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Effect Of Electron Beam Irradiation On Dispersion And Optical Constant Behavior For Polyurethane Sheets

S.Abd El All

Nasr City, Cairo (EGYPT)

S.M.El-Sayed National Center for Radiation Research and Technology, Nasr City, Cairo, (EGYPT) E-mail: smelsayed@hotmail.com

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ABSTRACT

Radiation - induced polyurethane sheets have been investigated. The irradiation doses were conducted at the values 10, 30,60,90 kGy respectively. An ultra violet visible spectrophotometer (UV-VIS) was used to characterize the changes in the optical constants as a result of electron beam irradiation. The optical constants and the absorption coefficient of polyurethane sheets are determined from the reflectance as well as the transmittance. These parameters are related to the Fresnel interface reflectance and transmittance by the attenuation of light inside the sheet. The cross linking (induced by electron irradiation) limits the immovability of the polyurethane molecular chains, the refractive index, and the dispersion parameters were consequently subjected to a change. It increased with decreasing electron irradiation doses up to 90 kGy. At higher dose of irradiation (90 kGy), degradation of polyurethane rather than cross-linking was raised. The irradiation PU sheets indicated that the cross-linking and degradation are likely to have an effect on their dispersion parameters.

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INTRODUCTION

Although polymers are widely used in several applications over many years, the environmental degradation by oxidation, hydrolysis and irradiation is

still a disadvantage. Radiation covers a very broad field of polyurethane, with numerous potential applications in frequency conversion devices electro optic modulators, optical communications and highdensity optical data storage systems. All optical pol-

ing of a polyurethane film grafted with a cyano-chromophore type, Second -order nonlinear optical properties was studied^[1-2] Because of its high tensile strength, chemical resistance, good process ability and mechanical properties, polyurethane is being used in many technical applications. Both polyurethane and composition based are widely used as protection films and /or agents for modification of the surface properties of various materials. The behavior of two semi - interpenetrating polymer networks based on polyurethane (PU)under exposure to UV radiation for long period of times (up to 200 h) was investigated^[3]. Also, some authors studied fire retardants tend to accelerate scorching by interaction with polyurethane degradation products and formation easily ox disable structures^[4]. Radiation effects on the polymer properties present the information valuable for investigation of the molecular structure and transport processes. Radiation effects on a segmented aromatic poly ether-urethane induced by electron beam irradiation were studied by using Fourier transform infra red spectroscopy^[5]. Also, photo degradation of polyurethane coating by Xe-arc lamp irradiation as a function of time was studied by positron annihilation spectroscopy^[6].

With regard to portable information display, many research groups to satisfy many new and emerging portable product categories have aggressively pursued reflective flat panel technology. Holographic polymer dispersed liquid crystals were prepared from photo-curable polyurethane acrylate of various structures and a nematic liquid crystal mixture upon curing the reactive diluents and hydroxy ethyl acrylate terminated (HEA) polyurethane^[7,8]. The series of photo chromic polyurethane was obtained by modification of precursor polymers and showed good photo chromic properties manifested by a change of spectral features and refractive index under illumination and by grating formation under four - wave mixing arrangement^[9,10]. A device-quality non-linear optical thermosetting polyurethane with improved process ability has been used to fabricate an electro optic attenuated-total-reflection modulator successfully and its performances was discussed^[11,12]. In the anti-reflection optical element such as polyurethane, the plastic constituting the optical component on

which a multi-layered anti-reflection film is provided has no particular restriction as long as it can be used as a material for an optical element, but typically includes the following. Polymer structure modifications and cross-linking are important parameters that can affect the behavior of these materials. The objective of this work was to study the effect of electron beam irradiation on the modification of polyurethane and study of theses modification through optical properties. The basic assumption was that the increase in doses would decrease the sensitivity of the polyurethane slapes to treatment.

EXPERIMENTAL

Stevens urethane MP 1880 Natural G-29 B10/S 604 with thickness (0.76mm) Gloss; was purchased from Stevens urethane U-A division of d PS Elastomeries Crop. (USA) samples were irradiated by electron beam radiation. It was prepared by electron irradiation process. The irradiation process was performed using dc electron accelerator (ICT type) of beam energy 1.5 MeV and current density to the sample were 10, 30, 60 and 90 kGy respectively. The transmittance, reflectance and absorbance were measured using a double beam UV / VIS / NIR spectrophotometer (Jasco Model 470) in the wavelength range 190-2500 nm. These studies are quite important because they lead to an insight into the molecular structure of the slap polyurethane and the effects of the irradiation doses were recorded.

RESULTS AND DISCUSSION

Effect of electron beam irradiation on the UV properties of polyurethane

The polyurethane is a linear polymer with an average molecular weight of 13,750 and polydispersity index 1.7. The glass transition temperature of this precursor PU was 31.9 °C. The polyurethane is most preferable because of its high refractive index and high impact resistance. While UV is not particularly information on the structure modification of the polyurethane network, it shows that different species are involved in the radiation doses. The change in the UV absorption spectra shows that the

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chemical structures have been altered due to electron beam irradiation. The yellowing tendency of polyurethane due to photo degradation has been observed^[13]. The origin of the absorption near 300 nm is speculated due to the unsaturated carbonyl groups^[14] High energy radiation; such as electron beam; change the physical properties of the materials. The changes are strongly dependent on the internal structure of the absorbed substances. It may be expected that EB can cause ionization (or excitation) of the optical electrons and; possibly displacement of atoms from their sites in the lattice of solids. The photoconduction electrons produced will go back and forth and then become freely or loosely bound to trapping centers in material structures, these new electric configuration would cause a change in the optical properties of the materials in addition to the possible displacement of atoms. Figure (1) shows the UV-spectral behavior of transmittance T (λ) and absorbance A (λ) of the polyure than thick film with a thickness of 0.79 mm as blank. UV absorption bands show fine structure in sense; the anomalous dispersion at the IR end corresponds to one broad absorption band which is hard to exhibit fine structure.

The principle of this technique is that a photon with energies greater than of the band gap energy will be absorbed.

The law of the optical absorption of light $I=I_{o}exp$ (α d) was used to calculates the absorption coefficient



Materials Science An Indian Journal $(\alpha\omega)$ in cm⁻¹ where $(\alpha\omega)=A/d$. A is defined by ln(I/I_o); where I_o and I are the intensity of the incident and transmitted light beams, respectively and d is the film thickness in cm.

Figure (2) shows the absorption characteristic for the un-irradiated and irradiated PU. It is clear from figure (2) that the as blank sheet shows one absorption bands. The absorption at 325 nm is identified as the soret band (B- band), The absorption at 1200 nm and 1400 nm are the Q band. Both arise from π to π^* transitions^[15]. It is noted in general that the sheets of PU have a strong absorption bands at the extreme ends of the spectrum. A distinct decrease of absorbance ascribed to trans form was observed a new band characteristic of the CIS form appeared at the maximum absorption band of the more stable trans from in the range 320nm. By increasing the radiation dose, the intensity of the peaks around 320nm was found decrease. This effect may be explained by decrease of NH-bond intensity by EB irradiated and the appearance of OH-bond. In order to determine the distribution of the energy electron





deposition versus depth, the spectral distribution of reflectance R(h) of sheets before and after irradiation is studied and shown in figure (3). It is clear that the as-blank and irradiated spectra are nearly identical. Since there is no much difference between the as blank and irradiated samples in terms of transmittance and reflectance experimental results. The measured values of A, R, T were used to calculate the optical parameters.

Effect of electron beam irradiation on the optical constant

The optical constants of solid materials can be precisely deduced from transmittance, T, and the reflectance, R, of its sheet^[16]. Considering the incoherent interference of light inside the sheet, its R and T are rigorously expressed in terms of its attenuation factor, η and the Fresnel reflectance, R and transmittance T_s of its plane-parallel interfaces. The attenuation factor η is related to the extinction coefficient, K, and sample thickness, t. To deduce the optical constants n and K of a solid from R and T of its slap, a standard iteration technique is used to find the unknowns R_s, T_s. The slap transmittance T is defined as^[17]

$$T = \frac{\eta T^2}{1 - \eta^2 R_s^2}$$
(1)

and its reflectance R becomes

$$\mathbf{R} = \mathbf{R}_{s} + (\mathbf{1} + \eta \mathbf{T}) \tag{2}$$

In these expressions, the reflectance, Rs, and transmittance, Ts of the slap are defined for normal incidence by the Fresnel formula^[18]

$$R_{s} = \frac{(n - n_{a})^{2} + K^{2}}{(n + n_{a})^{2} + K^{2}}$$
(3)

$$T_{s} = \frac{4n_{a}\sqrt{n^{2} + K^{2}}}{(n + n_{a})^{2} + K^{2}}$$
(4)

The interface coefficient R_s , T_s can be expressed in terms of measurable coefficients R, T of the sheet^[19]

$$\mathbf{R}_{s} = \frac{\mathbf{R}}{1 + \eta T}, \ \mathbf{T}_{s} = \sqrt{\frac{\mathbf{T}(1 - \eta^{2} \mathbf{R}^{2})}{\eta}}$$
(5)

These equations can be used, as shown below, to deduced R_s , T_s from experimentally found R and T.

The optical parameters were calculated from the transmission, absorption, and reflection data.

$$\alpha = -\left(\frac{1}{t}\right) \ln(\eta), \ \mathbf{K} = \frac{\alpha \lambda}{4\pi} \tag{6}$$

$$n = n_{a} \left[\frac{1 + R_{s}}{1 - R_{s}} + \sqrt{\frac{4R_{s}}{(1 - R_{s})^{2}}} - \frac{K^{2}}{n_{a}^{2}} \right]$$
(7)

Equations (6) and (7) follow directly from definitions of the attenuation factor η and the absorption coefficient, but equation (7) is obtained from Fresenal formula by means of elementary algebraic manipulation. The graphs in figure (4) show the slape absorbance A and the Fresenel reflectance R and transmittance T_s of its interface vary with λ inside the spectral range (190-2500 nm). The agreement of the experimental and the calculated R and T is excellently performed when the stationary solutions for R_a and T_a and $\eta = (1-A_s)$ in figure (4) are made use of for simulation. The calculations of n and k were performed for films with different radiation dose ranging from (10-90 kGy). The results of calculations showed that n and k are independent of film thickness for polyurethane, therefore each value of n and k depicted in figure (5) represents the average value of n and k for different doses at a given wavelength. The dispersion at ($\lambda < 1000$ nm), in which a single oscillator model can be applied; while at ($\lambda > 1000$ nm), the anomalous dispersion and the appearance



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of many peaks in n spectrum (figure (n)) may attributed to multiossillator model^[20]. Figure (5) shows normal dispersion in the range of wavelength 1100-2500 nm where the refractive index slightly until about 1200nm. Then, a very low rate of decrease is seen, followed by a sudden rise around 2200-2500 nm. At high doses, the intensity of refractive index decreased factor with increasing doses. The analyses spectra showed that there were two components the evolutions of all band associated with hard or soft segment bond linearly dependent with the doses. Fi-



nally the refractive index become wavelength independent above wavelength $\cong 2500$ nm.

Effect of electron beam irradiation on the optical dispersion parameters

The real and imaginary parts of the optical dielectric constant $\mathbf{\varepsilon}_1$ and $\mathbf{\varepsilon}_2$ were calculated using the following expression.

$$\mathbf{\varepsilon}_1 = \mathbf{n}^2 - \mathbf{K}^2$$

 $\mathbf{\epsilon}_2 = 2\mathbf{n}\mathbf{K}$

Where ε_1 and ε_2 are shown as a function of photon energy as in figure (6) the real part generally relat to the dispersions while the imaginary part provides a measure to the dissipative rate of the wave in the polyurethane medium. The degradation of the bands associated with soft signet and appearance of hydroxyl begun to be significant only for dose less than 90 KGY, moreover, beyond 90 KG the rates of the band evolution in PU were very close. In range 1200-2500 nm, the results suggested that the stabilizer that pratected only soft segment from oxidation was excluded from the micro domains of hard segment but after irradiated dose and absence of stabilizer, oxidation was manly located chains, which led to decrease in bands of refractive index. Nitroxyle radicals signal and symmetrical singlet observed in irradiated polyurethane sheets. They could be summarized as follows a large decrease of urethane bonds and aromatic bands that indicates soft segment and





hard segments degradations. It appeared that concentrations of new oxidation groups represented.

CONCLUSION

The absorption spectrum and dispersion on optical constants of a dielectric material is deduced from the reflectance and transmittance of its sheets whose faces are plane and parallel. The refractive index changes under irradiation in the range 190-2500 nm depending on the thickness of the sheets. Increasing irradiation doses leads to decreasing absorbance without changing peak position. Irradiation shifts these bands towards low energy side of spectra. The transmission spectra recommends these slaps as a good band pass or a good band stop optical filter material depending on the incident wavelength. The irradiation of aromatic polyurethane induced the formation of new chemical groups hydro peroxides. Degradation of hard segments was not influenced by the presence of stabilizer. Consequently, it appeared that oxidation was mainly located in the soft segment bond and the stabilizer is excluded from the hard segment micro domains. A mechanism of degradation was accounting for PU under electron beam irradiation.

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