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INFLUENCE OF ELECTRON BEAM TREATMENT ON THE CRYSTALLIZATION AND THERMAL STABILITY OF LDPE/EPDM BLENDS

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ABSTRACT

The effect of blend composition and Electron Beam (EB) irradiation on the crystallization and thermal behavior of Low Density Polyethylene (LDPE)/Ethylene-Propylene-Diene elastomer (EPDM) blends had been studied. Melting temperatures were found to remain unchanged upon variation of blend composition as well as irradiation dose. But the degree of crystallinity and T_c (crystallization temperature) were decreased with increase in EPDM content and EB dose. On the other hand, thermal stability (in terms of onset temperature and degradation temperature) and activation energy were increased with increase in EPDM content and irradiation dose. But the speed of degradation slowed down with increasing EPDM content and EB dose. Interestingly, once Trimethylolpropane Triacrylate (TMPTA) and Triallyl Cynuerate (TAC) were incorporated into the blends, the degrees of change of these properties were more in same direction upon irradiation. At higher irradiation dose properties were demoted due to chain scission.

Keywords: Low Density Polyethylene (LDPE), Ethylene-Propylene-Diene Elastomer (EPDM), Crystallinity, Degradation, EB Irradiation, TMPTA and TAC

1. INTRODUCTION

Radiation cross linking becomes an effective tool to improve properties of polymeric materials (Ray Chowdhury and Sabharwal, 2011; Zaharescu *et al*., 1999). Radiation processing of polymers starts with gamma irradiations in industry and academia (Cleland *et al*., 2003; Machi, 1995). Gamma radiation plays a significant role in polymer crosslinking and chain scission to alter properties. Many reports on gamma radiation processing are available with successful and useful outcomes (Ray Chowdhury *et al*., 2012a). However, now-a-days fascination is increasing towards electron beam irradiation due to some limitations of gamma irradiation instead of the later having less initial investment and high penetration power due to electromagnetic nature (Ray Chowdhury *et al*., 2012b; Magida, 2012). The limitations of gamma irradiation are difficulties of large scale processing, time consumption, handling of isotopes, transportation, safety of worker (Sam *et al*., 2012; Jamal *et al*., 2011). Electron beam irradiation affects mechanical, chemical, electrical and thermal properties of polymers as gamma radiation does. Upon irradiation polymer generates macro radicals, which combine and form inter chain or intra chain network (Mohamed *et al*., 2012; Abdel-Aziz *et al*., 1992). Such compact crosslinked network with and without involvement of crosslinker or chain scission can alter

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the above mentioned properties (Hung *et al*., 2004; Wang *et al*., 2009).

Radiation processing changes the thermal stability and crystallization behavior i.e., associated properties of polymers significantly (Vranjesn and Rek, 2007; Chattopadhyay *et al*., 2001). Both are important from application point of view. There are many reports on radiation processing and properties of LDPE, HDPE, PP, EP, SEB, PDMS. Among the polyolefins, Low Density Polyethylene (LDPE) and Linear Low Density Polyethylene (LLDPE) are widely used in the packaging and consumer industry because of their advantages like excellent mechanical properties, thermal stability, good environmental stress crack resistance, flexibility, excellent dielectric properties, availability and low cost (Maziyar *et al*., 2012; Santra *et al*., 1993). Most of the synthetic rubbers (styrene butadiene rubber, chloroprene rubber) have been replaced by LDPE. Crosslinked LDPEs are widely used in heat shrinkable materials, wire and cables and construction (Ray Chowdhury *et al*., 2000; 2012b). On the other hand, Ethylene Propylene Diene (EPDM) has attractive crosslinking ability, heat and ozone resistance properties and dynamic damping properties (Sen Majumder and Bhowmick, 2000).

By judicial selection of properties of LDPE and EPDM, scientists have made blends of two, to get selected combination of properties. That is why, LDPE-EPDM blends have got their application in automobile, wire and cable insulation and construction applications (Morteza *et al*., 2009; Senna *et al*., 2007). Needless to say that the use of radiation can be a good option to improve the properties of LDPE-EPDM blends.

To study different aspects, such as mechanical, thermal, rheological and morphological properties, PE/EPDM blends have been prepared and investigated (Airinei *et al*., 2013; Sadek *et al*., 2003; Nouri and Mehrabzadeh, 1996; Mukhopadhyay and Das, 1990).

Some studies on radiation processing (gamma) of polyolefins/EPDM have been reported (Zaharescu *et al*., 1999; Abdel-Aziz *et al*., 1992; Rizk *et al*., 2009). So far our knowledge is concern there is no reported literature on the influence of EB on crystallization and thermal stability of LDPE/EPDM blends.

Thus, our present work represents the effect of EB crosslinking on crystallization properties and thermal stability of LDPE/EPDM blends. We have also used polyfunctional monomers such as Trimethylolpropane Triacrylate (TMPTA) and Triallyl Cynuerate (TAC) as cross linking agent to improve the properties in a higher degree.

2. EXPERIMENTAL

2.1. Materials

Low Density Polyethylene (LDPE; MFI 4 gm/10 min, density of 0.922 gm/cc) in form of pellets are supplied by Reliance Petrochemicals. Ethylene Propylene Diene elastomer, KELTAN (EPDM; propylene content = 55% with 5.5% of ENB, MFI10 gm/10 min and density of 0.88 gm/cc) was procured from DSM Netherland. The polyfunctional monomers (crosslinking agent) like Trimethylolpropane Triacrylate (TMPTA) and Triallyl Cynuerate (TAC) were procured from Sigma Aldrich (India).

2.2. Preparation of Blends

LDPE was blended with EPDM in different compositions using twin screw extruder at the temperature profile of 120:140:160:180°C at 80 rpm. Blends were prepared in various proportions with and without crosslinker as in **Table 1**. Cross linkers (TMPTA and TAC) were used in 1phr. For study purpose dumble shaped samples were prepared by injection molding at 180°C. The codes of the samples are in **Table 1**. Mentioning ‘TMPTA’ or ‘TAC’ in the sample codes, implies that 1phr (w.r.t total mass of blend) of TMPTA or TAC is incorporated in the formulation.

2.3. Electron Beam Irradiation of Test Specimens

The injection molded specimens were irradiated by high energy electron beam in an inert environment using 2 MeV, 20kW EB accelerator (Model ILU-6) under forced air cooling at a radiation dose of 40, 80 and 120 kGy (kilo Grey). Only one side of the sample was exposed to irradiation, as the thickness of the sheets was 2 mm, which was thin enough for penetration of the electron beam of 2MeV energy.

The distance of the sample from the scan horn was 20 cm and the conveyer speed was set at 0.94 m/min. The dose rate was 10 kGy/pass and beam current was 1mA.

2.4. Characterization

2.4.1. Determination of Gel Fraction (% Gel Content)

Gel fractions were measured by solvent extraction technique using xylene as solvent. The samples were extracted in hot xylene for 48 h at 110°C. Extracted samples were dried in a vacuum oven at 80°C till constant mass. The gel content (% gel fraction) was determined using the following formula Equation 1:

Table 1. Blend compositions

Samples	1	2	3	4	5
LDPE	100	80	50	20	0
EPDM	0	20	50	80	100
Sample code	L 100	LE 82	LE55	LE 28	E 100

where, 'L' stands for LDPE and 'E' for EPDM, 'TMPTA'-Trimethylol propane triacrylate, 'TAC'- Triallyl cyanurate. If TMPTA and TAC are mentioned in sample code that means 1 phr (parts per hundred) TMPTA or TAC has been added respectively

$$(\%)\,Gel\ content = \frac{Mass\ after\ extraction}{Mass\ before\ extraction} \times 100 \quad (1)$$

2.4.2. Differential Scanning Calorimetry (DSC)

DSC analysis was carried out at heating and cooling rate of 10°C $\min^{-1}$ in N_2 atmosphere using Perkin-Elmer DSC thermal analyzer from room temperature to 160°C. The samples were heated at 10°C $\min^{-1}$ up to 160°C and held for 5 min at 160°C (molten stage). Then samples were cooled at the same speed up to room temperature. T_m (melting temperature), ΔH_m (heat of fusion) and % C (% crystallinity) are calculated from the melting (heating) curve (endothermic peak). Crystallization Temperatures ($T_c s$) are calculated from crystallization of cooling curve (exothermic peak). The degree of crystallinity (X_c) is calculated from heat of fusion under melting endotherm, using following formula Equation 2:

$$X_c = \frac{\Delta H_m}{\Delta H_m 0} \times 100 \quad (2)$$

where, ΔH_m is the melting enthalpy of sample and $\Delta H_m 0$ is the melting enthalpy of 100% crystalline sample (where $\Delta H_m 0$ for 100% crystalline LDPE is taken as 239 Jg^{-1}(Morawiec *et al*., 2005). The melting enthalpy of 100% crystalline EPDM has been considered as the heat of fusion of 100% crystalline LDPE as hydrocarbon chain only is responsible for EPDM crystallinity (Britton *et al*., 1978).

2.4.3. Thermogravimetric Analysis (TG)

Thermogravimetric analysis (TG) of the virgin polymers, their blends with and without crosslink coagent (TMPTA and TAC) before and after electron beam irradiation were carried out using a Thermogravimetric analyzer (TG Q 100) under N_2 atmosphere at a heating rate of 10°C $\min^{-1}$. To compare the nature of degradation of various samples, T_i (onset), T_d (degradation temperature), T_{30} (temperature corresponding to 30% mass loss), T_{50} (temperature corresponding to 50% mass loss) and T_{90} (temperature corresponding to 90% mass loss) were calculated from TG graphs.

The determination of the activation energy of degradation is important parameter for evaluating the ease of thermal decomposition of polymer. In our work, the integral method of Coats and Redfern has been used to determine the activation Energy of degradation (E) (Coats and Redfern, 1964; Baloch *et al*., 2011). However, different investigators have been using different methods to calculate the activation energy of polymer (Flynn and Wall, 1996; Kissinger, 1957; Kayacan and Doğan, 2008). The Coats and Redfern model gives the best linear fit and also this model has been mostly and successfully used for studying the kinetics of decomposition and dehydration. This approach is applied for single TG graph. That is why this model is chosen.

3. RESULTS AND DISCUSSION

3.1. Gel Fraction Analysis

The crosslinking efficiency of LDPE, EPDM and various LDPE/EPDM blends, at various doses, in absence and presence of crosslinker, is estimated from the gel fraction determination. Results are presented in **Fig. 1**. Higher is the gel content greater will be the amount of crosslinking, as gel content is the measurement of amount of crosslinking (Charlesby *et al*., 1959; Charlesby, 1954). There is no gel formation observed for control systems. It is clear from the **Fig. 1** that neat LDPE shows 50.43, 71.94 and 78.01% gel fraction at 40, 80 and 120 kGy EB doses. On the other hand, for pure EPDM, the gel contents are 76.81, 87.69 and 92.38% at the same doses respectively. Thus it is revealed that with increase in doses the gel content i.e., crosslinking ability is increased steadily with increase in radiation doses. That proves up to 120 kGy, in both the polymers, crosslinking process dominates over the chain scission process as the gel content is the measurement of crosslinking. From the findings it is again obvious that, at a certain dose, EPDM shows higher gel fraction than LDPE and that is true for all studied doses. That is due to higher crosslinking ability of EPDM than LDPE (Dikland and Van Duin, 2002). The crosslinking ability of EPDM is more due to higher amorphousness and molecular structure of EPDM. So it is expected that with increase in EPDM content in blends, gel fraction will keep on increasing. That is the finding throughout the experiments.

Interestingly, as in LDPE and EPDM, the gel contents of LDPE/EPDM blends with and without crosslinker are also in increasing trend with increase in irradiation dose. In LE 82 blends without crosslinker, the percentages of gel fractions are observed to be 57.6, 76.54 and 81.7% for different electron beam doses (40, 80 and 120 kGy). In LE55 blends, the gel fractions are higher than that of LE 82 blends due to greater amount of EPDM content in blends. The increased gel content in LE 55 blends are 63.39, 77.00 and 85.02 % at 40, 80 and 120 kGy EB. It is seen that LE 28 blends shows significant enhancement in gel fraction compared to LE 82 and LE 55 blends. The value of gel fraction for LE28 blends are 68.86, 82.35 and 89.68% at same dose rate of 40, 80 and 120 kGy, respectively.

Further, it is noticed that the gel content i.e., crosslinking ability of blends is increased after adding TMPTA and TAC. The TMPTA and TAC containing samples exhibit higher amount of gel than without ones due to higher degree of crosslinking.

In TMPTA and TAC added LE 82 samples, gel fractions are found to be 64.54, 80.93 and 85.34% and 61.57, 78.93 and 83.67% at 40, 80 and 120 kGy respectively. The TMPTA and TAC containing LE 55 samples show 71.58, 83.92 and 90.13% and 68.54, 80.03 and 87.66% gel fraction values at 40, 80 and 120 kGy doses.

Thus, TMPTA is found to be more efficient crosslinker than TAC for LDPE/EPDM system (**Fig. 1**). Both of these multifunctional monomers are three functional. Both join two polymer chains through C-C bridge formation and form three dimensional networks in a same fashion (Pyun *et al*., 1982). But why is this difference? According to Handlos (1979), the gel promoting efficiencies of these functional monomers depend on the initial ‘G’ values (crosslinking) value of monomers. In fact TMPTA possesses higher number of reactive double bonds than TAC (Waldron *et al*., 1985). R. Wiedenmann reports that there are so many unreacted double bonds in TAC-blended PE after irradiation (Wiedenmann, 1977). A similar trend is observed for TMPTA and TAC added LE28 samples, which exhibits 75.58, 89.19 and 93.95% and 72.26, 85.98 and 92.03% gel content at above-mentioned doses.

3.2. Differential Scanning Calorimetry (DSC)

The effect of blend compositions and electron beam radiation dose on the melting temperature (T_m), crystallization temperature (T_c), heat of fusion (ΔH_m) and degree of crystallinity (X_c) of LDPE/EPDM blends system have been analyzed by DSC. DSC curves of neat LDPE, EPDM and their blends before and after electron beam irradiation at different doses (40, 80 and 120 kGy) are represented in **Fig. 2 to 4**. The value of melting temperature (T_m), heat of fusion (ΔH_m) and degree of crystallinity (X_c) computed from the DSC endothermic and crystallization temperature (T_c) from exothermic curves are tabulated in **Table 2**. **Figure 2a** shows that for neat LDPE and EPDM prominent melting peaks (T_m) appear at 110.03 and 52.62ºC respectively. In all blends (LE 82, LE 55 and LE 28) two melting peaks corresponding to LDPE and EPDM phase have been observed.

The addition of higher amount of EPDM in LDPE causes little decrease of melting point of LDPE (**Table 2**). In LE 82 blend, the melting temperatures of LDPE and EPDM have been observed at 109.01 and 52.14ºC respectively. In LE 55 blend, where both LDPE and EPDM are in equal proportions, the melting peak of LDPE shifts slightly towards lower temperature (105ºC) while there is no considerable change in melting temperature of EPDM which is found at 54.0ºC. LE 28 blend shows the melting peak of LDPE and EPDM at 104.22 and 51.94°C respectively.

The electron beam irradiation of LE 82, LE 55 and LE 28 blends by 40, 80 and 120 kGy has not imparted considerable effect in melting temperatures of both LDPE and EPDM (**Fig. 2a to 4a and Table 2**). Even after incorporation of cross linking agent (TMPTA and TAC), i.e., higher degree of crosslinking no change of T_m is observed.

Figure 2b to 4b show DSC exothermic curves (cooling curve) of unirradiated and irradiated LDPE, EPDM and blends. The crystallization peak of LDPE has appeared as a sharp and narrow peak at 95.03°C (T_c). EPDM shows a blunt and somewhat wide crystallization peak at 32°C (**Fig. 2b**). It is seen that blending of EPDM with LDPE causes the shifting of crystallization temperature of LDPE to lower temperature range though for LE82 Tc does not change (**Table 2**). The T_cs of LDPE and EPDM in LE 82 blends are found to be 94.68 and 50.0°C and LE 55 shows the $T_c s$ of LDPE and EPDM at 88.03 and 43.0, while LE 28 exhibits the crystallization temperature of LDPE and EPDM at 84.12 and 36.1°C respectively. So it is revealed that EPDM, being in a molten state during crystallization of LDPE, does not act as nucleating agent for LDPE crystallization.

Again, interestingly it is noticed that as the LDPE content is increased in blends Tc of EPDM keeps on increasing (Tc of LE28, LE55 and LE82 are 36.1, 43.0 and 50°C respectively). This is due to the presence of already formed solid LDPE crystals in molten EPDM phase (**Table 2**), which acts as nucleating agent turning the nucleation process of EPDM heterogeneous (Ray Chowdhury and Sabharwal, 2011).

The electron beam crosslinking shows influence on the crystallization Temperature (T_c) of the blends, which is prominent at higher doses (**Table 2**). For all crosslinked blends, T_c of LDPE is decreased due to movement restriction of polymer chains engaged in network formation. Due to compact network formation crystallizing efficiencies of chains are reduced. In all blends T_c of EPDM has a tendency to go down at high irradiation dose (**Table 2**). Once the EPDM content is high (LE55 and LE28) then after crosslinking T_c of EPDM does not appear at all. As crosslinking efficiency of EPDM is high, thus at high dose, higher EPDM containing blends will show higher degree of crosslinking. That's why crystallization is very much discouraged due to higher degree of restriction of polymer chain movement.

However, the irradiation of TMPTA and TAC added blends (80 kGy dose is reported here) bring the similar effect on Tc of LDPE and EPDM in all three blends (**Table 2 and Fig. 2b to 4b**).

Another important parameter, the heat of fusion (melting peak area) i.e., amount of crystallinity is significantly affected by blend compositions as well as radiation dose (**Table 2 and Fig. 2a to 4a**). Neat LDPE and EPDM exhibit heat of fusion to be 83.01 and 25.79 Jg^{-1}, consequently 34.73 and 10.79% crystallinity respectively (**Table 2**). The addition of EPDM in LDPE leads to decrease heat of fusion i.e., crystallinity of LDPE in blends of higher EPDM content. But crystallinity of EPDM is almost same in all unirradiated blends. LE 82 illustrates 85.25 and 21.13 Jg^{-1} heat of fusion i.e., 35.66 and 8.84% crystallinity for LDPE and EPDM respectively. LE 55 shows 68.94 and 26.78 Jg^{-1} heat of fusion i.e., 28.84 and 11.20% crystallinity for LDPE and EPDM respectively. While LE 28 blend exhibits the 55.0 and 23.4 Jg^{-1} heat of fusion i.e., 23.01 and 9.79% crystallinity for LDPE and EPDM respectively. EPDM being amorphous in nature does not encourage crystallization of LDPE while mixed with the later.

Upon exposure to electron beam irradiation, the degree of crystallinity of all LDPE/EPDM blends (for both the phases) decreases with increase of electron beam dose level (**Table 2**). In LE 82 the crystallinities of LDPE and EPDM come down to 27.26 and 4.28% after irradiation at 120 kGy. For crosslinked (120 kGy) LE 55, the crystallinities of LDPE and EPDM go down to 24.59 and 3.93%. For LE 28, irradiated at 120 kGy, the % crystallinities become 15.12 and 2.79% for LDPE and EPDM respectively.

It is well known that due to interwoven conformation of polymer chains crosslinking takes place mainly in amorphous zone (Ray Chowdhury *et al*., 2012a). Once in amorphous phase the crosslinking takes place, the crosslinked phase may shrink. That may reduce the crystallinity rupturing some crystal domains, as common chains are involved in crystalline as well as amorphous phase of polymer. In addition to that due to interaction of crystalline phase with high energy radiation, some crystal domains may be destroyed while crosslink formation, reflecting reduced crystallinity.

The expected trend of reduction in degree of crystallinity has been seen in TMPTA and TAC added LE 82, LE 55 and LE 28 blends. As from the gel content analysis (**Fig. 1**) we have seen that for TMPTA and TAC added samples the degree of crosslinking is more, TMPTA having an edge over TAC. Thus, due to increased degree of crosslinking the effect of radiation dose on the crystallinity should be higher in presence of TMPTA and TAC. That's why it is obvious from **Table 2 and Fig. 2a to 4a** that the degree of crystallinity for TMPTA and TAC containing sample are considerably lesser than that of crosslinked blends without crosslinking agents. The reduction of crystallinity for TMPTA containing sample is more than TAC containing ones. That is certainly due to higher degree of crosslinking in presence of TMPTA.

3.3. Thermogravimetric Analysis (TG)

Thermogravimetric analysis (TG) has been used to study the degradation behavior of unirradiated and EB irradiated LDPE/EPDM blends. The Thermogravimetric analysis (TG) graphs of neat LDPE, neat EPDM and their blends before and after irradiation are depicted in **Fig 5a and b** and the results are presented in **Table 3**. Both unirradiated and irradiated blends show single step degradation (**Fig. 5**) as the degradation temperature of EPDM and LDPE are very close.

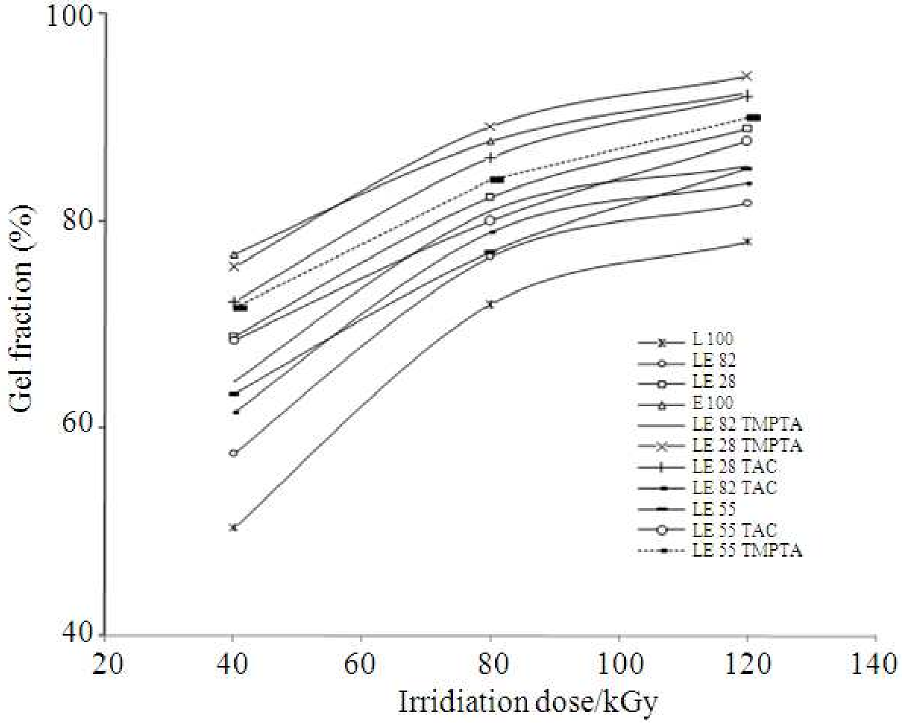
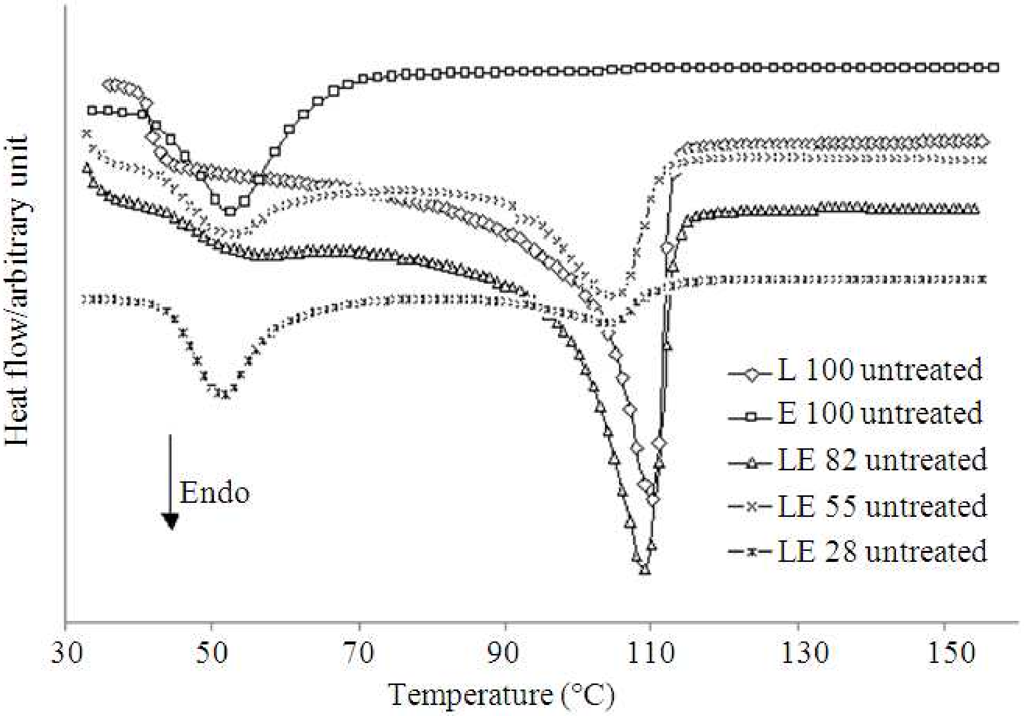
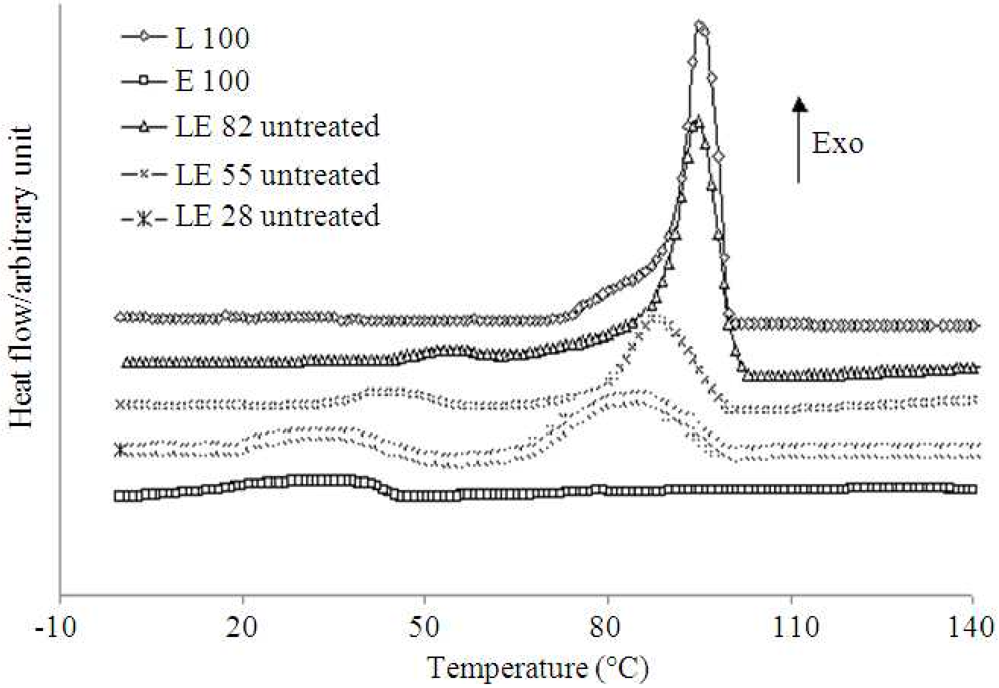


Fig. 1. Variation of gel fractions with blend composition and electron beam irradiation dose

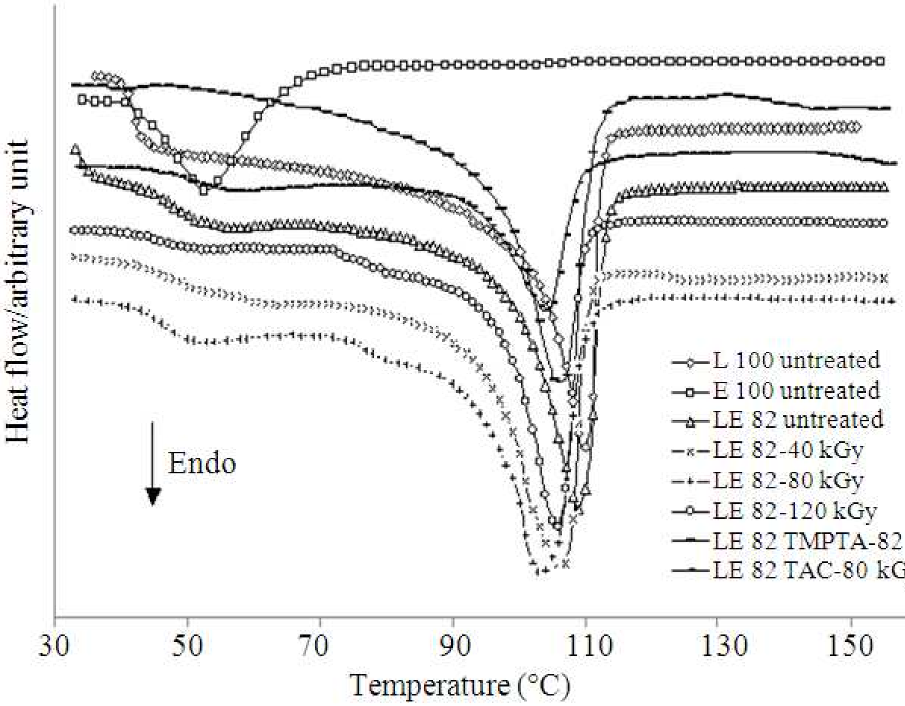


(a)

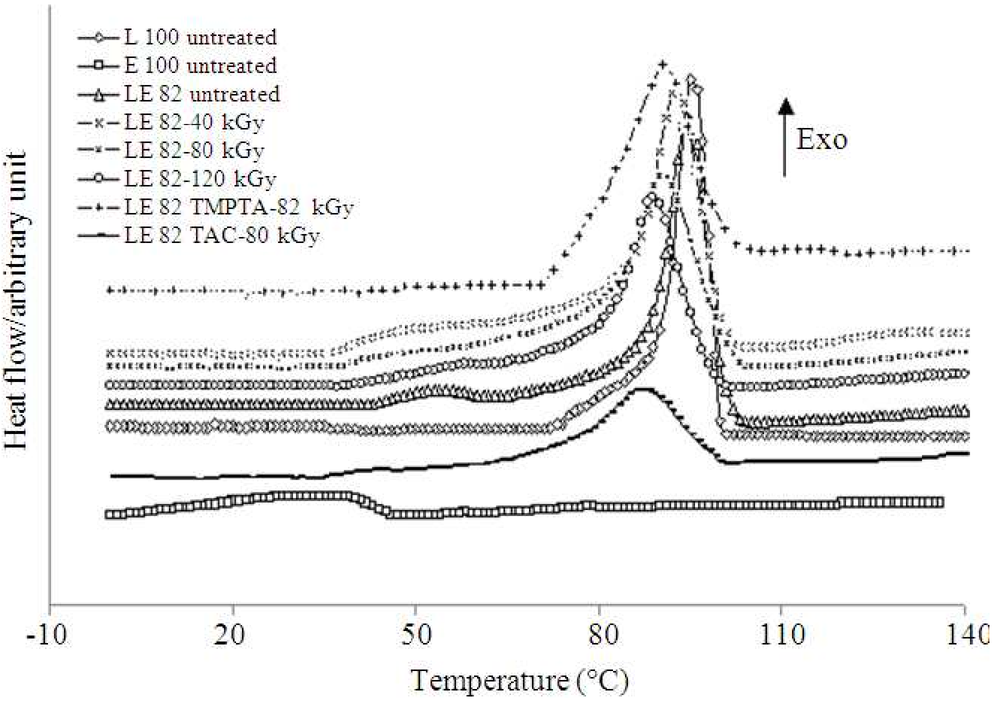


(b)

Fig. 2. (a) Effect of blend ratio on the melting behavior (heating mode) of LDPE/EPDM blends. (b) Effect of blend ratio on the crystallization behavior (cooling mode) of LDPE/EPDM blends

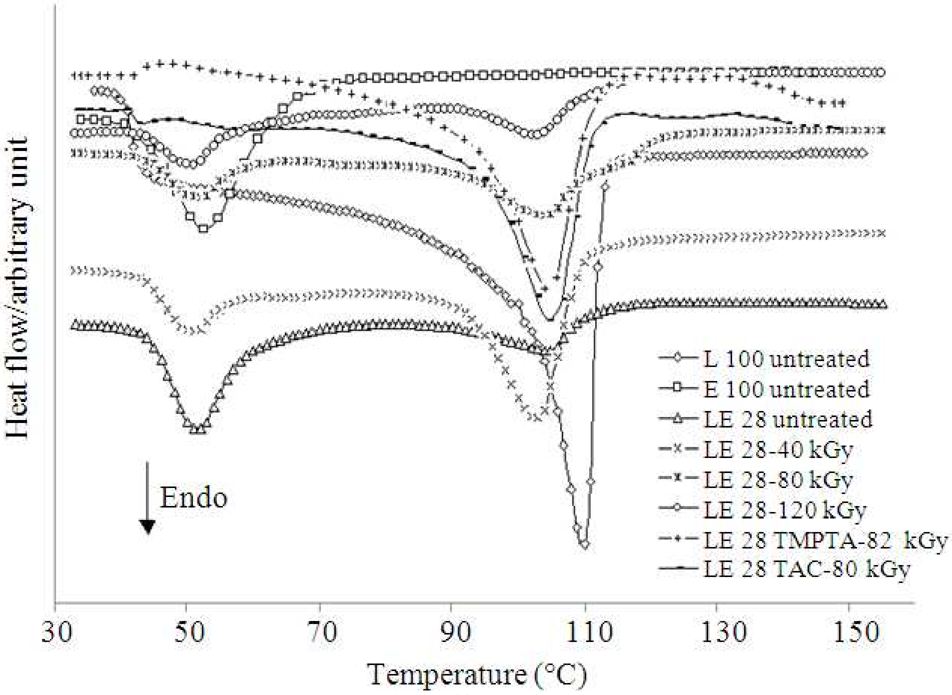


(a)

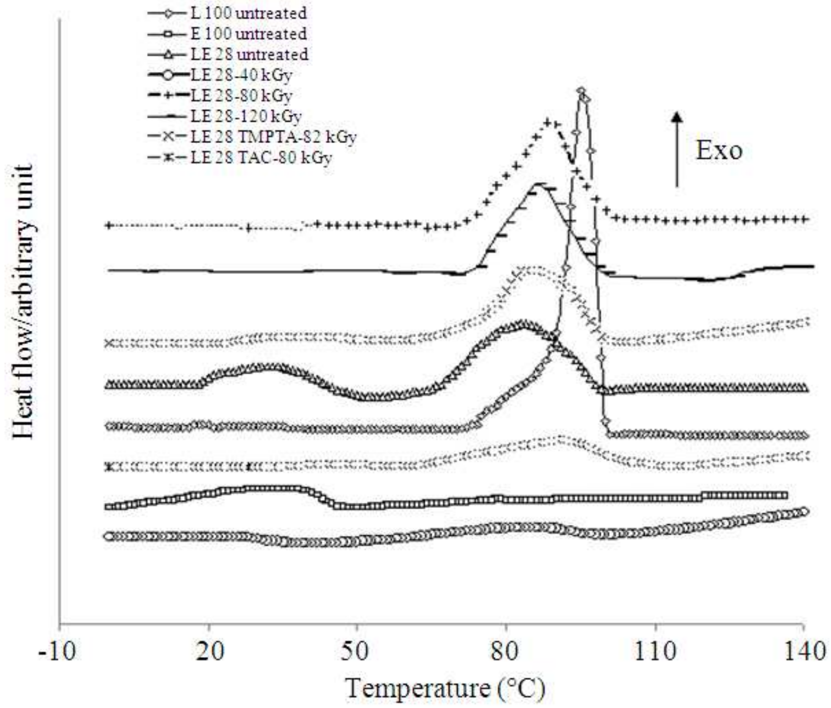


(b)

Fig. 3. (a) Effect of irradiation on the melting behavior (heating mode) of LE 82 blends. (b) Effect of irradiation on the crystallization behavior (cooling mode) of LE 82 blends

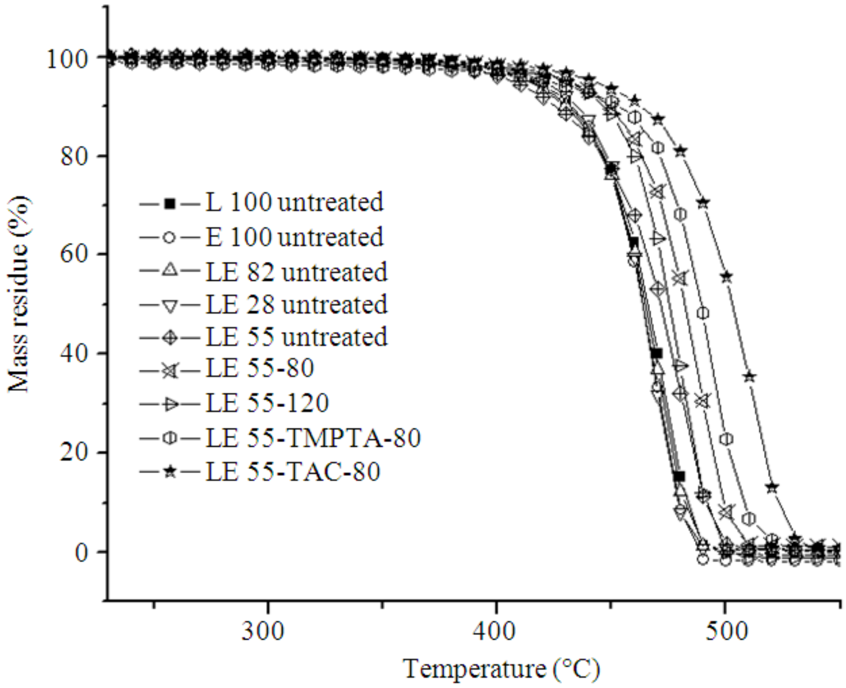


(a)

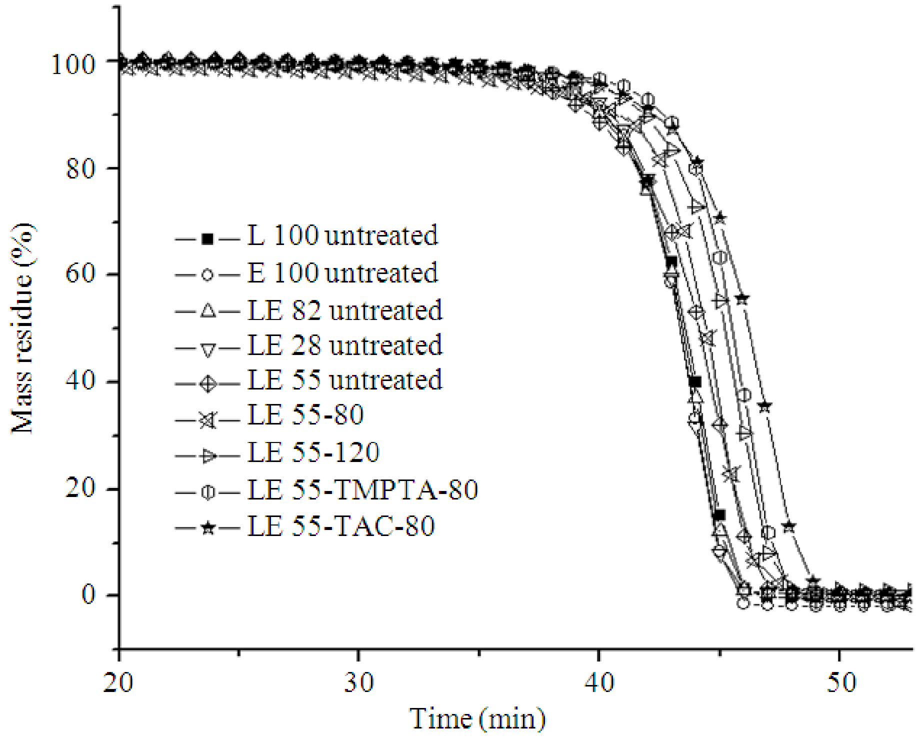


(b)

Fig. 4. (a) Effect of irradiation on the melting behavior (heating mode) of LE 28 blends. (b) Effect of irradiation on the crystallization behavior (cooling mode) of LE 28 blends



(a)



(b)

Fig. 5. (a) TG: Change of mass of LDPE/EPDM blends before and after irradiation with temperature. (b) TG: Change of mass of LDPE/EPDM blends before and after irradiation with time

Table 2. DSC parameters

	Tm/ºC		Tc/ºC		ΔHm/Jg^{-1}		% Crystallinity/Xc	
Samples	LDPE	EPDM	LDPE	EPDM	LDPE	EPDM	LDPE	EPDM
LDPE	110.03	-	95.030	83.010	-	34.73	-	
EPDM	-	52.62	-	32.000	-	25.79	-	10.79
LE 82 untreated	109.01	52.14	94.680	50.000	85.25	21.13	35.66	8.84
LE82-40 kGy	106.01	53.02	93.010	48.020	78.42	16.21	32.81	6.86
LE82-80 kGy	104.61	51.40	90.000	44.000	66.17	14.25	27.68	5.96
LE82-120 kGy	106.01	49.01	89.000	46.000	65.17	10.25	27.26	4.28
LE82 TMPTA-80 kGy	105.27	-	91.340	-	39.01	-	16.32	-
LE82 TAC-80 kGy	104.01	53.00	87.010	45.000	58.88	9.90	24.64	4.14
LE 55 untreated	105.00	54.00	88.030	43.000	68.94	26.78	28.84	11.20
LE 55-40 kGy	104.01	52.01	89.050	45.020	71.48	12.74	29.61	5.33
LE 55-80 kGy	103.02	51.06	85.020	-	62.96	11.16	26.34	4.67
LE 55-120 kGy	102.31	49.02	79.130	-	58.78	9.38	24.59	3.93
LE 55 TMPTA-80 kGy	104.35	52.54	83.310	-	51.30	4.70	21.46	1.96
LE 55 TAC-80 kGy	105.52	51.79	84.020	-	59.00	7.32	24.68	3.06
LE 28 untreated	104.22	51.94	84.120	36.100	55.00	23.40	23.01	9.79
LE28-40 kGy	103.08	51.35	85.000	-	49.25	9.17	20.60	3.83
LE28-80 kGy	105.02	52.13	89.700	-	39.20	7.88	16.40	3.30
LE28-120 kGy	103.03	50.80	86.010	-	36.15	6.67	15.12	2.79
LE28 TMPTA-80 kGy	104.92	52.93	88.410	-	24.85	7.33	10.39	2.45
LE28 TAC-80 kGy	105.40	54.47	86.810	-	32.90	5.86	13.76	3.07

Table 3. TG parameters

Sample code	Onset temperature (T_i/°C)	Degradation temperature (T_d/°C)	Temperature corresponding to 30% mass loss (T_{30}/°C)	Temperature corresponding to 50% mass loss (T_{50}/°C)	Temperature corresponding to 90% ass loss (T_{90}/°C)	Activation energy, (E/kJmol^{-1})
L 100 untreated	370	430	455	465	480	270.00
E 100 untreated	380	440	460	470	490	333.04
LE 82 untreated	370	431	454	463	482	297.24
LE 28 untreated	390	442	459	466	480	324.34
LE 55 untreated	368	448	459	471	489	345.28
LE 55-80	379	457	475	480	498	376.00
LE 55 -120	330	460	465	480	494	332.66
LE 55-TMPTA-80	380	473	476	493	508	410.05
LE 55-TAC-80	388	488	491	505	528	458.76

The **Table 3** shows onset temperature (T_i, temperature corresponding to 1% mass loss), degradation temperature (T_d) and temperatures corresponding to 30, 50 and 90% mass loss (T_{30}, T_{50} and T_{90}). Neat LDPE shows degradation at 430°C (T_d), whereas neat EPDM shows degradation at 440°C (**Table 3**). The higher degradation temperature of EPDM indicates its higher thermal stability than LDPE. Same trend is noticed for T_i of LDPE and EPDM also i.e., LDPE starts degradation earlier (370°C) than EPDM (380°C). Interestingly, T_{30}, T_{50} and T_{90} of EPDM are also found higher than those of LDPE. The T_i, T_d and speed of degradations (T_{30}, T_{50} and T_{90}) depend on structural factors, such as molecular structure, crystalline structure and degree of crystallinity. In this case though amount of crystallinity of LDPE is higher than that of EPDM, but due to presence of aliphatic cyclic ring in EPDM molecule, thermal stability becomes higher for EPDM (Barra *et al*., 1999).

Thermal Degradation temperatures (Td) for blends increase with increase in EPDM content. Interestingly, for LE 55, T_d and T_{90} are higher than those of LE 82 and LE 28. Though, no appreciable change is observed for T_i, T_{30} and T_{50}.

Blend composition is an important decisive factor for degree of compatibility and morphology of blends (Jose *et al*., 2008). Due to equal proportion of two polymers the degree of compatibility may be higher than LE28 and LE 82 or the generated morphology is such that can discourage thermal degradation.

For LE 82 and LE 55, Tis are almost same but for LE 28, Ti increases to 390°C. This is due to presence of more thermally stable EPDM in higher proportion.

However, electron beam irradiation of polymer may promote or demote the thermal stability by interchain crosslinking or degradation. We have investigated here the influence of electron beam irradiation on the thermal stability of LE55 blends in absence and presence of TMPTA and TAC, two widely used crosslinkers.

Ti of LE 55-80 (LE55 irradiated at 80 kGy as denoted in **Table 1**) appears at 379°C, where as for unirradiated LE55, T_i occurs at 368°C. Again, Td of LE55 increases by 12°C after irradiation at 80 kGy (**Table 3**). On the other hand, T_{30}, T_{50} and T_{90} of LE55 also increase by 17, 9 and 7°C respectively after irradiation. But at higher dose (120 kGy) Ti of LE55 goes down to 330°C (T_i of LE55 is 368°C). Also from the T_d, T_{30}, T_{50} and T_{90} values it is obvious that the changes are not expected as compared to sample irradiated at 80 kGy (**Table 3**). This may be due to two reasons. It is well known that during high energy irradiation, degradation and crosslinking of polymer occur simultaneously at different speeds and resultant effect is obtained. One reason may be occurrence of high degree of polymer chain scission along with crosslinking at higher dose (120 kGy). The other possibility is that as the degree of crosslinking is very high, so samples are under internal stress, which leads to less thermal stability. Second explanation is more acceptable as gel content results hint no degradation of polymer chains while irradiating at higher dose (**Fig. 1**).

Again irradiation at 80 kGy (LE55-80), in presence of TMPTA and TAC promotes the thermal stability of LE55 remarkably. In presence of TMPTA and TAC the degree of crosslinking is more as seen in **Fig. 1**. Due to the high degree of crosslinking TMPTA and TAC containing samples are more thermally stable than without one. Interestingly, TAC containing LE55 shows more thermal stability than TMPTA containing LE 55 at 80 kGy. T_i, T_d, T_{30}, T_{50} and T_{90} all of LE55-TAC-80 is higher than LE55-TMPTA-80, though degree of cross linking of TMPTA containing sample is more than TAC containing sample. It is apparently controversial but due to presence of aromatic hexagonal moiety in Tri Allyl Cynuerate (TAC), heat resistant of TAC is higher than aliphatic Trimethyl Propane Triacrylate

(TMPTA) (Makuuchi and Cheng, 2012). Thus thermal stability of TAC containing sample is higher as it has become a part of the crosslinked network structure of polymer bridging two polymer chains.

To observe the effect of blend composition and electron beam irradiation on the activation Energy (E), Coats-Redfern integral method as mentioned in experimental part has been used. These results are tabulated in **Table 3**. The E of pure LDPE (L-100) and EPDM (E-100) are found to be 270.81 and 333.04 kJmole^{-1} respectively before irradiation, which are in agreement with reported values of Ea of LDPE and EPDM (Kayacan and Doğan, 2008; Abadir, 2013). From **Table 3**, it is noticed that for LE 82 and LE28, E are found to be 297.24 and 324.34 kJmole^{-1}, thus with increasing EPDM content thermal degradation of the blend is discouraged obviously due to higher inertness of EPDM towards degradation. For LE55, the E is even more than E of LE28 like T_i, T_d, T_{30}, T_{50} and T_{90} due to same reason, the effect of blend composition as discussed above. Upon irradiation at 80 kGy, E of LE55 increases remarkably (E of LE55 at 80 kGy is 376.43 kJmole^{-1}). E of LE55 further is increased in presence of crosslinkers (E for LE55-TMPTA-80 and LE55-TAC-80 are 410.05 and 458.02 kJmole^{-1}) due to higher degree of crosslinking. TAC containing samples, due to having aromatic unit in molecular structure and involvement of the later in crosslinking, show higher Ea than TMPTA containing samples.

For LE55-120, E is reduced compared to LE55 like T_i and T_d. The reason is same as discussed above.

4. CONCLUSION

The present research work dealt with the investigation of the effect of blend ratio and EB irradiation on the crystallization and thermal stabilities of LDPE/EPDM blends. Blend composition and EB dose has been found to have significant effect on crystallization as well as thermal stability of the blends. DSC reveals that melting Temperatures of (T_m) of blends are found to remain unchanged by irradiation. The degree of crystallinity and T_c has been found to be decreased with increase of EPDM content as well as electron beam radiation dose. Crosslinkers (TMPTA and TAC) further reduce the crystallinity (X_c) in irradiated blends. Thermal stability of blends (with respect to T_i, T_d, T_{30}, T_{50}, T_{90} and E) is enhanced with increase in the proportions of EPDM in the blends as well as electron beam irradiation. In presence of TMPTA and TAC, due to higher degree of crosslinking the effect is more on the above mentioned properties. Due to presence of aromatic moiety in TAC, TAC containing blends are thermally more stable than TMPTA containing blends. At higher dose (120 kGy) chain scission takes place reducing the effect of crosslinking on the properties.

Appendix

Calculation of activation energy of degradation by integral method of Coats and Redfurn.

Theory

The fractional degradation of polymeric material can be expressed in terms of mass change by the following Equation 3:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \tag{3}$$

where, w_o, w and w_∞, are the initial, at any instant during thermal analysis and final mass of the samples, respectively.

Rate of degradation can be expressed in order based reaction kinetics and it can be written as:

$$-\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{4}$$

The rate of reaction is proportional to the nth power of un-reacted part of the sample. The power n is considered as the order of the reaction and k is reaction rate constant. But this rate constant is a function of temperature which can be expressed by Arrhenius Equation:

$$k = Ae^{-E/RT} \tag{5}$$

where, E is the activation energy of the reaction. Substituting k from Equation 5 into Equation 4 results the following Equation:

$$-\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^n \tag{6}$$

After separating the variables from Equation 6 the following Equation can be obtained Equation 7 and 8:

$$-\frac{d\alpha}{(1-\alpha)^n} = Ae^{-E/RT}dt \tag{7}$$

$$The\,rate\,of\;\;heating\,\beta\;=\frac{dT}{dt}$$

Or:

$$dt=\frac{dT}{\beta} \tag{8}$$

Putting the expression of *dt* in Equation 7 and integrating between limits T_1 and T_2 Equation 9:

$$-\int_{0}^{\alpha}\frac{d\alpha}{(1-\alpha)^n}=\frac{A}{\beta}\int_{T_1}^{T_2}e^{-\frac{E}{RT}}\,dT \tag{9}$$

But the integral at the right side $_{T1}\;^{T2}e^{-E/RT}dT$ has no analytical solution. Therefore several approximate solutions of the equations have been given in literature (Coats and Redfern, 1964; Baloch *et al*., 2011; Flynn and Wall, 1966; Kissinger, 1957).

But in our investigation, the solution given by (Coats and Redfren, 1964; Baloch *et al*., 2011) has been used to determine the activation energy of the degradation reaction. The approximate solution of the integral as per this method is like the following:

$$In\left[\frac{-In(1-\alpha)}{T^2}\right]-In\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}\;\;(\,for\;\,n=1) \tag{10}$$

Integral as per this method is like the following.

And Equation 11:

$$In\left[-In\left\{\frac{1-(1-\alpha)^n}{(1-n)^{T^2}}\right\}\right]=In\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] -\frac{E}{RT}\;\;(\,for\;\,n\neq 1) \tag{11}$$

Thermal degradation of LDPE and EPDM is considered as first-order reaction as (Kayacan and Doğan, 2008) reported it as first order from the reasonable data fit to straight lines (Kayacan and Doğan, 2008). Thus Equation 10 has been considered for our system.

As $2RT/E$ is much lower than unity then a plot of ln [-*ln* (1-α)/T^2] against $1/T$ from Equation 10 should give a straight line. From the slope of that line the activation Energy (E) was calculated.

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