

Rheological and Mechanical Behavior of Ethyl Vinyl Acetate/Low Density Polyethylene Blends for Injection Molding

Antonio Iannaccone,¹ Salvatore Amitrano,² Roberto Pantani¹

¹Department of Industrial Engineering, University of Salerno, Fisciano 84084, Salerno, Italy

²AMIFLEX SRL, Montoro Inferiore 83025, Avellino, Italy

Correspondence to: R. Pantani (E-mail: rpantani@unisa.it)

ABSTRACT: Ethyl vinyl acetate (EVA) is normally injection molded to produce parts with specific properties of flexibility and energy absorption. However, the produced objects often present an excessive flexibility. Furthermore, EVA presents a high viscosity for injection molding technology, and this compels the operator to apply high hydraulic pressures. The addition of PolyEthylene (PE) can provide a higher rigidity to the products, improve the flowability of the melt during processing, and at the same time reduce the cost of the products. In this work, several blends of EVA and low density polyethylene are prepared by melt mixing and injection molded. Rheological, calorimetric, and tensile tests are conducted on the molded specimens with the aim of understanding the performances of the materials also in the view of scrap recycling. On pursuing the mentioned goals, the behavior of the blends in the molten state, during crystallization and in the solid state was analyzed by comparing the experimental data with mixing rules to gather information concerning the morphology of the systems. All the results show that both the melt viscosities of the elastic moduli present significant deviations from the mixing rules, indicating that a phase inversion takes place on increasing the amount of EVA, both in molten and in solid state. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Blending two or more polymers is an effective strategy to improve plastic material performances, because polymer blends can offer properties not available in a single polymer. Blending ethyl vinyl acetate (EVA) with low density polyethylene (LDPE) is an economical and efficient alternative to the development of polymeric materials with specific properties. With particular reference to the injection molding technology, EVA is normally adopted to produce parts with specific properties of flexibility and energy absorption.¹ Typical applications includes tubing, hoses, bumpers, and feet for household appliances. However, the produced objects often present an excessive flexibility, which causes the part to escape from the slots when subjected to stress. Furthermore, EVA presents a high viscosity for injection molding technology, and this compels the operator to apply high hydraulic pressures. The addition of PE can provide a higher rigidity to the products and at the same time improve the flowability of the melt during processing. Eventually, since EVA is more expensive than PE, blending can also be an effective way for cost saving. However, the use of a blend requires a

specific study, because the behavior of these systems can be surprisingly different from the behavior of the starting polymers.

Indeed, the properties of a blend deeply depend on the microstructure of the blend itself,² and in particular for a binary blend some degree of miscibility is necessary to achieve the optimization of properties. Although many miscible binary polymer blends have been reported, those comprising two commercially important polymers are comparatively few.³ For these systems, mixing rules exist, which can efficiently describe viscosity and mechanical properties. However, most of the polymer blends present some degree of immiscibility, which induces a multiphase morphology, and this strongly affects the rheological behavior⁴ and also the mechanical properties,² which depend not only on the type of morphology but also on the interfacial interaction between phases. Furthermore, also the crystallization kinetics can be influenced by the presence of interfaces.^{5,6}

With a specific reference to the blends of EVA and LDPE, literature works indicate a morphology depending on composition. In particular, it can be found that, on increasing the EVA content,

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the morphology of these blends changes from a two-phase structure, if EVA is dispersed, to a cocontinuous morphology and, at large EVA content, a two-phase morphology again with LDPE dispersed as domains on EVA matrix.^{7,8} This obviously influences not only the rheology of the melts but also the mechanical properties in the solid state.⁹ Eventually, also the crystallization behavior of these blends is influenced by the morphology, with a crystallization kinetics depending on composition.^{10,11} It should be considered that the morphology is influenced also by process conditions (temperatures and flow fields)¹² and by the presence of compatibilizers.⁹ This complicates the phenomena involved and makes the study of these blends quite challenging, so that, despite the number of articles already written on the subject, a full understanding of the behavior of these systems has not been reached yet.

In this work, several blends of EVA and LDPE are prepared by melt mixing and subsequently processed by injection molded. The rheology is measured as a function of temperature and shear rate. Also, differential scanning calorimetric (DSC) analysis and tensile tests are carried out on the molded specimens. One of the aims is to analyze the rheological behavior of the blends and to gather information concerning the crystallization kinetics, both aspects being obviously of fundamental importance for processing. A further objective is to correlate the mechanical properties to the blend composition, because the elastic response of the moldings is of primary importance for practical applications. On pursuing the mentioned goals, the behavior of the blends in the molten state during crystallization and in the solid state is analyzed by comparing the experimental data with mixing rules to gather information concerning the morphology of the blends. This can for sure be helpful for understanding the complex behavior of these systems.

Obviously, when blending of two materials is considered for production, a deeper understanding of the behavior of the blends can be of great importance not only for understanding what will the performances of the materials be but also for scrap recycling.

MATERIALS AND METHODS

The adopted EVA in this work was a commercial grade produced by Arkema (Colombes, France) with the name of Evatane 1040. It presents a content of vinyl acetate of 14%, a density of 0.94 g/cm³, and Melt Flow Index (measured according to ASTM D1238) of 4 g/10 min.

The LDPE was supplied by ITI Polymers (Italy) and presents an average molecular weight distribution characterized by $M_w = 90$ kDa and $M_n = 60$ kDa, a density of 0.92 g/cm³ and Melt Flow Index (measured according to ASTM D1238) of 24 g/10 min.

The blends studied in this work were prepared by means of an ICMA San Giorgio corotating twin screw extruder, operating at 180°C with a screw speed of 300 rpm.

Different blends were prepared, which differ in the percentage of pure materials on mass basis. The blends were coded on the basis of the mass content of EVA: for instance, Mix25 indicates a blend containing 25% of EVA on mass basis. Also, the pure materials were processed by the extruder, so that they experienced the same thermomechanical treatment of the blends.

All the blends were injection molded into a rectangular cavity (thickness = 3 mm and width = 5 mm, $L = 20$ mm). The injection temperature was 135°C, and the mold temperature was 30°C. These temperatures resulted from a compromise between ease of flow (which increases on increasing temperature) and cycle time (which decreases on decreasing temperatures).

As the specimens adopted for mechanical testing are the result of an extrusion step followed by an injection molding step (each one possible cause of degradation¹³), also calorimetric and rheological measurements were carried out on molded samples. In this way, all the results reported in this work can be referred to materials that experienced the same thermomechanical history.

The molded specimens were analyzed by DSC in nitrogen atmosphere. The protocol followed consisted in a heating ramp at 10°C/min from room temperature to 200°C; an isothermal step at 200°C for 5 min; a cooling ramp at 10°C/min from 200°C to -20°C (first cooling); and a heating ramp at 10°C/min from -20°C to 200°C (second heating).

The viscosity of each blend was measured by both rotational (in dynamic mode) and capillary rheometers at three temperatures, 125, 135, and 145°C. The measurements were conducted on the molded samples, so that they can be referred to the material injected inside the cavity.

Tensile tests were conducted on molded samples, according to ASTM D638 standard. In particular, five tests were performed on each sample, at room temperature, with a cross-bar speed of 50 mm/min.

RESULTS AND DISCUSSION

Calorimetry

During the first heating ramp (not reported here), the thermograms did not show any cold crystallization but just the melting peaks. Furthermore, the heat absorbed during melting was essentially the same measured during the second heating scan, indicating that the crystallization kinetics of all the materials were fast enough to reach the maximum crystallinity degree also after injection molding.

The thermograms measured during the first cooling and the second heating ramps are reported as thick lines in Figure 1(a,b), respectively.

An additive rule was applied to describe the thermograms of the blends. In particular, the heat flow, \dot{Q} , measured on a blend containing a mass fraction of EVA equal to w_i was calculated as

$$\dot{Q}_{\text{blend}} = \sum w_i \dot{Q}_i \quad (1)$$

where \dot{Q}_i is the heat flow measured for the pure component. Obviously, this rule does not take into account any possible interaction among the components.

The results of Eq. (1) are reported as thin lines in Figure 1. It can be noticed that during the cooling scan the measured peaks of PE (at about 95°C) appear at temperatures slightly higher than what predicted by the additive rule. This happens for amounts of EVA lower than 65%: the PE fraction inside the blends crystallizes earlier and at higher temperatures

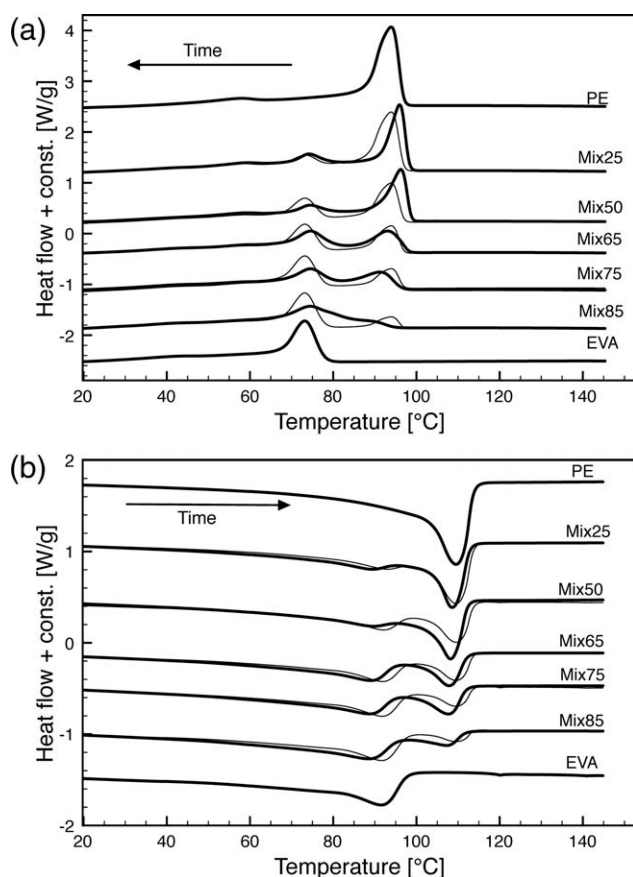


Figure 1. Thermograms of injection molded samples. (a) first cooling and (b) second heating. Thick lines: measurements; thin lines: results of Eq. (1). Endothermic heat flow is downward.

indicating that the presence of EVA somewhat enhances the crystallization kinetics of PE. This could be due to the presence of interfaces between different phases that act as a nucleant. The effect reverts for EVA contents larger than 65%: at these percentages the crystallization kinetics of PE seems to be hindered by the presence of EVA. This is a clear clue that the blends change their morphologies on changing the percentages of the two materials. On its turn, the measured peak of EVA (at about 75°C) appears at higher temperatures, so that it partially overlaps to the higher-temperature peak (due to LDPE). This is probably due to

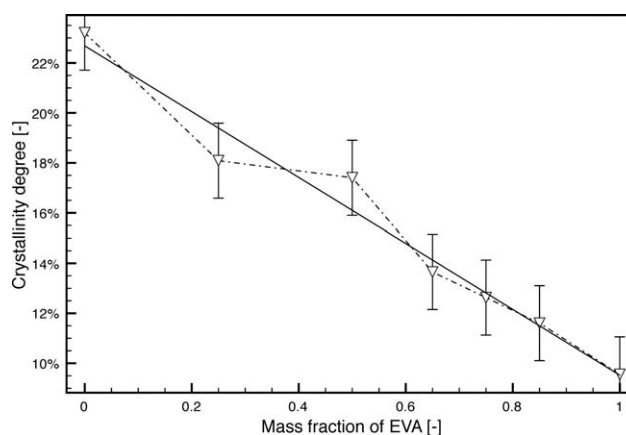


Figure 2. Crystallinity degree as a function of the EVA content.

the nucleating effect of the crystals of PE, which can enhance the crystallization kinetics of EVA.

Similar effects are also present during the subsequent heating scan: the melting peaks of both EVA and PE start at lower temperatures with respect to what predicted by the additive rules. This melting point depression can be taken as an index of an interaction between the two phases, which leads to the presence of smaller, less perfect crystals. The phenomena observed are in line with what reported in the literature.¹⁴

The measured temperatures of the peaks and the enthalpies of melting and crystallization (namely the areas of the peaks) are reported in Table I.

The crystallinity degree was calculated from the melting enthalpies, according to the equation

$$\chi_c = \frac{\Delta H}{\lambda_m} \quad (2)$$

in which ΔH is the area of the melting peak, and λ_m is the latent heat of melting of PE, considered here as 288 J/g.¹⁵ The results are reported in Figure 2, and they reveal that the crystallinity degree linearly depends on the EVA content, decreasing from a value of about 23% (for a sample made of pure LDPE) to a value of about 10% (for a pure EVA sample). This indicates that, if an effect of the presence of another material can influence the crystallization kinetics of each of the

Table I. Values of Peak Temperatures and Crystallization and Melting Enthalpies

Mass fraction of EVA	Cooling			Heating		
	Peak of PE (°C)	Peak of EVA (°C)	Heat released (J/g)	Peak of PE (°C)	Peak of EVA (°C)	Heat absorbed (J/g)
0	94.0		68	109.3		65
0.25	95.7	73.9	53	108.5	88.9	52
0.5	96.1	74.8	51	108.2	88.9	52
0.65	92.9	74.2	40	107.9	88.7	39
0.75	91.0	74.2	37	107.6	88.4	39
0.85	88.3	74.2	34	107.0	88.4	34
1		72.9	28		91	33

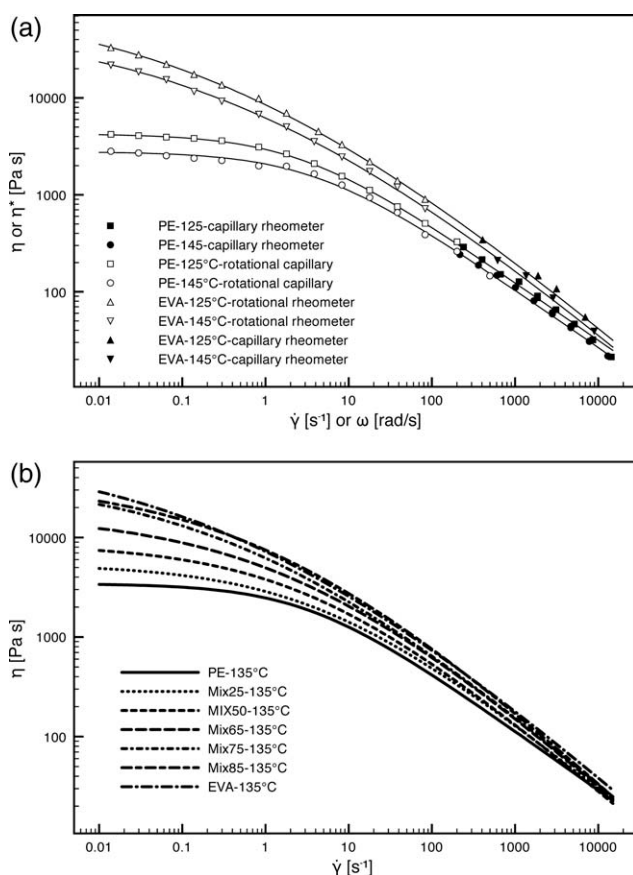


Figure 3. viscosity of the melts at different temperatures and shear rates. (a) viscosity of pure PE and EVA melts; symbols represent the experimental data, lines the description by means of eqs. (3) and (4) and (b) viscosity of all the blends at 135°C, as described by eqs. (3) and (4).

component of the blend, this does not have any effect of the final crystalline value.

Rheology

As mentioned above, the viscosity of each blend was measured by both rotational (in dynamic mode) and capillary rheometers. The Cox–Merz rule, which allow to equate the complex viscosity and the shear viscosity, resulted to be valid for all the blends analyzed in this work, thus allowing to measure the effect of shear rate in the range from 0.01/s to 10,000/s.

Table II. Parameters for the Carreau-Jasuda and WLF Models

Mass fraction of EVA	η_{ref} (Pa s)	A	B (K)	τ^* (Pa)	a	b
0	885	20.2	1030.1	11,104	0.41	0.67
0.25	880	19.3	755.9	26,086	0.33	0.43
0.5	1287	15.6	598.4	29,072	0.29	0.41
0.65	1966	13.8	483.8	41,535	0.26	0.33
0.75	10,186	13.2	669.0	30,991	0.27	0.28
0.85	5572	10.5	417.5	50,481	0.23	0.31
1	18,934	7.6	409.6	46,535	0.25	0.24

The viscosities of pure LDPE and EVA melts are reported in Figure 3(a) (only data at 125 and 145°C are reported): PE resulted to be significantly less viscous than EVA at all the shear rates, thus justifying the blending for reducing the viscosity. The rheological data in the whole ranges of shear rates and temperatures could be nicely described by the following Carreau-Jasuda model:

$$\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{[1 + (\eta_0(T)\dot{\gamma}/\tau^*)^a]^{\frac{1-b}{a}}} \quad (3)$$

in which η_0 is the low shear rate viscosity, described by the Williams-Landel-Ferry (WLF) equation:

$$\eta_0(T) = \eta_{\text{ref}} e^{\frac{-A(T-T_{\text{ref}})}{B+T-T_{\text{ref}}}} \quad (4)$$

τ^* is the critical stress value (the viscosity starts to deviate from the newtonian plateau for shear rates higher than τ^*/η_0), b is the power-law index at high shear rates.

The parameters for the eqs. (3) and (4), obtained by a best fitting analysis of viscosity data, are reported in Table II. It can be noticed that about all the parameters gradually change with the EVA content. Indeed, as reported in Figure 3(b), the rheological behavior of the blends progressively change from the curve of PE to that of EVA on increasing the EVA content, essentially in the whole range of shear rates

The viscosity of the blends can be described by a logarithmic mixing rule¹⁶

$$\log(\eta_{\text{blend}}) = \sum w_i \log(\eta_i) \quad (5)$$

where w_i is the mass fraction, and η_i is the viscosity of the pure component.

In Figure 4, the low shear rate viscosity, η_0 , of the blends at 135°C is reported versus the blend composition. The result of Eq. (5) is also reported as a line. It can be noticed that, at least for EVA contents lower than 75%, the blends present a negative deviation from the mixing rule. Negative and positive deviations from the mixing rule are normally found in immiscible blends in which a phase inversion occur on increasing the amount of one of the two components.¹⁷ The behavior reported in Figure 4 can therefore be taken as an indication that the system analyzed in this work presents a phase inversion at a EVA content of about 70%. Similar results are obtained also at 125 and 145°C and are not shown. The result obtained is in line with literature findings.⁷

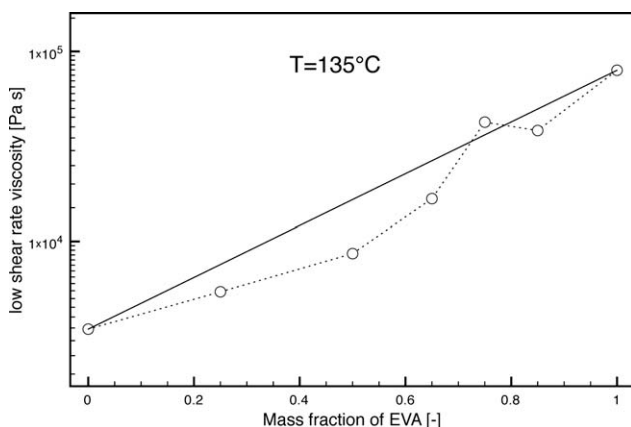


Figure 4. Low shear rate viscosity, η_0 , of the blends at 135°C versus the blend composition.

Mechanical Properties

The results of tensile tests are reported in Figure 5(a) in terms of “true stress” versus “true strain”. If L is the current length of the gage, L_0 is its initial value, P is the load, and A_0 is the initial cross-sectional area, the “true strain” was calculated as $\epsilon = \ln(L/L_0)$ and the “true stress” as $\sigma = P/A_0 L/L_0$. It can be noticed that, as already found for rheological and DSC tests, also the stress–

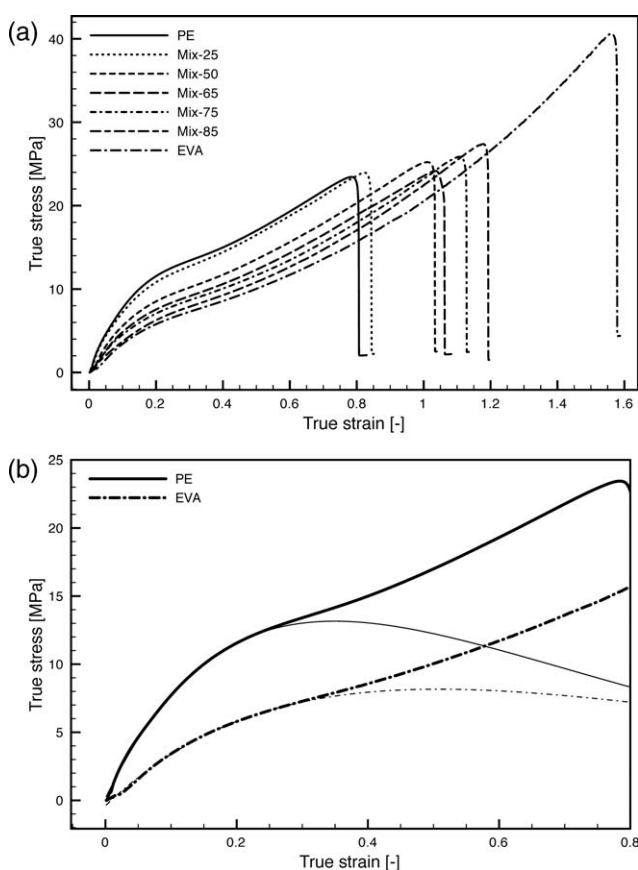


Figure 5. (a) Stress–strain relationship during tensile tests at room temperature and 50 mm/min. (b) Analysis by Eq. (6) of the stress–strain curves for pure PE and pure EVA samples: thick lines = data and thin lines = results of Eq. (6).

strain curves gradually pass from the plot representative of the pure PE to that representative of the pure EVA sample.

The elastic modulus was calculated by the equation proposed by Matsuoka,¹⁸ which describes the stress–strain relationship of a polymer up to the yield point as:

$$\sigma(\epsilon) = E_0 \epsilon e^{-\alpha\epsilon} \quad (6)$$

in which E_0 is the tensile modulus (namely the slope of the curve at very low strain). The description obtained by Eq. (6) for pure PE and pure EVA samples is reported in Figure 5(b). It can be noticed that the equation perfectly describes the experimental curves up to the yield point, at which the predictions start to deviate from data.

The elastic modulus of the samples is reported in Figure 6 versus the mass fraction of EVA: as expected, the modulus reduces on increasing the EVA content. The results of tensile tests are summarized in Table III.

Several theories have been proposed to predict the tensile properties of blends in terms of various parameters. The two simplest theories are the so-called series and parallel models, which should represent the upper and lower bounds, respectively, of the tensile properties¹⁹:

$$E_S = \sum w_i E_i \quad (7)$$

$$E_P = \frac{1}{\sum \frac{w_i}{E_i}}$$

These two limits are reported in Figure 6. It can be noticed that if the EVA content is lower than about 50%, the experimental data are larger than what predicted by both the simple mixing rules; at larger EVA fractions, the modulus reduces to follow the description of the series model and, for the blend with 85% of EVA, the description of the parallel model. These positive and negative deviations from the mixing rules have already been noticed.^{9,20} This cannot be ascribed to crystallinity, because as stated above the crystalline content linearly depends on EVA fraction. The deviation from simple mixing rules can be justified on the same basis of what already noticed for viscosity: at

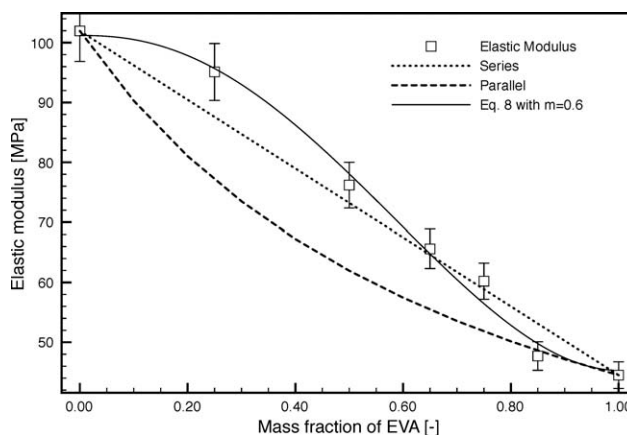


Figure 6. Elastic modulus of the samples as a function of EVA content. The continuous line represents the result of Eq. (8).

Table III. Tensile Properties of the Blends

Mass fraction of EVA	E (MPa)	Strain at break (%)	Ultimate stress (MPa)
0	102 ± 5	80 ± 5	23 ± 3
0.25	95 ± 5	84 ± 5	24 ± 3
0.5	76 ± 4	103 ± 10	25 ± 3
0.65	66 ± 4	106 ± 10	24 ± 3
0.75	60 ± 4	113 ± 10	26 ± 3
0.85	48 ± 2	119 ± 10	27 ± 3
1	45 ± 2	157 ± 15	41 ± 7

low EVA fractions, PE-rich phases form and induce to the blend properties closer to those of PE. In the solid, the increase of elastic modulus could be due to strong interfacial interactions with the other phase, which could be also ascribed to cocrystallization.²⁰ On increasing the EVA fraction, this phenomenon disappears and the data tend to follow the behavior of a system in series. At EVA fractions higher than 75%, the system is well described by a model in parallel.

Several models have been proposed in the literature to analyze the behavior of composite systems,^{21,22} however, none of them is able to describe the data reported in Figure 6.⁹ We decided to adopt a modified version of the Coran–Patel model.²³ This model describes the elastic modulus of heterogeneous polymer compositions on the basis of a phenomenological adjustment between an upper bound and a lower bound (x is the volume fraction of the soft phase, in our case nearly corresponding to the weight fraction of EVA):

$$E = (1 - x)^{\frac{1}{1-m}} \left(\frac{x}{1-m} + 1 \right) (E_U - E_L) + E_L \quad (8)$$

The parameter m represents the point of phase inversion.

In the original formulation, E_U and E_L correspond to E_S and E_B respectively. In this work, we replaced E_U and E_L with the moduli of pure LDPE and pure EVA, respectively. The application of this equation, with a value for the parameter m equal to 0.6, gives rise to the description reported in Figure 6 as a continuous line, which runs very close to the data.

Morphology of the Solid Samples

In Figure 7, some micrographs obtained by polarized optical microscopy in transmission mode of 10- μm thick slices of solid samples are reported. It can be noticed that the morphology of the sample containing 25% of EVA is quite homogeneous. On increasing the amount of EVA, some domains start to appear, which increase their characteristic dimensions. On passing from 75% of EVA to 85% of EVA, the morphology undergoes an abrupt change, with a sudden change in the dimensions of the domains despite the relatively small change in the EVA content. This can explain the differences in the mechanical properties of the samples.

CONCLUSIONS

In this work, several blends of EVA and LDPE were prepared by melt mixing and then processed by injection molding. The rheology of the blends was measured as a function of temperature and shear rate. Also calorimetric analysis and tensile tests were carried out on the specimens. DSC results show that the

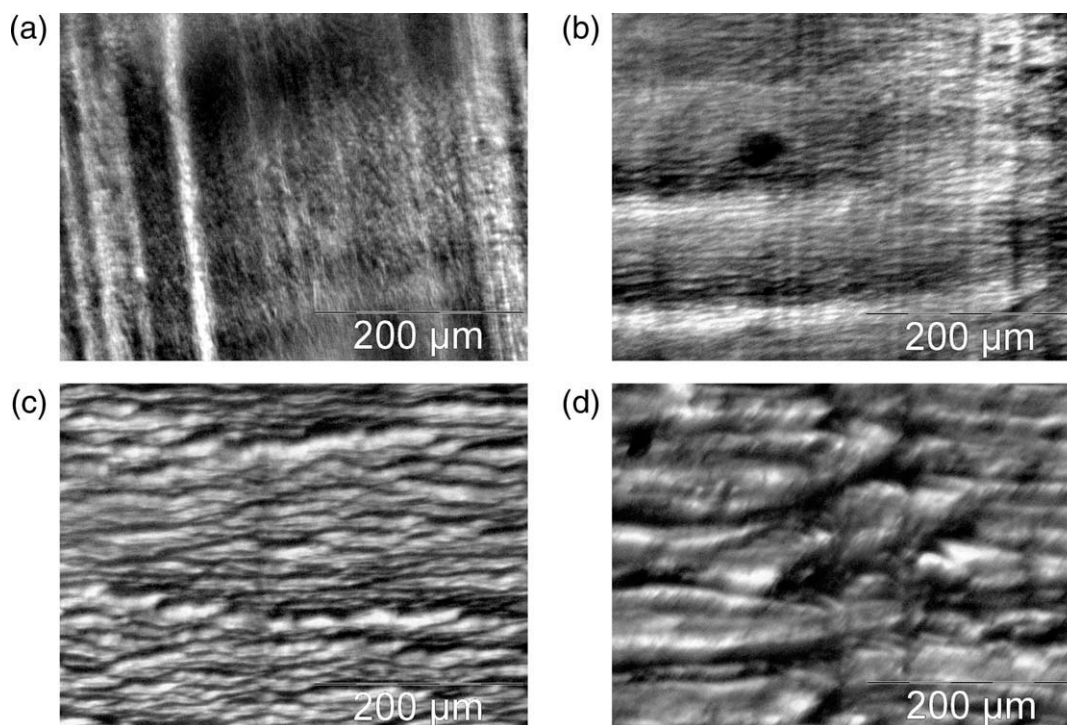


Figure 7. Micrographs obtained by polarized optical microscopy in transmission mode of 10- μm thick slices of solid samples. (a) Mix25; (b) Mix65; (c) Mix75; and (d) Mix85.

presence of EVA somewhat enhances the crystallization kinetics of PE. This could be due to the presence of interfaces between different phases that act as a nucleant. On its turn, also an enhancement of the crystallization kinetics of EVA was noticed.

The rheological characterization revealed that a phase inversion occurs at an EVA content of about 70%.

This behavior was also confirmed by tensile tests carried out on the molded samples: at low EVA fractions, PE-rich phases form and induce to the blend properties closer to those of PE; on increasing the EVA fraction, the data tend to follow the behavior of a system in series and, at EVA fractions higher than 75%, the system is well described by a model in parallel.

An optical observation of the solid samples was carried out, revealing a sudden change in the dimensions of the domains on passing from 75% of EVA to 85% of EVA. This can explain the differences in the mechanical properties of the samples.

This clearly indicates that the system presents different arrangements at different fractions of EVA, both in molten and in solid state.

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