Isothermal and Nonisothermal Crystallization of HDPE Composites Containing Multilayer Carton Scraps as Filler

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ABSTRACT: The influence of multilayer carton scraps (MC) on crystallization kinetics of high-density polyethylene (HDPE) is detailed in this contribution. HDPE/MC composites were prepared by melt mixing, and a maleated linear low density polyethylene (MAPE) was added as compatibilizer. The crystallization kinetics of HDPE/MC/MAPE was analyzed as function of composition both in isothermal and nonisothermal conditions. The multilayer carton scraps appear to promote the onset of crystallization of HDPE, act- ing as efficient nucleating agent. The presence of MAPE as compatibilizer slightly reduces the nucleating efficiency of MC: the compatibilizer induces a delay in the onset of crystallization, caused by the need to exclude the bulky pendant groups of maleated linear low-density polyethylene from the crystals, as HDPE and MAPE chains cocrystallize. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: composites; crystallization; polyethylene (PE)

INTRODUCTION

One of the most diffused commodities is polyethylene, that, in its branched (LDPE) and linear (HDPE, LLDPE) forms, is used for applications ranging from packaging to furniture, as well as to agricultural films. A wide variety of organic and inorganic fillers have been employed for the compounding of polyethylene-based composites, with the aim of reinforcement and cost reduction, further extending its applications.

Quite recent is the fabrication of composites made with polyethylene and cellulosic fibers, recovered from different sources such as sawdust, wood, and paper scraps.[1] The use of recycled cellulose in composites can represent a market for industrial scraps thus reducing problems related to waste disposal and recycling. Moreover, paper is a common contaminant in polyethylene recovered from municipal solid waste, then the compounding of PE/cellulose composites could represent a cost-effective route for the easy recycling of contaminated plastics.

While the tensile strength of the recycled plastics is usually good, the materials generally have fairly low stiffness and creep resistance, limiting their use in a number of applications.[2] If these recycled plastics are combined with cellulose or other natural fibers in a composite, the stiffness and creep resistance can be improved substantially.

Polyethylene and cellulose are used in multilayer packaging materials for liquid foods; these materials, named multilayer cartons (MC), are constituted by cellulose (80 wt %) and polyethylene (20 wt %) layers. Usual MC recycling essentially involves the separation of paperboard from other layers, then the polymer residues are separately recycled, with an overall recycling processes that is very complex and expensive. If the separation step is avoided, a simpler and more economic recycling process can be achieved. To obtain this, MC can be directly recycled by mixing with polyethylene, where MC are a source of cellulose fibers in the compounding of polyethylene-based composites.[3]

Previous studies have shown that HDPE-based composites can be processed using multilayer cartons as filler and maleated linear low-density polyethylene (MAPE) as coupling agent.[3,4] These composites exhibit improved properties compared with neat HDPE, since the addition of MC results in an improvement of mechanical properties at low- and high-deformation rates, as well as in a very interesting response of composites to water vapor permeability.

To more deeply investigate the properties of HDPE/MC composites, an analysis of crystallization kinetics of HDPE in the presence of multilayer cartons was carried out, and results detailed in this contribution. It is well known that the properties of polymer composites depend not only on dispersion and adhesion of the phases, but also on the crystalline

superstructure and morphology. The addition of a filler can affect the properties of the crystallizable phase, including the overall crystallinity, the crystal morphology, the dimensions of crystallites and their aggregates, as well as the amorphous–crystal interface. Therefore a complete understanding of the crystallization process in polymer composites is necessary to obtain products with tailored properties.

EXPERIMENTAL

Materials

Multilayer cartons, constituted by cellulose and LDPE (80/20 by mass), were kindly supplied by Tetra Pak Italiana S.r.l. (Latina, Italy), as production scraps. Scraps were milled in a Retsch SM100 cutting mill equipped with a bottom sieve (conidur holes, 1 mm diameter). The obtained powder was dried under vacuum at 90°C overnight and kept in a desiccator.

High-density polyethylene (Alathon M6580, density 0.965 g cm^{-3}, melt index 8.2 g/10 min at 190°C and 2.16 kg) was supplied by Equistar (TX).

Maleated linear low-density polyethylene (MAPE), trade name AgrimalHD, density 0.92 g cm^{-3}, was kindly supplied by Agricola Imballaggi (Pagani, Italy). The content of maleic anhydride grafted onto polyethylene is 1% by mass, evaluated by titration.[5]

Composites preparation

HDPE/MC composites were compounded in an internal mixer (Rheocord EC of HAAKE, NJ). HDPE was first blended with 0 or 5 or 10 wt % of MAPE at 175°C for 10 min, then cooled and pelletized. Successively these batches were mixed with 20, 40, and 60 wt % of dried MC powder to prepare uncompatibilized and compatibilized composites. The melt mixing was carried out at 175°C for 10 min. Composites and neat HDPE were finally compression-molded at 180°C. In Table I, compositions and codes of the prepared materials are reported.

Thermal analysis

Isothermal and nonisothermal crystallization kinetics of HDPE/MC/MAPE composites was investigated using a Mettler DSC 822^e calorimeter, Mettler-Toledo, equipped with a liquid-nitrogen accessory for fast cooling. The calorimeter was calibrated in temperature and energy using indium. Dry nitrogen was used as purge gas at a rate of 30 ml/min.

To set the structure for the analysis of crystallization kinetics, each sample was heated from 25 to 190°C at a rate of 30°C/min, melted at 190°C for 10 min to erase previous thermal history, then cooled at 30°C/min to the desired crystallization

TABLE I
Composition and Relative Codes of the HDPE/MC/MAPE Composites

Codes	HDPE + MAPE (%)	MC (%)	MAPE/(HDPE + MAPE) Weight ratio (%)
100/0_M0	100	0	0
80/20_M0	80	20	0
60/40_M0	60	40	0
40/60_M0	40	60	0
100/0_M5	100	0	5
80/20_M5	80	20	5
60/40_M5	60	40	5
40/60_M5	40	60	5
100/0_M10	100	0	10
80/20_M10	80	20	10
60/40_M10	60	40	10
40/60_M10	40	60	10

temperature (T_c) and maintained at T_c for the time needed for crystallization to reach completion.

Nonisothermal crystallization data were gained upon cooling from the melt at fixed scanning rates after melting the samples at 190°C for 10 min. The samples were rapidly cooled to 160°C, to avoid too prolonged permanence at high temperatures, then cooled to room temperature at a rate ranging from 0.5 to 4°C/min.

Crystallization is an exothermic process, and the heat evolved during the phase transition may cause some local heating and thermal gradients within the sample. As a consequence, transitions can occur at temperatures that do not correspond to those detected by the instrumentation.[6,7] The thicker the sample, the more critical this problem is. To reduce these problems, sample mass was limited to 3.0 ± 0.2 mg, and cooling rates not exceeding 4°C/min were used.

Morphology

Morphological analysis of HDPE/MC/MAPE composites was performed using a FEI Quanta 200 FEG environmental scanning electron microscope (ESEM) (Eindhoven, The Netherlands) in low vacuum mode (P_{H20} 0.60–0.75 torr), using a large field detector (LFD) and an accelerating voltage of 10–20 kV. Before the analysis, the composites were mounted on aluminum stubs by means of carbon adhesive disks.

RESULTS AND DISCUSSION

Crystallization kinetics of HDPE/MC/MAPE composites was investigated by differential scanning calorimetry in isothermal and nonisothermal conditions. For the isothermal analyses, a temperature range where all the analyzed compositions crystallize in a reasonable time was selected, to better compare the crystallization behavior of the various samples. For the

chosen temperature range, a cooling rate of 30°C/min from 190°C to the desired T_c was sufficient to prevent crystallization during cooling. However, in a few cases it was found that crystallization started during the instrumental drift that takes place after reaching the preset isothermal point.

In a DSC apparatus, due to the finite response time of the cell temperature controller, a sharp change of scanning rate, as for example a switch from cooling to isothermal step, always produces a transient overshoot, after which the signal gradually returns to the steady state.[8] In case the initial stages of the phase transition are masked by this overshoot, the latter needs to be separated from the exotherm associated to crystallization to estimate the time dependence of the evolved latent heat and determine the kinetics of phase transformation. To do this, after isothermal crystallization, blank experiments were performed with the same sample at a temperature above the melting point, where no transition takes place.[9–11] The blank runs were subtracted from the crystallization exotherms, and the intersection of the extrapolated baseline with the resulting exothermal curve was taken as the starting time for the phase transition (induction time, t_o), following the procedure detailed in Refs. [12] and [13]. The heat evolved during crystallization was recorded as a function of time, and the fraction of material crystallized after a period of time t (X_t) was calculated from the ratio of the heat generated at time t and the total heat developed during the phase transformation. Plotting X_t against time, the half-time of crystallization ($\tau_{1/2}$), defined as the time needed for 50% the final crystallinity to develop, was obtained.

The $\tau_{1/2}$ values of the analyzed HDPE/MC/MAPE samples are reported in Figure 1 as a function of temperature. The data are collected in three separate graphs, compared at parity of MAPE/HDPE ratio, for clarity of presentation. As expected, in the analyzed range the phase transition rate decreases with temperature of analysis. More importantly, Figure 1 reveals that much shorter crystallization times are attained by the composites, compared to plain polyethylene, suggesting that the filler fastens crystallization of HDPE, both in the presence and in the absence of the compatibilizer. A summary of the $\tau_{1/2}$ values of HDPE/MC/MAPE is reported in Table II.

Additional information on crystallization kinetics of HDPE/MC/MAPE composites comes from the analysis of the induction time (t_o), i.e., the time needed to initiate isothermal crystallization, measured as detailed above. The data are presented in Table II and exampled in Figure 2 for the composites containing MAPE/HDPE 5/95 ratio. At low crystallization temperatures, differences in t_o values are very close to the experimental uncertainty, at higher
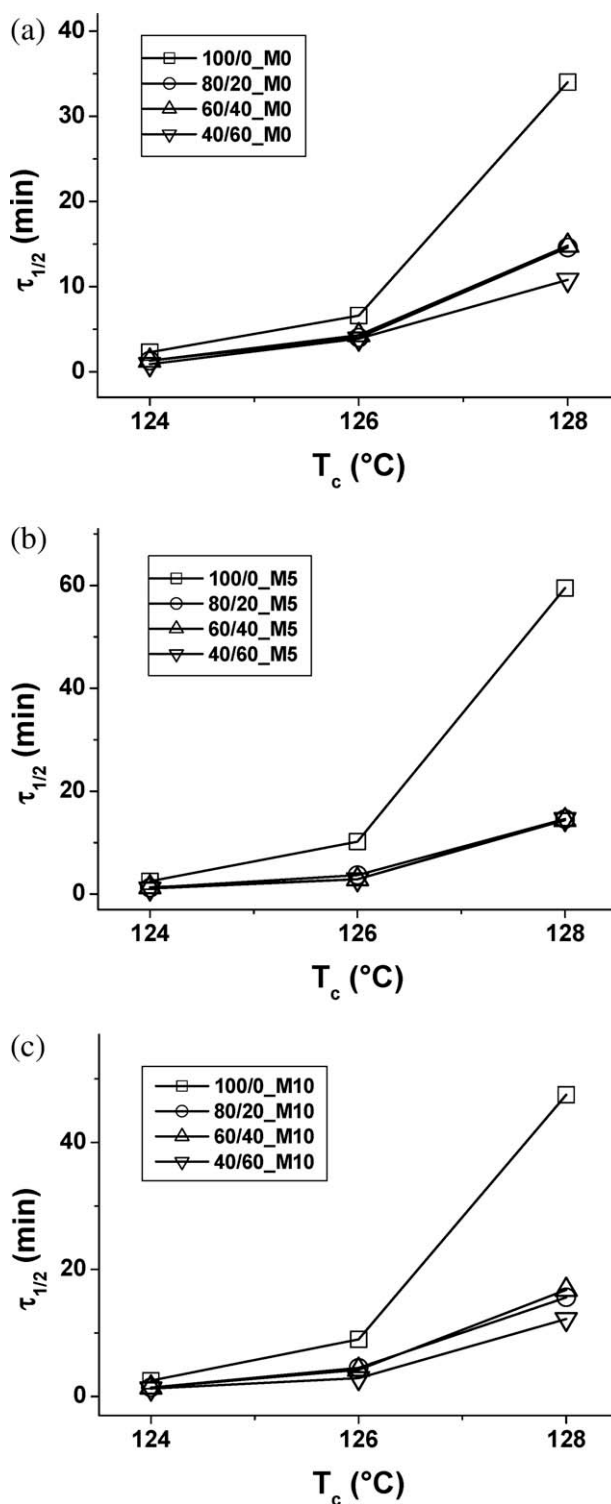

Figure 1 Half-time of crystallization ($\tau_{1/2}$) of HDPE/MC/MAPE composites as a function of the isothermal crystallization temperature (T_c): (a) MAPE/HDPE 0/100; (b) MAPE/HDPE 5/95 (c) MAPE/HDPE 10/90.

temperatures, instead, the presence of multilayer carton appears to promote the onset of crystallization of HDPE, acting as an efficient nucleating agent, similarly to the half-time of transition data shown in Figure 1.

Induction Time (t_o) and Half-time of Crystallization ($\tau_{1/2}$) of HDPE/MC/MAPE Composites at the Indicated Crystallization Temperatures (T_c)

Samples	t_o (min)			$\tau_{1/2}$ (min)		
	$T_c = 124°C$	$T_c = 126°C$	$T_c = 128°C$	$T_c = 124°C$	$T_c = 126°C$	$T_c = 128°C$
100/0_M0	1.5	3.2	23.5	2.3	6.6	34.0
80/20_M0	1.3	2.0	8.0	1.3	4.0	14.6
60/40_M0	1.5	1.8	9.2	1.3	4.3	14.8
40/60_M0	1.3	2.2	6.2	0.9	3.9	10.8
100/0_M5	2.2	3.4	27.5	2.5	10.2	59.5
80/20_M5	1.4	2.1	10.0	1.2_5	3.7	14.6
60/40_M5	1.3	2.0	3.6	1.3_5	2.9	14.4
40/60_M5	1.7	2.1	2.0	1.1	2.9	14.6
100/0_M10	2.1	4.0	36.5	2.5	9	47.5
80/20_M10	1.4	2	9.6	1.4	4.5	15.6
60/40_M10	1.4	2.6	6.0	1.4	4.2	16.8
40/60_M10	1.4	2.1	8.8	1.25	2.9	12.2

The subscripts are nonsignificant digits.

The nucleation efficiency of multilayer carton scraps on crystallization of HDPE was also probed by morphology analysis. The scanning electron micrograph of plain HDPE after isothermal crystallization at 128°C, presented in Figure 3a, is centered on a typical polyethylene spherulite with a diameter of about 7 μm. The linear boundaries between the spherulites suggest that the crystallites are nucleated at the same time,[14] as expected for polyethylene, whose homogeneous nucleation is reported to take place at temperatures below 85°C.[15] In Figure 3b, the morphology of polyethylene spherulites grown in the presence of 20% MC is presented. Multilayer carton scraps favor growth of much smaller polyethylene crystallites, with a diameter of about 1–2 μm, whose size is limited by the much higher number of simultaneously growing crystals,

being their nucleation facilitated by the presence of cellulose fibers.

The effect of compatibilizer on crystallization rate of HDPE/MC/MAPE composites is exampled in Figure 4 for the samples containing HDPE/MC ratio of 80/20. The data shown in Figure 4 illustrate the effect of a varied MAPE amount on the onset time of crystallization. At low crystallization temperatures, differences between the various samples are within the experimental error, due to the fast crystallization rate. At higher temperatures, the 80/20 composite that does not contain the compatibilizer (80/20_M0) appears to have a somewhat faster initiation of the phase transition, which, in turn, affects the overall crystallization kinetics. The presence of MAPE results in a slight delay of crystallization, not only for HDPE/MC/MAPE composites with (HDPE+MAPE)/MC 80/20 ratio, but also for the other analyzed compositions, as summarized in Table II.

Nonisothermal crystallization analysis of HDPE/MC/MAPE composites was also performed, to expand the temperature range of analysis of kinetics data. With the used DSC apparatus, controlled cooling rates higher than 30°C/min are difficult to achieve because of instrumental limitations, and this restricts the temperature range where isothermal crystallization after cooling from the melt can be performed. Therefore, nonisothermal crystallization at selected controlled cooling rates was preferred because this procedure allows a higher variation of crystallization conditions.

Nonisothermal crystallization analysis of HDPE/MC/MAPE composites is presented in Figure 5, which illustrates the heat flow rate plots of a few selected samples obtained during cooling from the melt at 2°C/min. Figure 5a compares the heat flow rate of HDPE/MAPE blends at various compositions. The addition of MAPE delays the onset of
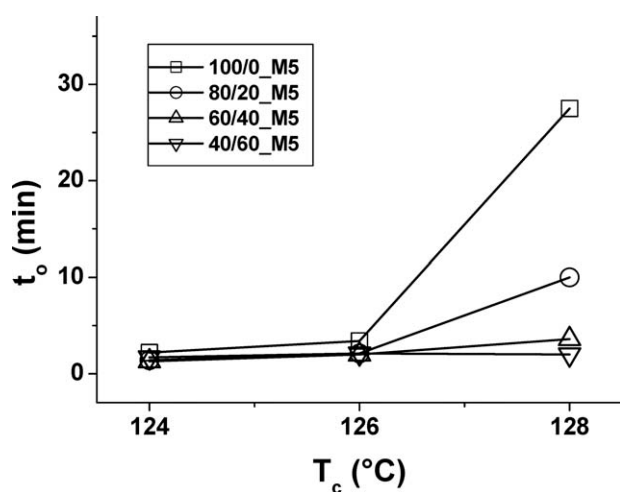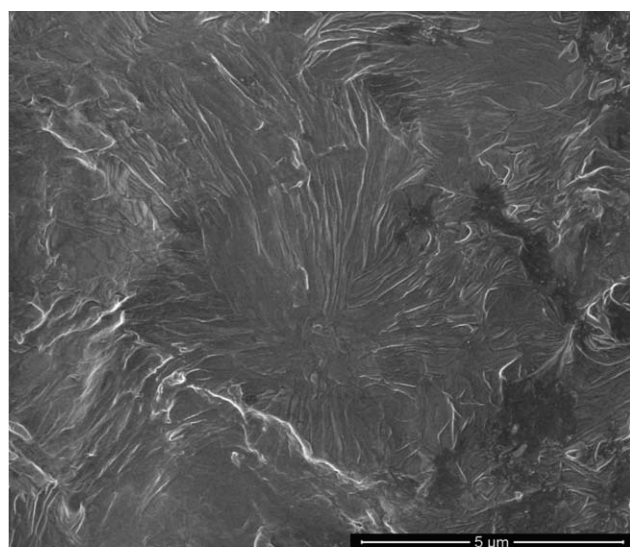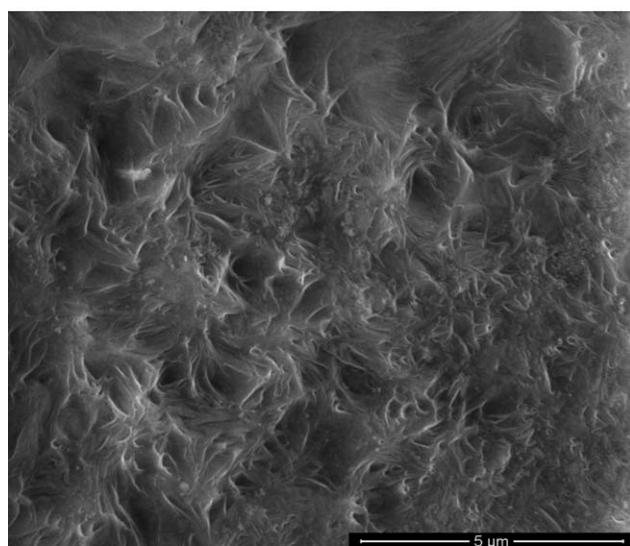

Figure 2 Onset time of crystallization (t_o) of HDPE/MC/MAPE composites with MAPE/HDPE 5/95 and varied (HDPE + MAPE)/MC ratio as a function of the isothermal crystallization temperature (T_c).

(a)

(b)

Figure 3 SEM micrographs after isothermal crystallization at 128°C of (a) neat HDPE and (b) HDPE/MC/MAPE composite 80/20_M0.

crystallization, as also seen in Figure 4 for the composites containing 20% MC, and results in a shift to lower temperatures of the whole crystallization exotherm. The extent of the shift seems to be unaffected by the amount of MAPE, at least for the analyzed compositions and cooling rates. The effect of multilayer carton scraps on crystallization of HDPE is illustrated in Figure 5b for the composites containing 5% of compatibilizer and refers to cooling from the melt at a rate of 2°C/min. Similar plots were obtained for all the other analyzed compositions and cooling rates. For the HDPE/MC/MAPE 100/0_M5 composite, that does not contain multilayer carton, crystallization has an onset at 122.7°C. The addition of MC induces an anticipated beginning of the phase

transition, that starts at 124.5 ± 0.2°C, independently of the amount of MC present in the composite.

In Figures 6 and 7, the onset (T_o) and peak (T_p) temperatures of the crystallization exotherms of the composites are compared in dependence of the cooling rate. The data are illustrated for the composite containing 5% of MAPE, similar plots were gained for all the other compositions. A summary of the crystallization onset and peak temperatures for all the analyzed cooling rates and compositions is presented in Table III. The onset point was taken as the intersection of the baseline before the transition and the inflectional tangent and the peak temperature as the maximum of the exotherm.[8] As expected, an increase in cooling rate results in a shift of the phase transition parameters of all the analyzed samples toward lower temperatures: at low cooling rates there is more time to form the nuclei, so that crystallization starts at higher temperatures.[16] Similarly, also the peak temperatures move toward lower values upon increasing the cooling rates, as result of the shift of the whole phase transition to lower temperatures. The addition of multilayer carton induces crystallization to start at higher temperatures, and has a limited effect on the shape of the phase transition exotherm, as seen by comparison of the data shown in Figures 5–7 as well as in Table III, indicating that MC can affect the nucleation of HDPE crystals and has a limited influence on crystal growth.

The influence of MAPE on nonisothermal crystallization kinetics of HDPE/MC/MAPE is exampled in Figure 8, for the composite containing 20% MC. Similar to the isothermal data shown in Figure 4, the presence of MAPE induces a delayed onset of crystallization, that starts at lower temperature when 5 or 10% of compatibilizer is added to the formulation.
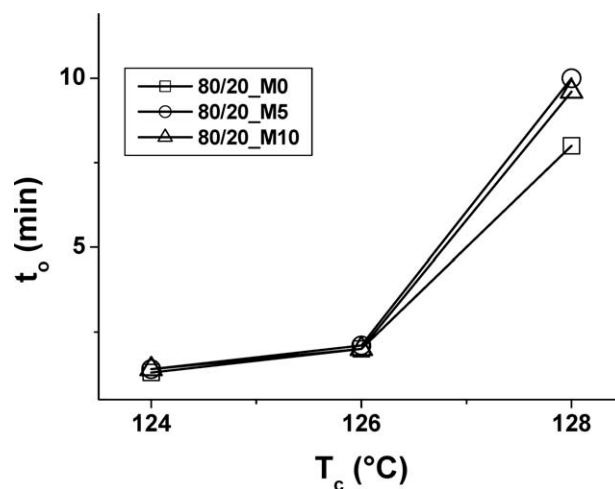

Figure 4 Onset time of crystallization (t_o) of HDPE/MC/MAPE composites with (HDPE + MAPE)/MC 80/20 and varied MAPE/HDPE ratio as a function of the isothermal crystallization temperature (T_c).
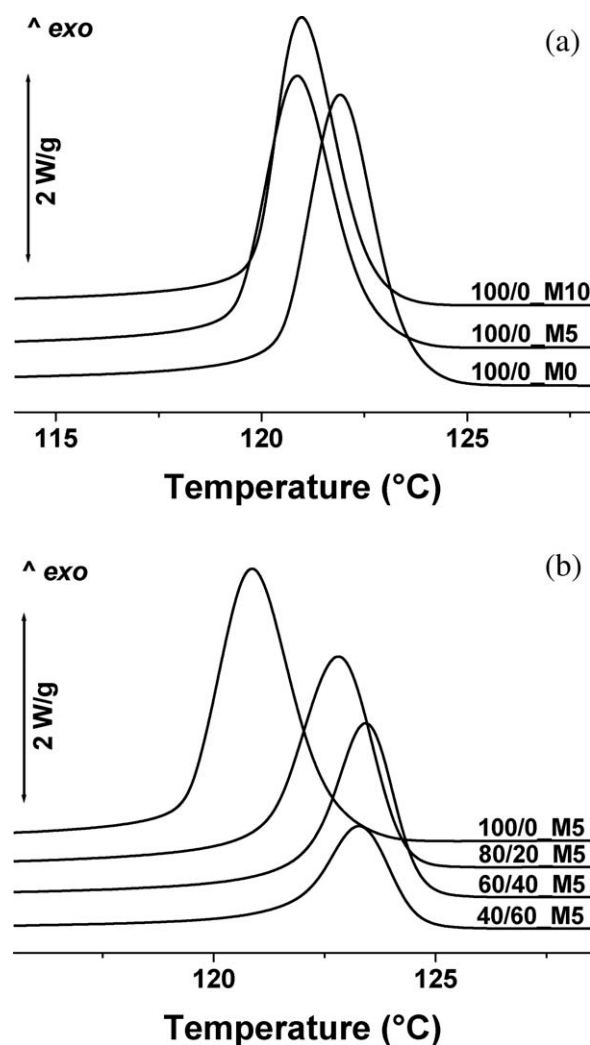
Figure 5 Heat flow rate plots of HDPE/MC/MAPE composites during nonisothermal crystallization from the melt at 2°C/min: (a) (HDPE + MAPE)/MC 100/0 and varied MAPE/HDPE ratio; (b) MAPE/HDPE ratio 5/95 and varied (HDPE + MAPE)/MC ratio.

The data reported above reveal that both the filler and the compatibilizer affect the onset of crystallization, then the phase transition proceeds without sizeable effects due to the presence of the filler or of the compatibilizer. In principle, the filler may affect crystallization also after crystal growth has started, since the dispersed MC fibers cannot be included within the polyethylene lamellae, but must be rejected and/or occluded by the growing crystals, which may disturb crystal growth.[17] This would result in a broadening of the phase transition, which was proven not to occur, as exampled by the data shown in Figure 5b. It is likely that low energy is needed to exclude the filler from the crystal growth front and the effect on crystallization kinetics is negligible.

MC is an effective nucleating agent for HDPE, but its efficiency is somewhat lowered by the presence
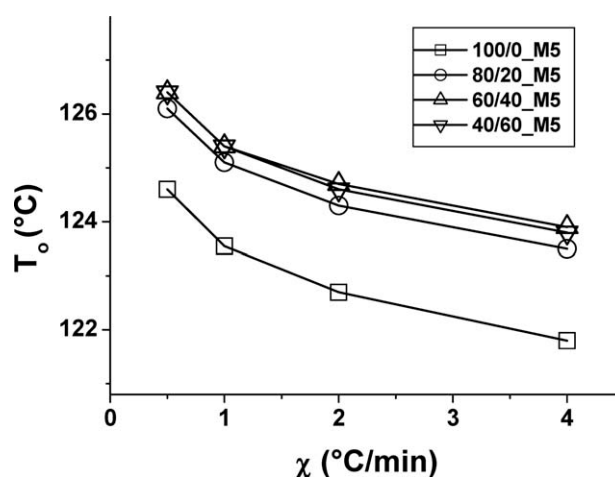
Figure 6 Onset temperature of crystallization of HDPE/MC/MAPE with MAPE/HDPE 5/95 as a function of cooling rate (χ).

of MAPE as compatibilizer. Morphological analysis of the cryogenically fractured surfaces of the composites, detailed in Ref.[3] reveal that, without the compatibilizer, multilayer carton fibers have a very poor adhesion to the polyethylene matrix. The addition of 5% of MAPE ensures partial adhesion between the polyolefin and the filler, and 10% of compatibilizer is necessary for a complete wetting of the fibrous phase with the polymer.[3] The degree of adhesion between filler and matrix does not affect the ability of MC to promote crystallization of HDPE, which can start on MC fiber surface, irrespective of the presence of the compatibilizer. Conversely, MAPE seems to slight delay the onset of the phase transition, as seen in Figures 4 and 8. At first analysis, this delay may be ascribed to a possible diminution of surface irregularities caused by wetting of the fiber by the compatibilizer, which may lead to a smoother
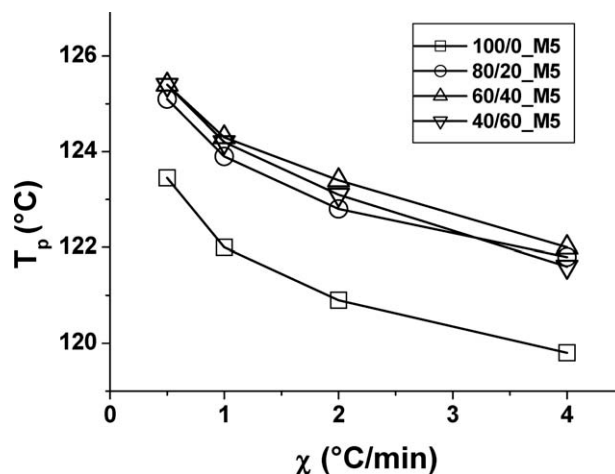

Figure 7 Peak temperature of crystallization of HDPE/MC/MAPE with MAPE/HDPE 5/95 as a function of cooling rate (χ).

TABLE III
Onset (T_o) and Peak (T_p) Temperatures of the Crystallization Exotherms of HDPE/MC/MAPE Composites
at the Indicated Cooling Rates

Samples	T_o (°C)				T_p (°C)			
	4°C/min	2°C/min	1°C/min	0.5°C/min	4°C/min	2°C/min	1°C/min	0.5°C/min
100/0_M0	122.8$_5$	123.6	124.5	125.7	120.8	121.9	123.1	124.4
80/20_M0	124.1	124.9	125.7	126.7	122.0	123.0	124.3	125.6
60/40_M0	124.1	125.0	125.8	126.8	121.6	123.0	124.4	125.4
40/60_M0	123.9	124.8	125.9	126.8$_5$	121.9	123.0	124.4	125.7
100/0_M5	121.8	122.7	123.5$_5$	124.6	119.8	120.9	122.0	123.45
80/20_M5	123.5	124.3	125.1	126.1	121.8	122.8	123.9	125.1
60/40_M5	123.9	124.7	125.4	126.4	122.0	123.4	124.3	125.4
40/60_M5	123.8	124.6	125.4	126.4	121.6	123.1	124.2	125.4
100/0_M10	121.9	122.7	123.7	124.8	119.8	121.0	122.0	123.5
80/20_M10	123.4	124.2	125.0	126.1	121.4	122.8	123.9	125.2
60/40_M10	123.5	124.4	125.1	126.1$_5$	121.8	123.0	123.9	125.2
40/60_M10	123.6	124.5	125.3	126.3	121.5	123.2	124.2	125.4

The subscripts are nonsignificant digits.

fiber surface, hence in a reduced amount of sites able to initiate crystallization. If this hypothesis were true, one would observe a progressively reduced nucleation efficiency of MC fiber with the amount of compatibilizer due to the increased adhesion of the phases,[3] which is not seen in Figures 4 and 8, as the onset of crystallization data practically overlap when either 5 or 10% MAPE is present in the composite.

The reduced efficiency of MC as nucleant for crystallization of HDPE in the presence of the compatibilizer has to be attributed to the delay of crystallization caused by MAPE itself on crystallization of HDPE. As illustrated in Figure 5a, that reports the DSC thermograms of HDPE/MAPE blends during cooling at 2°C/min, the addition of 5 or 10% MAPE delays the onset of crystallization of HDPE. A decrease in crystallization rate of HDPE in the presence of linear low-density polyethylene has often been reported in the literature, and ascribed to a reduced nucleation rate, which arises from the need to exclude the bulky pendant groups of LLDPE from the crystals, as HDPE and LLDPE chains cocrystallize.[18–20] Similarly, in the HDPE/MAPE blends, where MAPE is a linear low-density polyethylene, containing not only the branches typical of LLDPE, but also maleic anhydride groups grafted on the main polyethylene chain, MAPE induces a delay in the onset of crystallization. This delay affects the onset of crystallization also in the presence of the MC filler, and results in a slightly reduced nucleation activity in the presence of the compatibilizer in the HDPE/MC/MAPE composites, compared to the compositions prepared in absence of the compatibilizer.

CONCLUSIONS

Isothermal and nonisothermal crystallization analysis of HDPE/MC/MAPE composites reveals a marked influence of multilayer carton fibers on the crystallization process of high-density polyethylene. Both the filler and the compatibilizer appear to affect the onset of crystallization, then the phase transition proceeds without sizeable effects ascribable to the presence of the filler or of the compatibilizer. The multilayer carton scraps act as efficient nucleating agents for HDPE. The presence of the maleated linear low-density polyethylene as compatibilizer for the HDPE/MC composites slightly delays the onset of crystallization of polyethylene spherulites. This hindrance is caused by cocrystallization of HDPE and MAPE, as the bulky pendant groups of MAPE need to be excluded by the growing crystals, which slightly reduces the nucleating efficiency of MC in the composites.
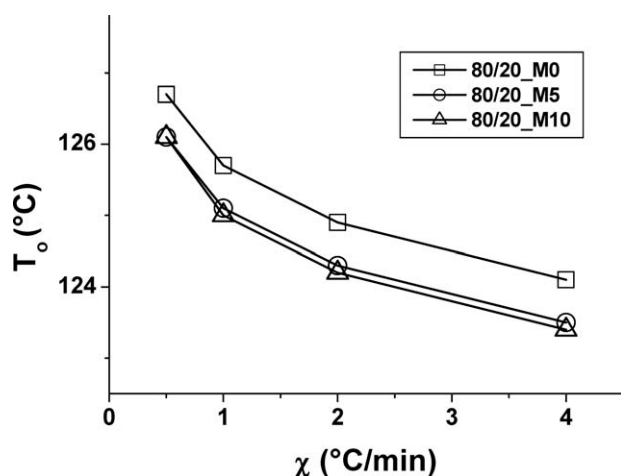

Figure 8 Onset temperature of crystallization of HDPE/MC/MAPE with (HDPE + MAPE)/MC 80/20 and varied MAPE content as a function of cooling rate (χ).

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