

Grafting of Butyl Acrylate and Methyl Methacrylate on Butyl Rubber Using Electron Beam Radiation

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ABSTRACT: Being nonpolar in nature, butyl rubber (IIR) has poor compatibility toward polar polymers and fillers. It can be improved by grafting polar substrates on the butyl elastomer. Radiation-induced polymer processing is getting increasing interest, as it leads to new and improved polymers with desirable and interesting properties. In this investigation, electron beam radiation has been used to graft methyl methacrylate (MMA) and butyl acrylate (BA) on IIR. This process has several advantages over conventional grafting processes such as cationic polymerization (which needs very low temperature and stringent reaction conditions) and solution radical polymerization (which often needs solvent

removal and recycling). The grafted polymers were characterized by using ^1H NMR, IR, TGA, and SEM analysis. The degree of grafting increases with a decrease in irradiation dose as well as with an increase in monomer concentration. It was observed that there was a decrease in intrinsic viscosity in irradiated IIR samples, indicating the chain scission. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1340–1346, 2006

Key words: graft copolymerization; butyl rubber (IIR); methyl methacrylate; butyl acrylate; electron beam radiation

INTRODUCTION

Butyl rubber (IIR) is an important commercial elastomer with many desirable and interesting properties such as low air permeability and broad damping characteristics.¹ Because of the presence of mostly saturated backbone, IIR has good resistance to aging and weatherability. The principal applications of this elastomer are in tire industry for the preparation of inner tubes and inner liners and also in adhesive industry in the preparation of pressure sensitive adhesives. Being nonpolar in nature, IIR has poor compatibility with polar elastomers, plastics, and carbon black. Research is going on to improve the interfacial adhesion of IIR with other elastomers, plastics, and carbon black. The use of graft and block copolymers as emulsifiers and interfacial compatibilizer are established techniques to improve the polymer–polymer interaction as well as the morphology in polymer blends.^{2–4} There are reports of grafting on IIR using sequential cationic polymerization.^{5–7} The cationic process provides well-defined graft copolymers with predictable molecular weights and narrow molecular weight distribution. However, this process is living only under complex conditions and involves high concentration of initiator, coinitiator, and electron donor. In addition, only few monomers undergo living cationic polymeriza-

tion, and most importantly, cationic polymerization can only be carried out at very stringent conditions and at very low temperature. Conventional radical graft copolymerization leads to ill-defined products, resulting in gel formation and/or simultaneous formation of homopolymerization. Solution graft copolymerization requires solvent removal and recycling, which often restricts commercial applications. The purpose of this article is to investigate a simple method for grafting of polar materials on butyl elastomers.

In recent time, radiation treatment of polymers is an important process for the production of new and improved polymers with desirable properties.^{8–10} The radiation-induced grafting of vinyl monomers has been found to be an efficient method and many reports have been published.^{8,11–15} Electron beam (EB) radiation is a new technique, which is increasingly being used in polymer processing and polymer modification.^{8,9} It has several advantages, such as it is very simple and fast process. Most importantly, this process can be used at the solid state of the polymer. The γ radiation has been used to graft methacrylic acid onto polypropylene,¹⁶ acrylonitrile onto natural rubber,¹⁷ and hydroxyethyl methacrylate (HEMA) onto EPDM.¹⁸ EB radiation has been used for the polymerization of acrylate-based monomers and modification of elastomers using polyfunctional acrylates.^{19–21} This investigation reports successful grafting of methyl methacrylate (MMA) and butyl acrylate (BA) on IIR by using EB radiation.

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TABLE I
Formulation of the Samples and Radiation Dose^a

Sample specification	Irradiation dose (Mrad)	Materials	Amount of materials (phr) (per hundred rubber)
IIR	0	IIR	100
IIR 8M	8	IIR	100
5P8M-MMA	8	IIR	100
		MMA	5
10P8M-MMA	8	IIR	100
		MMA	10
15P8M-MMA	8	IIR	100
		MMA	15
20P8M-MMA	8	IIR	100
		MMA	20
20P4M-MMA	4	IIR	100
		MMA	20
20P12M-MMA	12	IIR	100
		MMA	20
20P20M-MMA	20	IIR	100
		MMA	20
5P8M-BA	8	IIR	100
		BA	5
10P8M-BA	8	IIR	100
		BA	10
20P8M-BA	8	IIR	100
		BA	20

^a Samples are specified like this: for example, 20P8M-MMA = 20 phr (per hundred rubber) MMA was mixed with IIR and the irradiation dose was 8 Mrad.

EXPERIMENTAL

Materials

The butyl rubber (IIR; Polysar N.V., Belgium) was used as received. Methyl methacrylate (MMA) (Burgoyne Burbridges, Mumbai) and butyl acrylate (BA) (Loba Chemie., Mumbai) were purified using vacuum distillation.

Preparation of samples

IIR was first premasticated in a two-roll mill (model-Schwabenthan, Berlin) at room temperature for 4 min. The premasticated IIR was then passed into a two-roll mill to form a thin sheet of about 1 inch width. The sheet was then cut into small pieces and these pieces were taken in a Brabender Mixer. These IIR samples were mixed with other ingredients (as explained in Table I) at 30°C for 4 min. The mixed samples were placed between the two aluminum foils and then molded into a sheet of uniform thickness by placing inside the compressor for 30 min at a pressure of 50 kg/cm², at room temperature.

Irradiation of samples

The molded films were irradiated by electron beam (EB; model-RDI, Dynamitron DPC-2000, USA) at

room temperature of 25°C. The samples are irradiated with different radiation dose such as 4, 8, 12, and 20 Mrad. The radiation process was carried out at Nicco Corp. Limited (Kolkata, India). The radiation doses of various samples are shown in Table I.

Characterization

Sohxlet extraction

Sohxlet extraction was carried out to determine the extent of grafting. After the EB irradiation, the irradiated sample was sohxlet extracted for 24 h using acetone as the solvent. Acetone extracts the homopolymers of MMA or BA and unreacted MMA or BA monomer, which are not grafted. After the extraction, the samples were dried in a vacuum oven for 6 h at 45°C. The samples were kept under vacuum until it showed a constant weight. The percentage of solubility was measured in the following way

$$\% \text{ of solubility} = [(W_0 - W_s) / W_0] \times 100$$

where W_0 is the weight of sample before extraction and W_s is the weight of sample after extraction.

Instruments

¹H NMR spectra were recorded in a 200 MHz Bruker NMR spectrophotometer using CDCl₃ as solvent. IR spectra were recorded in a Perkin-Elmer IR-spectrophotometer with a range of 200–4000 cm⁻¹. For this, the samples were dissolved in CHCl₃ and were cast into films. These films were used for the IR analysis. Scanning electron microscopy (SEM) was carried out in a JEOL 5600 Electron Microscope to study the surface morphology of the samples. The grafted polymer

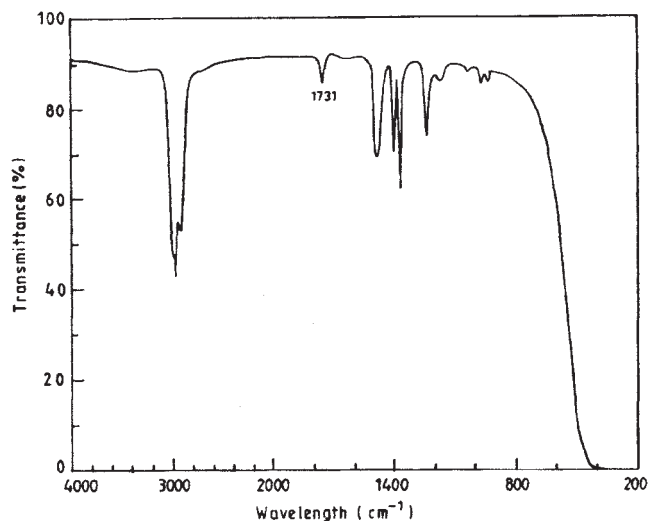


Figure 1 IR spectrum of IIR grafted with PMMA.

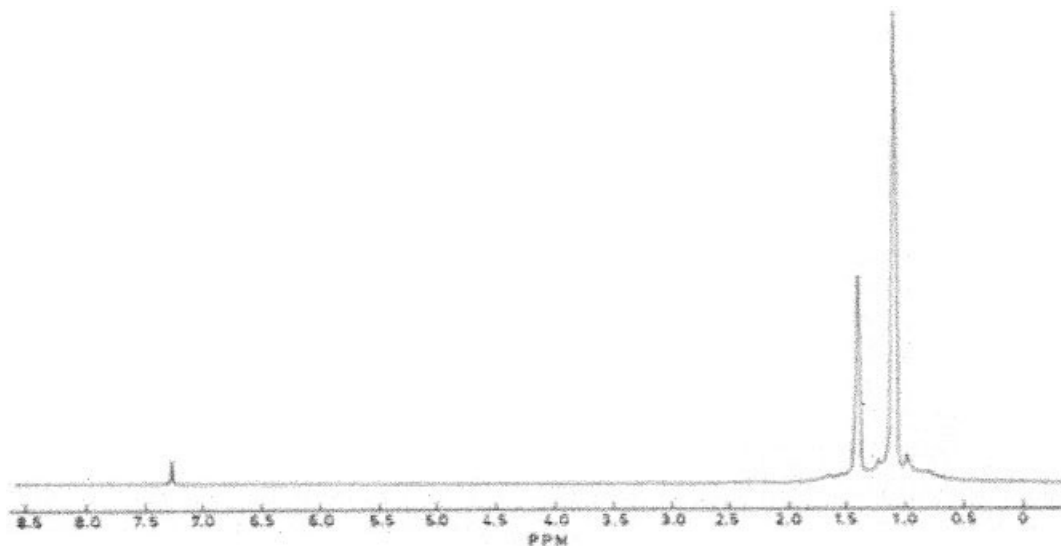


Figure 2 ^1H NMR spectra of IIR.

samples were dipped into the liquid nitrogen. The brittle polymer was then broken, and a small piece of the sample was collected and was gold coated using sputtering technique.

The thermogravimetry analysis (TGA) was carried out in TGA-7, Perkin-Elmer, USA, at the heating rate of $10^\circ\text{C}/\text{min}$ under argon atmosphere. From these thermograms, DTA as well as DTG analysis were carried out.

Viscosity measurement

Viscosity experiment was carried out in Ostwald's viscometer using CHCl_3 as solvent. Solutions of different concentration (0.3, 0.5, and 1.0%) were prepared. The time taken by the known volume of the solution (20 cc) to pass through the capillary was recorded for different concentrations. Each measurement was carried out for three times. Intrinsic viscosity was calculated from the intercept at Y axis (at $C = 0$) of the graph of the reduced viscosity (η_{red}) versus concentration (C).

RESULTS AND DISCUSSION

The IIR samples with different loading of MMA or BA were irradiated with EB radiation (Table I). The radiation dose was used from 4 to 20 Mrad. Grafted polymer may be associated with the homopolymer of PMMA and PBA or unreacted monomers. Soxhlet extraction was carried out to remove all these products. Acetone was used as the extraction solvent, as PMMA is soluble in acetone but IIR and grafted IIR are not soluble in acetone.

Grafted copolymer was characterized by IR and ^1H NMR spectra. After the Soxhlet extraction, the insoluble

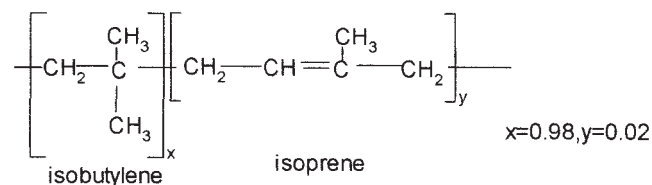
polymer was characterized by using IR spectroscopy (Fig. 1). It shows an intense peak at 1731 cm^{-1} , which is due to ester group ($-\text{COOCH}_3$) present in IIR-g-PMMA. Figure 2 shows the ^1H NMR spectrum of IIR. The chemical structure of IIR is shown in Scheme 1. The protons of $-\text{CH}_3$ group of isobutylene show a singlet peak at 1.09 ppm (Fig. 2). The IIR-g-PMMA shows a small peak at $\delta = 3.58$ ppm (Fig. 3), which is due to the methoxy protons ($-\text{O}-\text{CH}_3$) in PMMA. For the PMMA-grafted IIR, the percentage of copolymers can be determined by the ratio of peak area at 3.58 (X) and 1.09 (Y). X is for three protons of $-\text{O}-\text{CH}_3$ groups in PMMA segment and Y is for six protons of two $-\text{CH}_3$ groups in IIR. Hence, the ratio of these two types of protons is $X/3 : Y/6 = 2X : Y$.

Degree of grafting can be calculated as follows:

$$\% \text{ of grafting} = [2X/(2X + Y)] \times 100$$

In case of BA-grafted IIR, protons of $-\text{OCH}_2-$ ($\delta = 4.0$ ppm) were used as standard to quantify the BA portion in the grafted copolymer. The degree of grafting of MMA and BA in different irradiated samples is shown in Table II.

Figure 4 shows the extent of grafting of PMMA or PBA (in weight) per mol of isobutylene unit at the



Scheme 1

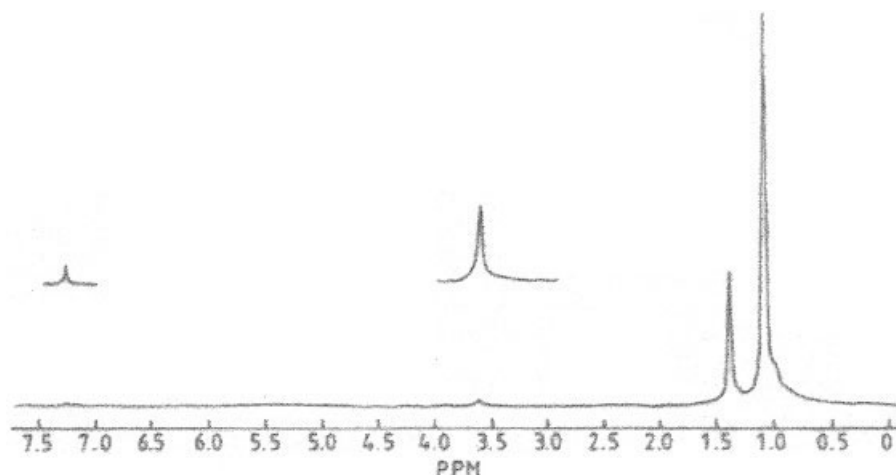


Figure 3 ^1H NMR spectra of PMMA-grafted IIR.

same irradiation dose (8 Mrad) but at different MMA/BA loading. In case of MMA, the extent of grafting increases initially with MMA loading. After certain loading of MMA, the degree of grafting levels off. In case of BA, the degree of grafting increases with increasing monomer loading. It is interesting to note that with the same loading of monomer and at the same irradiation dose the efficiency of grafting is greater in the case of BA (Fig. 4). It may be due to several factors. There may be different reactivity of the active species produced upon EB radiation. The reactions, which take place upon EB radiation, are primary and secondary in nature.⁸ The primary reaction in EB radiation is ionization (i.e., the production of an ion) as well as excitation (i.e., the formation of excited chemical species) of the molecules. The secondary reaction results from the excited ion dissociating into a radical ion and a radical.⁸ BA has higher rate of propagation (k_p) with respect to that of MMA.²² Greater

value of k_p leads to more incorporation of BA in the graft copolymer. The presence of longer alkyl chain in BA makes it more compatible with IIR, which is basically a polyolefin elastomer. The lower volatility of BA as compared to MMA may also make the graft copolymerization more effective in case of BA. It was observed that during EB irradiation the samples were heated up due to high energy radiation.

The intrinsic viscosity of the grafted IIR was determined after its sohxlet extraction. Figure 5 shows the variation of intrinsic viscosity with different loading of MMA/BA but at the same irradiation dose. It indicates that with increasing MMA/BA loading, intrinsic viscosity increases. With the same loading of monomer, the samples of IIR-g-PBA showed higher intrinsic viscosity (Fig. 5). It is due to the greater amount of grafting in case of BA and also due to the higher

TABLE II
Extent of Grafting on IIR in Different Samples^a

Sample	Irradiation (Mrad)	Grafting of MMA or BA (mol % w.r.t. isobutylene unit)
IIR8M	8	0
5P8M-MMA	8	3.0
10P8M-MMA	8	4.2
15P8M-MMA	8	4.4
20P8M-MMA	8	4.6
20P4M-MMA	4	8.5
20P12M-MMA	12	5.9
20P20M-MMA	20	3.7
5P8M-BA	8	2.6
10P8M-BA	8	3.9
20P8M-BA	8	7.1

^a Samples are specified like this: for example, 20P8M-MMA = 20 phr (per hundred rubber) MMA was mixed with IIR and the irradiation dose was 8 Mrad.

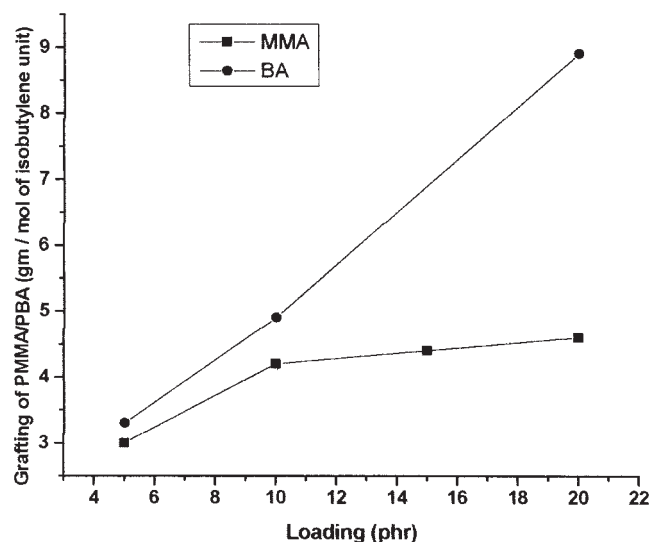


Figure 4 Effect of loading of MMA/BA on grafting on IIR at 8 Mrad irradiation.

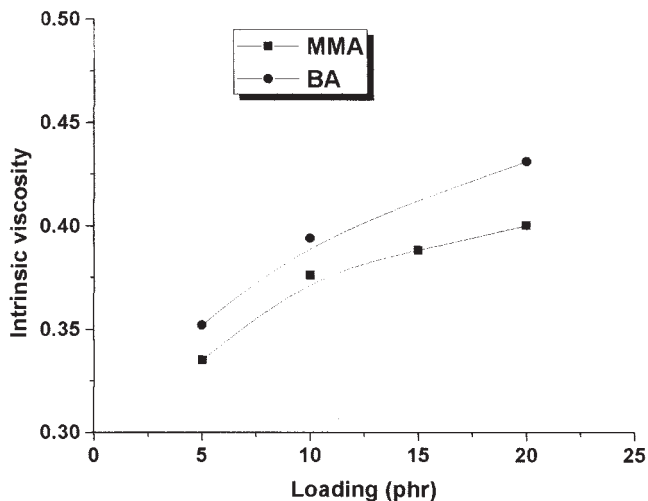


Figure 5 Effect of loading of MMA/BA on the intrinsic viscosity of grafted IIR (at 8 Mrad irradiation).

molecular weight of PBA unit with respect to the PMMA unit. Figure 6 shows that with increase in radiation dose, intrinsic viscosity decreases. All grafted materials have intrinsic viscosity lower than the intrinsic viscosity of IIR. It is because of the degradation during EB irradiation. In case of high dose of irradiation, viscosity is lowest, indicating greater amount of degradation. As explained earlier, EB radiation results in the formation of radical ions and radicals in the macromolecular chain. These species may undergo chain scission, crosslinking, and recombination of the broken chains, depending on the structure of the polymers. For IIR, the decrease in viscosity is mainly due to the main chain scission. On EB radiation, the formation of radical on tertiary carbon atom in IIR is favored because of its greater stability. Chan-

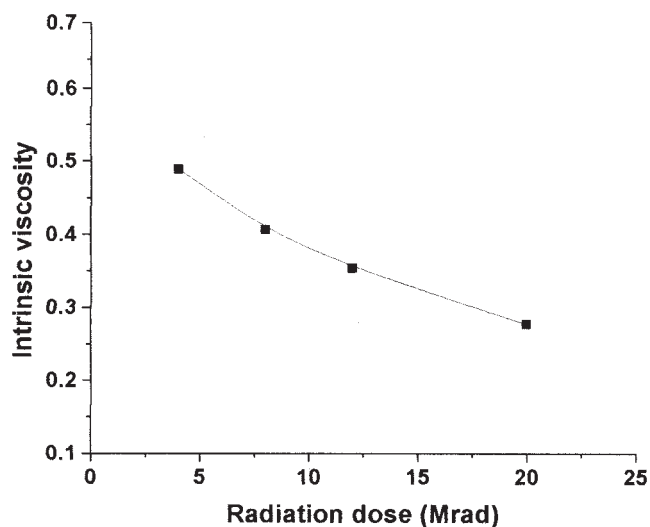


Figure 6 Effect of irradiation dose on the intrinsic viscosity of IIR grafted with PMMA.

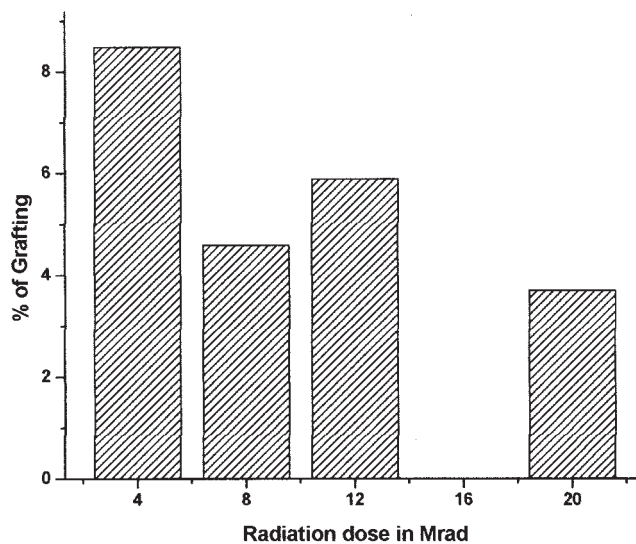


Figure 7 Effect of irradiation dose on grafting of PMMA on IIR (at 20 phr of MMA).

dra et al.²³ reported chain scission in IIR on γ irradiation and decrease in intrinsic viscosity of the irradiated elastomer. Intrinsic viscosity decreased as radiation dose increased, indicating greater amount of chain scission.

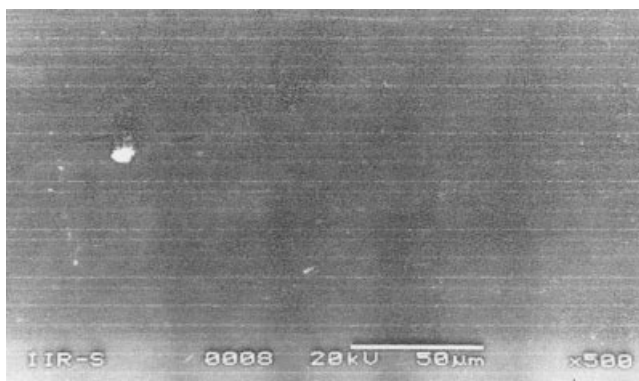


Figure 8 SEM picture of IIR.

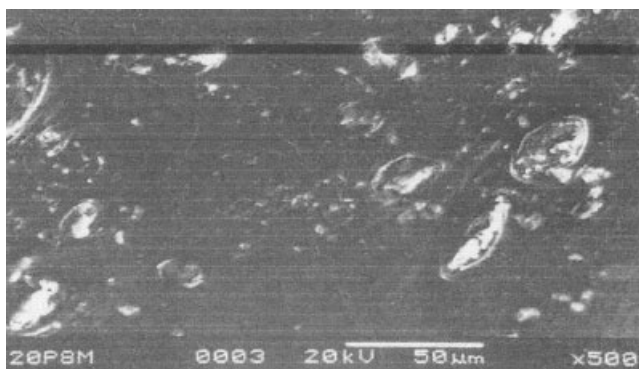


Figure 9 SEM picture of PMMA-grafted IIR.

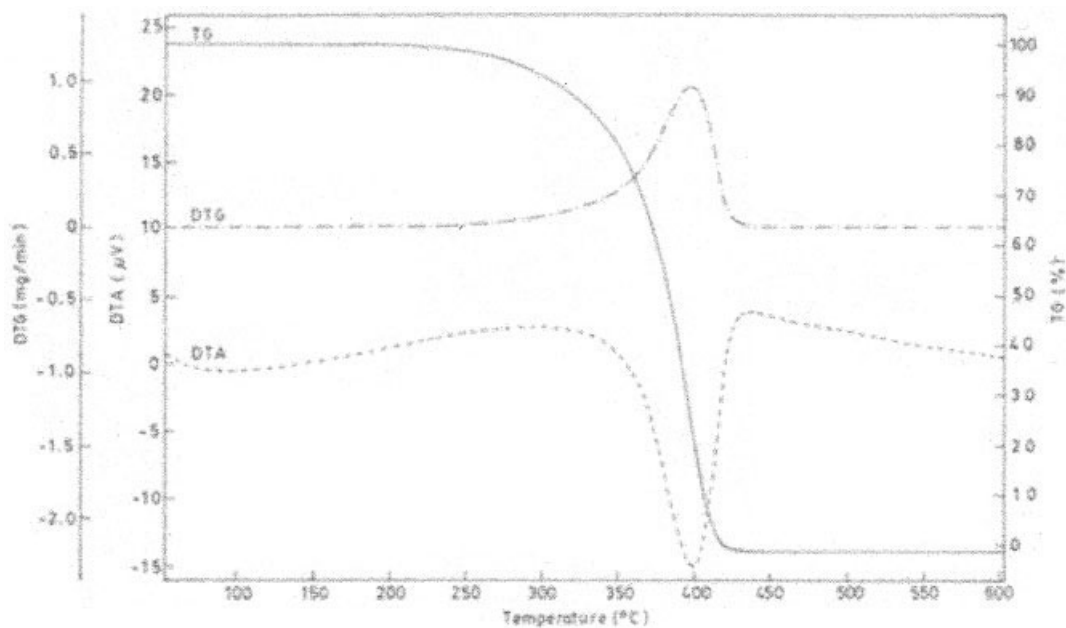


Figure 10 TGA of IIR.

The variation of degree of grafting of MMA at different irradiation dose is shown in Figure 7. It does not have a general trend in the degree of grafting. The complexity arises due to the several factors. On increase in radiation dose, there is degradation of IIR as well as the degradation of grafted PMMA, as reported in the literature.⁸ There is also possibility of the homopolymerization of MMA at high irradiation dose. However, in this case, at higher irradiation dose of 20

Mrad, the extent of grafting is very less. Irradiation dose of 4 Mrad was found to be optimum dose to get maximum grafting.

Figure 8 shows the picture of SEM of the IIR. Figure 9 shows SEM picture of IIR grafted with MMA. The formation of dense microlayer at the top of the extracted grafted samples and also different surface morphology as compared to the unmodified samples indicates that PMMA is grafted onto IIR. It is in ac-

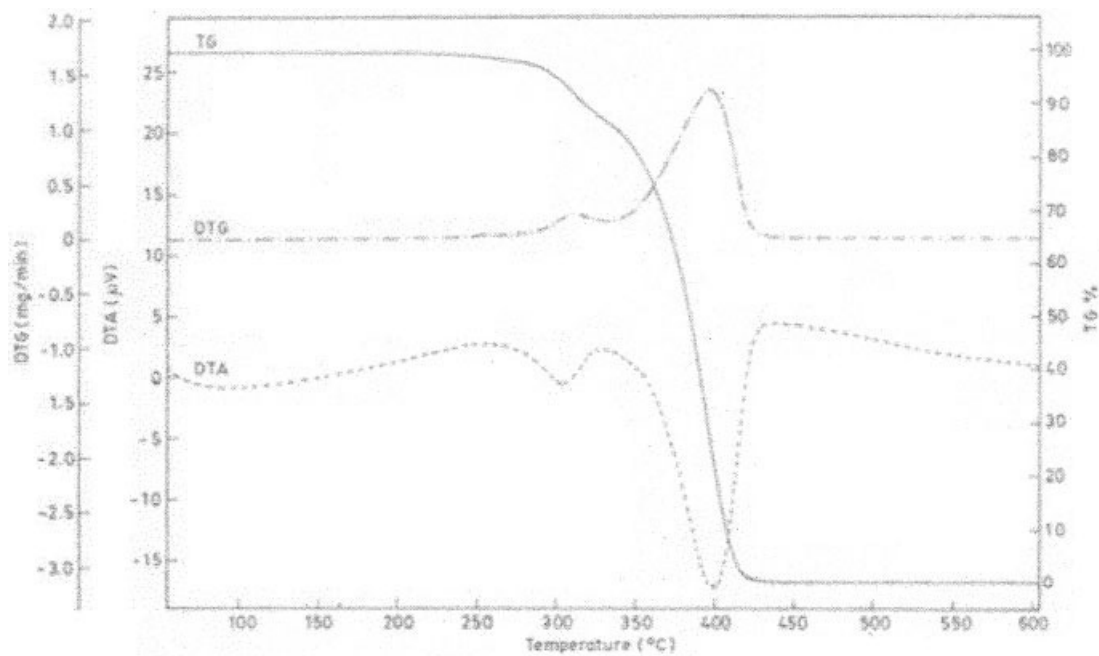


Figure 11 TGA of PMMA-grafted IIR.

cordance with the results obtained from ^1H NMR and IR analysis, which confirmed the grafting of PMMA on IIR.

The TGA, DTG, and DTA thermograms of IIR and IIR-g-PMMA are shown in Figures 10 and 11. In the thermogram of IIR (Fig. 10), the DTA curve shows only a single peak at T_{max} of about 400°C . The DTA curve of IIR-g-PMMA (Fig. 11) shows an additional small peak at 311°C , which is due to PMMA present in the elastomer. The DTG curve (Fig. 10) shows broad decomposition with a small hump, which indicates the presence of another component in the polymer. This is due to the PMMA segment of IIR-g-PMMA. T_{onset} of IIR and T_{onset} of IIR-g-PMMA are 262 and 215°C , respectively. Hatada et al.²⁴ reported a decomposition temperature (T_{onset}) of 210°C for PMMA prepared by conventional radical polymerization.

CONCLUSIONS

MMA and BA have been successfully grafted on IIR using EB radiation. The degree of grafting was quantified by using ^1H NMR. The extent of grafting varies from 2 to 9%, depending on the monomer loading and irradiation dose of EB radiation. BA was found to have better grafting efficiency compared with MMA. SEM picture showed that PMMA was distributed as a discrete phase in IIR. It was found that during irradiation there is degradation in IIR. At low irradiation dose, the extent of degradation is low and the degree of grafting is more.

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