



Optical properties of hydroxyethyl cellulose film treated with nitrogen plasma



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ABSTRACT

Hydroxyethyl cellulose (HEC) film has been prepared by casting technique. The prepared sample has been treated with nitrogen plasma at different exposure times. The optical absorption was recorded at room temperature in the wavelength range of 200–800 nm. Absorbance fitting procedure curves revealed a direct allowed transition with optical band gap, E_{opt} , of 4.9 eV for pristine film, and this value decreases to 4.30 eV for 20 min plasma treatment time. The band tail values (E_c) were found to be increased under plasma time treatment from 1.74 eV in case of the pristine film to 2.20 eV for 20 min. The dispersion of refractive index and complex dielectric constants under plasma treatment was also studied. Variation of color parameters under effect of the plasma treatment is analyzed in the framework of CIE $L^*U^*V^*$ color space.

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1. Introduction

Polymers are pretty class of materials that have several advantages, such as easy processing, low cost, flexibility, high strength, and good mechanical properties. Also they can perform various functions of light, such as modulation, generation, and switching. These properties make polymers an excellent candidate for electrical, electronic, optoelectronic, photonic applications and microelectronic fabrication industry [1].

Hydroxyethyl cellulose (HEC) is an important cellulose derivative. It has good chemical stability, biocompatibility, water solubility thickening, adhesion, dispersion, emulsification, film-formation, suspension, absorption, surface activity, salt tolerance, and water retention. It is widely used in food, cosmetic products, building materials, paint industry, petrochemicals, synthetic resin, ceramic industry, pharmaceutical, food, textile, agriculture, tobacco, ink, papermaking and other industries [2]. The β -D-glucose rings of the main chain of HEC, as well as the strong hydrogen bonds among the hydroxyl groups, make chemical modifications that mainly realized through solution process, is expensive, relatively complex and difficult to avoid byproducts [3–5].

Modification of polymer properties can optimize the performance of optoelectronic and photonic devices. Polymers characteristics are modified through the introduction of specific end groups, copolymerization, grafting, crosslinking, blending, and hybridization with other inorganic polymers and plasma treatment.

Physical and chemical properties of polymers can be modified owing to surface modification via plasma treatment. The plasma species such as excited and ionized particles, both atomic and molecular, photons and radicals are carrying significant energy to induce chemical

reactions, both in the plasma volume and at its interface with solid surfaces. Soft, low pressure, plasma has been successfully used as a dry process to change the surface properties of polymers and biological tissues. These plasmas are used for treatment of these surfaces, because they are heat sensitive and thermal damage must be avoided [6–10]. Many plasma parameters are effective on plasma treatment process such as the kind of plasma, the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time [11–13].

The aim of the present work is to enhance the optical properties of HEC via nitrogen plasma treatment.

2. Experimental

2.1. Samples preparation

HEC with average molecular weight approximately 250,000 and viscosity 80–125 mpa·s was supplied by Sigma-Aldrich Company. The solution method was used to obtain film sample. Weighed amounts of HEC were dissolved in double distilled water at room temperature using a magnetic stirrer. Film of suitable thickness (~50 μ m) was casted onto stainless steel Petri dishes, and then dried in an oven at 50 °C for about 2 days until solvent was completely evaporated.

2.2. Plasma treatment

The experimental setup of the present plasma is consists of three main parts, discharge cell, electrical discharge circuit and the high vacuum system. The discharge cell consists of two movable parallel electrodes enclosed in a vacuum vessel. Each electrode consists of a disk of

copper of 5 cm diameter coating with Perspex to prevent the discharge from the back of the electrode. The vessel consists of a cylindrical Perspex tube with outside diameter 11 cm and length 12 cm. It has two open holes one is connected to the vacuum system and other to the used gases. The electrical discharge circuit consists of, a DC power supply (high voltage power supply), which operate in range (0–2000 V; 200 mA). The discharge current in the circuit was measured by a digital multimeter (SK – 6160). The voltage on the discharge tube was measured by a digital multimeter (KIT –2704 B). The high vacuum system consists of two stages Edward rotary pump, diffusion pump and vacuum gauges.

The vacuum gauge of type pirani–penning 1005, which consists of two heads of pirani (PRM10K) standard pressure gauge head range 760 to 10^{-3} Torr and one pinning model (CO25K) of range 10^{-3} to 10^{-7} Torr.

2.3. Spectroscopic measurements

The absorption spectra of the samples were performed using a Perkin-Elmer lambda 4β spectrophotometer over the range of 200–800 nm. The tristimulus transmittance values (X, Y, Z) were calculated using the transmittance data obtained in the visible range according to CIE L*U*V* system. Also, the CIE three dimensional (L*, U*, V*) color constants, whiteness (W), yellowness (Y), chroma (C*), hue and color difference (ΔE) were studied.

3. Results and discussion

3.1. Optical properties

3.1.1. Absorbance spectra study

Fig. 1 shows the absorbance spectrum of hydroxyethyl cellulose film treated with nitrogen plasma under different exposure times from 200 to 800 nm. The spectrum shows an ultraviolet cut-off region with 34 nm width. A shoulder like band at approximately 270 nm which may be due to $\pi \rightarrow \pi^*$ electronic transition (k band) is shifted to approximately 267, 265, and 263 nm at 5 min, 10 and 20 min exposure times respectively. The increase in absorbance at different exposure times is due to the modifications occurred in the surface chemistry and morphology of the polymer. The plasma treatment increases the surface energy of the polymer and consequently, improves the adhesion between polymer chains [14,15].

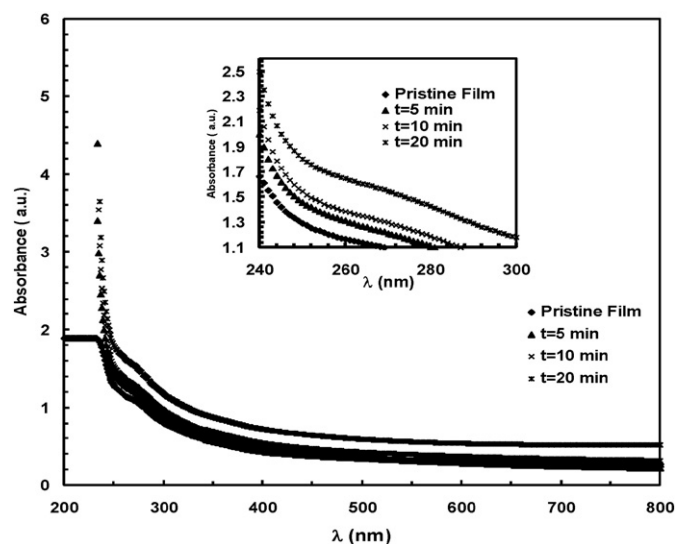


Fig. 1. Absorbance spectra of hydroxyethyl cellulose film under different plasma treatment times.

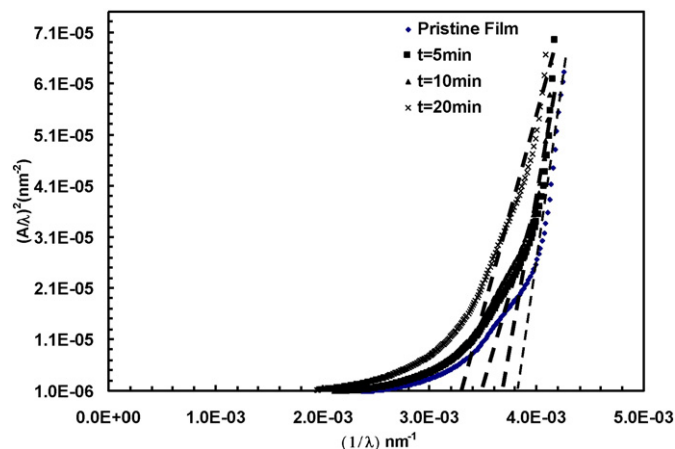


Fig. 2. ASF plots for hydroxyethyl cellulose film under different plasma treatment times.

Generally the change in absorption spectrum of the pristine polymer (untreated film with plasma) under different treatment times is an indication of structure variation of hydroxyethyl cellulose [16].

3.1.2. Determination of optical parameters by absorption spectra fitting procedure

The absorption coefficient, $\alpha(\nu)$ below and near the absorption edge was determined, using the relation:

$$\alpha(\nu) = \frac{2.303A}{d} \quad (1)$$

where A and d are the film absorbance and thickness respectively.

The observed shift in the fundamental absorption edge of UV–visible spectra can be correlated with the optical band gap by Tauc's expression [17,18]:

$$\alpha(\nu)h\nu = B(h\nu - E_{opt})^n \quad (2)$$

where B is constant called band tailing parameter; E_{opt} is the optical band gap energy; n is the index, which takes different values depending on the mechanism of interband transitions $n = 2, 3, 1/2, 1/3$ corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively.

Using the absorbance spectrum fitting (ASF) method [19], we will reformulate Eq. (2) as a function of wavelength (λ):

$$\alpha(\lambda) = B(hc)^{n-1} \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_{opt}} \right)^n \quad (3)$$

Where λ_{opt} , h and c are wavelength corresponding to the optical band gap, Planck's constant and velocity of light, respectively. Using Eq. (1), we can write Eq. (3) as follows:

$$A(\lambda) = B_1 \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_{opt}} \right)^n + B_2 \quad (4)$$

Table 1

Values of energy band gap (E_{gap}), Urbach energy (E_e) and refractive index (n_o) for hydroxyethyl cellulose film under different plasma treatment times.

Treatment time (min)	E_{opt} (eV)	E_e (eV)	n_o
0 (pristine film)	4.90	1.74	1.80
5	4.77	1.86	1.73
10	4.52	1.91	1.87
20	4.30	2.20	2.06

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