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## The influence of solar radiations to the physical and structural properties of CR-39

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**Abstract** : Long chain polymers owe many of their properties to the structural arrangements of their molecules and are extensively used for many industrial and applied sciences. One of such application is their perspective use in the field of solid-state nuclear track detectors. However they are profoundly influenced by low LET radiations exposure and new structural arrangements may emerge. CR-39 is one of the most popular polymeric track detectors, however its aliphatic nature restricts its applications. Thus in the present investigations the damage densities produced by solar radiations to the polymer have been estimated by analyzing the structural, physical and etching properties of the polymer. The polymer is found to be highly sensitive towards solar radiations and great changes in physical and structural properties of polymer have been observed. The sensitivity of the polymer has been found to decrease by 83.40% during eight months.

**Keywords** : Solar radiations, track registration, physical changes, CR-39.

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### 1. Introduction

CR-39 was introduced by Columbia Resins Pvt. Ltd. in 1939 to replace glass lenses, as it is highly unbreakable, lightweight and exhibits high transparency. The polymer consists of short polyallyl chains joined by the links containing carbonates and diethylene glycol groups into a dense three-dimension network. The monomeric unit of the polymer is shown in Figure 1.

At the branching point of this network, two links consist of polyallyl chains and other consists of diethylene glycol bisallyl carbonate. The polymer was commercialized in the field of solid state nuclear track detectors by Cartwright *et al* [1] and Casson and Benton [2] due to its ability to record even lighter particles. Thereafter the polymer get popularized in the field of SSNTDs and found versatile applications. CR-39 can also

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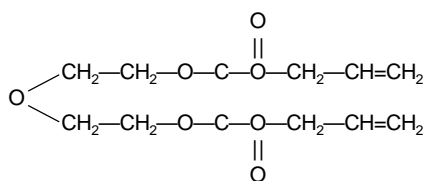


Figure 1. The monomeric unit of CR-39.

be used to detect the neutron [3–5] due to its ability to register recoil protons produced during neutron collisions with the molecules of the polymer. But the aliphatic nature of the polymer makes it highly sensitive towards environmental conditions and induces changes in the structural

optical and track registration properties of the polymer. Sometimes these induced changes also seem to be an obstacle to its use as track recorders in the open environment, for it easily absorbs solar radiation that initiate photolytic, photo-oxidative and thermo-oxidative reactions causing polymer degradation [6–8]. The degradation suffered during these processes may range from mere surface discoloration to extensive loss of mechanical properties that severely influence the performance of the polymer as a track recorder. Many authors [9–14] have analyzed the influence of solar radiations to CR-39 in different environmental conditions. However, no literature is available for the open exposure of the polymer in Indian environment.

The present investigations have been carried out to study the influence of solar radiations on CR-39 in the open environment. The modifications induced in the structural and track registration properties of the polymer have been analyzed.

## 2. Experimental

A set of CR-39 samples procured from Pershore Mouldings Ltd. of thickness 250  $\mu\text{m}$  was exposed to Cf-252 fission fragment source and thereafter to solar radiations for one year from February 1, 2003 to February 1, 2004 with a time interval of one month. The samples were fixed on the wire with the help of cellophane and hung in open environment. The changes in the structural properties of the polymer have been analyzed with the help of FTIR spectra of the pristine and solar radiation exposed CR-39. The spectra were taken using the Perkin-Elmer 7500 FTIR spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$ . The variations in bulk and track etch rates and sensitivity of the polymer have been determined at a constant temperature of 55°C. The method is illustrated elsewhere [15].

## 3. Results and discussion

Examining the physical changes induced in the polymer due to solar radiation may lead to the assessment of the damage caused to the polymer. Thus the variations in the morphology and discoloration of the polymer with solar radiation have been analyzed. The transparency of the polymer is found to diminish after three months and it gets yellowish tinge after 8 months exposure. These discolorations may be due to the entrapping of free radicals produced by heat and UV radiations of sunlight, to the molecular cages. Cracking and creeping effects also came into existence after duration of 8 months that may be attributed to the weather-inducing aging of CR-39. High

moisture content from overnight humidity and rainfall during this period can also be taken as an important parameter to exterior degradation of the polymer. Water may also accelerate the effect of radiation and converse may also be true. However the presence of oxygen cannot be ignored as polymers subjected to irradiation degrades much faster in the presence of oxygen [16]. For example discoloration of polystyrene occurs more rapidly when irradiation is performed in the oxygen atmosphere [17].

The physical analysis of the polymer is not enough to extract the information regarding the modifications induced in the track registration and structural properties. Thus the variation in the bulk and track etch rates and sensitivity of the polymer with exposure time has been determined and is reported in Table 1. It can be noticed that  $V_B$  and  $V_T$  increases with exposure time having exceptions at 6 months for  $V_B$  and 4–6

**Table 1.** The variation of bulk etch rate, track etch rate, and sensitivity in case of CR-39 exposed to sunlight.

Sunlight exposure (Months)	$V_B$ ( $\mu\text{m}/\text{h}$ )	$V_T$ ( $\mu\text{m}/\text{h}$ )	S
0	0.54	9.77	18.09
1	0.71	13.13	18.49
2	2.76	41.26	14.95
3	242.41	1312.50	5.41
4	585	988.86	1.69
6	143.25	953.70	6.66
7	195.06	1401.90	7.19
8	2470.62	6598.20	2.67
10	2644.95	—	—
11	4851.3	—	—
12	9720	—	—

months for  $V_T$ , the etch rates have been found to decrease during these times. The tracks could not be observed after 10 months exposure. It may be attributed to the greater enhancements in bulk etch rate as compared to that of track etch rates. The track etch rate is found to increase by 675 times than its initial value whereas the bulk etch rate has increased by 4574 times in the same duration (8 months) and thereafter increased to 18000 times in twelve months. Since the condition for track formation requires  $V_T > V_B$  and thus may be attributed as the reason of the disappearance of the tracks at higher exposures. The sensitivity of the polymer has been found to decrease by 83.40% during the exposure of eight months. The  $\alpha$ -sensitivity of the polymer has also been found to diminish with increasing exposure time as no  $\alpha$ -tracks could be revealed after two months. Our results corroborate the findings of Ansari *et al* [9], who have also observed the drop in track registration response of CR-39 for  $\alpha$ -particles from Am-Be source by about 87% for a sunlight exposure of 180 days.

Abu-Jarad *et al* [18] have also reported the increase in  $V_B$  and  $V_T$  in case of CR-39 exposed to sunlight followed by constancy after 30 hrs. Mattiulah and Kudo (1990) have also observed an increase in  $V_B$  and  $V_T$  with sunlight exposure of CR-39. They have observed the changes in sensitivity and critical angle too.

Henke *et al* [19] have also noticed a 5-fold increase in  $V_T$  for two-hour exposure of lexan to sunlight. Wong and Hoberg [10] showed that 8 days exposure of CR-39 to sunlight causes the increase in the bulk etch rate of the polymer by 80%. The reason may be the increased rate of chain scission and molecular unit cracking produced by solar radiations and other environmental conditions to the polymeric units.

For extracting more information about the changes in the internal structure of CR-39, FTIR analysis has been performed. Typical FTIR spectra of pristine and solar radiations exposed CR-39 for different time spans (1–12 months) in transmission mode is shown in Figure 2. The transmission bands for  $[-(C=O)-O-C=C]$  ( $1800-1750\text{ cm}^{-1}$ ) and C–H stretch ( $3000-2818\text{ cm}^{-1}$ ) with peaks at  $1696\text{ cm}^{-1}$  and  $2984\text{ cm}^{-1}$  for C=O

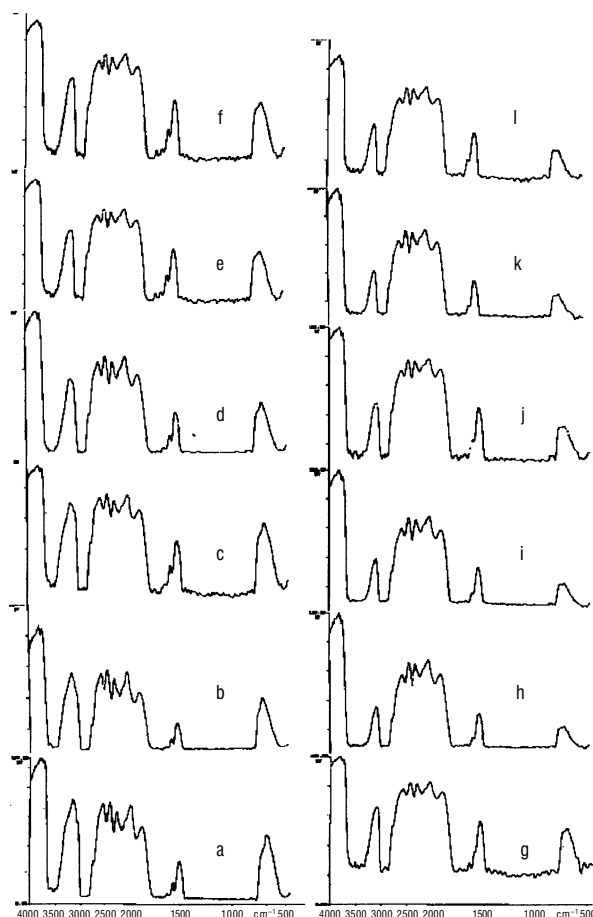


Figure 2. FTIR spectra of pristine (a) and sunlight (12 months) exposed (b-1) CR-39.

and  $sp^3$  C–H stretch respectively have been observed. The introduction of C=C band adjacent to carbonyl group ascertains the presence of  $[-(C=O)-O-C=C]$  molecular species and results in the delocalization of the  $\pi$ -electrons in the C=O and C=C bonds. This conjugation increases the single bond character of C=O and C=C bonds in the resonance hybrid and hence lowers its frequency by 25–45  $cm^{-1}$ . The assignment of these peaks is well summarized by William and Fleming [20]. On the other hand a sharp band of  $CO_2$  (2368  $cm^{-1}$ ) alongwith -OH group in the range of 3636–3454  $cm^{-1}$  can also be noticed. Another transmission bands at 2500, 785 and 501  $cm^{-1}$  are attributed to carboxylic acids, out of plane C–H bend and olefin stretches respectively.

Dependence of transmittance attributed to these bands on sunlight exposure has been estimated from the changes in the intensity of the respective bands. The transmittance for band attributed to  $[-(C=O)-O-C=C]$  has been found to increase consistently. However exceptions for the exposures of 3 and 8 months with a decrease in the intensity of carbonyl and unsaturated molecular species have been observed. The relative changes are smaller in case of C=O as compared to C=C as could be evidenced from the peak intensity of 1695 and 2984  $cm^{-1}$  during these months. The increases in the intensity of -OH band alongwith the appearance of new band at 3754  $cm^{-1}$  point to the hydrolysis of the polymer. It may be attributed to the absorption of water from the environmental humidity. The intensity of 3754  $cm^{-1}$  is higher during first three months and thereafter for last two months. It may be due the rainfall during these months. The increase in the intensity of -OH with low LET radiations has already been pointed out by Yamauchi *et al* [21] and is ascertained by Malek and Chong [22,23].

The FTIR spectra of the sunlight exposed CR-39 around  $CO_2$  band shows an increase in the intensity indicating the production and entrapping of the gas in the free sites of the polymer. The exceptions at one and six months' exposure indicate the evaporation of the gas from the entrapping centers. Some new weak bands at 1475, 1106 and 1078  $cm^{-1}$  that after 2 months and 3335  $cm^{-1}$  after 4 months exposure, are attributed to the production of alkenes and alkynes, respectively and indicate the domination of ether character of the polymer. Thus it may be concluded that the overall results indicate the enhancement of the unsaturated character of the polymer.

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