

# Electron-Beam Curing of Hydrogenated Acrylonitrile–Butadiene Rubber

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**ABSTRACT:** The electron-beam-induced crosslinking of hydrogenated acrylonitrile–butadiene rubber (HNBR) was investigated. HNBR sheets were exposed to electron-beam irradiation in air at a room temperature of  $25 \pm 2^\circ\text{C}$  over a dose range of 0–20 Mrad. An attempt was made to correlate the structure of the irradiated rubber with the properties. The ratio of chain scission to crosslinking and the gelation dose were determined by a method proposed elsewhere. The gel content and dynamic storage modulus increased

with the radiation dose. Fourier transform infrared studies revealed the formation of double bonds and carbonyl and ether groups. These observations were further supported by a thermogravimetric analysis of the carbonaceous residue of irradiated HNBR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 648–651, 2005

**Key words:** crosslinking; electron beam irradiation; gels

## INTRODUCTION

The electron-beam curing of polymers has been gaining commercial importance in recent times. It has certain advantages over conventional curing processes: it is quick and chemical-free, can be performed at the ambient temperature, and can be controlled very precisely. A wide range of dose rates (100–100,000 rad/s), an increased penetration depth with accelerating voltages as high as 10 MeV, and a high energy efficiency of radiation, available from high-power electron-beam accelerators, have made electron-beam radiation superior for polymer processing over other forms of ionizing radiation available, such as X-rays and  $\gamma$  rays.<sup>1</sup> Many publications have been devoted to the action of electron beams on polymers.<sup>2–7</sup> The effects of electron beams on polymers also have been reviewed.<sup>8</sup>

Hydrogenated acrylonitrile–butadiene rubber (HNBR) is a high-performance elastomer obtained by special hydrogenation of acrylonitrile–butadiene rubber (NBR). In addition to the excellent oil resistance and workability displayed by NBR, HNBR shows much improved heat, chemical, and ozone resistance. In comparison with conventional oil- and heat-resistant elastomers, including acrylic and fluorocarbon elastomers, HNBR shows greater tensile strength, wear resistance, and resistance to oils and fluids containing chemically aggressive additives. This unique set of

properties makes it ideal for use in various fuel, engine oil, and hydraulic oil parts such as hoses and seals.

Very little work has been published so far on the radiation processing of HNBR. Zhao et al.<sup>9</sup> studied the effects of  $\gamma$  irradiation on the radiation vulcanization of HNBR. This article presents the crosslinking behavior of HNBR by means of electron-beam irradiation.

## EXPERIMENTAL

### Materials

The HNBR Zetpol 2000L (Nippon Zeon Co., Ltd., Tokyo, Japan) was chosen for this study. Its main characteristics are shown in Table I.

### Sample preparation

HNBR was masticated in a Brabender PL 2207 plastimeter (Duisburg, Germany), at a rotor speed of 60 rpm and  $60^\circ\text{C}$  for 3 min. The stock was then hot-pressed at 5 MPa at  $150^\circ\text{C}$  for 2 min in an electrically heated press to obtain a smooth sheet 1 mm thick.

### Irradiation

The sheets were irradiated in air at room temperature with an ILU-6 electron-beam accelerator at the Bhabha Atomic Research Centre (Mumbai, India). The irradiation dose was 2–20 Mrad. A dynamic irradiation technique was used at a conveyor speed of  $0.9 \text{ m min}^{-1}$ . The acceleration energy and beam current were 1.8 MeV and 1 mA, respectively. A radiation dose of 1 Mrad was applied in a single pass.

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TABLE I  
Characteristics of HNBR

Acrylonitrile content (%)	36
Mooney viscosity (ML <sub>1+4</sub> , 100°C)	65
Density (g/cm <sup>3</sup> )	0.95
Unsaturation (%)	<1
Number-average molecular weight	200,000

### Measurement of the properties

#### Gel content

The gel content was determined by solvent extraction. The samples were extracted in boiling tetrahydrofuran (THF) for 24 h, and the extracted samples were dried to a constant weight. The gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{W_2}{W_1} \times 100$$

where  $W_1$  is the weight of the sample before extraction and  $W_2$  is the weight of the dried sample after extraction. The soluble fraction ( $S$ ) was calculated as follows:

$$S = 1 - \frac{W_2}{W_1}$$

#### Fourier transform infrared (FTIR) spectroscopy

FTIR (Lancklantralst, UK), spectra of thin films, cast from a THF solution, were taken with a PerkinElmer Paragon 1000 spectrometer. The instrument was operated at a resolution of 4 cm<sup>-1</sup>, and four scans were taken in all.

#### Thermogravimetric analysis (TGA)

The thermal decomposition behavior of the samples was studied with a PerkinElmer TGA-7 (Lancklantralst, UK), at a heating rate of 20°C/min over a temperature range of 70–600°C under a nitrogen atmosphere.

#### Dynamic mechanical analysis (DMA)

DMA was performed with a Metravib VA 4000 (Lyon, France), viscoanalyzer in the tension mode. The measurements were carried out at a heating rate of 3°C/min over a temperature range of –50 to 50°C and at a frequency of 1 Hz.

## RESULTS AND DISCUSSION

### Gel content

The gel content of the irradiated samples was determined to evaluate the efficiency of radiation-induced

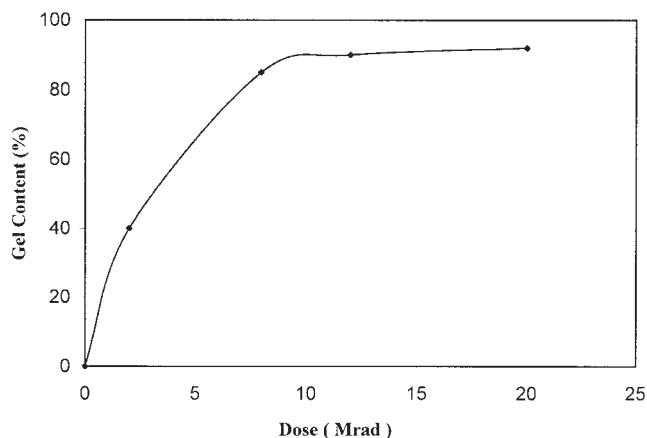


Figure 1 Effect of the radiation dose on the gel content.

crosslinking. Figure 1 shows the gel content of irradiated samples as a function of the radiation dose. The gel content increases with increasing radiation dose, and this indicates that more and more polymer molecules are crosslinked with the radiation dose.

It has already been established that crosslinking and chain scission occur simultaneously when polymers are exposed to irradiation.<sup>10,11</sup> The properties of a polymer ultimately depend on the process that predominates during the irradiation conditions. The theory of radiation crosslinking of polymers has been elaborated on the basis of a probabilistic approach.<sup>12</sup> The sol fraction ( $s$ ) becomes a measure of the ratio of the crosslinking probability to the chain-scission probability. This relationship is called the Charlesby–Pinner relationship and can be formulated as follows for an initial random molecular weight distribution:

$$(s + s^{1/2}) = p_0/q_0 + (2 - p_0/q_0)R_g/R \quad (1)$$

where  $q_0$  and  $p_0$  are the probabilities of crosslinking and chain scission, respectively;  $R$  is the radiation dose

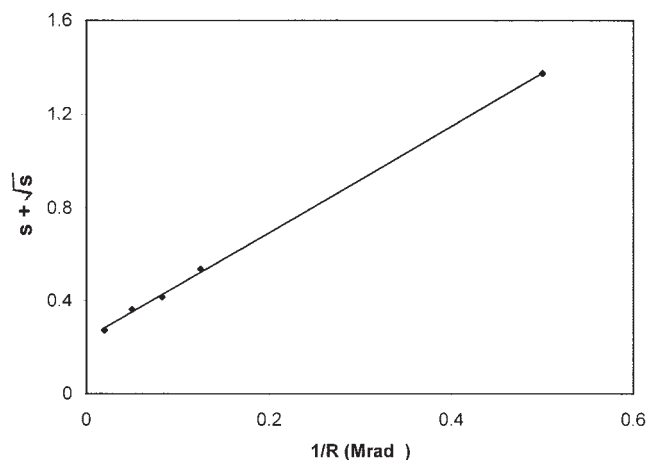


Figure 2 Dependence of  $s + \sqrt{s}$  on  $1/R$  for radiation-cured HNBR.

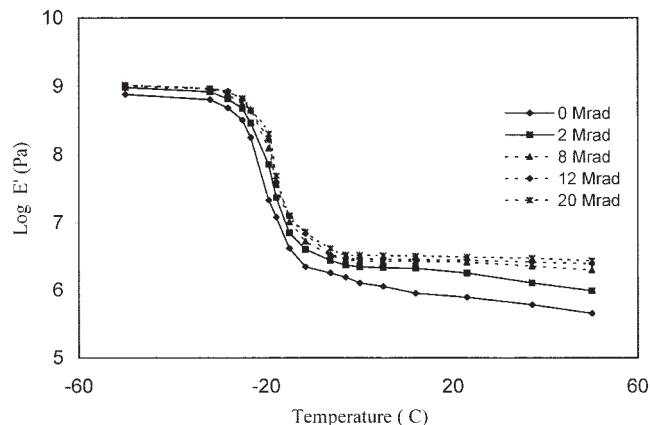


Figure 3 Temperature dependence of  $E'$  for HNBR.

(Mrad); and  $R_g$  is the gelation dose. The point at which an insoluble network first begins to form is termed the gel point, and the corresponding irradiation dose is  $R_g$ . A straight line can be drawn from the linear dependence of  $(s + s^{1/2})$  on  $1/R$ . In Figure 2, the dependence of  $s + s^{1/2}$  on  $1/R$  is shown, and on the basis of our experimental findings, the following equation is fit:

$$(s + s^{1/2}) = 0.238 + 2.276/R \quad (2)$$

The value of  $p_0/q_0$  obtained from the intercept is 0.238.  $R_g$ , calculated from eq. (2), is 1.29 Mrad. Both these values are lower than those of  $\gamma$ -irradiated HNBR in air reported by Zhao et al.<sup>9</sup> ( $p_0/q_0 = 0.41$  and  $R_g = 3.9$  Mrad). The exposure time for the electron beam is shorter than that for  $\gamma$  rays because of the higher dose rate of electron-beam radiation. As a result, the probabilities of radiation-induced oxidative chain scission are less during electron irradiation, and this accounts for the lower  $p_0/q_0$  and  $R_g$  values. Zhao et al. also studied compounded HNBR filled with additives such as carbon black, plasticizers, and antioxidants.

### DMA

Figure 3 depicts the effect of the temperature on the storage modulus ( $E'$ ) at different radiation doses. The modulus after the glass transition increases with the radiation dose. The modulus curve in the transition region also shifts toward higher temperatures with an increasing radiation dose. This is because with an increasing radiation dose, the crosslink density increases. A significant increase in the modulus at a low radiation dose (2 Mrad) indicates a high crosslinking efficiency of HNBR upon exposure to electron-beam radiation.

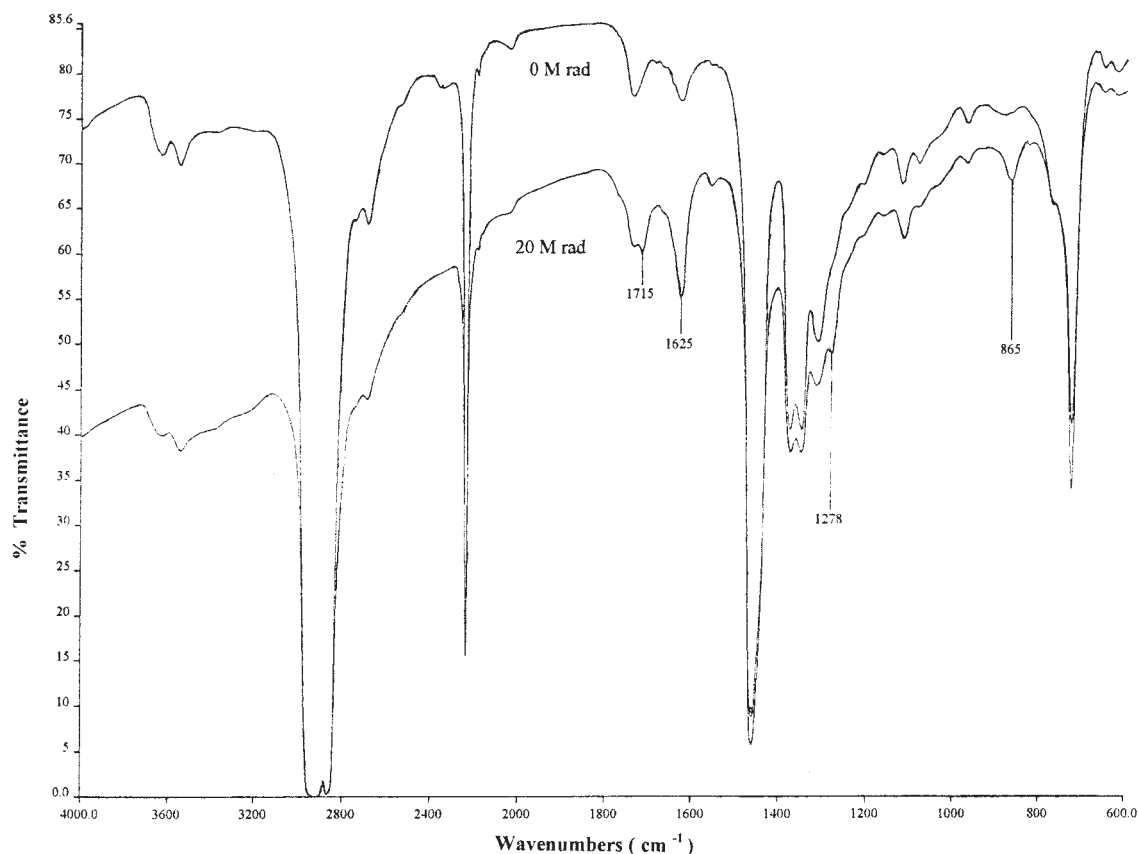


Figure 4 FTIR spectra of an HNBR film before and after irradiation.

TABLE II  
TGA Carbonaceous Residue at Various Irradiation Doses

Irradiation dose (Mrad)	Carbonaceous residue (%)
0	0.773
2	1.437
8	1.902
12	2.007
20	2.614

### FTIR analysis

Figure 4 illustrates the effect of irradiation on HNBR in the 4000–600-cm<sup>-1</sup> region at 0- and 20-Mrad radiation dosages. The appearance of an absorption peak at about 1715 cm<sup>-1</sup> indicates the formation of carbonyl group due to oxidation during irradiation. The absorption intensities at 1625 cm<sup>-1</sup>, due to C=C stretching, and at 865 cm<sup>-1</sup>, due to out-of-plane C—H of the —HC=CH— group, increase after irradiation. This can be attributed to the fact that double bonds are formed when a saturated polymer is subjected to irradiation.<sup>13</sup> A new absorption peak appears at 1279 cm<sup>-1</sup>, probably indicating the formation of a C—O—C group.

### TGA

To obtain information on the thermal degradation behavior, we analyzed irradiated samples with TGA. Most organic elastomers undergo thermal degradation when heated in nitrogen, and this is usually completed by 500°C. Many of them yield a carbonaceous residue, which is stable above 600°C in the absence of oxygen. Carbonaceous residues generally arise from elastomers containing heteroatoms, such as oxygen, nitrogen, and halogens.<sup>14</sup> Table II shows that the amount of the carbonaceous residues, obtained from TGA for HNBR, increases with the radiation dose. The unirradiated sample shows very little carbonaceous residue, unlike NBR, for which the amount is significantly higher.<sup>15</sup> The formation of carbonaceous residues is a result of a thermal cyclization reaction, and the extent of cyclization is much more for NBR be-

cause of the presence of an unsaturated butadiene segment. A gradual increase in the carbonaceous residue with an increase in the radiation dose strongly suggests that radiation induces oxidation and incorporates unsaturation in HNBR.

### CONCLUSIONS

HNBR can be crosslinked by an electron beam at a low radiation dose. DMA studies have revealed that irradiation has a significant influence on *E'* of HNBR. The increase in *E'* is believed to be due to irradiation-induced crosslinking. FTIR spectra show that double bonds, carbonyl groups, and ether linkages form upon the electron-beam irradiation of HNBR. This observation has been further confirmed by the measurement of carbonaceous residues with the TGA technique.

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