

# Studies on the Effect of Electron Beam Irradiation on Waste Polyethylene and Its Blends with Virgin Polyethylene

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**ABSTRACT:** Waste polyethylene (WPE) was segregated from the municipality solid waste, cleaned, dried, and chopped into pieces, then processed in a Brabender Plastimeter using the melt mixing technique. Blends of WPE and virgin polyethylene were prepared in various proportions under optimized process conditions. Of the various blend proportions studied, 70/30 blend of WPE/low density polyethylene (LDPE) and 50/50 blend of WPE/high density polyethylene showed better mechanical properties and hence selected for further modification involving electron beam irradiation. Aforementioned blends were exposed to various doses of electron beam irradiation and the effect of irradiation on physicochemical properties such as tensile

strength, flexural modulus, hardness, and impact resistance were studied. Thermogravimetric analysis, X-ray diffraction studies, Fourier transform infrared spectroscopy, scanning electron microscopy, and gel content were considered to characterize the blends. Physicochemical properties improved to an appreciable extent on irradiation but the elongation at break reduced drastically. Blow molding of the 70/30 WPE/LDPE blend could be done successfully to make bottles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 715–726, 2006

**Key words:** waste polyethylene; recycling; crosslinking; electron beam irradiation; fracture studies

## INTRODUCTION

The recycling of plastic wastes has tremendous potential as an alternate source of raw materials and has gained considerable attention of the environmentalists and the government agencies. It has become a channel for waste disposal throughout the world because of its non biodegradable nature, throwing a major task before the polymer scientists.<sup>1,2</sup> Recycling and reuse is the cheapest option for the waste plastics among all other options (incineration, landfill, and biodegradation), as it saves energy and cost. Also, it reduces plastic pollution, making the environment ecofriendly and green by increasing the flora and fauna on the earth, as it replaces wood and paper in majority of its applications. It also eliminates the pollution associated with the extraction and processing of virgin raw materials. Thus, recycling conserves the energy available on the earth's surface. Besides all these, recycling is a better option, as it is easier to process and can be

carried out at a lower cost resulting in low cost materials, when compared with biodegradation, which is presently not economically viable.<sup>3</sup>

With the advent of polymer science and technology in the last five decades, a large number of synthetic polymers were manufactured, used, and disposed in large quantities daily, generating huge quantities of plastic wastes. Different means of disposing of solid polymer waste has been reported earlier,<sup>1–3</sup> such as land filling, incineration, recycling, and biodegradation. The first two methods have been discarded because of environmental problems. Third option has been adapted for a majority of polymers and the fourth option is under investigation in different laboratories throughout the world. Several techniques for the recycling are used these days to solve the major issues of disposal. The major recycling techniques are pyrolysis,<sup>4–6</sup> flash pyrolysis,<sup>7</sup> copyrolysis,<sup>8</sup> ultra pyrolysis,<sup>9</sup> thermolysis or thermal pyrolysis,<sup>10</sup> dehydrochlorination,<sup>11</sup> melt reprocessing,<sup>12</sup> catalytic degradation,<sup>13,14</sup> chemical recycling<sup>14,15</sup> and cryo-communication.<sup>16</sup>

In India, the recycling of plastic wastes is around 60% when compared with the world figure, which stands below 30% while the per capita consumption of

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plastics is still the lowest at 1.8 kg in the country. On the other hand, the municipal solid waste (MSW; 1–4% of total waste plastics by weight) is growing at a tremendously high rate of 9–12%. Plastics mostly used as carry bags constitute the most formidable threat to public space and it is estimated that India generates 5600 tonnes of plastic wastes daily.<sup>17</sup>

Attempts have been made earlier to study the structural changes of virgin polyethylene as well as recycled polyethylene on treatment with different types of radiation such as gamma radiations, thermal and fast neutrons, and electron beam irradiation.<sup>18</sup> Electron beam irradiation is a clean and continuous process for affecting the physical and chemical modification of polymeric materials and is an important method for commercial applications.<sup>19,20</sup> Crosslinking, chain scission, and degradation are the prevailing mechanisms in polyolefins subjected to ionizing radiations. Crosslinking alters the properties of the polymeric materials by improving its toughness, chemical resistance, and expanding the temperature window for applications.<sup>21</sup>

Methods such as X-ray diffraction studies (XRD), Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM) help in the characterization of the polymer systems and in particular of polyethylene of different grades and to study the effect of electron beam irradiation on its performance.<sup>19,21–24</sup> Hardness, being one of the end performance property of the materials, is dependent on modulus and is used to compare the effect of crosslinking of the samples with and without radiation.<sup>19</sup> Tensile and flexural strength, although undergo marginal changes with irradiation, play an important role in predicting the structure property relationships and quality control.<sup>21,22</sup> Gel content as a measure of evaluating the extent of crosslinking in the irradiated as well as nonirradiated samples has been documented earlier.<sup>21–23</sup> Detailed investigations on the effects of gamma radiation on the mechanical behavior of recycled polyethylene and its blends have also been studied earlier.<sup>19,20,22,24,25</sup>

The present work deals with the re-utilization of waste plastic mostly consisting of low density polyethylene (LDPE), high density polyethylene (HDPE), LLDPE, PP from MSW in making value-added products of commercial importance. Blends of different grades of waste polyethylene (WPE) segregated from the MSW and virgin polyethylene were prepared and physicochemical properties were measured. Since these waste plastics are blends of a wide range of plastic materials with varying molecular weight, molecular weight distribution, and solubility parameter, their micro structures are expected to be coarse and weak, especially in the interfacial regions. Hence, the samples were further treated with high energy electron beam radiation at various doses to improve the

**TABLE I**  
**Characteristics of Virgin LDPE (Indothene 20 XL 020) and Virgin HDPE (B 6401)**

Material	Melt index (g/10 min)	Density (g/cc)
LDPE	2	0.91
HDPE	0.41	0.96

structural integrity and physicochemical properties without sacrificing the processability.

## EXPERIMENTAL

### Materials

Waste polyethylene (WPE) collected from municipality solid waste was segregated into different grades on the basis of density and melting temperature. All polyethylene grades were segregated from other polymer waste such as PET, PVC, etc. Virgin high density polyethylene (HDPE-blow molding grade, B 6401) was supplied by Haldia Petrochemicals Limited, India, and virgin low density polyethylene (LDPE-cable grade, Indothene 20XL 020) was supplied by Indian Petrochemicals Corp. Limited, Vadodara, India. Their properties are listed in Table I.

### Preparation of samples

The waste carry bags and pouches were segregated from the plastic wastes, cleaned, washed with detergent powder mechanically, and dried. This waste is expected to consist of mostly HDPE and LDPE with minor proportions of PP, LLDPE, and PS. They are chopped into formidable sizes for further processing in a Brabender Plasticorder. The pretreatment of WPE consisted of washing in water, removal of dirt, cleaning with detergent powder in a machine, and drying. Melt mixing was carried out in a Brabender Plasticorder (Model PLE 651), at optimized processing parameters such as mixing temperature, time, and rotor speed.

Blending of WPE with Virgin LDPE and HDPE were carried out separately in the Brabender Plasticorder in the proportions of 70/30, 50/50, and 30/70 at the optimized processing conditions. The optimum processing conditions as determined for melt mixing were as follows: a temperature of 180°C, rotor speed of 80 rpm, and residential time of 5 min. The molten mass was immediately sheeted into thin sheets of 3 mm thick on an open mixing mill (Schwabenthan, Berlin) at room temperature.

The sheets were compression molded between Teflon sheets at a temperature of 180°C and at a pressure of 5 MPa in an electrically heated compression mold-

**TABLE II**  
**Specification of the Electron Beam Accelerator (ILU-6)**

Energy range	0.5–2 MeV
Beam power through the whole energy range	20 KW
Beam energy speed	10%
Average current	15 mA
Adjusting limits of current	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration of pulse	100–200 $\mu$ s
Repetition rate	2–50 Hz
Pulse current	
Maximum	900 mA
Minimum	400 mA
Power supply voltage	3 $\times$ 380/220 V
P.S. voltage frequency	50 Hz
Consumption of power (total)	150 KW

ing hydraulic Press for 2 min to obtain tensile sheets of dimension 15  $\times$  15 mm<sup>2</sup>.

### Electron beam irradiation of samples

The molded sheets of WPE, WPE/HDPE blend (50/50), and WPE/LDPE blend (70/30) were subjected to electron beam irradiation at room temperature ((25  $\pm$  2) $^{\circ}$ C) by an electron beam accelerator at irradiation doses of 150, 200, 250, and 300 kGy (i.e., 15, 20, 25, and 30 Mrad). The specifications of the electron beam accelerator are given in Table II.

### Physico-mechanical property determination

Dumbbell specimens were punched out from the tensile sheets using ASTM cutting Die- C. The tensile property measurement was performed in an universal testing machine (Model No.H25KS of Hounsfield, UK) at a cross head speed of 50 mm/min at 25 $^{\circ}$ C as per the ASTM D 638. The average values of five test results are reported.

Flexural test specimens were also punched out from the tensile sheets and the flexural modulus tests were carried out as per ASTM D 790 in an universal testing machine (Model No.H25KS of Hounsfield, UK).<sup>21</sup>

Tensile impact specimens were punched out from the tensile sheet and the tests were performed as per DIN 53448 in an Impact Tester (Model No.6545/000 of Ceast make). The Shore D hardness measurement was performed according to ASTM D 1132 by a Shore-D Hardness Tester (STD-D). Each specimen was tested thrice at three spots, which were at a distance of at least 5 mm from each other and 13 mm from any edge of the test piece.

### Characterization of samples

#### Gel content studies

The gel fraction was determined according to ASTM D 2765 method using a Soxhlet extractor, taking xylene

as a solvent. Samples were refluxed in xylene close to its boiling point for at least 72 h, until the sample attained a constant weight. The residue after extraction was taken as the gel content.

$$\text{Gel fraction} = W_2/W_1$$

where  $W_1$  is the initial weight of the polymer and  $W_2$  is the weight of the insoluble portion of the polymer in the gel.<sup>21–23</sup>

#### FTIR studies

Thin films of WPE and its blends with LDPE and HDPE were prepared in a compression molding hydraulic press between two parallel plates. FTIR measurements on the thin film specimens were performed using the Perkin–Elmer Spectrum GX spectrometer in the range of 4000–400 cm<sup>–1</sup>.

#### XRD studies

The XRD patterns of the samples were recorded by a microprocessor controlled X-ray diffractometer (Phillips, model PW 1840) using Cu K $\alpha$  radiation in the angular range of 10–50 $^{\circ}$  (2 $\theta$ ) at an operating voltage of 40 kV and a current of 20 mA. The degree of crystallinity of the samples was determined by dividing the area under the crystalline peaks by the total area under the crystalline as well as amorphous regions.

#### SEM analysis

A JEOL-JSM-5800 SEM was used to study the topography of the tensile fracture surfaces of the specimens after testing to understand the failure mechanism. Before examination, the fracture surfaces were sputter-coated with a thin layer of gold in a vacuum chamber.

#### Thermo gravimetric analysis

Thermal degradation studies of the WPE and its blends were carried out using a thermo gravimetric analyzer, TA instruments (Model TG Q50) at a heating rate of 20 $^{\circ}$ C/min in an atmosphere of nitrogen, from room temperature to a temperature of 600 $^{\circ}$ C.

#### Product manufactured from WPE

Bottles were made by blow molding technique in the laboratory from the WPE/LDPE 70/30 blend by using the “Polylab” universal molding machine. The blow molding of WPE/LDPE 70/30 blend was carried out by using the extrusion cylinder fitted into the machine and the blow molding die was also fitted and ensured that it was in the open position. The cylinder temperature was set at 230 $^{\circ}$ C and the material was inserted

**TABLE III**  
Gel Content of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 Blend before and after Electron Beam Irradiation

Dose (KGy)	Gel Content (%)		
	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50
0	0	0	0
150	80	95	91
200	68	87	91
250	67	81	82
300	61	80	60

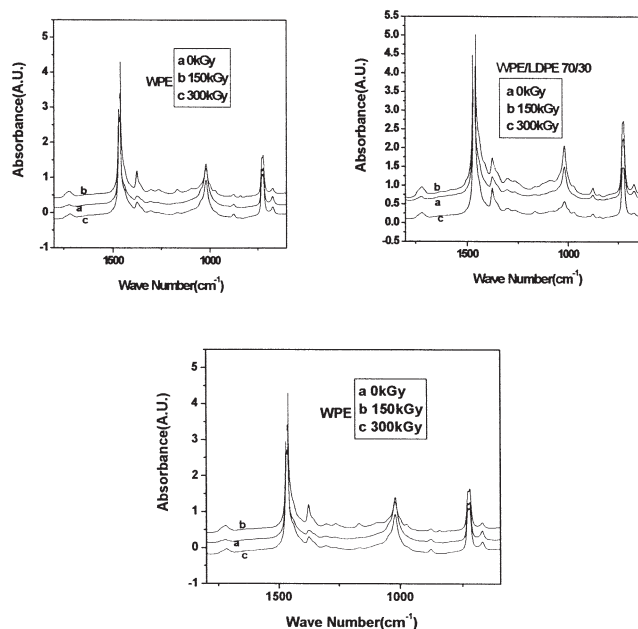
into it. After it was ready, a parason (round tubular section) of sufficient length was produced to carry out the extrusion. The mold was then closed firmly and clamped as quickly as possible, and then air was blown with the mouth into the drinking straw for 5–10 s; the parason formed into the shape of the cold mold and set.

## RESULTS AND DISCUSSION

### Gel content

Table III depicts the gel contents of the nonirradiated and irradiated samples at various doses. The gel content was determined by extraction of the irradiated samples in xylene at 25°C. It is found that electron beam irradiation increases the gel content of WPE rapidly, i.e., up to 80% at only 150 kGy. Similarly, the gel content of WPE/LDPE 70/30 and of WPE/HDPE 50/50 blend increase to 95 and 91%, respectively, at a dose of 150 kGy. However, on further increase in the dose of irradiation, i.e., beyond 150 kGy, the gel content of WPE and its blends with LDPE and HDPE decreases. This may be attributed to breakdown of crosslinks or the main chain, leading to a decrease in crosslink density; hence the gel content.<sup>22</sup> The gel content results indicate a maximum crosslinking occurring at a 150 kGy dose.

In WPE and its blends, crosslinking and chain scission occurs simultaneously. It is observed that the decrease in the gel content for WPE is significantly higher at higher doses of irradiation. However, on blending with LDPE, i.e., for WPE/LDPE 70/30 blend, a decrease in gel fraction at higher irradiation doses is comparatively lower after a irradiation dose of 200 kGy. Indeed, there is no marked difference in the values of gel content for this blend after a irradiation dose of 200 kGy, whereas for WPE/HDPE 50/50 blend, the gel content is drastically reduced at a higher dose of irradiation (after 250 kGy) owing to probable chain scission of the network, along with crosslink. Highly crystalline plastics such as HDPE generally exhibits a marked tendency of degradation at higher doses. At a high dose of 300 kGy, the radical concen-



**Figure 1** (a) FTIR spectra of WPE without and with exposure to radiation at 150 and 300 kGy. (b) FTIR spectra of WPE/LDPE 70/30 blend without and with exposure to radiation at 150 and 300 kGy. (c) FTIR spectra of WPE/HDPE 50/50 blend without and with exposure to radiation at 150 and 300 kGy.

tration is high, a greater chain scission reaction is induced, and hence the gel fraction reduces.

WPE contains significant amount of plastic materials (e.g., PP), those that degrade while exposing to electron beam radiation, particularly at higher dose of irradiation. LDPE degrades only at higher radiation doses. For HDPE at higher doses of irradiation, crystalline phase gets destroyed. In case of LDPE-based blends, the degradation is somewhat balanced by crosslinking of LDPE. HDPE-based blends contain more amount of virgin HDPE so that the degradation effects are somewhat marked at the initial stages.

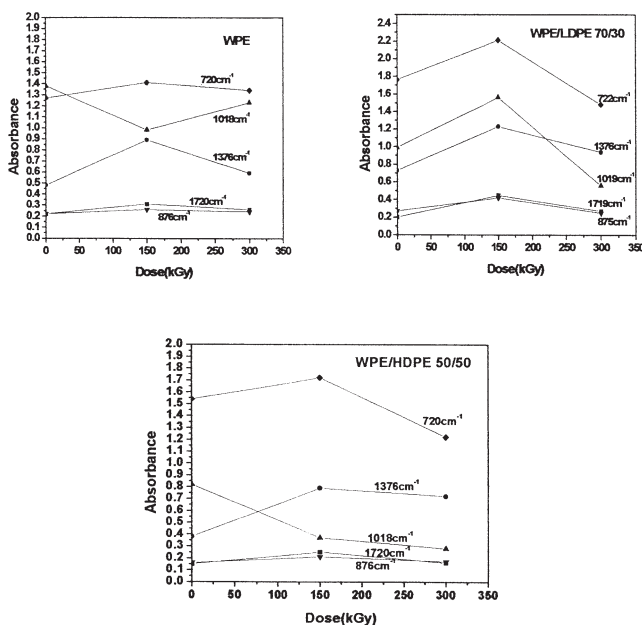
### FTIR study

FTIR spectra of WPE and its blend with LDPE and HDPE irradiated at various radiation doses are pre-

**TABLE IV**  
Peak Position and Assignment of Peaks in the IR Spectra of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 Blend

Wave number (cm <sup>-1</sup> )	Functional group
1720	>C=O stretching for carbonyl group
1460	H—C—H bending of methylene group (scissor)
1376	asymmetric vibration of methylene group
1018	C—O—C stretching of ether group
876	C—H deformation
720	H—C—H stretching





**Figure 2** (a) Plot of absorbance of asymmetric vibration of  $-\text{CH}_2$  group,  $\text{H}-\text{C}-\text{H}$  stretching,  $\text{C}-\text{O}-\text{C}$  stretching of ether group,  $>\text{C}=\text{O}$  stretching for carbonyl group,  $\text{C}-\text{H}$  deformation at different wave numbers with radiation dose for WPE. (b) Plot of absorbance of asymmetric vibration of  $-\text{CH}_2$  group,  $\text{H}-\text{C}-\text{H}$  stretching,  $\text{C}-\text{O}-\text{C}$  stretching of ether group,  $>\text{C}=\text{O}$  stretching for carbonyl group,  $\text{C}-\text{H}$  deformation at different wave numbers with radiation dose for WPE/LDPE 70/30 blend. (c) Plot of absorbance of asymmetric vibration of  $-\text{CH}_2$  group,  $\text{H}-\text{C}-\text{H}$  stretching,  $\text{C}-\text{O}-\text{C}$  stretching of ether group,  $>\text{C}=\text{O}$  stretching for carbonyl group,  $\text{C}-\text{H}$  deformation at different wave numbers with radiation dose for WPE/HDPE 50/50 blend.

sented in Figures 1(a)–1(c). Figure 1(a) shows the IR spectra of WPE, Figure 1(b) shows the IR spectra of WPE/LDPE 70/30 blend, and Figure 1(c) shows the IR spectra of WPE/HDPE 50/50 blend in the region of  $1800-600\text{ cm}^{-1}$  both before and after radiation. The various peaks and their corresponding vibrational frequencies are summarized in Table IV.

The absorbance at  $1376\text{ cm}^{-1}$  (asymmetric vibration of methylene group) and  $720\text{ cm}^{-1}$  (consecutive methylene linkages) for all WPE and its blends with LDPE and HDPE increases remarkably with radiation dose of 150 kGy, supporting crosslinking reactions and decreases as the dose is increased to 300 kGy, showing chain scission and break down of network structure. This confirms the modifications in the methylene group characteristic bands with radiation dose.<sup>19,20,22</sup>

In Figures 2(a)–2(c), absorbance due to asymmetric vibration of methylene group ( $1376\text{ cm}^{-1}$ ),  $\text{H}-\text{C}-\text{H}$  stretching ( $720\text{ cm}^{-1}$ ),  $\text{C}-\text{O}-\text{C}$  stretching of ether group ( $1018\text{ cm}^{-1}$ ),  $>\text{C}=\text{O}$  stretching for carbonyl group ( $1720\text{ cm}^{-1}$ ), and  $\text{C}-\text{H}$  deformation ( $876\text{ cm}^{-1}$ ) are plotted against irradiation dose for WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 blends. At first, an increase in the concentration of carbonyl group ( $1720\text{ cm}^{-1}$ ) is observed with radiation dose, which is due to the aerial oxidation of the samples under normal atmosphere. The band observed at  $1018\text{ cm}^{-1}$  is due to the oxidation effects.<sup>18</sup> In case of WPE, a decrease in the concentration of ether group ( $1018\text{ cm}^{-1}$ ) is observed at a lower dose of 150 kGy because WPE contains some radiation resistant polymers such as polystyrene in it, which has been confirmed from the occurrence of a peak at  $669\text{ cm}^{-1}$ . It increases at higher dose of 300 kGy, indicating that more free radicals are produced, which promotes the oxidation and chain scission. However, in case of WPE/LDPE 70/30 blend, there is an increase in the concentration of ether group at lower dose, indicating oxidation as well as synergistic occurrence of crosslinking, chain scission, and break down of network structure because of the availability of large number of free radicals. In WPE/HDPE 50/50 blend, the concentration of ether group is comparatively lower after irradiation, indicating less oxidative effect when compared with WPE and WPE/LDPE 70/30 blend. A slight change in the absorbance value at  $876\text{ cm}^{-1}$  is noticed, which may be due to the release of hydrogen and capturing of electrons, indi-

**TABLE V**  
Physicomechanical Properties of WPE, HDPE, LDPE, WPE/LDPE Blends (30/70, 50/50, 70/30), and WPE/HDPE (30/70, 50/50, 70/30) Blends before Electron Beam Irradiation

Sample	Density ( $\text{g}/\text{cm}^3$ )	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Hardness shore D	Tensile impact strength ( $\text{J}/\text{m}$ )
WPE	0.95	21.2	101.5	25.4	1154.0	27	574.5
HDPE	0.96	24.2	743.1	20.8	875.7	40	1747.5
LDPE	0.91	11.2	710.0	7.7	177.4	24	1596.0
WPE/LDPE (30/70)	0.94	13.1	391.1	11.2	284.3	23	1634.6
WPE/LDPE (50/50)	0.94	14.7	780.0	7.6	149.8	25	1383.9
WPE/LDPE (70/30)	0.94	16.1	129.9	15.8	431.7	30	1417.3
WPE/HDPE (30/70)	0.95	22.9	57.9	25.3	1176.6	30	1329.5
WPE/HDPE (50/50)	0.95	25.9	534	28.1	1268.4	36	1340.5
WPE/HDPE (70/30)	0.95	23.9	425	25.1	1215.5	36	1276.0

**TABLE VI**  
**Tensile Properties of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 before and after Electron Beam Irradiation**

Dose (KGy)	Tensile strength (MPa)			Elongation at break (%)		
	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50
0	21.2	16.1	25.9	101.5	129.9	534
150	21.2	19.0	24.7	24.4	64.0	40.6
200	23.0	19.0	26.2	25.5	93.6	35.4
250	23.6	19.1	25.9	21.7	57.4	14.7
300	24.5	18.5	23.8	14.6	72.9	8.8

cating chain crosslinking as well as scissioning in the samples.<sup>23</sup> It agrees well with the gel content data, in which a decrease is seen with an increase in the radiation dose. Also, the structural changes observed in all the three cases are coherent with the gel content and physicomechanical data. Thus, from the structural changes as seen in IR, it is clear that crosslinking, oxidation, and chain scission occur simultaneously giving rise to gross changes in physical properties due to irradiation.

### Physicomechanical properties

Physicomechanical properties such as tensile strength, elongation at break, flexural modulus and strength, hardness and tensile impact strength of the WPE, and blends of WPE with LDPE as well as HDPE before subjecting it to irradiation are shown in Table V.

Waste plastics (WPE) exhibit a tensile strength of 21.2 MPa, which is much higher than the neat LDPE (11 MPa) but close to that of neat HDPE (24.2 MPa), whereas the elongation at break of waste plastics is too low at 101.5% when compared with both neat LDPE and HDPE, which are 743.1 and 710% respectively. It is interesting to observe that waste plastics in general have higher flexural strength and flexural modulus when compared with both virgin LDPE and HDPE but has lower impact strength. It implies that waste plastics may contain some proportions of PP and PS, for imparting stiffness characteristics. Lower elongation at break and impact strength of WPE is probably due to the lack of adhesion between the various polymeric phases in the material.

Blends of WPE and LDPE impart lower tensile strength and flexural strength than WPE itself at all blend ratios, but exhibit higher impact strength and hardness. On the other hand, blends of WPE with HDPE exhibit moderately higher tensile strength and flexural strength as well as higher hardness and impact strength when compared with WPE itself. Thus, it may be concluded that WPE is more close to HDPE in most of its processing and technical properties than that of virgin LDPE, besides containing small proportions of other polyolefins such as LDPE, LLDPE, PP, and PS.

### Tensile properties of WPE and blends of WPE with LDPE and HDPE before and after irradiation

Table VI shows the tensile strength and elongation at break of WPE and blends of WPE/LDPE (70 : 30) as well as WPE/HDPE (50 : 50) before and after electron beam irradiation at various doses.

In case of WPE, as the dose of irradiation increases, the tensile strength marginally increases and the elongation at break decreases steadily. Almost the same trend is observed for the WPE/LDPE (70 : 30) and WPE/HDPE (50 : 50) blends, except that there is a marginal decrease in strength properties at higher dose of electron beam irradiation (300 kGy). Also, it is evident that exposure to 200 kGy radiation is sufficient to generate the necessary strength properties. This has been supported by a steady decrease in degree of crystallinity of the matrix after electron beam irradiation, which may be due to the formation of intermo-

**TABLE VII**  
**Flexural Properties of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 Blends before and after Electron Beam Irradiation**

Dose (KGy)	Flexural strength (MPa)			Flexural modulus (MPa)		
	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50
0	25.4	15.8	28.1	1154.0	431.7	1268.4
150	21.9	20.2	31.8	704.5	580.3	1026.3
200	25.5	21.6	22	849	566	705.3
250	25.7	21.5	25.7	743.3	571.8	743.3
300	29.4	20.3	31.2	935.3	613	958

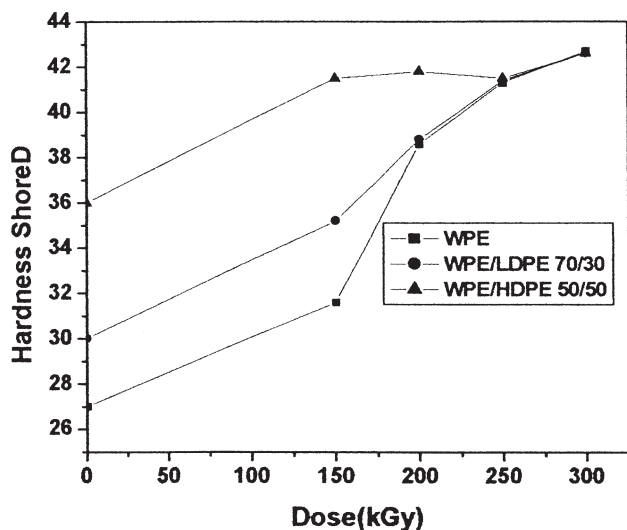


Figure 3 Variation of hardness of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 as a function of radiation dose.

lecular crosslinks in the crystalline regions, which destroys a significant portion of the crystalline structure.

The tensile strength of the irradiated WPE is marginally higher than that of the nonirradiated sample at lower doses of radiations. Thus, the WPE forms crosslinks on irradiation and as the elongation at break decreases, the ductility increases, whereas the tensile strength of the irradiated WPE/LDPE 70/30 blend increases reasonably at first followed by stabilization at higher doses. In the case of WPE/HDPE 50/50 blend, the tensile strength decreases first, followed by an increase and then decrease at higher doses of irradiation possibly as a result of severe chain scission. This is possibly due to the fact that chain scission is predominant over crosslinking reaction for this blend at a higher dose.<sup>21,22</sup>

In case of WPE/LDPE 70/30 blend, the tensile strength increases first by 12% at lower dose of irradiation (150 kGy) thereafter remain unaltered till 300 kGy irradiation. Introduction of LDPE to WPE marginally reduces the tensile strength, which may be attributed to decrease in the degree of crystallinity of the blend matrix because of lower crystallinity of LDPE. Moreover, LDPE crosslinks steadily with the increase in radiation dose, hence the degradation of minor constituents is effectively balanced out, whereas in case of WPE/HDPE 50/50 blend, the tensile strength increases by 20% even without radiation exposure, which may be attributed to higher degree of crystallinity of HDPE. It clearly suggests that WPE most closely resembles HDPE than LDPE. Density measurements as shown in Table V confirm this.

An increase in the tensile strength of WPE as well as its blends with LDPE and HDPE, although marginal, is an indication of crosslinking of the matri-

ces. This agrees well with the off repeated concept of chain crosslinking and chain scission occurring simultaneously in a polymer matrix. The final properties depend upon the mechanism that relatively predominates over the other. Decrease in elongation at break for the irradiated samples when compared with the unirradiated ones may be ascribed to the degradation events which may be pronounced among the minor constituents such as PP. Table V indicates that the WPE and its blends with LDPE and HDPE show a gradual ductile to brittle transition as the electron beam radiation dosages increases from lower values of 150 kGy to higher dose of 300 kGy. This transition is characterized by the reduction in the elongation at break with respect to that of the nonirradiated sample. The samples although show lower elongation at break after irradiation, the gel content values decrease at higher doses of radiation, can still be processed better.

#### Flexural modulus and strength

Table VII shows the values of flexural strength and modulus of the irradiated WPE and its blends with virgin LDPE and HDPE. It is observed that there is a marked increase in the flexural strength property of WPE with increase in dosage of electron beam radiation at higher doses. The modulus value, however, decreases first and then increases, showing no marked trend. In case of WPE/LDPE 70/30 blend the flexural strength increases first, followed by stabilization at higher doses of irradiation and also there is a significant rise in the modulus value. It implies that the degree of crosslinking increases with increase in radiation dose, whereas in the case of WPE/HDPE 50/50 blend, the flexural strength increases at first followed by a decrease and then an increase at higher doses of irradiation. The same trend has been observed for the flexural modulus too. This is a clear indication of simultaneous chain scission and crosslink formation in the matrix and has been explained earlier as due to destruction of crystalline structure of HDPE at higher radiation doses.

TABLE VIII  
Tensile Impact Values of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 with Variation in Radiation Dose

Dose (KGy)	Tensile impact strength (J/m)		
	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50
0	574.5	1417.3	1340.5
150	1011.4	1204.1	1036.4
200	604.1	1139.5	424.9
250	646.5	1279.7	646.6
300	932.4	1340.6	698.6

**TABLE IX**  
Degree of Crystallinity Versus Irradiation Doses for WPE and Its Blends with LDPE and HDPE as Obtained from X-ray Diffraction Study

Dose (KGy)	Crystallinity (%)		
	WPE	WPE/LDPE 70/30	WPE/HDPE 50/50
0	62.8	68.3	74.7
150	61.7	67.9	69.5
300	33.3	47.7	63.0

### Hardness shore D

Figure 3 illustrates the influence of radiation dose on the Shore D hardness of WPE and blends of WPE/LDPE 70/30 and WPE/HDPE 50/50. In all the three cases, the hardness value increases and then levels off. This may be due to the fact that without radiation, the incorporation of LDPE and HDPE contributes to the increase in modulus because of increase in crystallinity of the matrix. However, after electron beam irradiation, crosslinking takes place in the amorphous region, thus increasing the modulus values, hence the hardness. However at higher doses, there is a decrease in hardness and/or stabilization in hardness in case of WPE/HDPE 50/50 blend only because of opposite effect of increase in modulus, due to crosslink formation in the amorphous zone and destruction of crystallinity of HDPE in crystalline zone. Also, the presence of minor constituents such as PP and PS further enhances the stiffness and results in an increase in hardness and after which it remains steady.

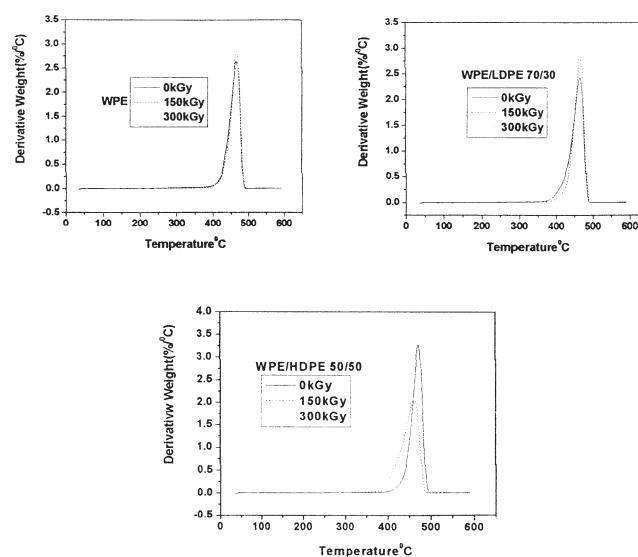
### Tensile impact strength measurements

Table VIII shows the results of tensile impact strength for WPE and its blends with LDPE and HDPE. It is observed that electron beam irradiation increases the toughness of the WPE and its blends. In case of WPE, the impact strength increases with radiation dose, reaching a maximum at 150 kGy dose followed by a decrease up to 250 kGy dose, beyond which the impact strength increases marginally. This may be explained as due to enhancement in the interphase crosslinking first, then competition between crosslink formation and chain scission of the minor constituents. In WPE/LDPE 70/30 as well as WPE/HDPE 50/50 blends, the samples exhibit decreased tensile impact strength in comparison with the values after irradiation. This may be attributed to the fact that LDPE and HDPE are both tough materials. Their incorporation into WPE would automatically toughen the matrix. If further crosslinked, then the impact strength would be lower. At a higher dose of 300 kGy, interphase crosslinking may be another factor for increased impact strength. It is an interplay between the interphase crosslinks, creation of defects from minor

constituents such as PP and PS, and a gross increase in number of crosslinks.

### X-ray diffraction study

The influence of the radiation dose on the degree of crystallinity of WPE, and the blends of WPE/LDPE 70/30 and WPE/HDPE 50/50 are shown in Table IX. WPE constitutes more of HDPE, the other components being LDPE and traces of PP and PS. Thus, its degree of crystallinity is high. On radiation exposure, the degree of crystallinity reduces may be due to partial breakdown of the crystalline structure and formation of crosslinks, as explained earlier. However, the strength property goes on increasing from a lower dose of 150 kGy to a higher dose of 300 kGy radiation, which has been explained earlier as due to the formation of more and more crosslinks in addition to the radiation resistant property of PP and PS, which contribute towards higher retention of strength property. LDPE undergoes crosslinking on radiation exposure and when blended with WPE, more crosslinks are formed when compared with that of blends of HDPE and WPE. Therefore, the mechanical strength property of WPE/LDPE 70/30 blend increases with increase in radiation dose and stabilizes at a high dose. Since HDPE degrades at higher radiation dose, its blend with WPE results in lower strength property. In all the three systems studied, the degree of crystallinity is decreased to a marked extent. This may be due to the interplay between the phases and increase in the crosslink density.



**Figure 4** (a) DTA curve showing the degradation peaks for WPE at 0, 150, and 300 kGy radiation dose. (b) DTA curve showing the degradation peaks for WPE/LDPE 70/30 blend at 0, 150, and 300 kGy radiation dose. (c) DTA curve showing the degradation peaks for WPE/HDPE 50/50 blend at 0, 150, and 300 kGy radiation dose.



TABLE X  
TGA Data of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 Blend (at Dose 0, 150, and 300 KGy) before and after Irradiation as well as That of Virgin LDPE and HDPE

	$T_i$			$T_{max}$			Percentage residue		
	0	150	300	0	150	300	0	150	300
WPE	393	395	395	465	467	465	4.5	3.7	2.6
WPE/LDPE	380	386	383	464	466	463	3.2	2.4	2.2
WPE/HDPE	403	386	395	471	464	461	2.6	1.8	1.5
HDPE	387	—	—	455	—	—	0.6	—	—
LDPE	387	—	—	465	—	—	0.6	—	—

It may be inferred that the electron beam irradiation brings forth modifications in WPE and its blends with LDPE and HDPE, practically decreasing the degree of crystallinity with radiation dose. Irradiation promotes intermolecular crosslinking. However, oxidation reactions are likely to decrease the strength property because of chain scission, resulting in decrease in degree of crystallinity. The scission process is especially important for the structural integrity of the polymer and irradiation reduces the branching as chains are broken. Also, because of the possible oxidative degradation reactions, the molecular chains are stiffened and the embrittlement of the material at higher radiation doses takes place as seen from the physicochemical properties. This has been further supported by the study of topography of the tensile fracture surface of the blends by SEM.

#### TGA study

Figures 4(a)–4(c) shows the thermo derivatograms of WPE and its blends with LDPE and HDPE. The initial decomposition temperature ( $T_i$ ) and the maximum decomposition temperature ( $T_{max}$ ) values are given in Table X. The thermal stability of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 blend are almost the same in comparison with the virgin LDPE and HDPE. Also, in all these three cases, there is no significant change in the values of  $T_i$  and  $T_{max}$  with radiation. This confirms that the thermal stability is not affected with radiation or remains the same for all WPE and its blends with LDPE and HDPE.

The residue in case of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 is around 4.5, 3.2, and 1.5% respectively, owing to contaminants present in it as the proportion of WPE is higher. Upon irradiation, the percent residue reduces steadily because of the degradation of contaminants, thus enhancing the processability of the samples.

#### SEM study

SEM photomicrographs of the tensile fracture surfaces of unirradiated WPE is shown in Figure 5(a), depicting large craters and mutilated surface after tensile failure. A magnified view of the surfaces shows longitudinal furrows indicative of high strength matrices and ductile fracture. However, after irradiation at 150 kGy, the fracture surface of WPE [Fig. 6(a)] shows generation of discontinuous fibrils. A magnified view of the surface [Fig. 6(b)] shows random ductile failure. When the radiation dose is increased to 300 kGy, the tensile fracture surfaces exhibit different surface topology as shown in Figures 7(a) and 7(b). Figure 7(a) does not show any fibrillar structure formation during failure, rather failure is initiated because of a flaw or a void, as clearly shown by the large crater on the side surrounded by smaller craters. A magnified view of the surface [Fig. 7(b)] shows smooth failure surface and normal failure may be due to chain scission or crosslink breakage. This is prevalent in tensile fracture surface of crosslinked structures.<sup>22,26,27</sup> This is in agreement with the increase in the mechanical

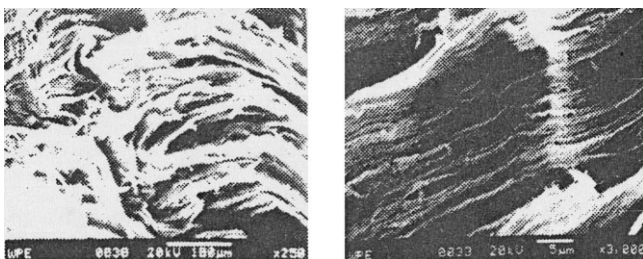


Figure 5 (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE without irradiation.

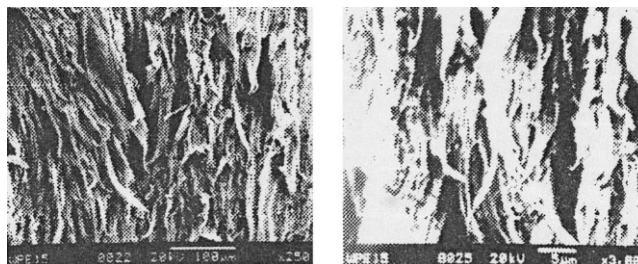
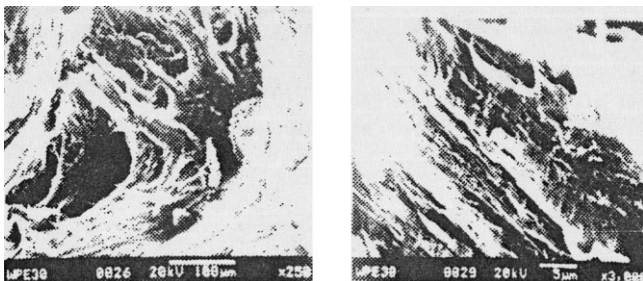


Figure 6 (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE at a radiation dose of 150 KGy.



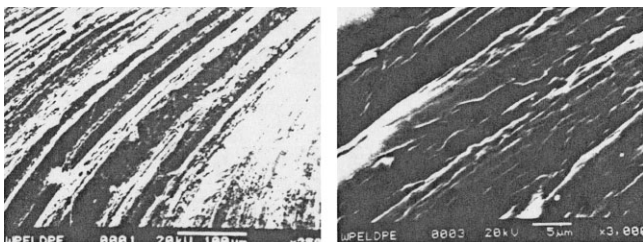
**Figure 7** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE at a radiation dose of 300 KGy.

strength of the matrix due to crosslinking, under high radiation doses.

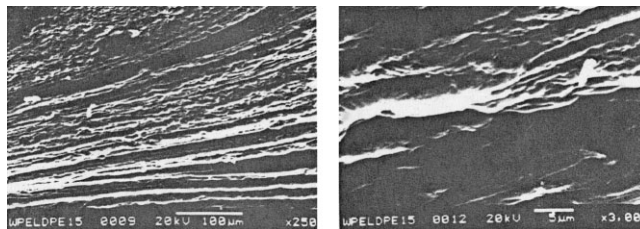
SEM photomicrographs of tensile fracture surfaces of WPE/LDPE 70/30 blend are shown in Figures 8(a) and 8(b) before irradiation. Figure 8(a) shows large furrows running from one end to the other end of the fracture forming periodic long ridges. This may be due to ease in tearing or peeling by introduction of LDPE into the matrix, which lowers the strength of the WPE matrix. It seems LDPE and WPE chains lie side by side giving a clear distinction from each other. Figure 8(b) shows the magnified view of the fracture surface with ripples on the furrows.

Also, the increase in the flatness of the fracture surfaces with increase in radiation dose for WPE and WPE/LDPE 70/30 blend may be an indication of some amount of microscopic degradation in the matrix and an evidence of ductile–brittle transition of the tensile fracture surface.

Figures 9(a) and 9(b) show the SEM photomicrographs of tensile fracture surfaces of WPE/LDPE (70:30) blend after exposure to radiation dose of 150 kGy. Figure 9(a) shows that the size of the furrows are reduced drastically and are narrowed, indicating formation of intermolecular crosslinks, leading to a less distinct LDPE and WPE phases and greater compatibility. This is quite evident from the magnified view of the fracture surface shown in Figure 9(b). Figures 10(a) and 10(b) show the tensile fracture surface of WPE/LDPE 70 : 30 blend after exposure to a radiation dose



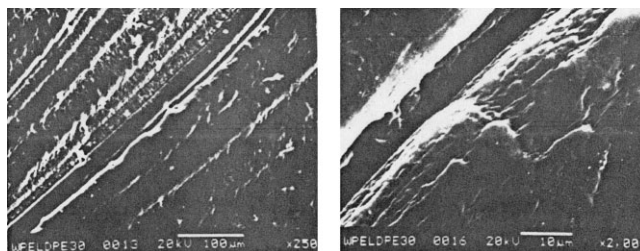
**Figure 8** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/LDPE 70/30 blend without irradiation.



**Figure 9** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/LDPE 70/30 blend irradiated with 150 KGy.

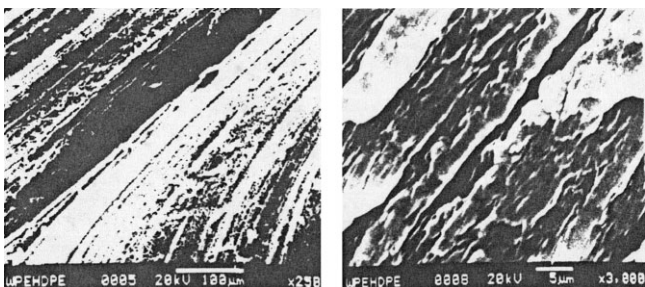
of 300 kGy. Figure 10(a) shows furrows only on the surface and not so deep and systematic. This may be due to a heavy radiation dose that has changed the network structure completely, supported by higher strength property. Figure 10(b) shows the magnified view of a single furrow. Their tensile failure of the blends characterizes ductile type of failure of the matrix.

In the case of WPE/HDPE 50/50 blend, the tensile fracture surfaces are smooth with localized plastic strain regions before irradiation, as indicated clearly in Figures 11(a) and 11(b). There are evidences of flow lines along the fracture path. Figure 11(b) shows the magnified view of the surface with smooth failures. At a dose of 150 kGy, the fracture surfaces are fibrous with highly stretched regions, as shown in Figures 12(a) and 12(b). This characterizes ductile fracture of the matrix. These observations are in agreement with the tensile properties of the blend, which show comparatively lower values. However, at a high dose of 300 kGy, the matrix undergoes tremendous changes, as shown in Figures 13(a) and 13(b). Figure 13(a) shows extremely corrugated surfaces clearly indicating brittle failure and high amount of degradation. Figure 13(b) shows the magnified view of the tensile fracture surface showing a mutilated and degraded matrix with craters and cavities. In all the three cases of WPE, WPE/LDPE 70/30, and WPE/HDPE 50/50 blend, the mode of failures observed at lower as well as higher doses of irradiation are in agreement with the tensile test results.<sup>22,26</sup>



**Figure 10** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/LDPE 70/30 blend irradiated with 300 KGy.





**Figure 11** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/HDPE 50/50 blend before irradiation.

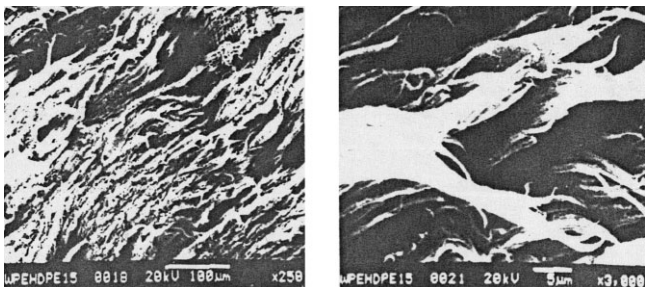
### Bottles prepared out of WPE/LDPE 70/30 blend

Figure 14 shows the blow molded bottles made in our laboratory from the blend of WPE/LDPE 70/30. The product obtained after electron beam irradiation has a better surface finish when compared with the original ones, indicating that the processability and surface finish are enhanced upon irradiation.

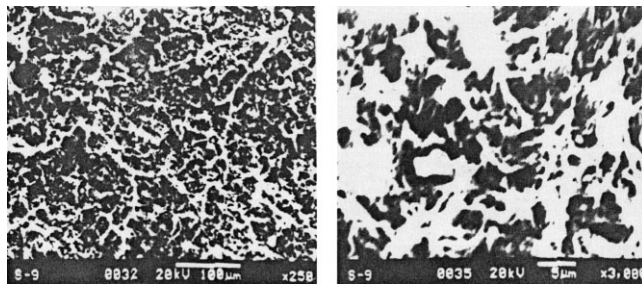
### CONCLUSIONS

The following conclusions have been drawn from the present article.

1. Gel content of WPE and its blends with virgin LDPE and HDPE show higher values after exposure to electron beam irradiation. The values are higher at lower doses of electron beam irradiation when compared with that at higher doses.
2. FTIR analysis clearly shows that modifications in the structure of the WPE backbone occur on irradiation. It increases the absorbance of consecutive methylene linkages, forms ether and carbonyl linkages due to oxidation and chain scission. However, crosslinking reaction predominates the degradation at low doses of irradiation than at higher doses.
3. Physicomechanical properties of the WPE and WPE/LDPE 70/30 blend increase with dose of



**Figure 12** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/HDPE 50/50 blend irradiated with 150 KGy.



**Figure 13** (a) and (b) SEM photomicrographs of tensile fracture surfaces of WPE/HDPE 50/50 blend irradiated with 300 KGy.

irradiation because of an increase in crosslink density. It results in higher ductility, toughness, and resistance to oxidative degradation. The WPE does not degrade completely but the degradation is high in case of WPE/HDPE 50/50 blend.

4. XRD study reveals that the crystallinity of the samples decreases with irradiation dose owing to the formation of intermolecular crosslinks in the crystalline regions.
5. TGA analysis confirms that the thermal stability is not affected by subjecting the materials to electron beam irradiation.
6. Fracture studies by SEM analysis supports all the physicomechanical property studied. The tensile fracture surfaces reflect clearly that fracture mechanism which changes from a ductile mode by void coalescence to a brittle failure mechanism as the radiation dose increases. Degradation is prominently high in case of WPE/HDPE 50/50



**Figure 14** Picture of bottles made out of WPE/LDPE 70/30 blend through blow molding technique. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

blend when compared with WPE and WPE/LDPE 70/30 blend as seen clearly by SEM, which is in agreement with the physicochemical property data.

All these observations confirm that electron beam irradiation of WPE and its blends with virgin LDPE and HDPE shall be useful for various commercial applications.

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