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Synthesis and controlling the optical and dielectric properties of CMC/PVA blend via γ-rays irradiation

A.M. El Sayed *

Physics Department, Faculty of Science, Fayoum University, Fayoum 63514, Egypt

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ABSTRACT

Carboxymethyl cellulose (CMC)/Polyvinyl alcohol (PVA) blend films were prepared by solution casting method. Then, these films were irradiated with γ-rays from a Co-60 source at doses over the range 0–70 kGy to investigate the modifications induced in the optical and dielectric properties. The dielectric constant (ε') was measured in the temperature range 303–408 K and in the frequency range 10 kHz–1 MHz. The indirect optical band gap was found to increase within the dose range 0–10 kGy, and to decrease at the higher doses. The refractive index values, however, showed a reversed behavior. The highest transmittance percentage was obtained at 10 kGy dose. According to the frequency and temperature dependence of ε', α- relaxation peaks were observed in all samples and assigned to the micro-Brownian motion of the blend chains. The values of ε' showed a decrease in the dose range 0–10 kGy and an increase in the dose range 10–70 kGy. The ac conductivity $\sigma_{ac}(T)$ showed an Arrhenius type behavior separated into two distinct regions. The results of the present system are compared with those of similar materials.

1. Introduction

Producing polymeric materials with improved properties by blending two polymers can often be implemented more rapidly than a realization of new polymer chemistry. Copolymers have been extensively studied because of their high potential of the application, as well as their significance in the basic science. The optical transparency, high refractive index, and bandgap tunability are important parameters for materials to be used in optoelectronic devices. Also, the dielectric constant and the dissipation factor of the polymeric materials as a function of temperature and frequency are crucial quantities required in the design of devices. They reveal information on the chemical and physical states of polymers [1–9].

Carboxymethyl cellulose (CMC), available as sodium salt NaCMC, the most popular and the cheapest cellulose ether, is an anionic water soluble polymer and of high transparency in the visible region [10]. CMC possesses many desirable qualities such as thermal gelation, filming, emulsification, bind and inspissations [11]. It is friendly to the environment due to non toxicity, degradability and good biological compatibility. NaCMC is a polyelectrolyte and shows sensitivity to pH and ionic-strength variations [4]. Therefore, CMC is used for many applications such as in medicine, food, textures, electrical elements, paper making, printing and dying [12–14]. Also, CMC hydrogel prepared by γ-ray irradiation has been used for the synthesis of Ag nanoparticles [15]. As another important material, polyvinyl alcohol (PVA) has fascinating properties and a wide variety of applications. It has high dielectric strength, good charge storage capacity, thermal stability over a wide range of temperature (173–473 K), high elasticity and hydrophilic characteristics, and good film forming by solution casting [5,16–18].

On the other hand, irradiation technique is a very convenient tool for the improvement or modification of polymer materials through crosslinking, grafting, or degradation [1–9,19,20]. γ-Irradiation with a dose of 250 kGy increased the dc conductivity of PVA doped with chlorophyll to about fifteen times [21]. Exposure of PVA blended with polyacrylamide to γ-radiation led to the occurrence of crosslinking upon exposure to a dose of 100 kGy [22]. Modifications in the dc conductivity, dielectric [23] and optical properties [24] of doped polymer electrolyte films induced by a 8 MeV e-beam irradiation were reported. Wang et al. [1], reported that CMC/PVP (poly-N-vinyl pyrrolidone) hydrogels possessed improved gel strength, flexibility and transparency compared with pure PVP and CMC hydrogels. E-beam irradiation of PVA blended with CMC was found to increase the gel fraction and reduce the swelling of PVA/CMC copolymer [25]. Previous experimental results showed that the composition 50/50 of CMC/PVA exhibits an enhanced thermal stability, low absorption edge and a minimum in dielectric constant (ε'). This indicates the compatibility between

* Address: Physics Department, Faculty of Science, Fayoum University, Fayoum 63514, Egypt. Tel.: +966 502608368.

E-mail addresses: ams06@fayoum.edu.eg, ad_286@yahoo.com

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CMC and PVA at this ratio. Such compatibility arises due to the presence of the carboxymethyl groups ($-CH_2-COONa$) bonded to some of the OH groups on the cellulose in CMC and the –OH groups in PVA capable of hydrogen bonding [14,26–28].

Due to its excellent control of the stoichiometry and its relative simplicity than the high temperature treatment, the solution casting method is used to prepare CMC(50%)/PVA(50%) blend films. This work presents the preliminary results of the influence of γ-rays irradiation, with doses of 0–70 kGy, on the optical and dielectric properties of the CMC/PVA blend.

2. Experimental

2.1. Materials preparation

Firstly, five CMC(50%)/PVA(50%) films were prepared as follows: For each film, 2 g PVA (Avondale Laboratories, Banbury Oxon, England, average molecular weight of 17000) was dissolved in 50 ml double distilled (*DD*) water under 90 °C and a magnetic stirring for 2 h till the complete dissolution of PVA. 2 g CMC (in the form of the sodium salt of commercial grade, supplied by El Nasr Pharmaceutical Chemicals Co., Egypt) was dissolved in 50 ml DD water at 50 °C and a magnetic stirring for 2 h till the complete dissolution of CMC, then mixed with the PVA solution. The mixed solutions stirred for another 1 h, then cast into glass petri dishes and placed in an oven at 60 °C for 24 h in the air. Finally, the films were peeled off from the Petri dishes and care was taken to obtain polymer films of uniform thickness for recording optical absorption spectra.

2.2. Irradiation facilities

One of the prepared films was left without irradiation, and the other four films were irradiated. Irradiation was performed using a Co-60 γ-source (irradiation cell) installed at the National Center for Radiation Research and Technology (NCRRT) at the Egyptian Atomic Energy Authority (AEA). The irradiation process was performed in the air, at room temperature (*RT*), where a cooling system was used in the irradiation chamber to avoid heating of the samples during irradiation. This source was giving a dose rate of 100 Gy/min. at the time of experiment. The doses were 5, 10, 30, and 70 kGy.

2.3. Measurements

The film thickness was evaluated using a digital micrometer with accuracy +/− 0.001 mm. Optical characterizations were carried out at *RT* using a Shimadzu UV-3600 UV–VIS-NIR spectrophotometer in the wavelength range 200–800 nm with an accuracy of ± 0.2 nm. From the measured absorbance (*A*) and transmittance (*T*), the absorption coefficient (α), the indirect optical band gap (E_g), and the refractive index (*n*) were calculated. Dielectric measurements were performed in the temperature and frequency ranges of 303–408 K and 10 kHz–1 MHz, respectively, by using a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR, with capacitance measurement accuracy on the order of 0.0001 pF. The temperature has been measured with a T-type thermocouple having an accuracy of ±1 °C.

3. Results and discussions

3.1. Optical properties

3.1.1. The absorption coefficient and the indirect band gap

The absorption coefficient (α) of the nonirradiated and γ-rays irradiated CMC/PVA films was calculated using the measured absorbance (*A*);

$$\alpha = A/d \tag{1}$$

where *d* is the film thickness. The values of *d* are listed in Table 1. The dependence of α on the wavelength for all samples is shown in Fig. 1. An absorption band is observed for all films at about 265 nm and is assigned to $\pi-\pi^*$ electronic transition [29]. It is noted that there is a decrease in the absorption coefficient till 10 kGy dose, followed by an increase in the dose range 10–70 kGy. The optical band gap (E_g) values of the CMC/PVA blend could be obtained from the optical absorption spectra by using Tauc's relation [29,30]:

$$\alpha = \frac{\beta(h\nu - E_g)^m}{h\nu} \tag{2}$$

where *m* is an empirical index that is equal to 2 for indirect allowed transitions in the quantum mechanical sense [29] and β is a constant having values between 1×10^5 and 1×10^6 $(\text{cm.eV})^{-1}$ [31,32]. The plot of $(\alpha h\upsilon)^{1/2}$ vs. the photon energy ($h\upsilon$) enables us to estimate the indirect optical band gap (E_g) by extrapolating the linear part of $(\alpha h\upsilon)^{1/2}$ to zero as shown in Fig. 2. The obtained E_g values are given in Table 1. As seen from Fig. 2 and this table, in the dose range 0–10 kGy, E_g is blue shifted from 4.84 to 5.0 eV. At 5 kGy dose, E_g = 4.92 eV. The same value was reported for nonirradiated PVA [33]. As the dose increased from 10 to 70 kGy, a reversed behavior occurred and E_g values show a decrease till approach 4.57 eV.

The microstructure modifications that may be induced by γ-rays irradiation during crosslinking and chain session processes cause a change in the molecular structure of the polymer, so modification within the optical band gap is expected. It is known from the density of state model that E_g decreases with increasing the degree of disorder of the amorphous phase [34]. In the dose range 10–70 kGy the rupture of the polymer bonds may take place. This

Table 1
Variation of the optical band gap (E_g), Urbach energy transmittance percentage (*T%*) and the refractive index (*n*) (at λ = 450 nm) with the dose.

Dose (kGy)	E_g (eV)	E_U (eV)	*T%* (at λ = 450 nm)	*n* (at λ = 450 nm)
0	4.84	1.166	83.5	1.575
5	4.92	1.041	83.6	1.572
10	5.00	0.556	88.2	1.462
30	4.75	1.116	77.5	1.752
70	4.57	1.237	73.6	1.809

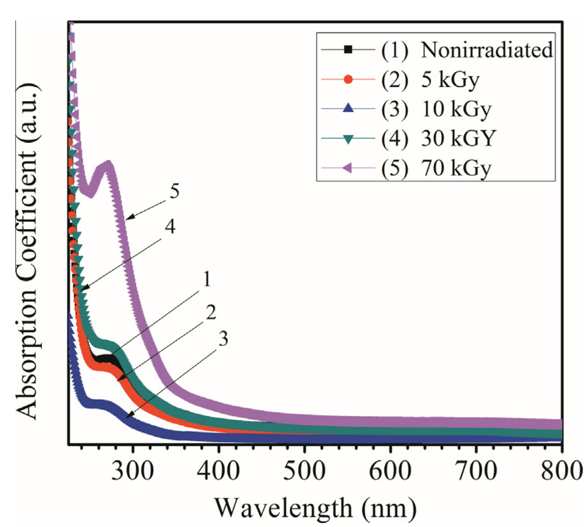

Fig. 1. The dependence of the absorption coefficient (α) on the wavelength of the nonirradiated and γ-rays irradiated CMC/PVA blend films.