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The effect of compatibilization in the reactive processing of the low density polyethylene/polyamide 6/EPDM blends ^{**)}

Summary — The compatibilizing effect of functionalized low density polyethylene (PE-LD) on PE-LD/polyamide 6 (PA6)/ethylene-propylene-diene terpolymer (EPDM) ternary blends has been studied. Compatibility was evaluated by means of differential scanning calorimetry, which was used also for studying the melting and crystallization phenomena. Torque-time measurements were performed in order to determine the processing behavior. The functionalized PE-LD modify the processing behavior, the crystallinity degree of PE-LD and PA6 and impact properties of the studied blends. These effects result from chemical reactions between functional groups of compatibilizing agents and the end groups of polyamide.

Key words: low density polyethylene, polyamide 6, functionalized PE-LD, miscibility, compatibilization, processing behavior, crystallinity degree, impact strength.

WPLYW KOMPATYBILIZACJI NA REAKTYWNE PRZETWÓRSTWO MIESZANIN POLIETYLEN MAŁEJ GĘSTOŚCI/POLIAMID 6/EPDM

Streszczenie — Zbadano kompatybilizujący wpływ polietylenu małej gęstości funkcjonalizowanego kwasem akrylowym (PE-LD/AA), bezwodnikiem maleinowym (PE-LD/MA) bądź bismaleinoimidem (PE-LD/BMI) na różniące się składem trójskładnikowe mieszaniny PE-LD/poliamid 6 (PA6)/terpolimer etylen-propylen-dien (EPDM) (tabela 1). Mieszalność oceniano za pomocą skaningowej kalorymetrii różnicowej, którą stosowano też do badania zjawisk topnienia i krystalizacji (rys. 1 i 2). W celu scharakteryzowania właściwości przetwórczych mierzono momenty obrotowe badanych układów w funkcji czasu oraz wartości jednostkowej energii mieszania po 1 minucie (tabela 1). Funkcjonalizowany PE-LD modyfikuje właściwości przetwórcze, stopień krystaliczności PE-LD i PA6 (rys. 3) oraz udarność mieszanin (rys. 4). Wpływ ten przypisano reakcjom chemicznym między grupami funkcyjnymi kompatybilizatorów oraz grupami końcowymi PA6. Określono wpływ składu na zbadane właściwości mieszanin.

Słowa kluczowe: polietylen małej gęstości, poliamid 6, funkcjonalizowany PE-LD, mieszalność, kompatybilizacja, przetwarzalność, stopień krystaliczności, udarność.

Plastics are present in almost every sector of our life, however after end of their life plastics constitute also a source of a substantial amount of waste that contaminate the environment. Therefore recovery and recycling of plastic materials are important issues in solving the environmental problems. Total amount of plastic waste generated in Western Europe in 2003 was 21 Mt, of which 39 % was recovered. Mechanical recycling of post-consumer plastics is a preferred recovery route, which recently is growing at more than 10 % per annum, with a total of 3.2 Mt in 2003.

Mechanical recycling of engineering plastics has also attracted attention of many researchers and significant achievements have resulted from this. The major concern is normally focused on the mechanical properties. In order to keep the mechanical strength at high level one has to implement blending of different components and provide high interfacial adhesion either by the physical or chemical compatibilization.

Reactive processing belongs to the methods being used to create multicomponent materials of superior properties, but recently also for the recovery of polymer waste by mechanical recycling [1–4]. In order to find optimal mixing parameters and suitable compatibilization methods for reprocessing of mixed plastic waste being composed of typical components a detailed study of virgin polymer blends is necessary. Polyolefins and polyamides are frequently found in plastic waste because of their numerous applications. Although their binary mixtures are incompatible, multicomponent blends exhibiting high mechanical properties can be obtained by finding proper methods of compatibilization.

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In our previous studies concerning reprocessing of mixed polymer waste containing among others iPP, PA6 and EPDM, it has been concluded that addition of reactive compatibilizing agents, such as iPP functionalized with different polar monomers, resulted in a good adhesion at the interface [5, 6].

This paper deals with a study on the effect of introducing small amounts of functionalized PE-LD on the processing characteristics and on selected thermal and impact properties of PE-LD/PA6/EPDM blends.

EXPERIMENTAL

Materials

The main characteristics of the polymers used for blending were as follows:

— Low density polyethylene (PE-LD) Malen-E FABS type (producer Basel Orlen Polyolefins SA, Poland): melt temperature 110 °C, melt flow rate 1.6–2.5 g/10 min, volatiles ~0.3 wt. %, density 0.919–0.923 g/cm³, Vicat softening temperature min. 90 °C, $M_n = 10,580$, $M_w = 66,000$.

— Polyamide 6 (PA6) — Stilamid S type (producer Stilon SA, Poland): melt temperature 225 °C, decomposition temperature range 297–492 °C, tensile stress at yield of 78 ± 4 MPa, tensile modulus E equal 2400 ± 100 MPa, free amine groups content 45–47 mval/kg, density 1.14 g/cm³.

— Ethylene/propylene/1,4 hexadiene terpolymer (EPDM) Buna EP 5450G type (producer Bayer AG): decomposition temperature range 223–487 °C, Mooney viscosity 46 ± 5 (MS 1+4 at 121 °C), density 0.86 g/cm³.

PE-LD functionalization

Melt functionalization was performed in a laboratory installation, according to the procedure previously described [7]. Low density polyethylene was functionalized with either acrylic acid (PE-LD/AA), maleic anhydride (PE-LD/MA) or bismaleimide (PE-LD/BMI). The results of FT-IR spectroscopy, elemental analysis and thermal methods proved the presence of the functional groups in polyethylene chains. The comonomer content was determined by the titration method. In respective samples it accounted to $1.05 \cdot 10^{-4}$ mole of grafted acrylic acid/100 g sample, $2.3 \cdot 10^{-4}$ mole of maleic anhydride/100 g sample or $0.7 \cdot 10^{-4}$ mole of grafted bismaleimide/100 g sample. The melting temperature was equal 117 °C for PE-LD/MA and PE-LD/AA, and 114 °C for PE-LD/BMI. Melting temperature measured for not functionalized PE-LD was lower (110 °C).

Blends and samples preparation

The blends were prepared using HAAKE RHEOCORD 9000 mixer at following conditions: mixing tem-

perature of 220 °C, rotor speed equal to 60 rpm, mixing time 10 min. The symbols of the blends (see the first column of Table 1) indicate the composition ratio of PE-LD, PA6, EPDM and the compatibilizing agents (*i.e.* functionalized PE-LD). The content of functionalized PE-LD in the ternary blends PE-LD/PA6/EPDM was 3 and 5 wt. % in respect with initial amount of PE-LD used in the blends. All components were dried before mixing in a vacuum oven at temperature of 80 °C for 24 hours.

After mixing the material was placed in a 4 mm thick steel frame between two Teflon sheets. The whole system was inserted between plates of a hydraulic press heated to 220 °C and kept without external pressure for 6 min, allowing a complete pre-melting. After this period, a pressure of 255 kPa was applied for 5 min. The specimens for impact tests have been cut from the press molded plates.

Investigation methods

The properties of PE-LD/PA6/EPDM blends were characterized with respect to the processing behavior, differential scanning calorimetry (DSC) and impact properties.

Processing

Processing behavior was evaluated from the torque-time curves recorded during previously described blend preparation. The following characteristics were evaluated: torque at 1 min mixing time ($TQ_{1 \text{ min}}$) and at the end of mixing (TQ_{fin}) as well as the specific energy after one minute of mixing (E_{mix} — energy required to process a unit mass of material) [8]. At a constant speed of mixing, variation in torque among samples at the same temperature is indicative of viscosity differences, the viscosity being directly proportional to the ratio of the torque and rotor speed.

Differential Scanning Calorimetry

DSC measurements were carried out using a Mettler DSC 12E instrument. All samples were heated from 50 to 250 °C at a heating rate of 10 °C/min and kept at 250 °C for 1 min in order to destroy any trace of crystallinity (run I). Afterwards the samples were cooled to 50 °C at a cooling rate of 5 °C/min. The second heating was performed with a heating rate 10 °C/min (run II). The mass of the samples was between 6 and 10 mg. The crystallinity degree has been evaluated using as reference the enthalpy of 100 % crystalline polymer found in literature: $\Delta H_m = 289$ J/g (for PE-LD) and $\Delta H_m = 190$ J/g for PA6 (the last value being the average of some controversial values) [9]. Calibration was made with Indium ($T_m = 156.6$ °C, $\Delta H_m = 28.43$ J/g).

Impact tests

Charpy impact was measured using a CEAST Resil 5.5 tester. The energy of breaking for notched samples

was 0.5 J for binary PE-LD/PA6 blends and 4 J for ternary and compatibilized blends. Hammer speed was 2.9 m/s for all measurements.

RESULTS AND DISCUSSION

Processing behavior

The processing behavior of the blends was evaluated from the torque-time curves received while mixing of the blend components.

The processing characteristics depend on blend composition (Table 1). The highest torque and E_{mix} values are observed for the blends with high amounts of polyamide *e.g.* for blends with 60PA6, due to the high melt viscosity of PA6. Increase in the viscosity is more obvious in the presence of the functionalized PE-LD. In the systems containing equal amounts of PE-LD and PA6 (45PE-LD/45PA6/EPDM blends), the highest values of the processing parameters were observed after addition of PE-LD/MA, both 3 and 5 wt. %. This increase can be explained by the reactions appearing in the systems between the functional groups of the compatibilizing agents and the amino or amide groups of PA6.

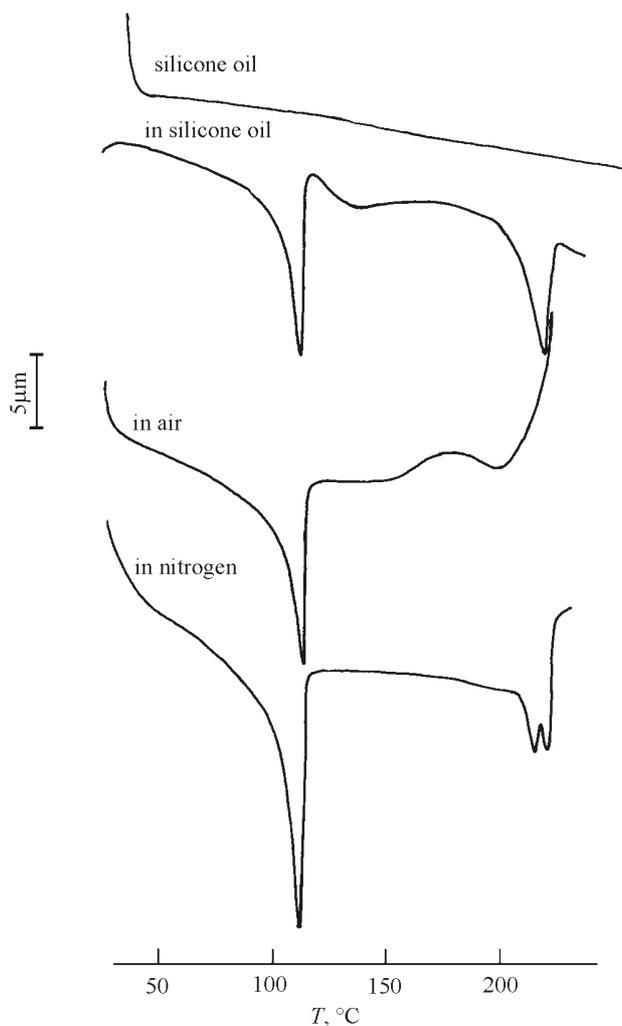


Fig. 1. DSC curves of 45PE-LD/45PA6/10EPDM + 5 wt. % of PE-LD/MA in an oil, air and in nitrogen

Table 1. Processing behavior of binary and ternary blends

Sample ^{a)}	$TQ_{1\ min}^{b)}$, Nm	$TQ_{fin}^{b)}$, Nm	$E_{mix}^{b)}$, kJ/g · 10 ⁻³
33PE-LD/67PA6	13.3	2.3	0.137
30PE-LD/60PA6/10EPDM	14.2	3.5	0.148
30PE-LD/60PA6/10EPDM + 3 % PE-LD/BMI	13.8	3.3	0.144
30PE-LD/60PA6/10EPDM + 3 % PE-LD/MA	13.3	3.1	0.140
30PE-LD/60PA6/10EPDM + 3 % PE-LD/AA	13.8	3.1	0.144
30PE-LD/60PA6/10EPDM + 5 % PE-LD/BMI	15.2	3.3	0.159
30PE-LD/60PA6/10EPDM + 5 % PE-LD/MA	13.6	3.4	0.142
30PE-LD/60PA6/10EPDM + 5 % PE-LD/AA	14.4	3.4	0.150
50PE-LD/50PA6	10.3	2.6	0.112
45PE-LD/45PA6/10EPDM	10.5	4.1	0.114
45PE-LD/45PA6/10EPDM + 3 % PE-LD/BMI	10.7	3.4	0.116
45PE-LD/45PA6/10EPDM + 3 % PE-LD/MA	12.2	4.6	0.133
45PE-LD/45PA6/10EPDM + 3 % PE-LD/AA	11.0	3.3	0.120
45PE-LD/45PA6/10EPDM + 5 % PE-LD/BMI	11.4	3.4	0.124
45PE-LD/45PA6/10EPDM + 5 % PE-LD/MA	12.2	3.8	0.133
45PE-LD/45PA6/10EPDM + 5 % PE-LD/AA	11.8	3.4	0.128
67PE-LD/33PA6	8.2	3.2	0.092
60PE-LD/30PA6/10EPDM	9.4	4.6	0.107
60PE-LD/30PA6/10EPDM + 3 % PE-LD/BMI	10.0	4.4	0.113
60PE-LD/30PA6/10EPDM + 3 % PE-LD/MA	9.6	4.4	0.105
60PE-LD/30PA6/10EPDM + 3 % PE-LD/AA	9.2	3.6	0.104
60PE-LD/30PA6/10EPDM + 5 % PE-LD/BMI	9.4	4.5	0.106
60PE-LD/30PA6/10EPDM + 5 % PE-LD/MA	11.0	5.4	0.124
60PE-LD/30PA6/10EPDM + 5 % PE-LD/AA	9.8	4.6	0.110

^{a)} The symbol of the samples includes weight percentage followed by respective polymer abbreviation.

^{b)} For meanings of $TQ_{1\ min}$, TQ_{fin} and E_{mix} — see text.

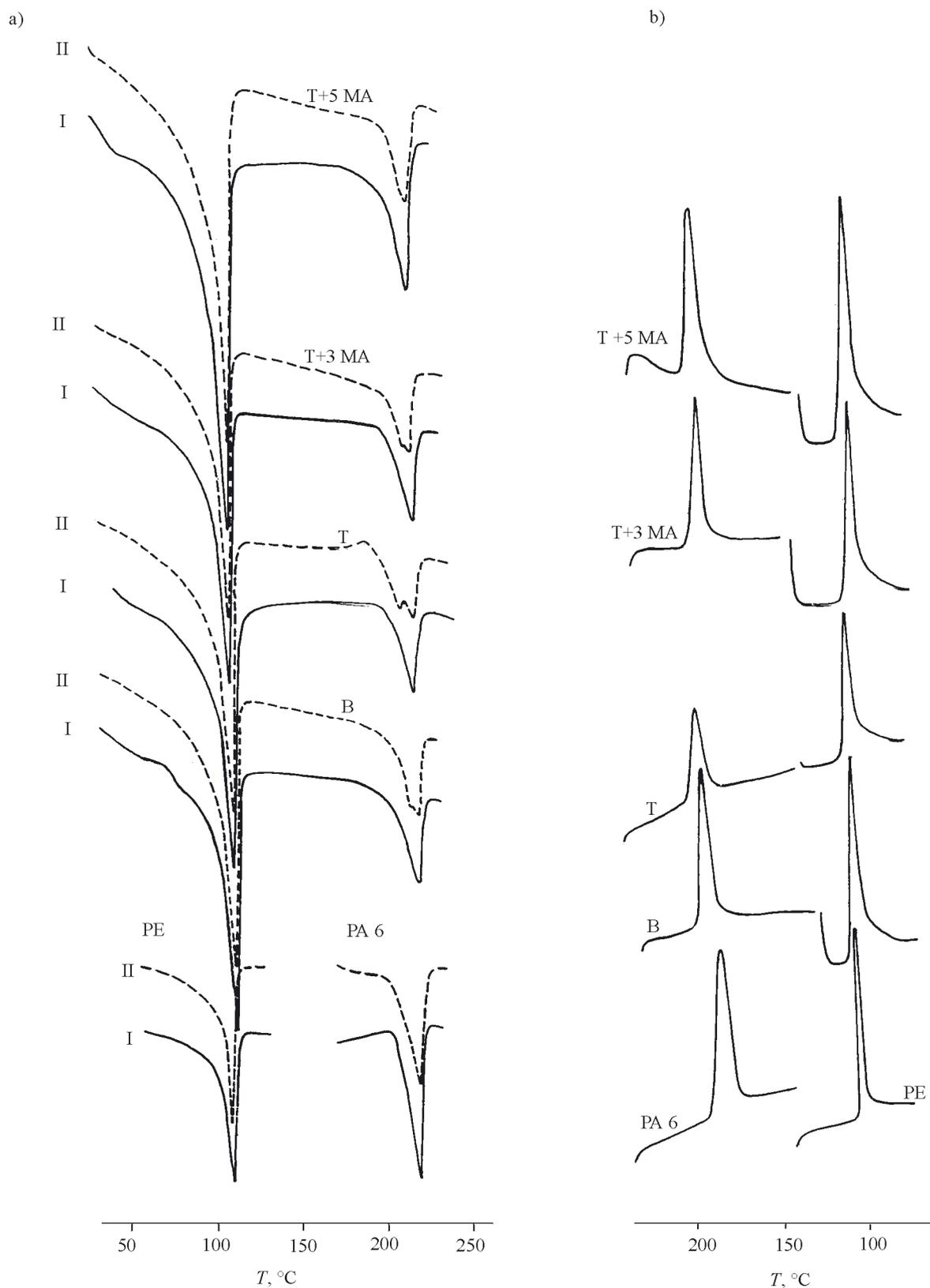


Fig. 2. DSC curves of 60PE-LD/30PA6/10EPDM ternary blends (T) and 60PE-LD/37PA6 binary blend (B): a) melting (I and II run of heating); b) crystallization

Differential Scanning Calorimetry

DSC measurements of the blends, both binary or compatibilized ones with different amounts of functio-

nalized PE-LD, have been performed in order to evaluate the influence of the addition of compatibilizers on the thermal characteristics of the blend components, mainly PE-LD and PA6.

Because the nitrogen flow was not symmetrical in respect with both crucibles, affecting the DSC thermogram's base line, for performing DSC tests we used an alternative way. Without nitrogen, the polyamide will be degraded in the melting process, so, in order to have an inert medium for DSC tests, the samples have been immersed in silicone oil, thermally inert up to at least 270 °C (Fig. 1).

The DSC recordings obtained have been improved by a double effect, firstly by isolation of the sample from an oxidative atmosphere and by better heat transfer between the sample and crucible (silicone oil was used in the amount of 5 mg, the same in both crucibles).

The melting/crystallization temperatures have been evaluated by the values corresponding to the endothermic/exothermic peaks and the melting/crystallization enthalpy has been calculated from the peak surface, using indium as a reference.

Most components of the polymer blends studied in this work exhibit a semi-crystalline feature, that is why a mutual effect of the crystallization behavior between the two main components may exist.

All DSC curves exhibit melting endothermic peaks well separated for main components — around 110 °C for PE-LD and 225 °C in the case of PA6 — and also separated exothermic crystallization peaks. The position of the peaks has not been affected by the blend composition. In the second run of heating, a new type of morphology was obtained due to the programmed cooling of the sample in the first run. In this case, the melting of PA6 is more affected, a double endothermic peak being observed especially for binary and ternary uncompatibilized blends. The shoulder at ~217 °C corresponds to PA crystals formed while cooling from the melt (γ polymorphous form) and the main peak at 220–224 °C is attributed to the melting temperature of α polymorphous form of PA crystals reorganized in the run I of heating. The intensity and position of the shoulder depend on the crystallization conditions of the blends and usually increase with increasing crystallization temperature (in isothermal conditions) or by decreasing crystallization rate [10].

For ternary PE-LD/PA6/EPDM blends there is a shift in the position of the shoulder peak toward lower temperature, with the double polyamide peak being more evidenced. The presence of the functionalized PE-LD does not change the position of the main melting peak of PA6, but slightly depress intensity of the shoulder peak. Broadening of the overall melting PA peak has been observed. The most effective compatibilizer is PE-LD/MA, especially if added to the blend in an amount of 5 wt. %.

These effects are more significant in the blends with a higher proportion of PE-LD, as presented in Fig. 2. In fact, the addition of functionalized PE-LD causes PA crystallization at lower temperature and also reduced enthalpy. The fractionated crystallization involves some

transformation of the usual heterogeneous crystallization mechanism into a homogeneous one, caused by the reduction of the PA particle size.

The cooling scans are presented in Fig. 2b. The crystallization exotherm of the neat PA6 appears at 185 °C and of PE-LD at 98 °C and seems to be independent on both the blend composition and the presence of the functionalized PE-LD. Interactions between the polar groups of compatibilizers and PA component of the blends retard the crystallization rate of the PA6 and decrease also ΔH_c values.

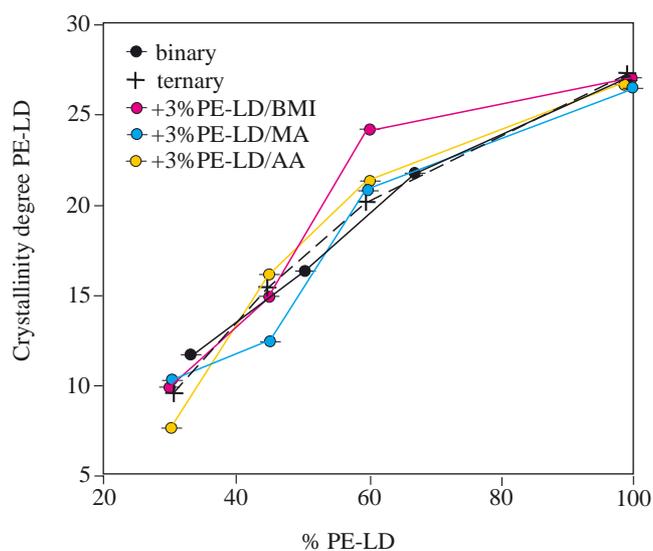


Fig. 3. Crystallinity degree versus PE-LD content in the blends (ternary with 10EPDM)

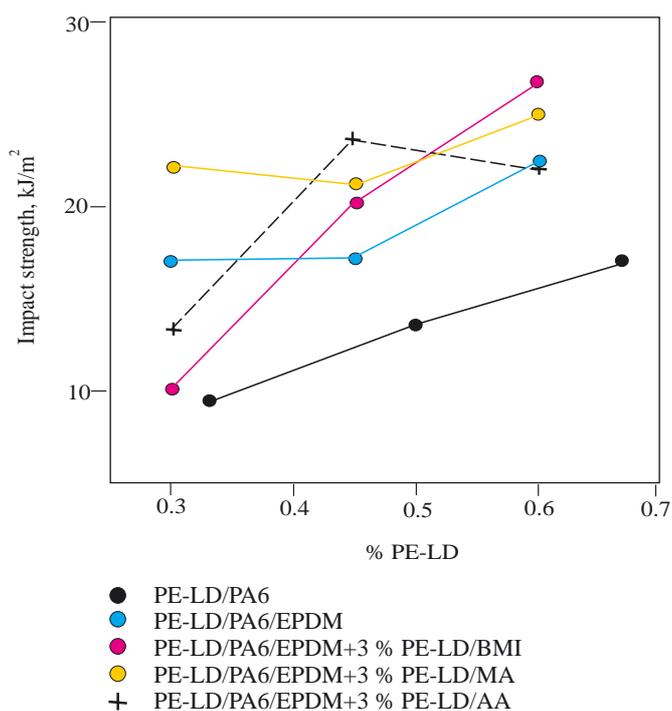


Fig. 4. Impact strength as a function of PE-LD content in the blends (ternary with 10EPDM)

The compatibilizing agents act as nucleation agents for PE-LD — variations in crystallinity degree are more obvious for a higher content of PE-LD, if PA creates a dispersed phase (Fig. 3). The increase in crystallinity is proportional to the improvement of mechanical properties.

Impact properties

Analyzing the impact results, one can observe an influence of the PE-LD/PA6 ratio and the type of the additive used (Fig. 4). The lowest values of impact strength have been observed for binary blends PE-LD/PA6 because of the incompatibility between these components. After EPDM addition impact strength values increased, because of the ability of the impact energy absorption by elastomer particles.

The impact behavior of the blends with functionalized PE-LD is superior in respect with both binary and ternary blends. The most effective compatibilizers are PE-LD/MA and PE-LD/BMI, especially for the blends containing a higher amount of PE-LD.

CONCLUSIONS

— Processing behavior indicated the occurring of the reactions between the blend components (*e.g.* PA6) and polar groups of the functionalized polyolefin. The interactions between the components (probably leading to the formation of a copolymer at the interface of the two phases) influence also the crystallization behavior and other properties of the complex PE-LD/PA6/EPDM systems.

— Thermal behavior (DSC) indicated small variations of the melting — crystallization temperatures, whereas main differences appeared in the values of the enthalpy and crystallinity degree, especially for PA6 component of the system.

— Impact enhancement has been observed for PE-LD/PA6/EPDM blends after addition of compatibilizing agents.

— Correlation of the processing behavior with the variation in the properties allows optimization of the composition (60PE-LD/30PA6/10EPDM) and the type of reactive compatibilizer (PE-LD/MA and PE-LD/BMI) as well as processing procedure, which allowed to obtain multicomponent polymer materials with satisfactory impact strength. These results can be used in the mechanical recycling of PE-LD and PA6 incompatible waste blends *via* reactive processing.

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