

Barrier Properties of Electron-Beam-Modified EPDM Rubber

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ABSTRACT: EPDM rubber was surface- and bulk-modified with varying concentrations of trimethylol propane triacrylate (TMPTA) in the presence of a constant electron-beam irradiation dose of 100 kGy and over a wide range of irradiation doses from 0 to 200 kGy at a fixed TMPTA concentration (10%). The permeation rate and absorption of three homologous nonpolar solvents, namely, *n*-hexane, *n*-heptane, and *n*-octane, along with an aromatic solvent, toluene, and a polar solvent, trichloroethylene, through unirradiated, unmodified control, and modified rubber membranes ($\approx 150 \mu\text{m}$) were studied. It was found that both the permeation rate and absorption decrease progressively with increase in the TMPTA concentration up to 10% for both the surface- and bulk-modified rubbers. With increase in the radiation dose, there also is an initial drop in the values up to 50 kGy for the control and surface-modified rubbers and up to about 100 kGy for the bulk-modified one. The control rubber shows the highest absorption and permeation for all the solvents except trichloroethylene, followed by the bulk-modified rubber membrane. Trichloroethylene is, however, absorbed and permeated most by the surface-modified sample. The observations are explained in terms of the structural modifications of the rubber, crosslinking, changes in the relevant thermodynamic properties such as surface energy, the penetrant size, and the transport mechanism of the penetrants. The influence of temperature on the permeability characteristics of the control and modified rubbers was also studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 784–795, 2000

Key words: rubber; EPDM; elastomers; surface modification; barrier property; electron beam; radiation; permeability; crosslinking; transport property

INTRODUCTION

Barrier properties of polymeric films are important for many polymeric applications. Because of their importance, the last few decades have witnessed a plethora of theoretical and experimental studies on the transport of solvents and solvent

vapors through polymeric films.^{1–3} A quantitative knowledge of the diffusion and permeation rates for polymer–solvent systems is required for the design of polymer membrane-based separation processes and protective seals. The scope of these studies has widened because of the development of new materials or new processes with the conventional materials.

Quite extensive research work has been carried out over the past years on the barrier properties of polymers based on different solvent systems. Cassidy and Aminabhavi⁴ reviewed the

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work done on water permeation through elastomers and plastics. Guo et al.⁵ reported the diffusion of organic solvents in rubber membranes. Popoola⁶ studied the effect of crystallinity on the kinetics of liquid absorption into poly(ethylene terephthalate) (PET). Pan et al.⁷ discussed the permeation of water vapor through cellulose membranes. Mehta et al.⁸ studied the sorption and diffusion of water in glass rubber-reinforced composites, while Sacher and Susko⁹ reported the permeation of polyimide films. Some recent studies were conducted on the transport of various organic solvents through rubbery polymers.^{10–12}

However, despite the several studies on the barrier properties of polymers, studies on the permeability behavior of polymeric membranes modified by radiation technology have been relatively fewer in number. Friedrich et al.¹³ reported the barrier properties of plasma-modified polypropylene and PET. The modification of polymer substrates also influences the resulting barrier effects by crosslinking.¹⁴ Friedrich et al.¹³ also showed that at longer plasma exposure times the plasma UV radiation has induced such effects in polymer surface layers to some micrometers.

However, a literature search clearly revealed that there has been a lack of systematic investigation on the influence of surface modification by *electron beam* treatment on the barrier characteristics of rubbers. Hence, this article describes the effect of electron beam-induced surface treatment in the presence of a polyfunctional monomer on the permeability behavior of EPDM rubber.

EXPERIMENTAL

Materials

EPDM rubber: Keltan 520-DCPD containing rubber, density = 0.86 g/cm³, diene content = 4.5 mol %, viscosity average molecular weight = 1.93×10^5 g/gmol, and ethylene propylene ratio = 58/42 mol/mol; supplied by DSM Chemical (Holland).

Dicumyl peroxide (DCP): Dicup (98% pure) obtained from Hercules Inc. (U.S.A.).

Trimethylol propane triacrylate (TMPTA): TMPTA was obtained from UCB Chemicals (Belgium). Flash point >100°C (Cleveland open cup); boiling point >100°C; specific density 1.11 g/cm³.

Methyl ethyl ketone (MEK, butan-2-one): MEK of chemically pure grade obtained from E. Merck (India) Ltd. (Mumbai, India).

Acetone (propan-2-one): Acetone of a chemically pure grade obtained from Ranbaxy Laboratories (Chemical Division), S.A.S. Nagar (Punjab, India).

Preparation of the Samples

Surface Modification

EPDM was mixed with 0.2 phr DCP on an open-roll mill (6 × 13 in., Schwabenthan, Germany) at 25°C. The mix was then compression-molded between Teflon sheets at a temperature of 150°C and a pressure of 10 MPa for 45-min optimum cure time (as obtained from the Rheometric studies using a Monsanto Rheometer, R-100) in an electrically heated press to obtain films of 150 μm thickness. The films thus obtained were washed with acetone to remove any trace of residual peroxide on the surfaces and air-dried at 25°C. These were then completely immersed vertically in different solutions containing 1, 2, 5, 10, and 20% TMPTA in MEK for 30 min. After immersion, the films were air-dried for 30 min at 25°C.

Bulk Modification

EPDM was mixed with 0.2 phr DCP on an open-roll mill. The mixes were then further compounded with TMPTA (1, 2, 5, 10, and 20% by weight) in a Brabender Plasticorder, PLE-330 at 30°C for 2 min at a 60-rpm rotor speed. The mixes were then sheeted out from a roll mill. Finally, the sheets were compression-molded at a temperature of 150°C for 45 min to obtain rectangular films of 150 μm thickness.

Irradiation of Samples

The molded rectangular EPDM samples (both surface- and bulk-modified) were irradiated in air by an electron-beam accelerator (Model ILU-6) at Bhabha Atomic Research Centre (BARC, Mumbai). Irradiation doses of 0–200 kGy were used. The samples were designated as E_{x/y} and EB_{x/y}, denoting control and surface- and bulk-modified samples, respectively, where *x* indicates the TMPTA level in percent, and *y*, the irradiation dose in kGy.

Characterization of the Samples

Measurement of Permeation Rate and Absorption

The permeation rate was measured gravimetrically using a permeation cell, filled with the test

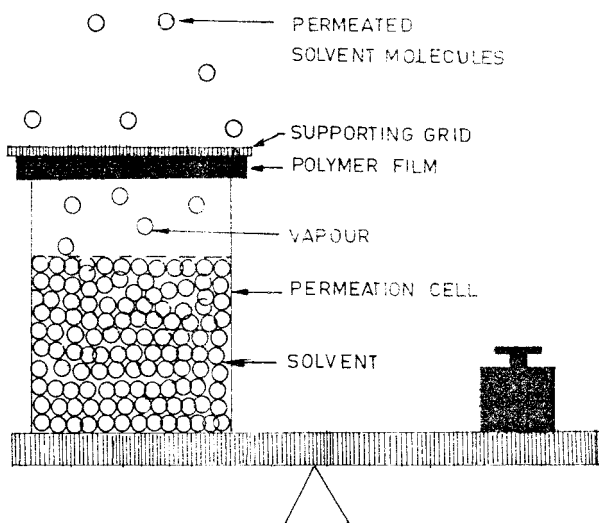


Figure 1 Schematic diagram of the permeation cell.

solvent, which was closed by the control and modified polymer films (Fig. 1). The weight loss of this permeation cell was measured using an analytical balance. Any polymer foil deformation was avoided by an aluminum grid which was fixed to the polymer film. From the loss in weight of the assembly and weight gain of the sample, the permeation rate (in $\text{mg h}^{-1} \text{cm}^{-2}$) and absorption (mass %) were calculated. Normally, all the experiments were carried out using *n*-hexane at 25°C. The other solvents used were *n*-heptane, *n*-octane, toluene, and trichloroethylene. The temperature was also varied from 25 to 55°C. The results reported are the average of three measurements.

Attenuated Total Reflection (ATR) Spectroscopy

IR-ATR spectra of the samples were taken using a Perkin-Elmer Model 843 infrared spectrophotometer in the ATR mode using a KRS-5 crystal. A total of four scans were taken with a resolution of 1 cm^{-1} .

Gel Fraction

Previously weighed samples were allowed to swell in *n*-heptane at 40°C for 12 h, the equilibrium swelling time. The test pieces were taken out and dried to a constant weight in a vacuum oven at 70°C. The gel fraction was calculated from the weight of the samples before and after swelling using the expression

$$\text{Gel content (\%)} = (W_2/W_1) \times 100 \quad (1)$$

where W_1 is the initial weight of the polymer, and W_2 , the weight of the insoluble portion of the polymer.

RESULTS AND DISCUSSION

Influence of Concentration of TMPTA on the Permeability Behavior

The permeability rates and absorption of *n*-hexane by the unirradiated, unmodified control, and modified EPDM samples were determined. These are shown in Figure 2. It was observed that both the permeation rate and absorption of the surface-modified samples decrease with the concentration of TMPTA to a 10% TMPTA level, beyond which there is no change in the values. The same behavior was observed in the case of the bulk-modified samples, although the values are higher in this case.

An electron-beam treatment changes the solvent absorption and swelling properties of polymers. In principle, two very different responses of

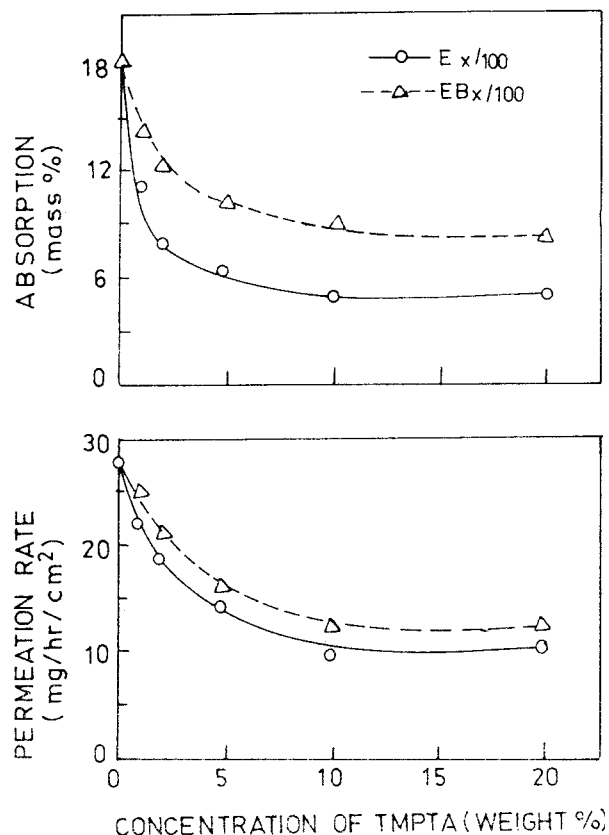


Figure 2 Plot of the variation of permeation rate and absorption against concentration of TMPTA.

Table I Principal Peak Assignments in the Spectra of Control and Modified EPDMs

Observed Peak (cm ⁻¹)	Peak Assignment
1730	>C=O stretching vibration
1630	>C=C< stretching vibration
1460	>CH ₂ scissoring vibration
1375	Symmetric C—H stretching vibration of —CH ₃
1260	Asymmetric C—O—C stretching vibration
1120	Symmetric C—O—C stretching vibration
1019	Symmetric C—O—C stretching vibration

a polymeric material are possible. On the one hand, an improvement in solvent compatibility accompanied by enhanced solvent absorption and polymer swelling can be achieved. On the other hand, the formation of a barrier layer, which hinders permeation of the solvent into and out of the polymer, can be the consequence. The compatibility of nonpolar polymers with nonpolar organic solvents can be modified with the help of polar groups formed on a polymer surface and in the bulk by electron-beam treatment. In this way, one can change the relevant thermodynamic surface properties, for example, the surface free energy. Other relevant effect is the formation of barriers by crosslinking of the polymeric material due to electron-beam irradiation. In this way, one obtains substantially reduced diffusion lengths of the solvent molecules. Finally, modified surface films deposited on a polymer can seal the substrates against solvent permeation because they are usually characterized by a denser structure.

The IR-ATR spectra of the control unmodified EPDM and EPDM surface-modified with different concentrations of TMPTA and irradiated at a constant radiation dose of 100 kGy were taken. The main peaks of interest were observed at 1730, 1630, 1375, 1260, 1120, and 1019 cm⁻¹. Their assignments are given in Table I. From a representative plot of peak absorbances against the concentration of TMPTA, it is seen that the absorbances at 1730, 1260, and 1019 cm⁻¹ increase initially with increase in TMPTA concentration up to 10%, after which there is a slight decrease in the absorbance values (Fig. 3). During irradiation, a large number of free radicals are generated

on the EPDM backbone. These radicals, being highly active, undergo aerial oxidation to produce carbonyl and ether linkages on the rubber surface. They may cause crosslinking as well as chain scission of the EPDM rubber (Scheme 1). On the other hand, active free radicals are also produced in profuse numbers on the TMPTA molecule itself. With the help of these radicals, TMPTA participates in several reactions, namely, self-crosslinking, grafting, cyclization, and cyclo-polymerization. The grafting of TMPTA onto the EPDM backbone, together with the carbonyl and

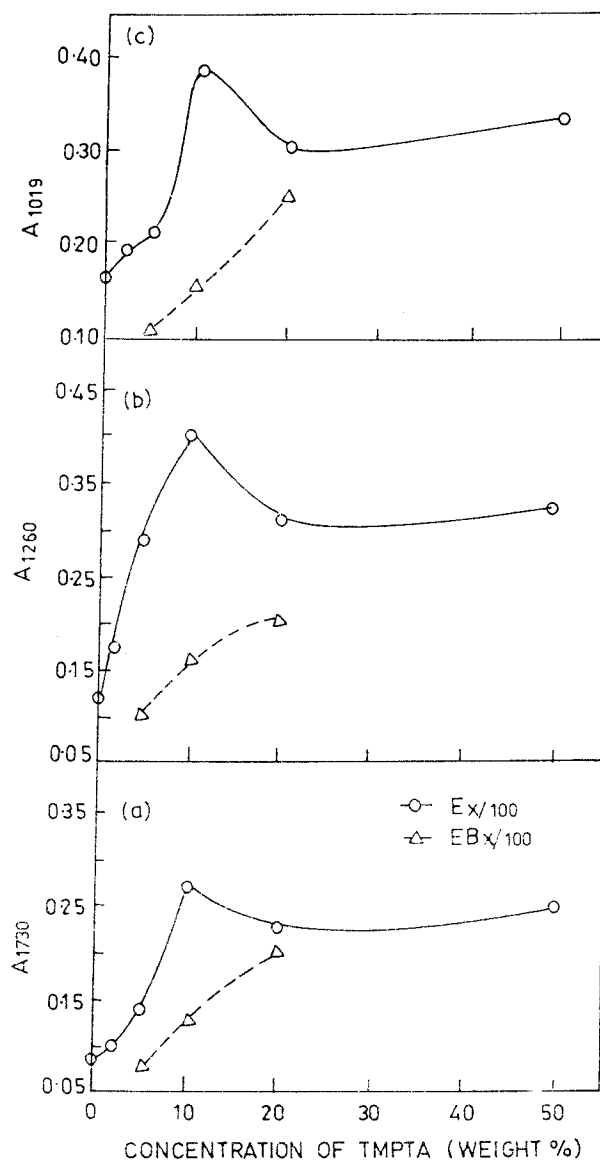
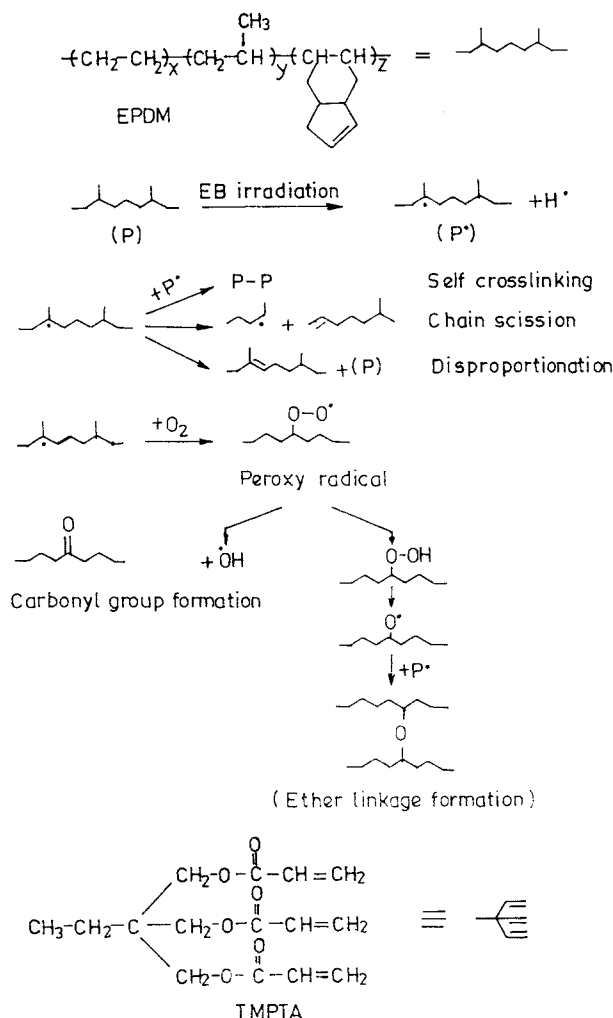


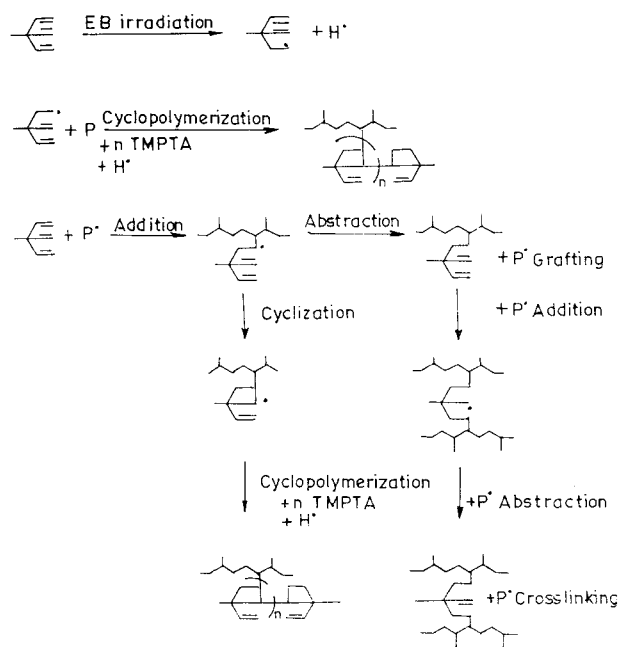
Figure 3 Change of absorbances at (a) 1730 cm⁻¹, (b) 1260 cm⁻¹, and (c) 1019 cm⁻¹ with the concentration of TMPTA.



Scheme 1 Reaction scheme for electron-beam irradiation of EPDM and plausible mechanism of interaction of TMPTA with EPDM.

ether groups generated on the rubber itself, causes the carbonyl and ether absorptions to increase.

As the concentration of TMPTA increases from 0 to 10%, the concentration of the active radicals also increases, thereby increasing the grafting and crosslinking level with EPDM. This is also clear from the plot of gel content against TMPTA concentration (Fig. 4), which also shows a similar increase. The introduction of polar groups on the surface such as $>\text{C}=\text{O}$ and $-\text{C}-\text{O}-\text{C}-$ is also reflected from the XPS studies.¹⁵ It shows that the C1s core peak for the $\text{E}_{0/0}$ sample appears at a 284.9 eV binding energy, but as the TMPTA level increases, there is a progressive shift of the C1s core peak as well as the other constituent peaks due to the formation of $\text{C}-\text{O}$ and $\text{C}=\text{O}$, to higher



Scheme 1 (Continued)

binding energies. This shift is maximum in the case of the $\text{E}_{10/100}$ sample, where an additional peak is also observed at 292.0 eV which may be ascribed to the $-\text{C}(=\text{O})-\text{O}-$ groups. A gradual decrease in the relative area of the C1s core peak

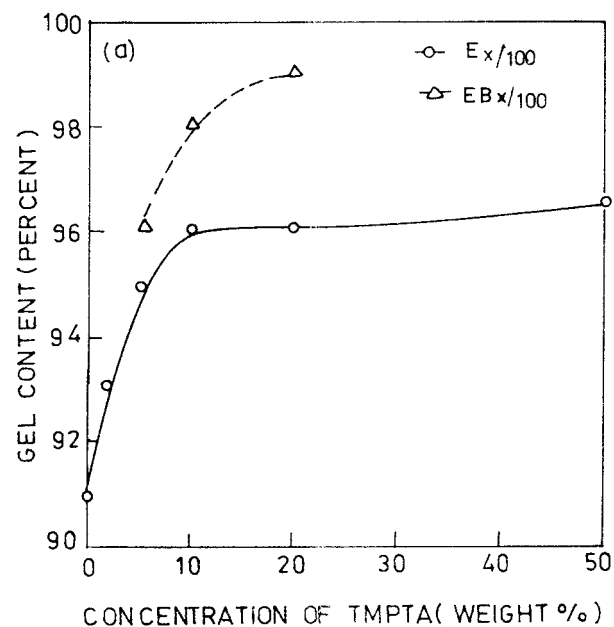


Figure 4 Plot of gel content against concentration of TMPTA.

with a corresponding increase in the area of the constituent peaks with modification also confirms this fact. The same effect is also corroborated from the appearance of the O1s peaks. The increase in the O/C ratio further supports these observations. The increase in the surface polarity is further accompanied by an increase in the total surface energy of the samples with TMPTA concentration. The surface energy increases from 44.8 mJ/m^2 ($E_{0/100}$) to 53.8 mJ/m^2 ($E_{10/100}$) for the surface-modified samples.¹⁵

As the TMPTA level is increased, the crosslinking of EPDM increases, which is clear from the plot of gel content versus concentration (Fig. 4). As permeation into or out of the polymer is mainly a diffusion-controlled process, this crosslinking of the EPDM rubber forms a barrier and a substantially reduced diffusion length of the solvent molecules is obtained. Thus, the absorption values decrease gradually with increase in the TMPTA level. Furthermore, due to the deposition of the modified slightly dense polar surface layers on both the surfaces of the polymer membrane, the entry and exit of a nonpolar solvent like *n*-hexane is prohibited. This explains the gradual drop in the permeation rate and absorption with an increase in the TMPTA level. The mechanism of transport of the solvents is discussed in terms of diffusion and solubility coefficients in a later section.

The same effects also explain the observations in the case of the bulk-modified samples. IR (Fig. 3) and XPS data¹⁵ of the representative bulk samples show that the concentration of the polar carbonyl and ether groups on the surface of the rubber is lower for the bulk-modified samples than for the surface-treated ones. Thus, the movement of the solvent molecules into or out of the rubber membrane is less restricted. This gives slightly higher absorption and permeation rate values than those of the surface-modified samples. The gradual decrease in the absorption and permeation rate values with increase in the TMPTA concentration is again due to the formation of an efficient barrier by crosslinking of the rubber in the presence of TMPTA, as discussed earlier.

Effect of Radiation Dose

Figure 5 illustrates the effect of radiation dose on the permeation behavior against *n*-hexane of the control unmodified and the surface-modified and bulk-modified samples at a fixed TMPTA concentration of 10%. As the irradiation dose is in-

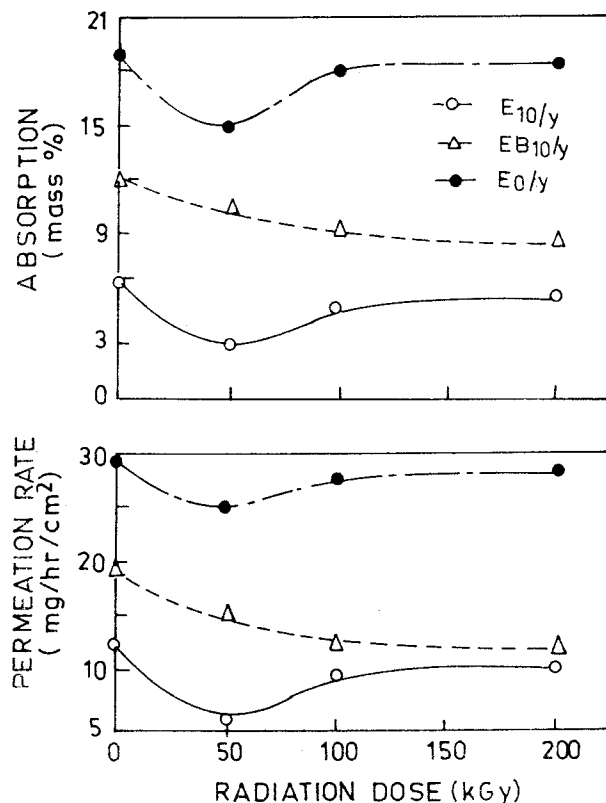


Figure 5 Plot of the variation of permeation rate and absorption against radiation dose.

creased, there is an initial decrease in the absorption and permeation values up to a 50 kGy radiation dose, beyond which they increase. The gel content of the control sample indicates a gradual increase in the gel content values with increase in the radiation dose due to self-crosslinking of the EPDM molecules (Fig. 6). Above the 50 kGy level, there is a marginal increase. Thus, the rubber forms a gelled barrier to the penetrant solvent which is maximum at the 50 kGy dose. The sorption of the solvent (*n*-hexane) thus decreases. IR-ATR studies of the control samples indicate that the deposition of a polar surface layer due to the aerial oxidation of the EPDM free radicals in the presence of electron-beam radiation is maximum at this dosage (Fig. 7). Consequently, the total surface energy of the control rubber is also maximum at this stage. (The total surface energy increases from 46.1 to 49.7 mJ/m^2 ; ref. 16.) At higher dose levels, the absorption values at 1730 , 1260 , and 1019 cm^{-1} decrease due to chain scission of the rubber, whereby the rubber is broken down into segmental moieties and a fraction of the polarity may be lost from the surface. Thus,

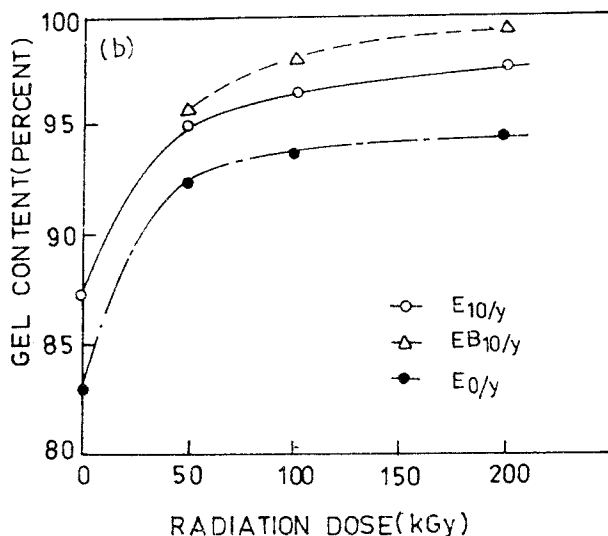


Figure 6 Change of gel content with radiation dose.

the permeation rate of the solvent molecules is the minimum at this stage due to the formation of a polar barrier layer on the surface which breaks down thereafter.

For the surface- and bulk-modified samples, the same behavior is noted. For the surface-modified samples, the permeation rate and absorption decrease up to a 50 kGy radiation dose, after which there is an increase in the values. For the bulk-modified samples, however, there is a decrease in the permeation rate and absorption up to 100-kGy dose, beyond which the values change very slightly. From the representative plot of the absorbances against the radiation dose, it was found that the 1730, 1260, and 1019 cm^{-1} absorptions increase with the radiation dose up to the 50-kGy level for the surface-modified samples, beyond which there is a slight decrease in the absorbance values (Fig. 7). Thus, the concentration of the polar groups is maximum at this stage on the surface, which explains the minima in the permeation rate and absorption curve. For the bulk-modified samples, however, the absorbances show an increase up to the 100 kGy level, after which the values change marginally. Thus, the concentration of the polar groups on the surface also increases up to the 100 kGy level. This explains the drop in the permeation rate and sorption values up to 100 kGy.

Influence of the Nature of Solvent

Figure 8 depicts the influence of the penetrant system on the permeability characteristics of

three representative samples, namely, $E_{0/0}$, $E_{10/100}$, and $EB_{10/100}$. It is observed that as the solvent changes from *n*-hexane to *n*-octane there is a gradual decrease in the absorption and permeation rates for the control, the surface-modified, as well as the bulk-modified samples. This may be because as the molecular weight and viscosity of the solvents increase with increase in the aliphatic chain length the movement into or out of the rubber membrane becomes progressively more difficult and, hence, the drop in the absorption and permeation values. However, the control sample absorbs and permeates at a higher rate as compared to the modified samples. This is obvious from the lower gel content of the control rubber (Fig. 6) as well as the much lower concentration of polar groups on the surface in the absence of any TMPTA.

On the other hand, the higher values of absorption of toluene in the case of all the three samples

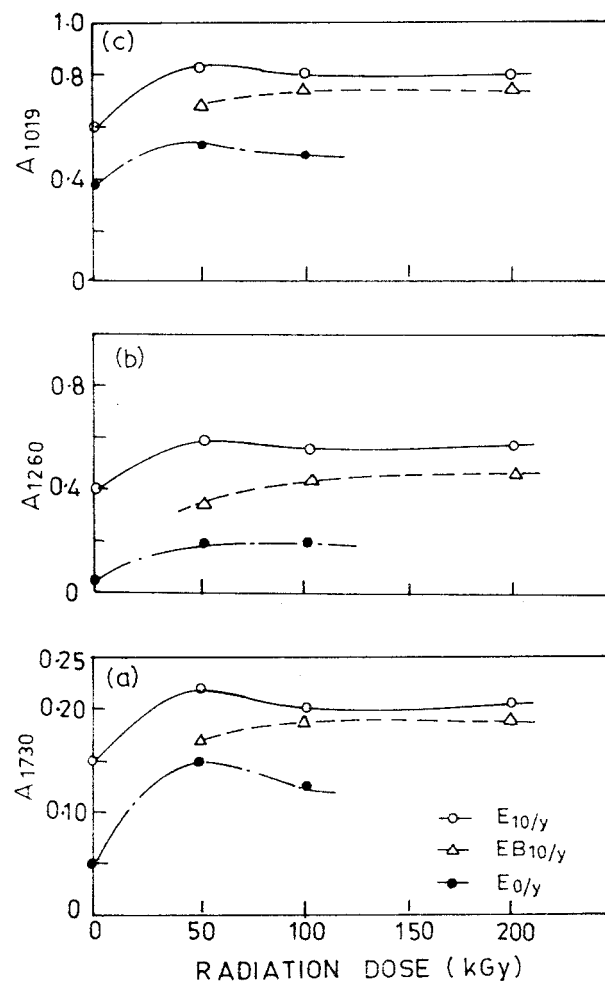


Figure 7 Change of absorbances at (a) 1730 cm^{-1} , (b) 1260 cm^{-1} , and (c) 1019 cm^{-1} with radiation dose.

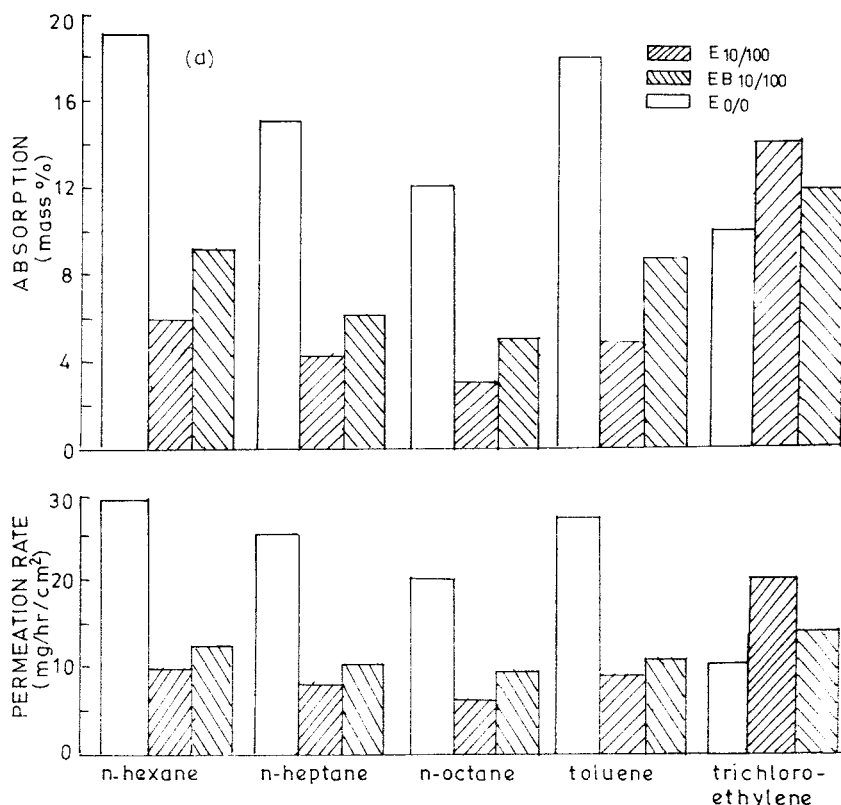


Figure 8 Plot showing the variation of permeation rate and absorption with the nature of the penetrant.

may be attributed to the solubility parameter of toluene, which is nearer to the EPDM rubber than to the above solvents ($\delta_{\text{EPDM}} = 8.4$, $\delta_{\text{toluene}} = 8.9$; here, the δ value of EPDM is slightly higher than the normal value for the raw rubber, which is 7.95, probably due to slight oxidation of the rubber due to its precrosslinking with 0.2 phr DCP). This value is higher than that of the three aliphatic solvents ($\delta_{n\text{-hexane}} = 7.3$, $\delta_{n\text{-heptane}} = 7.4$, $\delta_{n\text{-octane}} = 7.6$). The permeation rate is, however, lower than that of *n*-hexane, probably due to its higher molecular weight and larger penetrant size and viscosity.

Trichloroethylene, however, presents a somewhat different behavior. Probably, due to its inherent polar character, it is absorbed least into the control rubber. The modified rubbers, on the other hand, develop a compatibility toward the penetrant due to the deposition of a polar surface layer, which is even more prominent in the case of the surface-modified sample. Thus, trichloroethylene exhibits the most prominent permeation

behavior in the case of the surface-modified sample.

Mechanism of Transport

The dynamic sorption characteristics of the polymer-solvent system for circular sample geometry may be assumed to follow a Fickian transport mechanism. For such a transport system, the mutual diffusion coefficient, D , can be calculated using the expression¹⁷⁻¹⁹

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (2)$$

where M_t and M_∞ are the mass of solvent uptake at time t and at equilibrium, respectively, and l is the initial sample thickness. Thus, D can be calculated from a rearrangement of eq. (2) as

$$Dt = \frac{\pi l^2}{16} \left(\frac{M_t}{M_\infty} \right)^2 \quad (3)$$

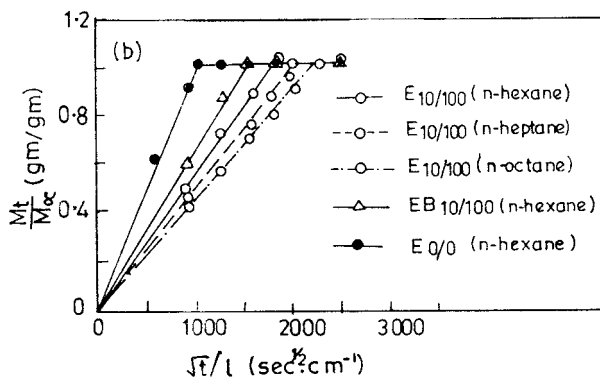


Figure 9 Plot of M_t/M_∞ against $t^{1/2}/l$.

D can be determined from the slope of a graph of M_t/M_∞ against $t^{1/2}/l$.

Figure 9 shows the plots of M_t/M_∞ against $t^{1/2}/l$ for n -hexane, n -heptane, and n -octane of three representative samples, $E_{0/0}$, $E_{10/100}$, and $EB_{10/100}$. The permeation of a penetrant molecule into a polymer matrix depends on the diffusivity as well as on the solubility or sorptivity of the penetrant in the membrane. The sorption coefficient, S , the maximum saturation sorption value, can be calculated using the equation²⁰

$$S = \frac{M_\infty}{M_p} \quad (4)$$

where M_∞ is the mass of the penetrant at equilibrium swelling, and M_p , the mass of the polymer sample. Permeation, in turn, is a collective process of diffusion and sorption and, hence, the permeability of a solvent into the polymer depends upon both the diffusivity and the solubility. The permeability may be defined as^{17,20}

$$P = DS \quad (5)$$

where D is the diffusion coefficient and S denotes the sorption coefficient. Table II gives the values of P , D , and S as a function of the penetrant size for the above three samples. It shows that the control sample has the maximum diffusivity, permeability, and sorptivity. This is obvious from the above discussion, which explains the maximum permeation and absorption in the case of the control sample for the solvents. It is also interesting to note that for the same solvent the diffusion coefficient and the sorption coefficient decrease with increase in the TMPTA level and irradiation

dose ($E_{10/100}$, $E_{0/100}$, cf. $E_{0/0}$), reducing the value of the permeability.

Influence of Temperature

To study the effect of temperature on the diffusion and permeation process, experiments were conducted from 25 to 55°C on the three samples, $E_{0/0}$, $E_{10/100}$, and $EB_{10/100}$, against n -hexane. It was found that the permeation rate increases with increase in temperature progressively. A major factor which affects the polymer chain segmental motion is temperature. An increase in temperature provides energy for a general increase in the segmental motion. If the energy density is sufficient, the polymer may pass through structural transitions, such as the glass and melting transitions, which further affect the solution as well as the permeation processes. The effects of an increase in temperature may also be expressed in terms of the increase in free volume directly related to the bulk expansion of the polymer due to increased segmental motions. Polymer segments and penetrant molecules jointly utilize the combined free volume of the components in the mixture.

The variation of the rate of permeation with temperature follows an Arrhenius relationship²¹:

$$K_p = K_{p0} \exp \frac{E_x}{RT} \quad (6)$$

where K_p represents the permeation rate and K_{p0} is a constant. K_p is calculated from the slope of a

Table II Transport Coefficients of Control and Modified EPDMs

Sample Code	$D \times 10^7$ (cm ² /s)	S (g/g)	$P \times 10^6$ (cm ² /s)
$E_{0/0}$ n -hexane	6.83	0.18	12.29
$E_{0/100}$ n -hexane	5.09	0.12	6.12
$E_{10/100}$ n -hexane	2.46	0.04	0.99
$E_{10/100}$ n -heptane	1.82	0.03	0.55
$E_{10/100}$ n -octane	1.52	0.02	0.30
$EB_{10/100}$ n -hexane	3.22	0.09	2.90

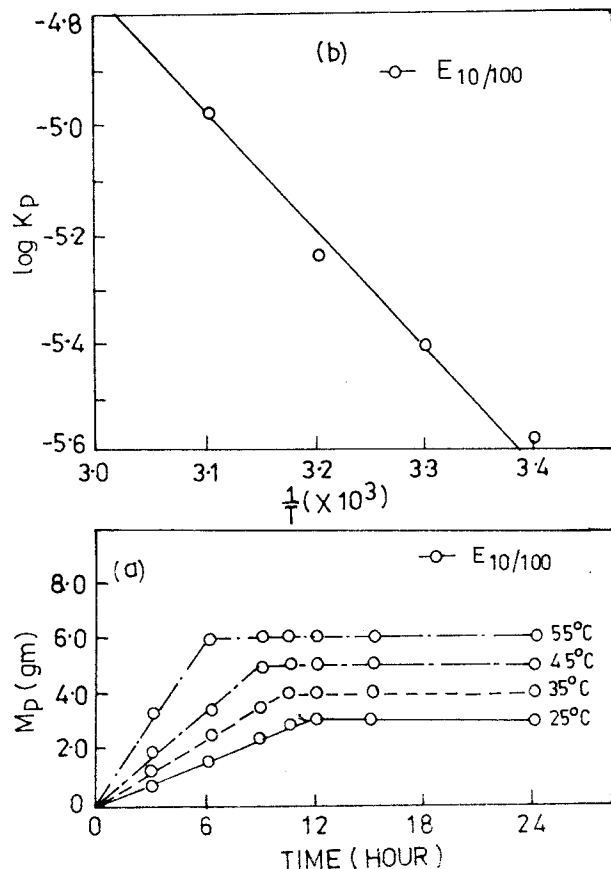


Figure 10 (a) Plot of mass permeated (M_p); (b) plot of $\log K_p$ against $1/T$.

plot of M_p (mass permeated) against t [Fig. 10(a)]. An Arrhenius plot of $\log K_p$ against $1/T$ was constructed [Fig. 10(b)], and from the slope of the curve, the value of the activation energy for permeation, E_p , was determined. Table III gives the values of E_p for the control ($E_{0/0}$), surface-modified ($E_{10/100}$), and bulk-modified ($EB_{10/100}$) samples with *n*-hexane.

The thermodynamic sorption constant K_s is defined as²²

Table III Thermodynamic Parameters of Control and Modified EPDMs

Sample Code	$-\Delta H$ (kJ/mol)	$-\Delta S$ (kJ/mol)	$-\Delta G$ (kJ/mol)	E_p (kJ/mol)
$E_{0/0}$	27.7	58.5	17.5	16.3
$E_{10/100}$	11.3	40.2	12.0	42.1
$EB_{10/100}$	20.5	55.5	15.3	36.5

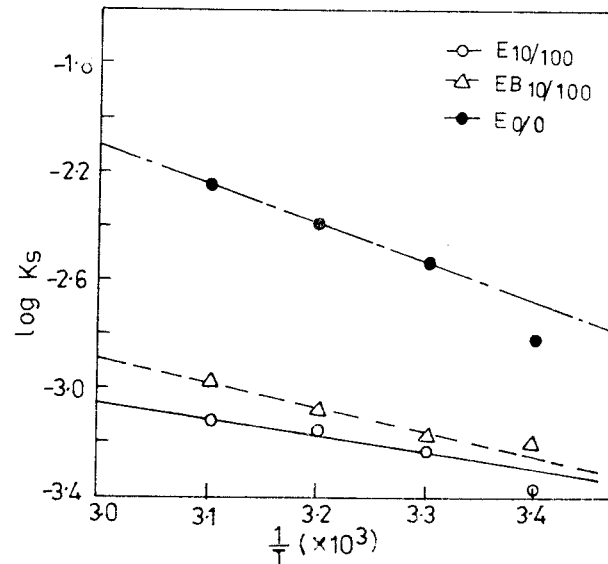


Figure 11 Plot of $\log K_s$ against $1/T$.

$$K_s = \frac{\text{no. moles of solvent sorbed at equilibrium}}{\text{mass of the polymer sample}}$$

The K_s value gives further understanding of the uptake of the solvent by the polymer. From the values of K_s and using the Van't Hoff relation,²³ it is possible to calculate the enthalpy (ΔH) and the entropy of the system:

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (7)$$

Van't Hoff plots of $\log K_s$ versus $1/T$ for the control ($E_{0/0}$), surface-modified ($E_{10/100}$), and bulk-modified ($EB_{10/100}$) samples for *n*-hexane was constructed (Fig. 11). From the slope and intercept of the plots, ΔH and ΔS can be determined. The free energy, ΔG of the process can be calculated using the expression

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

The values of ΔG , ΔH , and ΔS for the three solvent systems are given in Table III. The negative ΔH values indicate that the sorption is an exothermic process. The ΔG values are also negative, which show the feasibility of the process.

CONCLUSIONS

The permeability behavior of EPDM rubber, surface- and bulk-modified in the presence of an electron beam and a trifunctional monomer against various solvents such as *n*-hexane, *n*-heptane, *n*-octane, toluene, and trichloroethylene, was investigated. The following conclusions are drawn from this study:

1. There is an initial decrease in the permeation rate and absorption of *n*-hexane for the surface-modified samples up to 10% TMPTA concentration, after which it increases slightly. For the bulk-modified sample, there is almost no change in the values beyond 10% TMPTA after the initial decrease. The initial drop in the absorption and permeation may be due to the crosslinking of the rubber with TMPTA with a simultaneous rise in the total surface energy.
2. For the control and surface-modified rubber membranes, the absorption and permeation rates of *n*-hexane show a drop up to a 50 kGy irradiation dose, but increase at still higher doses. For the bulk-modified membrane, however, the initial drop is obtained until 100 kGy, beyond which there is marginal change in the values. The reason lies in the increase in crosslinking of the EPDM rubber itself as well as with TMPTA with an increase in irradiation dose initially, accompanied by an increase in the surface-energy values. However, at higher doses, the chain scission of the rubber predominates, which breaks down the rubber into segmental moieties and a fraction of the polarity is lost which increases the absorption and permeation values of *n*-hexane.
3. As the size of the penetrant molecules increases from *n*-hexane to *n*-octane, the diffusion rate decreases and lower absorption and permeation rates are obtained for the control and modified rubbers. However, the control rubber is most permeable to the above three solvents as well as to toluene. It, however, has the lowest affinity for trichloroethylene due to a high inherent polarity of the latter. Toluene is absorbed comparatively more than are *n*-heptane and *n*-octane in the

case of all the samples, which may be attributed to its higher solubility parameter which is nearer to the rubber. Trichloroethylene exhibits the highest absorption and permeation in the case of the surface-modified rubber due to the latter's highest surface polarity.

4. The transport coefficient values indicate that the diffusivity of the unmodified, un-irradiated control EPDM sample is almost three times that of the surface-modified one and double that of the bulk-modified one. The permeation coefficient is about 12 times and three times that of the modified samples, respectively.
5. The rate of permeation increases progressively with increase in temperature, showing that it is a temperature-activated process. The activation energy of permeation was found to be almost three times less in the case of the control rubber than of the surface-modified one. The negative enthalpy values show that the sorption is an exothermic process.

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