Morphological Modifications of the Gamma Induced Polymer

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ABSTRACT

Soon after the discovery of polymeric materials it became evident that they were quite sensitive to radiation of all kinds. In the present studies CR-39 polycarbonate was irradiated with gamma radiation at different doses from 1KGy to 125KGy. The morphological changes were studied by XRD technique. The structural parameters such as degree of crystallinity and crystallite size were found to increase with gamma irradiation in case of CR-39 which may be perhaps due to the increase in the Vanderwal bonding of more polymeric species in the crystallite. Microstrain had also been calculated which shows that the polymer has compressive strength. Interplanar and interchain distances are marginally changed in the sample.

Keywords: CR-39, Gamma radiation, XRD.

INTRODUCTION

The irradiation of polymeric materials with ionizing radiations [1, 2], (gamma rays, X rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates. These intermediates can follow several reaction paths, which result in rearrangements and/or formation of new bonds and leads to significant changes in structural [3-7] and thermal [8] properties. The ultimate effects of these reactions can be the formation of oxidized products, grafts, scission of main chains (degradation) or cross-linking. The degree of these transformations depends on the structure of the polymer and the conditions of treatment before, during and after irradiation. XRD technique has been utilized to detect changes in crystalline and amorphous regions along with the degree of crystallinity and micro strain of materials through interaction of X-ray beams with samples.

EXPERIMENTAL

For the present work, the sample CR-39 (procured from Pershore Mouldings Ltd. has been cut from a sheet of average thickness of 230 µm. The samples were washed in NaOH and then with running tap water to remove the dust impurities of the polymer.

For gamma irradiation the samples, of size 2 cm^2 each, were irradiated at IUAC, New Delhi by using gamma radiation source of ^{60}Co in the high vacuum radiation chamber (106 mm dia x 140 mm ht in the form of cylindrical chamber with dose rate 9 kGy/hr or 160 Gy/min) and source strength 185 TBq 5000 Ci) One sample was kept as virgin for reference and the other samples were exposed so as to achieve the doses of 1, 5, 25 and 125 kGy respectively

For XRD Panalytical's X'Pert Pro has been used at SAIF Chandigarh working at 40 KV and 25mA. The instrument consists of vertical theta-theta goniometer having range of 0°-160° 2 theta. The radiation used has been Cu K-alpha-1 where as nickel metal is used as beta filter.

COLOR CHANGES

Colour is also an issue for many materials. Colour transformations are common in irradiation processes of polymers [9, 10]. Most polymers turn yellow or brown upon exposure to relatively low radiation doses, due partly to inherent colour centre formation of macromolecular material arising from a combination of trapped radicals and permanent structural changes in the macromolecules which include conjugated chromospheres [11, 12].

The colour transformations have also been observed in CR-39 (fig.1) with the exposure to gamma radiations. The samples which had been originally colourless got yellowish tinge on exposure with IR radiation and thereafter become brown. This may be due to the dissolution of atmospheric oxygen to the polymeric conformation during the exposure which enhances the colour centres in the sample. It may also be attributed to the trapped free radicals or charge species in the polymer.

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Fig. 1 Color Changes in pristine and irradiated CR-39

STRUCTURAL CHANGES (XRD ANALYSIS)

The XRD spectra of pristine and gamma irradiated CR-39 polymer is as shown in fig.2. The crystallinity peak of CR-39 has been observed at 2θ = 20.27° corresponding to *d* spacing 4.40Å indicating the crystals beneath the top layer of the polymer and polymer is amorphous in nature.

The intensity variations are vibratory in case of CR-39 through an overall leaning inclination towards higher gamma irradiation. The overall decrease in intensity of peak shows the increase in amorphicity of the samples due to gamma irradiation, indicating that the structural conformation of the polymer has been modified due to irradiation at higher doses. However, no shift in peak position has been noticed. This implies that lattice parameter does not change during irradiation of CR-39 films under the studied conditions. Similar observations have been reported [13] in case of 35 MeV/u Ar^{+} irradiated PET.

The full-width at half-maximum height (FWHM) of the diffraction peaks were calculated by fitting the X-ray diffraction data with a Gaussian–Lorentzian function and the average crystallite size commonly known as grain size L for pristine and irradiated samples was estimated by calculating the broadening of the diffraction peaks

according to the Scherrer equation [14], as given below

$$\mathbf{L = K\lambda / \beta \, Cos \, \theta}$$

where *K* is the Scherrer constant, which depends upon lattice direction and crystallite morphology (0.9 is used in this study), and $\lambda = 1.54$ Å is the wavelength of the Cu- Kα x-ray radiation used, β is the FWHM of the diffraction peak and θ is the Bragg angle (radian). The change in the crystallinity of both of the polymers was calculated using the following formula: [15].

$$K = \frac{A}{A'} \times 100\%$$

The results obtained for grain size and percentage crystallinity of CR-39 has been summarized in table 1. The crystalline size has been found to increase with gamma irradiation in case of CR-39. The increase in the crystalline size when irradiated with gamma rays may be perhaps due to the increase in the Vanderwal bonding of more polymeric species in the crystallite. The result has been found to match with the study of Singh [16], carried out with Carbon ion beam irradiated PET at Dose 10^{11} ions/cm^2 and Narwal et al. [17] carried out with IR irradiated CR-39 polymer. However the crystallite size decrease at dose 25KGy, which indicates the weaking of vanderwal forces at this dose and detachment of polymeric units from the crystallite.

The interplanar spacing (d) of a set of planes in a crystal is related to the Bragg angle (θ) and the wavelength (λ) by the expression.

$$\mathbf{d = \lambda / 2 \sin \theta} \quad (1)$$

If d_u indicates the unirradiated spacing and d_i the spacing in the irradiated polymer, the variation in microstrain [18] δd/d to be calculated in the particles in the direction normal to the diffracting plane is

$$\boldsymbol{\varepsilon = \delta d/d = (d_i - d_u) / d_u}$$

The microstrain of the sample due to irradiation was calculated using the Eq. (1) and is given in table 1. Since $d_i<d_u$, then δd/d is negative indicating generation of residual compressive stress in the surface [19]. The compressive strength of a material is the compressive force per unit area that it can withstand. The graph between'd' and 'δd' for CR-39 is shown in fig.3. The interchain distance (r), and distortion parameters (lattice strain) (g) have been calculated using the following relations [20].

$$r = \frac{5}{8}\frac{\lambda}{\sin\theta},$$

$$g = \frac{\beta}{\tan\theta},$$

Interplanar and interchain distances were marginally changed in the sample because the angle of the peak (θ) did not vary significantly. The lattice strain decrease with dose in case of CR-39.

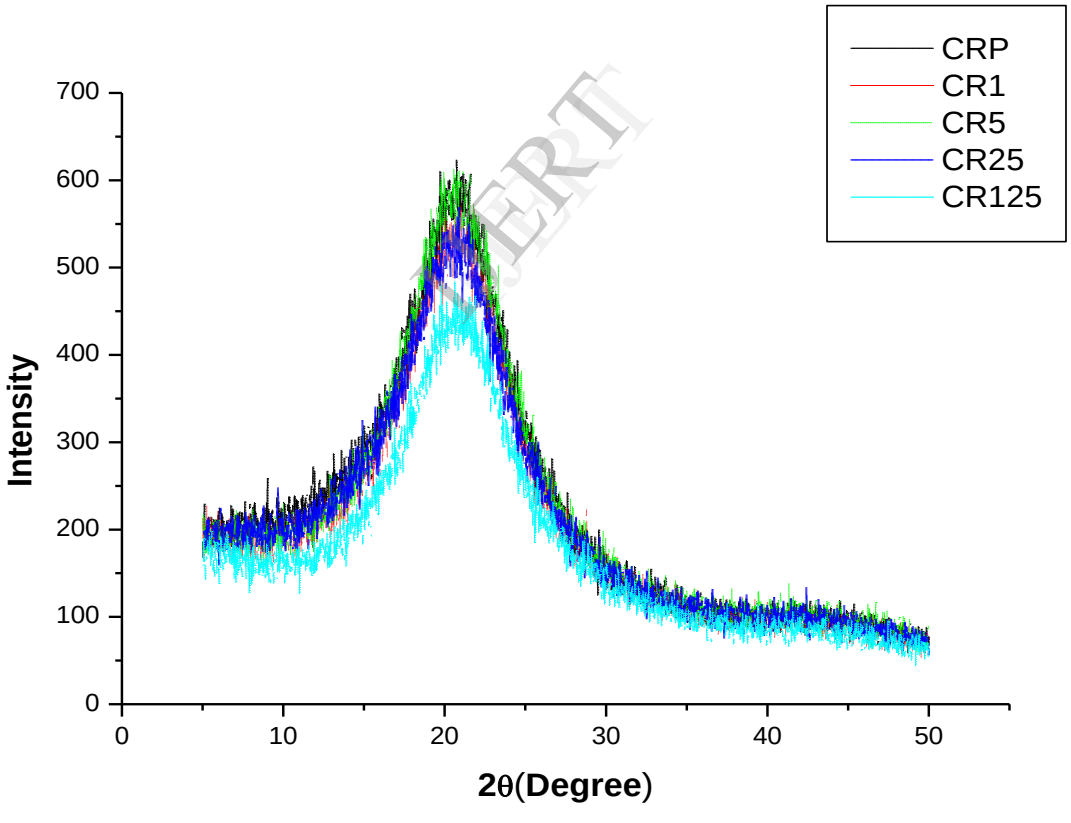

Fig.2 Intensity versus 2θ (degree) for pristine and IR irradiated CR-39

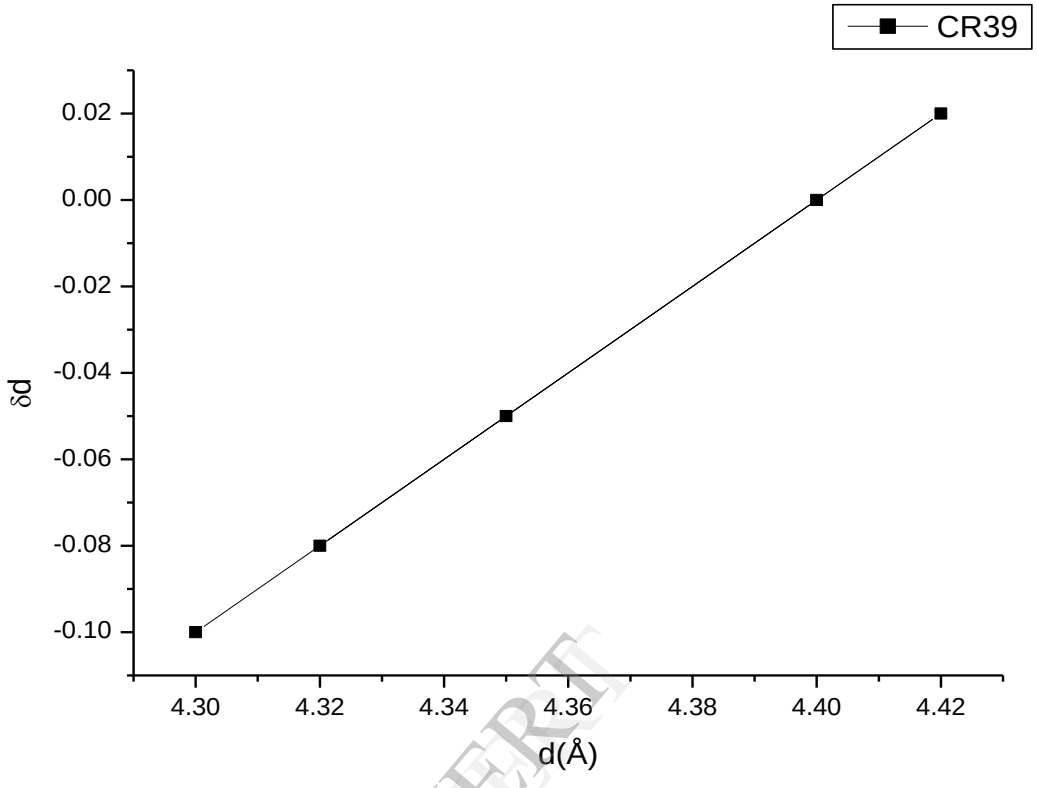

Fig. 3 The d versus δd of gamma irradiated CR-39 polymer

Table 1 XRD data for CR-39

Dose (KGy)	Peak angle (θ),degree	FWHM (β)	K (%)	L (Å)	r (Å)	g (%)	d (Å)	δd	ε
0	0.176	0.149	46	9.79	5.48	0.83	4.40	0	0
1	0.178	0.143	56	10.21	5.42	0.79	4.35	-0.05	-0.011
5	0.179	0.136	57	10.75	5.39	0.75	4.32	-0.08	-0.018
25	0.175	0.155	53	9.40	5.51	0.87	4.42	0.02	0.004
125	0.180	0.143	53	10.14	5.36	0.79	4.30	-0.10	-0.023

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