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Preparation of functionalised low-density polyethylene by reactive extrusion and its blend with polyamide 6

K. Kelar, B. Jurkowski*

Division of Plastics and Rubber Processing, Institute of Material Technology, Poznań University of Technology, 61-138 Poznań, Piotrowo 3, Poland

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Abstract

A maleic anhydride (MAH) was grafted to LDPE by the reactive extrusion in a single-screw Brabender extruder, equipped with a prototype static or dynamic mixer in the presence of a free-radical initiator—benzoyl peroxide (BP). It was found that the highest efficiency was for the dynamic mixer, next the static mixer and the lower for the shaping extruder's head. Here, the grafting process is not accompanied by cross-linking side reactions of the polyethylene chains.

For LDPE and PA6 blended in the presence of 5 wt.% of LDPE-*g*-MAH by using the extruder equipped with a typical shaping head, clearly improvement of compatibility of the mixed components was not observed and poor interfacial adhesion was noticed. This evidences that a single-screw extruder equipped with a typical extrusion-shaping head is a low-efficient mixer for the mechanochemical compatibilization of the immiscible polymers. The use of the dynamic mixer essentially improves the compatibility of the mixed components. Obtained in situ a graft copolymer LDPE-*g*-PA6 is created both because of reaction of the end amine groups in PA6 with carbonyl groups in MAH and because of recombination of the macroradicals generated under action of shearing stresses. Good stability of the phase structure during reprocessing and heating and good mechanical properties of the blend suggest that the dynamic mixer be suitable for reactive processing.

Keywords: Low-density polyethylene; Polyamide 6; Reactive processing

1. Introduction

Large demand for new engineering materials, sometimes with specific properties, results in development of different methods of the polymer modification. Here, physical modifications by the melt mixing of different polymers have principal importance. Most pairs of polymers are immiscible and are characterised by the two-phase structure [1–3]. Weak physicochemical interferences between the phases of the blend are usually a reason of low both processability and exploitation properties. Improvement of adhesion between the phases is possible to obtain by chemical compatibilization of the blend, i.e. by the introduction of third component into the two-polymer blend [4–10].

Good compatibility gives block and graft copolymers, which introduction improves adhesion on the phase boundaries and ensures also advantageous distribution of a dispersed phase within the polymer–matrix and stabilises a structure during next stages of the processing of such a blend [4,9]. Problems related with separate synthesis of the copolymers were the reason of development the different methods of manufacturing of polymers containing appropriate functional groups, which, next, create in situ the compatibilizer—block or graft copolymers [5,6]. The modification of polymers has been successfully achieved using solution [11,12], melts [13–15], and even solid-state rout [16]. Special attention should be paid for the reactive extrusion [17]. In many details were studied grafting reactions of a maleic anhydride on polyolefins occurring in a presence of a peroxide initiator. The process of functionalization of polyolefins is accompanied by side-reactions, as cross-linking or chain scission. For polyethylene the dominant reaction is cross-linking [17], for isotactic polypropylene—chains scission [18], and for ethylene–propylene copolymers could run both of them [19].

The mechanochemical processes during extrusion depends in a high degree on the design of the reactor used, here an extruder with attachments. This design determines mechanical and thermal interferences in the reactive blend. The aim of this study was the analysis of an influence of the prototype static and dynamic mixers on the grafting efficiency of low density polyethylene (LDPE) by means a

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* Corresponding author. Tel.: +4861-8782771; fax +4861-8782217.
E-mail address: jurkowsk@sol.put.poznan.pl (B. Jurkowski)

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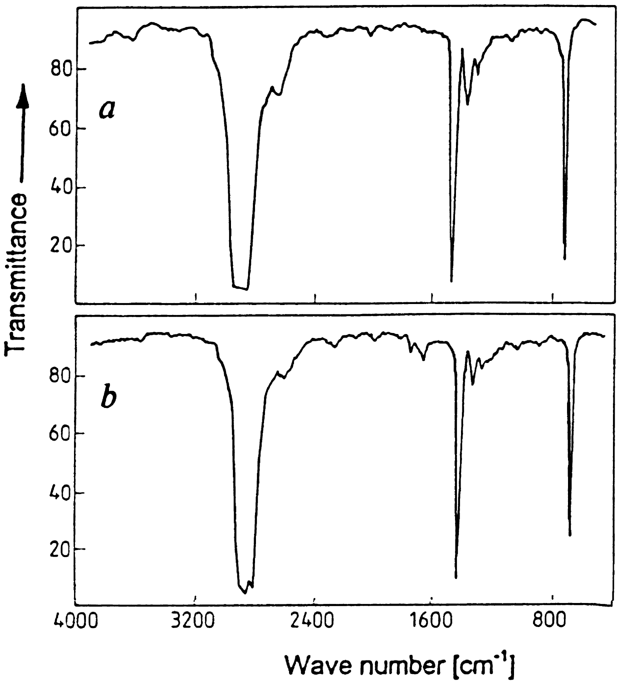

Fig. 1. IR spectra of the: (a) LDPE; (b) LDPE-*g*-MAH.

maleic anhydride (MAH) in a presence of benzoyl peroxide (BP). Obtained functionalised polyethylene (LDPE-*g*-MAH), was used as the third component of the blend of LDPE with PA6. Simultaneously with chemical compatibilization of the blend, mechanical compatibilization during its extrusion through the dynamic mixer was studied [20–22].

2. Experimental

2.1. Materials

The components used in the study were:

- low-density polyethylene (Petrochemical Plant in Płock, Poland) with a density of 0.92 g/cm^3 and a melting point of 107°C, the melt flow index MFI(190°C; 21.1N) = 2.0 g/10 min;
- polyamide six (Tarnamid T-27, Nitrogen Chemistry Plant in Tarnów, Poland) with a density of 1.12 g/cm^3, a melting point of 220°C and MFI(220°C; 21.1N) = 23.4 g/10 min. PA6 before the use had been dried in a vacuum chamber at 80°C for 48 h;
- a maleic anhydride (Fluka Chemie, Germany) with a melting point of 54°C, which was purified by recrystallization from benzene;
- benzoyl peroxide (Oxytop sp. z. o.o., Poland) with a melting point of 104°C, which was purified by recrystallization from acetone.

2.2. Functionalization of low-density polyethylene and blend preparation

The reactor used in the study was the modified Brabender plastograph (type FOD 234). Mixers of two types—static and dynamic—were attached to the typical single-screw extruder of 16 mm in diameter with $L/D = 22{:}1$ working here mainly as melting and conveying machine to allow, next, mixing and reacting of components under controlled conditions [11,20,22]. The dynamic mixer (Cavity Transfer Mixer type) provides the shear rates of the moving melt of about 100 s^{-1}. This shear rate was found as a difference of a linear speed between an outer surface of the rotated rotor and the immovable barrel of the mixer. The design of the static mixer was such that it allows the performance of grafting at shear rates of 50 s^{-1} [20].

A blend of LDPE with 1 wt.% of a maleic anhydride were mixed with BP (in the range 0–1 wt.%) and processed in nitrogen atmosphere at a temperature of 180 ± 5°C in a extruder at a rotational speed of a screw 50 min^{-1} with the use of a typical extrusion shaping head, or a static mixer or else a dynamic mixer.

LDPE/PA6/LDPE-*g*-MAH ternary blends were melt-mixed in nitrogen atmosphere at a temperature of 220 ± 5°C by using the Brabender extruder equipped with a extrusion shaping head and were also melt-mixed by using this extruder equipped with a dynamic mixer. The percent contributions of individual components in the blends LDPE/PA6/LDPE-*g*-MAH was between 90/5/5 and 45/50/5 wt.%.

2.3. Investigations

Infrared absorption spectroscopy (Specord 75 IR, Zeiss Jena, Germany) was used to study both the products of LDPE functionalization and obtained blends. Grafting efficiency of MAH on LDPE was evaluated in comparison with a peak responsible for stretching vibrations of a carbonyl group in MAH at a weave number 1780 cm^{-1} in comparison to C–H stretching vibrations in $-CH_2$ groups in LDPE at 719 cm^{-1} [13]. Studies of the blend were carried out for extruded samples and those after selective extraction by using formic acid. Analysis of gel fraction in LDPE-*g*-MAH was carried out by refluxing xylene [23]. Selective blends' extraction was performed in formic acid [24,25].

The blends' morphology was observed with the biological optical microscopy (type MSt 130, Polish Optical Plant, Warsaw). Phase contrast between the LDPE and PA6 was achieved by staining the polyamide phase with an alcohol solution (1 wt.%) of iodine. The morphology of the fracture surfaces were observed in a scanning electron microscope (SEM: JOEL type JMS-50A, Japan) at an accelerating voltage of 25 kV. The samples were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before SEM examinations.

The strength of the samples made of these blends was measured by use of a computer-operated Instron tensile

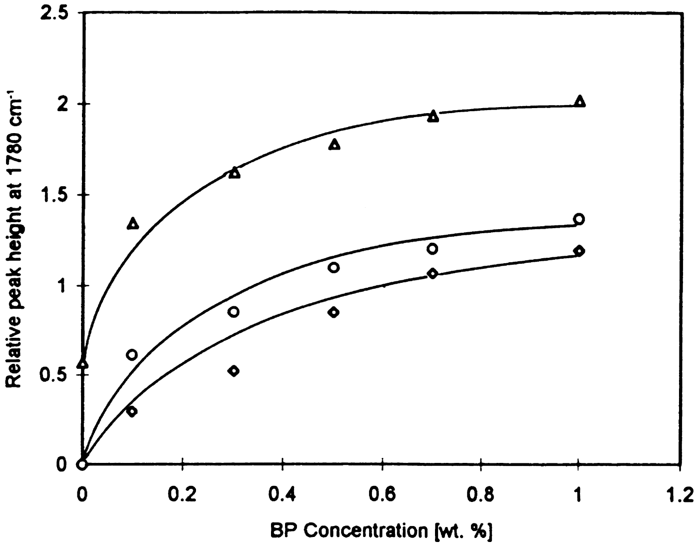

Fig. 2. Effect of the mixer design and BP concentration on the grafting efficiency (relative peak at 1780 cm^{-1}): (◇) a shaping head; (○) a static mixer; (△) a dynamic mixer.

testing machine Model 1115 (UK). All tests being done at a crosshead speed of 5 cm/min and a temperature of 20 ± 3°C.

3. Results and discussion

In Fig. 1 are infrared spectra of LDPE and LDPE-*g*-MAH. Characteristic absorption stretching vibrations of a carbonyl group in a maleic anhydride are present at a wave number of 1780 cm^{-1}. It was found that the intensity of a peak of stretching vibrations for carbonyl groups depends essentially on both the concentration of benzoyl peroxide and the processing method of the reactive blend. Dependencies of the grafting efficiency on a concentration of a benzoyl peroxide and a processing method evaluated based on infrared spectra are shown in Fig. 2.

The grafting efficiency grows as a concentration of BP grows for every processing method of the reactive blend.

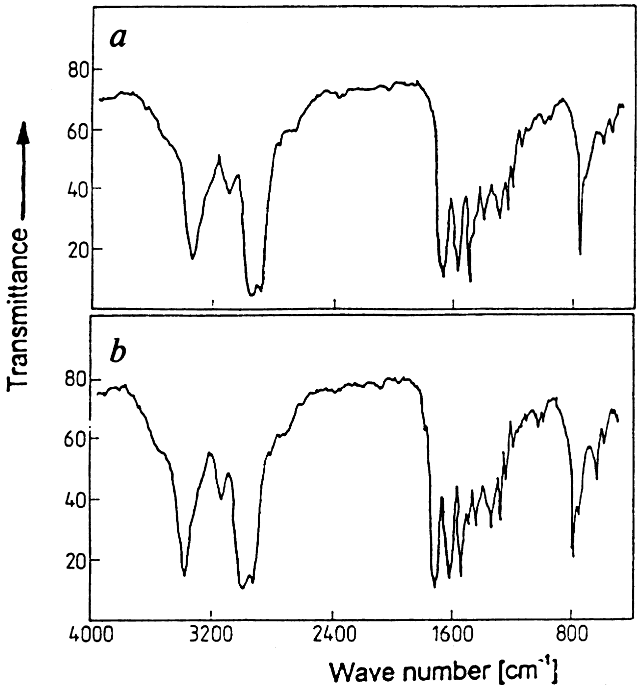

Fig. 3. IR spectra of the films of 65LDPE/30PA6/5LDPE-*g*-MAH ternary blends: (a) extruded with a shaping head; (b) extruded with a dynamic mixer.

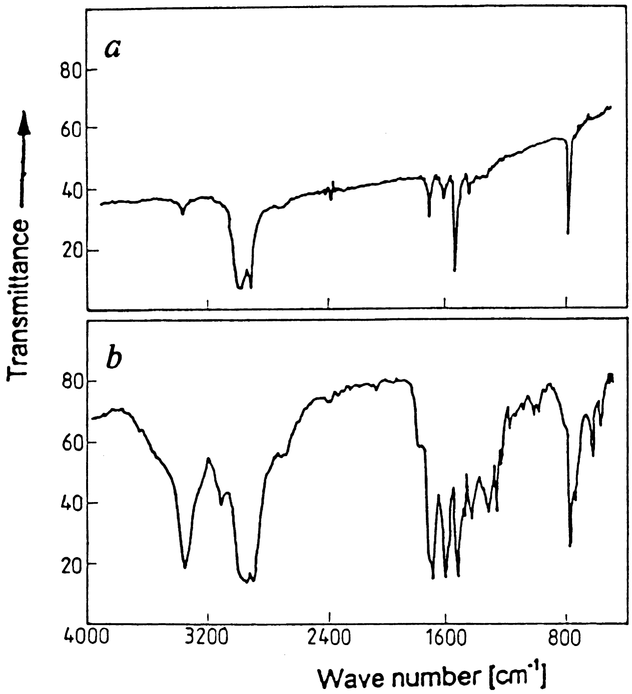

Fig. 4. IR spectra of the films of 65LDPE/30PA6/5LDPE-*g*-MAH ternary blends after selective extraction in formic acid: (a) extruded with a shaping head; (b) extruded with a dynamic mixer.

Table 1
Results of selective extraction of the blend with 98% formic acid (soluble weight fraction [wt.%])

Type of the mixer	Blend composition LDPE/PA6/LDPE-*g*-MAH					
	90/5/5	85/10/5	75/20/5	65/30/5	55/40/5	45/50/5
A shaping head	4.9	9.1	18.2	28.8	41.8	49.0
A dynamic mixer	0.0	0.0	0.24	5.5	22.8	45.9

The lowest efficiency was found for extrusion by using a typical shaping extrusion head, next, when the static mixer was used and the highest for the dynamic mixer. Spectral analysis of grafting when processing by using a dynamic mixer shows that also in the absence of BP at 1780 cm^{-1} it is visible a weak vibration of a carbonyl group, which was absent for processing by using a typical shaping head and the static mixer. A presence of this peak evidences that shearing stress applied to the batch when using a dynamic mixer make scission of macromolecules, affected by the creation of free radicals initiating the grafting reaction.

The studies of a gel content in LDPE-*g*-MAH show that all products of the mechanochemical reactions are dissolving in full in boiling xylene. In the studied range of both the BP and MAH concentrations, the grafting process is not accompanied by the side-reaction of polyethylene cross-linking. This confirms results of studies [12] where was found that BP cross-links LDPE only for the higher concentration of MAH.

In Fig. 3 are shown exemplary spectra of the ternary blends extruded with a shaping head and a dynamic mixer, respectively. The absorption of the polymer blends is additive, therefore, in every obtained spectrum of the blend are visible characteristic peaks for PA6 absorption as follows: at a wave number of 1640 cm^{-1} C=O stretching vibrations, at 1560 cm^{-1} N–H bending vibrations, and at 3300 cm^{-1} N–H stretching vibrations.

The exemplary IR spectra of the ternary blends after the selective extraction in formic acid are shown in Fig. 4. Analysis of these evidences by way of extrusion influences the intensity of absorption bands characteristic for an amide group. In spectra of blends extruded with a shaping head (Fig. 4(a)) the disappearance of the group characteristic for PA6 was observed. The IR spectra of the blends extruded with a dynamic mixer (Fig. 4(b)) are similar qualitatively to the spectra of the not extracted blends. Both of them contain the same absorption peaks characteristic for PA6.

In the spectra of the blends extruded with the dynamic mixer (both before and after the selective extraction) as distinct from the spectra of the ternary blends extruded with a shaping head at a wave number 1726 cm^{-1} it was found the presence of a new absorption peak. From

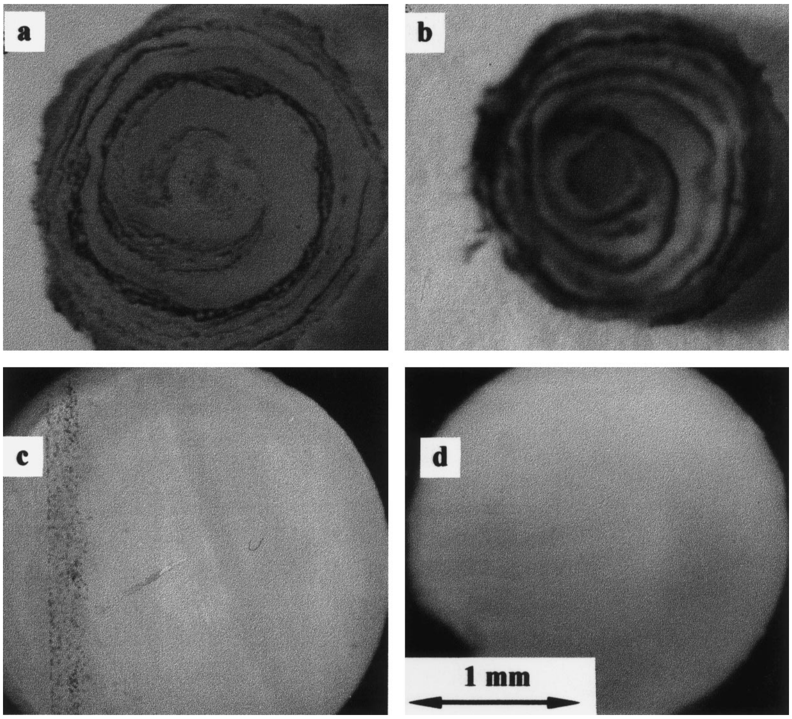

Fig. 5. Extrudates cross sections perpendicular to the flow direction of the blends: (a) 85LDPE/10PA6/5LDPE-*g*-MAH; (b) 55LDPE/40PA6/5LDPE-*g*-MAH (extruded with a shaping head); (c) 85LDPE/10PA6/5LDPE-*g*-MAH; (d) 55LDPE/40PA6/5LDPE-*g*-MAH (extruded with a dynamic mixer).

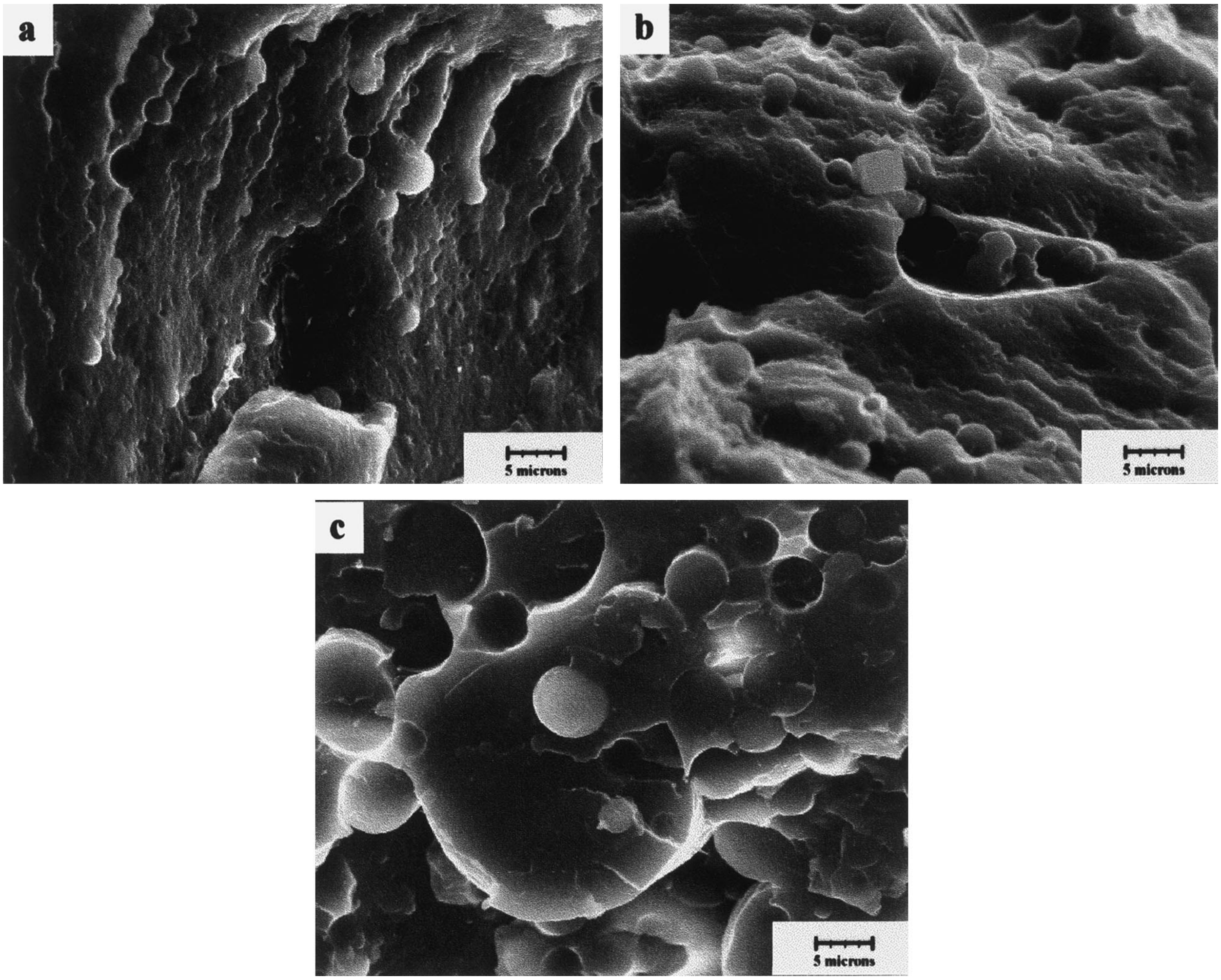

Fig. 6. SEM micrographs of cryogenically fractured surfaces for blends extruded with a shaping head): (a) 85LDPE/10PA6/5LDPE-*g*-MAH; (b) 65LDPE/30PA6/5LDPE-*g*-MAH; (c) 55LDPE/40PA6/5LDPE-*g*-MAH.

literature surveys [26] it is concluded that appearance of this result from changes in an amide group due to the addition of macromolecules of other polymers to a nitrogen atom in this group. In all the tested ternary blends the LDPE-*g*-MAH content was the same and equal to 5 wt.%. Therefore, here in a bound form should be the same quantity of polyamide accepting that the graft copolymer could be created only because of reactions of amine end-groups in PA6 with carbonyl groups in MAH of functionalised polyethylene. The results of selective extraction of the blend with 98% formic acid are given in Table 1.

The highest amount of PA6 was extracted from blends processed by using a shaping head. Much lower was for a dynamic mixer. Higher content of bound polyamide, which was determined for a dynamic mixer, evidence that because of shearing stresses caused by the dynamic mixer, scission of the macromolecules occurs with simultaneous creation of free radicals. A result of it is PA6 grafting on LDPE or

Table 2
Tensile strength R_r [MPa] of ternary blends and virgin material

Type of the mixer	Blend composition LDPE/PA6/LDPE-*g*-MAH					
	90/5/5	85/10/5	75/20/5	65/30/5	55/40/5	45/50/5
A shaping head	10.0	10.2	10.7	11.3	13.5	18.4
A dynamic mixer	10.9	11.2	11.8	12.3	17.5	24.7
Virgin material						
LDPE	10.4					
PA6	54.2					

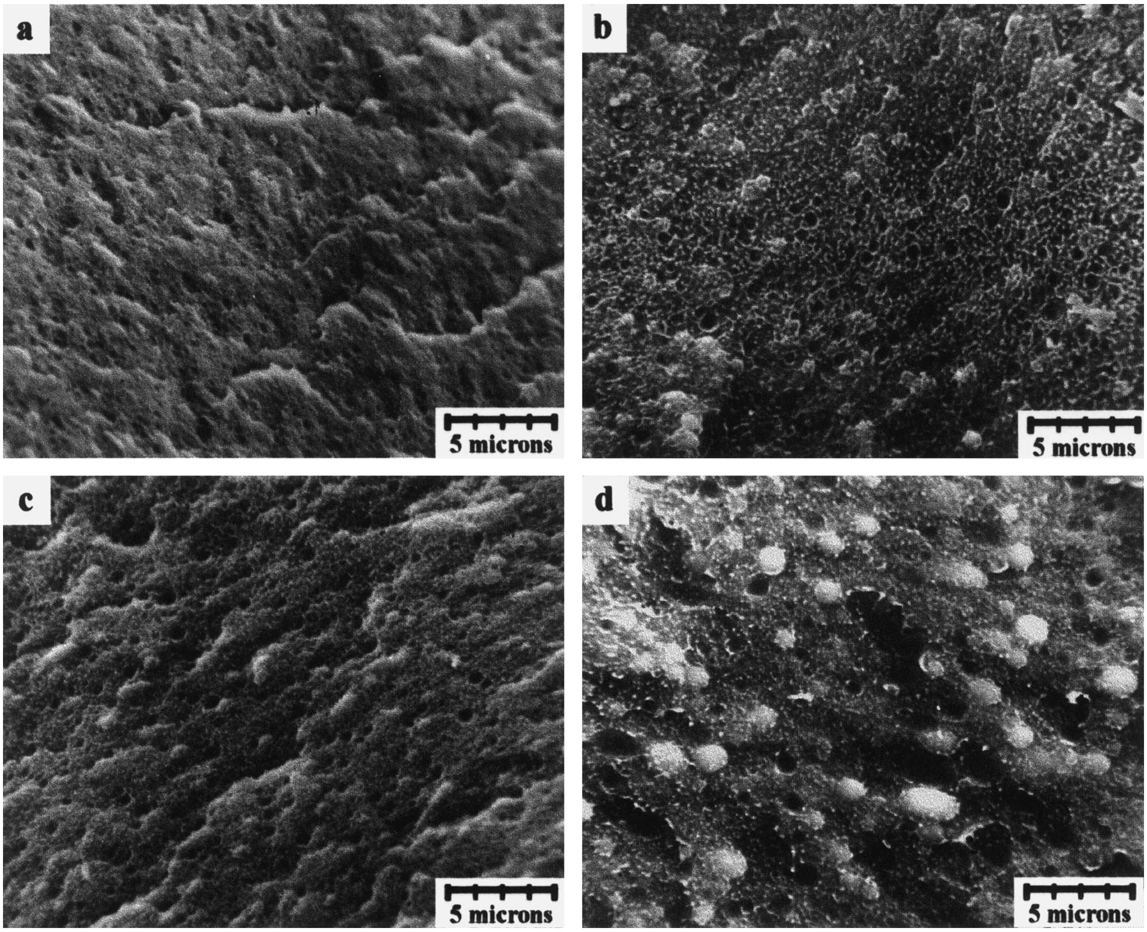

Fig. 7. SEM micrographs of cryogenically fractured surfaces for blends extruded with a dynamic mixer: (a) 85LDPE/10PA6/5LDPE-*g*-MAH; (b) 75LDPE/20PA6/5LDPE-*g*-MAH; (c) 65LDPE/30PA6/5LDPE-*g*-MAH; (d) 55LDPE/40PA6/5LDPE-*g*-MAH.

LDPE on PA6—advantageous effect of mechanical or mechanochemical compatibilization. It is different from that if a typical shaping head is used; it causes only some macroradicals generation. As the result, now the quantity of bound PA6 in the blend is small. The effect of washing out the not bound PA6 from the blend is visible in the spectra of the blend after extraction (Fig. 4(a)). For using a shaping head, a noticeable reduction of intensity of amide bands was found, whereas for spectra of the blends processed with the dynamic mixer it is preserved high (Fig. 4(b)).

In Fig. 5(a) and (b) cross-sections, made perpendicular to the flow direction, are shown as the example of morphologies of the ternary blends extruded with a use of a shaping head. Here, for all blends are clearly shown two separate phases (ribbon-type dispersion): dark—PA6 and light—LDPE. In these pictures is clearly visible that as the polyamide content in the blend increases, the surface of the tested samples became more rough and the cross-section of such samples has a shape essentially different from round in spite of the fact that a round shape of die was used. This effect results from the non-laminar flow of the molten polymers and it is more visible as the difference in the viscosity of mixed polymers is higher [8].

In Fig. 5(c) and (d) is shown the morphology of the ternary blends extruded with the help of the dynamic mixer. In these blends it is not visible separate phases, the surface of the extrudates is smooth and the cross-section of the extruded bars is round. This evidences the advantageous effect of mechanical compatibilization resulting from the dynamic mixer.

Typical morphology of a blend of immiscible polymers is the presence of spherulitic domains of different sizes [10,27]. In Fig. 6(a) and (c) is shown a SEM microphotograph of a fracture surface of the example morphology of the ternary blend extruded by using a shaping head. Poor interfacial adhesion was evident from the large voids left on the fracture surface where the particles had separated from the matrix and the smooth surfaces of the exposed PA6 particles.

In Fig. 7(a) and (d) are shown SEM microphotographs of a fracture surface of the ternary blends obtained when a dynamic mixer was used. The effect of the simultaneous chemical and mechanical compatibilization is visible in the relatively smaller-size particles of a dispersed phase and narrow is this size distribution. Better dispersion and improved interfacial adhesion were attributed to formation of an LDPE-*g*-PA6 copolymer during the melt mixing.

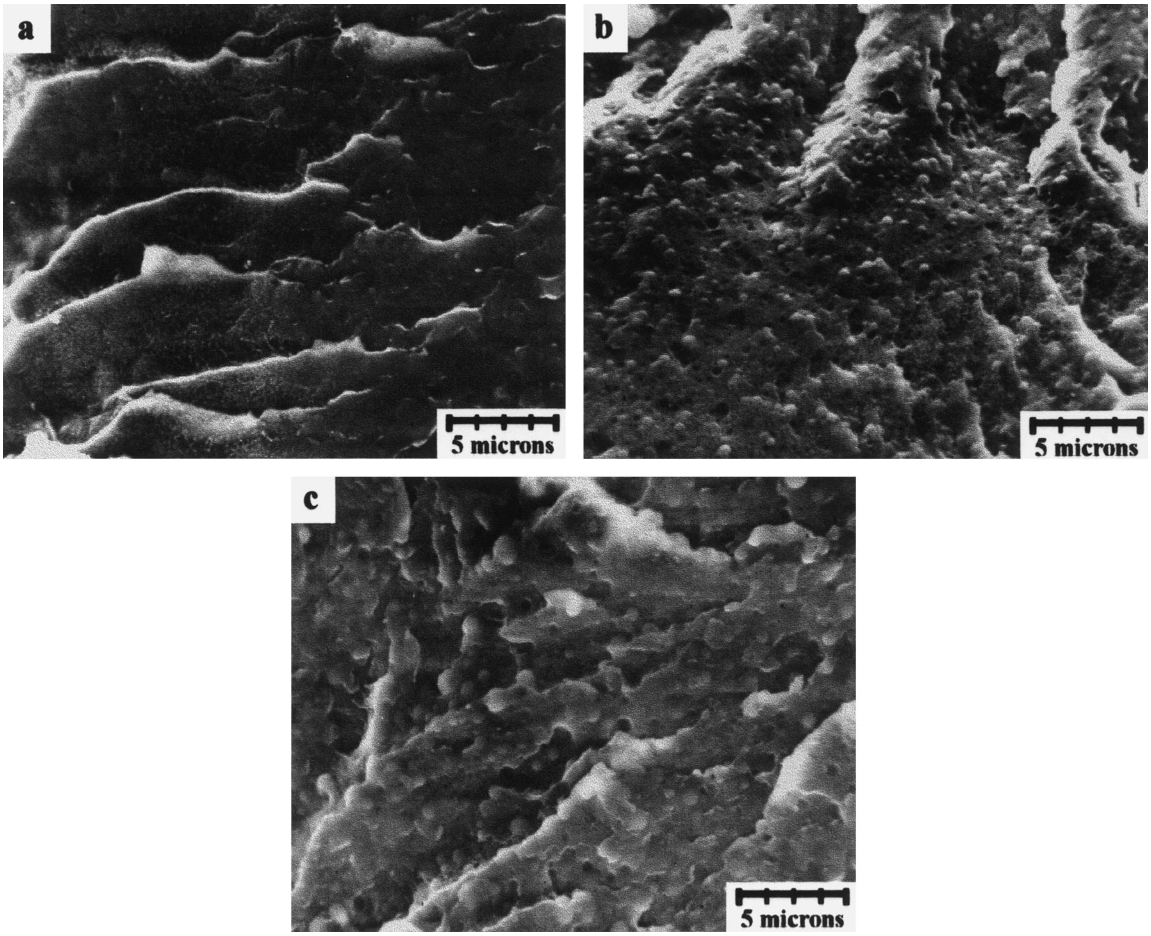

Fig. 8. SEM micrographs of cryogenically fractured surfaces for blends extruded with a dynamic mixer and molten again at 230°C): (a) 85LDPE/10PA6/5LDPE-*g*-MAH; (b) 65LDPE/30PA6/5LDPE-*g*-MAH; (c) 55LDPE/40PA6/5LDPE-*g*-MAH.

Finally, one may ask if the morphologies of ternary blends obtained by mixing with a dynamic mixer are stable or not during subsequent annealing. Fig. 8 (a)–(c) shows SEM microphotographs of a fracture surface of chemically and mechanically compatibilized ternary blends, annealed at 230°C for 10 min under nitrogen atmosphere. The pictures clearly show that all the blends have almost identical average particle size of the dispersed phase and the size distribution similar to unannealed blends. These results show that these blends are stable during subsequent annealing, and coalescence of the dispersed phase is not observed.

The mechanical properties of the materials and their blends are summarised in Table 2. In all tested samples, an increase in the PA6 content is followed by the growth of tensile strength. All blends extruded with a dynamic mixer are characterised by higher strength than that of the blends extruded with a shaping head. The low tensile properties of the blends extruded with a shaping head can be attributed essentially to the larger size of the PA6 particles with poor adhesion towards the LDPE matrix. These domains act as gross material defects, causing premature rupture of the specimen soon after the beginning of yield. On the contrary, in blends extruded with a dynamic mixer, both particle size reduction and an improvement of the interfacial adhesion, caused by the formation of LDPE-*g*-PA6 copolymers, seem to lead to the improvement of mechanical properties.

4. Conclusions

Grafting efficiency of MAH on LDPE increases as concentration of BP grows and depends on the way of reactive processing. The highest efficiency was found for the process when using the dynamic mixer, next the static mixer and the lower for a typical shaping extruder's head. Shearing stresses obtained by using the dynamic mixer results in the radicals' generation, the effect of which is grafting MAH on LDPE without the action of peroxide initiator. The dynamic mixer helps to obtain a high grafting efficiency on LDPE for a small concentration of a peroxide initiator. Here, process of grafting is not accompanied by the cross-linking side reactions of the polyethylene chains.

In the reactive extrusion of the LDPE with PA6 blended in a presence of 5 wt.% LDPE-*g*-MAH by using a single-screw Brabender extruder, equipped with a typical shaping head was not observed in the clear improvement of compatibility of mixed components. Studies by using both selective extractions in formic acid and IR spectroscopy show that, in the blend was created, only small amounts of the grafted copolymer LDPE-*g*-PA6. Investigation of these blends by using the optical microscopy with phase contrast shows that there is present two separate phases. Poor interfacial adhesion was evident from large voids left on the fracture surface where the particles had separated from the matrix and the smooth surfaces of the exposed PA6 particles. This evidences that a single-screw extruder equipped with a typical extrusion-shaping head is a low-efficient mixer for the mechanochemical compatibilization of immiscible polymers.

The use of the dynamic mixer as an attachment to the extruder for such processing causes the essential improvement of compatibility of mixed components. Obtained in situ a graft copolymer LDPE-*g*-PA6 is created both because of reaction of the end amine groups in PA6 with carbonyl groups in MAH and because of the recombination of macroradicals generated under the action of shearing stresses. Investigation of these blends by using optical microscopy with phase contrast showed the presence of a single phase. This evidences a good dispersion of the dispersed phase within the polymer–matrix. The same conclusion is confirmed by SEM of the fracture surface of samples. Good stability of the phase structure during reprocessing and heating; and good mechanical properties of the blend suggest that the dynamic mixer be suitable for the reactive processing, i.e. mechanical compatibilization of the LDPE/PA6 blends.

Acknowledgements

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