

# Effect of Electron Beam Irradiation and Vinyl Acetate Content on the Physicochemical Properties of LDPE/EVA Blends

Z. I. Ali

National Center for Radiation Research and Technology, P.O. Box, 29 Madinat Nasr, Nasr City, Cairo, Egypt

Received 27 February 2006; revised 8 October 2006; accepted 7 November 2006

DOI 10.1002/app.25885

Published online 28 February 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The radiation-induced crosslinking, compatibility, and surface modification of low density polyethylene/ethylene vinyl acetate blends (LDPE/EVA) were investigated. The structural and physical properties were characterized in terms of gel content, hot set, mechanical properties, contact angle, and surface free energy. The highest crosslink density was obtained at 20 wt % of EVA. Gel content of LDPE/EVA blends was increased with increasing irradiation dose, vinyl acetate (VA), and EVA contents. The hot set results are consistent with the gel content data. Mechanical testing showed that the tensile strength of samples increased with increasing irradiation dose up to 180 kGy, whereas the elongation at break was decreased with increasing irradiation dose. Contact angle measurements showed that the surface hydrophilicity of

LDPE blend was increased with increasing irradiation dose and contents of both VA and EVA. The surface free energy was greatly dependent on irradiation dose and content of both VA and EVA. The total surface free energies of different LDPE formulations were in the range 17.25–32.51 mN/m, in which the polar ( $P\sigma$ ) and disperse ( $d\sigma_s$ ) values were within the range 16.52–26.6 and 0.9–5.91 mN/m, respectively. In conclusion, electron beam irradiation and blending LDPE with EVA improved the wettability or adhesion properties of LDPE/EVA blends. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2886–2895, 2007

**Key words:** LDPE/EVA blend; electron beam irradiation; gel content; mechanical properties; contact angle and surface free energy characterization

## INTRODUCTION

Low density polyethylene polymer exhibits a wide range of properties such as light weight, chemical resistance, flexibility, toughness, good dielectric properties, thermal stability, electrical insulation, heat shrinkable properties, and relatively low cost compared with other plastics, which make it suitable for many applications. It is adaptable to add fillers, and copolymerizable with different ethylene vinyl acetate copolymers. Also, reinforcing materials are easily modified with thermal stabilizer, crosslinking agent, antioxidants, and ultraviolet blocking agent.<sup>1</sup> Ethylene copolymers such as ethylene vinyl acetate (EVA) exhibit high versatility in hot-melt formulations. Ethylene vinyl acetate (EVA)-based hot melts are able to fulfill various requirements in applications such as packaging, bookbinding, or label sticking. In other words, ethylene copolymers-based hot-melts will present a very good adhesion on various substrates such as paper, wood, plastics, metals, and on a broad operating window.<sup>2–6</sup> Radiation-induced

crosslinked LDPE/EVA blends are widely used in heat shrinkable materials for wire and cable industries because of the elastic memory that can be recovered by application of heat. The phenomenon is referred to as “memory effect” or elastic memory. The polyolefin blends like EVA copolymers with semicrystalline polymers like PE or PP give rise to materials with different structures and viscoelastic properties. The effect of electron beam irradiation and EVA content on the radiation crosslinking in LDPE/EVA blends have been studied by several authors.<sup>6–15</sup>

In recent years, increasing interest has been devoted to the surface modification of polymers, especially polyolefin, to obtain improved adhesion and wetting properties. Different treatments that have been used are as follows: chemical oxidation, high energy ion irradiation, X-ray, plasma etching, and electron beam irradiation; the last two being considered to be the most efficient techniques for surface modification of polymers. Blending of polyolefins with EVA is one of the most efficient methods for increasing the surface free energy by increasing the polar component in the polymer matrix.<sup>16–22</sup> The phenomenon of wetting or nonwetting of a polymer by a liquid is better understood by studying the contact angle (CA) and surface free energy (SFE). Most

Correspondence to: Z. I. Ali (zakariaismaiel\_59@yahoo.com).

of polymers show high contact angle behavior with many liquids. To improve the wetting properties, surface of polymers can be treated by electron beam irradiation. In this way, polar groups are introduced on the surface, and the SFE increases.<sup>18,22–25</sup> Low energy plastics, such as polyethylene, polypropylene, and teflon are essentially nonstick plastics and their molecular structure inhibits the adhesion and printing process. This molecular structure is basically inert or inactive, and these polymers are said to have low SFE.<sup>26</sup>

The aim of this work is to investigate the role of the type of EVA and its vinyl acetate content on the radiation crosslinking, physicochemical properties, and surface modification of LDPE/EVA blends.

## MATERIALS AND METHODS

### Materials

Three different Borealis batches of low density polyethylene (FA 3220, FT 5230, and FT 3030) were supplied in the form of pellets by Borealis A/S, Denmark. Also, Malen 23-D022 LDPE batch was supplied by PKN Orlen, Poland. Three commercial batches of ethylene vinyl acetate (Elvax 40w, Elvax 460, and Elvax 760) having different vinyl acetate contents were supplied in the form of pellets from Dupont and Industrial Polymer, Wilmington Delaware. The physical properties of both LDPE and EVA batches are listed in Tables I and II.

### Preparation of LDPE/EVA blends

LDPE and EVA resins were mixed in a Barabender plasticcorder PL 2100 (Installed at the National Center for Research and Technology (NCRRT) Cairo, Egypt) at 130°C and 50 rpm rotor speed. LDPE pellets were first allowed to melt for 2 min followed by the addition of the different types of EVA resins for a total mixing time of 5 min. Sheets of the melt of the different LDPE/EVA blends were obtained in an open roll mill. The plastic sheets were compression molded for 3 min at 160°C and a pressure of 15 MPa in an electrically heated hot press to obtain sheets of

thickness of about 1.0–1.1 mm. The different LDPE/EVA blends were denoted as shown in Table III.

### Irradiation procedure

Irradiation was carried out on the 1.5 MeV, 30 mA, and 25 kW electron beam accelerator (Installed at NCRRT, Cairo, Egypt). The total irradiation doses (60–180 kGy) were obtained by multipass runs at 3.0 m/min conveyer speeds with currents of 3.7 mA in which the maximum irradiation dose per one pass was 20 kGy.

### Gel content determination

Gel content percent (g %) was determined by refluxing the irradiated samples in xylene for 12 h. The initial weight ( $w_1$ ) and the final weight ( $w_2$ ) before and after extraction and drying the samples at 60°C for 24 h were recorded and the gel content percent was calculated from the following relationship:

$$\text{Gel content (\%)} = (w_2/w_1) \times 100 \quad (1)$$

### Mechanical properties

Tensile test was carried out on dumbbell-shaped specimen according to the ASTM specifications using the tension machine type M-10 Hung Ta Instrument LTD, Taiwan. The stress-strain measurements were carried out at ambient temperature using a stretching rate of 50 mm/min.

### Hot set properties

Hot set measurements were carried out in a ventilation oven equipped with air regulator giving 8–20 circulation per hour (Astfar SPA model F11, installed at El Sewaidy Co. for Wire and Cables, 10th Ramadan City, Cairo, Egypt) which insures a high uniformity and stability of temperature along with an easy setting of functions. Hot set test was done by determining the heat elongation percent of the samples under static load of 20N/mm<sup>2</sup> for 15 min at 200°C.

TABLE I  
Physical properties of Borealis and Malen LDPE batches

Properties	Boreolis LDPE batches			Malen batch
	FA 3220	FT 5230	FT 3030	
Density (kg/m <sup>3</sup> )	922	923	921	925
Melt flow index (MFI) (g/10 min)	0.30	0.77	0.20	1.6
Melting temperature (°C)	110	112	180	96
Softening temperature (°C)	96	97	–	90
Butyl acrylate content (wt %)	0.0	0.0	3.0	0.0

**TABLE II**  
Physical properties of different EVA batches

Properties	Elvax 40w	Elvax 460	Elvax 760
Vinyl acetate content (wt %)	40	18	9.3
Melt flow index (MFI) (g/10 min)	52	2.5	2
Density (kg/m <sup>3</sup> )	965	941	930
Softening point (°C)	104	199	167
Melting point (°C)	47	88	100
Freezing point (°C)	27	67	81

### Contact angle and surface free energy measurements

Contact angle and surface free energy of blank LDPE and LDPE/EVA blends were evaluated by contact angle goniometry (Kruss G 10) in a thermostate cell ( $25 \pm 1^\circ\text{C}$ ) interfaced to image capture software (installed at Polymer Chemistry Department, Technical University of Radom, Radom, Poland). Measuring was performed on six droplets of each test liquid (water, formamide and diodomethane). Using Owens–Wendt method, overall SFE and their components [polar ( $P\sigma$ ) and disperse ( $d\sigma$ )] were calculated from the contact angle data of the reference liquids throughout computer aided processor tensiometer with programmer software.<sup>18,22–28</sup>

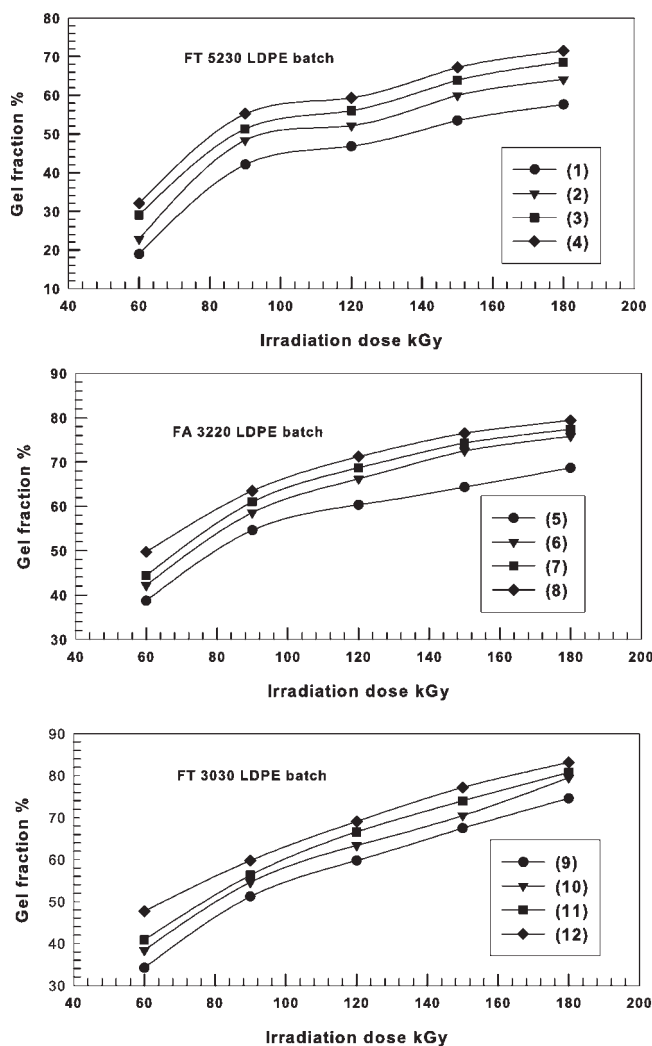
## RESULTS AND DISCUSSION

### Effect of EVA copolymer content on the gel content of LDPE samples

Figures 1 and 2 show the relationship between the gel content percent [using eq. (1)] and EB irradiation

**TABLE III**  
Composition of the prepared blends

Sample number	LDPE batch	Sample formulations	LDPE/EVA composition (wt %)
1	FT 5230	Blank LDPE	100/0.0
2		LDPE/Elvax 760	90/10
3		LDPE/Elvax 460	90/10
4		LDPE/Elvax 40w	90/10
5	FA 3220	Blank LDPE	100/0.0
6		LDPE/Elvax 760	90/10
7		LDPE/Elvax 460	90/10
8		LDPE/Elvax 40w	90/10
9	FT 3030	Blank LDPE	100/0.0
10		LDPE/Elvax 760	90/10
		LDPE/Elvax 460	
11		LDPE/Elvax 40w	90/10
12			90/10
13	Malen 23-D022	Blank LDPE	100/0.0
14			95/5
15		LDPE/Elvax 40w	92.5/7.5
16			90/10
17			80/20

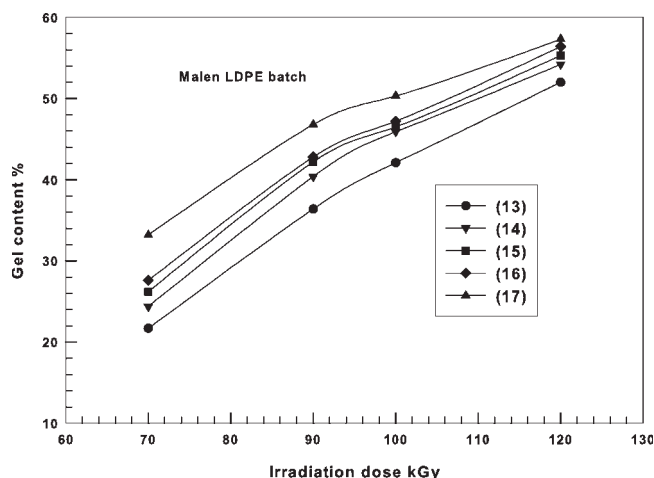


**Figure 1** Gel content percents of blank Borealis LDPE and Borealis LDPE/EVA formulations as a function of irradiation dose, kGy.

dose for the different LDPE/EVA blends. The gel content percent increased gradually with increasing irradiation dose up to 120 and 180 kGy for Malen and Borealis LDPE batches, respectively. LDPE/EVA blends showed higher gel content percent than did the blank LDPE sample. The enhancement of gel content for LDPE/EVA blends was greatly dependent on the types of LDPE and the ratio of EVA or VA content of the EVA copolymer. The order of crosslink density in LDPE/EVA blends based on the percentage gel content was as follows:

$$\text{Elvax 40w} > \text{Elvax 460} > \text{Elvax 760}$$

Thus, it is clear that the crosslinking efficiency of different LDPE/EVA blends is directly related to the physicochemical properties of blend compositions. Also, it can be seen that the crosslink density of the blends was greatly dependent on vinyl acetate content beside both melt flow index and density of EVA



**Figure 2** Gel content percents of blank Malen LDPE and Malen LDPE/EVA (Elvax 40w) formulations as a function of irradiation dose, kGy.

batch. The content of vinyl acetate in EVA copolymer influences the melt flow index which is considered as an inverse measure of the melt viscosity. The higher vinyl acetate content, the higher melt flow index and the higher density of EVA copolymer lead to increasing of crosslinking of LDPE/EVA blends. On the other hand, FT 3030 LDPE batch exhibited the highest percentage gel content compared with the other LDPE batches. This can be mainly attributed to the presence of ethylene butyl acrylate (EBA) copolymer containing 3 wt % of butyl acrylate which acts as an additional crosslinking agent.

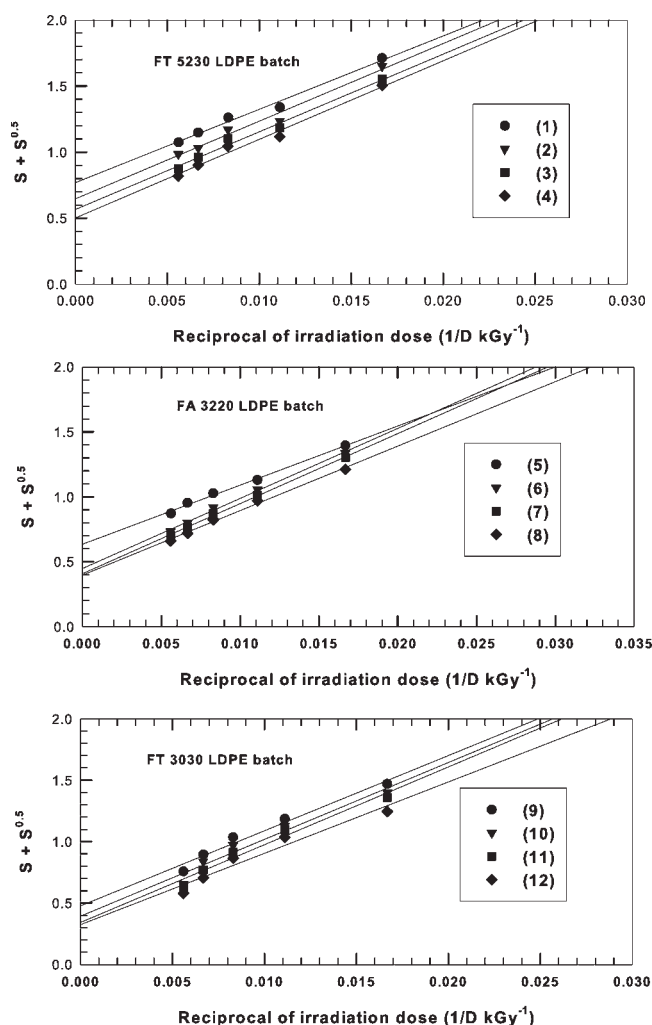
As shown in Figure 2, the blend of Malen LDPE and EVA copolymer (80/20 wt %) showed the highest gel contents compared with the other Malen LDPE blend compositions, in which the gel content is ~ 1.5 times that for blank Malen LDPE sample. Moreover, it can be noticed that blank Malen LDPE sample or its blend with 10 wt % EVA displayed lower gel content values with respect to the other Borealis LDPE batches blended with the same content of Elvax 40w. Finally, it may be concluded that the radiation-induced crosslinking of LDPE blends is largely dependent on the physical properties of the different LDPE batches and the content of either EVA or VA content of EVA copolymer.

When polymers are subjected to ionizing radiation, crosslinking and chain scission are usually observed. The processes ultimately cause formation of insoluble gel if crosslinking predominates over scission. Charlesby and Pinner first obtained a simple expression relating sol fraction ( $S$ ) to absorbed irradiation dose ( $D$  kGy)<sup>29–32</sup>:

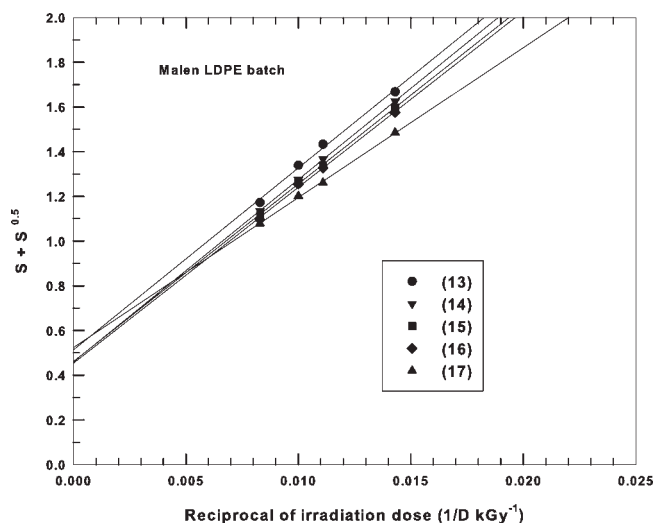
$$S + \sqrt{S} = \frac{p_0}{q_0} + \frac{2}{q_0 \mu D} \quad (2)$$

where  $p_0$  is the degradation density,  $q_0$  is the cross-linking density and  $\mu$  is the initial weight average degree of polymerization (units per initial weight average molecule). The Charlesby–Pinner equation is widely applied in radiation chemistry of polymers. This equation was derived based on the initial molecular weight distribution (MWD) of the most probable distribution with polydispersity index  $M_w/M_n = 2$ . The obtained soluble fraction data  $S + \sqrt{S}$  for the investigated blank LDPE and LDPE/EVA blends were plotted against the reciprocal of the irradiation dose (see Figs. 3 and 4). The obtained plots for all the investigated samples exhibited very linear behavior with higher regression in the range 97–99.5%. These plots allow obtaining the ratio ( $p_0/q_0$ ) and the gelling dose ( $D_g$ ) as shown in Table IV.

Another method was considered in the present work for the determination of crosslink density. The basic concept is to use the logarithm of sol fraction



**Figure 3**  $S + S^{0.5}$  of blank Borealis LDPE and Borealis LDPE/EVA formulations as a function of the reciprocal of irradiation dose,  $kGy^{-1}$ .



**Figure 4**  $S + S^{0.5}$  of blank Malen LDPE and Malen LDPE/EVA (Elvax 40w) formulations as a function of the reciprocal of irradiation dose,  $\text{kGy}^{-1}$ .

( $\log S$ , where  $S = 1 - g$ ) versus the logarithm of irradiation dose ( $\log D$ ). These coordinates, however, were used in the earlier stages of radiation chemistry of polymers but were not used widely. A possible reason for this is that the different slopes of the log-log plots were not explained at that time. However, it has recently been shown with computer simulation that logarithm of sol fraction has linear dependence on logarithm of irradiation dose<sup>33–34</sup>:

$$\log S = b + m \log D \quad (3)$$

The coefficients  $m$  and  $b$  have been computed with the least square method and all data are listed in Table IV. The coefficients enabled the dose of the starting gelation (gelling dose,  $D_g$  kGy) to be calculated. In fact, the gelling dose was determined to be the point where the approximation line intercepts the horizontal line at  $S = 1$ , i.e.,  $\log S = 0.0$ . Because of the high linearity of the plots, the gelling dose has been accurately obtained considering  $\log D_g = -(b/m)$ . The  $b$  value being related to the ratio of degradation and crosslinking densities and the  $m$  value is also sensitive to the chain scission rate in the crosslinked system.

Analyzing the obtained data regarding the ratio of chain scission to crosslinking events ( $p_o/q_o$ ), the gelling dose ( $D_g$ ) and the chain scission rate ( $m$ ) of the LDPE formulations can be correlated. These results have an important technological value when determining the intensity of the gel forming process at different irradiation doses. It can be seen that the extent of  $p_o/q_o$  values decreased according to the type of LDPE batch blended with EVA. It was found that the gelling dose decreased due to either blending LDPE with EVA copolymer or with increasing of

VA content of the blended EVA. Also, the obtained data ( $p_o/q_o$  and  $D_g$ ) confirmed that FT 3030 LDPE and also Elvax 40w EVA batches exhibited the highest crosslinking efficiency in comparison with other batches of either LDPE or EVA.

Ethylene vinyl acetate has a rubber-like property of highly flexibility. EVA can attain the same degree of crosslinking as LDPE at lower dose (100–150 kGy). Therefore it is possible by blending certain composition of EVA with LDPE to improve the radiation crosslinking performance of LDPE. Moreover, EVA is a block copolymer consisting of PE and PVA chains and both its alkyl radicals in the PE chains and methyl radicals on the acetoxy group in the PVA chains participated with the irradiation crosslinking reaction. LDPE/EVA blend has a structural similarity in the sense that EVA is a copolymer of a nonpolar methylenic chain ( $-\text{CH}_2-$ ) with a polar acetate group and LDPE is a completely nonpolar methylenic chain. Also, EVA makes the blend more amorphous in nature, which, in turn increases its efficiency towards crosslinking at a particular irradiation dose. In addition, the amorphous region's content of EVA is higher than that of LDPE. The radiation crosslinking and degradation reactions mainly occurred in the amorphous regions of semicrystalline polymers during the irradiation. Higher amorphous content is favorable to the radiation crosslinking of polymer, especially for higher dose rate irradiation, such as electron beam accelerator. The radiation crosslinking is lowered by oxidation of polymer during the irradiation in the air, especially for irradiation at higher doses.

**TABLE IV**  
Crosslink parameters of blank LDPE and Different LDPE/EVA blends

Sample number	Usual Charlesby–Pinner		log $S$ vs. log $D$		
	$p_o/q_o$	$D_g(\text{kGy})$	$b = (p_o/q_o)$	$D_g(\text{kGy})$	$m$
1	0.77	45.45	0.76	45.18	−0.459
2	0.65	43.48	0.62	43.79	−0.378
3	0.57	41.67	0.56	40.55	−0.348
4	0.50	40.00	0.49	39.79	−0.306
5	0.63	35.09	0.63	33.20	−0.414
6	0.45	34.48	0.44	34.72	−0.286
7	0.41	33.33	0.40	33.89	−0.261
8	0.40	31.25	0.39	30.90	−0.261
9	0.48	40.32	0.47	40.12	−0.293
10	0.40	39.22	0.39	38.99	−0.245
11	0.34	38.46	0.34	38.11	−0.215
12	0.32	34.75	0.32	34.69	−0.208
13	0.51	54.95	0.50	54.87	−0.288
14	0.46	52.91	0.45	53.09	−0.261
15	0.46	52.08	0.45	51.79	−0.262
16	0.45	51.28	0.44	50.98	−0.258
17	0.52	45.45	0.51	45.59	−0.307

LDPE/EVA blends are compatible in the amorphous region and both PE and PVA chains have high mobility in the amorphous region, in special PVA. The higher mobile methyl radicals on the acetoxy group in the PVA chains are more easily combined with alkyl radicals in the PE chains and they lead to more crosslinking of EVA, therefore, EVA has an enhancement effect on radiation crosslinking in the LDPE/EVA blend.

### Mechanical properties of different LDPE/EVA blends

The mechanical properties (tensile strength and elongation at break) of different LDPE/EVA blends exposed to various EB irradiation doses up to 180 kGy are shown in Tables V and VI. It can be seen that the tensile strength ( $\sigma_b$ , MPa) of the different LDPE/EVA blends increased with increasing irradiation dose up to 180 kGy. Also, the elongation at break ( $\varepsilon_b$ , %) decreased as a result of the increase of irradiation dose. The decrease in the elongation at break can be attributed to the increase in the crosslink density of LDPE formulations. In addition, the mechanical properties of LDPE blends are largely dependent on the type of both LDPE and EVA batches. In this regard, the blend of FT 3030 LDPE and Elvax 40w showed the highest drop in elongation % at break values, while FA 3220/Elvax 460 blends exhibited the lowest drop in elongation % at break values. Also, it can be observed that the increase of the vinyl acetate content of EVA copolymer is accompanied with an increase in the tensile strength causing a remarkable decrease in elongation at break. Similar trends were

observed in the case of the Malen LDPE/EVA blends, regardless of compositions. The results obtained illustrated that the level of change in the mechanical properties of Malen LDPE blends is being less than that for the Borealis LDPE blends.

### Hot set properties

Hot set testing provides a quick and accurate check on crosslinking of polymeric samples and can be correlated with percentage gel content. Basically, it is a test in which the sample is elongated under a given load at suitable temperature above or near the melting point of the polymer (200°C for crosslinked polyethylene at 20N/mm<sup>2</sup> for 15 min).<sup>6,35–37</sup> Figure 5 shows the dependence of heat percentage elongation for the different LDPE/EVA blends on irradiation dose. It should be noted that the unirradiated LDPE/EVA blends failed in the test immediately, i.e., they cut after 1–2 min at 300–450% elongation. On the other hand, the heat percentage elongation of irradiated LDPE/EVA blends decreased gradually with the increase of irradiation dose. Also, it was observed that the level of heat percentage elongation for Borealis LDPE blends decreased as follow: FT3220 > FT5230 > FT 3030. In addition, the vinyl acetate content (VA wt %) in the LDPE (FT 3030)/EVA blends was taken as a reference parameter for the change in the percentage elongation as a function of irradiation dose as shown in Figure 5(b). In this regard, it can be seen that the heat percentage elongation decreased as both VA content of EVA copolymer and irradiation dose were increased. Similar trends were observed with respect to the elongation

TABLE V  
Tensile strength ( $\sigma_b$ , MPa) and elongation at break ( $\varepsilon_b$ , %) of Borealis LDPE/EVA blends

Sample no.	LDPE blends	Property	EB irradiation dose					
			0.0	60	90	120	150	180
2	FT 5230/Elvax 760	$\sigma_b$ , MPa	19.0	20.49	21.44	22.37	23.35	24.15
		$\varepsilon_b$ , %	610	586	571	560	541	519
3	FT 5230/Elvax 460	$\sigma_b$ , MPa	20.10	21.10	22.60	23.40	23.95	23.90
		$\varepsilon_b$ , %	573	551	532	503	483	457
4	FT 5230/Elvax 40w	$\sigma_b$ , MPa	22.17	23.11	23.81	24.50	24.93	25.73
		$\varepsilon_b$ , %	547	510	501	471	430	387
6	FA 3220/Elvax 760	$\sigma_b$ , MPa	18.30	19.03	19.46	20.49	20.57	21.98
		$\varepsilon_b$ , %	653	622	588	567	526	485
7	FA3220/Elvax 460	$\sigma_b$ , MPa	19.01	20.90	21.10	21.64	22.30	22.90
		$\varepsilon_b$ , %	604	586	578	569	541	519
8	FA 3220/Elvax 40w	$\sigma_b$ , MPa	20.31	21.46	21.88	22.15	23.91	24.53
		$\varepsilon_b$ , %	589	563	530	506	482	454
10	FT3030/Elvax 760	$\sigma_b$ , MPa	21.50	23.56	23.86	25.01	25.71	26.09
		$\varepsilon_b$ , %	558	535	505	490	471	457
11	FT 3030/Elvax 460	$\sigma_b$ , MPa	22.70	24.35	25.41	25.93	26.4	26.90
		$\varepsilon_b$ , %	531	520	490	460	420	441
12	FT 3030/Elvax 40w	$\sigma_b$ , MPa	23.80	25.11	26.22	26.50	26.72	27.65
		$\varepsilon_b$ , %	463	438	388	361	350	323

TABLE VI  
Tensile strength ( $\sigma_b$ , MPa) and elongation at break ( $\epsilon_b$ , %) of Malen LDPE/EVA (Elvax 40w) blends

Sample no.	LDPE blends	Property	EB irradiation dose				
			0.0	70	90	100	120
10	Blank LDPE	$\sigma_b$ MPa	14.0	15.1	16.7	17.3	18.9
		$\epsilon_b$ %	790	776	753	741	695
11	LDPE/EVA 95/5	$\sigma_b$ MPa	14.5	16.3	16.9	18.0	19.5
		$\epsilon_b$ %	745	732	721	701	672
12	LDPE/EVA 92.5/7.5	$\sigma_b$ MPa	15.1	16.9	17.3	18.5	20.3
		$\epsilon_b$ %	713	700	691	650	605
13	LDPE/EVA 90/10	$\sigma_b$ MPa	17.8	18.2	19.8	20.5	21.3
		$\epsilon_b$ %	640	620	601	587	551
14	LDPE/EVA 80/20	$\sigma_b$ MPa	18.1	18.7	19.35	21.05	21.7
		$\epsilon_b$ %	564	541	521	489	455

for Malen LDPE/EVA blends with various EVA contents as shown in Figure 5(c). It can be observed that the heat elongation at the same irradiation doses for Malen LDPE/EVA (90/10 wt %) blends is higher than that for Borealis LDPE/EVA blends. This is due to Borealis LDPE batches still exhibited higher degree of crosslinking than that for Malen LDPE. At the same time, FT 3030 LDPE batch exhibit the higher overall degree of crosslinking when blended with EVA of higher VA content (Elvax 40w).

The hot set test results of blank LDPE and LDPE/EVA blends are strongly dependent on the blend compositions, degree of crosslink density and irradiation dose. This behavior is believed to be due the nature of EVA which easily crosslinks when exposed to electron beam radiation. Formation of adequate radiation crosslinking networks in the polymer blend render the blend better elongation at high temperature. The obtained results are well correlated with the gel content and mechanical properties data proving that FT 3030 LDPE, Elvax 40w and LDPE/EVA blend of the ratio (80/20 wt %) showed the maximum degree of radiation-induced crosslinking.

### Contact angle and surface free energy

Contact angle and surface free energy values are extremely important parameters characterizing surface modification such as wettability and adhesion properties. It is well known that contact angle ( $\theta$ ) is a decisive factor in evaluating the wetting phenomena of polymeric surfaces. The contact angles of reference liquids (water, formamide and diodomethane) on unirradiated and irradiated blank LDPE and LDPE/EVA samples are shown in Table VII. It can be seen clearly that unirradiated blank LDPE sample showed the highest values of contact angles in comparison with LDPE/EVA blends. Moreover, the contact angle values are dependent on the polarity of the reference liquids in which it increased as the polarity of the reference liquids increased. The

contact angles of LDPE/EVA blends decreased gradually as the electron beam irradiation dose increased up to 120 kGy. Also, the values of contact angles

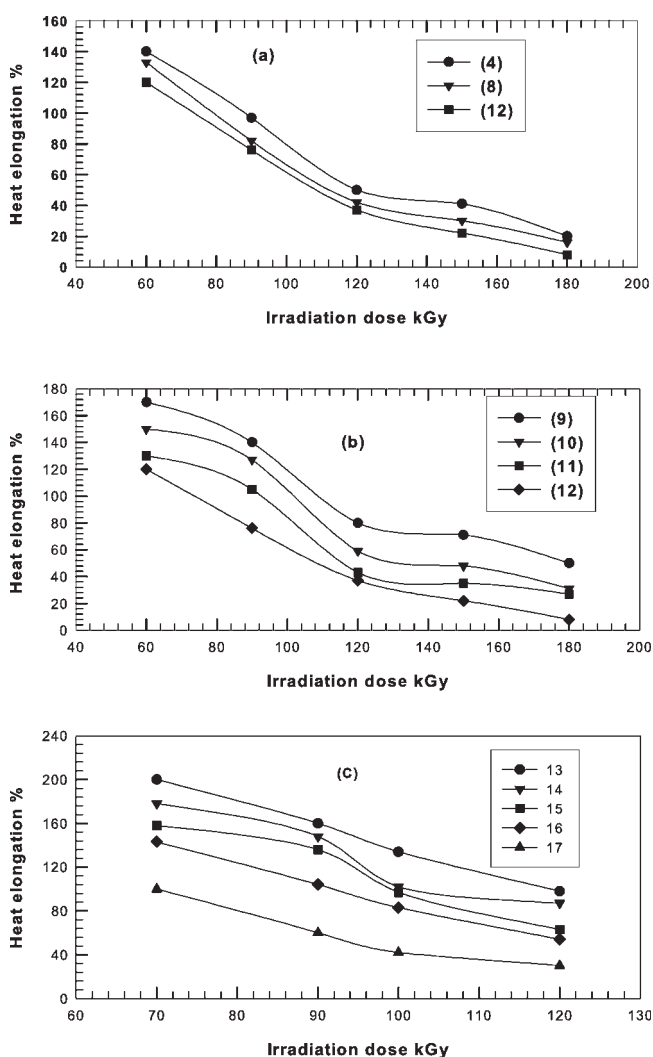


Figure 5 Heat elongation percent for different Borealis and Malen LDPE formulations as a function of irradiation dose, kGy.

TABLE VII  
 Values of contact angle, dispersion component ( $^d\sigma_s$ ), polar component ( $^p\sigma_s$ ), and overall surface free energy ( $\sigma_s$ ) for different LDPE formulations using three reference liquids {water, formamide (FM), and diiodomethane (DIM)}

Sample	Dose (kGy)	Contact angle ( $\theta^\circ$ )			Surface free energy parameters (mN/m)		
		DIM	FM	H <sub>2</sub> O	$\sigma_s$	$^d\sigma_s$	$^p\sigma_s$
Blank Malen LDPE	0.0	70.9	90.4	97.5	17.25	16.35	0.90
Malen LDPE/EVA 40w	0.0	65.4	87.4	93.2	18.25	16.90	1.35
95/5.0 wt %	70	63.3	87.1	92.1	20.03	18.24	1.79
	90	61.2	86.2	90.2	21.12	18.87	2.25
	100	60.0	85.2	88.7	22.85	20.40	2.45
	120	58.4	81.3	86.2	24.89	21.67	3.22
	0.0	64.3	85.1	92.5	19.23	17.55	1.68
92.5/7.5 wt %	70	63.2	82.6	90.7	20.88	18.99	1.89
	90	60.7	80.4	89.7	22.07	19.54	2.53
	100	59.1	79.8	88.1	25.03	22.25	2.78
	120	58.0	78.1	85.7	26.83	23.05	3.78
Malen LDPE/ EVA 40w	0.0	60.1	84.3	91.5	20.78	18.85	1.93
	70	58.7	80.1	88.3	23.61	21.60	2.01
	90	57.3	77.7	86.4	26.26	23.64	2.67
	100	55.2	76.3	84.9	27.87	24.64	3.23
	120	54.7	74.2	84.0	29.27	25.13	4.14
Malen LDPE/ EVA 40w	0.0	59.3	80.0	87.3	21.17	19.02	2.15
	70	57.8	77.3	86.0	24.37	21.92	2.45
	90	56.1	75.1	84.2	28.32	25.33	2.99
	100	53.2	73.2	80.3	29.91	26.40	3.51
	120	51.7	70.7	76.9	32.51	26.60	5.91
FT 3030/EVA 760	90	57.3	77.7	86.4	26.26	23.59	2.67
90/10 wt %	150	50.5	72.1	81.2	31.70	26.77	4.93
FA 3220/EVA 460	90	55.1	75.3	83.3	25.31	23.13	2.18
90/10 wt %	150	53.3	72.7	80.5	30.00	25.93	4.07
FA 3220/EVA 40w	90	52.4	71.3	79.2	24.30	22.51	1.79
90/10 wt %	150	51.1	96.1	78.7	28.60	25.03	2.57

decreased with increasing the EVA content in the blends.

Comparison of the contact angles for LDPE (FT 3030 batch) blended with 10 wt % of different EVA copolymers having different VA contents (Elvax 760, 460, and 40w) emphasized the relationship between surface modification (i.e., wettability) and the type of incorporated EVA in the blend samples. The contact angles for the reference liquids decreased with the increase of VA content of the EVA copolymer. Thus, it is clear that the modification of the surface polarity occurred when the content of VA of EVA copolymer increased. This is reflected in the lowering of contact angles of the reference test liquids {water, formamide (FM) and diiodomethane (DIM)} (see Table VII) which in turn raised the polymer surface free energy (also given in Table VII) due to increased polarity of the surface. The obtained results showed that electron beam irradiation with the aid of blending LDPE with EVA copolymer give the best wetting character, i.e., lowering contact angle. Conversely, the unirradiated and unblended LDPE with EVA (i.e., blank LDPE) displayed the highest contact angle values compared with irradiated and modified LDPE samples with EVA copolymer. Blending of LDPE with

EVA copolymer is an essential element of surface modification as it serves to exhibit higher level of surface wettability. Meanwhile, the irradiation of LDPE/EVA blends increased the surface wetting. The interaction of electron beam radiation with the polymer causes chemical and physical modification to their surface. These modifications produce more reactive surface, affect wetting properties and cross-linking.<sup>17,19,37</sup>

Surface free energy (SFE) of solid phase is a very sensitive method to investigate interfacial phenomena. Using Owens–Wendt method,<sup>17–18,22–28</sup> the SFE parameters {overall surface free energy ( $\sigma$ ), polar component ( $^p\sigma_s$ ), and disperse component ( $^d\sigma_s$ )} were estimated as shown in Table VII. When SFE increased, the hydrophilic character and consequently the wettability of polymer surface increased and *vice versa*. As expected, the blank LDPE sample has the lowest surface free energy values with low polar component values ( $^p\sigma_s$ ). On the other hand, LDPE/EVA blends showed extremely high surface free energy values associated with high affinity for the test liquids. It was noted that the surface free energy parameters increased gradually with the increase of either irradiation dose or EVA content.



Also, it can be concluded that the high increasing levels of the polar component ( $^P\sigma_s$ ) of surface free energy and consequently the overall surface free energy ( $\sigma_s$ ) is more remarkable due to irradiation and blending LDPE with EVA copolymer.

The obtained results may be explained based on the increase in the level of polar groups and also on the level of radiation-induced crosslinking of LDPE/EVA blends. It was established that radiation-induced reactions of polymer macroradicals (LDPE) and polar groups of vinyl acetate in EVA copolymer lead to change polarity of the blend. Also, crosslinking reaction results in the formation of compact structure with more reactive/hydrophilic surface which makes the functional groups to be close to each other in the blend matrix. In this context, the increase of the concentration of the polar groups would cause an increase in the surface free energy parameters which enhances the adhesion and wettability properties of the investigated samples.<sup>2,17,28</sup> The more common observations of the obtained data regarding contact angle and surface free energy showed that LDPE surface become more hydrophilic with higher increasing levels of polar components as compared with disperse one (i.e., the contact angle falls because of the better wetting property). High surface free energy values are favorable for wetting a surface. This means that polar interaction due to dipoles also have much higher bonding energies than dispersion forces, so that, one can also expect high increasing level of polar energy component ( $^P\sigma_s$ ) shares to lead to a good adhesion. The increase in surface free energy parameters is an indication of the increase of adhesion. It is evident that if the surface free energy of a LDPE plastic substrate is raised by irradiation and blending with EVA copolymer to a higher level, then the adhesion properties can be improved.

### CONCLUSIONS

This work has been dealt with the crosslinking of LDPE/EVA blends using electron beam irradiation. Based on the results obtained, few conclusions may be made:

1. Gel content of blank LDPE and LDPE/EVA blends increased as the irradiation dose increased up to 180 kGy. Moreover, the crosslink density of LDPE/EVA blends increased with increasing either VA or EVA content.
2. Tensile strength of LDPE/EVA blends increased with irradiation dose up to 180 kGy and also with increasing the EVA content, whereas elongation at break showed a decreasing trend.
3. EB irradiation of LDPE in the presence of EVA copolymer proved to be a simple and effective

way to improve the wettability and adhesion properties of polymer surfaces. The SFE of LDPE and all its polar and dispersive components ( $^P\sigma_s$  and  $^d\sigma_s$ ) can be improved through the electron beam irradiation and blending with different EVA copolymers leading to different adhesion levels. The results showed a high increasing level of polar component ( $^P\sigma_s$ ) with simultaneously high level of the overall SFE ( $\sigma_s$ ) of LDPE substrate leading to a better layer adhesion.

The author thanks Dr Wilczek M. E., and Dr Kostrzewa M., Polymer Chemistry Department, Technical University of Radom, Radom, Poland, for their assistance in the analysis of contact angle and surface free energy parameters.

### References

1. Mclaughlin, W. L.; Silverman, J.; Al-Sheikly, M.; Chapps, W. J.; Zhan-Jun, L.; Miller, A.; Pederson, W. P. *Radiat Phys Chem* 1999, 56, 503.
2. Legocka, I.; Zimek, Z.; Wozniak, A. *Radiat Phys Chem* 1998, 52, 277.
3. Singh, A. *Radiat Phys Chem* 2001, 60, 543.
4. Datta, S. K.; Chaki, T. K.; Tikku, V. K.; Pradhan, N. K.; Bhowmick, A. K. *Radiat Phys Chem* 1997, 50, 399.
5. Spenadel, L.; *Radiat Phys Chem* 1979, 14, 683.
6. Sharif, J.; Abdel Aziz, S. H. S.; Hashim, K. *Radiat Phys Chem* 2000, 58, 191.
7. Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 1996, 62, 75.
8. Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 1996, 86, 1296.
9. Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 2002, 86, 553.
10. Zhang, W. X.; Liu, Y. T.; Sun, J. Z. *Radiat Phys Chem* 1990, 35, 163.
11. Mateev, M.; Karageorgiev, S. *Radiat Phys Chem* 1998, 51, 205.
12. Chattopadhyay, S.; Chaki, T. K.; Bhowmick, A. K. *Radiat Phys Chem* 2000, 59, 501.
13. Chattopadhyay, S.; Chaki, T. K.; Bhowmick, A. K. *J Appl Polym Sci* 2001, 79, 1877.
14. Chattopadhyay, S.; Chaki, T. K.; Bhowmick, A. K. *J Appl Polym Sci* 2001, 81, 1936.
15. Salehi, S. M. A.; Mirjalili, G.; Amrollahi, J. *J Appl Polym Sci* 2004, 92, 1049.
16. Mirabedini, S. N.; Rahimi, H.; Hamedifar, Sh.; Mohseni, S. M. *J Adhes Adhesives* 2004, 24, 163.
17. Duca, M. D.; Plosceanu, C. L.; Pop, T. *Polym Degrad Stabil* 1998, 61, 65.
18. Luner, P. E.; Oh, E. *Colloid Surf A: Physicochem Eng Asp* 2001, 181, 31.
19. Devallencourt, C.; Marais, S.; Saiter, J. M.; Labbe, J. M.; Metayer, M. *Polym Test* 2002, 21, 253.
20. Yak, S. H.; Cho, S. H. *Eur Polym J* 2001, 7, 1985.
21. Oh, S. H.; Jung, J. C.; Zin, W. C. *J Colloid Interface Sci* 2001, 238, 43.
22. Chebbi, R. *J Colloid Interface Sci* 2000, 229, 155.
23. Lugscheider, E.; Bobzin, K. *Surf Coating Technol* 2001, 142-144, 755.
24. Michalski, M. C.; Hardy, J.; Saramoyo, B. J. Y. *J Colloid Interface Sci* 1998, 208, 319.
25. Nishino, T.; Meguro, M.; Nakamae, K. *Int J Adhes Adhesives* 1999, 1, 399.
26. Drummond, C. I.; Chan, D. Y. C. *Langmuir* 1997, 13, 3890.

27. Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1969, 13, 1741f.
28. Lugscheider, E.; Bobzin, K.; Moller, M. *Thin Solid Films* 1999, 355–356, 367.
29. Zhang, W. X.; Liu, Y. T.; Sun, J. Z. *Radiat Phys Chem* 1990, 35, 163.
30. Burns, N. M. *Radiat Phys Chem* 1979, 14, 797.
31. Rosiak, J. M. *Radiat Phys Chem* 1998, 51, 13.
32. Olejniczak, J.; Rosiak, J.; Charlesby, A. *Radiat Phys Chem* 1991, 37, 499.
33. Shyichuk, A. V.; Tokaryk, G. V. *Macromol Theory Simul* 2003, 12, 599.
34. Shyichuk, I.; Shyicuk, I.; Wu, G.; Katsumura, Y. *J Polym Sci Part A: Polym Chem* 2001, 39, 1656.
35. Adbin, S.; Frounchi, M.; Haji Saeid, M.; Gangi, F. *J Appl Polym Sci* 1959, 2002, 86.
36. Wiesner, L.; *Radiat Phys Chem* 1991, 37, 77.
37. Schultz, J.; Nardin, M.; Pizza, A.; Mittal, K. L. *Handbook of adhesive technology*; Marcel Dekker: New York, 1994.