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Influence of electron beam irradiation on fluorocarbon rubber vulcanizates

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The influence of electron beam irradiation on the fluorocarbon rubber vulcanizates at varying levels of the curative—hexamethylene diamine carbamate is reported. A higher crosslinking density, reduced elongation at break, increased modulus (both static and dynamic), decreased loss tangent value at T_g and increased glass transition temperature have been observed for the irradiated rubbers, as compared to the control rubber. The results are explained with the help of structure.

1. Introduction

In earlier papers we have discussed the influence of electron beam irradiation on pure fluorocarbon elastomers [1, 2]. It has been demonstrated that dehydrofluorination, crosslinking and grafting of the polyfunctional vinyl unsaturated monomer acrylates, when these are added, take place during electron beam irradiation. The above structural changes lead to drastic change of mechanical [3], dynamic mechanical [4], electrical [5] properties and thermal stability [6]. The properties are a function of radiation dose, level and nature of polyfunctional monomer. In this paper, diamine cured fluorocarbon elastomer has been exposed to electron beam irradiation. The structural changes associated with it and the mechanical and dynamic mechanical properties have been determined. An attempt has been made to correlate these properties with the structure of the fluorocarbon rubber vulcanizate.

2. Experimental

2.1. Materials

The fluorocarbon rubber (vinylidenefluoride-co-hexafluoropropylene-co-tetrafluoroethylene, F content 68%, H 1.4%) and the curative hexamethylene diamine carbamate (HMDAC, Diak #1) were obtained from E.I. duPont de Nemours & Co., USA. MgO used was of rubber grade. The rubber was mixed with various levels of HMDAC and cured in an electrically heated Moore Press, UK at a pressure of 5 MPa and temperature 150°C to their optimum cure times (determined from a rheometer, Monsanto R-100). The cured sheets of dimension $11.5 \times 11.5 \times 0.1$ cm were irradiated at Bhabha Atomic Research Centre, Trombay (Mumbai) by an electron beam accelerator (model ILU-6) in air over the dose ranges (0–200 kGy). The specifications of the electron beam accelerator were given in our earlier communications [1, 2, 4].

2.2. Sample designation

The samples were designated as $H_{x/y}$, where x denotes the level of the diamine in phr and y the radiation dose in kGy. The formulation of the mixes is given in Table I. The control rubber, without any conventional curing, is specified as $T_{0/y}$.

2.3. Mechanical properties

The tensile properties e.g. tensile strength, elongation at break and modulus at 100% elongation were performed in a Zwick GmbH UTM (model 1445) at a crosshead speed of 500 mm/min and at a temperature of 25 ± 2°C as per the ASTM method D-412-93.

2.4. Dynamic mechanical thermal analysis (DMTA)

The DMTA analysis of the rubber vulcanizates were performed in a DMTA-MK-II Analyzer (Polymer Laboratories, UK) at a frequency of 10 Hz and a strain of 64 μm (peak to peak displacement) in the temperature range of -25°C to $+100$°C using the samples of dimension $43.5 \times 12.5 \times 1$ mm. The data were analysed by an in-built COMPAQ computer.

2.5. Sol-gel analysis

The gel fraction was carried out gravimetrically using the solvent methylethyl ketone as reported in our earlier communications [1, 2]. The crosslink density was calculated using the Flory-Rehner Equations as given in our earlier paper [3].

3. Results and discussion

3.1. Effect of radiation dose

The stress-strain curves of the fluorocarbon rubber conventionally vulcanized with HMDAC (1 phr) at

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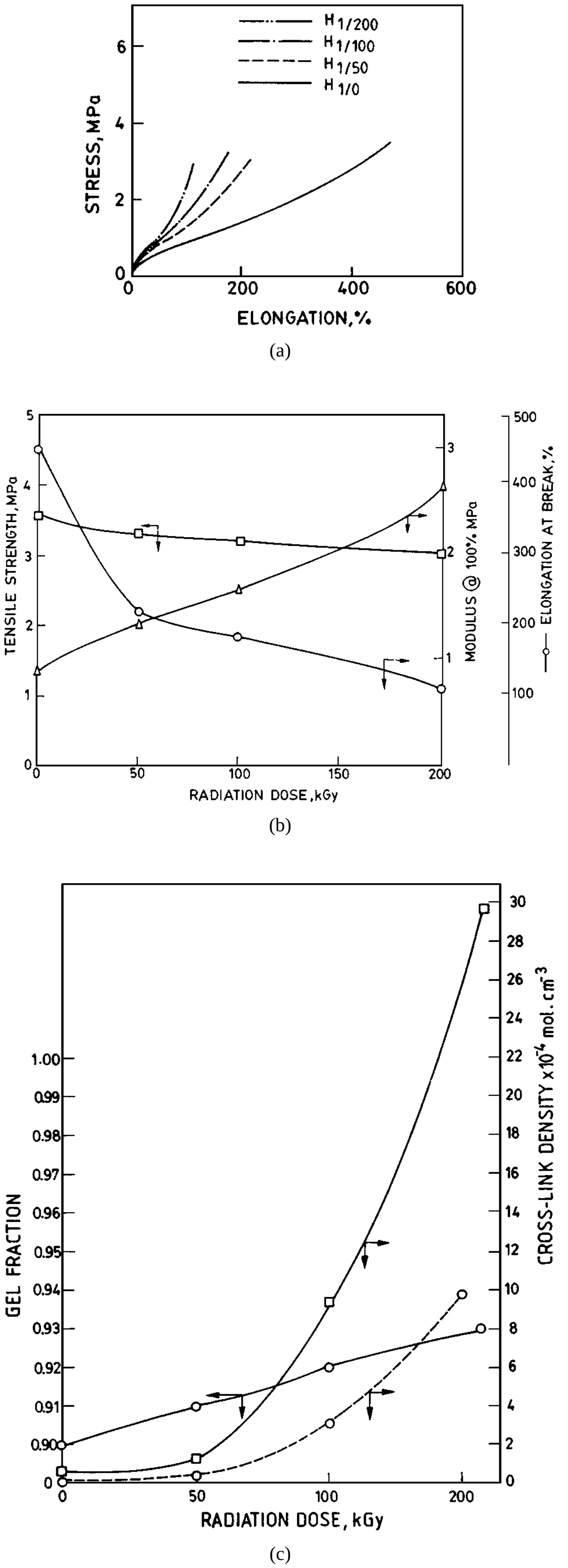
TABLE I Formulation of the mixes

Sample designation	HMDAC, phr	MgO, phr	Optimum cure time @ 150°C, min	Radiation dose, kGy
$H_{0.5/0}$	0.5	5	26	0
$H_{0.5/50}$	0.5	5	26	50
$H_{1/0}$	1	5	15	0
$H_{1/50}$	1	5	15	50
$H_{1/100}$	1	5	15	100
$H_{1/200}$	1	5	15	200
$H_{2/0}$	2	5	13	0
$H_{2/50}$	2	5	13	50
$T_{0/0}$	0	0	X	0
$T_{0/50}$	0	0	X	50
$T_{0/100}$	0	0	X	100
$T_{0/200}$	0	0	X	200



(a)

(b)

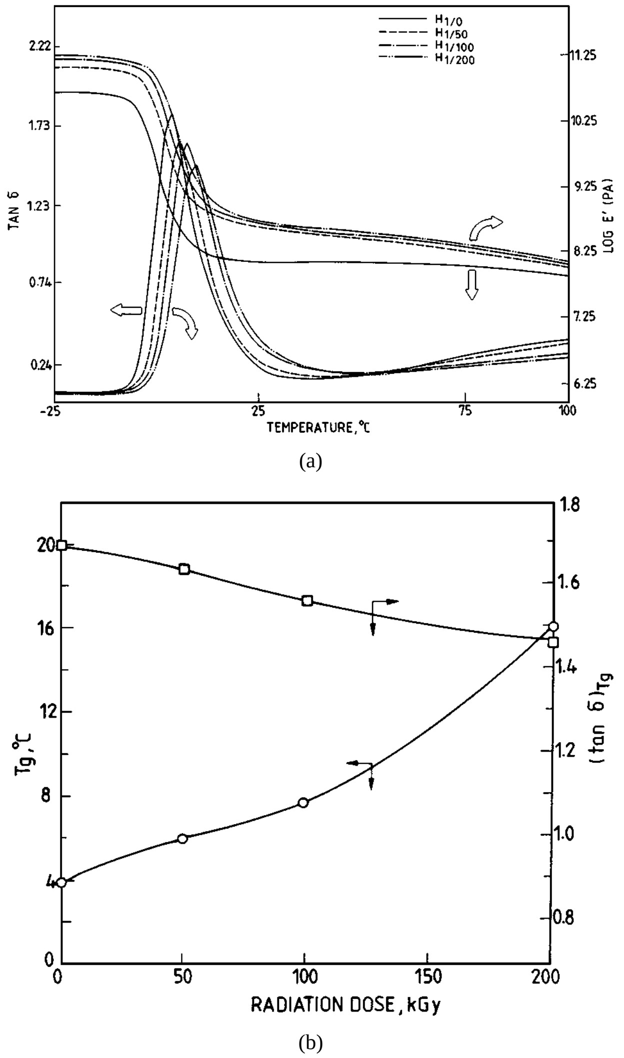
(c)

Figure 1 (a) Stress-strain curves of HMDAC (1 phr) cured fluorocarbon rubber (FKM) vulcanizates irradiated with different irradiation doses (0–200 kGy). (b) Plots showing the variation of tensile properties (tensile strength, modulus and elongation at break) of HMDAC (1 phr) cured FKM rubber vulcanizates at different radiation doses. (c) Variation of gel fraction and crosslink density of the above irradiated FKM rubber vulcanizates; crosslink density of the control fluorocarbon rubber i.e. $T_{0/y}$ irradiated to same different radiation doses is shown by the broken line.

different radiation doses (0–200 kGy) are shown in Fig. 1a. Fig. 1b depicts the variation of tensile properties (tensile strength, modulus and elongation at break) of the rubber vulcanizates calculated from Fig. 1a. It is observed that the modulus of fluorocarbon rubber vulcanizates increases with a corresponding decrease in elongation at break and a marginal decrease in tensile strength, as the dosage of radiation increases. Fig. 1c shows the gel fraction and the crosslink density of the samples irradiated to different radiation doses; the corresponding values of the pure (control) rubber are shown by a broken line. It is observed that there is an increase in crosslink density, on irradiating the rubber vulcanizates 50 kGy dose and above. Both the control and the rubber vulcanizate behave similarly. The increase in crosslink density is about 10–25 times and the change in crosslink density is more for the rubber vulcanizate. The increase in modulus and decrease in elongation at break are due to the enhanced crosslink density of the rubber vulcanizates on irradiation.

Dynamic mechanical properties of the samples have been measured. Fig. 2a shows the variation of tan δ (the mechanical loss factor) and log E' (the dynamic storage modulus) against temperature. As usual, tan δ passes through a maximum and E' drops at the glass transition temperature. Fig. 2b depicts the variation of the glass transition temperature (Tg) and the loss tangent peak $(\tan\delta)_{Tg}$, at the transition temperature of the various irradiated rubber vulcanizates with radiation dose. With increase in radiation dose there is an increase in Tg with a corresponding decrease in $(\tan\delta)_{Tg}$. The shifts in either ways are in line with the increase in degree of crosslinking. At Tg the free-segmental mobility, involving cooperative diffusional motion of the macromolecular chain, is reduced owing to crosslinking which then requires a higher temperature for the inception of rotation. The values of log E' increase with radiation dose over the temperature region studied.

Now the nature and degree of crosslinking of a polymer under the influence of radiation is a function of the structure of the polymer as well as the conditions under which the irradiation is carried out [7]. The crosslinking of fluorocarbon rubber can occur either through recombination of macroradicals formed by splitting-off of active (labile) hydrogens in the vinylidenefluoride

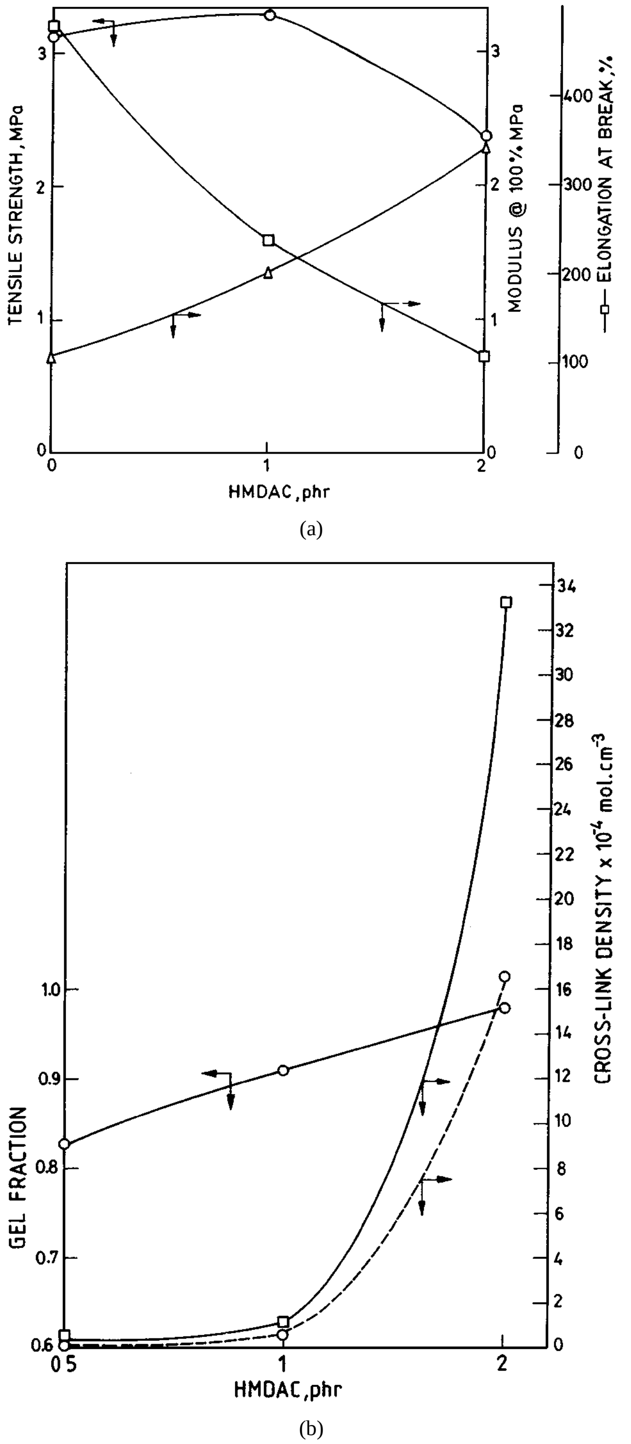


(a)

(b)

Figure 2 (a) Mechanical relaxation spectra, showing the variation of loss tangent (tan δ) and dynamic storage modulus (log E', PA) against temperature, of the fluorocarbon rubber vulcanizates at a fixed level of HMDAC (1 phr) and different radiation doses (0–200 kGy). (b) Plots showing the variation of glass transition temperature Tg and loss tangent at Tg, $(\tan\delta)_{\mathrm{Tg}}$ of the above fluorocarbon rubber vulcanizates at different radiation doses (0–200 kGy).

unit or addition of macroradicals across the π electrons formed by dehydrofluorination [1, 2]. With increase in radiation dose, probably the mobility of the macroradicals (generated by knocking-off the available hydrogen of the conventionally cured FKM) increases. The amount of radicals produced are also increased as the yield of radicals is proportional to the integral radiation absorbed [8]. Such an increase in the degree of crosslinking with increase in radiation dose due to the availability of more radicals and the greater freedom of polymer chains to undergo translational and segmental motion has been noted for silicon rubber [9]. All these are likely to favour the radical recombination process more leading to the progressive formation of denser network structure. This can also be explained on the lines of increase in the cross-linking yield for unsaturated rubbers with increase in hydrostatic pressure [10] to which the polymer is exposed during vulcanization. Greater yield of crosslinks is attributed to an enhancement of chain crosslinking furthered by the close proximity of polymer chains. Similarly, increasing tendency towards radical recombination (with increase in radiation dose) will perhaps set up molecular strain, bringing the reacting chain molecules closer together, thus increasing the chain reaction networking. Cases involving macroradical addition across the unsaturations generated on dehydrofluorination can not be ruled out [11]. Hence, increase in Tg and the decrease in $(\tan\delta)_{\mathrm{Tg}}$ with increase in radiation dose may well suggest that the degree of networking is enhanced thus imposing restriction on the mobility of the macromolecular chain



(a)

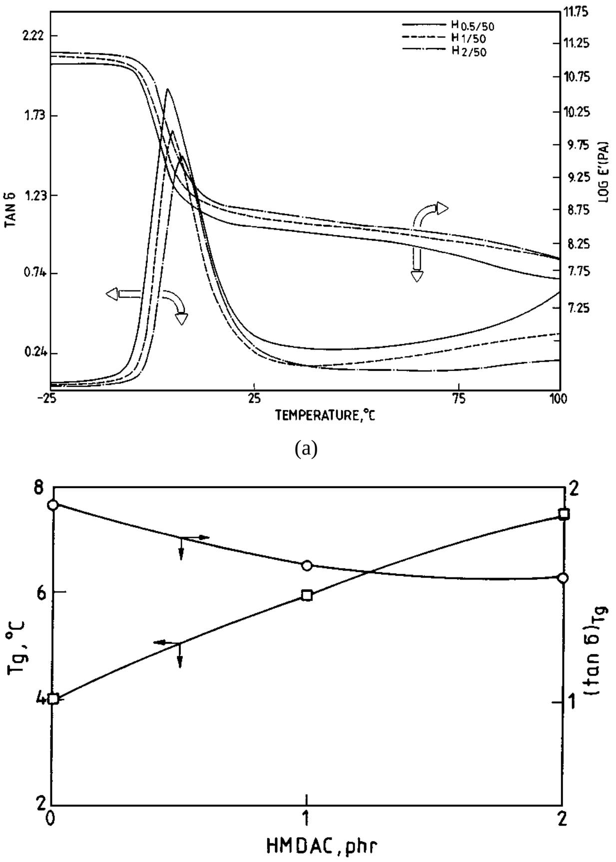
(b)

Figure 3 (a) Plots showing the variation of the tensile properties of the FKM rubber vulcanizates at different levels of HMDAC (0.5–2 phr) and fixed radiation dose of 50 kGy. (b) Plots depicting the variation of gel fraction and crosslink density of the above FKM rubber vulcanizates at a fixed radiation dose of 50 kGy.

segments. Increase in the crosslink density is in line with the increase in modulus and these are in agreement with the rise in degree of crosslinking. Increased resistance of the matrix to deformation can account for the decrease in elongation at break.

3.2. Effect of the level of HMDAC on the degree of crosslinking

Fig. 3a, b show variation of tensile properties and the gel fraction of rubber (along with the crosslink density) cured with various levels of HMDAC (hexamethylene diamine carbamate, 0.5–2 phr) and irradiated at a constant dose of 50 kGy. Dynamic mechanical properties of the same vulcanizates are shown in Fig. 4a, b. It is observed that the modulus increases with a concomitant reduction in elongation at break with increase in the level of HMDAC. This indicates the formation of a tightly knit network structure of the FKM rubber vulcanizes with HMDAC and no deterioration of properties on irradiation. Both the gel-fraction and the crosslink density increase with increase in the level of HMDAC. The glass transition temperature (Tg) and the dynamic storage modulus (log E') are also found to display an increasing trend with a corresponding decrease in the loss factor at the peak temperature, $(\tan\delta)_{\mathrm{Tg}}$. Since glass transition temperature is a sensitive indicator of crosslinking and the modulus is proportional to the degree of crosslinking [12], it is possible to infer that more crosslinks are introduced into the vulcanizates under the influence of radiation as the level of HMDAC is increased. With increase in the level of the curing chemical, as explained in the previous section, the probability that the reacting chain macroradical can come closer to each other is enhanced and this leads to the formation of a denser structure through the mechanisms as explained in the proceeding section and also in our previous communications [1, 2].



(a)

(b)

Figure 4 (a) Mechanical relaxation spectra of the fluorocarbon rubber vulcanizates at different levels of HMDAC (0.5–2 phr) and a constant radiation dose of 50 kGy. (b) Variation of Tg and $(\tan\delta)_{\mathrm{Tg}}$ of the above FKM rubber vulcanizates at a fixed dose of 50 kGy.

4. Conclusions

The fluorocarbon rubber vulcanizates ($H_{1/y}$) show on irradiation, an increase in modulus and decrease in elongation at break with an accompanying increase in density of crosslinking. A marginal variation is observed for the tensile strength $(\tan\delta)_{\mathrm{Tg}}$ at the peak temperature, Tg, decreases, followed by an increase in Tg (the glass transition temperature) and log E' (the dynamic storage modulus). The increase in the degree of crosslinking is due to an enhanced tendency towards the union of macro-radicals on account of increased macroradical mobility and progressive strain set up in chain molecules with rise in radiation dose. Similar change in tensile properties is observed for the vulcanizates ($H_{x/50}$) with increase in level of HMDAC with the tensile strength dropping at the highest level of HMDAC (2 phr) used. Both Tg and log E' have been found to increase with a corresponding decrease in $(\tan\delta)_{\mathrm{Tg}}$ at Tg. This is perhaps due to the increase in the degree of crosslinking with increasing strain imposed on the macromolecular chain radicals with the rise in the level of HMDAC.

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