N_2 pressure of 1.3×10^{-3} mbar [21]. The investigation of electron beam characteristics under different experimental conditions will be published elsewhere [23].

B. Optical Investigations

The pristine and irradiated PVA samples were characterized by UV-Vis spectrophotometer in the wavelength range of 100–1000 nm at room temperature. Figure 4 Figure 4: see original paper shows UV-Vis spectra of PVA sheets irradiated by N^+ ion beam for 0 min, 15 min, 30 min, and 60 min. A shift of the absorption edge towards longer wavelength with increasing ion dose is readily observed. The pristine sample was used as a reference material. UV-Vis spectroscopy provides information about the optical band gap energy (E_g), which is important for materials investigation. The absorption of light by polymeric materials in the ultraviolet and visible regions involves promotion of electrons in σ, π, and n-orbitals from the ground state to higher energy levels. The electronic transitions involved in the ultraviolet and visible regions are σ-σ, π-π, and n-π* [25]. In Fig. 4(a), two absorbance bands are related to the electronic transitions n-π and π-π*. The intensity of the two peaks increases with dose (0, 15, 30, and 60 min). The prominent peaks for ion effect are at (201, 288), (206, 275), (205, 283), and (205, 285).

The optical absorption coefficient (α) was calculated using Eq. (1) [26]:

$$\alpha(\nu) = 2.303[\log(I_0/I)]/l$$

where l is the sample thickness in cm, and $\log(I_0/I)$ is the absorbance with I_0 and I being the intensities of the incident and transmitted beams, respectively. The absorption coefficient near the band edge for non-crystalline materials shows an exponential dependence on photon energy (h) following the Urbach formula [27]:

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_u)$$

where α_0 is a constant, E_u is the Urbach energy interpreted as the width of the tail of localized states in the forbidden band gap, is the frequency of radiation, and h is Planck' s constant. The E_u values were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves.

Figure 4(b) shows the UV-Vis spectra for PVA sheets irradiated by electron beam for 0, 15, 30, and 60 min. The same behavior as in Fig. 4(a) can be observed. The two absorbance bands are related to the electronic transitions n-π and π-π^*. The intensity of the two peaks increases with electron dose. The two prominent peaks are related to criteria of the pure PVA irradiated by E-beams for 15, 30, and 60 min. The peaks for electron effect are at (205, 290), (206, 291), and (206, 275). Figure 4(b) shows a large shift with increasing electron doses, indicating a significant destructive effect that leads to the formation of more radicals and free electrons, hence the increase in UV-Vis spectra.

Tauc' s plot [28] is the standard method for determining the optical band gap (E_g) from UV-Vis spectrum by fitting the linear part of Tauc' s plots, $(\alpha h)^1/^n$ against (h), where α is the absorption coefficient, h is Planck' s constant, and is the frequency of incident UV-Vis radiation. The exponent n = 1/2 for direct electronic transition and n = 2 for indirect electronic transition [29]. The obtained band gaps are summarized in Table 3. The band gap of N^+ ion-irradiated PVA decreases with increasing dose, while the band gap of electron-irradiated PVA increases with dose. This variation in band gap can be attributed to structural deformation phenomena occurring in the polymer [30, 31]. In the case of indirect electronic transition, there is a shift in the position of the valence and conduction bands, requiring phonons to conserve momentum [32]. The phonon energy is the energy difference between direct and indirect band gaps [33].

The cluster size is correlated to the band gap energy and can be estimated from [34]:

$$E_g = 34.3N^{1/2}$$

where N is the number of carbon atoms per conjugation length. The calculated cluster sizes for PVA samples are given in Table 3 .

TABLE 3. Optical parameters of PVA films before and after ion/electron irradiation.

Samples	E_g (eV) Direct	E_g (eV) Indirect
Pristine	4.2	3.8
15 min EB	4.3	3.9
30 min EB	4.4	4.0
60 min EB	4.5	4.1
15 min N^+	4.0	3.6
30 min N^+	3.8	3.4
60 min N^+	3.6	3.2

Band gap energy decreases with increasing ion dose, while it increases with electron dose. This occurs because ions have a greater degradation effect than electrons. Ion/electron beam irradiation of polymers generates numerous charged species such as free radicals, ions, and other low molecular weight charged species, and the mobility of these species contributes to surface conductivity. The decrease in E_g of N^+ ion-irradiated PVA is attributed to a decrease in the mobility of molecular charged species compared with the band gap energy of electron-irradiated PVA.

C. Surface Morphology Analysis

SEM images were taken to visualize changes in the surface of PVA samples irradiated by N^+ ion beams for 15 min, 30 min, and 60 min [35] (Fig. 5 [Figure 5: see original paper]). The surface plot tool of ImageJ software was used to analyze the SEM image for pristine PVA and the N^+ ion-irradiated PVA samples. The N^+ ion beam effect is clearly visible. Among all N^+ ion-irradiated PVA samples, the surface morphology after 30-min irradiation (Fig. 5(c)) appears the most homogeneous and rough, representing the most suitable surface for substrate applications (coating and thin film deposition), as surface roughness enhances adhesion with added materials.

Figure 6 [Figure 6: see original paper] shows SEM images of PVA samples irradiated by electron beam for 15 min, 30 min, and 60 min. After 15-min electron beam irradiation, the surface was deformed (showing bubbles); after 30-min treatment, it showed less deformation (bubbles disappeared); and after 60-min treatment, surface deformation appeared again (without bubbles) and the surface became highly deformed and inhomogeneous.

The SEM images reveal significant differences before and after ion/electron beam treatment, indicating that roughness was induced on the PVA polymer surface following ion or electron treatment.

IV. CONCLUSION

A modified saddle field ion/electron source was used to modify the surface of PVA substrate for coating or thin film deposition. Nitrogen ion and electron beams were employed to irradiate the polymer surface, generating carbon clusters that improve surface conductivity with decreasing band gap under ion irradiation. SEM images reveal significant differences before and after ion/electron beam treatment, with the 30-min N^+ ion treatment producing the best surface homogeneity and roughness. UV-Vis spectra show small changes in energy gap and corresponding small changes in electrical properties. The induced defects on the polymer surface demonstrate that low-energy nitrogen ion/electron beam from a dual source is an effective tool (compared with large ion/electron accelerator machines) for improving surface morphology and enhancing the photoresponsive properties of treated samples.

ACKNOWLEDGMENTS

The authors are grateful to Dr. M. El-Desawy, Nuclear Physics Department, Nuclear Research Centre, Egyptian Atomic Energy Authority, Cairo, Egypt, for performing PM7 calculations using the semi-empirical PM7 quantum chemical method on PVA polymer.

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