Effect of starch concentrations on optical properties of Polyvinyl alcohol films

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Abstract: Polyvinyl alcohol (PVA) and its starch composite film with different concentrations were prepared in order to investigate the effect of starch additives (up to 10%) on the optical properties of PVA host at room temperature. The optical parameters such as optical energy band gap and Urbach energy were evaluated by measuring of the absorbance in the wavelength range 190-600 nm. It was found that the optical absorption is due to direct transition, the variation in the optical energy band gap and Urbach energy of the films have been observed on doping up to 10% starch in to PVA matrix. The changes in the optical parameter of composite films with increase in concentrations of starch in the film have been observed.

Keywords: Polymer, Optical energy band gap, Absorption coefficient, Extinction coefficient etc.

1. Introduction

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Polyvinyl alcohol is one of the most studied polymers due to its several interesting physical properties as observed by the researchers [1-2], which are very useful in technical applications [3-5]. The important feature of this semi crystalline polymer (PVA) is the presence of crystalline and amorphous regions. These two regions are well separated by portions of an intermediate degree of ordering, which enhances the mobility of the molecule, producing several crystalline and amorphous phases [1-6].

Recent studies have been done by Abdelaziz *et al* [2], Bhattacharyya *et al* [7], Gupta *et al* [8], Khan *et al* [9] and Rawat *et al* [10] on the electrical and optical properties of polymers have attracted much attention in view of their application in electronic and optical devices. Electrical conduction in polymers have been studied aiming to understand the nature of the charge transport prevalent in these materials, while the optical properties are aimed at achieving better reflection, antireflection, interference and polarization properties. Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal have considerable effect on the optical and electrical properties of PVA polymer [11-13].

Although most of the synthetic polymers can be recycled, environmental pollution caused by them is becoming more and more serious. To overcome this problem, numerous efforts have been made to develop environmental friendly biodegradable polymers in recent years [14,15]. Recently many efforts have also been made to blend starch with synthetic polymer like PVA, which is also recognized as a biodegradable polymer and its biodegradation in various microbial environments have been reported [16,17]. Blending

starch with other synthetic polymers to produce biodegradable composite materials with adequate mechanical strength could be practical way to reduce environmental pollution [18]. In this study we used starch as a composite material to make a polymerpolymer composite for the better understanding of the biodegradable polymers on behaves of the optical parameters like E_g , E_u , α , k and M in to optical applications for pure PVA and PVA/starch composite films.

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2. Experimental

Sample preparation

PVA with average degree of polymerization and molecular weight 1,25,000 was obtained from Central Drug House (P) Ltd., New Delhi (India), while starch was obtained from Hi Media Laboratories Pvt. Ltd., Mumbai. The films having thickness of the order of 150μm for virgin PVA and its composite with starch were prepared by solution cast method [10,19-21]. The deionised water was used as a solvent. The films of virgin PVA and its composites with starch were prepared in the laboratory by weight percentage method.

Initially PVA was dissolved in deionised water then starch was added in above solution for the preparation of composite films of varying weight percentage viz., 4%,6%,8% and 10%. A magnetic stirrer was used for few hours ensuring maximum dispersion and homogenous mixing. The solution was poured in to a cleaned Petri disc and then placed in a dust free chamber to evaporate the solvent at room temperature for five days. The average thickness of prepared films was found of the order of 150µm. Micrometer (Mitutoyo, Japan, M120-25) with a least count of 1µm was used in order to measure the thickness of the

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prepared films.

Optical Absorption Spectroscopy

Dual beam UV-visible PC based spectrophotometer (Model: UV5704SS) supplied by EC India Ltd., was used in order to measure the absorption spectra of pure PVA and its composite films with starch at room temperature, in the wavelength range 190-600 nm with a resolution ≤ 2 nm and wavelength accuracy \pm 0.5 nm at normal incidence. The absorption coefficient α (v) and optical energy band gap E_g were calculated from these spectra.

The α (v) was determined near the absorption edge, at different photon energies for all the investigated films using the relation [22,23].

$$\alpha(\nu) = \frac{2.303 A_b}{d} \qquad \dots (1)$$

where A_b is the absorbance [Fig-1] and d is the thickness of film.

The $\alpha(v)$ can be described by the Tauc relation [24,25].

$$\alpha h \nu = \beta (h \nu - E_g)^r \quad \dots \dots (2)$$

Where α is the absorption coefficient, hv the photon energy, E_{a} the optical energy band gap and β is a constant. The electron transition between the valence and conduction bands can be either direct or indirect. In both cases it can be allowed as permitted by the transition probability or forbidden when there is no such probability. The exponent r in the equation (2) is a number which characterizes the transition process, $r = \frac{1}{2}$ for direct allowed transition, r = 2 for indirect allowed transition $r = \frac{3}{2}$ for direct forbidden transition r = 3 and for indirect forbidden transition. Plots of $(\alpha hv)^2$ versus hv for the films of various composition are shown in figure 2. The straight line nature of $(\alpha hv)^2$ versus hv plots reveal that nature of transition in composite films is direct allowed (i.e $r = \frac{1}{2}$ for our case). Intercept of the linear portion of the plot on the hv axis gives the value of direct optical band gap energy E_a of the film.





Figure 1: The UV-Visible absorption spectra for pure



Figure 2: (ahv)2 versus hv (photon energy) plots for pure PVA and PVA/starch composite films

Table 1- Optical data for PVA and PVA/starch composite films					
Composition	Eg (eV)	E _u (eV)	α (cm ⁻¹)	k x10 ⁻⁶	М
			at 235 nm	at 235 nm	
Pure PVA	5.32	0.20	211.50	395.38	42
PVA+ 4% starch	5.26	0.31	129.40	241.91	43
PVA+ 6% starch	5.27	0.28	143.11	267.53	42
PVA+ 8% starch	5.28	0.25	145.24	271.51	42
PVA+ 10% starch	5.29	0.23	148.00	276.67	42

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Figure 1 represents the UV-Visible absorption spectra of pure PVA and PVA/starch composite films with varying concentration. It is clearly observed from these curves that there is very less absorption in the visible region as compared to the ultra-violet region for all the samples. The observed shift in the fundamental absorption edge of UV-Visible spectra can be correlated with the optical energy band gap E_{e} by Tauc's relation as given by equation (2). The values of E_{e} so determined are tabulated in Table 1. It is clear from the table that the value of E_{g} is 5.32 eV for pure PVA which is in agreement with the findings of Devi et al [12]. For PVA/starch composite films, E, changes due to addition of starch in the PVA matrix. This change has been observed for all the studied composite films of different concentrations. The E_a value for PVA/starch composites films lie within the range 5.26 eV to 5.29 eV. The decrease in the optical energy band gap on doping 4% amount of starch in PVA matrix may be explained on the basis of the fact that the incorporation of small amount of starch forms

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charge transfer complexes in the host lattice [26]. The starch molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carriers between two localized states [27] yields decrease of optical energy band gap [30]. But when starch concentration increases further (beyond 4%), it leads to segregation of the composite materials in the host matrix. These molecular aggregates impede the motion of charge carriers resulting in increased optical energy band gap, our results are in agreement with the earlier studies done by Devi et al [12].

The energy E_{μ} is linked to the absorption coefficient α (v) in the lower energy region of the fundamental edge and can also be described by the Urbach's relation [23,28].

$$\alpha(\nu) = \alpha_0 exp\left[\frac{h\nu}{E_u}\right] \qquad \dots (3)$$

In order to evaluate Urbach energy (E_{u}) , the natural logarithm of absorption coefficient $\alpha(v)$ is plotted as a function of photon energy (hv). Magnitudes of E_{μ} were estimated, by taking the reciprocal of the slopes of the linear portion of the curves. The energies E_{μ} obtained using equation (3) for pure PVA and PVA/starch composite films are listed in Table 1, for pure PVA, value of E_u is 0.20 eV and increases up to 0.31 eV on 4% addition of starch in PVA, thereafter on further addition of starch, E_{μ} decreases up to 0.23 eV. This indicates that among all investigate composite films, the 4% amount of starch with PVA has greater compositional and structural disorder as compared to the virgin PVA and other PVA/starch composite films. The variation of the magnitude of E_{μ} of these films, can be understood by considering the mobility concept as proposed by Davis et al [24], which suggests that blending significantly affects the Urbach energy. The process of blending introduces additional defect states (e.g. colour centres) in the polymeric matrix. The density of localized state is proportional to the concentration of these defects. The variation in E₁ for the investigated samples may be attributed to these defects in the lattice. Increasing starch content may cause the localized states of the defects to overlap and extend in the mobility gap. This overlap may give us an evidence for increasing E_w, when starch is included by 4% in the polymeric matrix. The larger the value of

 E_{u} , the greater is the compositional, topological or structural disorder [10,24].

The absorption coefficient (α) and extinction coefficient (k) have been obtained using equation (1) and (4) respectively at 235 nm wavelength for all samples.

$$k = \frac{\alpha \lambda}{4\pi} \qquad \dots (4)$$

The values of α and k for pure PVA and PVA/starch composite films are depicted in Table 1, initially the value of both parameters decrease on adding 4% starch in the PVA and on further addition of starch, the value of these parameters show an increasing trend for all investigated starch/PVA composite films. Further, the evaluated values of Eg can be correlated to the number of carbon atoms per molecule through the expression given by Eq. (5) according to Fink et al [29].

$$E_g = \frac{34.3}{\sqrt{M}} \qquad \dots \dots (5)$$

Where M is the number of carbon atoms in carbonaceous cluster. The calculated values of M for PVA and PVA/starch composite films are tabulated in Table 1. The value of M for PVA and its composites with starch lies within 42-43.

4. Conclusions

- The optical energy band gap for virgin PVA film is found 5.32 eV, on loading starch up to 10% in to PVA matrix, the optical energy band gap varies from 5.26 to 5.29 eV. These results identify PVA/starch composite films as a suitable material for being used in optical devices in order to reduce and control UV radiations. The Urbach energy for pure PVA is found to be 0.20 eV and for its composites with starch it varies from 0.31 to 0.23 eV.
- Blending starch with PVA to produce biodegradable composite materials with effective optical properties could be a practical way to reduce environmental pollution.

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