GAMMA-IRRADIATION-INDUCED BAND GAP NARROWING IN HEAT CURED ACRYLIC RESIN

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ABSTRACT

The response of heat cured Polymethyl-methacrylate resin (PMMA) to γ-irradiation has been investigated by measuring the change in the optical absorption spectra. Different exposure doses in the range of 0-100 Mrad were used. Characteristic changes in the band structure are predicted at different dose levels. The optical energy gap, E_{opt} was found to decrease with the increase of the radiation dose. This is suggested to be due to an increase of the tail width of the localized states in the band gap. The results are discussed on the basis of irradiation-induced changes in the structure.

***Keywords:** γ-irradiation, Acrylic resin, PMMA, Optical absorption.*

INTRODUCTION

The most common materials currently used in maxilla-facial fabrication are polymeric in nature. These include vinyl chloride polymers and copolymers, acrylic types and silicon rubbers [1]. Acrylic resin represents an ideal material for grafting as the properties required for implant material are possessed by it. It is well tolerated by the body tissues, and the completely polymerized material is chemically inert. The presence of free monomer and its effect need not be considered if the correct heat treatment has been carried out [2]. Thermal, electrical as well as heat capacity of such systems are extensively studied [3,4].

The study of optical absorption, and particularly the absorption band edge, is a useful tool for providing information about the band structure and optical energy gap in both crystalline and non-crystalline materials. The principal of this technique is that a photon with energy greater than or equal to the gap width will be absorbed by the system.

There are, in fact, three main kinds of absorption mechanisms in solids: i) free carrier absorption, ii) lattice absorption and iii) electronic interband absorption. The later one is very important in semiconductors, in which the electron is excited from filled to empty state by photon absorption. The absorption coefficient α (ω) in many disordered materials, near the band edge shows an exponential dependence on the photon energy hω, given by Urbach formula [5];

$$\alpha(\omega) = \alpha_o \exp (h\omega/\Delta E) \qquad (1)$$

Where α is constant, ΔE is the width of the band tail of the localized states, h is reduced Planck's constant and ω is the angular frequency of the optical radiation. The above expression was proposed originally by Urbach [5] to illustrate the absorption edge in alkali halide crystals. Davis and Mott [6] modified equation (1) to a more general formula of the form:

$$\alpha (\omega) = A (h\omega - E_{opt})^n / h\omega \qquad (2)$$

Where A is a constant and n is an index determined by the nature of the electronic transitions (direct or indirect) during the absorption process. E_{opt} in the above formula is the optical energy gap of the system. It was found that for many amorphous materials a reasonable fit of equation (2) with n = 2 is verified [7].

The action of ionizing radiation is known to be one of the major sources of altering the internal structure of polymers and, hence, leading to a wide span of interrelated changes in their properties. It may result in crosslinking of the molecular chains [8,9], destruction and degradation of the macro molecules with the simultaneous formulation of molecules with smaller chain length [9,10]. A possible change in the number and nature of double bonds may also be induced [11,12].

In case of gamma (γ) irradiation with energy equals to 1.25 MeV the atomic interactions are the predominant, producing photoelectrons and scattered electrons. The produced photoelectrons will go back and forth and then become freely or loosely bound trapping centers somewhere in the material structure. This new electronic configuration, besides the displacement of atoms, would cause a change in the optical properties of the material.

Many investigations of PMMA have been reported [13,14]. The effect of γ-irradiation on the molecular structure, thermomechanical and electrical properties of such systems were studied by the above authors. At low level of fast neutron fluences (10^5-10^8n/cm^2), the structure of PMMA is changed. These changes are assumed to be due to the formation of free radicals during irradiation process, i.e., new molecular configurations are formed such as degradation and/or crosslinking. Further exposure of PMMA ($\sim 10^{10}$n/cm^2) showed slight changes in the physical properties. The observations are correlated with the crystallinity produced by the accumulation of stable radiation defects.

The present study is devoted to investigate the effect of gamma irradiation on the optical properties and the band structure of the PMMA.

EXPERIMENTAL PROCEDURE

Samples of heat cured polymethyl-methacrylate resin (0.1 cm thickness) were prepared. Wax pattern in the form of discs were prepared and flasked. after washing, polymethyl methacrylates mixing, packing and curing according to manufacturers' instructions had been made in the same manner as for complete dentures processing. They were kept in water for release of excess monomer.

The specimens were gamma-irradiated at room temperature in air using Co^{60} gamma cell 220 manufactured by Atomic Energy of Canada. The exposure dose rate was 1.5 Mrad/h and a set of samples covering an integrated dose from 1 to 100 Mrad were prepared. Optical spectra were measured over the range of 200-110 nm using UV-60 Shimadzu spectrometer. The optical density (absorbance) was directly measured from the instrument.

RESULTS AND DISCUSSION

The experimental data of the optical absorbance plotted against the wavelength, for the as-prepared and γ-irradiated specimens are shown in Figure (1). It is obvious that the optical absorption spectral distribution is sensitive to the irradiation dose. The absorption band edge shifts towards a higher value of the wavelength as the irradiation dose is increased. The variation of the optical absorbance with the energy of the optical radiation is also shown in Figure (1).

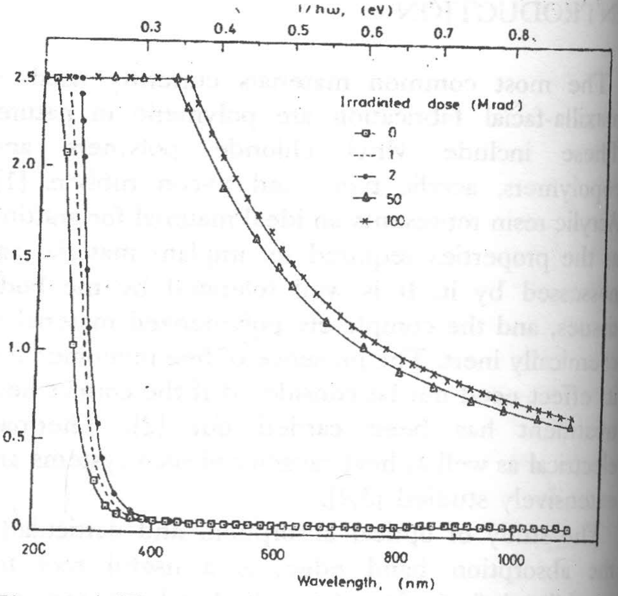

Figure 1. The variation of the absorbance versus the wavelength.

Figure (2) shows the variation of the absorption coefficient, α, with the photon energy $h\omega$ at the different γ-doses. A sharp increase in α can be seen at a particular energy. This sharp increase is followed by a flattening out at high photon energies depending on the γ-dose.

to find out an experimental value for the optical energy gap, E_{opt}, we have applied equation (2), Values of E_{opt} are determined from the intersection of the extrapolated straight portions of the curves with hω-axis.

Dose (Mrad)	o	1	2	50	100
E_{opt} (eV)	4.45	4.39	4.30	3.30	2.20

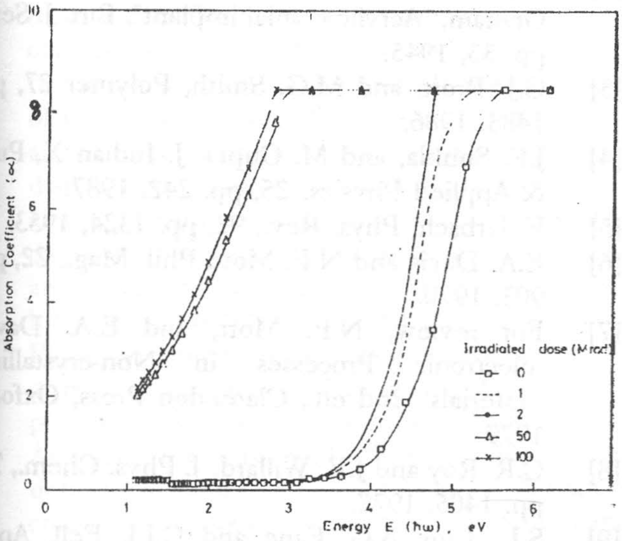

Figure 2. The absorption coefficient against the photon energy.

If the exponent n in equation (2) is chosen to be n=2, negative values of E_{opt} were obtained. A best fit of the experimental data is obtained if the exponent n is chosen to be 1/2. A plot of $(\alpha h\omega)^2$ versus hω is depicted in Figure (3). Such a behaviour is reported for systems with direct energy gap. The observed data of E_{opt} based on n=1/2 plots are summarized in the table for the different doses. It is worth noting that E_{opt} is a decreasing function of the γ-dose. An explicit plot of E_{opt} versus γ-dose is shown in Figure (4). The variation is almost exponential and can be represented by the empirical formula;

$$E_{opt} = B \exp(-\beta D) \tag{3}$$

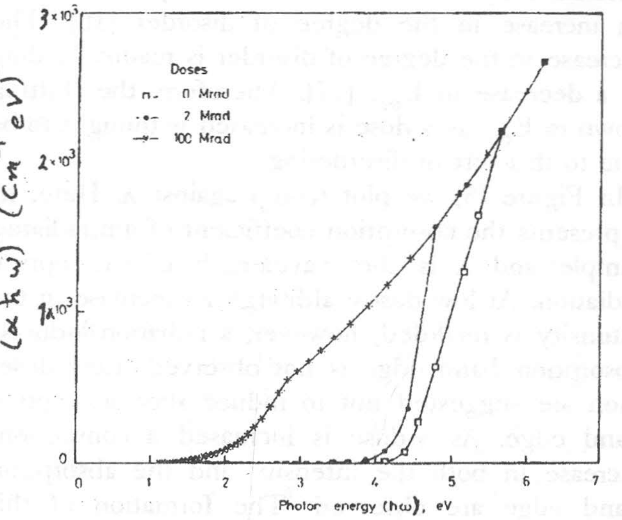

Figure 3. The variation of the parameter $(\alpha h\omega)^2$ with the photon energy (hw) for different doses.

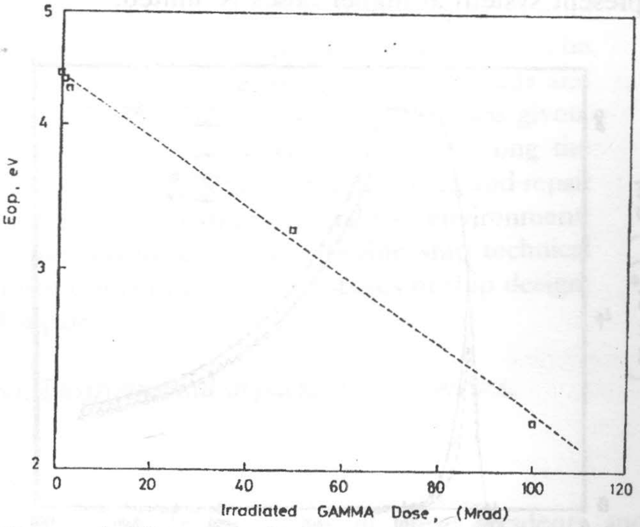

Figure 4. The optical energy gap against γ-dose.

where B = 4.45 eV, $\beta = 0.01$ $(\text{Mrad.})^{-1}$ and D is the dose (measured in Mrad.).

At this stage one may suggest that a band tailing is, probably, created due to γ-irradiation. The width of this band tailing increases as the irradiation dose is increased. An increases in the band tail width is readily leading to a lowering down of the optical energy gap E_{opt}. Formation of the band tail is well known in other systems such as heavily doped semiconductors [1].

It has been suggested that at low irradiation dose the crystalline structure, if any, of a system is perturbed by the irradiation. Obviously, this leads to an increase in the degree of disorder [16]. The increase in the degree of disorder is readily leading to a decrease in E_{opt} [17]. Therefore, the shifting down in E_{opt} as γ-dose is increased is thought to be due to this sort of disordering.

In Figure (5) we plot $(\alpha-\alpha_o)$ against λ. Here, α_o represents the absorption coefficient of unirradiated sample and λ is the wavelength of the optical radiation. At low doses, although an increase in the intensity is recorded, however, a radiation-induced absorption band edge is not observed. Low doses then are suggested not to induce such absorption band edge. As γ-dose is increased a consequent increase in both the intensity and the absorption band edge are observed. The formation of this absorption band is attributed to radiation-induced a local disorder in the system. One however should point out that the sensitivity to γ-irradiation of the present system at higher doses is limited.

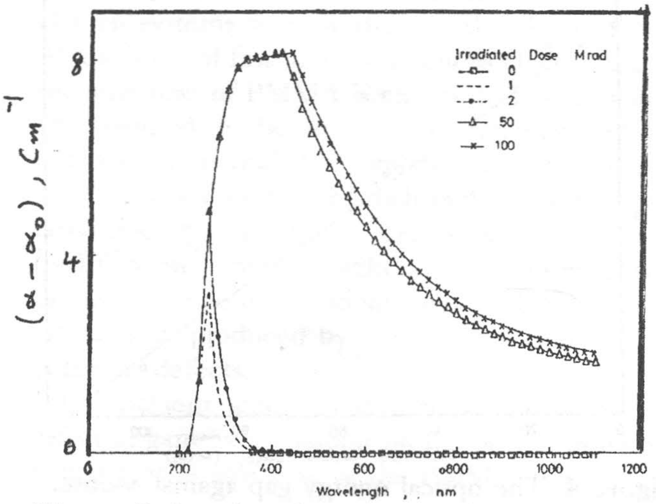

Figure 5. $(\alpha-\alpha_o)$ against the wavelength.

From the present study one may conclude that:

1- Optical absorption of heat cured polymethyl methacrylate resin is in general term sensitive to γ-irradiation dose.
2- An increase in γ-dose leads to consequent decrease in the optical energy gap.
3- Band tailing is assumed to take place, its width depends on the γ-irradiation dose.
4- The degree of crystallinity, if any, is suggested to decrease due to the γ-irradiation.

The use of PMMA as a biomedical polymer in the field of medicine and density requires careful avoidance of radiation exposure, depending on the type and the rate of irradiation.

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