

Thermal and Mechanical Properties of Uncrosslinked and Chemically Crosslinked Polyethylene/Ethylene Vinyl Acetate Copolymer Blends

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ABSTRACT: Uncrosslinked and chemically crosslinked binary blends of low- and high-density polyethylene (PE), with ethylene vinyl acetate copolymer (EVA), were prepared by a melt-mixing process using 0–3 wt % *tert*-butyl cumyl peroxide (BCUP). The uncrosslinked blends revealed two distinct unchanged melting peaks corresponding to the individual components of the blends, but with a reduced overall degree of crystallinity. The crosslinking further reduced crystallinity, but enhanced compatibility between EVA and polyethylene, with LDPE being more compatible than HDPE. Blended with 20 wt % EVA, the EVA melting peak was almost disappeared after the addition of BCUP, and only the corresponding PE melting point was observed at a lowered temperature. But blended with 40% EVA, two peaks still existed with a slight shift toward

lower temperatures. Changes of mechanical properties with blending ratio, crosslinking, and temperature had been dominated by the extent of crystallinity, crosslinking degree, and morphology of the blend. A good correlation was observed between elongation-at-break and morphological properties. The blends with higher level of compatibility showed less deviation from the additive rule of mixtures. The deviation became more pronounced for HDPE/EVA blends in the phase inversion region, while an opposite trend was observed for LDPE/EVA blends with co-continuous morphology. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3261–3270, 2007

Key words: polyethylene (PE); ethylene vinyl acetate copolymer; crosslinking; thermal properties; mechanical properties

INTRODUCTION

Blending of two or more thermoplastics may generate new materials with a combination of properties not found in pure polymers. Blending is often a faster and more cost-effective way of achieving the required properties than synthesizing new polymers. Over the years, numerous systems have been developed and commercialized. A large part of this family of new materials is based on polyolefins, which are the widest used polymers in industry.¹

Polyethylene is one of the most important thermoplastics, but its use is restricted in certain applications due to its low melting point, solubility, or swelling in hydrocarbons and tendency to crack when stressed. In an effort to tackle these disadvantages, considerable work has been carried out based on the crosslinking of polymer.^{2–6}

Crosslinking is a broadly used method for the modification of polymer properties. This process involves the formation of three-dimensional (3D) structure,

gels, causing substantial changes in material properties. Different procedures may be used for the initiation of polyolefin crosslinking. One of these procedures is based on macro-radical formation via thermal decomposition of organic peroxides. A detailed description of the various initiation procedures has been given in a comprehensive review by Lazar et al.²

The most usual method of crosslinking is the chemical method, especially by means of peroxides. Peroxide is incorporated into the polymer by extrusion below the activation temperature of the peroxide. The extruded crosslinkable polyethylene will later be formed by one of the processing methods and cured under pressure and temperature. Suitable peroxide has to be selected to give fast crosslinking without pre-curing in the extruder; hence, dicumyl peroxide is widely used for this purpose. For compounding in-line during the extrusion process, there are advantages in using a liquid instead of a powder. Di-*tert*-butyl peroxide is liquid and has some distinct advantages over di-cumyl peroxide, among them easier feeding into the polymer melt stream in the extruder and safer margin of temperature for preventing scorch or premature crosslinking inside the extruder.^{7,8}

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Crosslinked polyethylene (PE) has become widely adapted for a number of industrial applications requiring withstanding high-temperature environments. Examples of such applications include wire and cable coating, heat shrinkable materials, hot water tubing and steam resistant food packaging.^{9–13}

The use of ethylene vinyl acetate copolymer in blends and composites is most important from the technological point of view. Because of low-temperature flexibility, somewhat rubbery nature, low permeability, and good impact strength, it is becoming interesting as a stretched film for packaging technology. It has drawn interest as a cable insulating material because of the good resistance to stress cracking and because the polymer may be easily crosslinked.^{14–17}

The thermal and mechanical behavior of crosslinked polyethylene has been studied most extensively either at room temperature or at temperatures above the melting point of the polymer.^{18–23}

There is very limited available information on the combined effect of the morphology and crosslinking level on the tensile mechanical response of chemically crosslinked polyethylene and its blends with EVA at different temperatures.

In the present work, the effects of the chemical crosslinking, addition of EVA, the crosslinking level on the thermal, and mechanical properties of LDPE/EVA and HDPE/EVA blends at different temperatures were investigated. An attempt was also made to establish a correlation between the properties and morphology of the blends.

EXPERIMENTAL

Materials

Low-density polyethylene grade LD 00BW, with a MFI value of 2 g/(10 min) and a density of 923 kg/m³, was kindly supplied by Exxon Mobile (Köln, Germany). High-density polyethylene (HDPE) grade MG7547A, with a MFI value of 4 g/(10 min) and a density of 954 kg/m³, was obtained from the Borealis Group (Kongens-Lyngby, Denmark). This grade has high-impact strength and toughness, even at low temperatures, and also has good flow properties.

Ethylene vinyl acetate copolymer grade UL 00218, with a MFI value of 1.7 g/(10 min), density of 938 kg/m³, and vinyl acetate content of 18%, was kindly supplied by Exxon Mobile (Germany).

Tertiary-butyl cumyl peroxide (BCUP) with 96% purity and a density of 0.96 g/cm³ was obtained from Peroxide-Chemie GmbH (München, Germany).

Sample preparation

The LDPE/EVA and HDPE/EVA blends in different ratios of EVA (0–100 wt %) were melt-mixed in an in-

ternal mixer (Plasti-Corder, model PL 2000, Brabender, Duisburg, Germany) with a speed of 50 rpm at 145°C for 10 min. The samples were then compression molded to flat sheets, using Fontune 400 KN Laboratory (Rotterdam, Holland), hot press at a temperature of 190°C for 3 min under 10-MPa pressure; the sheets were then cooled at a cooling rate of 15 K/min to ambient temperature. To prepare the crosslinked samples, a new set of blends were melt-mixed with an EVA content of 0–40 wt % under similar processing conditions but, after completion of melt-mixing, peroxide (BCUP) was introduced in the system and was mixed for another 3 min. In this state, BCUP mixed with LDPE/EVA and HDPE/EVA blends. The crosslinking of sheet samples was carried out in the same compression molding hot press at a temperature of 190°C for 5 min under 10-MPa pressure; the sheet samples were then cooled by cooling rate of 15 K/min.

Gel measurement

The gel content of the crosslinked PE was determined gravimetrically, according to ASTM D 2765, using a 16-h soxhlet extraction cycle with *p*-xylene as the solvent at 140°C. Irganox 1010 was added at 0.5 wt % to inhibit polymer degradation during the extraction. Approximately 0.3 g of the crosslinked polymer sample was cut into small pieces and placed in a pre-weighed stainless steel fine wire mesh. After the extraction cycle, the sample was washed with acetone and vacuum dried to a constant weight. The gel fraction was calculated as the percentage ratio of the final weight of the polymer to its initial weight.

Thermal analysis

Differential scanning calorimetry (DSC) tests were performed on a DSC Q 1000 of TA (USA) with samples of ~ 5 mg sealed in aluminum pans under nitrogen atmosphere in a temperature range of –60–180°C at a heating rate of 10 K/min. The melting and crystallization enthalpy and melting temperature of the samples were determined. The degree of crystallinity was calculated via the total enthalpy method, according to the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^+}, \quad (1)$$

where X_c is the degree of crystallinity, ΔH_m is the specific enthalpy of melting, and ΔH_m^+ is the specific enthalpy of melting for 100% crystalline polyethylene. We used a ΔH_m^+ value of 288 J/g.²⁴

Mechanical properties

The mechanical properties of uncrosslinked and crosslinked LDPE/EVA and HDPE/EVA blends

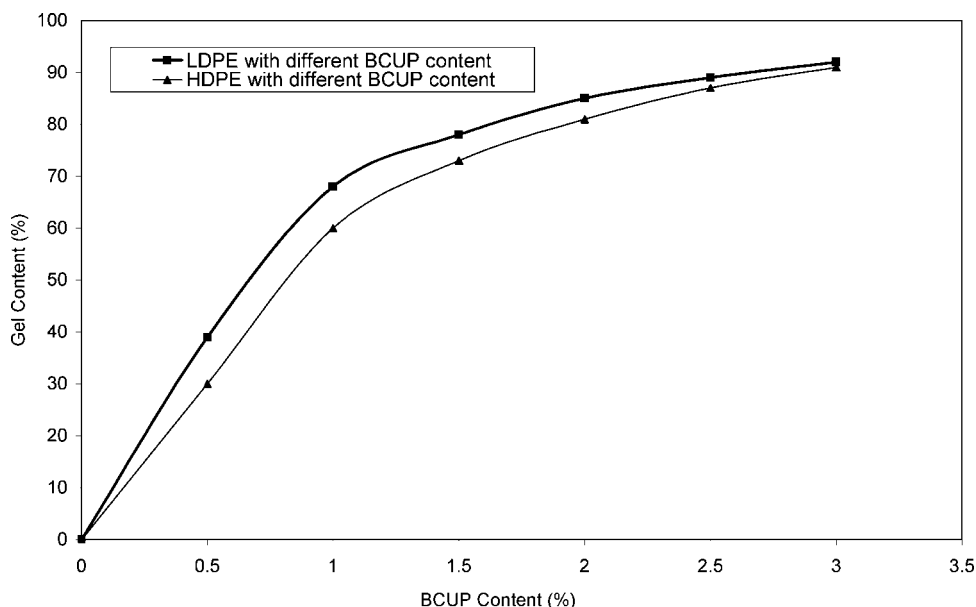


Figure 1 Effect of peroxide (BCUP) content on the gel content of crosslinked low- and high-density polyethylene.

were determined according to ISO 527-2: 1996 on an UPM 1456 (Zwick, Ulm, Germany). The test was carried out with a crosshead speed of 100 mm/min at three temperatures, i.e., at ambient temperature, at 90°C (below the maximum crystallization temperature), and also at 140°C (above the melting point) for the crosslinked blends, whereas the uncrosslinked blends were tested at room temperature and at 90°C only.

The hardness test of uncrosslinked LDPE/EVA and HDPE/EVA blends was determined according to ISO 868: 1998 on a hardness durometer (Zwick).

RESULTS AND DISCUSSION

Gel fraction

LDPE and HDPE are thermoplastic, consisting of a continuous amorphous phase in which the crystalline domains are distributed. Peroxide crosslinking takes place randomly at elevated temperatures in the molten state, where the polymer has only amorphous structure. Determination of gel content, which is an indication of extent of crosslinking, is reported elsewhere.^{12,21} Figure 1 shows the gel content against BCUP content for crosslinked LDPE and HDPE. As the curve indicates, there is a continuous increase of the gel content with peroxide content up to ~ 2.5 wt %, after which the curve gradually levels off; that is, an exponential variation of gel content was observed with increasing BCUP content. A comparison between the gel content of LDPE and HDPE shows that LDPE with its long-chain branching in its structure and presence of tertiary carbon atoms is more prone to the crosslinking and hence it has more gel content as compared with HDPE at the same peroxide content.

Thermal properties

The degree of crystallinity of semi-crystalline polymers has a considerable effect on their mechanical and thermal properties. Figures 2 and 3 show the DSC traces (heating curves) for LDPE/EVA and HDPE/EVA over a full composition range, respectively. As can be seen, both blends show two distinct peaks corresponding to the EVA and PE component of the blends. Moreover, the peak area corresponding to the PE component of the blends decreases with increased EVA content, whereas the corresponding EVA peak shows an increase depending on the blending ratio. This decrease in the PE peak area is due to the decrease in the PE ratio in the blend. These DSC

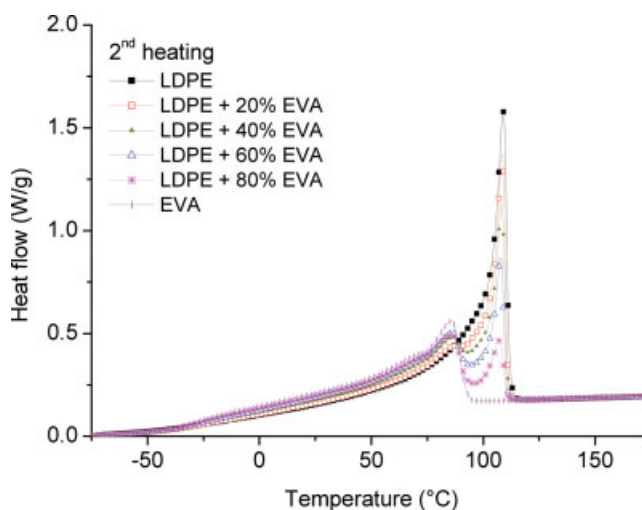


Figure 2 DSC thermograms of LDPE/EVA blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

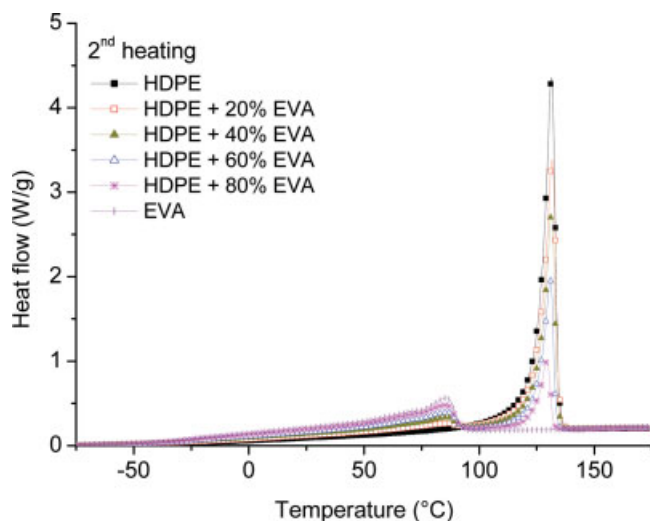


Figure 3 DSC thermograms of HDPE/EVA blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

curves were analyzed; the results corresponding to the melting and crystallization temperatures and heat of fusion (ΔH_m) of the blends with different EVA content are summarized in Table I. The EVA is observed to have no significant effect on the melting temperature of PE; rather, it decreases the total crystallinity of the blends. A comparison between effect of addition of EVA on reduction of crystallinity for LDPE/EVA and HDPE/EVA blends is shown in Table I. It is seen that this effect of reduced crystallinity is much more pronounced for HDPE/EVA blend as compared with LDPE/EVA blend. This is because the HDPE has higher crystallinity compared with LDPE. Thus, in this blend, EVA dispersed phase has a disrupting role in the arrangement of HDPE chain molecules in a crystal lattice when cooling from melt; as a result, crystallinity is reduced.

The effect of crosslinking on the thermal properties of LDPE, HDPE, LDPE/EVA, and HDPE/EVA blends will now be discussed. The DSC curves of

crosslinked LDPD and HDPE were analyzed and the results corresponding to the melting and crystallization temperatures, heat of fusion (ΔH_m) and percentage of crystallinity of samples with different peroxide content are summarized in Table II. Figures 4 and 5 show the effect of crosslinking on the thermal behavior of HDPE and its blends with 20 wt % and 40 wt % EVA, respectively. Figures 6 and 7 show the same behavior for LDPE.

It is seen that with increasing peroxide, the melting point and crystallinity of the crosslinked HDPE and LDPE decrease, although the melting peak areas of PE and EVA are decreased with blending; however, this decrease is more evident when the blend is crosslinked with 2% BCUP. In a blend with 20% EVA content, the EVA melting peak area almost disappears after the addition of BCUP, and only the corresponding PE melting point as observed with a lowered temperature. But, in a blend with 40% EVA content, two peaks still existed with slight shifts toward lower temperatures, as compared with uncrosslinked blends. Indeed, in this composition, we obtain blends that are less compatible in nature. This effect is much more pronounced for HDPE/EVA blend as compared with the LDPE/EVA blend.

Normally the glass transition temperature (T_g) is used as a tool for evaluating the degree of compatibility of a blend. In the present systems, since the T_g of the blend components are quite close to each other, it is very difficult to estimate the level of compatibility of the blends using this method. Therefore, the melting behavior of the blend components, and in particular the morphology of crystal formation, is taken into account for the compatibility evaluation. For uncrosslinked samples differences in the melting behavior and consequently differences in level of compatibility are better seen from variation in mechanical behavior and direct morphological observations (see Figs. 8–10).

Figure 8 depicts a lesser compatibility for blends with higher amount of EVA (> 40 wt %). This incom-

TABLE I
Melting Temperature (T_m), Heat of Fusion (ΔH_m), Crystallinity (X_c), and Crystallization Temperature (T_c) of Polyethylene Blends

EVA content (%)	LDPE/EVA blends						HDPE/EVA blends					
	T_m (°CC)		T_c (°CC)		ΔH_m (J/g)	X_c (%)	T_m (°CC)		T_c (°CC)		ΔH_m (J/g)	X_c (%)
	EVA	LDPE	EVA	LDPE			EVA	HDPE	EVA	HDPE		
0	—	108.8	—	96.0	141.3	49.8	—	131.4	—	119.7	220.5	76.2
10	86.0	108.5	69.6	96.6	130.4	47.6	86.3	131.2	69.6	119.7	209.3	73.3
20	87.5	108.3	69.4	96.2	124.6	44.5	85.9	131.6	70.2	119.1	193.5	66.8
30	86.7	108.0	69.7	96.7	123.5	42.9	86.3	131.2	70.6	119.2	178.8	63.1
40	86.6	108.0	69.8	96.1	119.6	40.4	86.2	131.3	70.9	119.3	162.8	56.9
50	86.4	107.9	70.2	96.5	110.1	39.4	85.9	131.0	71.0	119.2	152.4	51.4
60	86.2	107.7	70.4	96.1	109.8	36.5	86.3	130.8	71.0	118.9	134.2	48
80	85.9	107.2	70.7	95.1	91.4	32.5	85.9	129.6	70.8	116.1	106.0	36.5
100	85.7	—	69.2	—	81.0	27.5	85.9	—	69.2	—	81.0	27.5

TABLE II
Melting Temperature, T_m , Heat of Fusion, ΔH_m , Degree of Crystallinity, X_c , and Crystallization Temperature, T_c , of LDPE, and HDPE Crosslinked with Different Peroxide (BCUP) Content

Peroxide content (wt %)	LDPE				HDPE			
	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c	ΔH_m (J/g)	X_c (%)	T_m (°C)	T_c
0.0	141.4	49.1	108.8	96.0	220.5	76.5	131.4	119.7
0.5	135.9	47.2	107.0	95.2	195.5	67.8	129.9	117.3
1.0	130.5	45.3	106.1	93.3	192.8	66.9	128.5	116.7
1.5	127.6	44.3	103.9	91.7	182.2	63.3	126.8	115.6
2.0	126.8	44.0	103.1	91.0	178.9	62.1	125.9	114.7
2.5	126.3	43.8	101.4	90.4	164.8	57.2	121.6	111.4
3.0	124.8	43.3	99.5	88.8	158.3	54.9	121.0	111.2

patibility for the high-density grade of polyethylene due to a different molecular spatial structure with that of EVA is more distinct and it is quite clear in the melting behavior of HDPE/EVA blend containing more than 40 wt % EVA with two distinct melting endotherms corresponding to each component of the blends (Fig. 2).

As a result, one may conclude that incorporation of EVA into LDPE or HDPE reduces crystallinity and a two-phase dispersed morphology is obtained. When this blend is crosslinked, crystallinity is further reduced but compatibility is enhanced, so that at low levels of EVA (≤ 20 wt %), a compatible compound is attained with a lowered single melting point, whereas at higher levels of EVA (> 40 wt %) the compatible blends possess two melting endotherms shifted toward each other. Compatibility is more pronounced for cured LDPE/EVA as compared with HDPE/EVA blends.

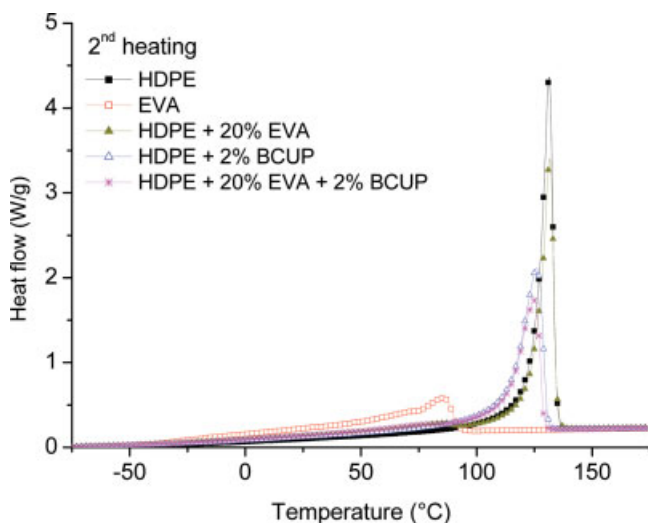


Figure 4 DSC thermograms of uncrosslinked and crosslinked HDPE with 20 wt % of EVA containing 2 wt % BCUP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

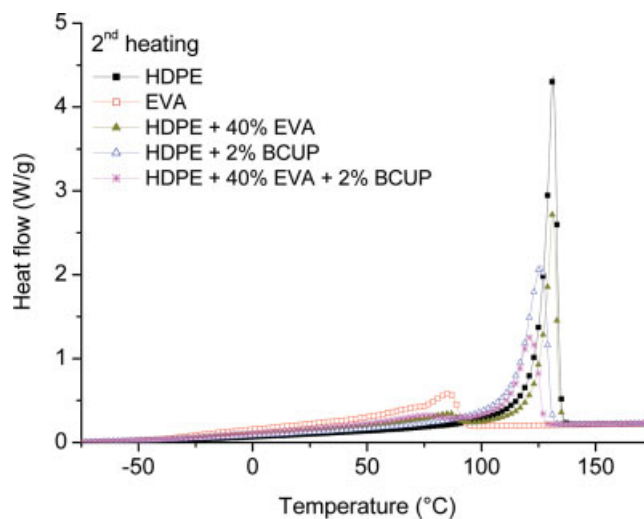


Figure 5 DSC thermograms of uncrosslinked and crosslinked HDPE with 40 wt % of EVA containing 2 wt % BCUP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mechanical properties

Effect of EVA content on tensile behavior

Table III shows modulus, elongation at the break, and tensile strength at room temperature for LDPE and HDPE blends with EVA. One of the important parameters that affects the modulus is crystallinity. As shown, by increasing the EVA content in PE/EVA blends, the crystallinity of LDPE/EVA and HDPE/EVA blends decreases. Therefore, the modulus of LDPE/EVA and HDPE/EVA blends decreases with the increase of EVA content.

At ≤ 20 wt % EVA, the EVA phase is dispersed in the LDPE matrix (Fig. 8). So, the elongation is not

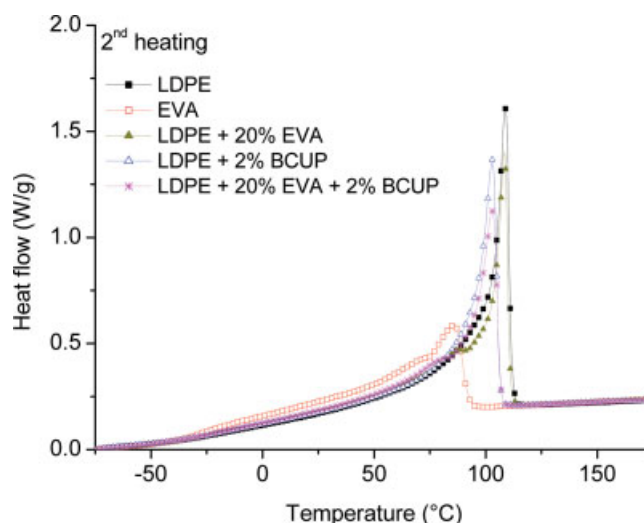


Figure 6 DSC thermograms of uncrosslinked and crosslinked LDPE with 20 wt % of EVA containing 2 wt % BCUP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

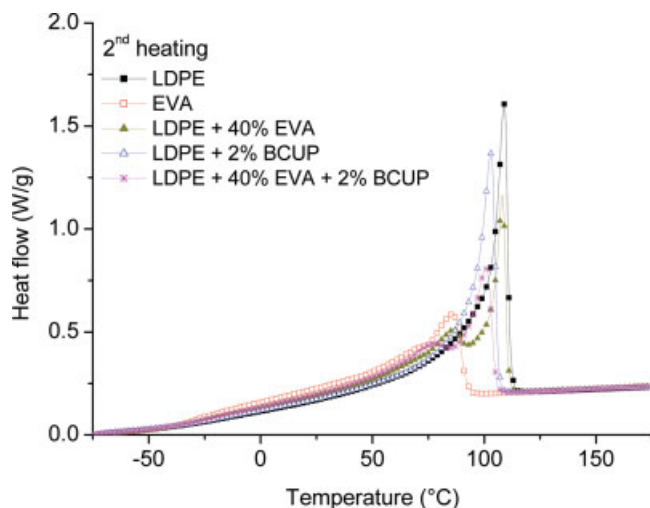


Figure 7 DSC thermograms of uncrosslinked and cross-linked LDPE with 40 wt % of EVA containing 2 wt % BCUP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

affected by the EVA rubbery dispersed phase. As the EVA percentage is increased, the properties of the blend approach the properties of the rubbery phase due to changes in the morphology of the blend. Therefore, the elongation at the break and tensile strength increase with increased EVA content.

The EVA particles are also dispersed in the continuous matrix of HDPE at ≤ 20 wt %. In this region (≤ 20 wt % EVA), small changes in the properties of HDPE/EVA blends are observed. These changes are due to the particle size of dispersed EVA phase. With increasing EVA ≤ 50 wt %, the elongation decreases as a result of the changes in the morphology of the blend. Beyond 50 wt %, because of the occurrence of phase inversion, the elongation of the blend increases to reach the elongation of pure EVA. Similarly, the tensile strength at the break initially decreases with an EVA of ≤ 40 wt %, and then increases. The initial decrease in the tensile strength and elongation at the break can be attributed to the biphasic nature of the blend. With increased disperse phase content due to the increased incompatibility of the blend components, the properties of the matrix phase (high super-tough HDPE) is decreased. After the phase inversion point, a reverse trend is observed since the properties of minor phase dominate the blend.

The influence of EVA content on the elongation at the break of the LDPE/EVA and HDPE/EVA blends is shown in Figures 9 and 10. An increase in the EVA content resulted in a decrease in the elongation at the break for HDPE/EVA blends. But the elongation at the break increases for LDPE/EVA blends, as shown in Figure 10, with increasing of EVA content. One of the most important factors influencing the final properties is the mutual miscibility of the components.

Most polymeric substances are not miscible with each other. A few methods can be used to investigate the miscibility: DSC, DMA, SEM, and others. In our previous article, we showed that the DMA curves for LDPE/EVA and HDPE/EVA blends had only one glass transition temperature,²⁵ while the DSC curves and SEM results of these blends proved the incompatible nature of these blend systems.

The log-additive rule is a better rule for investigation of compatibility of blends:^{26,27}

$$\log E = \sum \omega_i \log E_i,$$

where E is one of the properties of blend and the E_i is properties of the i th component, respectively, and ω_i is the weight fraction of the i th component. A strong negative deviation from the log-additive rule indicates that systems are not compatible. Thus, comparing Figure 9 with Figure 10, it is evident that LDPE and EVA are much more compatible than HDPE and EVA blends, which show distinct negative deviation from the mixture additive rule.

Figure 9 comprises three regions: region 1, ≤ 40 wt % EVA; region 2, 40–70 wt % EVA; and region 3, 70 wt % upward. In the whole blend composition range, a negative deviation from rule of mixtures, which is an indication of an anti-synergism behavior of the system, is evident that can be attributed to the difference between the linear and branched architecture of two polymer molecules. In region 2, in which the phase inversion occurs, the incompatibility, and hence the deviation, becomes more pronounced and gradually HDPE constitutes the dispersed phase in EVA matrix. Figure 8 depicts the phase inversion for a 50 wt % blend of HDPE and EVA blend. In region 3, the trend of the curves is similar to the region 1, but with a reversed matrix.

Similarly, Figure 10 can be interpreted in terms of four regions. But here, at all compositions, two highly branched polymers (LDPE and EVA) are much more compatible and show less deviation from the mixtures rule. In region 1 (< 40 wt % of EVA), a biphasic dispersed-type morphology is observed in which EVA phase are well distributed in the continuous LDPE phase. The elongation at the break decreases in this region. A co-continuous phase morphology occurs in region 2 (40–60 wt % of EVA), which is depicted in Figure 8 for the LDPE/EVA blend. It is noteworthy to see excellent compatibility between the two polymers in region 2, where EVA constitutes the matrix. Therefore, the obtained properties are close to the mixing rules. In region 3 (60–80 wt %), LDPE dispersed phase with lower melt viscosity compared with EVA has been broken easily to much smaller droplets. So, in this region, higher properties are observed as compared with region 1. In region 4 (> 80 wt % EVA content), the size and content of LDPE phase are small enough

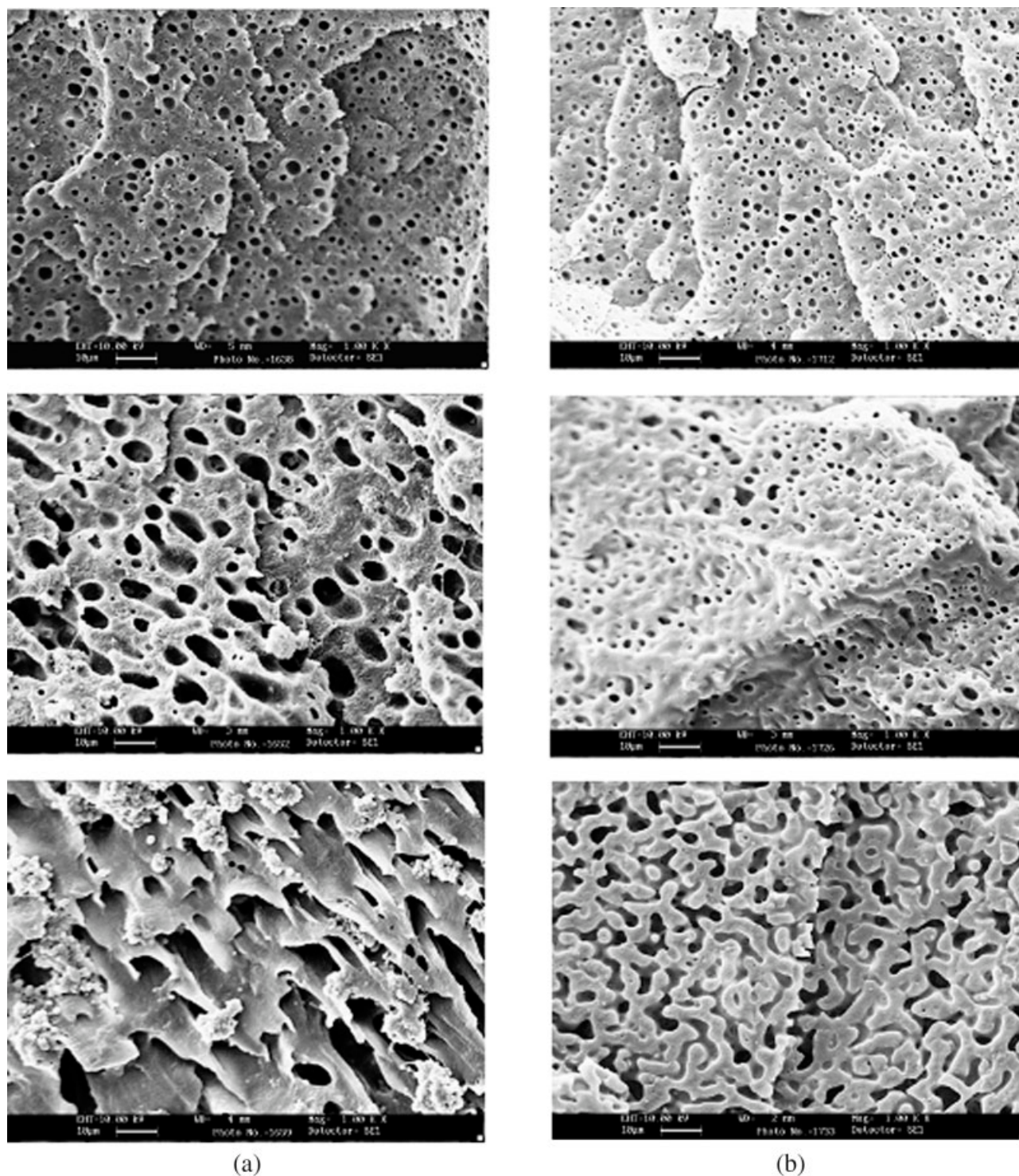


Figure 8 SEMs of LDPE/EVA and HDPE/EVA etched cryofractured surface containing 20, 40, and 50 wt % of EVA. (a) HDPE/EVA: 80/20, 60/40, and 50/50; (b) LDPE/EVA: 80/20, 60/40, and 50/50.

to have a compatible blend in which the properties of the EVA as matrix phase dominate the final properties hence in this region the blend obeys the mixing rule.

Hardness tests provide a rapid evaluation of variations in mechanical properties affected by changes in chemical or processing conditions, heat treatment,

microstructure, and aging. Morphological and textural changes in crystalline polymers can be detected by hardness tests. Table IV shows the results of hardness tests for the PE/EVA blends. As it is seen, the hardness decreases by increasing the EVA content. The reduction in hardness is more pronounced

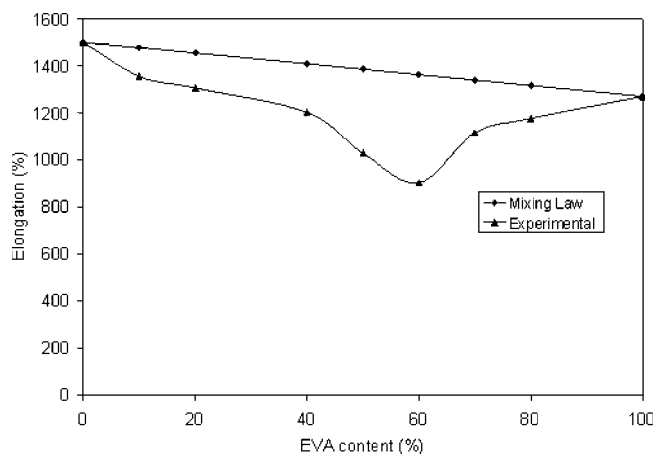


Figure 9 Effect of EVA content on the elongation at break of LDPE/EVA blends.

for HDPE/EVA blend as compared with LDPE/EVA blend. This is because the HDPE has higher crystallinity as compared with LDPE.

Effect of BCUP content and temperature on tensile behavior

PE is ductile and, under tension at room temperature, usually yields with necking and drawing followed by strain hardening effect and finally ruptures at relatively long elongation.

The data on the effect of temperature and BCUP content on the tensile properties of crosslinked LDPE and HDPE with two different contents of EVA (20 and 40 wt %) are summarized in Table V. Young's modulus decreases with increased crosslinking level and temperature, as it shown in Table V. The above results can be interpreted as follows.

Because of the restriction imposed by crosslink junctions for packing of chains units together in an ordered lattice while cooling from the melt, the crystallinity of the cooled solid polymer decreases with the increased crosslinking that takes place in the molten state (as shown in DSC data). These two structural parameters have an opposing effect on the mechanical properties of the polymer. At room temperature, there are both physical crosslinks (crystalline ties) and chemical crosslinks between polymeric chains. With increased chemical crosslinks, which are stronger than the physical crosslinks, the restriction imposed on the elongational behavior of the polymer increases. This restriction is due to the smaller length of segments available for stretching and lesser the probability of chain slippage resulting in decrease of elongation at the break. At low peroxide content (0.5 wt % BCUP), the increased temperature weakens the physical crosslinks, as a result of

disappearance of the crystallites, while the chemical crosslinks are not yet sufficient to hold the structure fully. Therefore, it behaves the same as virgin uncrosslinked PE. However, with increased chemical crosslinks and increased temperature, the chemical crosslinks are more effective, although the physical crosslinks are weakening. This reduces the elongation at the break at higher temperatures.

Below the crystalline transition temperature, that is the stress-strain behavior obtained at $< 90^{\circ}\text{C}$ (Table V), values of the Young's modulus and the yield strength are dominated by the amount of hard crystalline regions, unit cells of which are held together by relatively strong forces. This crystalline structure is being weakened and reduces with advancement of crosslinking degree so are the Young's modulus and the yield strength. The tensile stresses are borne by a larger number of crosslinks, resulting in rupture of samples at lower tensile stress. However, with increasing the crosslink points, apart from decreasing the stress-resistant crystalline domains, one reaches a circumstance in which no strain hardening occurs and the stress is not borne by the oriented backbone chain segment, but only by the single crosslink bonds, where the drop in tensile strength is observed. It is noteworthy that at temperatures higher than the crystalline transition temperature (Table V), owing to fewer crystalline ties, or even those that have disappeared, the number of crosslinks upon which the tensile strength is dependent is less than the critical value that would have been reached at the same degree of crosslinking at lower temperatures.

EVA containing tertiary type of carbons in its chain skeleton is more prone to crosslinking reaction by peroxide compared with polyethylene. In our previous studies, we have observed higher amount

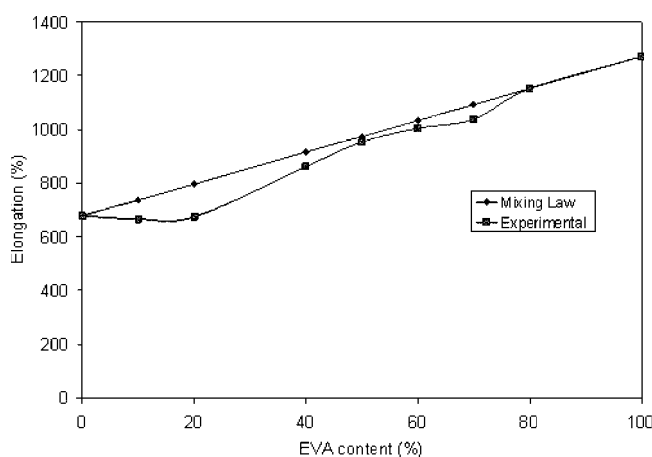


Figure 10 Effect of EVA content on the elongation at break of HDPE/EVA blends.

TABLE III
Tensile Properties of Polyethylene/Ethylene Vinyl Acetate Copolymer Blends at 25°C

EVA content (%)	LDPE/EVA blends			HDPE/EVA blends		
	σ_B (MPa)	ε_B (%)	E_t (MPa)	σ_B (MPa)	ε_B (%)	E_t (MPa)
0	13.2	678	210.6	*	*	728.9
10	12.5	666	178.3	13.8	1355	712.1
20	12.9	674	164.4	13.7	1306	627.4
40	15.0	861	121.2	14.4	1202	396.5
50	16.4	953	101.3	18.0	1028	262.8
60	16.9	1005	79.0	20.1	903	193.5
70	17.4	1038	62.1	21.1	1115	91.9
80	20.2	1151	51.0	21.2	1177	63.7
100	22.7	1270	35.6	22.7	1270	35.6

* The samples did not rupture in the range of tensile machine.

TABLE IV
Hardness (Shore D) of Polyethylene/Ethylene Vinyl Acetate Copolymer Blends

PE blends	EVA content (%)										
	0	10	20	30	40	50	60	70	80	90	100
HDPE/EVA	73	71	69	66	63	60	56	53	50	—	46
LDPE/EVA	60	59	58	56	55	52	53	50	48	—	46

of gel for EVA with respect to PE for the same amount of peroxide added. That is why the gel content increases with an increasing amount of EVA in the blend and gel affected blend properties are altered in the way as expected.²⁸

This effect on the mechanical behavior of PE/EVA blends is shown in Table V. At a given temperature and peroxide content, with increased EVA from 20

to 40 wt %, the elongation at the break decreases. Moreover, with increasing EVA, modulus of cured samples decreases due to the reduction in crystallinity; however, tensile stress at the break increases for the sake of higher gelation brought about by EVA.

CONCLUSIONS

Investigation of thermal properties of PE/EVA over a full composition range showed two distinct unchanged melting peaks corresponding to the EVA and PE component of the blends respectively. Moreover the peak area corresponding to PE component of the blends decreased with the increased EVA content, whereas the corresponding EVA peak showed an increase depending on the blending ratio. Overall degree of crystallinity of the blends decreased with

TABLE V
Tensile Properties of Crosslinked Polyethylene with 20% and 40% of Ethylene Vinyl Acetate Copolymer Blends at Different Content of Peroxide and Different Temperatures

PE	Temperature Samples/Tensile properties	20°C			90°C			130°C		
		σ_B (Mpa)	ε_B (%)	E_t (Mpa)	σ_B (Mpa)	ε_B (%)	E_t (Mpa)	σ_B (Mpa)	ε_B (%)	E_t (Mpa)
LDPE	LDPE	13.2	670	220						
	LDPE + 0.5% BCUP	12.9	535	213	6.1	653	29.9	1.7	476.5	10
	LDPE + 1.5% BCUP	9.9	307	165	4	252	21.7	.87	207.9	3.1
	LDPE + 20% EVA + 0% BCUP	12.0	650	165						
	LDPE + 20% EVA + 0.5% BCUP	14.6	675	153	5.1	842	15.4	.51	956	.8
	LDPE + 20% EVA + 1.5% BCUP	16.4	518.8	83	6.6	447	15.6	1.2	272	.6
	LDPE + 40% EVA + 0% BCUP	15.0	860	121						
	LDPE + 40% EVA + 0.5% BCUP	8.8	515	92.9	3.4	598	8.5	.95	403	5.2
HDPE	LDPE + 40% EVA + 1.5% BCUP	13	275	85.4	4.2	200	12.3	2.1	149	7.1
	HDPE	*	*	728.9	*	*	158.9			
	HDPE + 0.5% BCUP	32.9	1066	537	15.9	1066	99.5	2.9	1287	10.6
	HDPE + 1.5% BCUP	27.3	737.7	431.8	13.4	723.3	74.2	2.6	566	5.1
	HDPE + 20% EVA + 0% BCUP	*	*	627						
	HDPE + 20% EVA + 0.5% BCUP	29	967	443	12.0	1236	79	2.5	1350	—
	HDPE + 20% EVA + 1.5% BCUP	22.1	607	295	11.6	564	54	3.3	400	11.3
	HDPE + 40% EVA + 0% BCUP	12.75	1270	377						
HDPE + 40% EVA + 0.5% BCUP	27.3	807	299	7.4	890	44.3	.8	412.3	5.6	
HDPE + 40% EVA + 1.5% BCUP	24.2	659	230	8.9	563	25.9	2.6	397.9	4	

* The samples did not rupture in the range of tensile machine.

increase of EVA content. The effect of crosslinking on thermal behavior of HDPE, LDPE, and its blends with 20% and 40% EVA was investigated. It was found that with increasing peroxide, the melting point and crystallinity of the crosslinked HDPE and LDPE decreased, although the overall melting peak areas of PE and EVA were decreased with blending; however, this decrease was more evident when the blend was crosslinked with 2% BCUP. In a blend with 20% EVA content, the EVA melting peak almost disappeared after the addition of the BCUP but, in the 40% EVA content, two peaks corresponding to the melting points of PE and EVA still existed. On the whole dynamic crosslinking enhances the compatibility between EVA and polyethylene, with LDPE being more compatible than HDPE.

Investigation of mechanical properties of the uncrosslinked PE/EVA blends showed that with increased EVA content, the modulus and hardness decreased. The elongation at the break increased with increased EVA content for the LDPE/EVA blends, while a reverse trend was seen for the HDPE/EVA blends. A good correlation was observed between mechanical (elongation at the break) and morphological properties. The blends with a higher level of compatibility showed less deviation from the additive rule of mixture in mechanical properties. The deviation became more pronounced for HDPE /EVA blends in the phase inversion region, while an opposite trend was observed for LDPE/EVA blends with co-continuous morphology.

The effect of temperature and BCUP content on mechanical properties of crosslinked LDPE and HDPE with two different contents of EVA (20 wt % and 40 wt %) showed that the Young's modulus decreased with increased crosslinking level and temperature. The mechanical properties observed are influenced by opposing effects of extent of crystallinity and crosslinking degree, as well as temperature and blend morphology.

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