Changes in physical properties and molecular structure of butyl rubber during γ-irradiation

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Butyl rubber samples have been aged by γ-irradiation at 25°C in air. The change in molecular structure due to chain scission and formation of oxygenated groups also change the $\bar{M}_n$, tensile strength and density of butyl rubber. The rubber predominantly undergoes chain scission upon γ-irradiation up to a dose of 50 Mrad, but there is also substantial chain crosslinking above 50 Mrad. The yield $G(x)$ has been found, which provides an insight into the mechanism of the radiolytic degradation. Hydroperoxide is the major product and unsaturation is incorporated in the polymer back bone. The change in molecular structure due to recombination and chain scission are followed by the formation of a more ordered structure and hence an increase in density.

Keywords Butyl rubber; γ-irradiation; radiolytic degradation; chain scission; crosslinking

INTRODUCTION

In the previous papers[1–7] in this series the effect of u.v. irradiation on butyl rubber films has been studied by light scattering and u.v. techniques. It was observed that butyl rubber undergoes predominantly random chain scission upon treatment with 254 and 366 nm radiation in air. Jellinek and coworkers[8–9] have carried out the studies on photodegradation of butyl rubber in the presence of NO_2, SO_2 and O_3 using polychromatic u.v. radiations above 280 nm. They also concluded that the reactions are of a chain-scission type on the basis of viscometric studies of non-degraded and photodegraded polymer samples. Very little data on γ-irradiation of butyl rubber are available[10] and it has not been proved yet whether the values of $G(x)$ and $G(s)$ and also the nature of chain scission are dose-dependent.

Here we have investigated the mechanism of radiation degradation of butyl rubber by monitoring the changes in molecular weight, degree of unsaturation, hydroperoxide content, tensile strength and density as a function of radiation dose. The radiolysis products have also been determined. The change in molecular structure and its correlation with the properties and the dependence of $G(x)$ and $G(s)$ values on the dose have been investigated.

EXPERIMENTAL

Sample preparation

Butyl rubber (BR), a copolymer of isobutylene and isoprene (M/s Swastic Rubber Co., Poona, India) was purified by acetone and methanol extractions and kept in contact with petroleum ether (40°–60°C). The rubber was precipitated from 1 per cent solution in petroleum ether with acetone. It was dried *in vacuo* for 36 to 48 h to a constant weight.

Irradiation procedure

Small samples of BR (5–20 mg) for analysis were weighed into thin-walled pyrex glass tubes (4 mm in diameter) and sealed in a length of 30 mm. Irradiation was carried out in a Cobalt-60 Gammacell at a dose rate of 0.25 Mrad h^{-1} at 25°C in air. The sample were used as such for all the investigations.

Determination of kinetic parameters

The progress of degradation was followed by viscosity measurements in decaline at 30 ± 0.1°C using a modified Cannon-Ubbelhode type viscometer[11]. No kinetic energy correction was applied as the flow time of the pure solvent was more than 150 seconds. The viscosity-average molecular weight ($\bar{M}_v$) was obtained from the values of intrinsic viscosity $[\eta]$ at 30°C using Mark-Houwink equation:

$$[\eta] = 4.37 \times 10^{-4} \bar{M}_v^{0.614} \qquad (1)$$

The viscosity-average molecular weights ($\bar{M}_v$) were converted into number-average molecular weights ($\bar{M}_n$) by using the relation[12]

$$\frac{\bar{M}_v}{\bar{M}_n} = \left[\frac{\Gamma(3+a)}{2^{(1+a)}}\right]^{1/a} \qquad (2)$$

where $\Gamma(3+a)$ is the gamma function of $(3+a)$, 'a' being the exponent in the Mark—Houwink relation,

$$[\eta] = K \bar{M}_v{}^a \qquad (3)$$

Biswas *et al.*[13] have also used equation (2) to process the data on the ultrasonic degradation of BR in solutions.

The initial number-average chain lengths (p_{no}) and that at any time t, (p_{nt}) can be calculated from the corresponding values of the number-average molecular weights, $\bar{M}_{no}$ and $\bar{M}_{nt}$ respectively. Alternatively, the value of the average number of cuts s per original chain length can be determined by using the equation:

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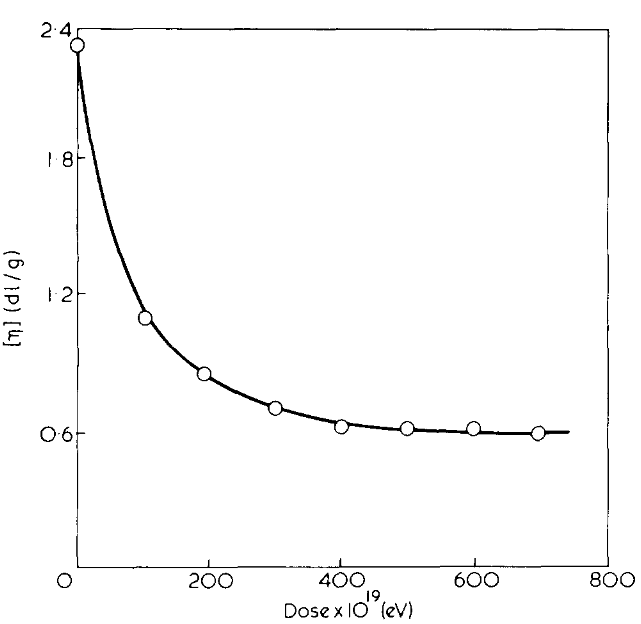

Figure 1 Change in intrinsic viscosity [η] of butyl rubber during γ-irradiation for different doses

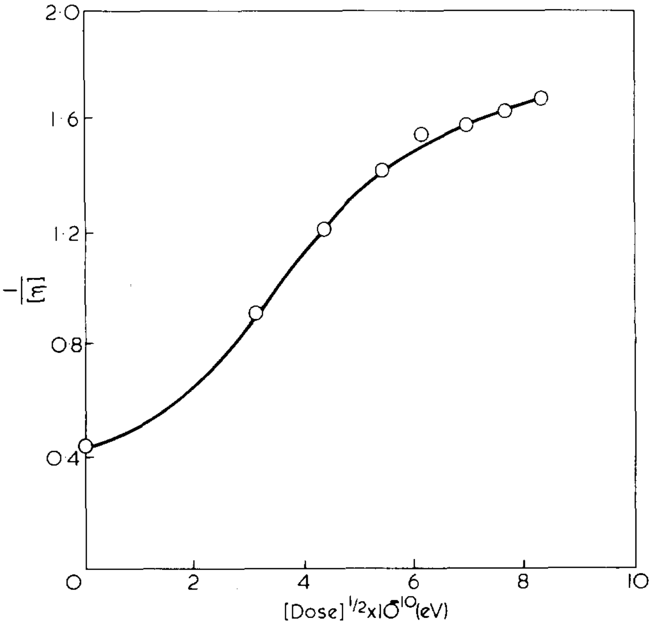

Figure 2 Change in 1/[η] of butyl rubber during γ-irradiation for different doses

$$p_{nt}/p_{no} = 1/(s+1) \tag{4}$$

This equation has been used successfully to study the kinetics of degradation of natural rubber[13], polyethylene[11] and SBR[14].

Determination of unsaturation

The unsaturation (i.e. the presence of ethylenic double bonds) was determined[15] from the 'iodine number' obtained by dissolving the BR sample in chloroform.

Determination of hydroperoxide contents

Polymer hydroperoxides produced during irradiation were determined by the method of Bocek[16]. This method is sufficiently sensitive to measure the very low concentrations (10^{-7} moles) of hydroperoxides found in degraded polymer samples.

Spectrophotometric measurements

Molecular changes were studied by i.r. spectroscopy using a Perkin-Elmer 21 spectrophotometer.

Determination of mechanical properties

The tensile strength was measured, according to ASTM D 412-68 by using Instron tensile tester, model TTCM, at an elongation speed of 50 cm min^{-1}. Density measurements were done using methanol–water mixtures.

RESULTS AND DISCUSSION

Inspection of *Figures 1–3* reveals that in the initial stages of degradation, the value of [η] decreases, and 1/[η] and $\bar{M}_{no}/\bar{M}_{nt}$ increase rapidly with the dose and a point of inflexion is reached after 50 Mrad. Such a sharp decrease in [η] and sharp increase of 1/[η] and $\bar{M}_{no}/\bar{M}_{nt}$ in the initial stages of degradation generally indicates a random breaking of bonds in the polymer chain. In fact, after a dose of 50 Mrad visible opalescence occurs, due to crosslinking and microgel formation by the fragments of the BR molecules and the reaction is predominantly crosslinking with negligible chain scission.

Using Kilb's equation[17] in the region up to 50 Mrad, the value of $[G(s)-4G(x)]$ was estimated with a plot of $1/\bar{M}_{nt}$ vs. dose.

$$\frac{1}{\bar{M}_{nt}} = \frac{1}{\bar{M}_{no}} + \frac{[G(s)-4G(x)]D}{200N} \tag{5}$$

In equation (5) $G(s)$ and $G(x)$ represent the number of chain scissions and crosslinks per 100 eV of absorbed dose respectively. D is the absorbed dose and N is Avogadro number. The value of $[G(s)-4G(x)]$ was found to be 0.11. At very low dose, where the dominant process is chain scission only, the value of $G(s)$ has been found to be 0.27. Thus, in this range $G(x)$ is 0.04 in the presence of air.

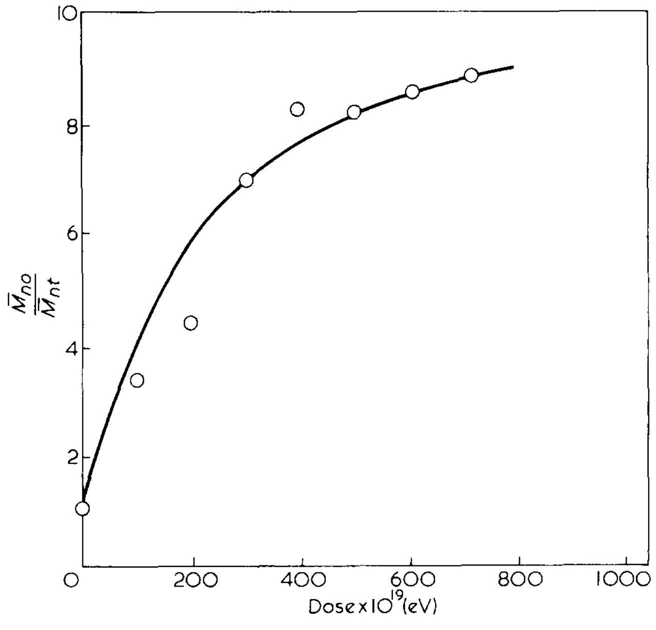

Figure 3 Change in the ratio of number-average molecular weight ($\bar{M}_{no}/\bar{M}_{nt}$) of butyl rubber during γ-irradiation

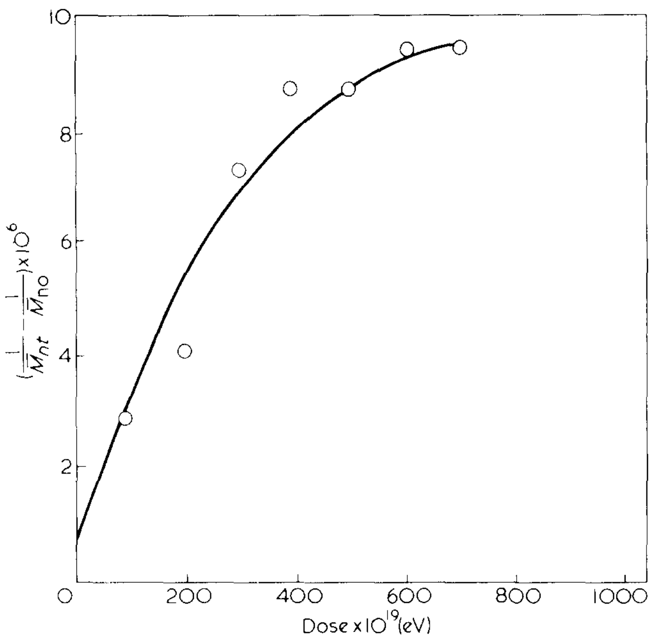

Figure 4 Change in $(1/\bar{M}_{nt} - 1/\bar{M}_{no})$ of butyl rubber during γ-irradiation

From *Figure 4*, it can be seen that the plot of $(1/\bar{M}_{nt} - 1/\bar{M}_{no})$ vs. dose is linear initially, proving that at the beginning of irradiation a random scission is dominating and the breaking of one type of bond is taking place.

This is true at low degrees of degradation, but then a significant deviation from linearity was observed. Similar relationships have been found in cases where crosslinking (branching) competes with chain-scission reactions at higher degrees of degradation[4].

The molecular changes, i.e. formation of carbonyl and unsaturated groups, in BR during γ-irradiation are shown in *Figure 5*. Different small bands appear in the carbonyl region 1760–1700 cm^{-1} after a dose of 1×10^{21} eV and form a broad band in the 1700–1690 cm^{-1} region after 3×10^{21} eV due to the formation of ketonic (1720 cm^{-1}), carboxylic (1705 cm^{-1}), aldehydic (1730 and 1735 cm^{-1}) and ester (1745 cm^{-1}) groups. Two weak bands at about 1790 and 1785 cm^{-1} appear during irradiation, due to the formation of γ-lactone and peracidic groups and their intensity changes with the dose. One more band centring at about 1680 cm^{-1} also emerges after 3×10^{21} eV showing the formation of unsaturated ketonic groups[18]. The carbonyl band in the spectra of BR aged with doses of 5×10^{21} and 7×10^{21} eV broadens and splits due to the formation of different kinds of oxygenated groups but the intensity gradually decreases. This decrease may be due to the photolysis of molecules having ketonic carbonyl groups. Two weak bands have been found to appear at 3440 and 3550 cm^{-1} (hydroxyl region), due to the formation of free and conjugated hydroperoxy groups, in the spectra of irradiated samples. Intensity of the bands at 1150 and 1025 cm^{-1} also changes with irradiation due to the change in concentration of ether type bands (C–O–C) in BR. The intensity of these bands decreases up to 5×10^{21} eV. These bands shift towards the lower wavenumber.

Bands in the region of 1000–940 and 930–860 cm^{-1} in the untreated BR are due to the presence of a few olefinic bonds in the molecular chains of BR. The intensity of these bands decreases sharply in 1×10^{21} eV of γ-ageing. The olefinic bands reappear at about 964 cm^{-1} (vinylidene, R–CH=CH–R′), 910 cm^{-1} (vinyl, R–CH=CH$_2$) and 888 cm^{-1} (*trans*-vinylene, [R(R′)C=CH$_2$] on further ageing up to 3×10^{21} eV and their intensity increases up to 7×10^{21} eV.

The presence of olefinic unsaturation, i.e. $\rangle C=C\langle$ bonds was determined (*Figure 6*) for unirradiated and irradiated specimens by measuring the 'iodine number' The original specimens already showed a small degree of unsaturation which was not directly related to the initial molecular weight, which was subtracted from the total unsaturation of the irradiated samples. In *Figure 6* the unsaturation of BR due to γ-irradiation in air is plotted against the reciprocal of $\bar{M}_n$.

Figure 7 shows that the tensile strength decreases up to 5×10^{21} eV and on further irradiation it increases slightly. The value of density increases initially and a point of inflexion is reached after 5×10^{21} eV.

On the basis of these results the steps of molecular changes can be correlated to the changes in properties of BR. The small concentration of unsaturated groups (*Figure 6*) in unirradiated BR and the scission of C–H bonds of methylenic groups in the α-position of the double bond in irradiated BR initiate degradation. The degradation proceeds through the formation of hydroperoxides which are formed (*Figure 8*) as the primary products of degradation and undergo a variety of reactions. The environmental oxygen molecules act like a diradical and are incorporated as such without the

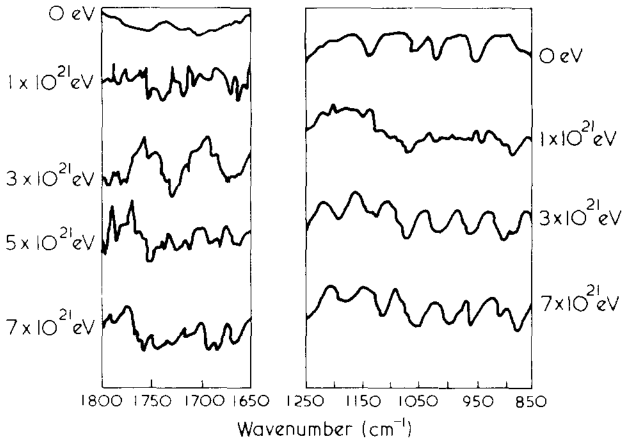

Figure 5 Change in i.r. spectra of butyl rubber during γ-irradiation

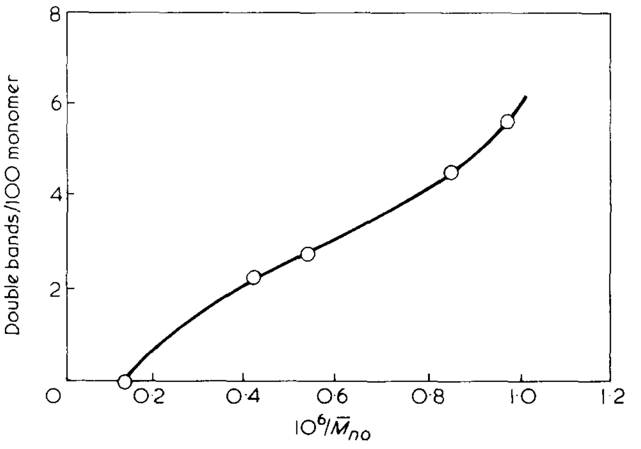

Figure 6 Change in unsaturation of butyl rubber during γ-irradiation

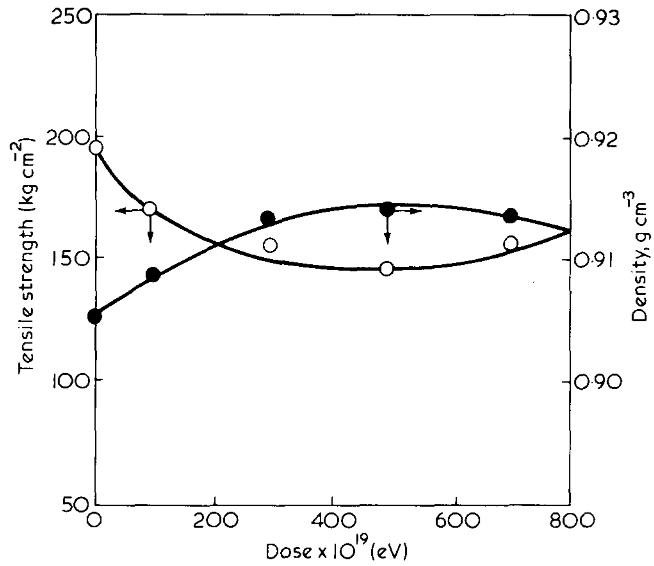

Figure 7 Change in tensile strength and density of butyl rubber during γ-irradiation

rupture of the O–O bond. The chain-scission may take place subsequently depending upon the rupture of the hydroperoxide bond which decomposes into free radicals. These radicals propagate the reactions by hydrogen capture from the polymer molecules. The RO free radical (R is a long chain) formed by the scission of O–O bond of hydroperoxy group can form terminal aldehydic and ketonic groups.

The carbonyl groups can also cleave the backbone chain of the polymer by Norrish type I and II reactions. The type II reaction does not produce free radicals and thus cannot initiate the reaction while the type I reaction produces free radicals but the quantum yield of this reaction has been estimated to be low[19]. The increase in intensity of the band at 910 cm^{-1} may be due to the formation of $-CH=CH_2$ type unsaturated groups. The carbonyl free radicals can also recombine with RO type free radicals to form ester or γ-lactone type groups. The formation of unsaturated groups such as $RCH=CH-R'$ (964 cm^{-1}) and $R(R')C=CH_2$ (888 cm^{-1}) may possibly occur at the hydrogen capture sites, where the availability of oxygen is less. The formation of wide variety of oxygenated groups at doses $>7\times10^{21}$ eV indicates that the rate of degradation increases on prolonged ageing due to the formation of more reactive sites. The molecular enlargement may also be due to the recombination of peroxy free radical:

$$ROO\cdot + R'OO\cdot \rightarrow ROOR' + O_2 \qquad (6)$$

The decrease in tensile strength up to 5×10^{21} eV may be due to the high quantum yield of ester bond by recombination of oxygenated free radicals, which may decrease the average strength of the molecular chain. The increase in density at the same time could be explained by the fact that a considerable amount of low molecular weight material is simultaneously formed up to 5×10^{21} eV and the rate increases up to 7×10^{21} eV. The shorter and more mobile molecular chains will have an increased probability of attaining a closer packing in the amorphous region and hence increase the density. The increase in secondary bond forces by ester groups (polar groups) formation also supports formation of a more ordered structure. The increase in tensile strength may be due to increase in crystallinity of BR as highly ordered structures are formed on prolonged ageing up to 7×10^{21} eV.

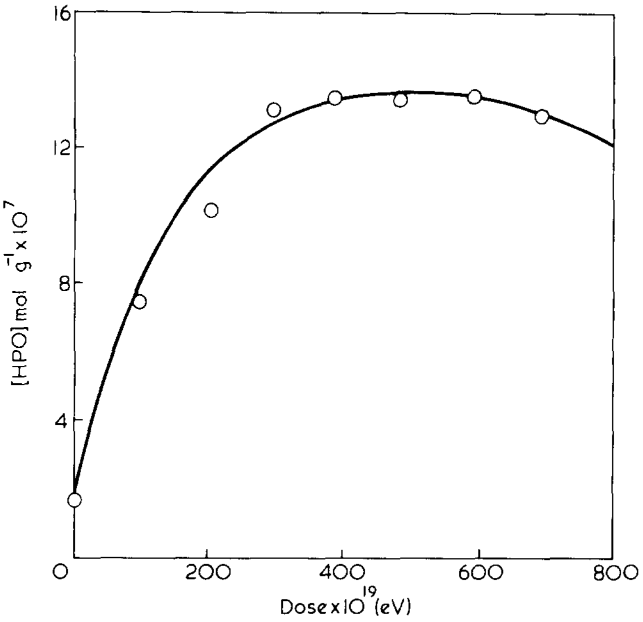

Figure 8 Change in hydroperoxide concentration of butyl rubber during γ-irradiation

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