

Effect of Crosslinking Monomers on the Performance of Electron Beam-Induced Biodegradable Bionolle–Rubber Blends

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ABSTRACT: To find out the better crosslinking monomer for vulcanization of natural rubber under electron beam (EB) radiation, the dry rubber was masticated with different polyfunctional monomers like TMPTA, NVP, and ethylene glycol diacrylate of different numbers of CH₂—CH₂—O group, such as 1G, 3G, 7G, and 10 G. The masticated films were irradiated with different doses under EB at 10 kGy/pass. The highest tensile strength (25 MPa) of the rubber was observed in the presence of TMPTA (3phr) at 150 kGy dose. The gel content of the rubber increased with an increase of dose. Bionolle was mixed with the masticated rubber containing 3 phr TMPTA at different proportions; films of these blends along with Bionolle were irradiated under EB with different doses. The concentration of rubber in Bionolle and radiation dose were optimized. The elastomer with 5% masticated showed the highest tensile strength (62 MPa). The gel content of the blends was found to increase with an increase of radiation dose as well as rubber concentration in Bionolle. The elastomers or blends were found to possess good thermal properties. The elastomers exhibited a much lower loss of tensile strength due to the thermal aging compared with pure Bionolle. The elastomers sustained their original shape for 300 min at 180°C, whereas Bionolle sustained its shape for only 3 min at 120°C under the same load (50 g). Among all the elastomers, 5% rubber containing elastomer was found to be better in all respects. It was observed from scanning electron microscopy and differential scanning calorimetry studies that 5% rubber is well mixed with Bionolle. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 799–807, 2001

INTRODUCTION

Increased polymer consumption for different uses has threatened the environment. This has led to intensive research activities for new polymers, blends of polymers, and elastomers that would at-

tain better physico-mechanical and thermal properties as well as allow removal of the polymer waste economically, e.g., biodegradable.^{1–3} Blends of biopolymers with nondegradable polymers as well as with elastomers can partly solve this problem.⁴ The use of biodegradable polymers in plastics is limited because of their poor physical properties. Recently, thermoplastic elastomers have become increasingly important in industrial application.⁵ Duchacek,⁶ in his review article, mentioned that the

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latest development of thermoplastic elastomers is block copolymers⁷⁻⁹ and polymer blends.¹⁰⁻¹⁴ Most of the research is conducted with nondegradable plastics [polyvinyl chloride (PVC)], acrylonitrile-butene rubber,¹⁵⁻¹⁷ and styrene-butadiene rubber.¹⁸ Dynamically vulcanized blends of PVC with chloroprene rubber are superior in respect to flame-retardant and aging resistance.¹⁹ A disadvantage of the chloroprene rubber/PVC blends is that they cannot be recycled because the blends undergo thermocrosslinking.²⁰ A Biopol-rubber blend was prepared recently²¹ by the controlled incorporation of a small amount of natural rubber (NR) into the host Biopol. The blends produced a biodegradable character with far superior mechanical properties than the Biopol alone. Bionolle is a synthetically biodegradable aliphatic polyester thermoplastic, chemically known as polybutylene succinate. Bionolle is a polymer of 2- and 4-carbon diacids and glycols.²² Bionolle has many interesting properties such as biodegradability, melt processability, thermal, and chemical resistance.²³ Ratto and Strenhouse²⁴ have investigated Bionolle as well as Bionolle-starch blends for their processable mechanical properties and also thermal properties. Very recently, Khan et al.²⁵ studied the enzymatic degradation of Bionolle and its blends with NR. Blends of 5% rubber in Bionolle showed the higher degradation in comparison with pure Bionolle; the blend showed 93% degradation within 90 h.

Radiation processing is a powerful, energy-efficient, and nonpolluting method for the production of advanced materials. NR was vulcanized by radiation in place of sulfur, the conventional process. Vulcanization of NR by electron beam (EB) radiation has become popular in many applications because of several advantages over conventional sulfur vulcanization, e.g., absence of *N*-nitrosamines, degradability, transparency, softness, low cytotoxicity, etc.^{26,27} In addition, the use of the EB radiation process offers some other advantages such as performing irradiation at ambient temperature in reduced irradiation time with less atmospheric pollution.²⁸ Banil et al.²⁹ demonstrated EB curing and modification of fluoro elastomers in the presence of polyfunctional monomers; they also studied the dynamic mechanical properties of EB-modified fluorocarbon rubber.³⁰

The present study was conducted to prepare and characterize the biodegradable elastomer of Bionolle and NR with different functional monomers using EB radiation; the effect of radiation on

the performance of mechanical and thermal properties of the elastomers was also studied.

EXPERIMENTAL

Materials

Bionolle no. 1020 of average molecular weight of 6.33×10^4 and melting point 112.6°C was procured from Showa Highpolymer Co. Ltd., Japan. Dry NR was obtained from Okamoto Co. Ltd., Japan. Monomers monoethylene glycol dimethacrylate (1G), triethylene glycol dimethacrylate (3G), heptaethylene glycol dimethacrylate (7G), and trimethylol propane trimethacrylate were obtained from Merck, Germany.

Methods

Preparation of Rubber Films

Dry rubber was masticated with crosslinking or processing monomer by roller mill (Fuji Electronic Co. Ltd., Japan). The monomer was added drop by drop on the rubber during mastication. The concentration was varied from 1 to 5 phr. The rubber sheets were prepared by hot-press technique at 160°C and 150 kg/cm².

Preparation of Blends

The masticated rubber (containing TMPT) was mixed with Bionolle at different concentrations using Labo Plastomill (model 50C I50; Toyoseiki Seisakushe Co. Ltd., Japan) at 160°C for 5 min and 30 rpm. Sheets of 0.5-mm thickness were prepared with these mixtures by using hot-press methods. Temperature, pressure, and time were 160°C, 150 kg/cm², and 6 min, respectively.

Irradiation

Rubber sheets masticated with different monomers and Bionolle rubber blend sheets were irradiated to vulcanize under EB accelerator at a beam current of 1 mA and acceleration voltage of 1 MeV generated by a Cockcroft-Walton type accelerator. The dose rate was 10 kGy/pass.

Tensile Properties

Tensile strength of rubber, Bionolle, and their blends were measured by using a Toyosciki Strogaph R1. The samples were cut into dumbbell shapes using cutter ASTM-D1822-L.

Gel Content

The gel content of irradiated samples of rubber, Bionolle, and the blends were determined by extracting the soluble portion with hot toluene in a Soxhlet for 48 h.

Thermal Properties

To study the thermal aging property, dumbbell-shaped blend samples, both irradiated and unirradiated, were placed on a rotary rack in a thermostated oven for different periods of time, with a maximum of 15 days. The loss of tensile strength was measured as a function of rubber concentration in the blends at different irradiation doses.

Heat resistance properties of the Bionolle and the blends were studied by hanging the samples ($10 \times 4 \times 0.5$ mm) with a 50-g load in an oven at a fixed temperature of 120°C . The breaking time of the samples was monitored as a function of blend composition with respect to irradiation dose.

Differential Scanning Calorimeter (DSC)

DSC measurements of both the irradiated and unirradiated blend samples were performed by using a Perkin-Elmer Thermal Analyzer under nitrogen gas at a flow rate of 30 mL/min. Samples of 10 mg were encapsulated in an aluminum pan and heated from 30 to 160°C at a rate of $10^\circ\text{C}/\text{min}$ and then cooled to 30°C at the same rate.

Thermogravimetric Analysis (TGA)

TGA of the samples was performed by using a Thermal Analyzer (Shimadzu TGA-50, Japan). The samples (10 mg) were encapsulated in an aluminum pan and heated to 500°C at $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The main object of the investigation was to blend NR with polybutylene succinate (Bionolle) in the presence of suitable crosslinking monomer additives under EB radiation so that the materials, thus formed, can be used in diverse applications. Different experimental parameters were optimized as follows.

Dose Optimization

The masticated NR sheet with TMPTA at different proportions of rubber was irradiated under EB at

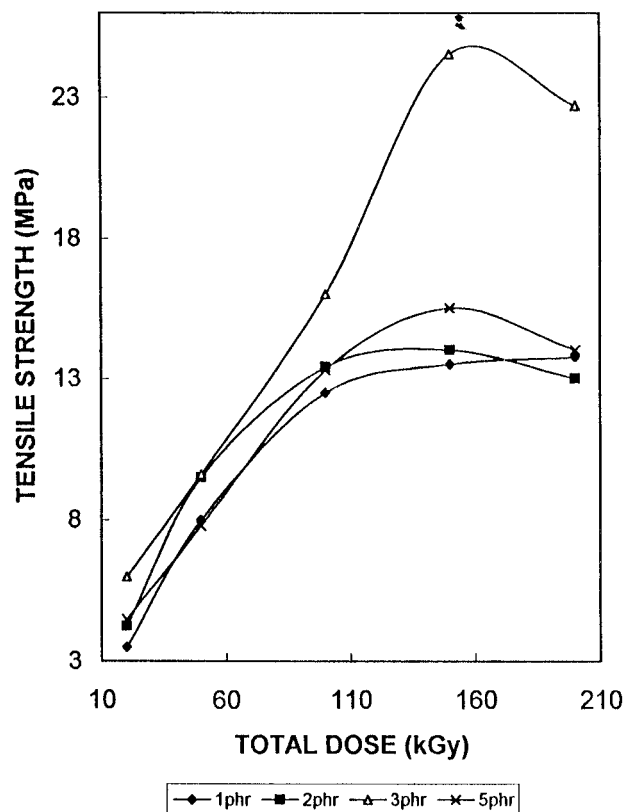


Figure 1 Tensile strength of irradiated rubber against radiation dose with respect to TMPTA concentration.

different total doses using a dose rate of 10 kGy per pass. The tensile strength of irradiated rubber was determined. The results are shown in Figure 1, where tensile strength is plotted against different total doses as a function of TMPTA concentration. The tensile strength increases with increase of dose, becomes maximal at 150 kGy, and then decreases. The decrease of the tensile strength at a higher dose could be caused by degradation effect with higher radiation on the rubber materials. Higher doses of radiation causes crosslinking and scission in the polymeric materials; this causes segmentation of polymeric chains, introducing heterogeneity into the system.³¹ The highest tensile strength of the rubber was observed at 3 phr of TMPTA. A multifunctional vinyl monomer promotes rapid free radical propagation reaction³² leading to network (crosslinking) polymer structures through grafting via their double bonds.^{31,33} When TMPTA concentration is increased, the amount of residual unsaturation also increases as a consequence of a faster rate of formation of the three-dimensional network causing restricted mobility at an early stage. The

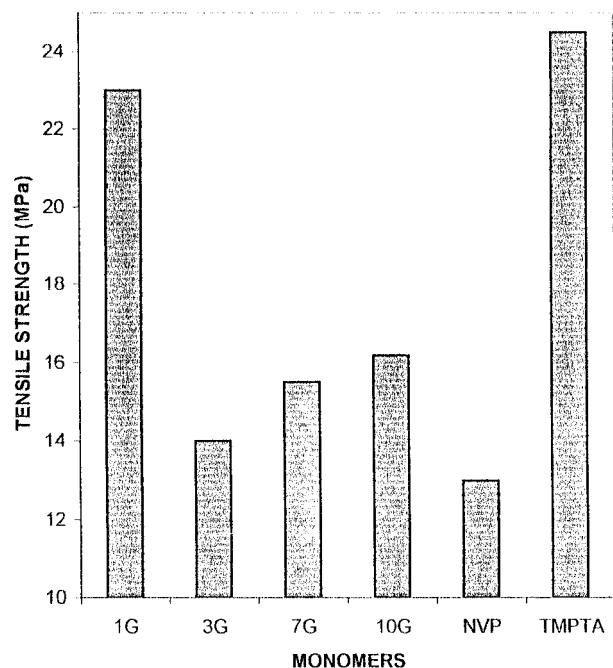


Figure 2 Tensile strength of irradiated rubber over crosslinking monomers (3 phr) at 150 kGy.

crosslinking rate, especially during the early stages of radiation is proportional to TMPTA concentration. TMPTA increases the radical-radical reaction termination and hence decreases the extent of scission reaction and oxidation.³⁴ In the higher concentration of TMPTA (5 phr), the tensile strength of irradiated rubber was found to decrease; this may be attributed to the fact that the free radical-radical of TMPTA is more dominant rather than the grafting and crosslinking reaction between TMPTA and rubber.

Selection of Crosslinking Monomer

Generally, multifunctional unsaturated vinyl monomers are used in radiation crosslinking with rubber to obtain optimum properties to reduce the radiation dose level or to achieve an increased state of dose.³¹ The reactivity of these monomers depends on various factors like number of double bonds,³⁵ shape, and size.³⁶

Having optimized the dose and concentration of monomer TMPTA at 3 phr, dry rubber was masticated with different monomers such as NVP, 1G, 3G, and 7G; concentration of each monomer was 3 phr to prepare rubber sheets. The rubber sheets were irradiated under EB at 150 kGy. The tensile strengths (TS) of these samples are shown in Figure 2. TMPTA exhibited the

highest TS values followed by 1G. TMPTA has a branch-like structure with three acrylate groups in each molecule. This helps for easy crosslinking mechanism with isoprene unit of rubber through these acrylated moieties. Ethylene monoglycol diacrylate (1G) produced the second-highest TS values with rubber. The 1G molecules make crosslinking with rubber through its diacrylate groups present at two ends of 1G molecules. Because 1G is a simple long chain molecule, it can easily diffuse into the rubber during crosslinking phenomena; but as the ethylene glycol chain ($-\text{CH}_2-\text{CH}_2-\text{O}-$) increases, the molecule becomes bulkier, thus causing a difficult situation for these molecules to easily diffuse into the rubber backbone chain like 1G molecule. NVP produced the lowest tensile strength; this may be attributed to its structure and cannot easily diffuse into the rubber, the reactivity of $-\text{C}=\text{C}-$ bonds of rubber backbone hindered by the aromatic ring.³⁷

Chain scission and crosslinking are among the chemical effects observed when polymers are subjected to ionizing radiation (like gamma or EB). The process ultimately causes formation of an insoluble gel if crosslinking predominates over

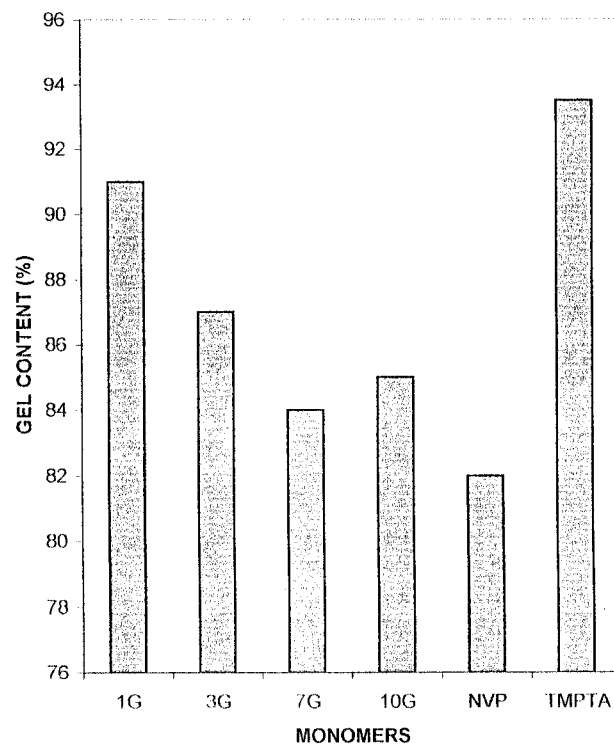


Figure 3 Gel content of irradiated rubber over crosslinking monomers (3 phr) at 150 kGy.

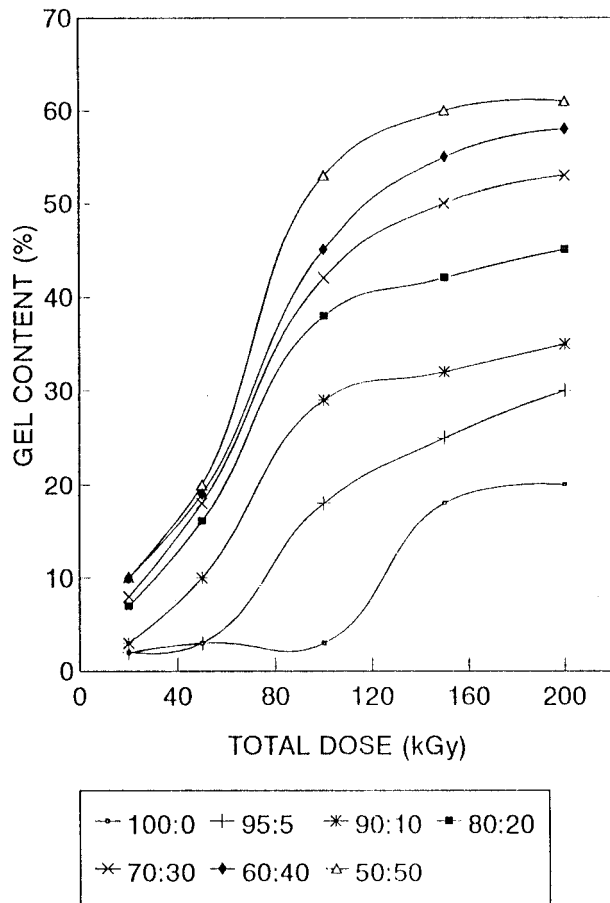


Figure 4 Gel content of irradiated Bionolle and its blends against radiation dose with respect to rubber content in Bionolle.

scission. The gel contents of irradiated rubber were plotted against monomers in Figure 3. Gel content is the amount of crosslinked polymer present in the entire material. As the crosslinking increases, the gel content value increases. The highest gel content is attained in the presence of TMPTA followed by 1G (like TS results in Fig. 2).

Bionolle-Rubber Blends

The blends were prepared with Bionolle and masticated dry rubber (3 phr TMPTA) at different proportions and irradiated with different total doses at 10 kGy/pass. The gel content of the irradiated Bionolle and blends were determined and the results are shown in Figure 4, where gel contents are plotted against irradiation dose as a function of different compositions of Bionolle and rubber. The gel contents of pure Bionolle and the elastomers of different concentrations of rubber

were found to increase with an increase of irradiation dose. Bionolle yields the least gel values and as the Bionolle ratio decreases, with increases of rubber in the blend, the gel content increases. The highest gel content (65%) is obtained with the blend, Bionolle/rubber = 50:50.

Tensile Strength

The tensile strengths of Bionolle and its blends are presented in Figure 5 against irradiation dose with respect to rubber content in the blends. The tensile strength of Bionolle increased (83 MPa) at 20 kGy and thereafter decreased with an increase of radiation. The same trends were observed in the blends. The increase of the tensile strength is due to the rearrangement of the polymer chain during the extension process. At sufficiently high crosslinked density above 20 kGy, the rearrangement of the polymer chain became much more

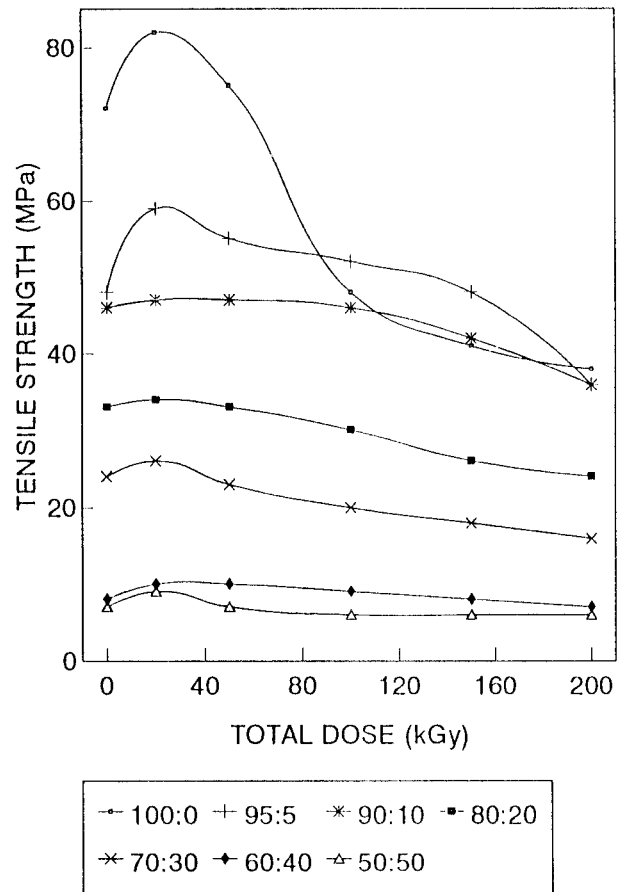


Figure 5 Tensile strength of irradiated Bionolle and its blends against radiation dose with respect to rubber content in Bionolle.

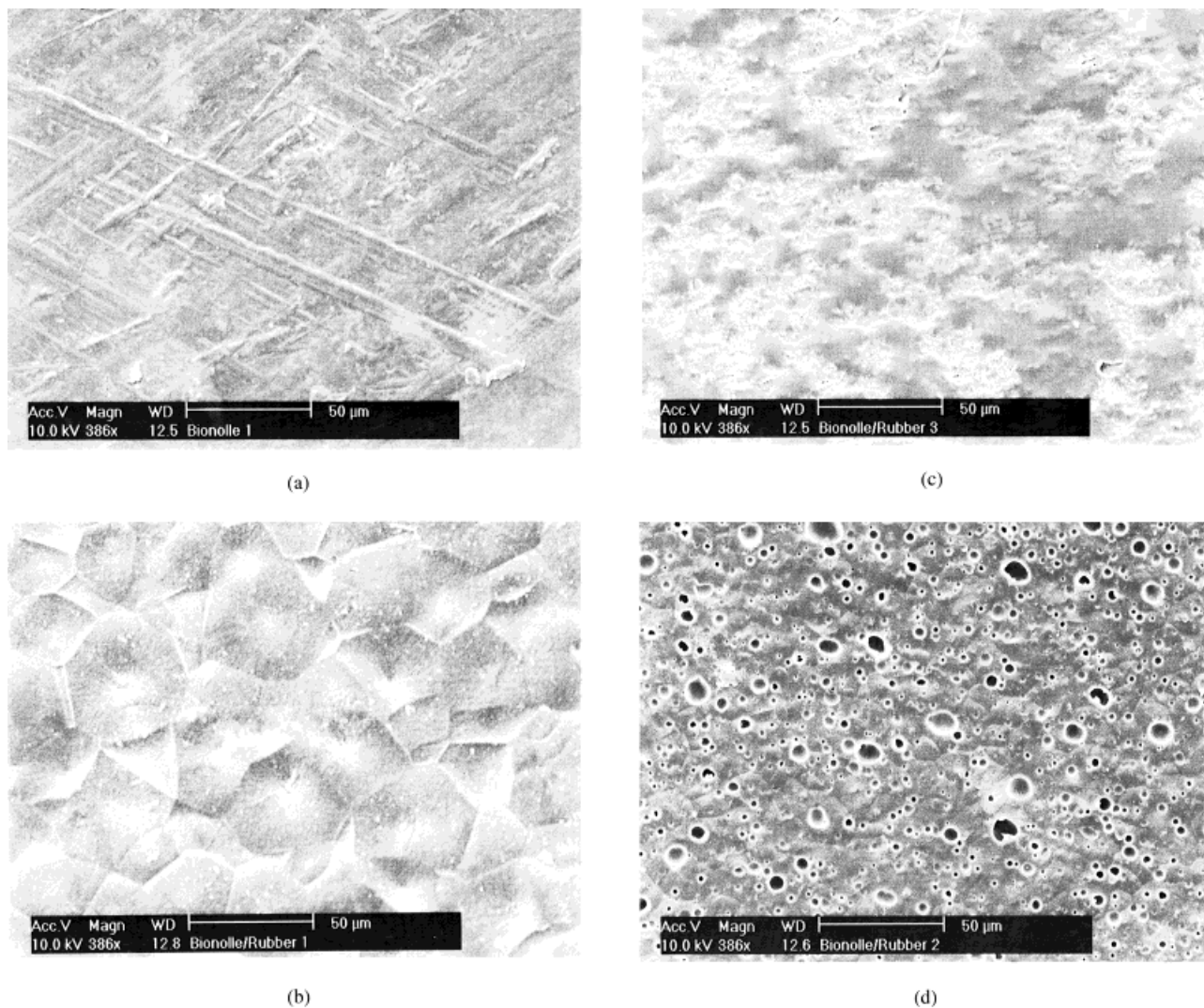


Figure 6 Scanning electron microscope photographs of (a) Bionolle, and its blends (b) 95:5, (c) 80:20, and (d) 50:50.

difficult and because of this, the tensile strength reduction occurred.³⁸ The blend of 5% rubber showed the highest tensile strength value of 60 MPa at 20 kGy and the tensile strengths of other blends decreased with an increase of rubber concentration. The mechanical properties of the rubber polymer blends strongly depend on the sub-micro particles and volume fraction of the rubber in the blends.³⁹ With an increase of rubber portion in the blends, the volume fraction and the particle size increase. The compatibility between rubber and Bionolle is also decreased with an increase of rubber content in the blends. This can be performed by scanning electron microscopy (Fig. 6). The elastomer of 5% rubber showed the best dispersion of rubber with Bionolle compared with other blends.

Thermal Aging

The thermal aging property was determined by heating the samples (both unirradiated and irradiated of different doses) at 70°C for 15 days in an oven. The loss of tensile strength as a result of treatment was measured, and the values are shown in Table I. The unirradiated Bionolle showed the maximum loss of strength. The minimum loss of strength was obtained with the blend samples that contained 5% rubber, and then as the rubber quantity increased, the loss of strength also increased under the heating process. It indicates that there is good stability of the strength when 5% rubber is incorporated into the blend. It was also noticed that strength stability of the blends increased as the dose was increased

Table I Tensile Strength (MPa) of Bionolle and Its Blends after 15 Days of Thermal Aging

Blends	0 kGy			50 kGy			100 kGy			200 kGy		
	0 Days	15 Days	% Loss	0 Days	15 Days	% Loss	0 Days	15 Days	% Loss	0 Days	15 Days	% Loss
100 : 0	70	36	48.5	73	40	45.2	50	43	14.0	41	35	14.6
95 : 5	49	43	12.2	58	52	10.3	55	53	3.6	40	39	2.5
90 : 10	48	41	14.5	50	44	12.0	49	47	4.1	40	38	5.0
70 : 30	32	26	18.7	26	21	19.2	22	18	18.2	19	17	10.5
50 : 50	6	4	33.3	7	5	28.6	6	5	16.7	7	6	14.3

in each case. Unirradiated Bionolle showed 50% tensile strength in 15 days of heating at 70°C.

Heat Resistance

Blends of different compositions of Bionolle and rubber, irradiated with different doses were hung with 50-g load at 120°C in an oven. As a result of this treatment, Bionolle and blends with lower amounts of rubber were broken within a few minutes, whereas the blends containing rubber at more than 30% showed heat resistance for a substantial period. The results of breaking time (heat resistance time) are plotted in Figure 7 against radiation dose. The resistance increased with an increase of dose and increase of rubber quantity in the blends. The blends containing 40% rubber and above possess very high resistance and are quite stable. These blends are suitable in making materials that can be used for special purposes. Although rubber as well as Bionolle have very low heat resistance, the blends of rubber and Bionolle possess good heat resistance at higher temperature and at higher radiation dose.

When the temperature is increased from 120 to 190°C, the profile of the heat resistance under 50-g load is different. The results are shown in Figure 8. The breaking time of these blends sharply decreases with an increase of temperature. There is virtually no resistance at 190°C for both the samples of the blends containing 40 and 50% rubber in Bionolle.

Melting and Crystallization Character

The melting and crystallization behavior of Bionolle and its elastomers of different quantities of rubber both irradiated at 300 kGy and unirradiated were studied by DSC. Different parameters of DSC are shown in Table II. The results of the

blends indicate that the melting temperature as well as the crystallization temperature of the blends slightly shifts as the quantity of rubber is increased in the blend. The sharp peak and smooth DSC curves of the blends indicate the

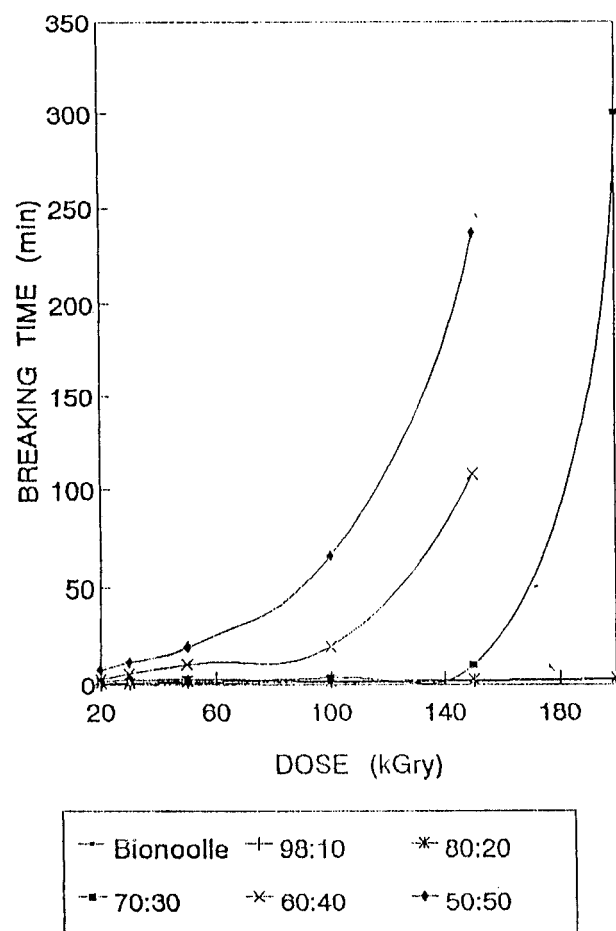


Figure 7 Breaking time of Bionolle and its blends due to thermal treatment against total dose with respect to rubber content in Bionolle.

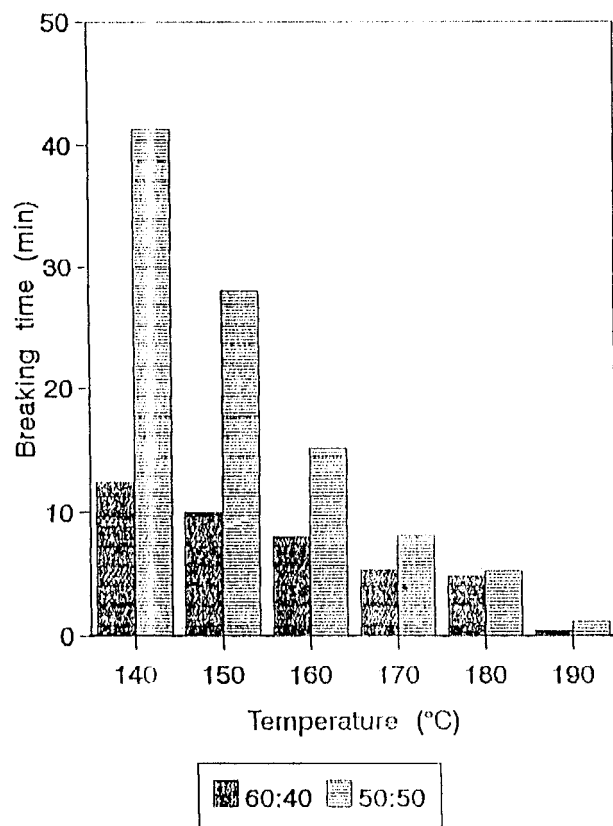


Figure 8 Breaking time of blends (60:40 and 50:50) as a result of heat treatment versus temperature.

Bionolle was well mixed with rubber and was compatible for making the blends.

When these samples are irradiated at 300 kGy their DSC data (Table II) indicate that the melting temperature of these samples further reduce but the crystallization temperatures of the irradiated Bionolle and blends increase. Enthalpy changes of both irradiated and unirradiated sam-

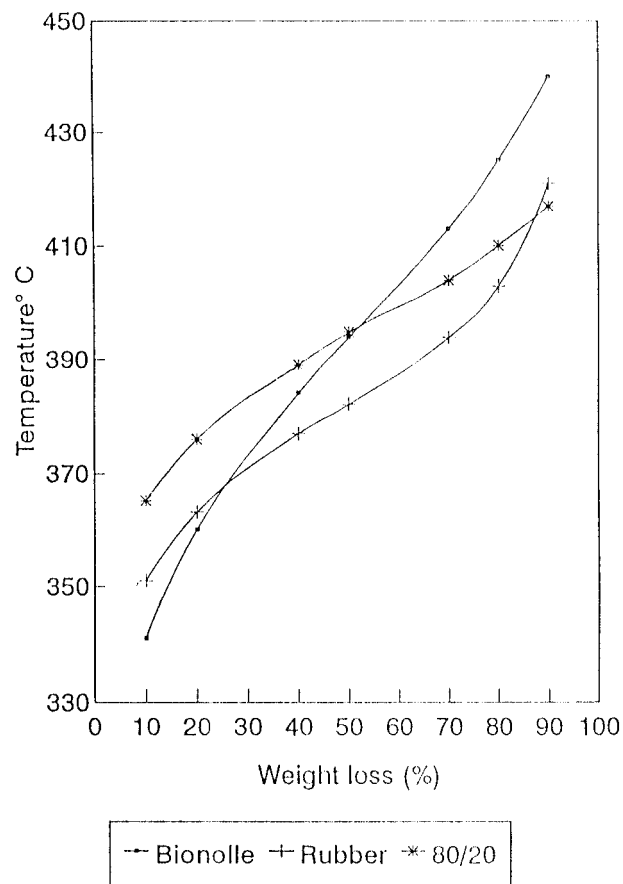


Figure 9 Loss of weight of Bionolle, rubber, and blends (80:20) against temperature.

ples of Bionolle and blends were determined and the results are also shown in Table II. With a decrease of melting temperature and crystallization temperature, the enthalpy (ΔH) values also decrease.

TGA was performed with the samples of Bionolle, rubber, and the blend (80:20). The weight

Table II Different Parameters of DSC for Both Irradiated and Unirradiated Bionolle and Its Blends

Blends (Bionolle/ Rubber)	Melting Temperature				Crystallization Temperature			
	T_m (°C)		ΔH (J/g)		T_c (°C)		$-\Delta H$ (J/g)	
	0 kGy	300 kGy	0 kGy	300 kGy	0 kGy	300 kGy	0 kGy	300 kGy
100 : 0 (Bionolle)	114.72	111.91	76.01	85.90	78.52	69.15	59.74	63.15
95 : 5	115.48	113.45	73.46	80.46	78.13	69.15	56.05	60.56
90 : 10	115.20	112.63	72.27	75.35	71.50	70.01	54.27	56.29
70 : 30	114.55	112.58	56.55	57.75	75.45	71.45	41.52	44.14
50 : 50	113.55	111.58	34.16	39.55	74.58	—	27.38	—

loss due to heating at different temperatures was recorded, and the results are shown in Figure 9. The Bionolle shows 10% weight loss at 230°C, rubber at 350°C, and blends at 365°C; however, the Bionolle needs more heating (above 430°C) for 90% weight loss than the blend and the rubber for the corresponding loss of 90% at 410°C.

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