Effects of Reactive Melt Mixing on the Morphology and Thermal Behavior of Linear Low-Density Polyethylene/Rubber Blends

Maurizio Penco,[1] Stefania Della Sciucca,[1] Elisa Passaglia,[2] Guido Giordani,[3] Serena Coiai,[3] Luca Di Landro[4]

[1]Dipartimento di Chimica e Fisica per l'Ingegneria e per i Materiali, Università degli Studi di Brescia, Via Valotti 9, 25133 Brescia, Italy
[2]Istituto di Chimica dei Composti Organometallici (Consiglio Nazionale delle Ricerche), Sezione di Pisa, c/o Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy
[3]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Via Risorgimento 35, 56126 Pisa, Italy
[4]Dipartimento di Ingegneria Aerospaziale, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy

ABSTRACT: Linear low-density polyethylene (LLDPE)/polybutadiene (PB) and LLDPE/poly(styrene-*b*-butadiene-*b*-styrene) (SBS) binary blends were prepared by simple melt mixing or by reactive blending in the presence of a free-radical initiator, and for comparison, pure LLDPE was treated under the same conditions with a comparable free-radical initiator concentration. The effect of the reactive melt mixing on the morphology of the blends was studied with transmission electron microscopy, and the corresponding particle size distributions were analyzed and compared to highlight the effects of the crosslinking and grafting phenomena. Thermal properties of the obtained materials were investigated with differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA). In particular, the effect of the reactive mixing parameters on the amorphous phase mobility was investigated. The influence of the chemical modification on the crystallization behavior of LLDPE, neat and blended with PB and SBS, was also studied with dynamic and isothermal differential scanning calorimetry tests, and the isothermal thermograms were analyzed in light of the Avrami equation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1014–1021, 2008

Key words: blends; polyethylene (PE); reactive processing; thermal properties

INTRODUCTION

For many years, plastics based on polyolefins have been of paramount interest in technological fields: their low cost and easy processability are the most important factors ascribed to the success of these materials, especially in packaging applications.

In a recent article,[1] we studied the crosslinking of modulated polyolefins through radical processes in the melt; in particular, we studied poly(ethylene-*co*-butylene) [linear low-density polyethylene (LLDPE)] and its blends with polybutadiene (PB) rubber prepared by reactive melt mixing. The aim was to tune the crosslinking of the materials without substantially reducing the crystallinity and at the same time increase the melt strength. This would allow higher stretching ratios to be reached and thus increase the chance of obtaining thinner films with convenient strength.

It is well known that low compatibility exists between polyethylene and rubbers such as natural rubber, PB, and poly(styrene-*b*-butadiene-*b*-styrene) (SBS), and the blending processes produce heterogeneous materials.[2–6] On the other hand, the compatibility can be modified by the promotion of grafting reactions at the rubber–LLDPE interface.[7–10] In principle, the use of a free-radical initiator during the melt-mixing processes should allow grafting to be promoted, although other competitive reactions must be considered, particularly the crosslinking of the components.[11,12]

In general, if polyethylene is crosslinked, a material having a higher glass-transition temperature (T_g) and a lower degree of crystallinity is obtained;[13,14] also, the crystallization behavior is modified, and a lower crystallization rate results. In the case of complex materials such as heterogeneous LLDPE/rubber blends, the degree of crystallinity as well as the crystallization rate and T_g can be strongly affected by the presence of the second rubber phase.[3,15,16] The use of a free-radical initiator during the melt mixing increases the complexity because grafting and crosslinking are both promoted. From a technological

Correspondence to: M. Penco (maurizio.penco@ing.unibs.it).

point of view, the ideal result should be to obtain grafting for increasing the compatibility and to obtain crosslinking of the sole amorphous domains of LLDPE for preserving the crystallinity. In this way, materials having a higher melt strength without the loss of the crystalline phase could be obtained.

In this article, the effect of chemical modification on the morphology and thermal behavior of LLDPE/PB and SBS binary blends obtained by melt mixing or reactive blending in the presence of peroxide is discussed in detail. For comparison, a set of samples of LLDPE melt-mixed with the same initiator amount used in the blends is considered.[1] The reactive melt-mixing conditions results were studied from different points of view and with different analytical techniques. The morphology was analyzed with transmission electron microscopy (TEM), and the obtained particle size distributions were compared; the thermal properties were determined with differential scanning calorimetry (DSC). The crystallization behavior, determined with DSC isothermal measurements, was analyzed on the basis of the Avrami equation[17–19] to compare the primary composite constant rate of crystallization (Z) and exponent of time (n); the mechanical properties were determined by dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

Materials

LLDPE (Lupolex 18QFA, Basell Polyolefins S.p.A.), PB (Intene 40, Polimeri Europa S.p.A.; 38 wt % cis units), and SBS (Kraton D 1102, Shell; 11 mol % 1,2 butadiene units) were used as received. Dicumyl peroxide (DCP) was purchased from Aldrich S.p.A. (Gallarate Mi, Italy) and not purified before the use.

Instruments

Morphological analysis was performed by TEM with a Philips EM420 instrument (Eindhoven, The Netherlands) after treatment of the specimens with OsO_4.

The calorimetric studies were performed with a PerkinElmer DSC 7 (Norwalk, CT) with a liquid nitrogen cooling system. Mercury (mp = $-38.4°C$) and indium (mp = $156.6°C$) standards for low-temperature scans and indium and zinc (mp = $419.3°C$) standards for high-temperature scans were used for instrument calibration. Heating and cooling thermograms were carried out at a scan rate of $5°C$/min; two scans were performed for each sample.

DMTA was performed with a Rheometrics Scientific MkII DMTA apparatus (Reichelsheim, Germany), three-point-bending tests being run with samples of about 11 mm $\times$ 5 mm $\times$ 1.5 mm. Measurements as a function of frequency (0.2–10 Hz) and temperature ($-150°C$ to $100°C$) were taken.

Blend preparation

Physical and reactive (with initiator) blends were prepared in a Brabender W30E discontinuous internal mixer (Duisburg, Germany) with a 30-cc chamber at $180°C$ at a mixing rate of 50 rpm with a 20-min mixing time. The obtained materials were molded in a plate form (5 cm $\times$ 5 cm $\times$ 1.5 mm) at $180°C$. The procedure is described in detail elsewhere.[1]

RESULTS AND DISCUSSION

LLDPE and the rubbers, PB and SBS, were melt-mixed with and without the addition of DCP in a discontinuous mixer; in Table I, the feed compositions of the prepared materials are summarized.

First, the influence of reactive mixing on the morphology of the blends is presented and discussed; second, the effects on the thermal properties and, in particular, on the crystallinity and crystallization rate of the LLDPE phase are considered.

Blend morphology

As reported in the introduction, low compatibility exits between LLDPE and rubbers, so heterogeneous materials with a poor interface must be expected

TABLE I
Composition of the Mixing Machine Runs and Calorimetric Data

Sample	LLDPE (wt %)	Rubber (wt %)	DCP (mol %)	T_m (°C)	X_c (wt %)[a]	$T_{g,\text{LLDPE}}$ (°C)	$T_{g,\text{rubber}}$ (°C)
LLDPE	100	—	—	122.1	40.8	−120	—
LLDPE-R1	100	—	0.01	122.0	35.7	−109	—
LLDPE-R2	100	—	0.1	121.4	33.2	−106	—
PB	—	100	—	—	—	—	−80
LLDPE/PB	90	10	0	120.7	37.7	−117	−81
LLDPE/PB-Ra	90	10	0.01	121.5	39.7	−109	−76
SBS	—	100	—	—	—	—	−86
LLDPE/SBS	90	10	—	121.3	38.5	−121	−84
LLDPE/SBS-Ra	90	10	0.01	121.1	40.8	−116	−74

[a] Degree of crystallinity.

from their physical melt mixing. As shown by TEM analysis, in the explored composition range (90 : 10 wt %/wt % LLDPE/rubber), blends with LLDPE matrices containing dispersed rubber particles were obtained. It is known that the average particle diameter (d) is related to the matrix (η_m) and rubber (η_r) melt viscosities under the mixing conditions, the interfacial tension (γ), and the shear rate in the mixing machine (G), as suggested by Wu:[20]

$$G\eta_m d/\gamma = 4(\eta_r/\eta_m)^\beta \qquad (1)$$

where β is a coefficient worth 0.84 if $\eta_r/\eta_m > 1$ and -0.84 if $\eta_r/\eta_m < 1$.

It is clear that if the blending is performed in the presence of a free-radical initiator, these parameters could change in a significant way, particularly because crosslinking and grafting phenomena affect the melt viscosity and the interfacial strength.

All blends obtained by reactive melt mixing (via the addition of the peroxide) showed the finest particles. In Figure 1, a comparison of the two materials obtained with and without DCP is shown, whereas the particle size distribution curves of these samples are reported in Figure 2. The major effect of the chemical modification, in terms of decreasing particle size, occurred for the LLDPE/PB system. On the other hand, in the physical blends (without DCP), no significant differences were noticed in the distribution curves if PB or SBS were used.

The reduction of the dispersed particle size, observed for both LLDPE/PB-Ra and LLDPE/SBS-Ra samples, could be due to the following: (1) the improved compatibility between the two polymers as a result of graft polymer formation between LLDPE and the rubbers via macroradical coupling, which is able to improve γ in eq. (1), and (2) the crosslinking reaction of the elastomeric phase. The crosslinked rubber particles exerted more torque, and this eventually resulted in particle breakup and more effective mixing,[21] thus lowering the particle size, as could be seen by the application of eq. (1) under conditions of an improved shear rate. Therefore, a lower grafting degree or a lower crosslinking level should be expected with SBS rubber, which contains fewer double bonds than PB; this explains the higher particle dimensions.

Thermal properties

The melting temperature (T_m) of the LLDPE phase did not change in a significant way in the different blends: it was 122.1°C for the unmodified LLDPE and 122.0 and 121.4°C for samples LLDPE-R1 and LLDPE-R2, which were obtained by the addition of 0.01 and 0.1 mol % DCP, respectively. Various
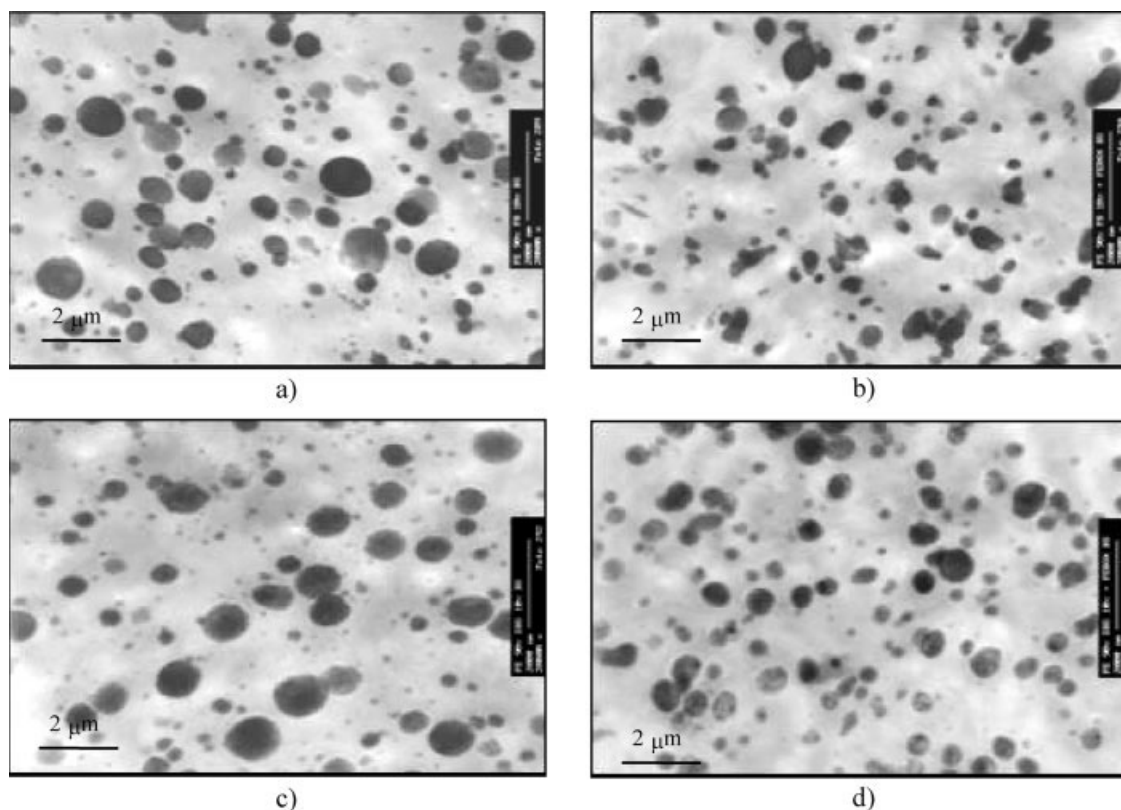
Figure 1　TEM analysis of (a) LLDPE/PB, (b) LLDPE/PB-Ra, (c) LLDPE/SBS, and (d) LLDPE/SBS-Ra.
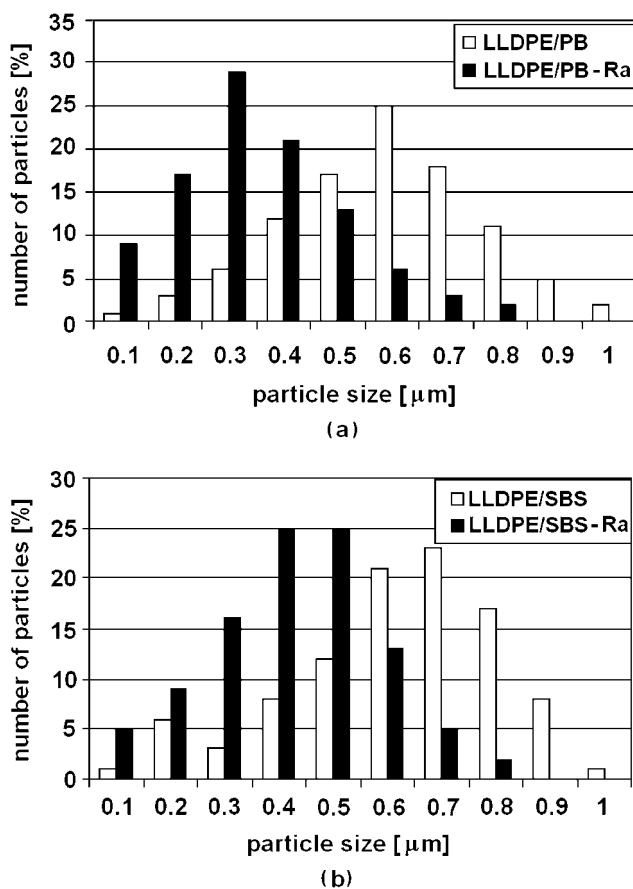
Figure 2 Particle size distribution for (a) LLDPE/PB-LLDPE/PB-Ra and (b) LLDPE/SBS-LLDPE/SBS-Ra blends obtained with and without the addition of DCP.

authors have shown that because the effect of crosslinking polyethylene on the T_m values strongly depends on the type and crosslinking degree, significant or modest T_m variations can be obtained,[22,23] and our results agree with those studies, as shown in Figure 3(a,b). On the other hand, the crystalline phase amount decreased from 40.8 to 33.2 wt % in the same series, in which the crystalline fraction was evaluated with the melting enthalpy of 100% crystalline polyethylene.[24]

The crosslinking effect on T_g, which increased from −120 to −106°C, is well shown in Figure 3(c), in which the calorimetric traces in the T_g range are reported. This result is in agreement with the amount of gel previously determined for these samples by boiling xylene extraction.[1] In particular, the gel fraction was 34% for LLDPE-R1 and 89 wt % for LLDPE-R2. In fact, the LLDPE-R2 sample with the highest crosslinking level also showed the highest T_g value and the lowest heat capacity variation.

Isothermal tests were performed to estimate the influence of the crosslinking on the crystallization behavior. The DSC traces at 115°C for the samples LLDPE, LLDPE-R1, and LLDPE-R2 are compared in

Figure 4. A longer time was required to reach the minimum of the curve for LLDPE-R2.

The following Avrami equation was employed to evaluate the kinetic parameters Z and n:

$$X = W_c/W_0 = 1 - \exp(-Z \cdot t^n) \qquad (2)$$

where X is the crystallized fraction at time t; W_c and W_0 are the weights of the crystalline phases at time t and at a very long time, respectively; Z is the rate of
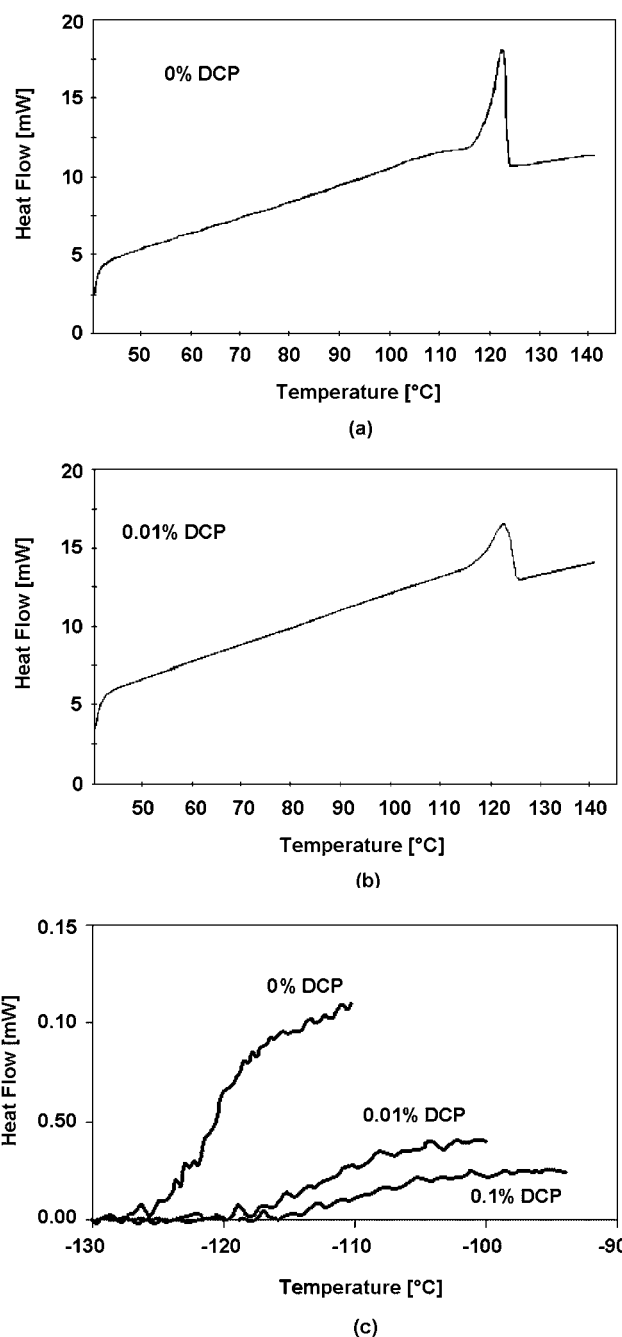
Figure 3 DSC traces of the LLDPE samples (a,b) in the range of fusion and (c) in the range of −130 to 90°C treated with different amounts of DCP.
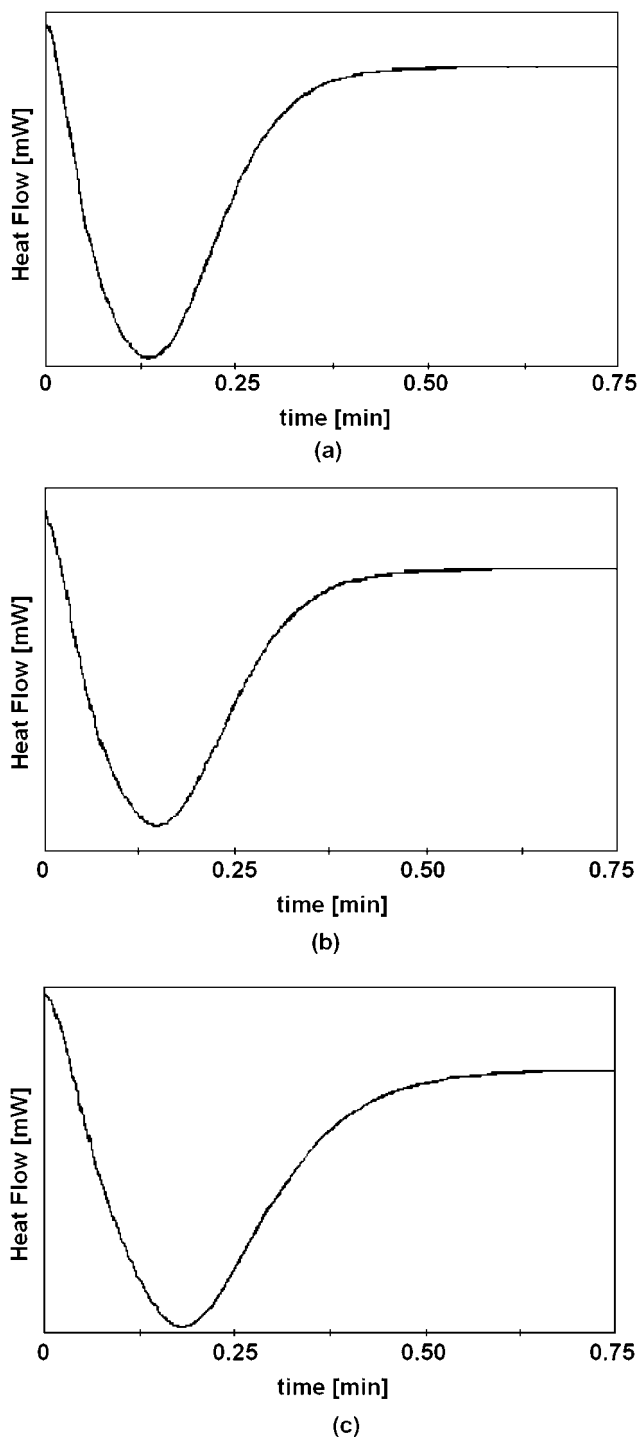
Figure 4 Isothermal DSC traces at 115°C for (a) LLDPE, (b) LLDPE-R1, and (c) LLDPE-R2 samples.

the crystallization process; and n is a parameter related to the type of nucleation process and growth.[25]

Z and n parameters for LLDPE, LLDPE-R1, and LLDPE-R2 are reported in Table II. Both Z and n decrease with the increase in the crosslinking degree.

Now the effect of reactive blending on the thermal properties of LLDPE/rubber blends is discussed. The mixing conditions employed to prepare these

blends were the same ones previously used for LLDPE samples; the compositions and calorimetric data for both series of blends, LLDPE/PB and LLDPE/SBS, are summarized in Table I.

In general, two criteria can be used to estimate the degree of compatibility in a blend: the shift of the T_g's of the components in comparison with the starting materials and, if one component contains a crystalline phase, the shift of T_m.[5] In particular, when the compatibility is increased, approaching T_g and a depression of T_m should be expected.

The reactive blending performed with the addition of a free-radical initiator can produce crosslinking and grafting reactions, and both these processes can change the T_g values of the polymers involved. As shown previously, the increment of the LLDPE crosslinking degree gave rise to an increase in the T_g value and a decrease in the crystalline degree; on the other hand, it is known that grafting reactions during reactive blending increase the compatibility, the T_g's of the components approaching each other. In this contest, it is obviously difficult to discriminate the role of each process involved; however, some important considerations can be made.

It should be noticed from the T_g's of the samples prepared by physical blending (LLDPE/PB and LLDPE/SBS) that some compatibility exists if PB is used. In fact, as reported in Table I, T_g of LLDPE increases from −120°C in the starting polymer to −117°C in the physical blend, whereas no significant change can be observed for T_g of the PB phase, the value of which shifts from −80°C for the starting PB to −81°C.

In the case of the LLDPE/SBS blend, on the contrary, the glass transition of the LLDPE phase seems to be not affected by the melt mixing; in fact, it goes from −120°C for pure LLDPE to −121°C for the blend, and T_g of the SBS phase shifts from −86°C to −84°C in the direction opposite of the expected one.

Neither blend showed significant variation of T_m with respect to the starting LLDPE; nevertheless, a decrease in the crystalline degree was observed, and it was more evident in the case of LLDPE/PB (see Table I), in agreement with the good compatibility between the two polymers.

TABLE II
n and Z Parameters for the Isothermal Test at 115°C and Calculated $t_{1/2}$ Values for Crystallization

Sample	n	Z (s^{-1})	R^2	$t_{1/2}$ (s)
LLDPE	1.97	0.0109	0.9999	8.2
LLDPE-R1	1.91	0.0098	0.9991	9.3
LLDPE-R2	1.89	0.0087	0.9994	10.1
LLDPE/PB	1.73	0.0600	0.9999	4.1
LLDPE/PB-Ra	1.78	0.0571	0.9997	4.1
LLDPE/SBS	1.75	0.0564	0.9999	4.2
LLDPE/SBS-Ra	1.73	0.0604	1.0000	4.1

When the peroxide was added to the polymers blends, it caused an appreciable increment of the T_g's in both phases. The chemical process appeared more efficient for the LLDPE phase when PB rubber was employed versus SBS: as shown in Table I, there was an increment of 11°C for T_g of LLDPE in LLDPE/PB-Ra and an increment of only 4°C for T_g in LLDPE/SBS-Ra. It should be underlined that this difference could be due to a lower double-bond content in SBS rubber, in comparison with PB, leading to a lower grafting degree.

As in the case of the physically mixed blends, LLDPE/PB-Ra and LLDPE/SBS-Ra did not show a significant variation of T_m, and from the point of view of the crystalline phase content, a very modest decrement was observed only for the LLDPE/PB-Ra sample. This result is in contrast with the effect of crosslinking expected and suggests that grafting reactions were probably prevailing over crosslinking. An increment of the compatibility cannot be based on the increase in T_g of LLDPE alone but can be supposed by consideration also of the finer particle size dispersion. On the other hand, the grafting products should explain why the crystalline phase in reacted blends is maintained or slightly increased in comparison with the physical blends; in fact, higher mobility could be produced in the interfacial zone as the kinetic parameter of secondary crystallization processes suggests (discussed later).

Although the Avrami equation was developed for studying the crystallization process in pure polymers, various articles describe the use of this equation for studying the crystallization behavior of polymer blends.[16,18,26] However, here it was used merely as a fitting equation for DSC isothermal data of the blends; Z and n parameters, obtained with high correlation coefficients, should be considered as fitting parameters and compared.

The isothermal tests were carried out at two different temperatures, 115 and 110°C, and the fitting with the Avrami equation was performed in both cases.

For the isothermal tests at 115°C, the evaluated Z and n parameters are summarized in Table II. The blends showed Z values about 5 times higher than those obtained for LLDPE samples but lower n values; the blends showed similar n parameters, all near the value of 1.7. In the same table, the half-time ($t_{1/2}$) values calculated from the Avrami equation at $X = 0.5$ are also reported. In general, lower $t_{1/2}$ values were observed in the blends.

In the case of the tests performed at 110°C, the blends prepared with and without the addition of DCP showed two different crystallization peaks, as shown in Figure 5 for LLDPE/PB and LLDPE/PB-Ra. The same behavior was not observed for LLDPE samples at the same temperature.
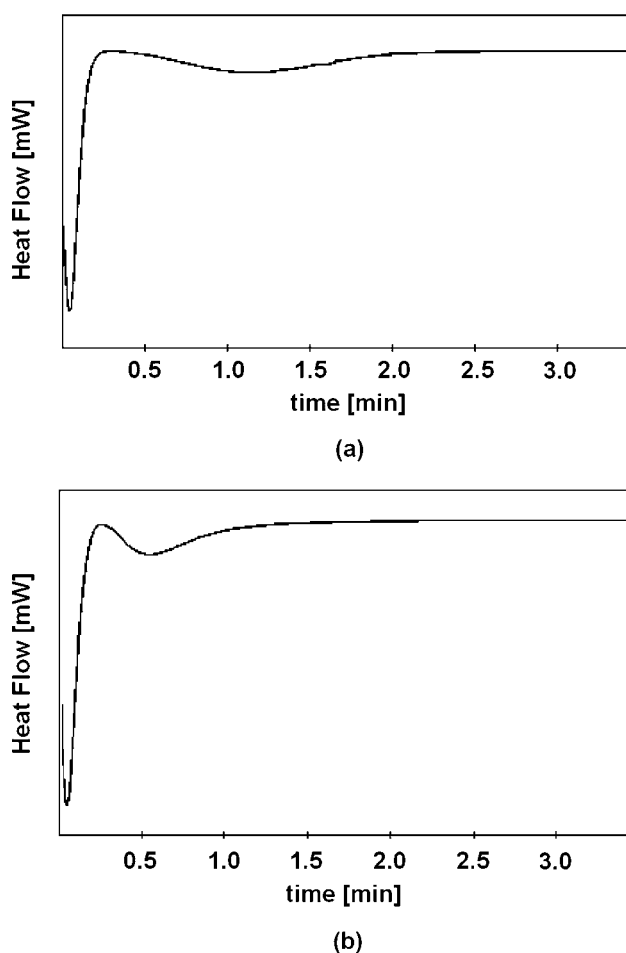
Figure 5 Isothermal DSC traces at 110°C for (a) LLDPE/PB and (b) LLDPE/PB-Ra samples.

The Avrami's parameters of the blends evaluated at 110°C are reported in Table III. If we consider the first peak, only little differences are observed with respect to the isothermal run at 115°C; also, in this case, no appreciable effect of the presence of DCP was observed.

On the contrary, when we consider the slower crystallization process, in general, reactive mixing increases the rate in a remarkable way; in fact, a Z increment of 2 decades was observed. On the other hand, the fitting parameter n decreased from 2.51 to 1.98 for the LLDPE/PB and LLDPE/PB-Ra samples and from 2.66 to 2.23 for the LLDPE/SBS and LLDPE/SBS-Ra samples, respectively. $t_{1/2}$ values clearly show the rate increment of this step due to the reactive blending. These results could be explained by the consideration of two different factors: a probable nucleation effect of the rubber particles and an increment of LLDPE molecular mobility due to the grafting processes.

The nucleation effect of rubber should explain the higher rate of crystalline phase formation in the blends. On the other hand, the presence of a slower

TABLE III
n and Z Parameters for the Isothermal Test at 110°C and Calculated $t_{1/2}$ Values for Crystallization

Sample	I peak				II peak			
	n	Z (s^{-1})	R^2	$t_{1/2}$ (s)	n	Z (s^{-1})	R^2	$t_{1/2}$ (s)
LLDPE/PB	1.66	0.0766	0.9998	3.8	2.51	6.5×10^{-6}	0.9998	100.7
LLDPE/PB-Ra	1.68	0.0759	0.9997	3.7	1.98	6.1×10^{-4}	0.9991	34.9
LLDPE/SBS	1.73	0.0631	1.0000	3.9	2.66	7.5×10^{-6}	0.9993	73.6
LLDPE/SBS-Ra	1.63	0.0821	0.9998	3.7	2.23	1.1×10^{-4}	0.9981	50.6

crystallization process should be due to a constraining phenomenon at the LLDPE/rubber interface. The chemical modifications do not substantially affect the rate of the main crystallization process in comparison with a physical blend. This suggests that a limited extent of crosslinking was obtained. On the contrary, the large effect of chemical modification on the slower step could be explained by grafting polymer formation in the interfacial zone with a consequent increment in the molecular mobility near the particle surface.

DMTA was also employed to better understand the transition processes in crosslinked LLDPE and in the blends. Different loss modulus peaks were evidenced around −110°C (glass transition), around −25°C, and in the range of +40 to 70°C (α transition). In particular, attention was paid to the α-transition temperature (T_α), which involves intralamellar motions in the crystalline phase and is associated with different molecular motions under the constraints imposed by the crystalline region near T_m.[27,28] Measurements performed in the range of 40–100°C at frequencies of 0.2, 1, 3, and 10 Hz, respectively, were used for evaluating the activation energy of the α transition, the T_α values being estimated from the traces obtained at 0.2 Hz.[28]

The data for all the samples studied are summarized in Table IV. T_α in LLDPE samples decreased, whereas the corresponding activation energy increased with the crosslinking degree increasing (the DCP content). A reasonable explanation of this behavior is probably the presence of a higher defect content (chain extension and branching) in the intralamellar phase, which affects the molecular

constraints within this region. On the contrary, all blends showed higher T_α and activation energy values than pure LLDPE. In this case, the presence of DCP during the blending generally emphasized the phenomena. These results suggest that a more regular packing of the crystalline phase occurs in the blends in comparison with LLDPE in agreement with the increased crystallinity and crystallization rate observed for the blends in the isothermal DSC tests previously discussed. This effect, particularly evident for the reactive blending procedure, can be ascribed to the presence of an elastomeric phase able to reasonably act as a free-radical scavenger preserving the LLDPE phase.

CONCLUSIONS

The preparation of LLDPE/PB and SBS binary blends by reactive melt mixing through the addition of a peroxide appreciably increased the compatibility of the phases. In particular, a finer rubber dispersion in the LLDPE matrix was obtained, as determined by TEM analysis. The occurrence of competitive grafting and crosslinking reactions has been considered and discussed on the basis of their effects on the thermal properties.

The isothermal DSC traces at 110°C of physical blends showed the presence of a secondary crystallization peak at a longer time that was probably related to the crystallization of LLDPE near the interface zone. The reactive blending showed a negligible effect on the rate of the main crystallization process but strongly increased the rate of secondary phenomena.

A significant effect of the blending process on the LLDPE α-transition was also observed.

TABLE IV
T_α and Activation Energy (E_a) as Determined from the DMTA Data

Sample	T_α (°C)	E_a (kcal/mol)
LLDPE	71.7	55.0
LLDPE-R1	69.4	61.6
LLDPE-R2	50.7	67.4
LLDPE/PB	69.4	56.9
LLDPE/PB-Ra	74.4	56.9
LLDPE/SBS	72.0	57.4
LLDPE/SBS-Ra	80.9	58.6

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