

Compatibility of Low-Density Polyethylene/Poly(ethylene-co-vinyl acetate) Binary Blends Prepared by Melt Mixing

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ABSTRACT: The compatibility of low-density polyethylene and poly(ethylene-co-vinyl acetate) containing 18 wt % vinyl acetate units (EVA-18) was studied. For this purpose, a series of different blends containing 25, 50, or 75 wt % EVA-18 were prepared by melt mixing with a single-screw extruder. For each composition, three different sets of blends were prepared, which corresponded to the three different temperatures used in the metering section and the die of the extruder (140, 160, and 180°C), at a screw rotation speed of 42 rpm. Blends that contained 25 wt % EVA-18 were also prepared through mixing at 140, 160, or 180°C but at a screw speed of 69 rpm. A study of the blends by differential scanning calorimetry showed that all the prepared blends were heterogeneous, except that containing 75 wt % EVA-18 and prepared at 180°C. However, because of the high inter-

facial adhesion, a fine dispersion of the minor component in the polymer matrix was observed for all the studied blends with scanning electron microscopy. The tensile strengths and elongations at break of the blends lay between the corresponding values of the two polymers. The absence of any minimum in the mechanical properties was strong evidence that the two polymers were compatible over the whole range of composition. The thermal shrinkage of the blends at various temperatures depended mainly on the temperature and EVA-18 content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 841–852, 2003

Key words: polyethylene (PE); compatibility; blends; differential scanning calorimetry (DSC); mechanical properties

INTRODUCTION

Ethylene copolymers such as poly(ethylene-co-vinyl acetate) (EVA) are produced by free-radical polymerization in a bulk process, like that used for low-density polyethylene (LDPE) production, involving high pressures and temperatures.¹ Because the vinyl acetate monomer has the same reactivity with the ethylene monomer, a variety of copolymers, containing different vinyl acetate contents, can be produced. The vinyl acetate content affects straightforwardly the degree of crystallinity and generally all the properties of the copolymers. The copolymers are more flexible and have higher transparency, lower modulus of elasticity, and improved barrier properties to oxygen and water vapor than LDPE. However, the major drawback of EVA is its low melting temperature (T_m) and melt strength, which restrict its applications at high temperatures.

There has been increasing interest in LDPE/EVA blends, which offer high performance at low cost. The addition of EVA to LDPE improves its environmental stress crack resistance, toughness, film transparency, and flexibility. For all these reasons, these blends have

gained great technological and economic importance, and they can be used in various applications. Many studies concerning foam production with LDPE/EVA blends have also been performed.^{2–4} Such blends are used in the electric, electronic, wire-cable-coating, and automotive industries, among others. However, for the polymers to have efficient melt strength, the existence of crosslinks between the polymer chains is necessary; in the case of polyolefins, they are mainly formed by irradiation at room temperature. EVA has a higher capacity for crosslinking and lower thermal conductivity than LDPE.^{5,6} The gel content of irradiated LDPE/EVA blends depends not only on the irradiation dose but also on the atmosphere and EVA content. The extent of crosslinking in a blend increases with increasing EVA content.⁵

The greater capacity of EVA for crosslinking has also been used for grafting larger amounts of acrylamide in LDPE/EVA films.⁷ Polyacrylamide can be used for copper recovery from aqueous solutions, but it is soluble in water. For this problem to be overcome, acrylamide is grafted in an insoluble matrix, such as LDPE/EVA, and in this way, copper can efficiently be recovered (up to 98%) from water solutions. Besides, such films can be used as photodegradable materials because acrylamide accelerates photodegradation and the mechanical properties of the films deteriorate rapidly.

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Blends of random EVA copolymers of different commercial grades with high-density polyethylene (HDPE) and carbon black were used for the preparation of conducting polymer composites.⁸ The idea was to produce a smart fiber capable of sensing the environmental conditions of its immediate surroundings through the electroactive response of the fiber. The whole technology was based on the reversible electroactive responses exhibited in conducting polymer composites. For these composites to have sufficient mechanical properties and also retain their electrical conductivity, the filler content should be as small as possible. The addition of EVA resulted in composites containing only 3.6–4.2 wt % carbon black for lower resistivity; this meant higher conductivity attributed to vinyl acetate units.

The largest amount of end-use LDPE is used for film applications. It is preferred as a packaging material because it can be produced in various thicknesses, is low-cost and highly transparent, and has low toxicity and a limp feel. LDPE/EVA blends can be used alone or in combination with other polyolefins such as HDPE, polypropylene (PP), and poly(ethylene-co-vinyl alcohol) (EVOH) for the production of multilayer packaging films.⁹ Such coextruded and oriented films offer an ideal combination of oxygen barrier properties, toughness, shrinkability, and good optical properties.^{10,11} Furthermore, LDPE/EVA blends can be used for shrinkable films suitable for the packaging of meats and other products.¹² After air evacuation, the films can suffer shrinkage very easily through mild heating.

EVA, except from the preparation of blends with LDPE, can also be used to produce compatible or miscible blends with several kinds of polymers or as a compatibilizer in incompatible blends.^{13–15} For EVA/poly(vinyl chloride) (PVC) blends, an increase in the impact strength depends on the amount of EVA and vinyl acetate. The polar ester groups of vinyl acetate can interact strongly with the polar C—Cl groups of PVC, and this can lead to truly miscible blends if the amount of vinyl acetate groups is higher than 60 wt %.¹⁶ Therefore, EVA-chlorinated polyethylene blends are also miscible.¹⁷ The existence of hydrogen bonds between the carbonyl groups and hydroxyl groups, as in EVA/phenolic resin blends, can also enhance miscibility.¹⁵ Because of this ability, EVA containing 8 wt % vinyl acetate units was used as effective compatibilizer in LDPE/starch biodegradable blends.¹⁸ It was also used as a compatibilizer between HDPE and poly(butylene terephthalate)¹⁹ or poly(ethylene terephthalate)²⁰ and melt-blended with other polyolefins such as PP to increase their impact strength.²¹

The aim of this study is to study the effect of functional parameters, such as the temperature of mixing and screw rotation speed, on the thermomechanical properties and morphology of blends of LDPE and

TABLE I
Characteristics of the LDPE and EVA-18 Copolymers

	LDPE	EVA-18
Density (g/cm ³)	0.921	0.936
Melt-flow index (190°C g/10 min)	2.5	2
Tensile strength at break (MPa)	19	21
Tensile strength at yield point (MPa)	11	—
Elongation at break (%)	>500	>750

poly(ethylene-co-vinyl acetate) containing 18 wt % vinyl acetate units (EVA-18), which have been prepared by melt mixing. These properties generally characterize the miscibility or compatibility of a studied binary system. The blends consist of two distinct phases but exhibit sufficient mechanical properties. Therefore, they have been characterized as immiscible but compatible blends. These blends are commercially available, have great technological importance, and are used for the industrial production of tubes for medical applications.

EXPERIMENTAL

Materials

LDPE (Stamylan LD-2102TN37) was provided by BP Chemicals. EVA-18 (PA-538) was supplied by Novex Co. Some characteristics of these polymers are presented in Table I.

Blend preparation

Blends containing LDPE and various amounts of EVA-18 (25, 50, or 75 wt %), were prepared via melt blending in a Devis BCC50/B6055 standard single-screw extruder (length/diameter = 30). For each composition, three sets of blends were prepared, corresponding to the three different temperatures used in the metering section and the die of the extruder (140, 160, and 180°C). The temperatures in the feed and transition sections were kept constant in all runs (130 and 140°C, respectively). The screw rotation speed was 42 rpm. Blends containing 25 wt % EVA-18 were also prepared via mixing at 140, 160, or 180°C but at a screw rotation speed of 69 rpm. All the blends were extruded in the form of tubes with an external diameter of 10 mm and a thickness of 1 mm; they were cooled immediately in a water bath.

Thermal analysis

A thermal analysis of the blends was performed with differential scanning calorimetry (DSC; Pyris 1, PerkinElmer) calibrated with metal standards. For each measurement, a sample of about 10 mg was used. It was placed in an aluminum pan that was sealed and

heated to 180°C at a scanning rate of 20°C/min. From these scans, the values of T_m and the heat of fusion (ΔH_m) of the blends were measured.

Mechanical properties

Tensile tests were performed on an Instron 1122 dynamometer in agreement with the ASTM D 638 method at a crosshead speed of 50 mm/min. Before the measurements, the samples were conditioned at $50 \pm 5\%$ relative humidity for 36 h and placed in a closed chamber containing a saturated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution in distilled water (ASTM E 104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value. The specimens for the mechanical properties were prepared by compression molding of the extruded tubes in a heated press (PW30 hydraulic press, Paul-Otto Weber). The T_m 's were the same as those used for the preparation of each blend, and the applied load was 6 kN on a ram of 110 mm, followed by rapid cooling in the molds.

Morphology of the blends

The morphology of the blends was examined with scanning electron microscopy (SEM; JMS-840, JEOL). For this examination, fractured samples of each blend tube were used. The samples were etched with xylene for 4 h at 50°C for the removal of the EVA-18 copolymer. The specimens were covered with a carbon coating for good conductivity of the electron beam. Microphotographs were taken within a magnification range of 500–8000 \times .

Shrinkage

So that there would be sufficient results for the shrinkage estimation, the shrinkage percentage was measured for the stretched samples, which were elongated to 500% in the Instron 1122 dynamometer, as described before. The measurements were performed at three different temperatures (80, 120, and 160°C). The shrinkage (Shr) was calculated as follows:

$$\text{Shr} (\%) = (L_{\text{str}} - L_{\text{shr}})/L_{\text{str}} \times 100$$

where L_{str} is the length of the sample after stretching and L_{shr} is the length of the sample after shrinkage.

RESULTS AND DISCUSSION

Thermal analysis

The effects of the blend composition and mixing temperature on the thermal properties of the prepared LDPE/EVA-18 blends have been studied with DSC.

The blends containing 75 wt % EVA-18 are transparent, not depending on the mixing temperature, whereas those containing 25 or 50 wt % EVA-18 are white, especially the former with the highest LDPE content. This behavior is an indication that these blends are inhomogeneous. The DSC thermograms of the blends containing different amounts of EVA-18 prepared by melt mixing at 180°C are presented in Figure 1.

For all samples, a small peak between 45 and 65°C, before the main melting peak, has been recorded, which is due to the melting of crystals formed during the storage of the samples at room temperature because, after the first melting and rapid quenching of the blends, these peaks are not recorded during the second heating run.

In the DSC traces of the blends containing 25 or 50 wt % EVA-18, two well-distinguished melting peaks, at temperatures close enough to the T_m 's of LDPE and EVA-18, can be observed, revealing the formation of separate crystal phases of the two polymers. EVA-18 has lower crystallinity than LDPE, and its T_m at 87°C, is almost 25°C lower than that of LDPE (112°C). In the literature, it has been reported that T_m of EVA depends almost linearly on its vinyl acetate content.²² As the content of vinyl acetate increases, T_m decreases because the acetate branch points reduce the packing and folding of chains and, therefore, interrupt the crystallization of the polyethylene backbone.

The melting peaks of the blends, corresponding to LDPE and EVA-18 phases, are both shifted by about 2–3°C toward lower temperatures with respect to the peaks of the original polymers. This shifting indicates a plasticizing action of one component to the other, probably caused by the interpenetration during melt mixing of some macromolecules of one component into the phase of the other. During the cooling of the blends, the crystallization of the components takes place, and these macromolecules are enclosed, probably in different polymer phases, acting as diluents within the crystalline regions. From the DSC traces of the blends containing 25 or 50 wt % EVA-18, it seems that, despite the great similarity of the chemical structures of the macromolecular chains of the two polymers, immiscible blends are formed. This phenomenon has also been observed for other polymers with such great similarity in molecular structure, such as nylon 6 and nylon 6,6 and polyethylenes with differently sized branches that crystallize into separate crystalline phases.^{23,24} For LDPE/HDPE blends²³ and linear low-density polyethylene (LLDPE)/LDPE blends,²⁴ two distinct T_m 's have been observed that are attributable to the separate melting of the low-crystalline and high-crystalline regions of the blends. The only difference in the structures of these polymers is the existence of short branches in HDPE and LLDPE and

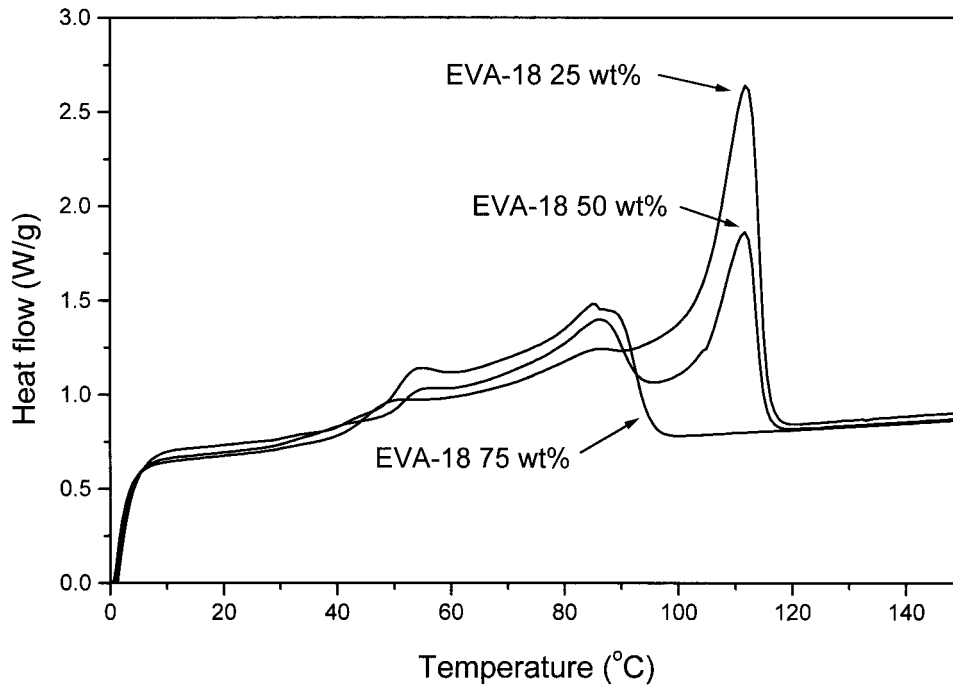


Figure 1 DSC thermograms of LDPE/EVA blends prepared at 180°C.

long branches in LDPE, but they form immiscible blends.

However, the behavior of the blend containing 75 wt % EVA-18 is different from that of the blend containing 25 or 50 wt % EVA-18. As can be seen in Figure 1, this blend exhibits only one melting peak at 85°C, which is indicative of the existence of a single crystalline phase. The samples containing 75 wt % EVA-18

but blended at lower temperatures (160 or 140°C) show an extra small peak (ca. 110°C) corresponding to the melting of a separate LDPE crystalline phase, which is larger at 140°C ($\Delta H_m = 6.2$ J/g) than at 160°C ($\Delta H_m = 1.2$ J/g; Fig. 2). These results show that a large amount of EVA-18 (75 wt %) and a high mixing temperature (180°C) are necessary to obtain a blend with a single crystalline phase.

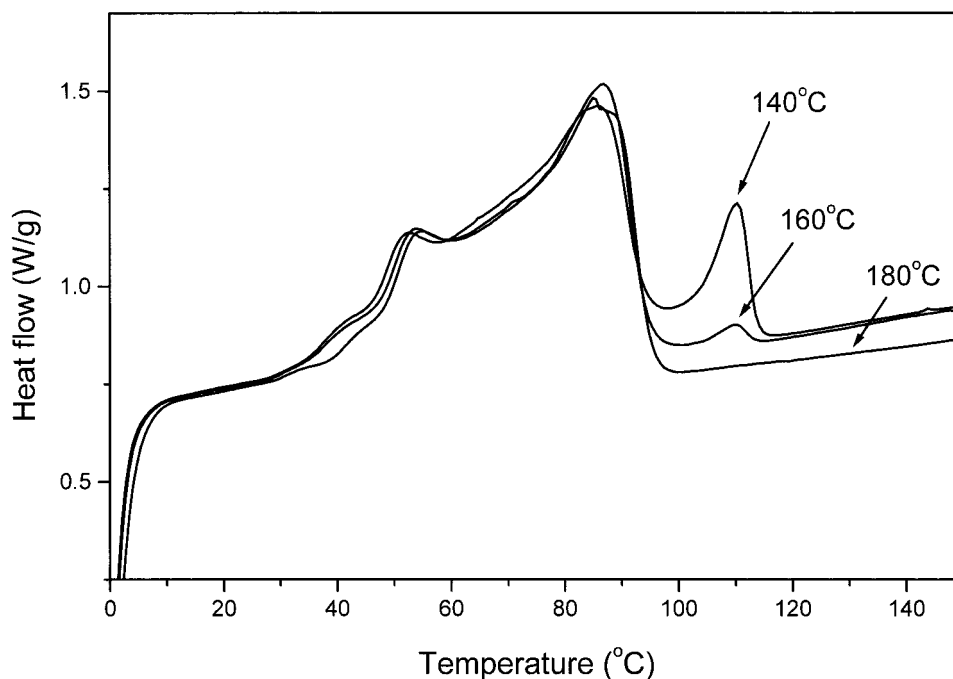


Figure 2 DSC thermograms of 25/75 (w/w) LDPE/EVA blends prepared at different temperatures.

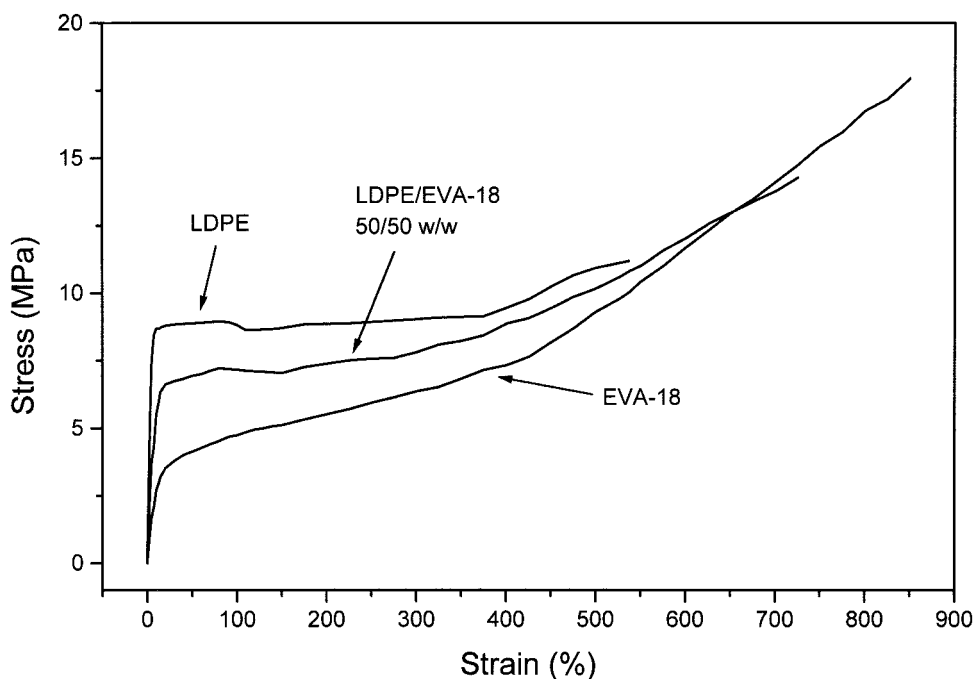


Figure 3 Stress-strain curves of LDPE, EVA-18, and a 50/50 (w/w) blend.

For the interpretation of the aforementioned behavior of the blends, the influence of the blending temperature and blend composition on the resulting morphology has been analyzed. It is well known that at temperatures far above T_m of a polymer, the chains are extended. If both LDPE and EVA chains are more extended at the higher T_m of 180°C, more effective mixing is achieved under the stress field. Besides, melting at such a high temperature results in the destruction of the majority of crystal nuclei. Therefore, entanglements between the chains of the different polymers, combined with reduced crystal nuclei, result in slower rates for a subsequent crystallization of LDPE. Then, crystallization of LDPE probably takes place at temperatures comparable to those at which EVA crystallizes (close to 65°C). The simultaneous crystallization of the two components means that phase segregation is no more favored by crystallization. With respect to the composition, it is plausible to assume that if the amount of LDPE is small, at a T_m of 180°C, its chains are quite finely dispersed among the EVA chains and effectively trapped because of the entanglements occurring between the chains of the different species. With the amount of LDPE increased, its chains can no longer be trapped by EVA chains, and this, in turn, leads to the formation of a separate LDPE crystal phase during cooling.

Crystallization at low temperatures or in a constrained environment results in poor crystals because of the presence of crystal defects as well as a small crystal size. This explains the low T_m 's of EVA and the LDPE crystals in the case of the blend containing 75 wt

% EVA-18 after blending at 180°C. All these poor crystals melt at comparably low temperatures, giving a single melting peak.

Mechanical properties

In Figure 3, the stress-strain curves of LDPE, EVA-18, and a blend with 50 wt % EVA-18 are presented. LDPE shows a clear yield point, after which a small decrease appears in the stress; the stress increases again after 350% strain. On the contrary, EVA-18 does not show a yield point but, during the applied stress, is uniformly elongated, without forming a neck. EVA-18 has a larger amorphous fraction than LDPE, and the macromolecules can slip more easily and can be oriented in the direction of the applied stress more easily than LDPE. Also, EVA-18 shows a strain hardening after 400–450% elongation, and this results in an increase in the tensile strength of the sample because of higher orientation and probable crystallization. Because EVA-18 is less crystalline than LDPE, the effect of strain hardening is more prominent. The elongated part of the specimen becomes white, revealing the occurrence of crystallization. The tensile stress at break for EVA-18 is higher than that for LDPE.

The stress-strain curves for all the blends lie between these of the constituent polymers. The blends containing 50 and 25 wt % EVA-18 show a clear yield point.

In Figure 4, the tensile strength at break for neat polymers and the studied blends are presented. In the latter, an increase in the amount of EVA-18 results in

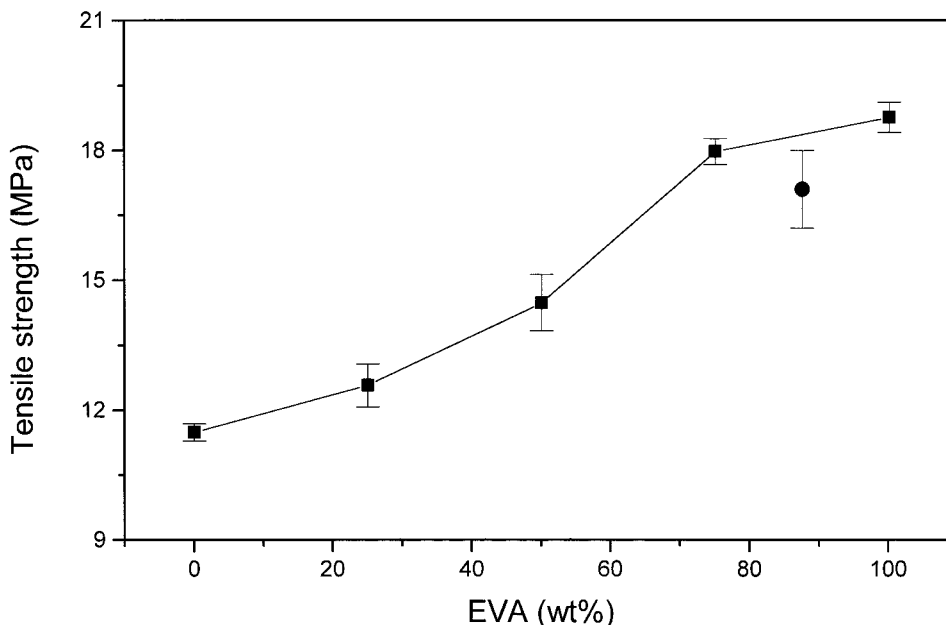


Figure 4 Tensile strength of LDPE, EVA-18, and their blends.

an almost linear increase in the tensile strength. This behavior indicates that the two polymers are compatible. It is known that for incompatible blends, the tensile strength and especially the elongation at break follow a negative deviation from the linear variation with the blend composition, exhibiting a minimum because of the high interfacial tension between the different components.²⁵ In incompatible polyolefin blends, this minimum in mechanical properties appears for a blend containing equal amounts of each component or almost such a composition.²⁶ Also, it has been reported in the literature that a blend system of LDPE and poly(ethylene-co-vinyl acetate) with 28 wt % vinyl acetate units (EVA-28) showed a minimum in tensile properties corresponding to the blend containing 70 wt % EVA.²⁷ This result is in contrast with our findings, which, however, are concerned with blends of LDPE with EVA containing 18 wt % vinyl acetate units. The higher amount of acetate groups in EVA-28 most likely increases the polar character of EVA-28 and decreases the affinity and, therefore, compatibility of LDPE with EVA-28. The LDPE/EVA-28 blends after being crosslinked show a positive variation of the mechanical properties from linearity, and the tensile strength for blends containing 50 and 70 wt % EVA-28 copolymer has been increased to levels higher than those in the neat EVA-28 copolymer.²⁷ This effect has been attributed to the *in situ* compatibilization and the formation of interpenetrating networks between the different phases, which result in an increase in the interfacial adhesion.

In Figure 4, it is shown that the 25/75 (w/w) LDPE/EVA-18 blend has a tensile strength value slightly higher than that predicted by the linear dependence of

the strength values on the blend composition. Such a positive variation is also observed for the same blend for the elongation at break (Fig. 5). This finding, in combination with the thermal analysis results (i.e., single phase melting), indicates a higher compatibility of the two components and/or a synergistic effect between the two polymers. Such a synergistic effect on the ultimate tensile strength and elongation at break has been mentioned for poly (butene-1) (PB-1)/PP blends prepared by injection molding, which are also immiscible.²⁸ To check if this also occurs in our blends, we have prepared one more blend containing 87.5 wt % EVA-18 and 12.5 wt % LDPE by melt blending in the extruder at 180°C. However, the tensile strength (Fig. 4) of this new blend is close to the linear fit. Therefore, it seems that there is not any synergistic effect between the two polymers even in the case in which one component exists in a very low amount. The high compatibility is perhaps the result of the occurrence of crosslinking between LDPE and EVA-18, which forms macromolecules acting as compatibilizers.

The elongation at break shows a dependence on the blend composition (Fig. 5) similar to that observed for the tensile strength. EVA-18, because of its higher amorphous fraction with respect to LDPE, has a more intense elastomer-like behavior, exhibiting very high elongation at break, as high as 880%, whereas that for LDPE is only 530%. This, in addition to the lower crystallinity of EVA-18, should be connected with the absence of long side chains. Neither the high crystallinity nor the side chains permit easy slippage of macromolecular chains during extension. The linear dependence of the values of the elonga-

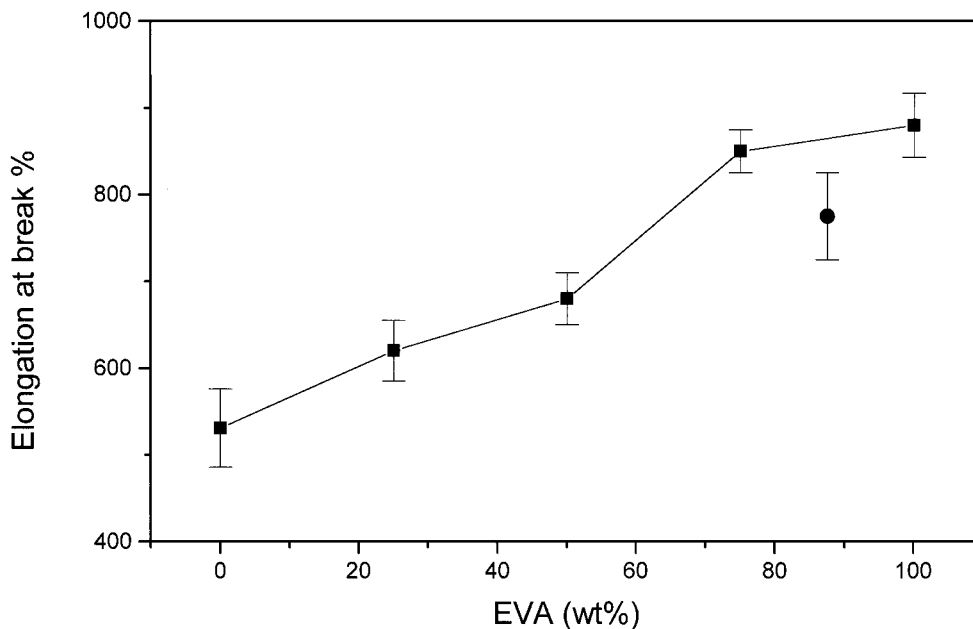


Figure 5 Elongation at break of LDPE, EVA-18, and their blends.

tion at break on the blend composition and the absence of a minimum strongly support the assumption of high compatibility for the two-component polymers.

In Figure 6, Young's modulus of LDPE, EVA-18, and their blends is shown. It is higher for LDPE than for EVA-18. In a tensile test, the yield strength and especially Young's modulus depend on the degree of crystallinity. Because EVA-18 has lower crystallinity than LDPE, it is expected to also have a lower elastic modulus. Crystalline regions can act as physical

crosslinks and this action enhances amorphous areas to restore the storage stress. For this reason, in semi-crystalline polymers, Young's modulus increases with an increasing degree of crystallinity.²⁹ The same trend is also found in the blends, for which Young's modulus decreases with an increasing amount of EVA-18 (Fig. 6). The degree of crystallinity of the blends increases with increasing LDPE contents and, therefore, ranges within the limits of the neat components. Consequently, in every case, it is lower than that of LDPE.

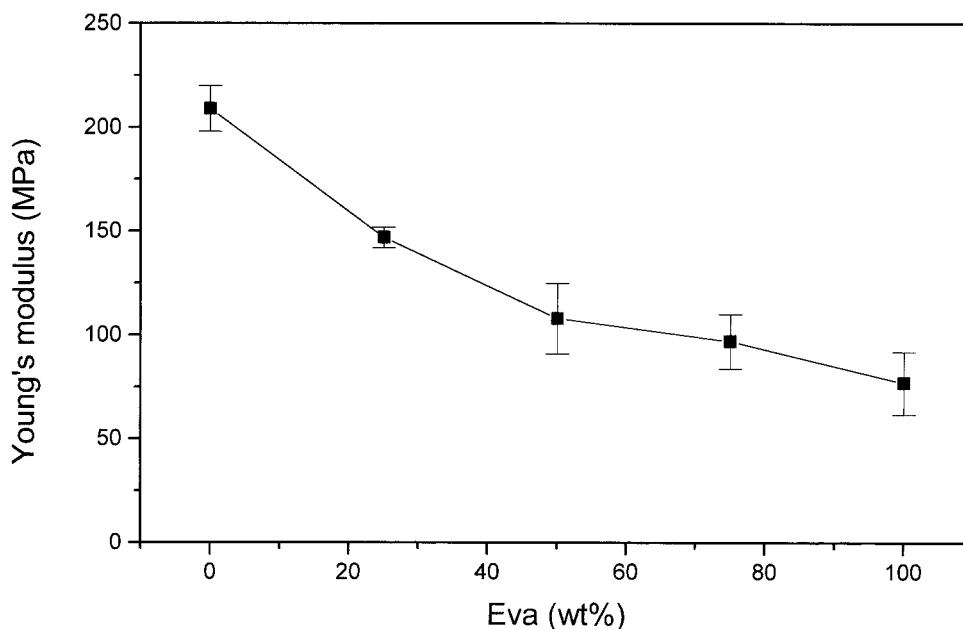


Figure 6 Young's modulus of LDPE, EVA-18, and their blends.

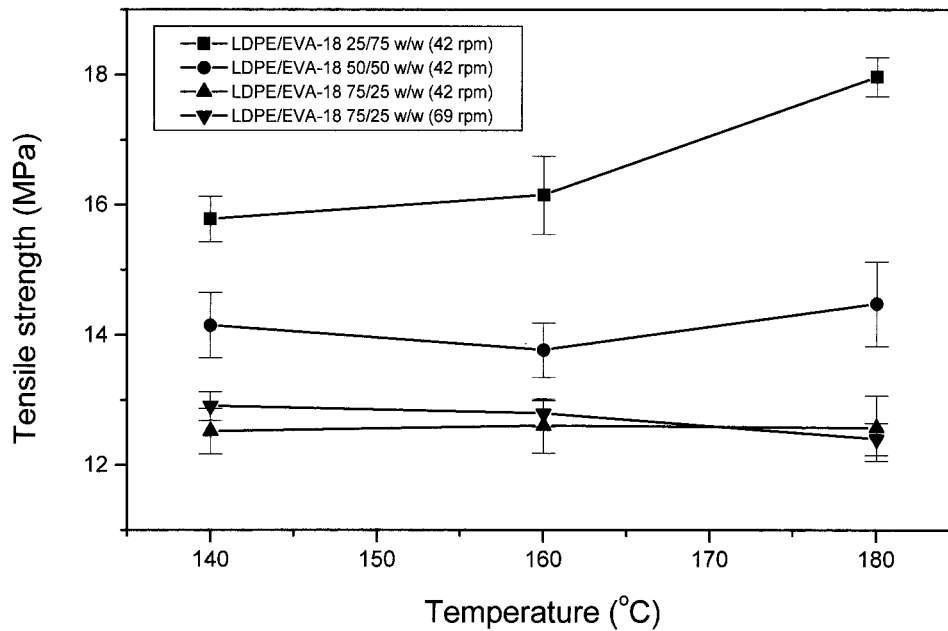


Figure 7 Tensile strength of LDPE/EVA blends prepared by melt mixing at different temperatures and screw speeds.

The mechanical properties are generally the key parameters for all blends, in combination, of course, with satisfactory physical properties, for commercial applications. From the previously discussed results, it can be concluded that all the studied blends have sufficient mechanical properties to meet the demands of industrial products, such as tubes for medical uses.

In Figures 7 and 8, the effects of the melt mixing temperature on the tensile strength and the elongation at break of the blends are shown. There is an effect,

mainly for the blend containing 75 wt % EVA-18 and prepared at 180°C.

The increases in the mechanical properties that appear in these blends with increasing mixing temperatures at 180°C agree with the DSC measurements. The same blends prepared at 160 or 140°C show a small melting peak indicating the existence of a separate LDPE phase, which could justify their reduced mechanical properties.

In the same figures, the effect of the screw rotation speed is shown on the mechanical properties of blends

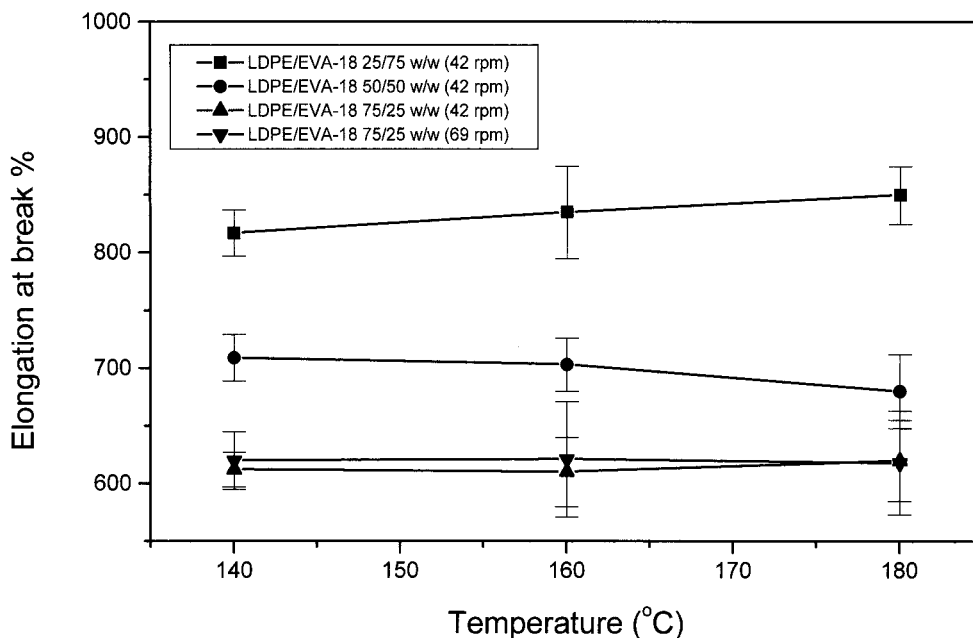


Figure 8 Elongation at break of LDPE/EVA blends prepared by melt mixing at different temperatures and screw speeds

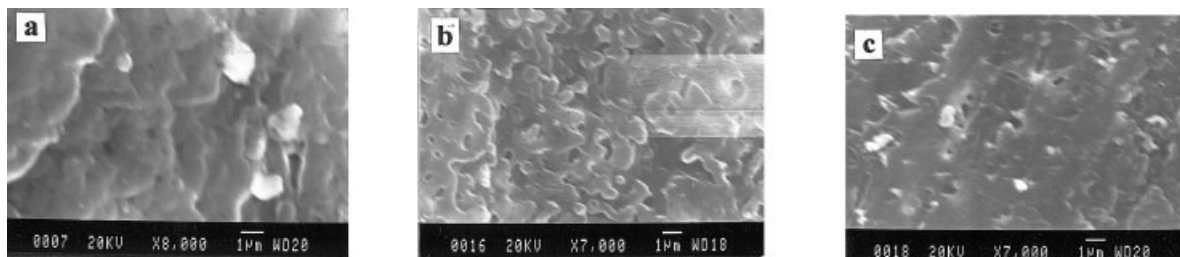


Figure 9 SEM microphotographs of LDPE/EVA blends prepared at 180°C: (a) 75/25, (b) 50/50, and (c) 25/75 (w/w).

containing 25 wt % EVA-18. Although a minor dispersion of the minor component in the polymer matrix is expected to occur with an increasing screw rotation speed in the extruder, no significant effect has been observed.

Morphological study

In miscible blends, the mechanical properties vary monotonically between the properties of the neat components,³⁰ or they may exhibit a positive deviation from linearity if strong interactions take place between specific groups of the components.³¹ In immiscible blends, such as those studied in this work, the thermomechanical behavior is strongly influenced by the size distributions of different phases and their interfacial characteristics.³² Therefore, a morphological study of our blends has been undertaken to provide useful observations for the interpretation of their mechanical properties (discussed in the previous section). Generally, the dispersion characteristics of a blend depend on the composition ratio and the melt viscosity of the neat components at the preparation temperature of the blend. The dependence of these characteristics on the composition for our blends prepared at 180°C is demonstrated in Figure 9. In this figure, SEM microphotographs of these blends after etching with xylene at 50°C are presented; xylene extracts EVA-18 from the blend surfaces.

In the SEM microphotograph of the blend containing 25 wt % EVA-18, small, spherical holes and a few elongated shapes are observed. These correspond to EVA-18, which is extracted with xylene. The EVA-18 domain size in all cases is smaller than 1 μm , and its distribution in the LDPE matrix is very fine. The small size of the EVA particles and their fine dispersion show that a small interfacial tension exists between LDPE and EVA-18.

In the blend containing equal amounts of its components, LDPE is also the matrix because EVA-18 has been removed. This result shows that at 180°C, EVA-18 has a lower melt viscosity than LDPE, and the latter, being more viscous, creates the continuous phase (matrix). This behavior could be predicted by the melt-flow index because LDPE has a higher index

than EVA-18 (Table I). For this blend, small holes and a network of canals has appeared, creating in some cases an interpenetrating network [Fig. 9(b)]. From this microphotograph, it can be seen that LDPE also creates canals, but they are joined together in all cases.

The morphology of the blend containing 75 wt % EVA-18 is different from that discussed previously [Fig. 9(c)]. Because EVA-18 predominates, it forms the matrix, and LDPE is in the form of small, spherical particles pulled out from the matrix after the partial removal of EVA-18 from the sample surface. The LDPE particle size and size distribution are greatly reduced and become more uniform in shape. These particles are smaller than 0.2 μm and are detectable only at higher magnifications. The lower sizes, combined with the finer dispersion, indicate the existence of a better interfacial adhesion between EVA-18 and LDPE in the blend, which can justify the better mechanical properties that this particular sample exhibits. This blend seems to be a two-phase system [Fig. 9(c)], although by DSC, it has been observed to form a single phase with one T_m (Fig. 1). The latter could be attributed to the fact that LDPE is in the form of very small particles consisting of very small crystals; this small crystal size most likely results in low stability because of increased crystal surface energy and, therefore, in a low T_m about the same as that of EVA-18 crystals.

The fine dispersion of the minor component in the polymer matrix observed by SEM for all the studied blends can explain the high compatibility between LDPE and EVA-18 noticed in the mechanical property study. However, the question to be answered is where this compatibility can arise. EVA is a random copolymer and has a more polar and hydrophilic character than LDPE. As the amount of acetate groups in EVA increases, its compatibility with PE should be reduced because the penetration of LDPE macromolecular chains into the EVA phase would be limited and the adhesion between the two phases would be reduced. Besides, LDPE does not have functional groups to form hydrogen bonds with carbonyl groups of vinyl acetate, and the interfacial tension will be higher for EVA with high vinyl acetate contents. Optical microscopy studies of blends of LDPE with EVA containing

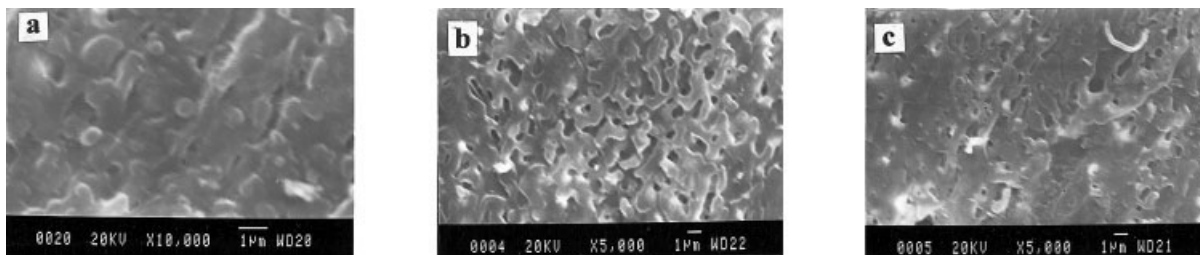


Figure 10 SEM microphotographs of LDPE/EVA blends prepared at 160°C: (a) 75/25, (b) 50/50, and (c) 25/75 (w/w).

9, 14, and 18 wt % vinyl acetate groups showed that only in blends containing 9 wt % vinyl acetate groups were transcrystalline zones formed at the interfaces of the two polymers.³³ Moreover, only PE oligomers with a molecular weight of 507 were completely miscible with an EVA copolymer containing 18 wt % vinyl acetate groups.³³ Therefore, in that study, the miscibility and compatibility of LDPE and EVA were found to be restricted.

The enhanced compatibility of the LDPE/EVA blends prepared in our work can be attributed to the occurrence of chemical reactions during the melt blending performed in our work under different experimental conditions and temperatures higher than those used in previous work.³³ These reactions can form *in situ* block copolymers between LDPE and EVA-18 placed in the interface and reduce the interfacial tension. It is well known that diblock copolymers have extensively been used as effective compatibilizers in incompatible blends.

EVA has a greater capacity for crosslinking than LDPE because macroradicals can be formed very easily on account of α - or β -hydrogen group subtraction. According to Ray et al.,³⁴ EVA macroradicals can react with vinylidene groups or macroradicals of LDPE at elevated temperatures. Also, the thermal decomposition of EVA at 150–180°C results in the evolution of acetic acid and the formation of unsaturated groups,³⁵ which can also very easily form radicals. As the EVA amount increases in LDPE/EVA-18 blends, the gel content increases, too.⁵ It is also expected that as T_m increases, a larger number of EVA macroradicals will form. Therefore, crosslinkings between LDPE/EVA macromolecules can be formed, increasing the adhesion between the blend components. For this reason,

for the blends containing 75 wt % EVA-18, an increase in the mechanical properties has been observed as the temperature of blending has increased.

In Figures 10 and 11 are shown SEM microphotographs of blends prepared at 160 and 140°C, respectively. As the temperature decreases, the LDPE particle size increases. At 140°C, there are many LDPE particles with sizes close to 1 μm with a fine dispersion [Fig. 11(c)], whereas in the blend prepared at 160°C, the domain particle is smaller than 0.5–0.6 μm [Fig. 10(c)]. These morphological differences between blends of the same composition are due to the differences in the interfacial adhesion between the two polymers, which is lower in the blend prepared at 140°C and higher in the blend prepared at 160°C, when the LDPE particles are very small. Such a temperature effect has been noticed to a lesser extent for other blends containing 50 and 25 wt % EVA-18.

Shrinkability

One of the most important properties of LDPE/EVA-18 blends for practical applications, especially for film or tube preparation such as in this study, is their shrinkability. The ability of LDPE/EVA-18 blends to shrink after heating at different temperatures depends on the particular temperature and the composition (Fig. 12).

EVA-18 shows a high shrinkability (ca. 53%) even at the low temperature of 80°C. This is due to its low T_m , which is close to that temperature. On the contrary, LDPE has no shrinkage at 80°C, and only at higher temperatures such as 120 and 160°C is considerable shrinkage observed. This behavior of the two initial polymers affects the shrinkage of the prepared blends,

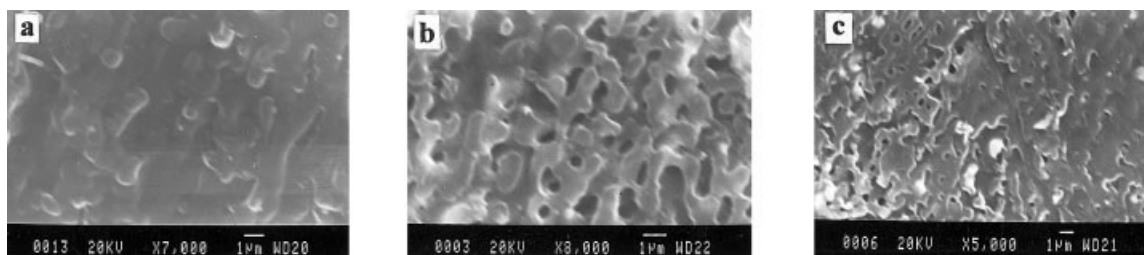


Figure 11 SEM microphotographs of LDPE/EVA blends prepared at 140°C: (a) 75/25, (b) 50/50, and (c) 25/75 (w/w).

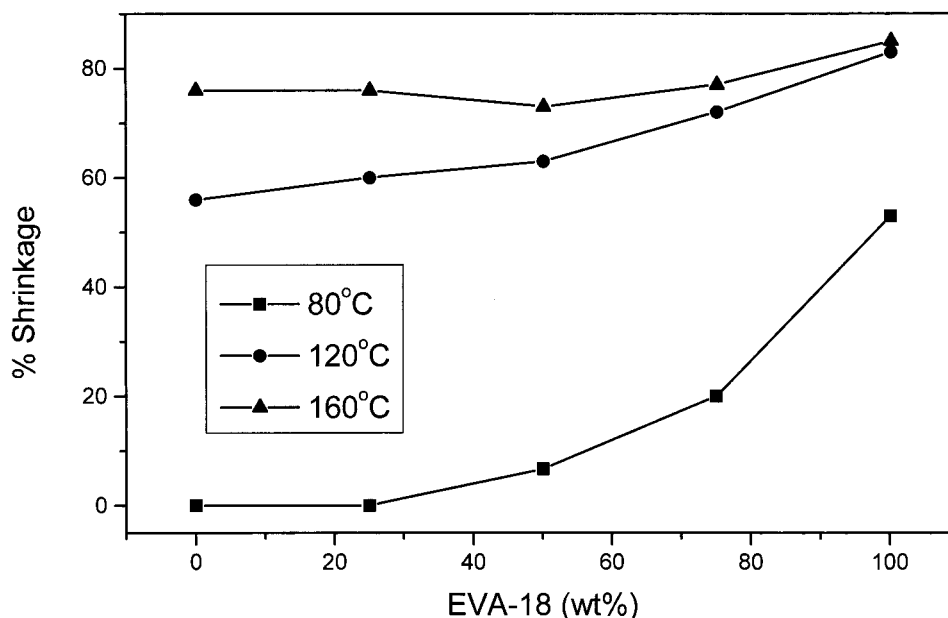


Figure 12 Shrinkage variation (%) of EVA, LDPE, and their blends at different temperatures.

especially at 80°C. As the amount of EVA-18 increases, shrinkage becomes higher, except for the blend containing 25 wt % EVA-18. Because in this blend LDPE predominates, the shrinkage is negligible. In the other two blends containing 50 and 75 wt % EVA-18, the shrinkage is 6.5 and 20%, respectively. The blend composition has a small effect on the shrinkage measured at 120°C. This effect is even smaller at 160°C because of the higher ability of LDPE to shrink, which is almost equal to that of EVA-18 at that temperature.

CONCLUSIONS

LDPE/EVA-18 binary blends containing 25 or 50 wt % EVA-18 have been found by DSC to be immiscible, showing two well-defined melting peaks, because of the molecular similarity of the two polyolefins and separate crystal phases. On the contrary, the blend containing 75 wt % EVA-18 and prepared at 180°C shows only one peak. However, when this blend is prepared by blending at 160 or 140°C, the beginning of phase separation is recorded, that is, a small melting peak for an LDPE phase, which is higher for 140°C than that for 160°C. In the blends that show two melting peaks, these are about 3°C lower than the melting peaks of the corresponding pure polymers. This shifting indicates a high compatibility between LDPE and EVA-18.

This compatibility has also been verified by a mechanical property study. In all the blends, the tensile strength and elongation at break ranged between the corresponding values of the initial polymers, without the appearance of a minimum. This high compatibility is probably the result of LDPE macromolecule diffu-

sion in the EVA-18 phase or the *in situ* formation of crosslinks between EVA-18 and LDPE macromolecules.

The melt mixing temperature has an influence on the mechanical properties, mainly for blends containing 75 wt % EVA-18 at 180°C, which show increased values. The melt mixing temperature also affects the morphology of blends containing 75 wt % EVA-18. As the mixing temperature decreases, the particle size becomes larger. The screw rotation speed does not affect the mechanical properties and morphology of the blends.

All the blends have sufficient mechanical properties to be used for the industrial production of tubes. A melt mixing temperature higher than 180°C is preferred because it results in an improvement in the mechanical properties and increased compatibility of the blends.

References

- Whiteley, K. S.; Heggs, T. G.; Koch, H.; Mawer, R. L.; Immel, W. Ullmann's Encyclopedia of Industrial Chemistry; VCH: 1992; Vol. A21, p 494.
- Mateev, M.; Karageorgiev, S. Radiat Phys Chem 1998, 51, 205.
- Martinez-Pardo, M. E.; Zuazua, M. P.; Hernandez-Mendoza, V.; Cardozo, J.; Montiel, R.; Vazquez, H. Nucl Instrum Methods Phys Res Sect B 1995, 105, 258.
- Rodriguez-Perez, M. A.; Duijsens, A.; De Saja, J. A. J Appl Polym Sci 1998, 68, 1237.
- Sharif, J.; Aziz, S. S. A.; Hashim, K. Radiat Phys Chem 2000, 58, 191.
- Dalai, S.; Wenxiu, C. J Appl Polym Sci 1996, 62, 75.
- Abdel-Bary, E. M.; El-Nesr, E. M. Radiat Phys Chem 1996, 48, 689.
- Fouglar, S. H. J Polym Sci Part B: Polym Phys 1999, 37, 1899.

9. Schinner, H. G.; Nelson, N. Eur. Pat. 0,474,376 (1991).
10. Shah, G. P. U.S. Pat. 4,755,419 (1988).
11. Gaetan, P. World Pat. 9,216,358 (1992).
12. Newsome, D. L. U.S. Pat. 4,457,960 (1984).
13. Yoon, J.-S.; Oh, S.-H.; Kim, M.-N. *Polymer* 1998, 29, 2479.
14. Feldman, D.; Rusu, M. *Eur Polym J* 1974, 10, 41.
15. Huang, M.-W.; Kuo, S.-W.; Wu, H.-D.; Chang, F.-C.; Fang, S.-Y. *Polymer* 2002, 43, 2479.
16. Hammer, C. F. *Macromolecules* 1971, 4, 69.
17. Walsh, D. J.; Higgins, J. S.; Rostani, S. *Macromolecules* 1983, 16, 388.
18. Prinos, J.; Bikiaris, D.; Theologidis, S.; Panayiotou, C. *Polym Eng Sci* 1998, 38, 954.
19. Legros, A.; Carreau, P. J.; Favis, B. D.; Michel, A. *Polymer* 1997, 38, 5085.
20. Chen, C.; Lai, F. S. *Polym Eng Sci* 1994, 34, 472.
21. Gupta, A. K.; Ratnam, B. K.; Srinivasan, K. R. *J Appl Polym Sci* 1992, 45, 1303.
22. Motta, M. *J Therm Anal* 1997, 49, 461.
23. Donatelli, A. A. *J Appl Polym Sci* 1979, 23, 3071.
24. Ree, M.; Kyu, T.; Stein, R. *J Polym Sci Part B: Polym Phys* 1987, 25, 105.
25. Lovinger, A. J.; Williams, M. L. *J Appl Polym Sci* 1980, 25, 1703.
26. Robertson, R. E.; Paul, D. R. *J Appl Polym Sci* 1973, 17, 2579.
27. Ray, I.; Khastgir, D. *Polymer* 1993, 34, 2030.
28. Lee, M. S.; Chen, S. A. *Polym Eng Sci* 1993, 33, 686.
29. Ray, I.; Khastgir, D.; Mukunda, P. G. *Angew Makromol Chem* 1993, 205, 59.
30. Prinos, J.; Thesios, C.; Bikiaris, D.; Panayiotou, C. *Polymer* 1997, 38, 5921.
31. MacKnight, W. J.; Karasz, F. E. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: London, 1978; Vol. 1.
32. Barlow, J. W.; Paul, D. R. *Polym Eng Sci* 1984, 24, 525.
33. McEvoy, R. L.; Krause, S. *Macromolecules* 1996, 29, 4258.
34. Ray, I.; Roy, S.; Khastgir, D. *Polym Bull* 1993, 30, 685.
35. Sultan, B. A.; Sörvik, E. *J Appl Polym Sci* 1991, 43, 1737.