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Influence of gamma irradiation on the formation of methanol induced micro-cracks in polycarbonate

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The effects of γ-irradiation on the methanol diffusion behaviour in polycarbonate have been investigated by UV-visible, Fourier Transform Infra-red (FTIR) Spectroscopy, Positron Annihilation Lifetime Spectroscopy (PALS), Differential Scanning Calorimetry (DSC), Sorption, and Optical Microscopy. Positron results show that the free volume size and its content decreases after γ-irradiation which is due to cross-linking of chains. The cross-linking process is further confirmed by DSC measurements, which indicate an increase in glass transition temperature (T_g) after γ-irradiation. Sorption results reveal that methanol diffuses faster in virgin polycarbonate as compared to cross-linked polycarbonate (after gamma irradiation) in agreement with the results of supplementary techniques. Interestingly, the optical microscopic examination of the sample surfaces provides clear evidence of decreased micro-crack formation in γ-irradiated polycarbonate as compared to the virgin sample. This decrease in crack formation can be related to the decrease in the rate of methanol diffusion. © *2003 Kluwer Academic Publishers*

1. Introduction

Polymeric materials when subjected to γ-irradiation are known to undergo cross-linking and/or chain-scission accompanied by free radical formation. The former is reflected by an increase in molecular weight and glass transition temperature (T_g) of the polymer whereas the latter has an opposite effect [1]. Some polymers like polyethylene and polystyrene undergo cross-linking upon γ-irradiation while chain-scission is observed in some other polymers like poly (methyl methacrylate) (PMMA) [1]. Certain polymers like polycaprolactone show both cross-linking and chain-scission on exposure to γ-radiation [2].

One of the interesting physical properties of a polymer that gets influenced significantly upon γ-irradiation is diffusion [1, 3]. Diffusion occurs due to natural process tending to equal out the concentration of given species of particles in a given environment [4]. In polymers, diffusion of molecules is assisted by the 'free volume,' which in its simple form is the difference between the total volume and the occupied volume of the polymer [5]. As such, the rate of diffusion will depend to a large extent both on the size of the diffusing molecules as well as on the fractional free volume [4, 6]. So, the rate of diffusion is expected to change on exposure to γ-radiation [1, 3] if γ-irradiation changes the free volume of the polymer. Various models have been proposed to explain the diffusion process in polymers [7–10] and excellent review articles are available on this subject [11, 12].

Gravimetric sorption is widely used to measure the diffusivity in polymer-solvent systems [11, 13, 14]. In this method, the relative weight gained by the sample after different sorption times is measured. A sorption experiment provides information on the kinetics of sorption, the process of swelling, plasticization, change

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in crystallinity etc. [15]. The merits of the sorption method lie in its simplicity and the broad range of diffusivities (from 10^{-10} to 10^{-16} m^2/sec) measured [15]. Most of the experimental data available today is invariably from the sorption method [13, 16].

Upon diffusion of molecules of low solubility, the physical state of the polymer is unaffected and the diffusion is expected to follow Fick's laws [17]. Generally, diffusion proceeds in the direction of diminishing concentration and Fick's law relates the flux of the diffusing particles to the concentration gradient [14, 15]. If the rate of diffusion is much less than the polymer segmental relaxation, it is termed as Fickian behaviour and if the rate of diffusion is much faster than the polymer segmental relaxation, it is termed as non-Fickian behaviour [18–20]. It is interesting to note that diffusion in systems of almost similar character do not always follow Fick's law [20, 21].

As pointed out earlier, the free volume in a polymer plays a vital role in the diffusion process. The existence of free volume holes in polymers was proposed by Doolittle to explain the molecular motion and physical behavior of glassy and liquid states [22]. The free volume holes or cavities are defined as low electron density regions present mainly in the amorphous domains of the polymer matrix [23]. These free volumes provide pathways for the diffusing species. The amount of free volume in a polymer is called the fractional free volume (F_v) or free volume content. According to the free volume theory of transport, the greater the free volume content in a polymer, the higher is the rate of diffusion [11, 13, 24]. In other words, the free volume in a polymer controls the diffusion kinetics [11, 13]. In recent times, Positron Annihilation Lifetime Spectroscopy (PALS), a sophisticated and well-established tool, is commonly used to probe the angstrom sized free volume holes and their concentration in polymers [13, 23].

The basis of PALS involves the injection of positrons from a radioactive source into the material of interest in which they thermalise very rapidly through inelastic collisions with the molecules. Thermalised positrons annihilate with electrons of the medium. A positron can also form a bound state with an electron, called positronium (Ps), which can exist, in two spin states. The singlet state (or para state referred to as p-Ps) with antiparallel spins tends to annihilate with its own electron has a lifetime of 0.125 ns and it decays with the emission of two photons. The triplet state (or ortho state referred to as o-Ps) with parallel spins has longer lifetime and it annihilates in free space into three photons with a lifetime of 140 ns. In polymers, this o-Ps annihilates predominantly via a fast channel called pick-off annihilation (positron of Ps annihilates with an outside electron from the medium) by two photon emission and its lifetime gets reduced to 1–10 ns. The o-Ps pick-off lifetime depends on the overlap of the Ps wave function with the wave function of the electron in the free volume cavity. The larger the cavity size, the smaller is the overlap and hence the longer is the lifetime [25]. Thus, the formation of o-Ps and its yield in polymers is determined by the positron lifetime measurement, attributing the long-lived component to the o-Ps decay [23].

Diffusion of certain organic liquids in polymers seems to be a serious aspect due to the formation of micro-cracks in polymers [3, 26]. For any application, cracks in the system are very dangerous faults which bring down the mechanical strength of the polymer. Micro-crack formation poses problems to a greater extent in transparent polymers like poly(methyl methacrylate) (PMMA) due to loss of transparency in them [3]. Interestingly, it is reported that the transport of methanol in PMMA after γ-irradiation has resulted in many surface cracks whereas no such cracks were seen for the case of virgin PMMA [3]. In order to probe this interesting feature of solvent induced crack formation, we found it worthwhile to investigate the transport behaviour of methanol in another technologically important transparent polymer, polycarbonate, before and after γ-irradiation. We also hope this investigation might shed more light on the possible relation between free volume, diffusion rate and the process of crack formation which has not been addressed extensively so far.

Polycarbonate (PC) is an attractive polymer due to its excellent characteristics like impact strength, stiffness, transparency, heat stability and water resistance [27]. The transparency of PC is exploited in applications such as aircraft light housing, aircraft dials, windscreens for cars and in making contact lenses. The effect of γ-irradiation on this polymer was studied [28]. Studies on the transport of a few organic liquids in PC have been reported [1, 29, 30]. Our group has reported [13, 31, 32] iodine diffusion studies in polymers including PC using Sorption and Positron Annihilation Lifetime Spectroscopy (PALS) methods. In the present study, we have extended the sorption measurements by studying the surface morphology to understand the process of micro-crack formation, if any, upon methanol diffusion in un-irradiated PC or PC in the as received state (here afterwards referred to as PC-ARS) and γ-irradiated polycarbonate (here afterwards referred to as PC-γ). UV-visible and Fourier Transform Infra-red (FTIR) spectroscopic measurements have been used to confirm the structural changes in PC in terms of absorbance at different wavelengths after γ-irradiation. Change in free volume upon γ-irradiation is measured from Positron Annihilation Lifetime (PAL) technique and Differential Scanning Calorimetry (DSC) has been used to find the change in the glass transition temperature (T_g) of PC upon γ-irradiation. Using an optical microscope, the surface morphology of the sample during the sorption is observed.

2. Experimental

2.1. Sample and its treatment

The polycarbonate sample with a molecular weight of 28,000 and density 1200 kg/m^3 procured from Goodfellow, UK in the form of a sheet of 0.001 m thick was used in the present investigation. Gamma irradiation was carried out with a ^{60}Co source available at the Malignancy Disease Treatment Center (MDTC), Department of Radiation Oncology, Pune, India. The sample was positioned properly for full exposure to the source so as to receive a total dose of 10 Mrad at 3.13 Mrad/hr.

2.2. Methanol sorption

Analytical grade methanol has been used in the present study. Sorption of methanol was carried out at room temperature by soaking the samples in methanol for different intervals of time. After each sorption time, the samples were dried with a blotting paper for removal of surplus methanol and weighed using a Mettler digital balance to a good accuracy.

2.3. UV-visible and FTIR measurements

The UV-visible measurements were carried out using a HP model 8452A diode-array UV-visible spectrophotometer at 2 nm resolution in the wavelength region 190 to 790 nm. A Shimadzu FTIR spectrometer model 8201-PC at 2 cm^{-1} resolution was used for FTIR measurements in which each datum point is an average of 64 scans. Both UV-visible and FTIR measurements were done with the facility available at the National Chemical Laboratory, Pune, India. The spectra were background corrected with a Au sample in place.

2.4. Positron Annihilation Lifetime measurement

Positron Annihilation Lifetime measurements were performed using a fast-fast coincidence system consisting of a KL-236 plastic scintillator coupled to a RCA-8575 photomultiplier assembly as detectors. A 15 μCi ^{22}Na deposited on a pure kapton foil of 0.0127 mm thickness was used as the positron source. The standard source-sample sandwich geometry (sample on either side of the ^{22}Na positron source) was employed for positron lifetime measurements. More details of the experimental procedures can be found in literature [23, 33]. Positron lifetime spectra with more than one million counts were recorded for each sorption time.

The instrumental time resolution and source correction terms were obtained from the measured spectrum of a medium of known lifetime (well annealed aluminium) fitted with a computer program RESOLUTION [34]. A time resolution of 340 ps was obtained with 40% ^{22}Na energy gating. The lifetime spectra were analysed using the program PATFIT-88 after source and background corrections [34]. The lifetime spectra were resolved into three lifetime components as it gave better χ^2 values and standard deviations than the 2 and 4 component analyses.

2.5. Calorimetry measurements

Thermal characteristics of the samples like the glass transition temperature were measured using a Mettler FP-900 DSC system at a scan rate of 10°C/min.

2.6. Light microscope

The surface fractography of samples upon methanol sorption was observed using a Nikon-Labophot-2 optical microscope.

3. Results and discussion

3.1. UV-visible absorption results

After γ-irradiation, the PC turned slightly yellowish in colour; such yellowing of polymers upon γ-irradiation is due to the formation of conjugated double bonds [3]. Hence, we can expect more groups having conjugated double bonds after γ-irradiation. To explore the possible changes in the structure of PC upon γ-irradiation, UV-visible absorption spectra have been taken and are depicted in Fig. 1a. The spectra show a clear increase in absorbance in the entire wavelength region of 190 nm to 790 nm after γ-irradiation, indicating that the polymer has turned slightly opaque as compared to the PC-ARS. In order to extract the changes more clearly, the difference spectrum of these two is also made and is presented in Fig. 1b. This figure clearly shows a prominent absorption band around 386 nm and a weak one near 210 nm.

A recent thermal degradation study on PC reports that the C—O bond adjacent to the carbonyl group (bond energy 330 kJ/mol) is a vulnerable bond in PC [35]. Hence, upon γ-irradiation, there are more chances that this bond can break and the reaction can proceed as reiterated in Fig. 2, resulting in the production of phenoxy (type I) and phenyl radicals (type II) radicals. The phenoxy radical (I) can initiate further reaction with the polymer and can lead to a radical of type (III) [28]. In a γ-irradiation study on PC, Torikai *et al.* [28] attribute the broad UV-absorption band which is close to 390 nm to the production of the aforesaid anionic species. In agreement with this, we attribute the broad absorption peak around 386 nm to the production of these anionic species. Furthermore, the benzene chromophore displays a forbidden transition around 204 nm (molar absorptivity at maximum absorption $\varepsilon_{\max} = 7900$) [36]. The presence of an alkyl group like OH and substituents at para positions can result in a bathochromic shift.

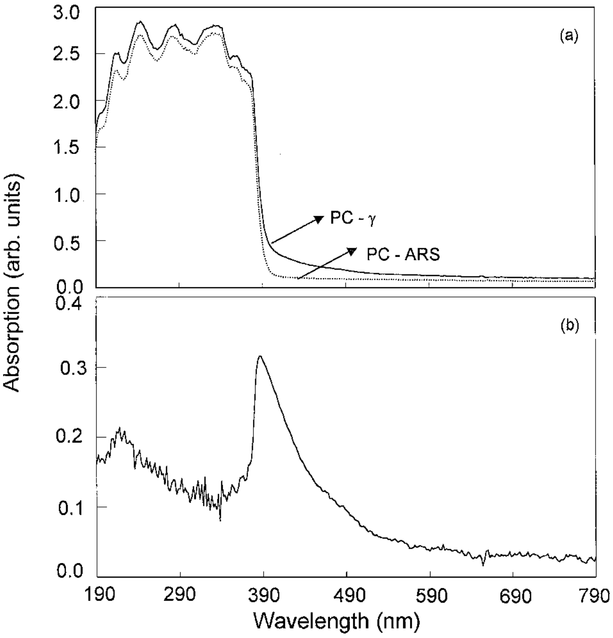


Figure 1 (a) UV-visible absorption spectra for PC-ARS and PC-γ. (b) The difference UV-visible absorption spectrum of PC-ARS and PC-γ.

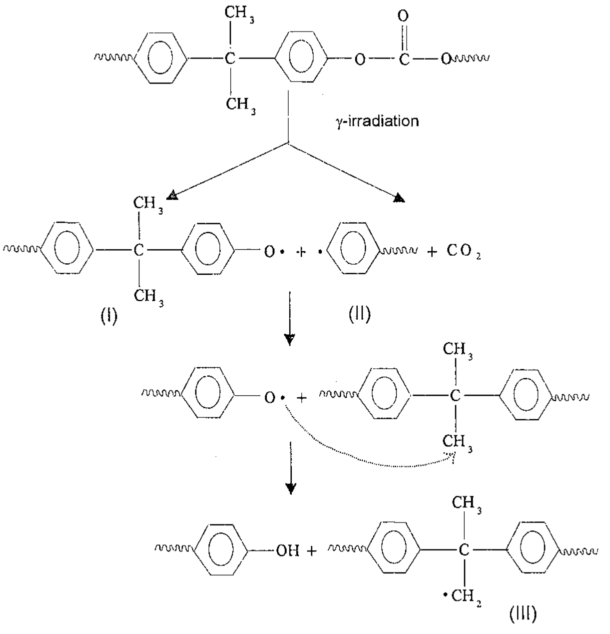


Figure 2 The mechanism of production of anionic moieties in γ-irradiated PC.

Hence the weak absorption band around 210 nm can be attributed to these para substituted benzene end groups formed upon γ-irradiation.

3.2. FTIR results

The FTIR measurements were performed before and after γ-irradiation to identify the changes of the functional groups in PC due to γ-irradiation. To understand the modifications in the functional groups more clearly, a difference spectrum is made similar to that in the UV-visible case and is shown in Fig. 3. A broad absorption band, which appears around 3450 cm^{-1}, indicates the formation of OH groups [27]. The absorption peak at 1520 cm^{-1} is due to phenyl groups and the one at 1780 cm^{-1} is because of the C=O moiety of PC [27, 37]. The peak close to 1200 cm^{-1} is caused by the C—O bond of PC [27]. If γ-irradiation has resulted in the products as detailed in Fig. 2 owing to chain-scission at the C—O bond, the difference spectrum should have been completely free from absorption peaks corresponding to C=O and C—O groups. But a considerable absorption peak at 1780 cm^{-1} and the one close to 1200 cm^{-1} points that chain-scission has taken place only at a moderate level.

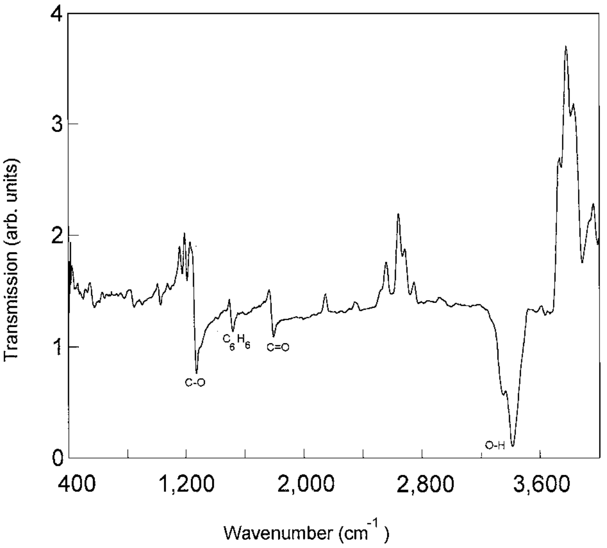


Figure 3 The difference FTIR spectrum of PC-ARS and PC-γ.

3.3. Positron lifetime results

The Positron Annihilation Lifetime measurements have been performed to identify the change in free volume after γ-irradiation. Generally, the attribution of the three resolved lifetime components to various states of positron annihilation is as follows: The first short lived component τ_1 with intensity I_1 is attributed to p-Ps and free positron annihilations. The intermediate lifetime component τ_2 with intensity I_2 is considered to be caused mainly by the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline-amorphous interface. The longest lived lifetime component τ_3 with intensity I_3 is due to pick-off annihilation of the o-Ps in the free volume sites present in the amorphous regions of the polymer matrix [23].

In polymers, of the three lifetime components, the o-Ps lifetime (τ_3) and intensity (I_3) are important since τ_3 is related to the average free volume size and I_3 is related to the population of free volume holes [13, 38] and hence are the prime parameters of this study. Further, the diffusion in polymers is dependent on the free volume content, [11, 13, 24] and for understanding the diffusion kinetics in terms of free volume, we need to look at τ_3 and I_3 only. The o-Ps lifetime (τ_3) is related to the free volume hole size by a simple relation developed by Nakanishi *et al.* [39] based on theoretical models originally given by Tao [40] and later by Eldrup *et al.* [41]. As per this model, the o-Ps is assumed to be localised in a spherical potential well having an infinite potential barrier of radius R_o. It is further assumed that the o-Ps annihilates in a homogeneous electron layer of thickness ΔR (where $\Delta R = R - R_o$; R being the radius of the free volume) inside the well where its lifetime is the spin averaged Ps lifetime of 0.5 ns and the relation is

$$\tau_3^{-1} = 2[1 - (R/R_o) + (1/2\pi)\sin(2\pi R/R_o)]\,\text{ns}^{-1} \quad (1)$$

The parameter ΔR has been determined by fitting the experimental values of τ_3 obtained from molecular materials of known hole sizes like zeolites and its value is 0.1656 nm. This equation is used to calculate the free volume radii of PC-ARS and PC-γ. Then, the average free volume size is evaluated as $V_{f3} = (4/3)\pi R^3$. From this average free volume size, the fractional free volume (F_v) or the free volume content is calculated using the relation [38]

$$F_v = C V_{f3} I_3 \quad (2)$$

where C is the structural constant and can be obtained from a measurement of the thermal expansion coefficient of free volume (α_o). The experimentally calculated value of C for PC is 0.969 nm^{-3} [13]. This value of

TABLE I Free volume data of PC-ARS and PC-gamma samples

Sample	τ_3 (ns)	I_3 (%)	V_{f3} (nm^3)	F_V (%)
PC-ARS	1.87 ± 0.0078	35.9 ± 0.18	0.0854 ± 0.61	2.97%
PC-γ	1.82 ± 0.0085	33.3 ± 0.19	0.0814 ± 0.66	2.71%
% change	2.4%	7.2%	4.8%	8.8%

C is used in the calculation of F_V in PC-ARS and PC-γ and is tabulated in Table I. As can be seen from this table, there is a decrease in the average free volume size (4.8%), its number density (7.2%) and fractional free volume (8.8%) in PC-γ which points to cross-linking of chains. Owing to cross-linking, the molecular weight of the polymer increases [1] and hence a decrease in the average free volume size is quite obvious.

3.4. Calorimetric results

To explore the influence of γ-irradiation on T_g, DSC scans were made and are shown in Fig. 4. This figure clearly indicates a transition at 152°C for PC-ARS, which is the T_g of this polymer [42]. This transition gets shifted to 155°C after γ-irradiation. This increase in T_g certainly indicates cross-linking of chains upon γ-exposure and is in agreement with PAL results.

Previously, it has been experimentally found that low doses of γ-irradiation (up to 5 Mrad) increase the molecular weight of PC and enhance its physical properties [1, 43]. An independent experiment of γ-irradiation on PC by Torikai *et al.* [28] also reports a large change in molecular weight only after a dose of 25 Mrad. From these reports and from the present experimental results, it can be concluded that the effect of γ-irradiation is mainly cross-linking. However, the observed scission products from UV-visible and FTIR must have been due to mild chain-scission. Thus, the overall effect of γ-irradiation on PC at the exposed dose of 10 Mrad is mainly cross-linking of chains.

3.5. Diffusion results

In order to understand the sorption mechanism of methanol in PC and to determine the diffusion coefficient (D), we have invoked Fick's second law of diffusion [17] which is

$$\delta C_d/\delta t = D(\delta^2 C_d/\delta x^2) \tag{3}$$

where 'C_d' is the concentration of the diffusing substance and 't' is the time. A solution to the above equation for diffusion in a plane sheet with surfaces maintained at a constant concentration is given by Crank [14] as

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} 8/\pi^2(2n+1)^2 \times \exp(-D(2n+1)^2\pi^2 t/L^2) \tag{4}$$

where 'L' is the thickness of the sheet, 'M_t' and 'M_∞' are the masses of the penetrant sorbed at times 't' and '∞' (time taken at the final stage of sorption equilibrium). The ratio (M_t/M_∞) in Equation 4 can be expressed as

$$M_t/M_\infty = (W_s - W_d)/(W_\infty - W_d) \tag{5}$$

where 'W_d' is the weight of the dry sample 'W_s' is the weight of the sample which has been soaked for a time 't' and 'W_∞' is the weight of the sample in the final stages of sorption. The ratio (M_t/M_∞) is evaluated according to the above equation with the measured values of W_s, W_d and W_∞. A widely used approximation is that at short time (up to $M_t/M_\infty = 0.5$ to 0.65), the amount of substance diffused is proportional to $\sqrt{t}$ which is called as square-root-of-time law [44] or Stefan's approximation [14] which is given as

$$M_t/M_\infty = 4[Dt/\pi L^2]^{1/2} \tag{6}$$

This approximation is derived under the assumption that 'D' is constant. The diffusion coefficients can also be calculated from the late-time approximation of Equation 4 [45] taking $n = 0$ which results to

$$M_t/M_\infty = 1 - [(8/\pi^2)\exp(-D\pi^2 t/L^2)] \tag{7}$$

A plot of M_t/M_∞ versus square root of sorption time ($\sqrt{t}$) is generally termed as 'sorption curve' and D is calculated from the slope of the initial linear portion of this curve. Fig. 5 depicts the methanol sorption curves for both PC-ARS and PC-γ. The (M_t/M_∞) ratios vary linearly with $\sqrt{t}$ up to (M_t/M_∞) ~ 0.65 in both PC-ARS and PC-γ and level-off at the final stages of sorption (see Fig. 5).

Sorption kinetics are often explained using the Berens and Hopfenberg model [16] which is otherwise called as dual-mode sorption model [46] which incorporates both Fickian diffusion and polymer structural relaxation. According to this model, if the sorption curve is linear during the initial stages of sorption (up to $M_t/M_\infty = 0.5$ to 0.65) and reaches a plateau region over an extended period of time, it is termed as Fickian sorption [14]. The existence of an upward curvature over an extended period of sorption indicates the presence of a relaxation contribution to the overall

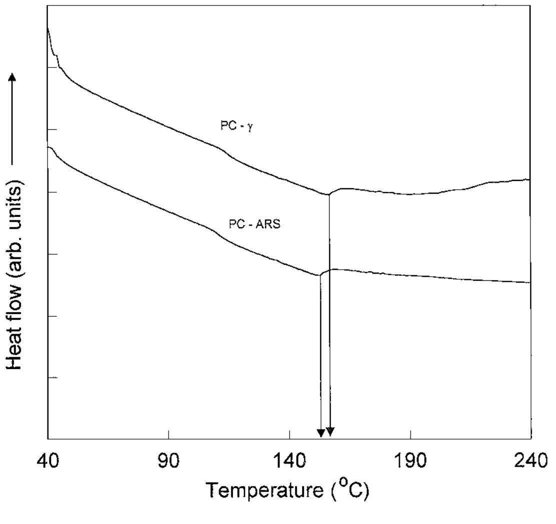


Figure 4 DSC heat flow curves of PC-ARS and PC-γ.

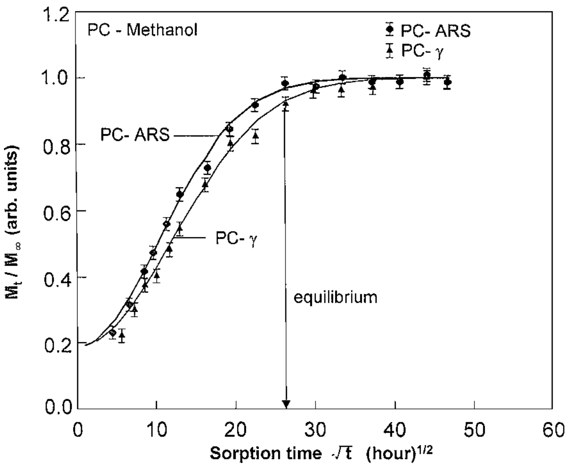


Figure 5 Variation of (M_t/M_∞) as a function of square root of methanol sorption time (t) for PC-ARS and PC-γ. The solid lines represents fits to the experimental data.

sorption [13, 16]. In other words, the diffusion is non-Fickian. The Fickian type of diffusion is characterized by the rate of diffusion to be much less than that of the polymer segmental relaxation due to mechanical, structural etc., modes of penetrant-polymer system interaction. Non-Fickian type of diffusion is the one for which the diffusion occurs faster than the segmental relaxation process [18–20]. The theory of non-Fickian diffusion was extensively investigated by Thomas and Windle [19]. From the description of Fickian and non-Fickian sorption processes and a careful examination of sorption curves in Fig. 5, it can be concluded that the methanol sorption in PC-ARS and PC-γ are of Fickian type.

In order to support the above mechanism of methanol transport in PC-ARS and PC-γ matrices, the sorption results have been further fitted to a relation of the type [47]

$$M_t/M_\infty = Kt^n \tag{8}$$

where 'K' is a constant which depends on the structural characteristics of the polymer network in addition to its interaction with the solvent. The value of the exponent 'n' indicates the type of transport mechanism. A value of $n = 0.5$ is suggestive of the normal Fickian behaviour. A value of $n = 1$ refers to non-Fickian transport mode. If the magnitude of 'n' lies between 0.5 and 1, the diffusion process is of anomalous type for which the diffusion and the relaxation rates are comparable [13]. From the least-squares fit of Equation 8, the values of 'n' for PC-ARS and PC-γ are obtained as 0.51 and 0.50 respectively and the corresponding 'K' values are 4.715×10^{-2} and 4.731×10^{-2}. These values of 'K' are of the same order as that of diffusion of organic liquids studied in polymers and iodine diffusion in PC [13]. The obtained values of 'n' further confirms that methanol sorption in PC-ARS and PC-γ is of Fickian nature [13]. Further, the type of diffusion in a polymer may get modified by changing its free volume by any one of the processes like subjecting it to a change in temperature, pressure, radiation treatment etc. [20, 21]. Interestingly, in the present case, even for a free volume change of 8.8%, (see Table I) the diffusion still remains Fickian and at the moment we do not find a plausible explanation for this.

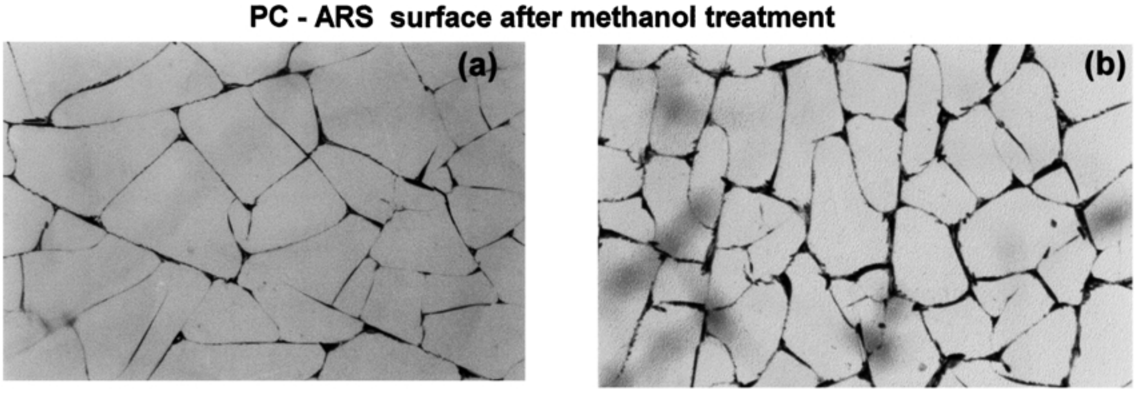
Furthermore, to compare the experimental results with Crank's theoretical expression for Fick's law, we have fitted our experimental results in the initial linear region (up to $M_t/M_\infty = 0.65$) of the methanol sorption curve (Fig. 5) to Stefan's approximation (Equation 6) and the values of 'D' obtained from the best fit are 13.15×10^{-14} m^2/sec for PC-ARS and 9.91×10^{-14} m^2/sec for PC-γ. The decrease in the value of D in PC-γ is due to cross-linking of chains, which puts stiffer resistance for the incoming diffusing species. The solid curves in Fig. 5 are obtained by fitting Crank's diffusion expression (Equation 4) with the above values of D. As can be seen from this figure, there is a good agreement between the experiment and the theory. The positron results indicate a reduction in free volume content (F_v) by 8.8% due to cross-linking after γ-irradiation (see Table I). According to the free volume theory of transport, 'D' should decrease with the decrease in F_v [11, 13, 24]. The present results are in agreement with this theory.

Polymers are known to exhibit swelling in liquid media [16]. The process of swelling involves tension between the swollen and non-swollen parts of the polymer because the latter resists further swelling. The solvent transport in the polymers depends greatly on the polymer chain flexibilities and type of polymer backbone structure. In the case of PC, the absence of long chain flexible groups and the presence of two strong phenyl groups in the chain backbone prevents it from swelling. Since γ-irradiation induces cross-linking in PC, the rigidity of the polymer gets further enhanced and hence there will be no swelling. If a polymer exhibits swelling upon sorption, it is an indication of departure from Fickian diffusion [13, 16]. In the absence of any departure from Fickian behaviour, it can be concluded that there is no swelling upon methanol sorption in PC-ARS and PC-γ. Earlier works on the transport of a mixture of acetone and methanol [29] and iodine in PC [13] also report a Fickian type diffusion without any swelling effects in agreement with the present results.

3.6. Optical microscopy results

In view of the advantage of the transparency of PC, the surface modifications in PC-ARS and PC-γ at different methanol sorption levels were examined with a Nikon-Labophot-2 optical microscope and the microphotographs at selected sorption times are displayed in Fig. 6a–d. These microphotographs reveal direct evidence of cracks appearing on the PC surface. Fig. 6a and b show the surfaces of PC-ARS after a methanol sorption period of 2 and 3 months respectively whereas Fig. 6c and d show the surface modifications in PC-γ at the same sorption period.

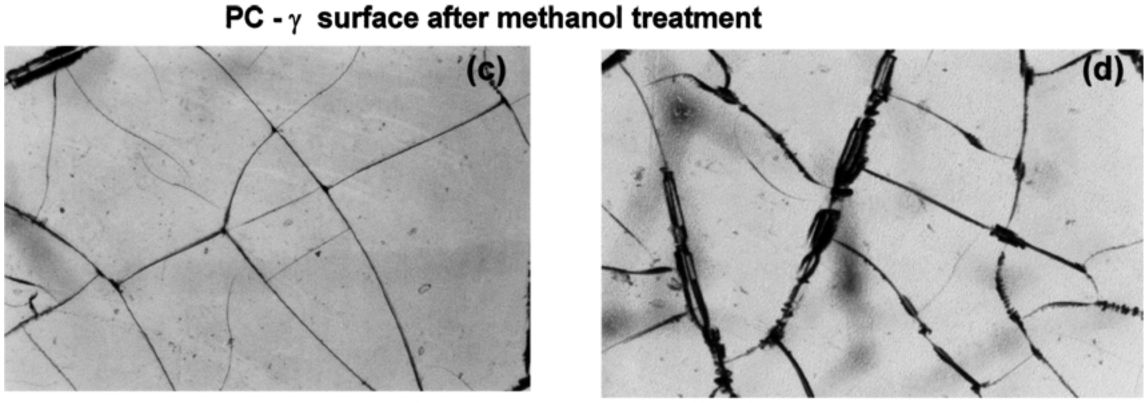
The driving force for the micro-cracks formation is usually the internal stress in the polymer inherently introduced during injection molding, machining, extrusion etc. [48]. The process of micro-cracks formation



PC - ARS surface after methanol treatment

(a) After 2 months (X 200)

(b) After 3 months (X 200)



PC - γ surface after methanol treatment

(c) After 2 months (X 200)

(d) After 3 months (X 200)

Figure 6 (a) and (b). The surface morphology of PC-ARS treated with methanol. (c) and (d). The surface morphology of PC-γ treated with methanol.

is generally termed as Environmental Stress Cracking (ESC), which is the accelerated brittle failure occurring in glassy polymers due to the simultaneous action of internal stress and the specific fluid in contact. More precisely, ESC is due to a combination of internal stress and diffusion of the aggressive chemicals and would not cause this effect (ESC) if the polymer encounters either the residual stress or the chemical fluid individually [49].

When a polymer comes in contact with a specific organic liquid, the small molecules of the organic liquid diffuse into the polymer matrix and induce plasticization which might trigger a ductile–brittle transition to form cracks by debonding in order to release the internal stress [48]. Further, the reduction of polymer surface energy by adsorption of the organic liquid may also contribute to the embrittlement phenomenon.

In a γ-irradiated polymer in which cross-linking has occurred, there will be reduction of chain mobility, which might alter the effect of internal stress. When high levels of stresses are present in a material, the impact strength is lowered and ESC becomes the dominant process [49]. However, since ESC is due to the combined effect of two parameters, as internal stress increases due to cross-linking, the decreased rate of diffusion reduces the micro-cracks formation, which is clearly evident from the microphotographs shown in Fig. 6a–d.

In an earlier study on methanol sorption in an unirradiated and γ-irradiated PMMA, the crack nucleation was reported to have been observed only for γ-irradiated PMMA but not in virgin PMMA [3]. This is attributed to the prominent chain-scission resulting from γ-irradiation, which enhanced the methanol transport in PMMA leading to the appearance of cracks. In the present study, crack generation was observed after the attainment of sorption equilibrium ($\sim$697 hrs; see Fig. 5). Initially, cracks were generated along the boundary of the sample and later seen spreading to the entire surface. The crack density increases and deepens on further sorption period. In case of PC-γ, the crack initiation starts nearly 240 hrs late compared to PC-ARS and the crack density was also found to be less as compared to PC-ARS. This is because, as explained earlier, the increased cross-linking in PC-γ opposes the free entry of the diffusing species; the rate of diffusion thus becomes less and hence the possibility of methanol induced crack generation gets reduced. Thus compared to PC-γ, more cracks are seen in PC-ARS. In both the cases, the intensity of cracks increases as the sorption period advances (see Fig. 6a–d). Thus, in the present study, the main effect of γ-irradiation on ESC process appears to restrict the entry of methanol into PC matrix thereby minimizing the release of internal stress and the number of cracks.

4. Conclusions

Using UV-visible, FTIR, PALS, DSC, Sorption and Optical Microscopy techniques, we have studied methanol diffusion in virgin and γ-irradiated PC and the following observations are made:

- The UV-visible results show that the transparency of the polymer is decreased after γ-irradiation.
- Although the combined results of UV-visible and FTIR results point towards chain-scission to some extent, the presence of C=O and C—O groups after γ-irradiation as per FTIR scan reveal that the scission process is not pronounced at 10 Mrad irradiation.
- The positron results show a decrease in the average free volume size and free volume content after γ-irradiation, which is due to cross-linking of chains and this fact, is supported by DSC results.
- Diffusion of methanol in PC-ARS and PC-γ are of Fickian type and the rate of methanol diffusion gets reduced after γ-irradiation.
- Methanol sorption leads to environmental stress cracking on the PC surfaces and the micro-crack density is less in PC-γ compared to virgin PC.

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