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Thermochimica Acta 438 (2005) 70–75

thermochimica acta

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Thermal stability of LDPE, iPP and their blends

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Received 27 March 2005; received in revised form 10 August 2005; accepted 10 August 2005
Available online 3 October 2005

Abstract

The thermal decomposition reaction of LDPE, iPP and LDPE/PP blends irradiated with accelerated electrons has been investigated with TGA and DSC. TGA showed only one degradation step at different temperatures according to the type and composition of the samples. LDPE exhibited the highest thermal stability compared with either iPP or LDPE/iPP blends; LDPE/iPP blends showed intermediate thermal stability. TMPTMA loading and irradiation enhanced the thermal stability of all samples. The obtained TGA data by the stimulation method illustrated that the compatibility between LDPE and iPP in their blends takes place during mixing and irradiation processes, where only one degradation step was observed in the experimental TGA data instead of two degradation stages that appeared in the arithmetic calculation curve of the blend. The melting temperature decreased for TMPTMA loaded LDPE, whereas irradiation and/or loading with TMPTMA did not change the melting temperature of iPP. LDPE/iPP (50/50 wt%) showed a drop in melting temperature compared with the components. The glass transition temperatures increased as a result of modification either by TMPTMA loading or irradiation.

Keywords: LDPE; iPP; LDPE/iPP; TMPTMA; EB-irradiation; TGA and DSC

1. Introduction

Blending of different plastic resins has long been practiced to tailor blends for specific processing and performance requirements. Blends of PE and PP are among those binary systems that have attracted much attention [1]. Radiation-modified blends of polyolefins are commercially important. Radiation crosslinked polyethylene is widely used in wire and cable and heat shrinkable tubing. Ionizing radiation causes chain scission and crosslinking of the polymer chains of PP in roughly equal probability, while crosslinking is predominant in the case of PE [2,3].

Preparation of LDPE/PP blends is hindered by the low compatibility of this polymer pair. The compatibility might be improved by addition of a compatibilizing agent and electron beam irradiation. When two polymers are mixed together, the most frequent result is a system that exhibits almost total phase separation due to the entropy of mixing [4]. Addition of TMPTMA during sample processing is used to improve miscibility. The polyfunctional monomer (TMPTMA) may reduce the interfacial tension and increase the adhesion force between the polymer phases allowing a finer dispersion and more stable morphology [5]. The compatibility of a polymer blend can be affected by species produced during thermo-oxidation, e.g. carbonyl groups. These species may act as a compatibilizer, and play an important role in enhancing crosslinking. PP degradation can be avoided by addition of antioxidants such as phenols, quinines and polyfunctional monomer [6–8].

The purpose of this study is to gain knowledge about the thermal stability of unirradiated, unmodified, irradiated and TMPTMA modified LDPE, iPP and LDPE/iPP blends. TGA and DSC were used to determine the effects of different blending ratios of LDPE and iPP and the degradation characteristics of the blends on their thermal stability, melting point, crystallinity and glass transition temperature.

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doi:10.1016/j.tca.2005.08.017

2. Experimental

2.1. Materials

Low density polyethylene pellets were produced in Lortrene, CDF Company, France, and supplied by El Sewedy Company for plastic industry (Sedplast), 10th Ramadan city, Cairo, Egypt. The density of the LDPE is 935 kg/m^3, melt flow index (MFI) ≅ 3.5 g/10 min and its crystallinity ratio is about 45%.

Isotactic polypropylene pellets (PRO-FAX) were supplied from Tecno Back Company, Cairo, Egypt. The density is about 900 kg/m^3, MFI = 0.8, its crystallinity ≅ 65%.

The polyfunctional monomer used throughout this work was trimethylol propane trimethacrylate (TMPTMA) (M.wt. = 338) (produced by Shin Nakamura Chemical Co., Ltd., Japan), with the molecular structure:

$CH_3{-}CH_2{-}C{-}(R)_3$

where R = {$-CH_2{-}O{-}C(O){-}C{-}(CH_3){=}CH_2$}, $C_{18}H_{26}O_6$.

2.2. Irradiation process

Irradiation was carried out in air at ambient pressure and temperature with a 1.5 MeV electron beam accelerator. All polymeric samples were irradiated on one side with a current of 10 mA and scan width variable up to 90 cm. The polymeric samples were exposed to an irradiation dose of about 5 kGy on each pass. Higher irradiation doses were collected in multipass runs.

2.3. Sample preparation

LDPE, iPP and LDPE/iPP blends with different ratios (LDPE/iPP, 100/0.0, 80/20, 50/50, 20/80 and 0.0/100 wt%) were prepared by melt mixing in a laboratory mixer (Plasticorder PL2100). The mixing process was carried out at 413 K for LDPE pellets and thereafter, raising the temperature to 438 K after adding iPP pellets till complete mixing was obtained. Different concentrations (1, 3, and 5 wt%) of polyfunctional monomer (TMPTMA) were added after complete mixing. This process was carried out at 60 rpm for 5 min. The polymer mixture was immediately transferred from the mixer to an open roll-mill to sheet. Sheets of 1.0 mm thickness were obtained by hot pressing at 438 K for 5 min (2 min preheating and 3 min at 15 MPa). The molded plastic sheet was then immediately transferred to water-cooled press at the same pressure.

2.4. Thermal analysis

TGA studies were carried out on a TGA-50 (Shimadzu, Japan), in the temperature range 298–873 K in an atmosphere of nitrogen gas at a heating rate of 10 °C/min.

DSC was done with a Perkin-Elmer DSC-7. The sample weight (5.0 mg) was sealed inside an aluminum pan. DSC measurements were carried out in nitrogen atmosphere at 153–473 K at 10 °C/min.

3. Results and discussion

3.1. Low density polyethylene (LDPE)

Fig. 1 displays the thermogravimetric curves of LDPE. The start and end temperatures of the degradation depends on irradiation and the presence of TMPTMA. An increase in the degradation temperature due to irradiation and to incorporation of 3 wt% of TMPTMA is observed. The onset temperature (T_i) and the weight loss percents at different temperatures show that irradiation and/or 3 wt% TMPTMA results in increasing the onset temperature T_i, T_s (temperature at maximum rate of reaction ($\mathrm{d}\alpha/\mathrm{d}t$), where α is the reacted fraction for a weight loss system at constant rate of heating, α is given as $(w_0 - w_t)/(w_0 - w_\infty)$ where w_0, w_t and w_∞ are the initial sample weight, sample weight at time t and at infinite time, respectively) and lower weight loss (Table 1). This can be attributed to the larger extent of three-dimensional networks (i.e., crosslinking). At a given temperature, the values of weight loss is in the order: unmodified LDPE > irradiated > TMPTMA loaded > loaded and irradiated.

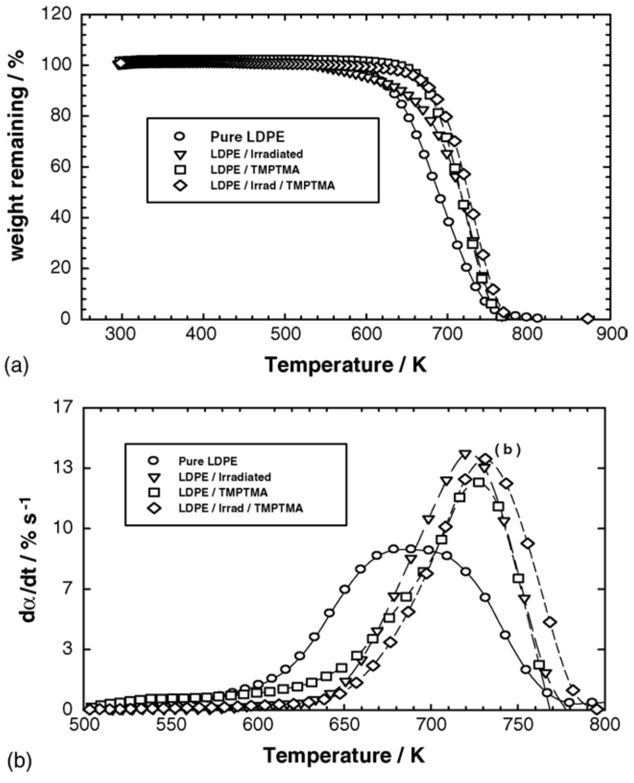

Fig. 1. Thermogravimetric curves and $\mathrm{d}\alpha/\mathrm{d}t$ as functions of temperature for LDPE.

Table 1
Beginning and ending temperatures and weight loss % for LDPE, iPP and LDPE/iPP (50/50 wt%)

Sample	Dose (kGy)	TMPTMA (wt%)	T_i (K)	T_s (K)	Weight loss % at different temperatures (K)			
					573	623	673	723
LDPE	0.0	0.0	618	690	2.1	6.5	33.5	74.3
	30	0.0	633	720	1.2	6.2	17.5	56.2
	0.0	3.0	643	725	0.75	3.4	5.8	55.5
	30	3.0	653	730	0.05	1.2	5.2	41.7
iPP	0.0	0.0	513	568	62.5	93.1	95.0	96.2
	30	0.0	538	633	15.2	45.1	85.5	89.3
	0.0	3.0	573	653	6.2	31.1	92.3	100
	30	3.0	603	680	1.8	10.1	48.4	95.8
LDPE/iPP, 50/50 wt%	0.0	0.0	588	638	3.9	13.5	60.3	92.5
	30	0.0	593	663	2.6	10.6	55.1	94.5
	0.0	3.0	598	673	2.2	7.2	44.5	85.5
	30	3.0	633	693	0.1	4.5	29.0	85.5

3.2. Isotactic polypropylene (iPP)

TGA curves of unstabilized and stabilized iPP samples are depicted in Fig. 2a. The variation in the TGA curves differ more than for LDPE. Fig. 2b shows dα/dt versus temperature for iPP. The effect of both irradiation and incorporation of TMPTMA led to enhanced thermal stability of iPP in the same manner as with LDPE. T_i, T_s, and weight loss at temperatures through the entire range showed that unstabilized iPP exhibited lower thermal stability than unstabilized LDPE (see Table 1).

3.3. LDPE/iPP blends

Fig. 3 represents the TGA curves of LDPE/iPP (50/50 wt%) blend. The shift in T_i, T_s and the weight loss at different temperatures for LDPE/iPP blends compared to iPP indicated that the LDPE/iPP blend is of intermediate thermal stability between iPP and LDPE (see Table 1).

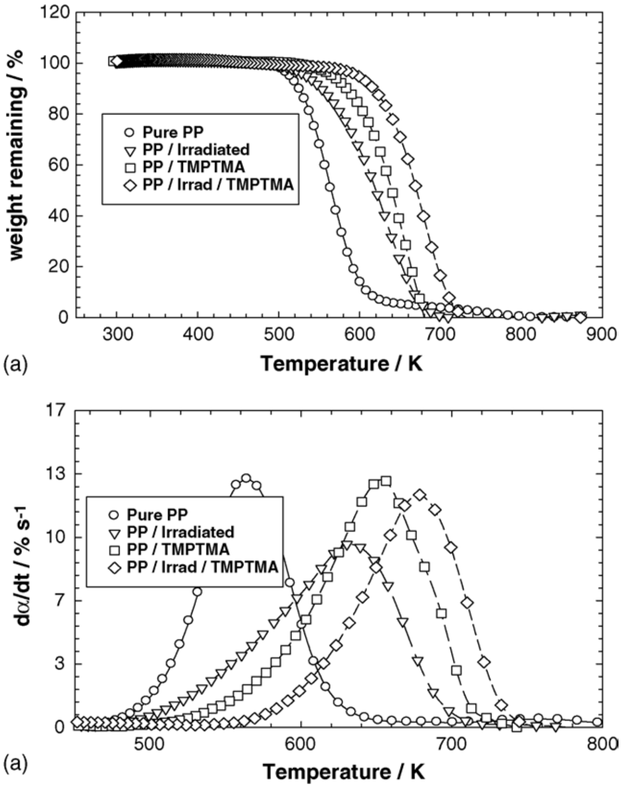

Fig. 2. Thermogravimetric curves and dα/dt as functions of temperature for iPP.

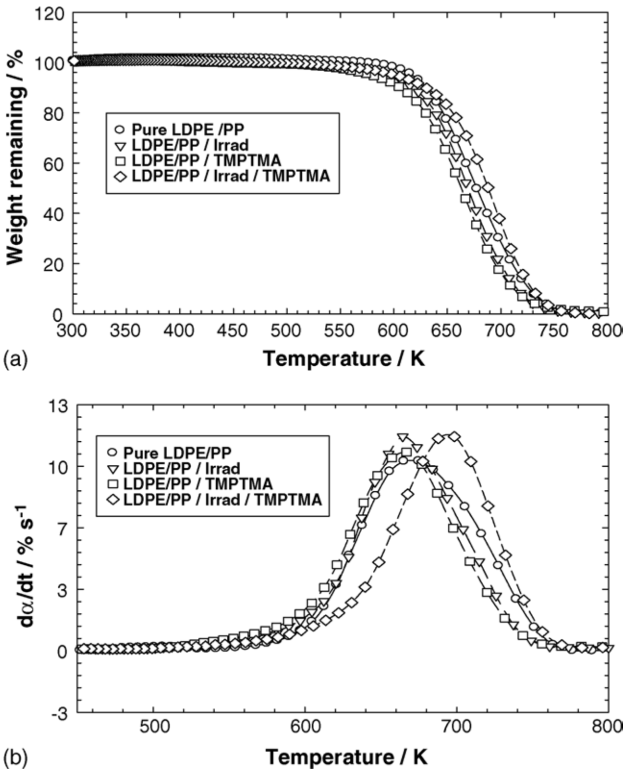

Fig. 3. Thermogravimetric curves and dα/dt as functions of temperature for LDPE/iPP (50/50 wt%) blends.

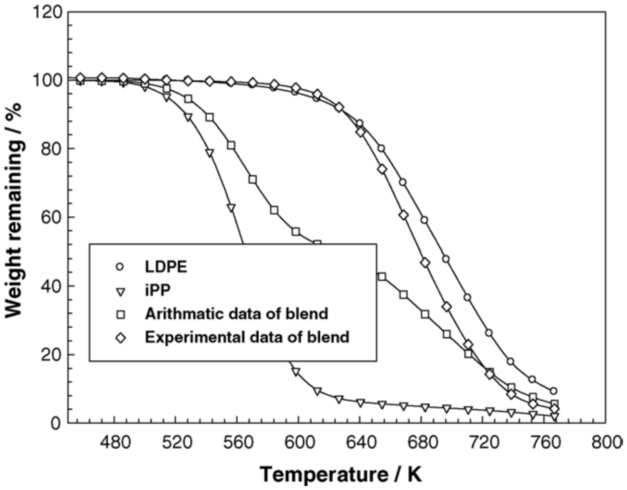

Fig. 4. TGA curves of LDPE, iPP, as well as the experimental and arithmetic data for unmodified LDPE/iPP (50/50 wt%) blend.

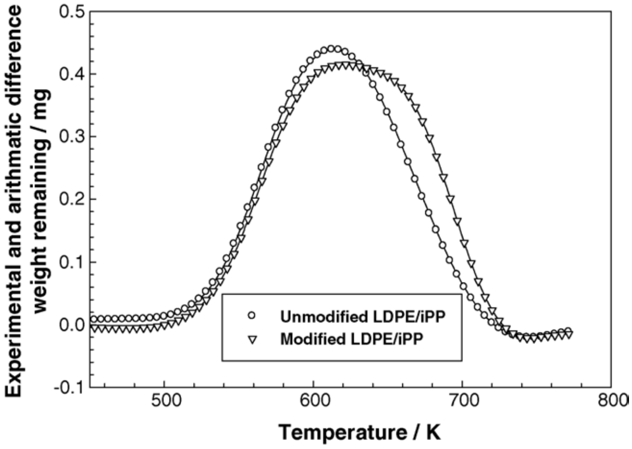

Fig. 5. The experimental and arithmetic difference in residue weight of unmodified and modified LDPE/PP (50/50 wt%) blends.

3.3.1. Simulation of LDPE/iPP (50/50 wt%) blends with individual LDPE and iPP data

Polypropylene is more sensitive to thermal heating than polyethylene which can sustain higher temperatures without substantial chain scission or degradation compared to polypropylene [6–9]. If polyethylene and polypropylene are blended together by 50/50 wt% assuming no chemical interaction between the degradation products, then the degradation characteristic of the blend, i.e., the weight loss at a given temperature appears as the summation of weight losses of each individual polymer. If there are interactions between the degradation products of the two individual polymers, the thermal characteristics of the blend will differ from the summation. This accelerates or retards the gradation [7,10].

Fig. 4 represents the weight remaining percents of individual LDPE and iPP, as well as experimental and arithmetic residues of LDPE/iPP (50/580 wt%) blend as a function of temperature. The difference between the experimental remaining weight and the arithmetic values of unmodified and modified (loaded with TMPTMA and 30 kGy irradiated) blends are plotted in Fig. 5. The difference between the experimental and arithmetic remaining weight values appears at 513 K, the temperature at which unmodified iPP begins to degrade. Thereafter, the values of the difference between the experimental and arithmetic data continue to increase up to maximum values at 613 and 633 K for unmodified and modified blend, respectively. Beyond the maximum difference, the difference decreases to reach zero at 733 K (Fig. 5). The temperature at which the decrease begins at about 613–633 K, is equivalent to the beginning of LDPE decomposition. The difference in remaining weight of unmodified and modified LDPE/iPP (50/50 wt%) blend is the same through the region before LDPE begins to decompose. After the beginning of LDPE decomposition up to complete degradation, the modified blend exhibited a larger residue weight than unmodified blend. The reason is the induced crosslinking reaction that occurred with higher proportion in LDPE than iPP upon irradiation and presence of the TMPTMA.

The positive difference means that the experimental remaining weight is higher than the arithmetic one; hence, there is a protection against thermal degradation in the LDPE/iPP blend. The LDPE acts as stabilizer for iPP in the blend by retarding the autocatalytic propagation of tertiary carbon radicals, probably by crosslinking. The efficiency of LDPE as stabilizer diminishes beyond the temperature corresponding to the start of degradation of LDPE. The efficiency of LDPE continues to decrease as the temperature increases to 733 K.

The compatibility between LDPE and iPP takes place during mixing and processing of the blend through the interaction of the carbonyl group, on oxidation product [6]. Also, the compatibility of LDPE/iPP blend was mainly due to the interaction of LDPE and iPP during processing and irradiation. The role of irradiation and loading the blend with TMPTMA monomer appeared only at temperatures higher than 623 K.

3.4. Differential scanning calorimetry (DSC) analysis

3.4.1. Thermal characterization of LDPE and iPP samples

Fig. 6 shows the DSC scans of LDPE and iPP samples (unirradiated, loaded with 3 wt% TMPTMA and the loaded sample after it was exposed to 30 kGy of accelerated electrons). Table 2 shows the glass transition temperatures and the melting temperatures for LDPE and iPP samples. The glass transition temperature (T_g) of LDPE is 241 K in agreement with previous reports [11]. Loading LDPE with 3 wt% TMPTMA shifts T_g to 274 K. Exposing the loaded LDPE to 30 kGy irradiation dose increases the glass transition temperature (T_g) to 282 K. The increase in T_g could be attributed to introducing polar groups of TMPTMA; enhancing hydrogen bonding. Also, TMPTMA could disrupt the symmetry of LDPE molecular chains, converting it to an unsymmetrical matrix, with T_g about 306 K. TMPTMA may also induce

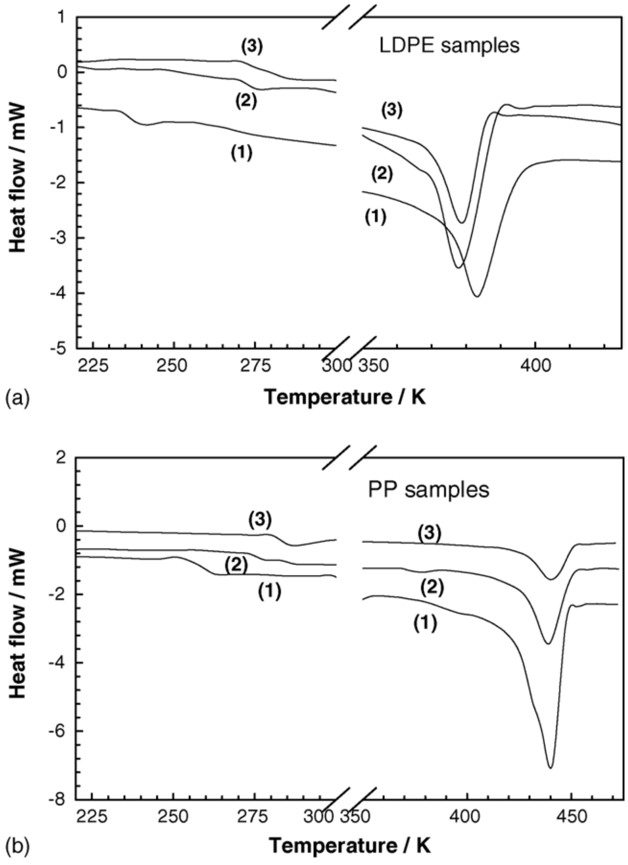

Fig. 6. DSC scans for LDPE and iPP samples {(1) unirradiated, (2) loaded with TMPTMA, and (3) irradiated/loaded with TMPTMA}.

crosslinking during sample processing but the influence on T_g is small [11–14].

From the proceeding, it is expected that the melting temperature (T_m) for LDPE treated by TMPTMA would increase; instead it was decreased by about 278 K. Presumably, the unreacted TMPTMA acts as a plasticizer causing the decrease in the melting temperature. The melting temperature is nearly unchanged for irradiated and TMPTMA loaded LDPE. The decrease in melting temperature may be attributed to the addition of 3 wt% TMPTMA which may reduce crystallinity, whereas irradiation (30 kGy) had no significant effect on the melting temperature for LDPE [11,12].

Table 2
Melting points and glass transition temperatures for unmodified and modified LDPE, iPP and LDPE/iPP

Polymer	TMPTMA (wt%)	Dose (kGy)	T_m (K)	T_g (K)
LDPE	0.0	0.0	383	241
	3.0	0.0	379	274
	3.0	3.0	378	282
iPP	0.0	0.0	440	263
	3.0	0.0	439	281
	3.0	3.0	440	286
LDPE/iPP	0.0	0.0	380 (LDPE), 436 (iPP)	255, 268
	3.0	0.0	380 (LDPE), 439 (iPP)	263
	3.0	3.0	379 (LDPE), 438 (iPP)	278

Table 2 shows the variation in the glass transition temperatures of the iPP samples. T_g for iPP behaved the same as LDPE (i.e., the same reason for T_g increase could be applied). The T_g of TMPTMA loaded iPP (281 K) was higher than the unloaded one (263 K). The radiation effect on loaded iPP may lead to crosslinking through the graft copolymer between iPP and TMPTMA and cause a significant increases in the glass transition from 263 to 286 K. The difference in the T_g values caused by loading and irradiation for loaded LDPE (306 and 283 K) are higher than that for iPP (291 and 278 K), respectively. This can be attributed to iPP being more sensitive to degradation than LDPE, hence decreasing the molecular weight during processing and mixing.

The DSC scans of unmodified iPP, loaded iPP with 3 wt% TMPTMA and 30 kGy irradiated loaded iPP showed a melting peak at 440, 439 and 440 K, respectively (see Fig. 6b). In contrast to LDPE, the melting temperature of iPP remains nearly unchanged upon TMPTMA incorporation. It seemed that the plasticization effect observed in the case of LDPE was absent for iPP. This can be attributed to the consumption of TMPTMA monomer in the crosslinking reaction during mixing and irradiation.

3.4.2. LDPE/iPP (50/50 wt%) polymer blends

Fig. 7 shows the DSC scans of LDPE/PP (50/50 wt%) blend. The DSC scans of this blend showed two endothermic peaks at about 380 and 436 K corresponding to the melting temperatures of the individual polymers. The melting temperature of iPP in the blend is however, increased from

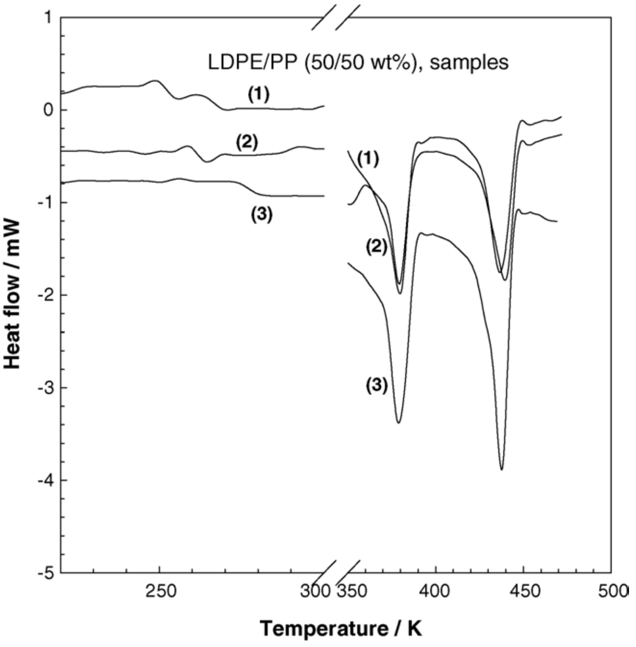

Fig. 7. DSC scans for LDPE/iPP (50/50 wt%) blends {(1) unirradiated, (2) loaded with TMPTMA, and (3) irradiated/loaded with TMPTMA}.

436 to 439 K by addition of TMPTMA. Upon exposing the TMPTMA loaded blend (LDPE/iPP, 50/50 wt%) to 30 kGy, the melting point decreased by 274 K. The melting temperature of LDPE in the loaded blend did not change and then decreased by 274 K upon exposing the TMPTMA loaded sample to 30 kGy irradiation (see Table 2).

4. Conclusion

Unmodified LDPE exhibited the highest thermal stability, whereas unmodified iPP has lower thermal stability than either unmodified LDPE or LDPE/iPP blend. The presence of LDPE in the blend affords protection against degradation. The addition of 3 wt% TMPTMA as a crosslinking agent enhances the thermal stability, especially unmodified iPP. Generally, the improvement in the thermal stability was: unirradiated < irradiated < incorporated by TMPTMA < irradiated and incorporated by TMPTMA. The compatibility between LDPE and iPP takes place during mixing and processing and instead of two degradation stages; only one decomposition step was observed. The melting temperature (T_m) decreased for TMPTMA loaded LDPE (3 wt%), whereas irradiation and/or TMPTMA loading did not show a significant effect on the melting temperature for iPP. The LDPE/iPP (50/50 wt%) blends showed a decreased melting temperature in comparison with individual polymers. The T_g for blend containing equal amounts of LDPE and iPP indicated a single T_g. An increase in T_g for the modified blends (30 kGy irradiation dose and/or 3 wt% TMPTMA loading) may be attributed to the occurrence of crosslinking reaction via the graft copolymerization between the blend components and the TMPTMA monomer.

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