

Study of Some Properties of Waste LDPE/Waste Butyl Rubber Blends Using Different Compatibilizing Agents and Gamma Irradiation

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ABSTRACT: Blends of waste low-density polyethylene with waste butyl rubber of equal quantities containing reactive compatibilizing agents, namely: malic anhydride; glycidyle methacrylate, divinyl benzene, tetraethyleneglycoldimethacrylate and diethyleneglycoldimethacrylate were prepared and exposed to different γ -irradiation doses up to 400 kGy. The swelling behavior in organic solvent of the gel and soluble fractions and the degree of crosslinking were investigated. The mechanical properties, namely tensile strength and elongation at break were also studied. Thermal properties using thermo gravimetric analysis and differential

scanning calorimetry analysis follow analyses have been followed up to follow the change of the structure for the irradiated and nonirradiated blends. Results obtained indicated improvement in physical, mechanical and thermal properties on irradiation of the prepared blends which incorporate compatibilizing agents, but with varying degrees. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4157–4163, 2007

Key words: waste butyl rubber; waste polyethylene; mechanical properties; morphological structure; compatibilization

INTRODUCTION

One of the various problems which mankind faces upon entry into the 21st century is the problem of waste disposal management. The main goal of combining two or more polymers is to obtain a material with appropriate features and conditions for processing. Postuse polymers are mixed to recycle such materials, and to reduce the environmental impact generated by these solid residues. Plastics represent a serious environmental problem when they become waste at the end of their useful lifetimes. The drawbacks underlying the disposal of waste rubbers by methods such as landfills, pyrolysis, and incineration encouraged further research on the recycling technology. Reutilization of powdered waste rubber in mixtures with virgin rubbers^{1–7} and plastics^{8–12} is an attractive alternative. A recent advancement in this field is the use of ground rubber tire (GRT) in the preparation of thermoplastic elastomeric blends based on rubbers and thermoplastics. Osborn¹³ studied the feasibility of using activated tire rubber as a modifying ingredient in thermoplastic elastomers such as Santoprene. Baker and coworkers^{14–17} reported the use of functional monomers as compatibilizers in enhancing the properties of GRT-poly-

olefin blends. Al-Malaika and Amir¹⁸ found that reclaimed rubber in a thermoplastic elastomeric blend of natural rubber (NR)/polypropylene (PP) could replace half of NR without adversely affecting the mechanical properties of the blend. Preparation of thermoplastic elastomers consisting of ultrasonically devulcanized GRT and PP was also reported.¹⁹ Apart from the tire rubbers, other automotive rubbers such as ethylene–propylene–diene monomer (EPDM) rubber also contribute to the disposal problems. General immiscibility of polymers has been turned into a unique advantage in the development of rubber toughened plastics.^{20,21} Blending of elastomers with a selected plastomer provides a convenient means of making thermoplastics elastomers of diverse nature. Polyolefin thermoplastics such as polypropylene and polyethylene were blended with such elastomers as EPDM and NR or waste butyl rubber (WBR) and such materials find applications in packing kitchen wears, toys, furniture, electronic, electrical goods, etc.

It is known that the radiation crosslinking of polymer blends can produce many materials with better properties and high stability when subjected to aging, weathering and aggressive media, etc.^{22–26} The treatments of such blends with high-energy radiation lead to additional and unpredictable changes in their structure and properties. This is so because the irradiation itself or the usage of different additives may have a significant and ambiguous effect upon the same polymer.

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In this work, the mechanical, physical and thermal behavior of recycled 50/50 blends of waste low density polyethylene (WLDPE) and waste butyl rubber using different compatibilizing agents, after exposure to gamma rays in the air, was investigated.

EXPERIMENTAL

Materials

Powder of waste butyl rubber of particle size 80 meshes (150 μ m) was kindly provided by Rouse Rubber Industries, MS, USA, and waste low-density polyethylene was obtained from local market. The reactive compatibilizing agents supplied by Merck, Germany, were used as received and are listed in Table I.

Techniques

Sheet preparation

Waste butyl rubber and waste low-density polyethylene were washed several times with petroleum ether and then with boiling water and were dried at 50°C in vacuum oven. The mixing of WBR and WLDPE with different compatibilizing agent was achieved using extruder at a temperature of about 150°C for 7 min and open mill at temperature 70°C. The sheets were compression molded between aluminum at 180°C for 5 min under 200 bar pressure in an electrically heated press to prepare sheets of 2 ± 0.05 mm thickness and to ensure the melting of WLDPE and homogeneity of the blend.

Gamma irradiation

The samples were submitted to gamma irradiation, in air, at room temperature and in ambient humidity. The absorbed doses were 100, 150, 200, and 400 kGy at irradiation dose rate 5–7 kGy/h. Irradiation was carried out at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt.

Physical measurement

A weighed amount of blend film was immersed into toluene for 48 h. The blend film was taken out from

the solvent and the swollen film was weighed. The swelling ratio was calculated from the difference of the weight of the films before and after swelling.

The crosslink density was calculated from Flory and Rehner equation as follows:²⁷

$$\begin{aligned} \text{Crosslink density (number of crosslinks/ml)} \\ = K \times Q^{-5/3} \end{aligned}$$

where K is a constant having a value of 4.71×10^{20} for a system of toluene-rubber and Q is the swelling ratio.

The gel fraction (W_g) was determined by extracting the soluble component in boiling toluene for a total of 21 h at $t = 140^\circ\text{C}$ and by drying the residue for about 4 h at $t = 50^\circ\text{C}$. The weight of the treated samples was marked as m_1 , while the initial weight was registered as m_0 . The gel fraction was defined as: $W_g = m_1/m_0$. Three samples were used to determine the average gel fraction for each case.

Mechanical measurements

Mechanical properties of the films were measured by using HOUNS FILD testing machine, England, connected to a computer. The ISO 37-1977 (E) and ISO 34-1975 (E) standards were followed up to measure tensile strength (TS) and elongation at break (E_b), respectively.

Thermogravimetric analysis

A type TGA-50 system from Shimadzu, Kyoto, Japan, was used under nitrogen atmosphere at 20 mL/min. in this study in the temperature range from ambient to 600°C at a heating rate of 10°C/min.

Differential scanning Calorimetry

Shimadzu DSC system of the type DSC-50 was used under nitrogen atmosphere at 20 mL/min in this study in the temperature range from ambient to 600°C at heating rate of 10°C/min.

TABLE I
List of Reactive Compatibilizing Agents Used for Irradiation WLDPE/WBR (50/50) Blends

Chemical name	Molecular formula	Molecular weight (g/mol)
Malic anhydride	$\text{C}_4\text{H}_2\text{O}_3$	98.06
Glycidyle methacrylate	$\text{C}_7\text{H}_{10}\text{O}_3$	142.15
Divinyl benzene	$\text{C}_{10}\text{H}_{10}$ ($\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)_2$)	130.19
Diethylene glycol dimethacrylate	$[\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2]_2\text{O}$	242.27
Tetraethylene glycol dimethacrylate	$\text{O}[\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2]_2$	330.37

RESULTS AND DISCUSSION

Gel fraction

In general, the yield of irradiation-induced crosslinking can be estimated from gel fraction determination. The variations of gel fraction % with irradiation dose for WLDPE with WBR of equal quantity for the blank and for the same blend containing various additives are shown in Figure 1.

For all cases, it is observed that gel contents increase gradually with increasing irradiation dose and reach about 60% at 200 kGy. It also reveals that the materials are crosslinked properly with subsequent formation of a three-dimensional network structure. However, the sensitivity of the blends is higher at low-radiation doses in comparison with control and the most sensitive blend is the blend with TEGDMA.

Over the whole irradiation range, the following order, for the capacity of utilized compatibilizing agents in enhancing radiation induced crosslinking, is as follows:

$$\text{DEGDMA} > \text{DVB} > \text{TEGDMA} > \text{GMA} > \text{MA} > \text{Blank}$$

Apparently, the efficiency of the compatibilizing agents is affiliated with the number of double bonds, i.e., the functionality (F) of each agent molecule.

A further confirmation of the above results may be obtained from following up the swelling behavior of enhanced and irradiated samples, from which the

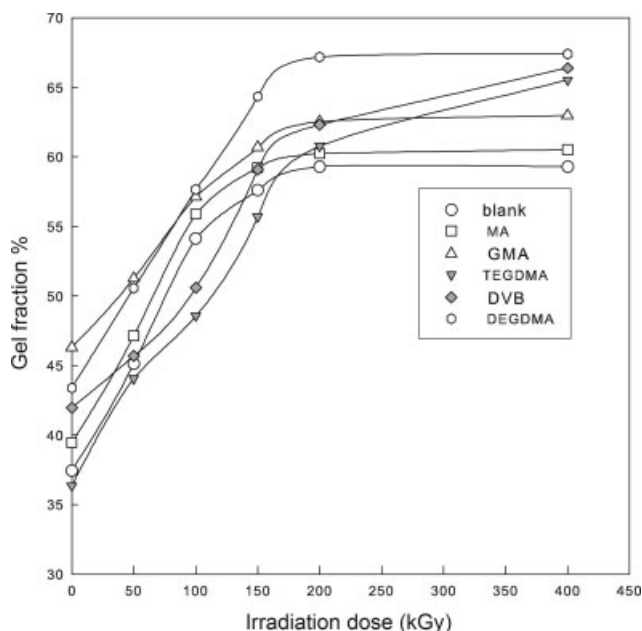


Figure 1 Gel fraction % variations versus irradiation dose for WLDPE/WBR blends (50/50)% with different compatibilizing agents. Y axis: Gel fraction; X axis: irradiation dose (kGy).

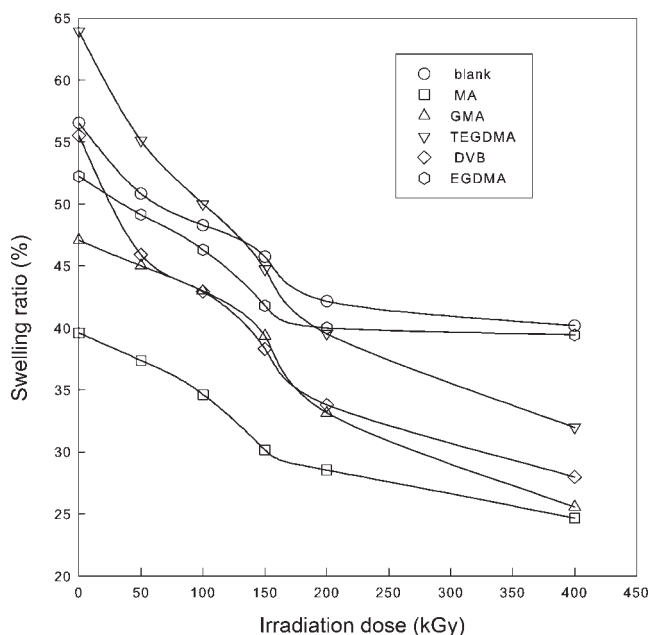


Figure 2 The relationship between percentage of swelling and irradiation dose for compatibilizing agents of WLDPE/WBR blends (50/50)% at a room temperature. Y axis: Swelling ratio (%); X axis: Irradiation dose (kGy).

number of crosslinked units per unite volume, i.e., crosslinking density, can be calculated.

Figure 2 shows the swelling of WLDPE/WBR blend with different reactive compatibilizing agents as a function of irradiation dose. It can be seen that the swelling decreases with increasing irradiation dose in accordance with the increasing degree of crosslinking, which normally results in lower degree of swelling.

Figure 3 depicts the plot of percent crosslinking density of the same blends as a function of irradiation doses. All these blends show similar trend of variation with doses. The crosslinking density increases up to 200 kGy and remains almost constant with further increase in irradiation dose.

Crosslinking density percent at a particular dose is slightly higher as compared to their control. The increase of crosslinking density with increase in irradiation dose in presence of compatibilizing agent is due to the formation of a three-dimensional network structure. On the other hand, beyond an optimum irradiation dose, the increase is marginal due to the balance of various competitive reactions like ether formation, chain scissoring, etc. It can be noted that the extent of swelling is an inverse function of the crosslinking. This means the crosslinking increases with decreasing swelling (%).

Mechanical properties

The effects of ionizing radiation on polymers have been investigated by many researchers over the past

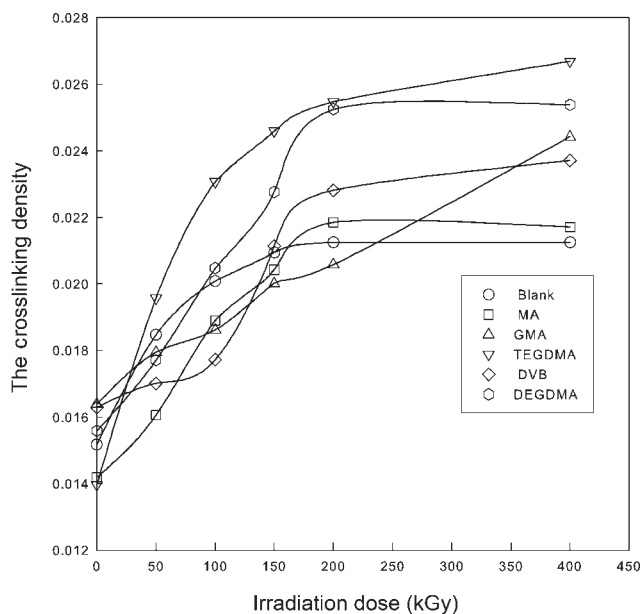


Figure 3 The relationship between percentage of the crosslinking density and irradiation dose for different compatibilizing agents of WLDPE/WBR blends (50/50) % (cured at 150°C) at a room temperature. Y axis: The crosslinking density; X axis: Irradiation dose (kGy).

few decades. Among the effects is that high-energy irradiation causes crosslinking and degradation in polymers. As a result of crosslinking the tensile strength increases while the elongation at break decreases.

Figure 4 shows the variation of the tensile strength properties of WLDPE/WBR blend (50/50) in presence of different compatibilizing agents at different

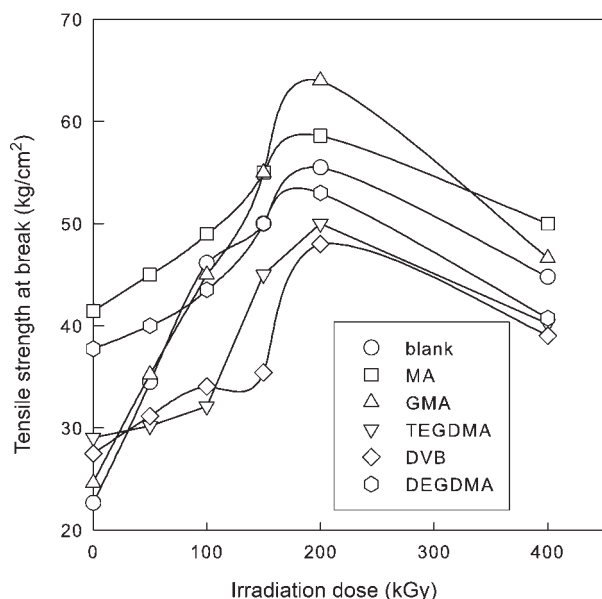


Figure 4 Tensile strength at break of WLDPE/WBR blends (50/50)% with different compatibilizing agents at different irradiation doses. Y axis: Tensile strength at break Kg/cm²; X axis: Irradiation dose (kGy).

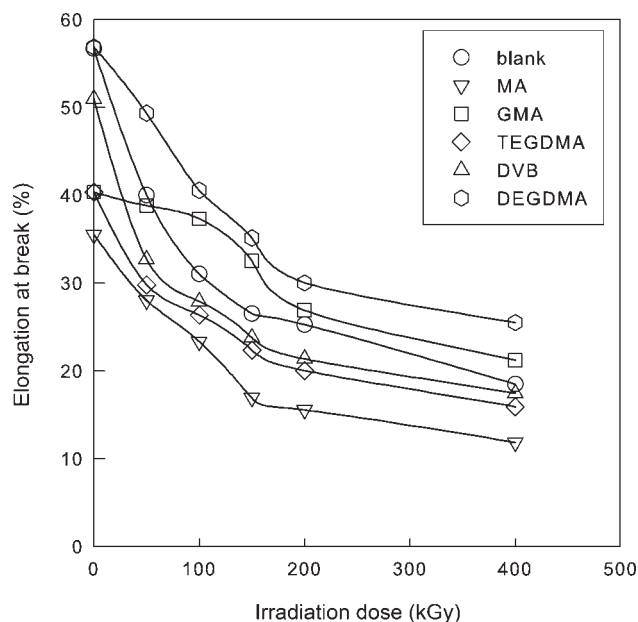


Figure 5 Elongation at break of WLDPE/WBR blends (50/50)% with different compatibilizing agents at different irradiation doses. Y axis: Elongation at break (%); X axis: Irradiation dose (kGy).

gamma irradiation doses up to 400 kGy. It is clear from this figure that TS of the blends increases with the irradiation dose up to 200 kGy, indicating that up to a dose of 200 kGy crosslinking is the predominant process; however beyond that dose the degradation dominates over the crosslinking process for all the samples.

This can be explained by two reasons: (i) a high-energy irradiation of polymers creates free radicals

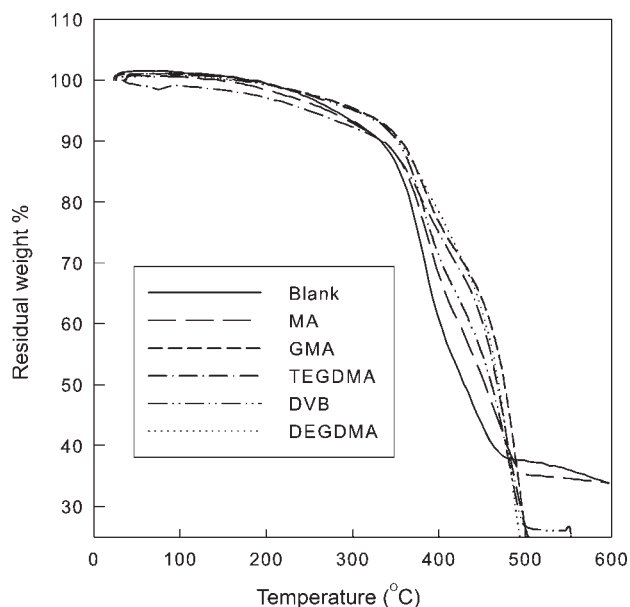


Figure 6 TGA curves of unirradiated (WLDPE/WBR) blends (50/50)% using different compatibilizing agents. Y axis: Residual weight %; X axis: Temperature (°C).

TABLE II
Temperatures for Different Percentage of Weight Losses for Irradiation WLDPE/WBR Blends
Using Different Compatibilizing Agents

Sample WLDPE/WBR	Dose (kGy)	TWL 5% (°C)	TWL 10% (°C)	TWL 50% (°C)	Remain ^{WL} % at 600°C
Blank	0	250	320	428	33.7
	100	319	325	450	34
	400	319	325	450	34
MA	0	257	326	452	34
	100	266	328	470	30
	400	295	347	472	24
GMA	0	302	352	475	23
	100	325	365	470	37
	400	300	348	440	39.4
TEGDMA	0	250	330	465	36
	100	302	353	477	32
	400	296	346	467	37.4
DVB	0	302	353	465	9
	100	360	393	485	14.6
	400	360	393	485	14.6
DEGDMA	0	303	355	468	24
	100	301	359	477	14.3
	400	301	359	477	14.3

by the scission of the weakest bonds. These new entities react with each other or with molecular oxygen if the exposure environment contains it; (ii) the presence of carbon black in the reclaim. The increase in crosslink density of the blends from addition of reclaimed rubber was due to the presence of active crosslinking sites in the reclaimed rubber, which continued to form crosslinking. The additives used produce free radicals on irradiation. These radicals might react with polymer radicals to enhance crosslinking and chain scission in polymer matrix with an increase in irradiation dose. The enhanced crosslinking density may not necessarily increase the tensile properties of the polymer, because of the radiation-induced scission of long polymer backbone chain as well as brittleness character of the polymer induced at higher crosslinking density.

Elongation at break of the samples depends upon the nature of the polymer as well as on the degree of crosslink, which restricts the movement of the polymer chain against the applied force. Figure 5 shows the variation of elongation at break E_b , as a function of irradiation dose for unenhanced as well as enhanced blend with different compatibilizing agents. It can be seen that E_b values decreases with a semileaner manner up to irradiation dose of 200 kGy, after which it decreases very slowly for higher doses up to 400 kGy. This behavior offers confirmation to data obtained for TS as an almost reverse order is obtained when comparing both parameters at the same irradiation dose.

Thermo gravimetric analysis

The thermal stability behavior of the unirradiated WLDPE/WBR blends using different compatibilizing agents is displayed in Figure 6 and the results are tabulated in Table II. It can be seen that for tempera-

ture up to ~ 350°C, the weight loss for blends with additives is lower than that of its blank copolymers, indicating that the additives incorporated provide thermal stability to the copolymer matrix. The evaluation of temperature for a loss of 5%, 10%, and 50% weights are given in Table II. On close examination, it may be observed that the thermograms show that the blank sample has lower thermal stability than the formulations containing the compatibilizing agents. In addition, it can be seen from the data given in Table II that unirradiated samples of the blank as well as WLDPE/WBR/MA, WLDPE/WBR/GMA, WLDPE/WBR/TEGDMA, WLDE/WBR/DVB, and WLDPE/WBR/DEGDMA have samples

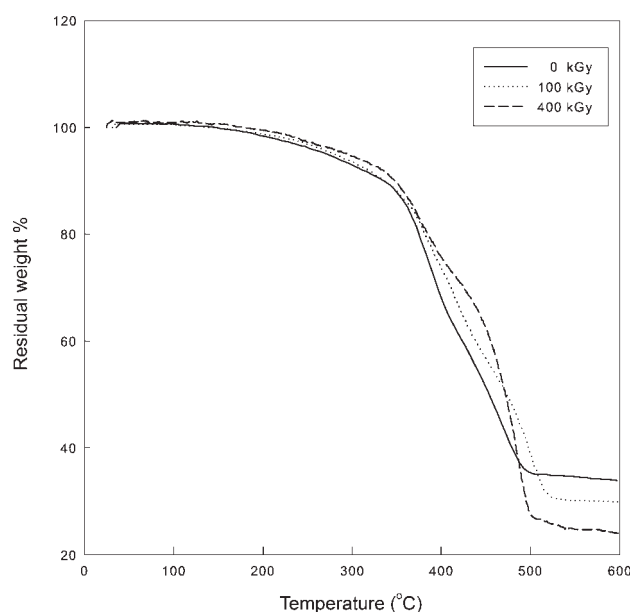


Figure 7 TGA curves of (WLDPE/WBR) blend (50/50)% with MA at different irradiation doses. Y axis: Residual weight %; X axis: Temperature (°C).

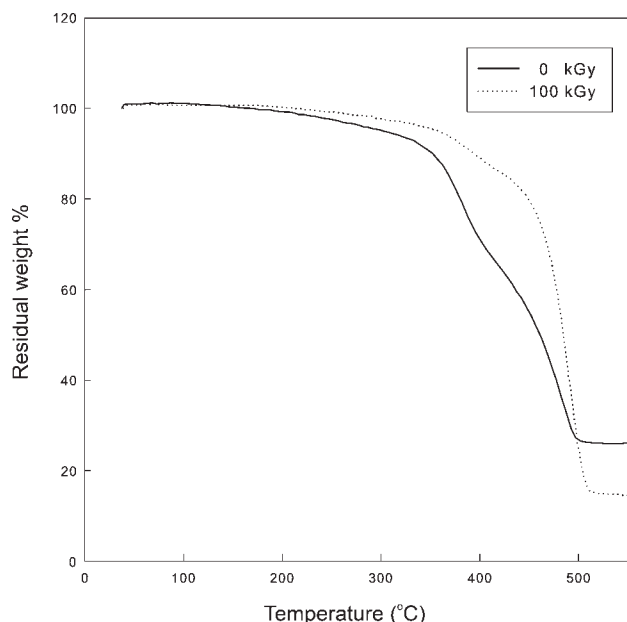


Figure 8 TGA curves of WLDPE/WBR blends(50/50)% with DVB at different irradiation doses. Y axis: Residual weight %; X axis: Temperature (°C).

5% weight loss at acquired 250, 257, 302, 250, 302, and 303°C where as for the same samples with an irradiation dose of 10 kGy, the same weight loss is observed at 319, 266, 325, 302, 360, and 301°C, respectively. This shows that the addition of compatibilizing agents to unirradiated blend does not seem to exert any detrimental influence on the thermal stability. Figures 7–9 show TGA thermograms of irradiation WLDPE/WBR blends using different

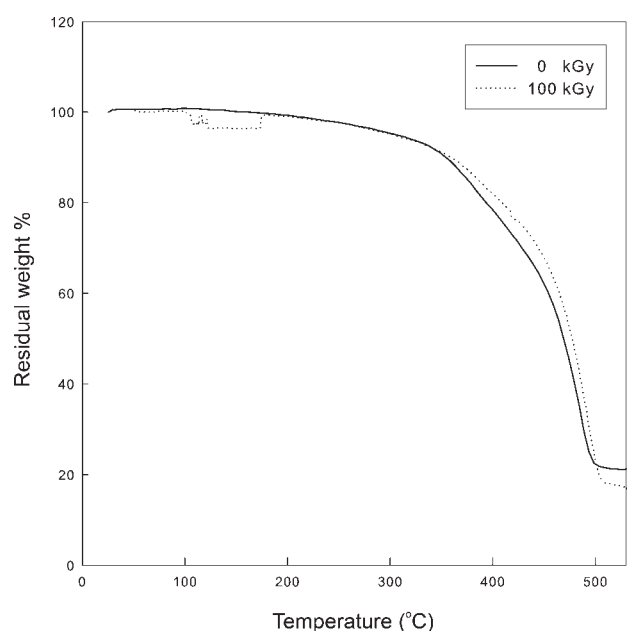


Figure 9 TGA curves of WLDPE/WBR blends (50/50) % with TEGDMA at different irradiation doses. Y axis: Residual weight %; X axis: Temperature (°C).

compatibilizing agents to a dose of (0,100,400) kGy. In the region of TWL 0–5% and TWL 5–10%, thermally initiated homolysis of the groups causes the scission of the rubber chains and this chain scission is associated with the weight loss. In the region of TWL 10–85%, maximum decomposition of blends takes place. This may be attributed to enhanced crosslinking of the matrix in presence of compatibilizing agents that causes further increase in the crosslink density of the matrix.

Differential scanning calorimetry

Variation of the melting point of the compounds against the radiation doses has been plotted in Figure 10. It is seen that the melting point gradually decreases with the augmentation of the radiation dose. This denotes that size of the crystallite becomes small, and crystallites with small size are dispersed in the crosslinked polymer matrices. This feature of melting point depression may be accounted for as a result of the diluent's effect of the amorphous component.

The variation of heat of fusion ΔH versus irradiation dose has been plotted in Figure 11 for the blends using different compatibilizing agent. It is seen that as the irradiation dose increase, the value of ΔH decreases, which corresponds to the reduction in the crystallinity of the compound. It is also seen that ΔH decreases marginally with irradiation dose. In addition, in all the blends considered this drop in the melting temperature T_m value is accompanied by

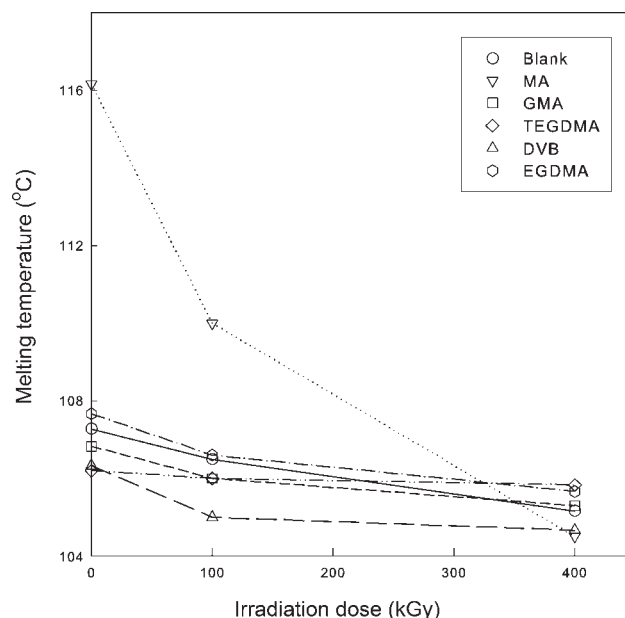


Figure 10 Variations of melting point versus irradiation dose of (WLDPE/WBR) blends (50/50) % with different compatibilizing agents. Y axis: Melting temperature (°C); X axis: Irradiation dose (kGy).

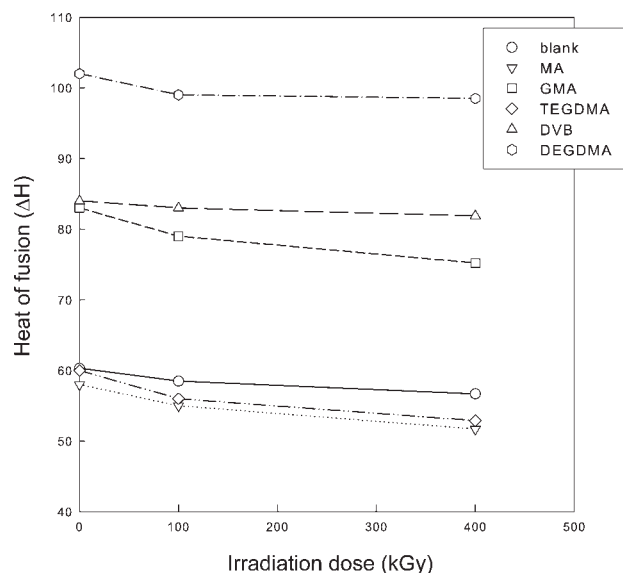


Figure 11 Change of heat of fusion (ΔH) versus irradiation dose of WLDPE/WBR blends (50/50) % with different compatibilizing agents. Y axis: heat of fusion (ΔH); X axis: Irradiation dose (kGy).

a consistent decrease in the ΔH value. The total degree of crystallinity of the blends also decreases rapidly with the increase in the rubbery component.

CONCLUSIONS

The results of the investigations of the study of some properties of WLDPE/ (WBR) blends using different compatibilizing agents and gamma irradiation described above lead to the following conclusions:

- The gel fraction results before irradiation, the control exhibits higher gel fraction compared to the compound with additives.
- The incorporation of EGDMA was found to improve the gel fraction of (WLDPE/WBR) (1/1) compared to DVB, GMA and control sample.
- It is clear that TS of the blend increases and the elongation at break decreases with irradiation dose increase up to a dose of 200 kGy and latter on it decreases in TS indicating initially up to a

dose of 200 kGy crosslinking is the predominant process.

- It can be seen that at a particular temperature weight loss for blends with additives is smaller than that of its blank copolymers indicating the additives incorporated provides thermal stability to the copolymer matrix.
- The melting point gradually decreases with the augmentation of the radiation dose.

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