Characterization of Optical Properties of Hydroxyethyl Cellulose Doped Erbium Nitrate Composites

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Abstract

Hydroxyethyl cellulose (HEC) doped erbium nitrate films have been prepared by casting technique. The optical absorption was recorded at room temperature in the wavelength range of 190-800 nm. Tauc's curves revealed a direct allowed transition with optical band gap, E_{opt}, of 4.40 eV for HEC film, and this value decreases to 4.10 eV for 5wt% erbium nitrate doped HEC sample. The dispersion of refractive index and complex dielectric constants was also studied. Variation of color parameters composite samples are analyzed in the frame work of CIE L*u*v* color space.

Keywords: Refractive index; HEC; Optical properties; Erbium nitrate.

1. Introduction

One of the changeless of polymer research is to create and develop new materials tailored to a particular application and to understand the physical mechanisms that determine their properties. Depending on the chemical nature of the doping substance and the way in which they interact with the host matrix, the dopant alters the physical properties to different degrees [1].Hydroxyethyl cellulose (HEC) is one of the leading cellulose derivatives. It has good chemical stability, biocompatibility, water solubility thickening, adhesion, dispersion, emulsification,film-formation, suspension, absorption, surface activity, salt tolerance, water retention. It is widely used in food, cosmetic products, building materials, paints industry, petrochemicals, synthetic resin, ceramic industry, pharmaceutical, food, textile, agriculture, tobacco, ink, papermaking and other industries [2]. The blends and composites formation is realized through the β-D-glucose rings of the main chain of HEC, as well as the strong hydrogen bonds among the hydroxyl groups [3-5].

The aim of the present work is to study the effect of erbium nitrate on optical properties of hydroxyethyl cellulose.

2. Experimental

2.1 Samples preparation

HEC with average molecular weight approximately 250000 and viscosity 80-125 mpa.s was supplied by Sigma – Aldrich Company. Hydrated erbium nitrate was supplied by Strem Chemicals Company, USA, with purity 99.9%. The solution method was used to obtain film samples. Weighed amounts of HEC and erbium nitrate were dissolved in double distilled water at room temperature using a magnetic stirrer. Weighted amounts were mixed together to obtain 3,4 and 5wt% erbium nitrate doped HEC samples using magnetic stirrer at room temperature. Films of suitable thickness (~ 60μm) were casted onto stainless steel Petri dishes, and then dried in an air for about 7 days until solvent was completely evaporated.

2.2. Spectroscopic measurements

The absorption spectra of the samples were performed using Perkin-Elmer lambda 4β spectrophotometer over the range of 190-800 nm. The tristimulus transmittance values (X, Y, Z) were calculated using the transmittance data obtained in the visible range according to CIEL*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 doped with erbium nitrate from 190-800 nm. The spectrum shows abroad band at approximately 226 nm which may be due to $\pi \rightarrow \pi^*$ electronic transition (k band) is shifted to approximately 238, 250, and 274 nm at 3, 4 and 5wt % erbium nitrate respectively. The increase in absorbance at different dopant concentrations is due to the structural modifications occurred through bonding between erbium nitrate and hydroxyethyl cellulose [6].

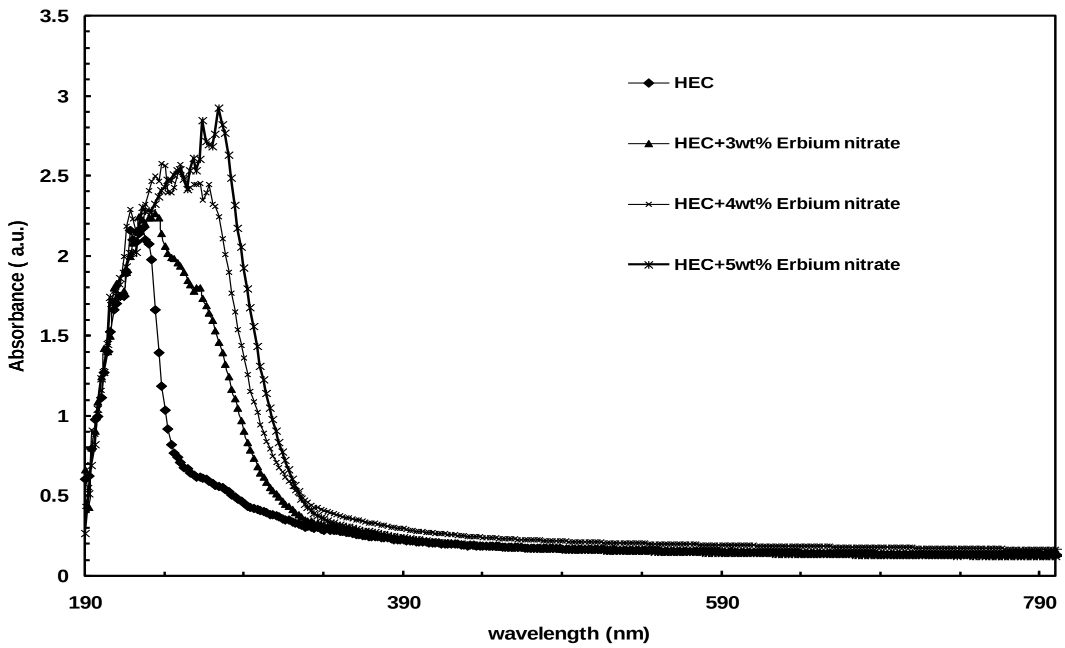

Figure 1. Absorbance spectra of hydroxyethyl cellulose doped erbium nitrate composites

3.1.2. Determination of Optical parameters

The absorption coefficient, α (ν) below and near the absorption edge was determined, using the relation:

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

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 [7, 8]:

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

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.

The values of optical band gap E_{opt} can be deduced from the intercept of the linear fitted lines in the plots of $(\alpha h\nu)^2$ versus $h\nu$, as shown in Fig. 2(a,b).

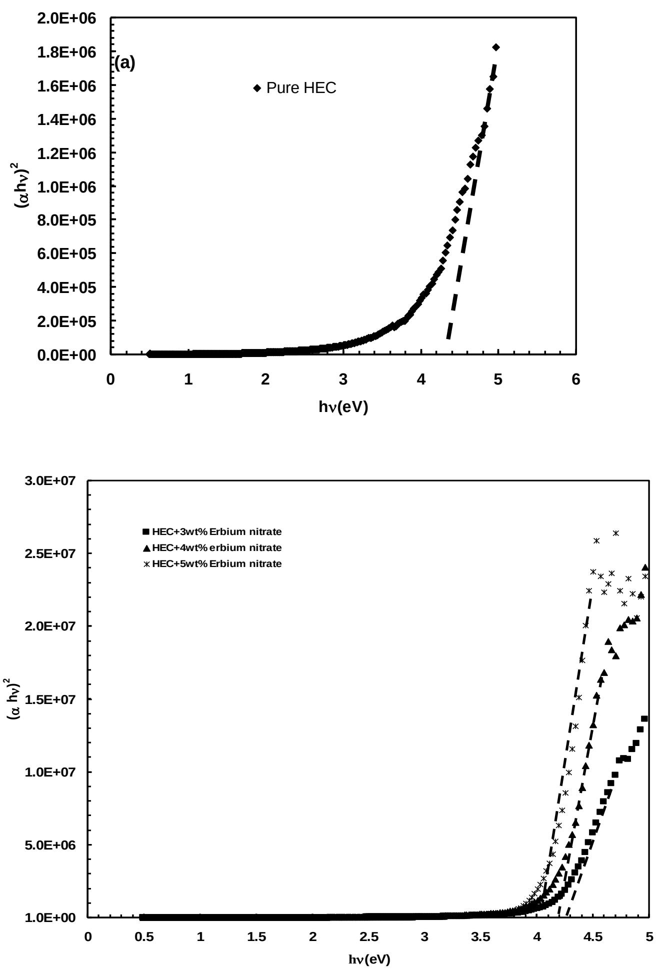

Figure 2. Tauc's plots of hydroxyethyl cellulose doped erbium nitrate composites

The values of optical band gap so determined are listed in Table 1. It is clear from the table that the value of E_{opt} increases from 4.4 eV (HEC) to 4.10 eV for 5 wt% erbium nitrate doped hydroxyethyl cellulose sample.

Such decrease in the value of E_{opt} can be attributed to the formation of bonds between erbium particles and HEC molecules. Therefore, the trap levels between the HOMO and LUMO energy states are formed and make the lower energy transitions feasible and results in the reduction of optical band gap [9].

Table 1. Values of energy band gap(E_{gap}) and refractive index (n_o) of hydroxyethyl cellulose doped erbium nitrate composites

Composite sample	E_{opt} (eV)	n_o
HEC	4.40	1.80
HEC+3wt% Erbium nitrate	4.21	1.81
HEC+4wt% Erbium nitrate	4.19	1.88
HEC+5wt% Erbium nitrate	4.10	1.76

3.1.3. Refractive index dispersion

The refractive index of a material is one of its fundamental and useful optical properties. Accurate knowledge of the refractive index over a wide range of wavelengths is indispensable for many applications such as integrated optics devices such as switches, filters and modulators. The values of refractive index n and extinction coefficient k have been calculated using the theory of reflectivity of light [10, 11]

$$R = \frac{[(n-1)^2 + k^2]}{[(n+1)^2 + k^2]} \qquad (3)$$

where k= αλ/4π is the extinction coefficient of the material; λ is the wavelength of the incident photon. As shown in Fig.3, the refractive index decreases with increasing wavelength of incident photon and finally, almost saturates at values n_0 (longer wavelength values) (as shown in Table 1) for pristine and those doped with erbium.

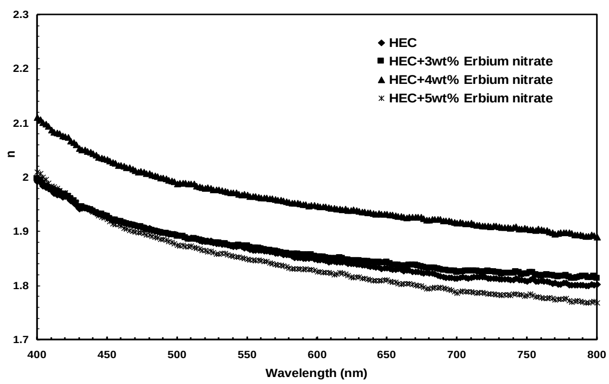

Figure3. Variation of refractive index n with wavelength of hydroxyethyl cellulose doped erbium nitrate composites

It is also clear that as the dopant concentration increases, the refractive index increases and this can be attributed to the reduction in free volume in the polymer sample as a result of crosslink formation. The increase in crosslink density in polymeric system will lead to an increase in refractive index due to the effect of closeness and tightness between chains [14].

3.1.4. Determination of complex dielectric constant

The complex dielectric constant is a fundamental intrinsic property of a material. The real part of the dielectric constant shows how much it can slow down the speed of light in a polymeric material. The imaginary part shows how a dielectric in the polymer absorbs energy from an electric field caused by dipole motion [12].

The real and imaginary parts of the complex dielectric function are related to the refractive index through the following expressions [13]

$$\varepsilon'(\lambda) = n^2(\lambda) - k^2(\lambda) \qquad (4)$$

$$\varepsilon''(\lambda) = 2n(\lambda)\,k(\lambda) \qquad (5)$$

From Fig. 4(a, b), it is noticed that as incident photon energy and dopant concentration increase ε' and ε'' increase. The increasing of dopant concentration leads to an enhancement of the polarization processes in the samples and increase the dielectric parameters and this seems to follow the polar dielectric behavior.

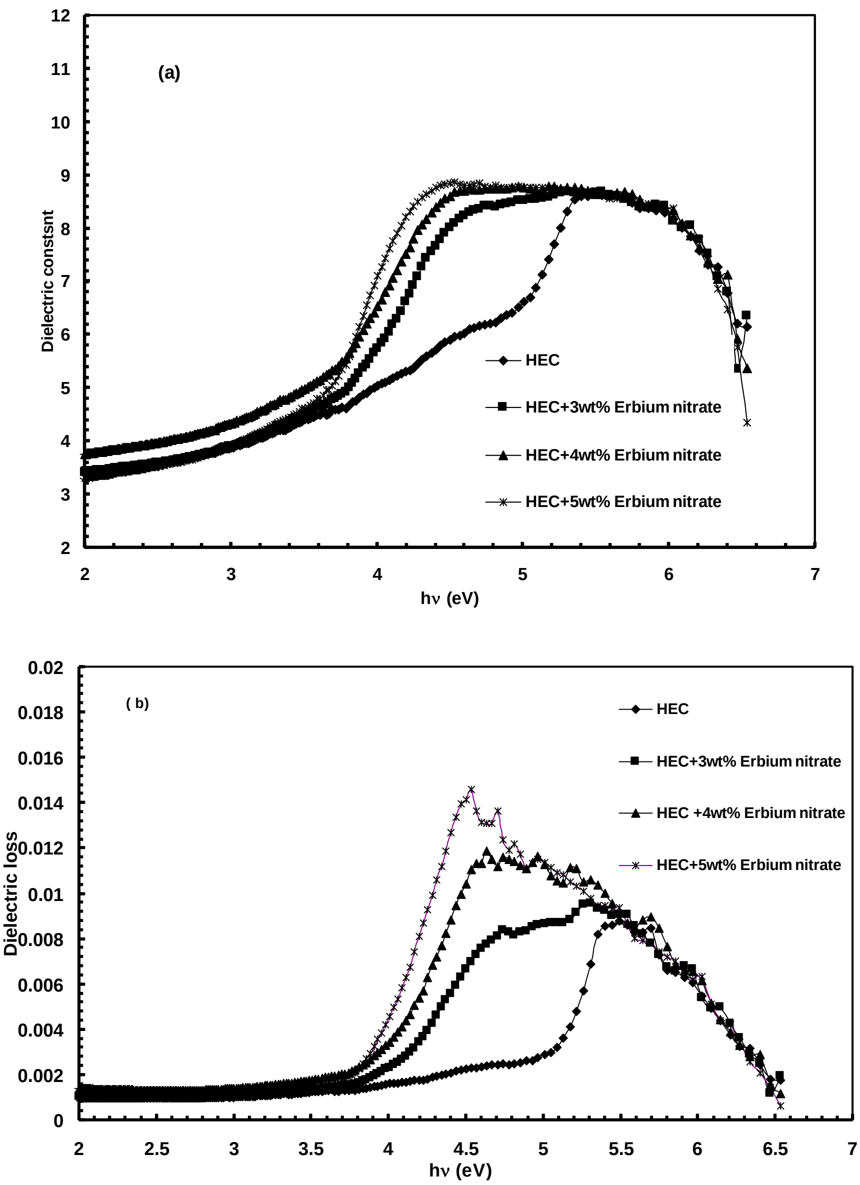

Figure 4. Plots of (a) dielectric constant , (b) dielectric loss versus photon energy (hν) of hydroxyethyl cellulose doped erbium nitrate films

3.2.5. Color detection

Fig. 5 illustrates the variation of the tristimulus transmittance (Y_t) with wavelength in the range of 380-760 nm for pristine and doped samples under different dopant concentration. We can see that the behavior of Y_t for all dopant concentrations is similar since they have the same peak position at about 560 nm and a peak with lower intensity at 470nm. Also it is observed that Y_t (max) has irregular trend with dopant concentration.

Table 2 represents the color parameters L*, U*, V*, h_{ue}, W, Y_e [15] and color difference data, ΔL*, ΔU*, ΔV*, ΔC*, and ΔE between pure polymer and those doped with erbium nitrate.

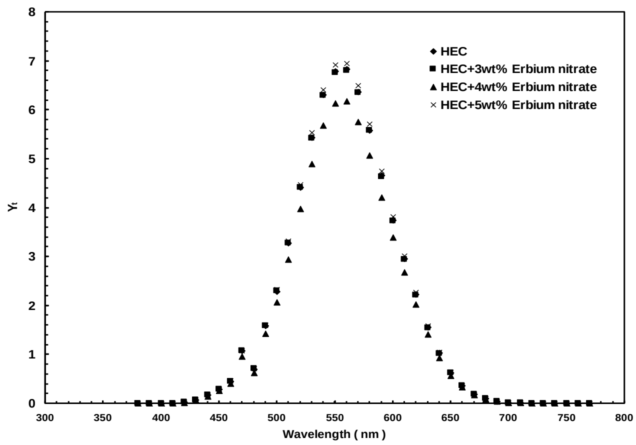

Figure 5. Tristimulus transmittance of hydroxyethyl cellulose doped erbium nitrate composites

It is observed that the color parameters change noticeably with a variation of dopant concentration. Moreover, the color difference data indicate that, the dopant concentration has pronounced effect on color parameters. The 5wt% sample is less light, more saturated than other samples. In addition, it has high h_{ue} value. The observed changes in the color parameters for doped samples may be due to the formation of new color centers of pristine sample.

Table 2. Color parameters of hydroxyethyl cellulose doped erbium nitrate composites

composite sample	L*	U*	V*	C*	ΔL*	ΔU*	ΔV*	ΔC*	ΔE	h_{ue}	W	Y_e
HEC	86.61	2.15	5.2	5.63	-----	------	-----	-----	----	67.46	-828	0.07
HEC+3wt%Erbium nitrate	86.52	1.78	4.98	5.29	-0.09	-0.37	-0.22	0.43	0.43	70.33	-825	0.06
HEC+4wt%Erbium nitrate	83.19	2.40	6.53	6.94	-3.42	0.25	1.33	1.35	3.67	69.76	-748	0.09
HEC+5wt%Erbium nitrate	68.96	2.37	6.36	6.79	-17.65	0.22	1.16	1.18	17.68	69.51	-842	0.08

4. Conclusions

Doping process has a pronounced effect on the optical properties of hydroxyethyl cellulose film. Optical band gap of pure polymer film changed remarkably with dopant concentration. The refractive index also is strongly modified by doping. The variation of optical parameters under doping makes these samples useful in fabrication of electronic and optoelectronic devices.

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