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Thermal studies on unirradiated and γ-irradiated polymer of allyl diglycol carbonate

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Abstract

The thermal decomposition of unirradiated and γ-irradiated (5.93–15.5 MRad dose range) allyl diglycol carbonate polymer (trade name, CR-39) was studied by thermogravimetry (TG) and differential thermal analysis (DTA). These studies indicate four main decomposition steps in CR-39 polymer in air. Assessment of the influence of radiation dose on the above range shows that while the 5.93 MRad γ-irradiated polymer CR-39 degrades in three steps, the 15.5 MRad γ-irradiated polymer degrades in only two steps. The kinetics of the different stages of degradation were also evaluated from the TG curves. Irradiation enhances the decomposition rate and the effect increases further with increasing radiation dose. The activation energy values calculated for all the decomposition stages decrease on irradiation.

Keywords: Activation energy; Allyl diglycol carbonate; Decomposition; DTA; Gamma radiation; Polymer; SSNTD; TG

1. Introduction

Allyl diglycol carbonate polymer [1–4] (trade name, CR-39) is a well known and widely used solid-state nuclear track detector in nuclear science and technology [1]. Solid state nuclear track detectors (SSNTDs) are insulating solids, both naturally

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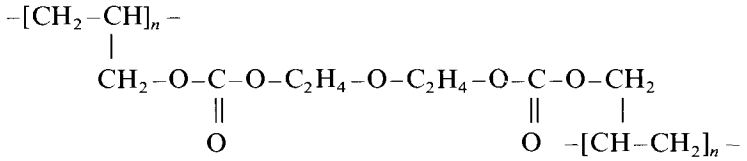
occurring and man-made. Allyl diglycol carbonate is one of the most promising plastics used as SSNTDs [1]. One of the important applications of these detectors is in fission studies [2–4]. In studies connected with nuclear fission induced by neutrons, the detectors are exposed to high doses of radiations such as β- and γ-rays, neutrons, etc. in a nuclear reactor. It was thought interesting to investigate the thermal behaviour of these SSNTDs and to see the influence of γ-irradiation on the thermal stability of these SSNTDs. In the present work, these studies are carried out with CR-39. The thermal behaviour of CR-39 has not been reported in the literature.

2. Experimental

CR-39 is a thermoset plastic made by the polymerization of either allyl diglycol carbonate or diethylene glycol bis-allyl carbonate. The polymer structure is



The thermal decomposition of unirradiated and γ-irradiated CR-39 film was carried out in flowing air using differential thermal analysis (DTA) and thermogravimetry (TG). The thermograms were recorded at the heating rate of 6 K min^{-1} up to 600°C in a ULVAC thermoanalyser using sintered Al_2O_3 as the reference material for DTA. For the γ-irradiation, CR-39 pieces, 2 cm^2 in area, were cut from a big sheet. These samples were irradiated with ^{60}Co γ-rays for doses of 5.93 and 15.5 MRad at the Radiochemistry Division, BARC.

3. Results and discussion

The TG and DTA curves of unirradiated CR-39 in air showed four main stages in its decomposition. These four steps are clearly indicated by four arrests in the TG curve. The corresponding DTA curve also showed four exothermic peaks with respect to the four stages of decomposition. The DTA data and TG temperatures for all these stages are given in Table 1. The effect of ^{60}Co γ-irradiation on the thermal decomposition of CR-39 was to reduce the number of decomposition stages: 5.93 MRad γ-irradiated CR-39 decomposed in three steps while 15.5 MRad γ-irradiated decomposed in two steps. Irradiation lowers the temperature at which the decomposition begins (T_i) for each stage. The temperatures corresponding to complete decomposition (T_f) and to maximum decomposition rate (T_s) were also lowered in the irradiated samples (Table 1). The salient features of the thermal decomposition of γ-irradiated polymer are listed in Table 1. The TG curves (Fig. 1)

Table 1
Thermal decomposition data and kinetic parameters calculated using the Horowitz–Metzger method

Sample	DTA peak temp. range/°C		TG			Wt. loss/%	E/kJ mol^{-1}
			T_i/°C	T_f/°C	T_s/°C		
Unirr. CR-39							
Stage 1	290–380	(Exo)	55	370	360	69.0	156.3 ± 2.9
Stage 2	380–410	(Exo)	370	415	410	79.3	134.7 ± 7.6
Stage 3	410–480	(Exo)	415	445	430	91.4	321.3 ± 9.5
Stage 4	480–550	(Exo)	460	565	530	100	334.9 ± 7.0
5.93 MRad γ-irr. CR-39							
Stage 1	265–370	(Exo)	50	365	355	72.8	101.7 ± 7.6
Stage 3	370–465	(Exo)	365	435	420	95.0	278.0 ± 8.2
Stage 4	465–530	(Exo)	450	540	520	100	286.7 ± 13.7
15.5 MRad γ-irr. CR-39							
Stage 3	360–460	(Exo)	45	430	415	93.0	249.1 ± 6.0
Stage 4	460–530	(Exo)	440	530	500	100	228.8 ± 8.0

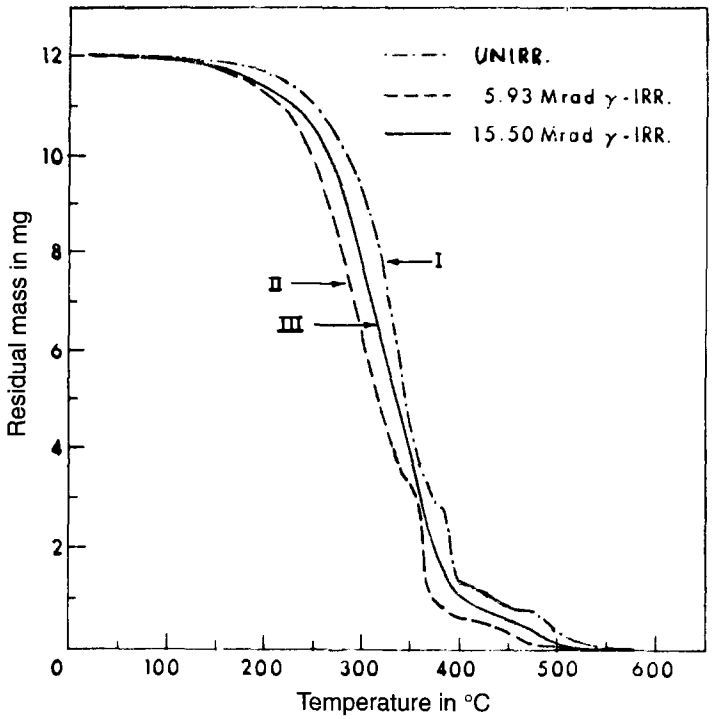


Fig. 1. Thermogravimetric curves of unirradiated and γ-irradiated allyl diglycol carbonate.

show that 100% weight loss occurs in the TG experiments up to 600°C in unirradiated as well as irradiated CR-39 polymer, leaving no residual material. The volatile products have not been analysed in the present experiments. It appears that CR-39 polymer combines with oxygen and gives oxidative degradation products, noted by exotherms in the DTA (Table 1). A thermogram of the polymer in an argon atmosphere yielded a little carbon residue and endothermic-type reactions, which confirmed the participation of oxygen in the thermo-oxidative process.

In order to compare quantitatively the effects of γ-irradiation on the thermal decomposition of CR-39, the kinetics of the different stages of decomposition were investigated from the TG thermograms according to the various methods suggested [5–7] and applied [8,9] in the literature for the calculation of kinetics parameters. The data for both unirradiated and irradiated CR-39 polymer were found to fit well to Horowitz–Metzger's method [7] for the kinetic analysis of non-isothermal data of a first-order reaction.

In this method $\ln[\ln(W_0/W)]$ is plotted versus θ, as shown in Fig. 2, where W_0 and W are the weights of the polymer initially and at time t, and $\theta = T - T_s$, where T is the temperature at weight W of the polymer and T_s is the temperature at which W/W_0 equals $1/e$. The slope of the straight line thus obtained is given by $\Delta E/RT_s^2$, where R is the gas constant and ΔE is the energy of activation. The ΔE values

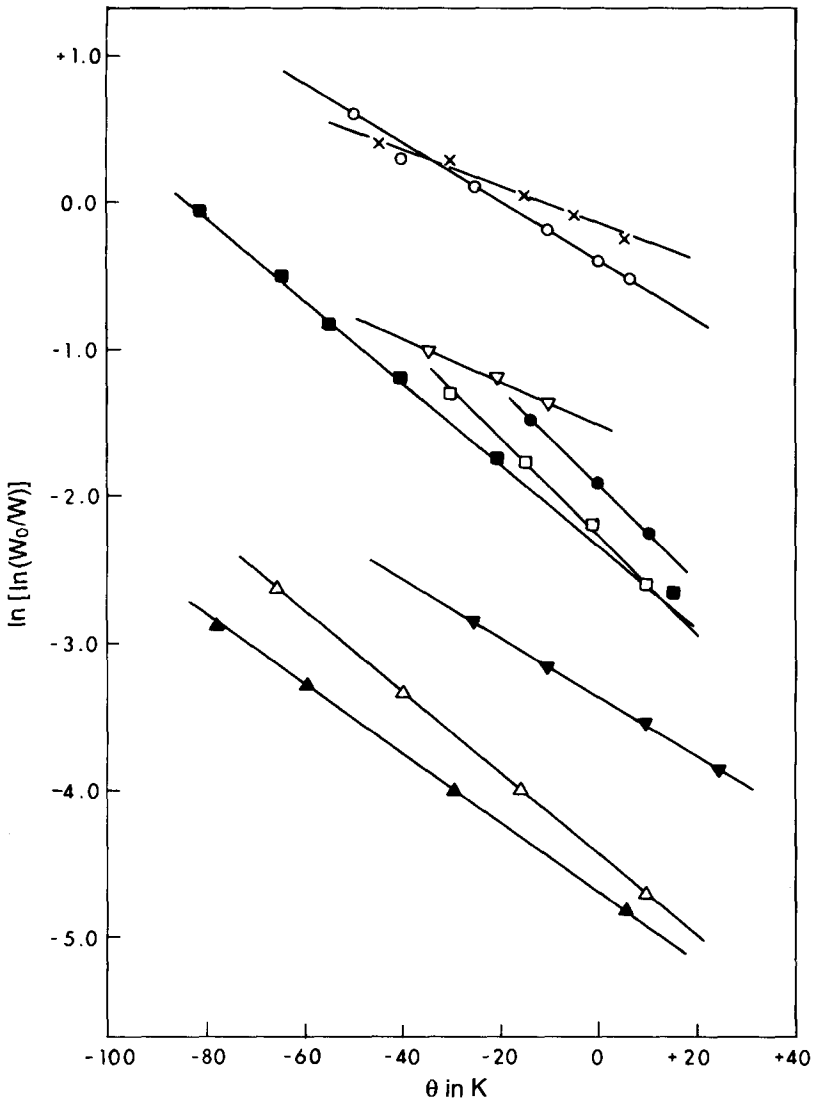


Fig. 2. Horowitz–Metzger analysis of the kinetics of different stages of the thermal decomposition of unirradiated and γ-irradiated allyl diglycol carbonate. Unirradiated: ○, 1st stage; △, 2nd stage; ●, 3rd stage; ▽, 4th stage. 5.93 MRad irradiated: ×, 1st stage; □, 3rd stage; ▼, 4th stage. 15.50 MRad irradiated: ■, 3rd stage; ▲, 4th stage.

calculated from the TG curves by this method for the different stages of thermal degradation of unirradiated and γ-irradiated CR-39 polymer are presented in Table 1. It is obvious that γ-irradiation results in a substantial decrease in ΔE in that values decrease with increasing dose. This decrease indicates that main-chain

scission is predominant in γ-irradiation of CR-39. Studies by Stenjay and Portwood [4] on γ-irradiated CR-39 have also shown that the main chains are relatively inert and it is the cross-links that are damaged by scission of the diethlyene glycol dicarbonate units.

4. Conclusions

γ-Irradiation cleaves the cross-links in CR-39 and makes it less stable to decomposition in air. Similar studies will be carried out on CR-39 irradiated with the electrons, neutrons, alpha particles and heavy ions.

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