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Positron annihilation study on γ-irradiated cellulose acetate matrix

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A cellulose acetate matrix was irradiated in the dose range 0–250 kGy by γ radiation from a ^{60}Co source under an argon atmosphere; positron lifetime experiments were performed under the same atmosphere at room temperature. The results reveal a dominant intermediate component τ_2 (~430 ps) attributable to a crystalline macrocellulosic domain. Important changes are shown by the long-lived pick-off component τ_3 due to the degradation in the polymer matrix.

(Keywords: cellulose acetate; γ-irradiation; positron annihilation)

Introduction

Studies on the interaction of ionising radiations, such as ^{60}Co γ-radiation or fast electrons, with cellulose have gained momentum mainly due to the industrial significance of cellulose acetate (CA). Cellulosic materials find their use in medical appliances and packages which are often subjected to radiation doses. Therefore, there is a need to study the changes initiated by radiation on the cellulosic materials so that the dose limits do not adversely affect the functional properties[1]. Ionising radiations have the ability to remove electrons from saturated molecules, since the energy of the quanta is substantially greater than the binding energy of an electron. Labile ionic and radical states can thus be produced[2]. Such microstructural changes in the molecular matrix of a polymer may involve free volume changes in the polymeric solids[3,4]. Positron annihilation spectroscopy (PAS) serves as a sensitive probe to yield information about free volume hole sizes and any kind of microstructural change involving electron density changes in the matter[5]. A brief report by Doyle and Pethrick[6] has been found in the literature concerning PAS on a fibrous CA structure.

This paper reports the changes of CA material upon high energy γ-irradiation as probed by PAS.

Experimental

CA (in the form of flakes) with an acetyl content of about 53.5% to 54.5%, procured from BDH, was ground to powder. A Perkin Elmer die was used to pelletise the CA into discs of 12 mm diameter and about 2 mm thick. The pelletisation was done at a pressure of about 560 MPa.

A pair of CA pellets were placed in a specially made glass vial with an air-tight lid and a side inlet for flushing out air. The vial was degassed and filled with argon. The vial was then placed in a γ-irradiation chamber, with the ^{60}Co γ source. The dose rate was about 455 rad min^{-1}. Different pairs of identical samples were irradiated to doses in the range (0–250 kGy).

Positron lifetime measurements were made on the pure and γ-irradiated samples, under argon atmosphere. The positron source was made by depositing ^{22}Na(Cl) onto a thin nickel foil and covering it with an identical foil. This source was sandwiched between two CA samples. The glass vial containing the source–sample sandwich (under argon atmosphere) was placed between two NE111 plastic scintillators, coupled to RCA8575 photomultipliers. The timing pulses were processed by a fast–fast coincidence system. The prompt resolution of the lifetime system was about 260 ps for the prompt γ-rays of ^{60}Co. Each lifetime spectrum contained about 1×10^6 counts. The lifetime data were analysed using the PATFIT-88 package.

Results and discussion

The positron annihilation lifetime spectra of the pure and γ-irradiated samples of the CA matrix could be resolved by a three-component fit analysis. The first component τ_1 was attributed to annihilations within the source foil and self-annihilations of parapositronium, the intensity I_1 of which changes at the higher irradiation doses. The intermediate lifetime component τ_2 (~430 ps) remained almost a constant (*Figure 1*). However, the intensity I_2 ($\geq$ 42%) showed a gradual increasing trend, suggesting a dominant middle phase which could be assigned to the molecular caged structure of the matrix (*Figure 2*). It is found that the primary effects of high energy localisation in cellulose (due to irradiation by ionising radiation) results in long-lived, trapped macrocellulosic radicals[1,7] up to a certain dose rate. These cellulosic radicals are located in the more ordered or crystalline regions of cellulose. The intermediate component could result from this domain, which further declines due to the deterioration of the structure at higher dose rates and upon long-term exposure[8]. The complex morphological structure[9] of CA material restricts further inference from being drawn at the higher dose rates.

The longest lived component, τ_3, showed profound

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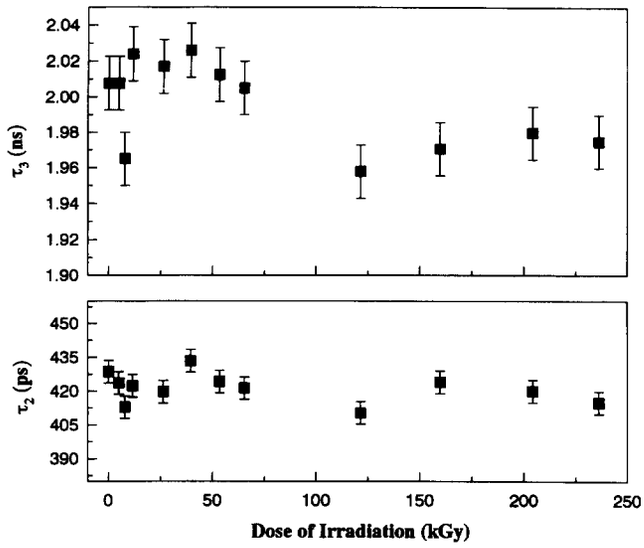

Figure 1 The positron lifetime components τ_2 and τ_3 plotted as a function of the dose of irradiation

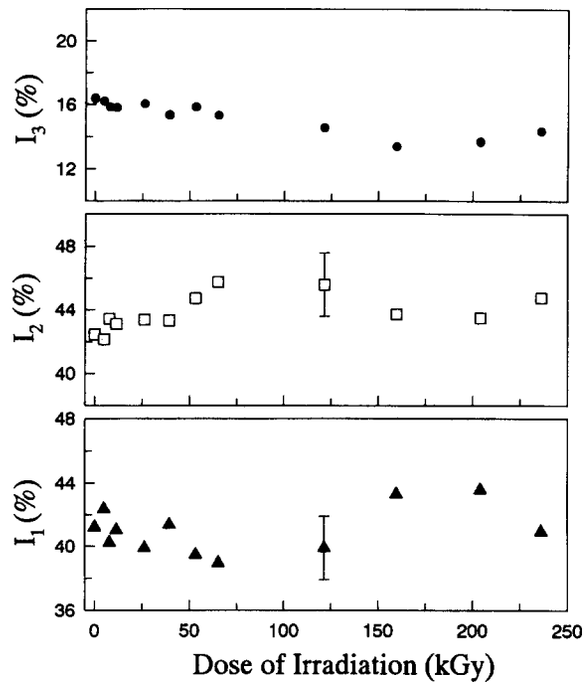

Figure 2 The intensities I_1, I_2 and I_3 plotted as a function of the dose of irradiation. The size of the point accounts for the error in I_3

changes with the irradiation dose (*Figure 1*). The corresponding intensity I_3 (*Figure 2*) showed a gradual decrease at higher doses. This component is generally attributed to pick-off annihilation of orthopositronium in the free volume sites of the amorphous polymer material, due to the fact that a positronium atom can be trapped in these atomic-sized holes with sizes ranging up to several Ångströms[5]. At the dose rates of the high energy ionising radiation to which the cellulosic matrix is subjected in the present study, it is expected that the polymeric structure would undergo subsequent depolymerisation, changing the free volume sites; thus, the probability of overlap of electron and positron wave functions increases with the production of free radicals and a rise in the electron density due to fragmented products[8]. Accordingly, τ_3 showed a prominent change after a certain dose (*Figure 1*) and I_3 showed a gradual decrease in free volume sites. It is to be noted that in this region of higher dose, there is a consequent increase in I_1 (~2%) which may be attributable an to increase in parapositronium annihilation owing to an increase in free radicals, though this may be difficult to depict from the lifetime spectroscopy alone.

Conclusion

The positron annihilation data presented here reflect the important changes in the CA matrix upon high energy γ-irradiation up to doses of about 250 kGy, under argon atmosphere.

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