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Polymer 43 (2002) 6195–6204

polymer

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Characterization of blends of LDPE and PA6 with functionalized polyethylenes

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Received 15 May 2002; received in revised form 22 July 2002; accepted 31 July 2002

Abstract

Blends of low density polyethylene (LDPE) or polyamide 6 (PA6) with two types of functionalized polyethylenes compatibilizers, namely: poly(ethylene-*co*-acrylic acid) (Escor5001 by Exxon) and ethylene–glycidylmethacrylate copolymer (Lotader GMA AX8840) in the LDPE/compatibilizer or PA6/compatibilizer composition 80/20 w/w, have been prepared. The morphology, crystal structure, isothermal crystallization behavior and microhardness of the blends have been studied by optical and electron microscopy, DSC, WAXS and microhardness tests. The peculiarities in the new characteristics of the blends investigated have been revealed. The isothermal crystallization rate of both LDPE and PA6 decreases in the presence of the two types of compatibilizers. The crystallization enthalpy only of the LDPE blends is a function of the crystallization temperature. In the presence of the compatibilizer, PA6 or LDPE crystallize into spherulites with dimensions smaller than those of the corresponding neat polymers. The crystallites dimensions and degree of crystallinity do not change in LDPE/compatibilizer blends, while there are strong reductions of the degree of crystallinity and the crystallites dimensions of the components in the PA6/compatibilizer blends if compared to those of the neat polymers. The microhardness values of the PA6/compatibilizer blends are lower than the corresponding additive values, while the microhardness of LDPE/compatibilizer blends corresponds to the additive values. The results have been interpreted by different types of interactions between the functionalized polyethylenes and LDPE or PA6, correspondingly. The results indicate that the compatibilization efficiency of Escor towards PA6 is higher than that of Lotader. © 2002 Published by Elsevier Science Ltd.

Keywords: LDPE/compatibilizer blends; PA6/compatibilizer blends; Characterization

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1. Introduction

The physical and mechanical properties of incompatible heterogeneous polymer blends may be enhanced by compatibilization through the introduction of physical or/and chemical interactions between the components. The compatibilization of polyethylene–polyamide blends has gained attention in the recent years mainly due to the technological application of these materials.

Many different compatibilizers that proved useful for blends of polyethylene (PE) with polyamide 6 (PA6) have been described in the scientific and patent literature [1,2]. It has been demonstrated that the polyolefins functionalized with maleic anhydride or with acrylic acid are capable of reacting with the amine end groups of PA6, leading to efficient compatibilization [3–8]. Copolymers of ethylene with vinyl acetate [5], or with esters of the acrylic (or methacrylic) [9,10], and succinic [11] acids have shown to be effective compatibilizing agents. Some authors have also attributed the mechanism of their action to the formation of block copolymers through a reaction with the end groups of PA6.

Blends of low density polyethylene (LDPE) with PA6 compatibilized with poly(ethylene-*co*-acrylic acid) (Escor 5000, 5001 and 5010, by Exxon) having different concentration of acrylic acid (from 6 to 11 wt%) has been investigated [12]. It has been shown that Escor 5001 with acrylic acid concentration of 6% has the optimum compatibilizing efficiency as it exhibits comparable affinity towards the polyethylene phase as well as to the polyamide one. The strong compatibilizing effect of only 1–2% Escor 5001 has been explained by the formation of an Escor-PA6 copolymer, which compatibilizes the LDPE phase through the formation of polar interactions such as hydrogen bonds

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0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00532-3

between the Escor component of the copolymer and the LDPE bulk phase. On the contrary, the compatibilization efficiency of the copolymer formed towards PA6 phase is due to the miscibility of PA6 component of the copolymer with the PA6 phase [12].

In this work, binary blends of both phases, namely LDPE and PA6 as matrixes and Escor 5001 as a dispersed phase, have been studied in order to establish how the type of the interaction between the components (physical or chemical) affects the crystallization behavior, crystal structure, morphology and microhardness of the blend components. Binary blends of LDPE and PA6 with another type of functionalized polyethylene (ethylene–glycidylmethacrylate copolymer (Lotader GMA AX8840)) have been studied too. The isothermal crystallization, the microhardness and the morphology of the matrix phase of such type of blends have not been studied yet.

2. Experimental part

2.1. Materials

LDPE Riblene FF20 with a melt flow index (MFI) equal to 0.8 g/10 min, kindly provided by Polimeri Europa, was used for the blend preparation. PA6 was a commercial sample (kindly supplied by Snia Tecnopolimeri) with a relative viscosity of 3.5 dl/g (measured at 20 °C in 96% sulfuric acid with a concentration of 20 g/l). An acrylic acid functionalized polyethylene, Escor 5001, produced by Exxon, was used for the blends preparation. Escor 5001 contains 6% (w/w) acrylic acid (AA) branches and its MFI is equal to 2.0 g/10 min. Another functionalized polyethylene was ethylene–glycidylmethacrylate copolymer (Lotader GMA AX8840), provided by Elf-Atochem.

2.2. Blending

Blends of LDPE (FF20) and PA6 with Escor or Lotader were prepared by one and the same procedure. The following blends were prepared: LDPE/Escor 80/20 w/w; LDPE/Lotader 80/20 w/w; PA6/Escor 80/20 w/w, PA6/Lotader 80/20 w/w. The blend components were charged to a 30 ml mixing bowl of a Brabender Plastograph and blended 4 min at 230 °C at 100 rpm in nitrogen atmosphere. The neat components were subjected to the same thermal treatment.

2.3. Methods

Scanning electron microscopic analysis (SEM) was made with a JEOL JSM-5300 apparatus, on polymer specimens fractured under liquid nitrogen and coated with gold.

The isothermal crystallization kinetics were studied using a Perkin Elmer DSC-7 apparatus, calibrated with indium and tin standards, under nitrogen atmosphere. LDPE and LDPE/compatibilizer blends were heated to 190 °C, while PA6 and PA6/compatibilizer blends were heated to 250 °C in order to destroy the LDPE or PA6 crystal nuclei, kept at this temperature for 5 min, and cooled to the appropriate crystallization temperature T_c with a rate of 200 °C/min. T_c was in the range 102–106 °C for the crystallization of LDPE component, in the range 195–199 °C for the crystallization of PA6 component and in the range 90–96 °C for the crystallization of the neat functionalized polyethylenes. The starting time of crystallization was taken when thermal equilibrium had been reached at T_c.

The melting temperature T_m of the isothermally crystallized samples was determined from the maximum of the melting endotherm in a heating experiment starting from T_c, at a rate of 10 °C/min.

Optical microscopic observations were made with a Reichert Zetopan polarizing microscope equipped with a hot stage. Small amounts of the samples were melted between glass slides in order to obtain thin films. The films were transferred quickly onto the hot stage of the microscope, preliminarily pre-set at the temperature of crystallization T_c. The photomicrographs were taken after the completion of the crystallization at T_c and subsequent cooling of the samples to room temperature. The H_ν diffraction patterns of low-angle light scattering were obtained by applying the Bertran lens and using the microscope in the diffraction mode. The average dimensions of the spherulites were determined from the H_ν patterns, using the Stein equation [13].

WAXS investigations of the neat Escor, Lotader, LDPE and PA6, as well as their blends were carried out at room temperature in a powder Philips APD 15 diffractometer, using Ni-filtered Cu Kα radiation (1.54 Å). The diffraction scans were collected between 2θ values of 10 and 35° in reflectance mode using a step of 0.05°. The computer program FIT [14] was used for decomposition of the powder diffraction patterns.

The specimens used for the measurement of microhardness were cylindrical tablets with diagonal 8 mm and height 1 mm. They were prepared by hot pressing the materials at temperature above the corresponding melting point and subsequent cooling to room temperature. Microhardness of the blends was measured on a standard Vickers microhardness tester mhp-160 for a light microscope NU-2 (Germany). The indentor was a square shaped diamond pyramid, with top angle of 136°. Loads of 0.4, 0.6, 0.8 and 1.0 N were employed to correct the instant elastic recovery. A loading cycle of 0.1 min was used. The standard Vickers microhardness (H) was determined by the equation [15,16]

$$H = kP/d^2,$$

where P is the applied load, k a geometric factor equal to 1.854 and d the mean diagonal length of the imprint after removing the indentor.

At least 10 imprints were made under each load. The H value was determined within $\Delta H/H = 0.05$.

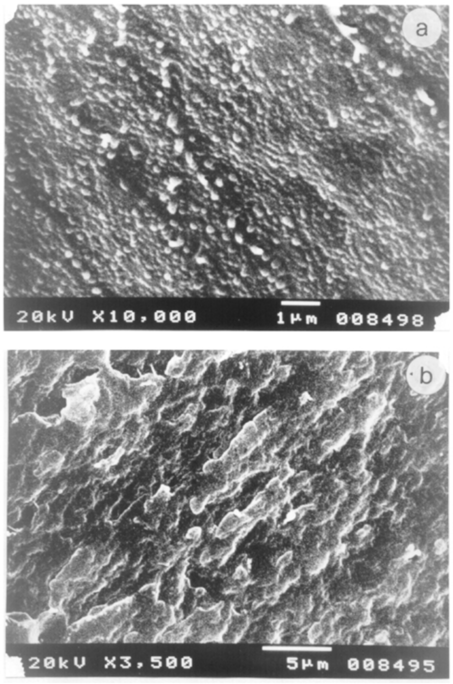

Fig. 1. SEM micrographs of LDPE/Escor 5001 80/20 w/w blend (a) and of PA6/Lotader 80/20 w/w blend (b).

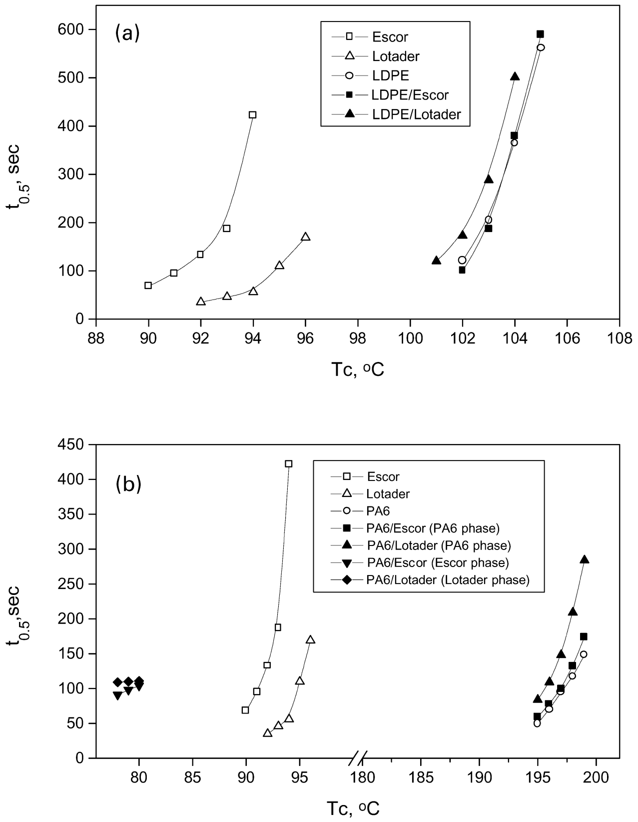

Fig. 2. Dependence of half-crystallization time ($t_{0.5}$) on crystallization temperature (T_c) for LDPE/compatibilizer blends (a) and for PA6/compatibilizer blends (b).

3. Results and discussion

The SEM observations of the fracture surfaces of the blends LDPE/Escor 80/20 w/w and LDPE/Lotader 80/20 w/w show a two phase morphology (Fig. 1(a)). The functionalized polyethylene forms the dispersed phase with rather small droplets; the droplet dimensions almost do not depend on the type of the compatibilizer and vary between 0.15 and 0.30 μm. The SEM observations show that the functionalized polyethylenes form immiscible, yet highly compatible blends with LDPE [12]. The SEM micrographs of the blends PA6/Escor 80/20 w/w and PA6/Lotader 80/20 w/w demonstrate an almost indistinguishable dispersed phase with droplet dimensions of 0.1–0.2 μm (Fig. 1(b)). It should be noted that a blend between PA6 and LDPE with similar composition 80/20 w/w demonstrates dispersed LDPE droplets with much larger sizes of about 4 μm [12]. The strong reduction of the size of the dispersed particles in PA6/functionalized polyethylene blends could be attributed to the interaction between the functional groups of polyethylenes and the reactive groups of polyamide chain, giving rise to the formation of a copolymer which can act as a compatibilizer for the blend, thus decreasing the interfacial tension and enhancing the phase dispersion [12].

In order to reveal the compatibilization efficiency of both types of functionalized polyethylenes towards LDPE and PA6 matrix phases, respectively, investigations on the crystallization behavior, crystal structure, morphology and microhardness of the blends have been carried out.

3.1. Isothermal crystallization behavior

The isothermal crystallization parameters are collected in Table 1. As shown the enthalpy of the isothermal crystallization decreases with increasing T_c in the investigated range for neat Escor and Lotader as well as for LDPE/compatibilizer blends. Similar behavior was observed for other branched polyethylenes [17,18] and was interpreted by the rejection of the polyethylene macromolecules of lower structural order into the amorphous zones between the crystalline lamellae. The higher the T_c, the larger is the fraction of the polymer segregated during crystallization. The enthalpy of the isothermal crystallization of neat PA6 and PA6 component of the blends almost does not depend on T_c. Moreover, the normalized enthalpy of isothermal crystallization of PA6 in the presence of a compatibilizer at each T_c is slightly lower than that of the neat PA6.

The dependence of the half-crystallization times $t_{0.5}$ on T_c of the samples are shown in Fig. 2(a) for LDPE/compatibilizer blends and in Fig. 2(b) for PA6/compatibilizer blends. It is apparent that the addition of a compatibilizer into LDPE increases slightly the half-crystallization times in LDPE. It could be interpreted by the disturbance of the LDPE crystallization in the presence of the functionalized polyethylenes, due to the creation of polar interactions such as hydrogen bonds between both

Table 1
Isothermal crystallization parameters for LDPE, PA6, Escor, Lotader and their blends

Sample	T_c (°C)	$t_{0.5}$ (s)	n	K_n (s^{-n})	$\Delta(_{cr}$ (J/g)[a]	T_m (°C
LDPE	105	562	2.2	6.2×10^{-7}	28.6	112.7
	104	365	2.1	2.9×10^{-6}	41.3	112.4
	103	205	2.0	1.6×10^{-5}	56.2	112.6
	102	121	2.0	4.7×10^{-5}	57.5	112.3
LDPE/Escor (LDPE phase)	105	590	2.3	2.9×10^{-7}	13.6	112.6
	104	380	2.3	8.0×10^{-7}	40.0	112.7
	103	187	2.0	2.0×10^{-5}	63.4	112.4
	102	100	2	6.9×10^{-5}	67.5	112
LDPE/Lotader (LDPE phase)	104	501	2.1	1.5×10^{-6}	29.6	112.4
	103	288	2.2	2.7×10^{-6}	55.2	112.3
	102	173	2.0	2.3×10^{-5}	64.4	112.2
	101	120	2.0	4.8×10^{-5}	63.2	111.8
Escor	94	422	2.5	1.9×10^{-7}	46.5	105.9
	93	187	2.2	6.9×10^{-6}	56.9	104.8
	92	133	2.2	1.4×10^{-5}	56.3	104.2
	91	95	2.1	4.8×10^{-5}	57.4	103.7
	90	68	2.1	9.8×10^{-5}	57.4	103.4
Lotader	96	169	2.1	1.4×10^{-5}	52.9	–
	95	110	2.1	3.6×10^{-5}	64.6	109.1
	94	56	2.1	1.5×10^{-4}	63.2	108.8
	93	46	2.0	3.3×10^{-4}	61.7	107.4
	92	35	2.0	5.6×10^{-4}	70.4	106.6
PA6	199	148	2.3	7.1×10^{-6}	51.5	218.7
	198	117	2.3	1.2×10^{-5}	50.6	218.2
	197	95	2.2	3.1×10^{-5}	50.3	217.7
	196	70	2.2	6.0×10^{-5}	49.9	217.5
	195	50	2.3	8.5×10^{-5}	51.4	217.7
PA6/Escor (PA6 phase)	199	174	2.5	1.7×10^{-6}	51.5	217.3
	198	132	2.5	3.5×10^{-6}	50.3	217.0
	197	100	2.4	1.1×10^{-5}	48.9	216.5
	196	78	2.3	3.1×10^{-5}	47.4	216.3
	195	59	2.3	5.8×10^{-5}	47.3	216.2
PA6/Escor (Escor phase)	80	104	–	–	12.4	102.1
	79	101	–	–	12.1	101.9
	78	91	–	–	2.9	101.7
PA6/Lotader (PA6 phase)	199	284	2.0	8.6×10^{-6}	50.3	222.1
	198	209	2.3	3.2×10^{-6}	49.5	221.9
	197	148	2.3	7.1×10^{-6}	47.7	221.5
	196	109	2.1	3.6×10^{-5}	50.5	221.1
	195	84	2.1	6.3×10^{-5}	51.0	220.9
PA6/Lotader (Lotader phase)	80	111	–	–	14.2	105.4
	79	110	–	–	14.7	104.5
	78	109	–	–	13.1	104.4

[a] The enthalpy has been normalized to the content of the corresponding crystallizing component of the blend.

components [8,9]. Evidently, the compatibilization efficiency of both Escor and Lotader towards LDPE leads to the reduction of LDPE overall crystallization rate. Concerning the PA6/compatibilizer blends it could be observed that the PA6 overall crystallization rate decreases in the presence of both Escor and Lotader (Fig. 2(b)). It should be also noted that the reduction of the PA6 crystallization rate in the presence of Lotader is slightly higher than that in the presence of Escor. This reduction is due to the compatibilization of PA6 phase through the formation of a PA6-compatibilizer copolymer by a chemical reaction between compatibilizer carboxyl groups and PA6 reactive end groups [8,9,12].

The minor phase (Escor or Lotader) in PA6/compatibilizer blends crystallizes isothermally at a very large supercooling (Table 1, Fig. 2(b)). This is due to the very fine dispersion of the functionalized polyolefins in the PA6 matrix, caused by the formation of a copolymer between PA6 and the compatibilizers. This result is explained in the terms of a fractionated crystallization process [19]. If the number density of the dispersed polymer particles in the blend is larger than the number of heterogeneities which usually induce nucleation in this component, the crystallization of the dispersed phase may take place in several steps at higher undercoolings (at which other types of heterogeneities are activated) and eventually,

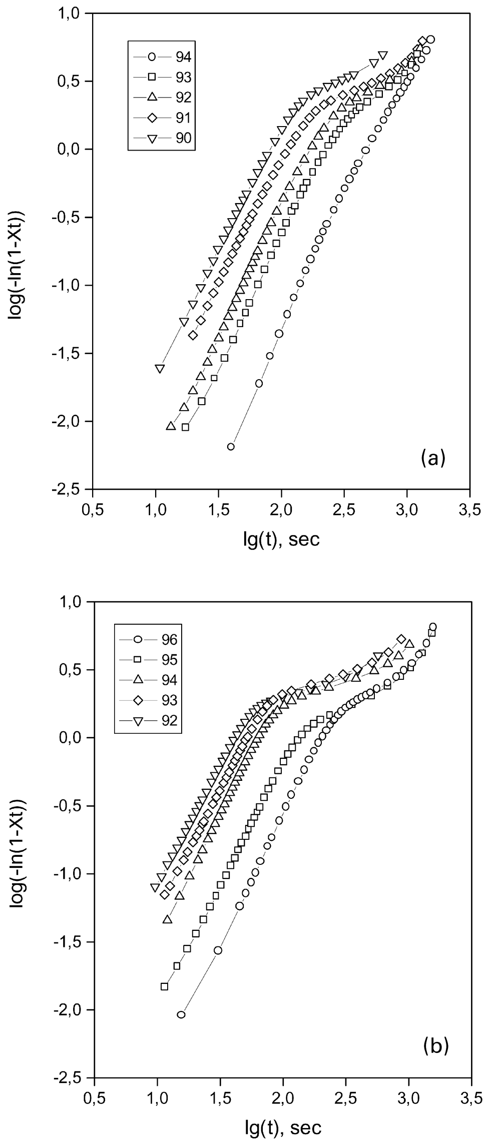

Fig. 3. Dependence of $\log(-\ln(1-X_t))$ on $\log t$ for Escor (a) and for Lotader (b).

homogeneous nucleation may take place [20]. It should be noted also that the extent of crystallization of the dispersed phase of functionalized polyolefins is definitely low (Table 1). Moreover, the experiments of isothermal crystallization of the minor phase in LDPE/compatibilizer blends fail to succeed. This confirms the strong disturbance in the compatibilizer crystallization in PA6/compatibilizer blends and in LDPE/compatibilizer blends.

The crystallization kinetics of Escor, Lotader, LDPE, PA6 and PE and PA component in the blends at each T_c have been analyzed by means of an Avrami-type equation

$$X_t = 1 - \exp(-K_n t^n),$$

where X_t is the fraction crystallized at time t, K_n the kinetic constant and n the Avrami exponent, depending on the nucleation type and the growth geometry of the crystals. It should be noted that the shape and the low enthalpy of the

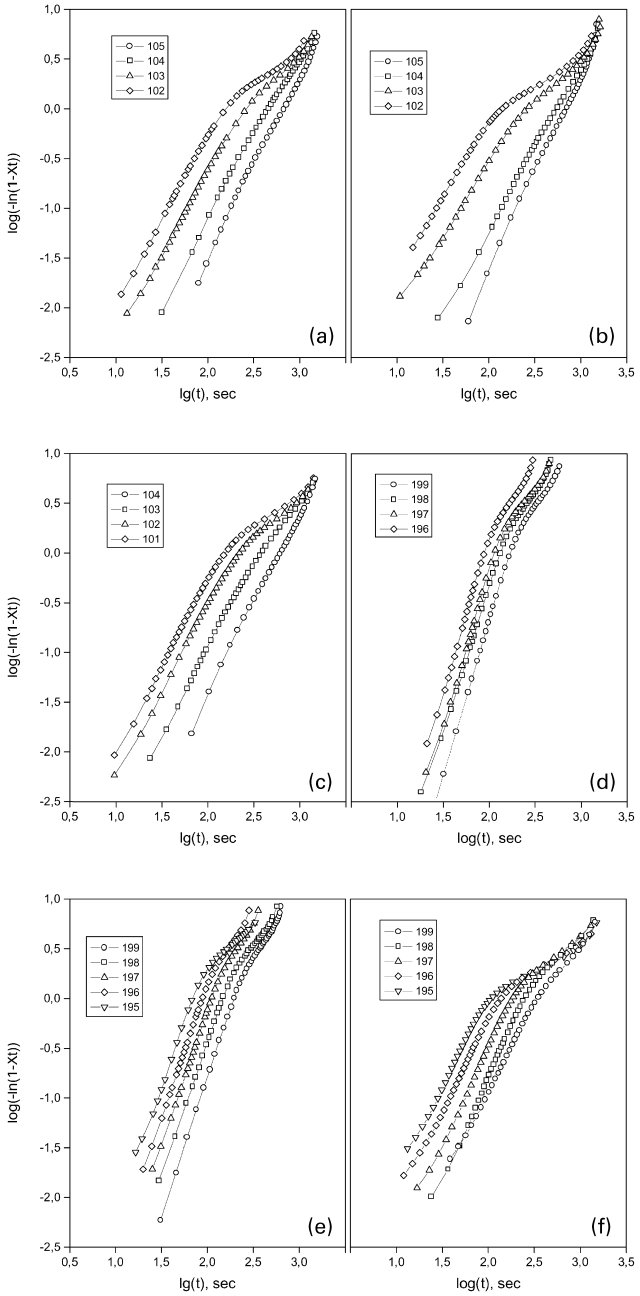

Fig. 4. Dependence of $\log(-\ln(1-X_t))$ on $\log t$ for LDPE (a), LDPE/Escor 80/20 w/w blend (b), LDPE/Lotader 80/20 w/w blend (c), PA6 (d), PA6/Escor 80/20 w/w blend (e), PA6/Lotader 80/20 w/w blend (f).

Escor/Lotader crystallization peaks in the PA6/compatibilizers blends do not allow precise determination of the isothermal parameters.

Values of K_n and n can be obtained from the intercepts and slopes, respectively, of the linear plots of $\log(-\ln(1-X_t))$ versus $\log t$. Examples of these plots are shown in Fig. 3 for Escor and Lotader isothermally crystallized at $T_c = 90$–96 °C and in Fig. 4 for LDPE, PA6 and their blends with compatibilizers. The Avrami exponents n are in the range 2.0–2.5 (Table 1), indicating athermal nucleation and mixed two-dimensional/three-dimensional growth. The results

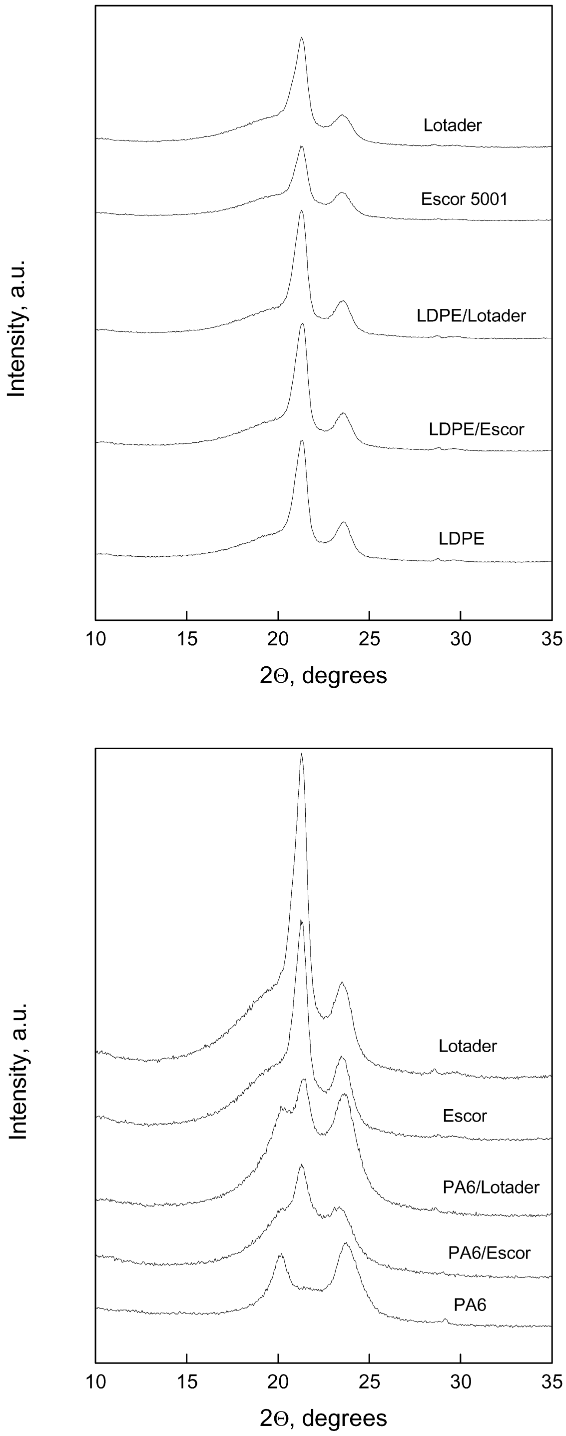

Fig. 5. X-ray diffraction patterns of Escor 5001, Lotader, LDPE, PA6 and their blends.

show that the addition of Escor or Lotader to LDPE or PA6 does not change the crystallization mechanism of the corresponding matrix phases. The values of the kinetic constant K_n for the LDPE and PA6 phases in the blends are lower than those established for neat LDPE and PA6. The values of K_n and $t_{0.5}$ show that the overall isothermal crystallization rate of either LDPE or PA6 decreases in the presence of compatibilizers. The overall crystallization rate may vary due to a change either in the crystal growth rate or in the nucleation rate. The compatibilization mechanism of Escor and Lotader includes physical interactions with LDPE phase and a formation of copolymers between PA6 and the functionalized polyolefins. The decrease of the crystal growth rate of the copolymers in comparison to the corresponding homopolymer is a common finding explained by the lower mobility of the crystallizable segments of the copolymers [21]. Hence, it could be assumed that the overall LDPE and PA6 crystallization rate in the blends decreases due to the unchanged or increased nucleation rate and due to the decreased crystal growth rate.

The melting temperatures of the isothermally crystallized phases are shown in Table 1. The T_m values for the neat PA6 and PA6/Escor blend are slightly lower than those for PA6/Lotader blend (Table 1). It could be assumed that crystals in α form and γ form coexist in the samples, but in PA6/Lotader blend crystals in α form predominate slightly ($T_m^\alpha = 223$ °C, $T_m^\gamma = 215$ °C) [22]. It is worth noting that the measured T_m values of Escor/Lotader phases in the PA6/compatibilizer blends are lower than those of the corresponding neat functionalized polyethylenes (Table 1). That means that the fine dispersed compatibilizer particles in PA6/compatibilizer blends crystallizing at large supercooling with low rate exhibit low degree of crystallinity and perfectness.

3.2. Crystalline structure

The X-ray diffraction patterns of melt crystallized samples are shown in Fig. 5 for LDPE, PA6, Escor, Lotader and their blends. The fitted profiles of PA6 and PA6/Lotader 80/20 w/w patterns are shown in Fig. 6 as an example. The fitted peaks' positions are collected in Table 2. It could be observed (Table 2) that the peaks positions almost do not change for the blends LDPE/Escor 80/20 w/w and LDPE/Lotader 80/20 w/w. However, SEM observation of the fracture surface of these blends shows that LDPE and both functionalized polyethylenes are not miscible. Thus, the X-ray patterns of the LDPE/compatibilizer blends could not be interpreted by a co-crystallization of both components. The diffraction patterns of the blends PA6/Escor and PA6/Lotader are characterized by the reflections of both components. It is worth noting that the γ crystalline reflection is not taken into consideration because as it has been shown [19], the weight content of PA6 γ crystals increases only when PA6 is the minor component in PA6/functionalized polyolefin blends. No significant variations of the peak positions are found for PA6 component in the blends; analogously the position of the (110) reflection for Escor/Lotader component do not vary. Such results indicate that there are no interactions in the crystal phase or co-crystallization between the components.

In Table 2 the calculated crystallite sizes determined by the half-widths of the decomposed peaks of PE and PA6 are

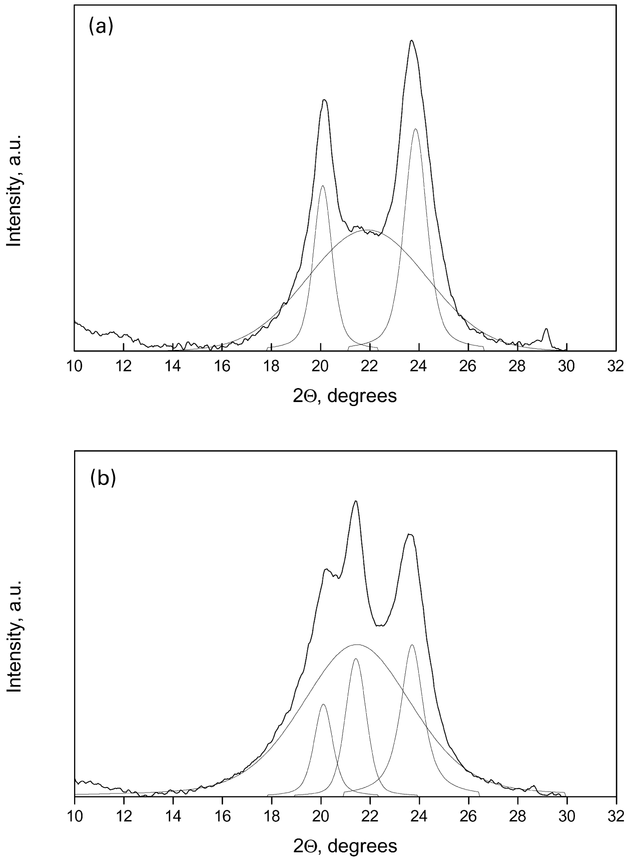

Fig. 6. Fitted profiles of PA6 X-ray pattern (a) and of PA6/Lotader 80/20 w/w X-ray pattern (b).

listed. As seen these dimensions almost do not change in LDPE/compatibilizer blends in comparison to the neat polymers. On the contrary, the crystallite dimensions of either PA6 or functionalized polyethylenes in the PA6/compatibilizer blends are smaller than those in the corresponding neat samples. These results could be interpreted by a disturbance of the crystallization of PA6 in the presence of the compatibilizer; the crystallization of functionalized polyethylenes is also strongly disturbed. The results are in agreement with the isothermal crystallization behavior of these blends.

In order to gain insight into the nature of the blend crystalline structure, we have tried to determine LDPE, PA6 and compatibilizer degree of crystallinity as the ratio of the main peaks areas A_c of the corresponding component and the sum of these areas and the amorphous area of the diffractogram A_a, namely $(A_c/(A_c + A_a))$, as it is done in Refs. [23,24]. The amorphous area on each blend diffractogram has been drawn in one and the same angle interval using one and the same curve profile (as it was done for the corresponding neat matrix component), in order to minimize the errors normally appearing for such complicated systems. It should be noted that practically the amorphous area of the compatibilizer component is included in the amorphous area of the blends. Table 2 presents the crystallinity degree of the samples thus determined.

Noteworthy Escor and Lotader have slightly lower degree of crystallinity than neat LDPE. The degree of crystallinity of LDPE almost does not change with the addition of the compatibilizer. On the contrary, the degree of crystallinity of PA6 component in the blends is strongly reduced in comparison to that of the neat PA6. Similar behavior presents the value of the degree of crystallinity of Escor/Lotader in the blends. Evidently, the compatibilization increases the amorphous halo, indicating a good dispersability of the components in the amorphous phase [25].

3.3. Morphology

The isothermal crystallization of molten films of LDPE ($T_c = 105$ °C), LDPE/compatibilizer blends ($T_c = 105$ °C), PA6 ($T_c = 198$ °C), PA6/compatibilizer blends ($T_c = 198$ °C) leads to spherulite structure (Fig. 7). The morphology of isothermally crystallized Escor and Lotader has not been studied yet according to our knowledge. Both functionalized polyethylenes crystallize also into spherulites ($T_c = 95$ °C) with well defined boundaries (Fig. 7). The average dimensions of the spherulites have been determined from the H_ν patterns by means of the equation

$$R_{\mathrm{sph}} = c\lambda/(n\pi \sin Q_{\mathrm{m}}),$$

where R_{sph} is the spherulite radius, c a constant ($c = 2.05$ for spheres), λ/n the wavelength of the light in a medium of

Table 2
Peaks' positions, crystallite size (L), and the degree of crystallinity ($A_c/A_c + A_a$) of the samples

Sample	α_1 (PA) (°)	110(PE) (°)	200(PE) (°)	α_2 (PA) (°)	$L_{\alpha 1}$ (Å)	L_{110} (Å)	L_{200} (Å)	$L_{\alpha 2}$ (Å)	$A_c/A_c + A_a$
LDPE	–	21.29	23.58	–	–	202	180	–	0.40
PA6	20.09	–	–	23.73	231	–	–	180	0.41
Escor	–	21.29	23.43	–	–	202	163	–	0.34
Lotader	–	21.29	23.48	–	–	202	163	–	0.36
LDPE/Esc 80/20	–	21.33	23.58	–	–	202	180	–	0.43
LDPE/Lot 80/20	–	21.35	23.53	–	–	202	180	–	0.41
PA6/Esc 80/20	20.14	21.29	–	23.33	162	180	–	90	0.23 (0.21)[a]
PA6/Lot 80/20	20.14	21.44	–	23.63	202	180	–	148	0.26 (0.15)[a]

[a] The values in the brackets represent the degrees of crystallinity of the compatibilizer.

refractive index n, Q_m the angle of the incident and scattered beams corresponding to the maximum intensity.

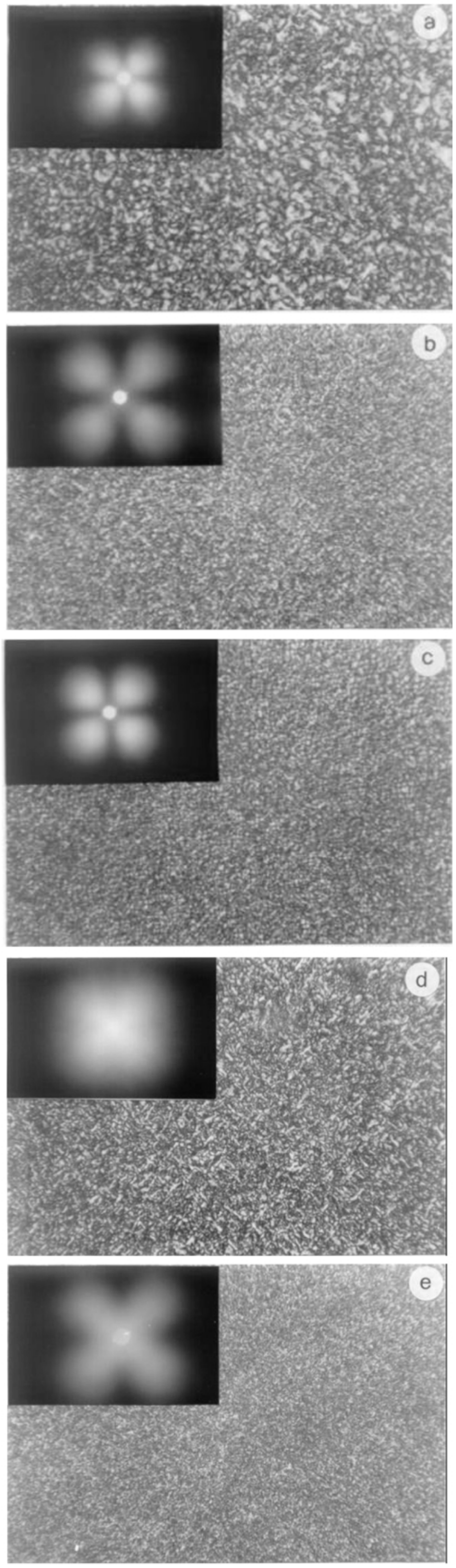

Fig. 7. Optical micrographs of isothermally crystallized LDPE (a), LDPE/Escor 80/20 w/w blend (b), Lotader (c), PA6 (d) and PA6/Escor 80/20 w/w blend (e). The corresponding H_ν patterns are also presented.

The average radius of the LDPE spherulites decreases from ca. 8 to 4 μm when the compatibilizer is added into the matrix polymer. A strong decrease of the dimensions of PA6 spherulites in the presence of compatibilizer could be clearly observed (from ca. 7 μm of neat PA6 to ca. 3 μm of PA6/Escor blend and to ca. 4 μm for PA6/Lotader blend). It is well known that the spherulite size is predominately determined by the nuclei density when athermal nucleation occurs. The smaller LDPE and PA6 spherulite dimensions in the presence of the compatibilizers could be interpreted by the reduced overall crystallization rate, which in turn is due to the increased nucleation rate and decreased crystal growth rate.

3.4. Microhardness

The experimental hardness values of LDPE based blends are shown in Fig. 8(a), while those of PA6 based blends are shown in Fig. 8(b). The dashed lines represent the corresponding additive values. As observed the experimental hardness values of LDPE/compatibilizer blends coincide with the corresponding additive values (Fig. 8(a)), while the experimental values of PA6/compatibilizer blends are lower than the additive values (Fig. 8(b)). It should be also noted that the microhardness of PA6/Escor blend is lower than that of PA6/Lotader blend.

As shown [26,27] the microhardness of LDPE phase depends on the degree of crystallinity α according to the equation

$$H^{\mathrm{PE}} = \alpha^{\mathrm{PE}} H_{\mathrm{c}}^{\mathrm{PE}},$$

where $H_{\mathrm{c}}^{\mathrm{PE}}$ is the hardness value for the crystalline phase. The hardness of the amorphous phase could be neglected because the glass transition temperature of PE is much below 0 °C. The functionalized polyethylenes Escor and Lotader should have similar behavior. The X-ray measurements have demonstrated that the degree of crystallinity of LDPE/compatibilizer 80/20 w/w blends almost does not change. Thus, the fact that the experimental hardness values of the LDPE/compatibilizer blends are almost equal to the corresponding additive values could be interpreted by the unchanged degree of crystallinity of the samples.

However, the hardness of the amorphous phase of PA6 ($H_{\mathrm{a}}^{\mathrm{PA6}}$) should be taken into account for the PA6/compatibilizer blends ($H^{\mathrm{PA6}} = \alpha^{\mathrm{PA6}} H_{\mathrm{c}}^{\mathrm{PA6}} + (1 - \alpha^{\mathrm{PA6}}) H_{\mathrm{a}}^{\mathrm{PA6}}$). This is due to the fact that the measurements of microhardness are performed at room temperature, i.e. below the glass transition temperature of PA6 (50 °C). Thus the expression for the total microhardness of the PA6/compatibilizer materials is obtained:

$$H = 0.8\alpha^{\mathrm{PA6}} H_{\mathrm{c}}^{\mathrm{PA6}} + 0.8.(1 - \alpha^{\mathrm{PA6}}) H_{\mathrm{a}}^{\mathrm{PA6}} + 0.2\alpha^{\mathrm{comp}} H_{\mathrm{c}}^{\mathrm{comp}}.$$

The X-ray measurements showed that the degree of

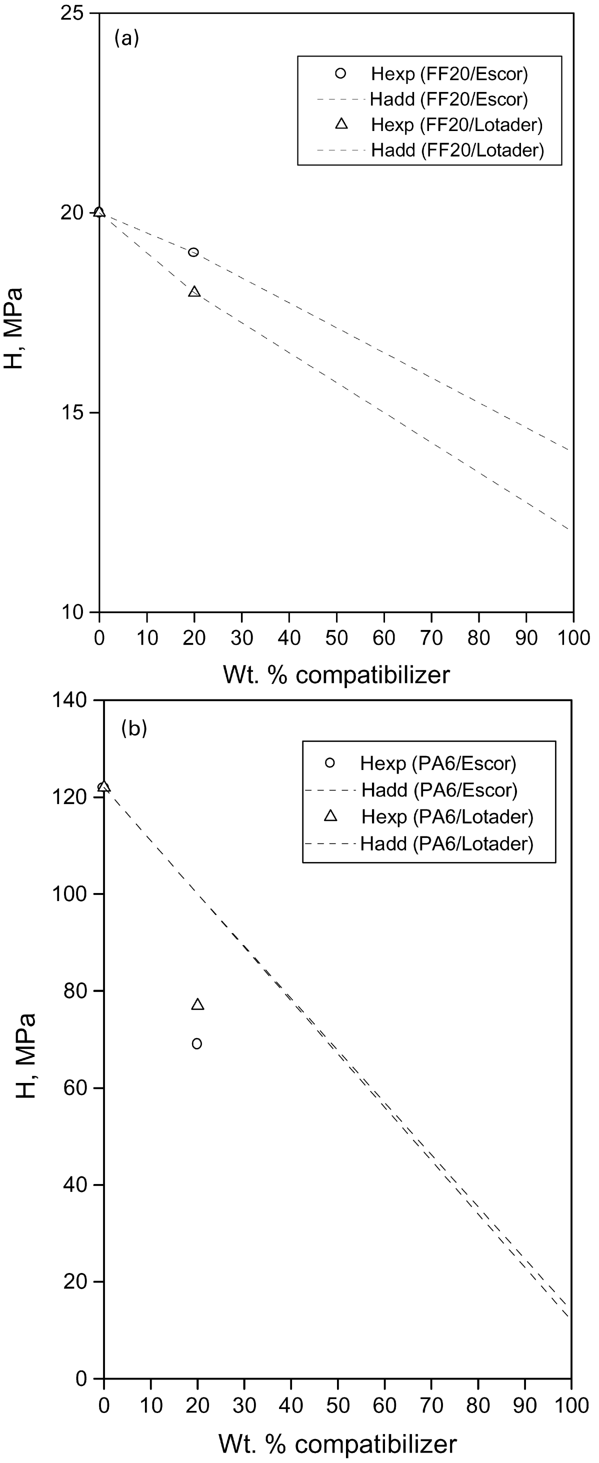

Fig. 8. Dependence of microhardness values on wt% compatibilizer for LDPE/compatibilizer blends (a) and for PA6/compatibilizer blends (b). Dashed lines represent the corresponding additive values.

crystallinity of PA6 component in the blends is strongly reduced in comparison to that of neat PA6; similar behavior presents the value of the degree of crystallinity of Escor/Lotader in the blends. Hence, assuming that H_c^{PA6}, H_a^{PA6} and H_c^{comp} do not change, the microhardness values of the blends lower than the additive ones are due to the decreased degree of crystallinity of the blend components.

4. Conclusion

The detailed characterization of blends of LDPE and PA6 with both types of functionalized polyethylene (Escor and Lotader) in a 80/20 w/w composition reveals the peculiarities in the new characteristics of the blends investigated. The dimensions of the dispersed droplets of the functionalized polyethylenes in the blends are rather small. Moreover, the size of the droplets in PA6/compatibilizer blends is smaller than that of the droplets in LDPE/compatibilizer blends. The isothermal crystallization rate of both LDPE and PA6 decreases in the presence of the two types of compatibilizers, while the crystallization mechanism does not change. The fine dispersed compatibilizer particles in PA6/compatibilizer blends crystallize at large supercooling exhibiting low degree of crystallinity and perfectness. PA6 or LDPE in the presence of the compatibilizer crystallize into spherulites with dimensions smaller than those of the corresponding neat polymers. The X-ray measurements demonstrate that there are no interactions in the crystal phase or no co-crystallization occurs between the components in the PA6/compatibilizer blends. However, while the crystallite dimensions and degree of crystallinity do not change in LDPE/compatibilizer blends, there are strong reductions in the degree of crystallinity and the crystallite dimensions of the components in the PA6/compatibilizer blends in comparison to those of the neat polymers. The lowered degree of crystallinity of the blend components in the PA6/compatibilizer blends leads to microhardness values of the blends lower than the corresponding additive values. On the other hand, the microhardness of LDPE/compatibilizer blends corresponds to the additive values.

The results could be interpreted by different types of interactions occurring between the functionalized polyethylenes and LDPE or PA6, correspondingly. The functionalized polyethylenes Escor/Lotader interact with the polar groups of polyamide chain giving rise to the formation of a copolymer, which can act as a compatibilizer for the matrix PA6 phase. On the contrary, only physical interactions proceed between LDPE and the compatibilizers. The type of the interaction between the components (chemical or physical) influences the crystallization behavior, crystal structure, morphology and microhardness of the blend components. The results obtained from X-ray studies, optical microscopy observations and microhardness measurements indicate that the compatibilization efficiency of Escor towards PA6 is higher than that of Lotader.

Acknowledgements

This work was financed by Bulgarian Science Research

Foundation (Contract X-1104) and was carried out within a Joint Research Project between CNR Italy and the Bulgarian Academy of Sciences.

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