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One-step functionalization and reactive blending of polyolefin/polyamide mixtures (EPM/PA6)

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Abstract

Diethyl maleate, maleic anhydride and dicumyl peroxide in different ratios were directly added to molten polymeric mixtures based on ethylene-*co*-propylene (EPM) and polyamide 6 (PA6) to perform in one-step the functional groups grafting and branched copolymer formation necessary to obtain compatibilized products.

The characterization of the blends by selective solvent extraction and IR and NMR analysis of the various fractions allowed to evidence the occurrence of maleate grafting on both EPM and PA6 as well as the formation of graft copolymers at the interface. The effect of the reactions on phase morphology development and thermal properties was evaluated by SEM and DSC analysis respectively in order to investigate the compatibilization extent in comparison with the conventional two-steps procedure. Besides tests about mechanical properties of samples produced by the extrusion were carried out.

Keywords: Ethylene-*co*-propylene (EPM)/nylon-6 (PA6) blends; Functionalization; Reactive processing

1. Introduction

Polyolefin (PO)/polyamide (PA) blends, when properly compatibilized, can potentially offer a wide range of desirable and useful characteristics such as high impact toughness [1], improved tensile behaviour [2] and barrier properties [3] which usually answer to the market requirements of high performance materials. These properties can be modulated by acting on composition and morphological features of the blends.

Generally the morphological properties, such as the phase distribution and the dispersed phase size depend on several parameters. These are chemical and physical interactions, interfacial tension, processing conditions, coalescence phenomena and rheological characteristics of the two polymeric immiscible phases [4,5]. A functionalized polyolefin bearing reactive groups towards polyamide is conventionally added to the polyolefin (PO)/polyamide (PA) mixture before the reactive processing. The grafted groups inserted onto the backbone of the polyolefin react with the amino-end groups of the polyamide to give a polyolefin–polyamide grafted copolymer (PO-*g*-PA) which acts at the interface as a compatibilizer [6–9,11]. This conventional process therefore is characterized by two distinct steps:

Step 1. Treatment of the PO in a mixer or extruder by adding a functional monomer and a radical initiator with the aim of anchoring reactive groups to the polyolefin backbone through free radical grafting in the melt.

Step 2. Reactive blending between the polyolefin and the polyamide (PA) in the presence of the added PO with grafted reactive groups obtained in step 1; during this blending step PA terminal groups can react with the functionalized PO to give PO-*g*-PA compatibilizing graft copolymers at the interface.

The new structural and morphological properties are responsible of improved mechanical properties in terms of tensile and impact behaviour [12–14] with respect to the uncompatibilized blends.

Only a few papers have been published about the one-step reactive blending, that consists in the addition of functionalizing agents during the blending of PO with PA. Lambla et al. [15] studied the free radical reactivity of blends between low density polyethylene (LDPE) and polyamide 11 (PA11)

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(80/20 w/w) towards different amounts of various peroxides. The initiator structure and concentration were accurately chosen to obtain an optimal concentration of radical sites on the polymer backbone (the macroradicals) by hydrogen abstraction reaction from primary radicals, preventing the crosslinking reactions, which are statistically favoured by macroradicals concentrations. The use of maleic anhydride led to a significant improvement of the morphology and mechanical properties, in comparison to the poor results obtained with peroxide alone.

This process was applied also to high density polyethylene/polyamide-6 (HDPE/PA6) blends [16] produced in a co-rotating twin screw extruder in the presence of both peroxide and maleic anhydride. The improvements of tensile, morphological and thermal properties with respect to the reference blends obtained without chemicals were explained on the basis of a high level of reciprocal grafting reactions between the two polymers (PO-*g*-PA6 copolymers formation), due to the effectiveness of the reacting system acting at the interface. The authors proposed that the formation of graft HDPE-*g*-PA6 copolymer occurred by the termination reactions (by coupling) of radicals formed onto both the polymer chains and by condensation reaction between functionalized polyolefin and amino terminal groups of the polyamide.

Successively Hu et al. [17] modulated the optimal extrusion conditions to obtain HDPE/PA6 compatibilized blends in a single step by setting up the twin screw extruder configuration: the separated feed of polyolefin and polyamide and in particular the presence of a devolatilization valve of residual maleic anhydride produced resulting blends characterized by much better mechanical properties in terms of elongation at break and impact strength.

This paper concerns the one-step reactive process, which is attractive from an industrial point of view because it is less expensive and time consuming than the two-steps process. As the understanding of the mechanism and nature of the product of the compatibilization single step is still lacking, the present work is mainly focused on the detailed study of the one-step reactive blending of the ethylene–propylene copolymer (EPM) and polyamide 6 (PA6) in a discontinuous mixer.

Diethyl maleate (DEM) [18–22] or DEM/maleic anhydride (MAH) [23–26] mixtures were used in the presence of dicumyl peroxide (DCP) as radical initiator in different ratios as functionalization additives. The selective solvent extraction of the blends was also performed to isolate products of the various possible reactions and their characterization were performed by IR spectroscopy. Finally, morphology and thermo-mechanical properties were determined in comparison with the compatibilized blends obtained by the traditional two-steps process.

2. Experimental

2.1. Materials

Polyamide 6 ($M_n = 20{,}000$ D) has been used as provided (Ultramid-BASF) without further purification.

EPM-CO-O34 (22.7 wt% propylene), supplied by Enichem Elastomeri, is characterized by a Mooney viscosity (100 °C) of 40–48, $\bar{M}_w = 138{,}000$ D and $\bar{M}_n = 55{,}200$ D.

Diethyl maleate (DEM Aldrich) was distilled under reduced pressure. Maleic anhydride (MAH Aldrich) was purified by recrystallization from benzene.

Dicumyl peroxide (DCP, Aldrich) was used without further purification.

Poly(diethyl fumarate) (PDEF) was prepared by free-radical polymerisation of diethyl fumarate by using azobisisobutyronitrile as radical initiator [27].

2.2. Reactive blending

One-step reactive blending runs were performed at 230 °C and 30 rpm in a Brabender Plastograph© (model N° OHG47055, 30 ml) mixer equipped with a 30 ml mixing chamber. The EPM/PA6 mixtures (20 g, 80/20 wt/wt or 20/80 wt/wt) were introduced in to the mixer and the radical functionalizing mixture (a solution of functionalizing monomer(s) and peroxide) was added after the torque stabilization. The blending was carried out for 10 min then stopped and the material collected.

2.3. Characterization

The blends deriving from the one-step process were previously extracted with boiling acetone to remove unreacted monomers, peroxide decomposition products and oligomers. The residual fraction was extracted with formic acid to remove unreacted polyamide 6 and with hot toluene to remove unreacted EPM. The residue (the EPM-*g*-PA6 graft copolymers) was collected and characterized. Extractions with formic acid of 80/20 EPM/PA6 grinded blends have been carried out for 20 days by substituting fresh solvent each 3 days. This procedure was get ready on the basis of the extraction results obtained for the reference mechanical EPM/PA6 blend, produced by mixing the two polymer components in Brabender (in the same experimental conditions described before) without any low molecular weight chemicals addition.

IR spectra of residual and extracted fractions were measured with a Perkin–Elmer 1760-X Fourier transform infrared spectrometer on films obtained using a PM 20/20 press at 22 MPa and 230 °C (for 5 min).

^{1}H NMR analysis of polyamide extracted fractions were performed with a Varian Gemini -200 spectrometer at 200 MHz by dissolving about 35 mg of every sample in deuterated formic acid (DCOOD). Totally decoupled ^{13}C NMR spectra were obtained by using the same instrument (delay = 0.4 s and acquisition time = 0.6 s).

The titration of end –NH_2 and –COOH groups of polyamide samples was carried out on the formic acid extracted polyamide fractions with a visual method: about 1 g of each sample was dissolved in 70 ml of benzyl alcohol at 150 °C under nitrogen flux. After adding 20 ml of a mixture methanol/water 2:1 v:v, the resulting solution was titrated with a KOH 0.02 N ethylene glycol solution (which has been daily standardised against a 0.0196 N hydrochloric acid solution) by using phenolphthalein as visual indicator to determine the concentration of –COOH functional groups. In the same way the concentration of $-NH_2$ groups was determined by using a 0.0196 N hydrochloric acid solution with brominephenol blue as indicator.

The concentration of the end groups was determined, after subtracting blank contribution, with the following equation:

$$[\mathrm{TGroups}](\mathrm{mequiv/kg}) = \frac{(\mathrm{ml_s} - \mathrm{ml_b})T}{m_{\mathrm{PA6}}}1000$$

where [TGroups], terminal groups concentration; ml_s, titrating solution millilitres to titrate sample; ml_b, titrating solution millilitres to titrate blank; T, titrating solution concentration (moles/litres); m_{PA6}, sample weight (g)

Thermal analysis was carried out by a Perkin–Elmer DSC7 differential scanning calorimeter (DSC) in the temperature range 20–250 °C at 10 °C/min. The instrument was previously calibrated by using In and Zn as standard references.

Scanning electron microscopy (SEM) was performed on cryogenically fractured samples (with liquid nitrogen) after sputtering with gold with a Jeol JSM T-300 instrument.

3. Results and discussion

3.1. Blends preparation and characterization

The reactive blending was performed by using two different EPM/PA6 weight ratios (80/20 or 20/80) respectively and different amount of additives (Table 1). Two different reference blends BLref1a and BLref1b were prepared by mechanical mixing of the pristine polymers whereas BLref2 is a two-steps reactive blend obtained by using a previously functionalized EPM sample [19,22,24]. Two series of one-step runs were carried out: the former characterized by the use of diethyl maleate alone (DEM) as functionalizing reagent (from BL1 to BL7 runs and BL13 and BL14), and the latter by the contemporary presence of both DEM and maleic anhydride (MAH) (from BL8 to BL12 runs and BL15, BL16 and BL17). Dicumyl peroxide (DCP) was always used as radical initiator. In few cases (runs BL10, BL11 and BL17) amorphous silica was added as absorbing substrate of the chemicals reagents (DEM, is a liquid at room temperature) to favour their dispersion [28].

All the blends were extracted with acetone and toluene to remove low molecular weight species (unreacted monomers and degradation products of peroxide or polyolefin) and the unreacted polyolefin respectively. Few samples were extracted also with formic acid to remove the polyamide not grafted onto PO chains (Table 1).

IR spectra (Fig. 1) allow evaluating the composition of various fractions and the presence of grafted functional groups [10,24]. The spectra indicate the presence of functionalized polyolefin in the toluene and of polyamide in the formic acid extracted samples; the residue to both extractions can be considered to consist of EPM-*g*-PA6 graft copolymer for blends EPM/PA6 80/20 wt/wt whereas it is not possible to exclude also the presence of unreacted polyolefin for blends EPM/PA6 20/80 due to hindered accessibility of solvent to dispersed EPM (BLref1b run).

Table 1
EPM/PA6 blends and solvent extraction results

Run	Starting EPM/ PA6 wt ratio	Functional monomer (mol%)[a]	DCP (mol%)[a]	Acetone soluble fraction (wt%)	HCOOH soluble fraction (wt%)	Toluene soluble fraction (wt%)	Residue (wt%)
BLref1a	80/20	None	–	0.8	20.0	77.9	1.3
BLref2	80/20	DEM[b]	–	n.d	n.d	n.d	n.d
BL1	80/20	DEM (1.0)	0.13	1.6	n.d	87.3	n.d
BL2	80/20	DEM (2.1)	0.13	2.0	n.d	85.9	n.d
BL3	80/20	DEM (4.2)	0.13	3.2	20.4	76.4	0
BL4	80/20	DEM (6.3)	0.13	8.7	n.d	68.8	n.d
BL5	80/20	DEM (4.2)	0.07	3.7	n.d	83.9	n.d
BL6	80/20	DEM (2.1)	0.27	2.9	n.d	87.4	n.d
BL7	80/20	DEM (4.2)	0.27	2.5	17.6	78.8	1.1
BL8	80/20	DEM, MAH (1.6, 0.8)	0.07	3.2	n.d	17.8	n.d
BL9	80/20	DEM, MAH (1.6, 0.8)	0.13	3.2	13.4	31.5	51.9
BL10[c]	80/20	DEM, MAH (1.6, 0.8)	0.07	2.1	n.d	29.8	n.d
BL11[c]	80/20	DEM, MAH (1.6, 0.8)	0.13	3.4	12.2	38.7	45.7
BL12	80/20	DEM,.MAH (1.0, 1.9)	0.23	0.9	n.d	59.2	n.d
BLref1b	20/80	None	–	0.2	79.0	7.8	13.0
BL13	20/80	DEM (4.0)	0.25	0.3	n.d	n.d.	n.d
BL14	20/80	DEM (8.0)	0.25	2.2	75.9	2.7	19.2
BL15	20/80	DEM, MAH (1.5, 3.1)	0.13	0.9	n.d	1.0	n.d
BL16	20/80	DEM, MAH (1.5, 3.1)	0.25	0.6	69.9	0.8	28.7
BL17[c]	20/80	DEM, MAH (1.5, 3.1)	0.25	0.8	70.4	1.7	27.1

n.d, not determined.

[a] With respect to 100 monomer units calculated on the basis of blend composition.

[b] The EPM used in this run has been previously functionalized with DEM (FD = 0.64 mol% (18)).

[c] Five weight percent of amorphous silica has been used as inorganic substrate able to absorb the functionalizing mixture.

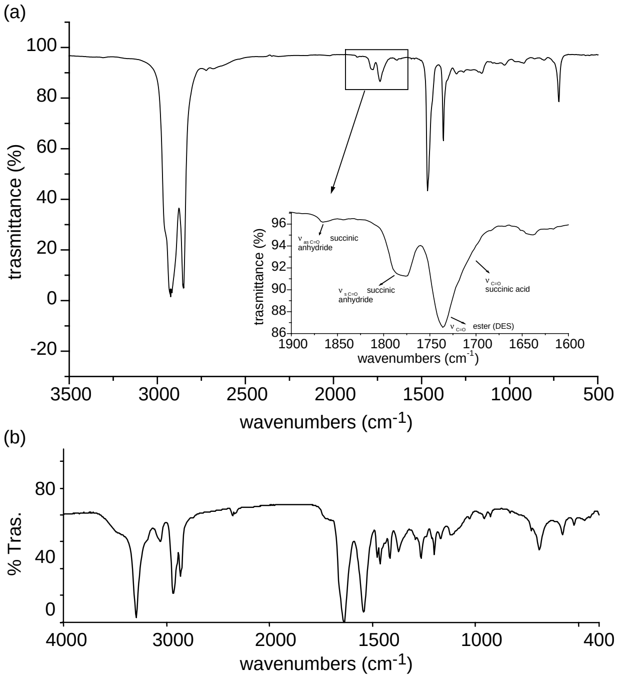


Fig. 1. IR spectra of toluene extracted fraction (a) and formic extracted fraction (b) of BL9 blend.

The amount of the acetone extracted fractions is in general low and comparable with those obtained for samples produced by mechanical mixing without the additives (BLref1a and BLref1b), apart of runs carried out by using more than 4% mol of DEM in the feed (BL14 and BL4). When treating the polymer mixtures with both MAH and DEM a very low amount of toluene extractable polyolefin with respect to the reference blends (respectively, BLref1a for EPM/PA6 80/20 wt/wt and BLref1b for EPM/PA6 20/80 wt/wt) and a notable quantity (more than 25 wt%) of residue to both toluene and formic acid were collected. For runs carried out with silica as monomers and peroxide dispersant (in particular BL11 and BL17) similar results in terms of residue content were obtained as for the corresponding samples produced without employing silica (BL9 and BL16).

3.2. Evaluation of functionalization degree (FD)

After the extraction with hot acetone the samples were characterized by infrared spectroscopy to determine the functionalization degree (FD), number of grafted DES groups derived from DEM (or MAH) per 100 monomeric units.

In the case of runs obtained with DEM alone the carbonyl region of the IR spectrum was characterized by well distinct bands attributable to the grafted diethylsuccinate and the amide groups for both compositions (Fig. 2).

The FD values were calculated on the basis of the ratio between the area of the signal of C=O stretching of diethylsuccinic grafted units at about 1738 cm^{-1} and the reference band [19] at about 1460 cm^{-1} due to the bending of –CH$_2$ and –CH$_3$ groups (Appendix A). The FD values reported in Table 2 were calculated neglecting the amount of the carbonyl groups eventually involved in the formation of cyclic imide groups as the related carbonyl stretching band at 1706 cm^{-1} [22] was not easily assigned in the IR spectra of the blends (Fig. 2).

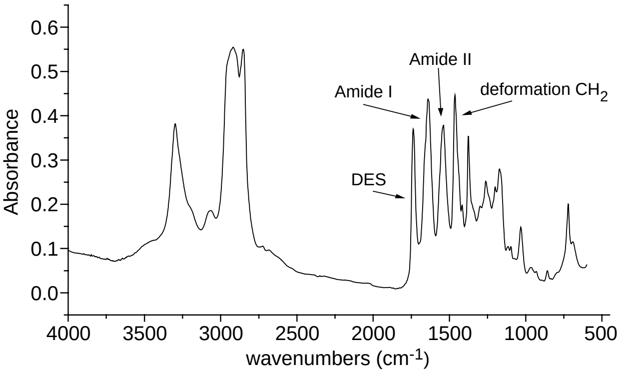


Fig. 2. FT-IR spectrum of BL7 blend after acetone washing.

In the case of blends treated with both MA and DEM, the profile of the bands associated to the inserted functional groups in the IR spectrum is very complex (Fig. 3): the contribution to the FD of the single grafted groups can be evidenced by using a deconvolution procedure [24] (Appendix B).

This methodology cannot be applied directly to the acetone residues IR spectra of the samples (BL8-BL12 and BL15-BL17) containing the polyamide fraction, as the amide I and II absorptions are partially overlapped to the region of interest for deconvolution (Fig. 3). For this reason with regards to EPM/PA6 80/20 wt/wt blends only, the deconvolution methodology was applied to IR spectra of the toluene soluble fractions [22]. The related functionalization degrees are reported in Table 2 (details of calculations and deconvolution procedure are discussed in Appendix B).

The results indicate that for EPM/PA6 80/20 blends FD increases linearly by increasing the amount of DEM and DCP only for low concentration of the reagents (graphs in Fig. 4), and levels off to a limit value due to the occurrence of side reactions [19,22,25].

Runs characterized by very similar concentration of functionalizing reagents showed a FD value larger for the PA6 rich blend (BL13 than BL7) suggesting that the polyamide takes part to the grafting reaction.

3.3. Characterization of formic acid extracted fractions and residue

Degradation reactions can occur when polyamide 6 is treated in heated formic acid [29]. To avoid this effect the extractions were carried out at room temperature and the successive titration was performed on the polyamide fraction recovered after 3 days of extraction.

The time dependence of the extractions with formic acid (Fig. 5) shows that the one-step reactive blending with MAH and DEM generates copolymers insoluble in the formic acid

Table 2
FD_{DEM} and FD_{MAH} values of different blends

Run	Functional monomer (M)	M (mol%)[a]	DCP (mol%)[a]	FD_{DEM}[b] (mol%)[c]	s_{FDDEM}[b]	FD_{MAH}[b] (mol%)[c]	s_{FDMAH}[b]	FD_{tot} (mol%)[c]
BL1	DEM	1.0	0.13	0.5	0.06	–	–	0.50
BL2	DEM	2.1	0.13	1.0	0.05	–	–	1.00
BL3	DEM	4.2	0.13	1.5	0.09	–	–	1.50
BL4	DEM	6.3	0.13	1.6	0.08	–	–	1.60
BL5	DEM	4.2	0.07	1.0	0.08	–	–	1.00
BL6	DEM	2.1	0.27	1.3	0.11	–	–	1.30
BL7	DEM	4.2	0.27	1.8	0.10	–	–	1.80
BL8	DEM, MAH	1.6, 0.8	0.07	0.33[d]	0.02	0.34[d]	0.04	0.67[d]
BL9	DEM, MAH	1.6, 0.8	0.13	0.63[d]	0.06	0.52[d]	0.07	1.15[d]
BL10[e]	DEM, MAH	1.6, 0.8	0.07	0.53[d]	0.05	0.43	0.06	0.96
BL11[e]	DEM, MAH	1.6, 0.8	0.13	0.53[d]	0.06	0.43[d]	0.06	0.96[d]
BL12	DEM,.MAH	1.0, 1.9	0.23	0.19[d]	0.01	0.36[d]	0.02	0.55[d]
BL13	DEM	4.0	0.25	2.2	0.1	–	–	2.2
BL14	DEM	8.0	0.25	2.6	0.1	–	–	2.6

[a] With respect to 100 monomer units calculated on the basis of blends composition.

[b] The procedure to calculate FD values and their standard deviation s_{FD} was reported in Appendices A and B for DEM and for both DEM and MAH functionalized samples respectively.

[c] Expressed as number of grafted units (diethylsuccinate and/or succinic anhydride) per 100 monomeric units.

[d] These values are referred only to the toluene soluble fractions.

[e] Five percent by weight of silica has been used as inorganic substrate able to absorb the functionalizing mixture.

presumably due to the reactions between the two polymers which produce EPR-*g*-PA6. The lower solvent capability of the formic acid in the case of BL9 and BL11 for short time (few days, Fig. 5) could be considered an indirect evidence of the better compatibility between the phases in these blends, prepared by using both DEM and MAH, as confirmed also by some difficulties to separate the polymer components as reported for Molau tests [30].

The same behaviour is observed for EPM/PA6 20/80 blends BL16 and BL17 which show the lower amount of PA6 extractable fraction and consequently a notable content of residue.

The residual and the extracted fractions were analysed by IR spectroscopy. In the case of sample treated with DEM alone (BL1-BL7, BL13, BL14) the well distinct signals of the functionalized polyolefin are present in the residue IR spectrum (Fig. 6(a)), but weak absorption bands attributable to the polyamide can be due to the formation of a very low amount of EPM-*g*-PA6 copolymers with probably short polyamide chains, soluble in the toluene. The formic acid soluble fraction contains the polyamide, but an evident peak at 1736 cm^{-1} (Fig. 6(b)) highlights the occurrence of the functionalization reaction also onto polyamide phase. In the spectrum of the

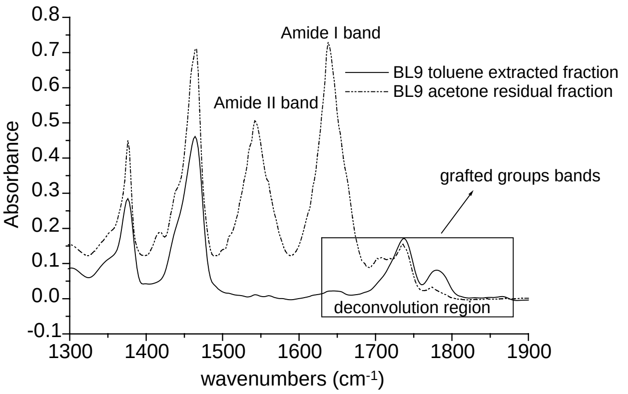


Fig. 3. IR spectra of acetone extraction residue and toluene soluble fraction of BL9 blend.

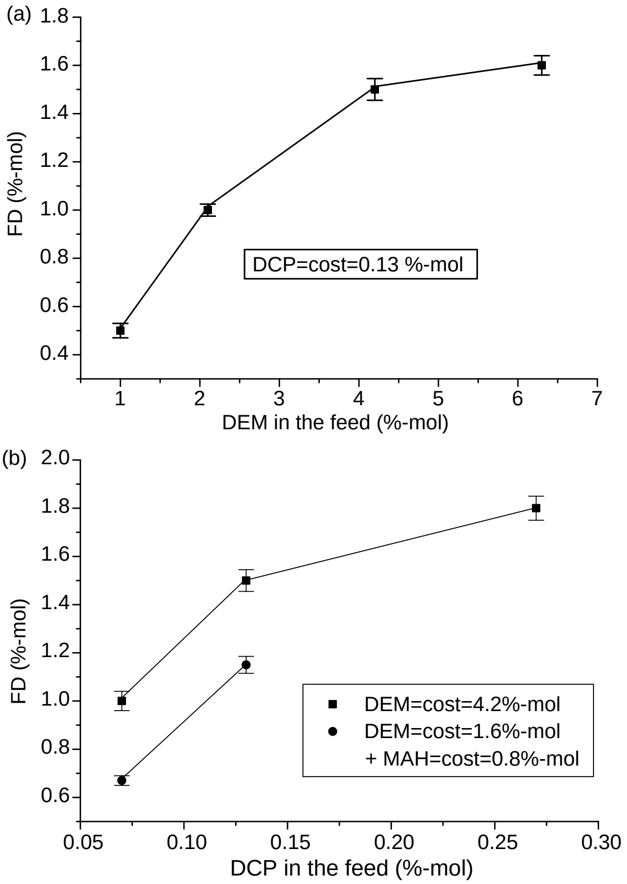


Fig. 4. FD dependence on the feed composition for EPM/PA6 80/20 blends.

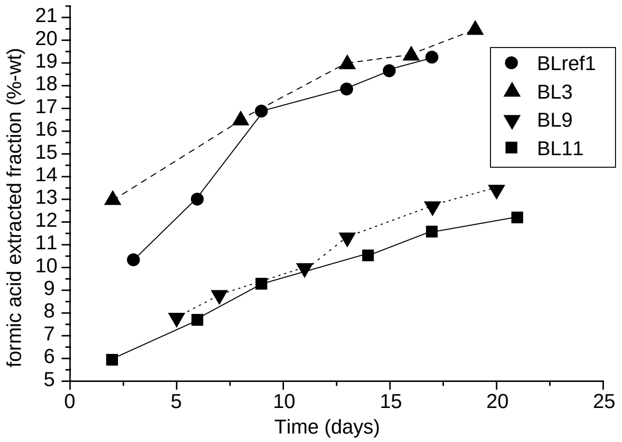


Fig. 5. Formic acid extraction curves obtained for reference blend (BLref1), BL3 (functionalised with DEM) and BL9 and BL11 functionalized with DEM: MAH 2:1 molar ratio.

residue of the sample treated with both the functionalizing reagents (BL9) strong signals related to the absorptions of EPR, PA6 and grafted functionalizing groups are well attributable (Fig. 6(c)).

The ^{1}H NMR spectrum of BL7 formic fraction (Fig. 7) shows main signals due to nylon 6 units protons. Moreover the 4.15 ppm resonance peak (resulting from $-CH_2-$ protons in ethoxyl groups) [19,31] confirms the presence of grafted maleate groups according to the occurrence of the functionalization reaction onto PA6 chains.

Again the ^{13}C NMR analysis (Fig. 8) shows six main bands that result from carbon atoms in the PA6 monomeric unit according to structure reported in the figure [32]; the weak signals at 60, 13 and 178 ppm could be attributed respectively to $-CH_2$ and $-CH_3$ and $-C{=}O$ carbon atoms of grafted ester units [33].

On the basis of the integrated area of the peaks present in the ^{1}H-NMR spectrum, the FD = 15 mol% related only to the polyamide phase soluble in the formic acid (that means the fraction which did not react with the polyolefin) was calculated. This value is very high by comparison with the average FD(s) of the blends (Table 2). The higher affinity of DEM towards the molten polyamide characterized by lower viscosity and higher polarity with respect to the EPM polymer fraction could explain this result. Indeed

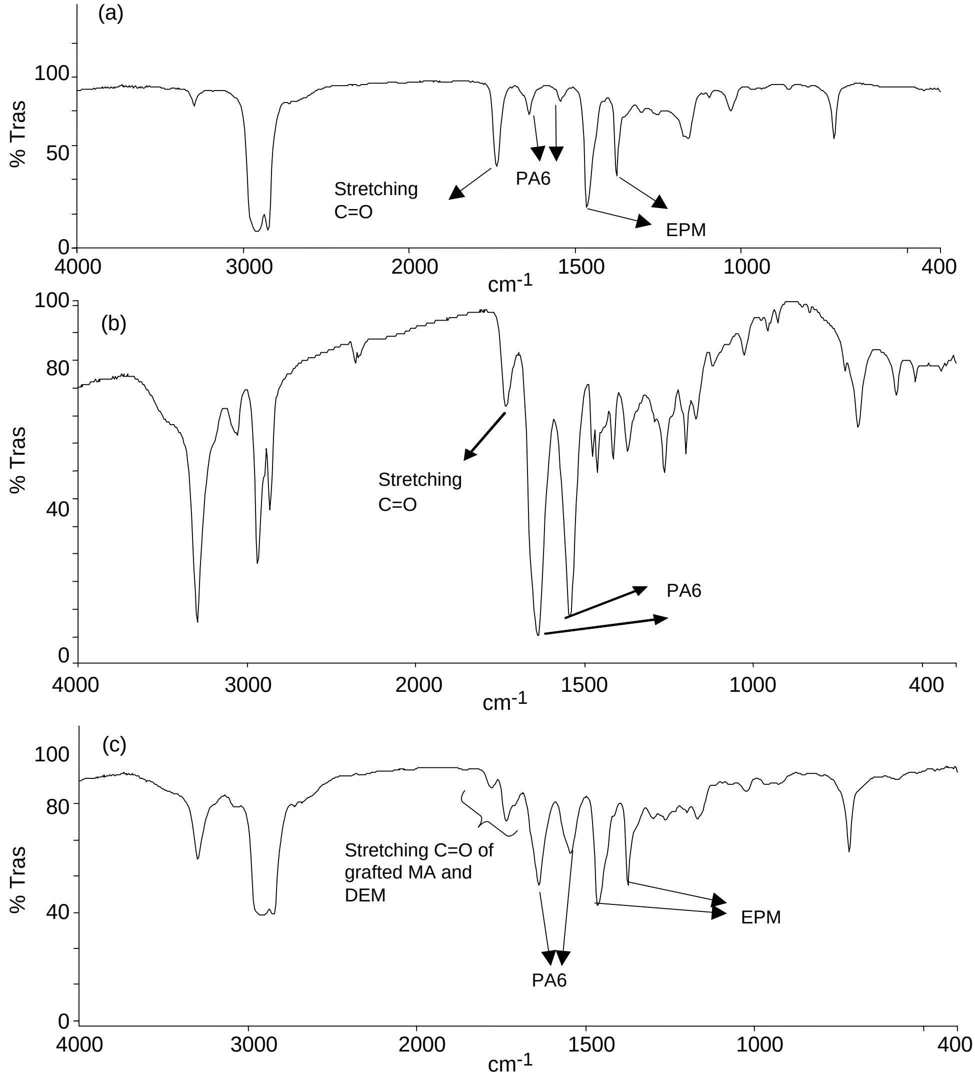


Fig. 6. IR spectra of residue (a) and formic acid soluble fraction (b) of BL3 blend and IR spectrum of residue (c) to the extraction with formic acid of BL9 blend.

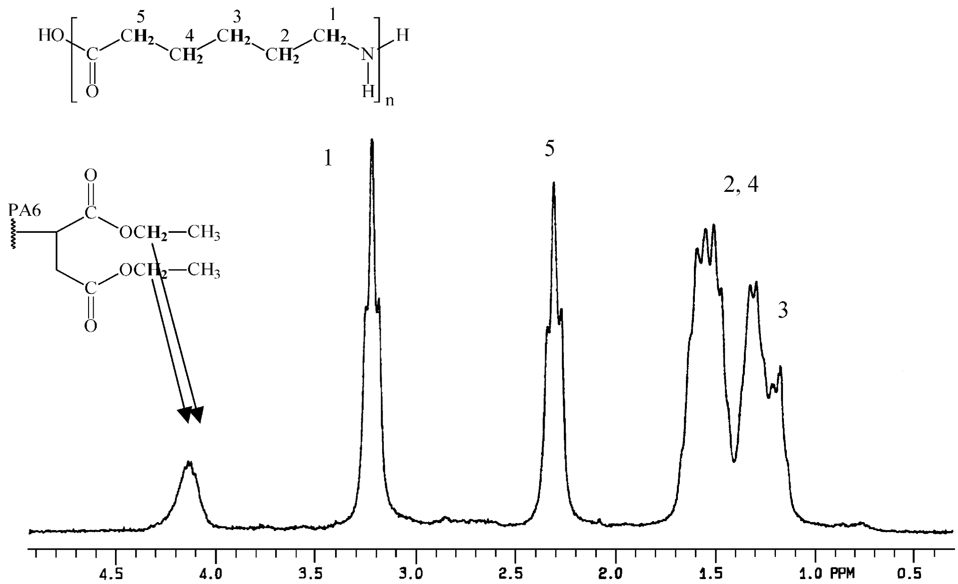


Fig. 7. ^{1}H NMR spectrum of extracted formic fraction of BL7 blend run (unreacted polyamide).

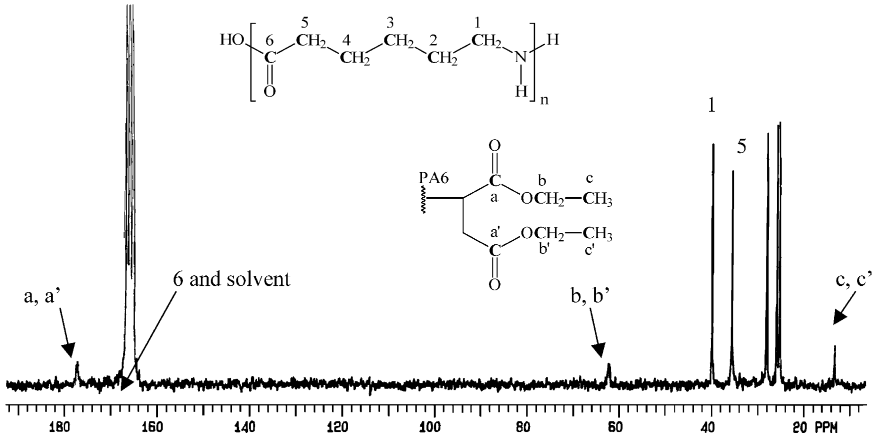


Fig. 8. ^{13}C NMR spectrum of BL7 formic extracted fraction.

when PA6 is the matrix a higher FD was reached with respect to the value obtained for the blend EPM/PA6 80/20 by using similar functionalizing feed composition (BL13 and BL7).

3.4. Molecular weight of polyamide fractions

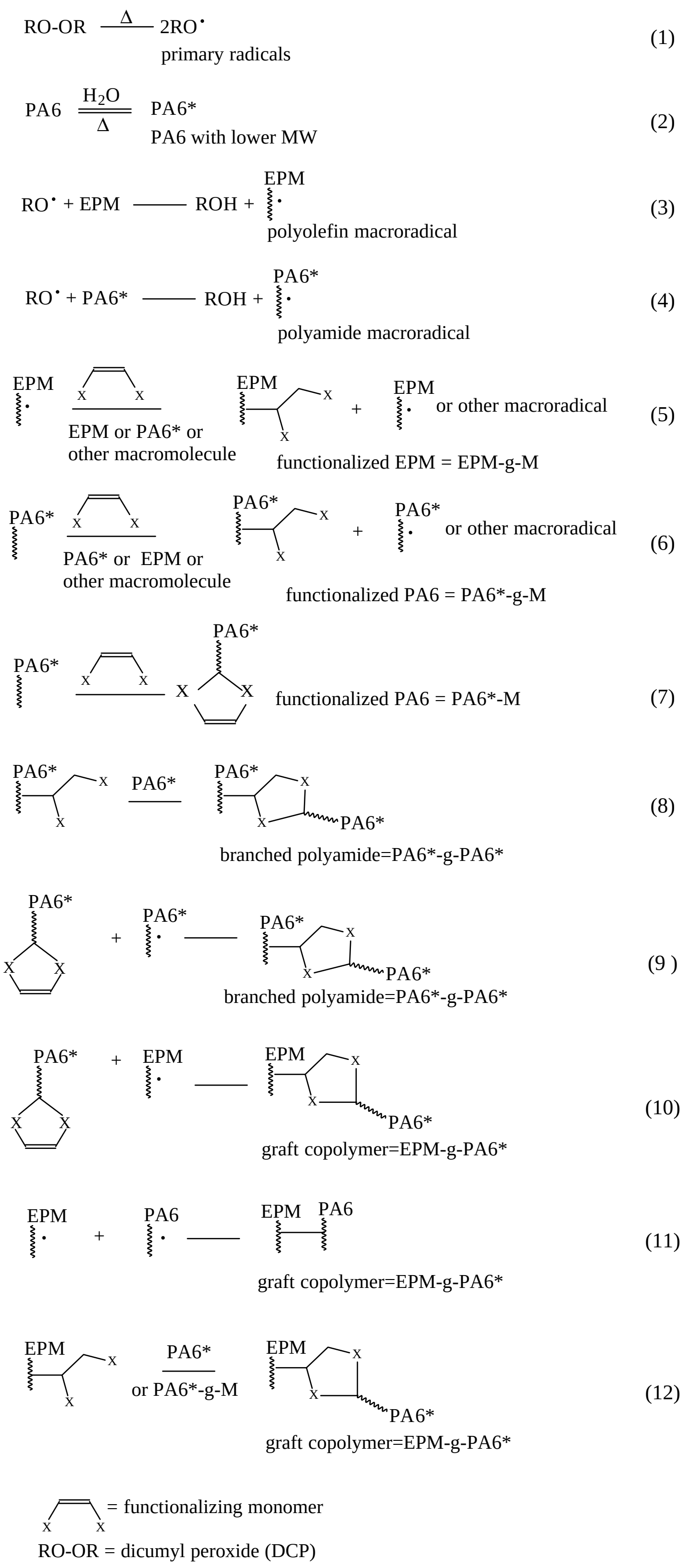
The molecular weight of the polyamide extracted from the EPM/PA6 80/20 reference blend was lower than that of

Table 3
Titration results obtained of the formic acid extracted fractions of some blends

Samples	Additives	–COOH groups (mequiv/kg)	–NH_2 groups (mequiv/kg)	Molecular weight[a]
PA6[b]	–	50	51	19,600–20,000
BLref1a formic acid extracted fraction	–	110	155	6500–9100
BL3 formic acid extracted fraction	DCP, DEM	188	200	5000–5300
BL9 formic acid extracted fraction	DCP, DEM, MAH	559	36	n.d
BLref1b	–	43	38	23,300–26,300
BL14 formic acid extracted fraction	DCP, DEM	79	46	n.d
BL16 formic acid extracted fraction	DCP, DEM, MAH	244	35	n.d

[a] Calculated on the basis of the end groups number.

[b] PA6 is the pure polyamide 6 not treated in the mixer.



Scheme 1. Hypothesis of reactions mechanism.

the original crude polyamide (Table 3), whereas that of the EPM/PA6 20/80 reference blend was increased according to the shift of the equilibrium between water and molten polyamide [34].

The titration analyses of selected formic acid extracted fractions gave a COOH/NH_2 molar ratio around 1 when maleates were not used. In the presence of DEM a slight larger value of COOH than NH_2 is observed, (from 1.1 to 1.7 with

Table 4
Evaluation of the number of PA6 grafted chains in the EPM–PA6 copolymer

Samples	Composition EPM/PA6 wt/wt	PA6 wt% in the copolymer	EPM wt% in the copolymer	R^a
BL9	80/20	12.9	87.3	1.0
BL11	80/20	17.1	82.9	1.5
BL16	20/80	35.1	64.9	1.2
BL17	20/80	35.4	64.6	1.2

[a] $R = ((\%\text{wtPA}/\text{MnPA})/(\%\text{wtEPM}/\text{MnEPM}))$ where wt% PA6 and wt% EPM derived from the composition of the residue; MnPA6 derived from titration results and MnEPM was 55,200 as reported in experimental part. The molecular weight of PA6 for blends was evaluated from the titration results of corresponding reference blends.

PA6 going from 20 to 80% in the mixture). In the presence of MAH this ratio assumes higher values, ranging from 7 to 15 (Table 3).

In particular when MAH is present (BL9, BL16) a high number of COOH end groups is present due to the hydrolysis of succinic anhydride grafted groups. The lowering of the number of NH_2 terminals for blends BL9, BL14 and BL16 is also related to the occurrence of the reaction of maleic anhydride, anhydride (DSA) or ester (DES) grafted groups with terminal amine groups of nylon (Scheme 1).

The number of PA6 chains grafted on a EPM macromolecule, R, (Table 4) was very indicatively evaluated on the basis of the residue composition and the ratio between the molecular weight of PA6 (derived from titration results for BLref1a and BLref1b) and the molecular weight of EPM.

As R is ranging from 1.0 to 1.5 in all the blends, the average structure of copolymer consists of a functionalized EPM macromolecule bearing a polyamide side chain.

3.5. Thermal and morphological properties of the blends

The DSC of the acetone extraction residues derived from the 80/20 EPM/PA6 blends shows a slight decreasing of PA6 melting temperature and ΔH_m (for functionalized blends). A weak fractionated crystallization phenomenon [35] is observed for the reference blend (BLref1a) and for few reactive blends (BL2, BL3, BL8) probably due to the poor dispersion of the polyamide phase.

In fact the SEM analysis for this kind of blends showed that the dispersed phase diameter does not decrease by processing the blend with the functionalizing reagents (BLref1a in comparison with BL3, Fig. 9), and the particles are well defined by shape (round) and dimension (about 1–2 μm). In the case of the treatment with both MA and DEM (BL9 Fig. 9(c)) the morphology of the dispersed phase is not homogenous: the shape is not round for all the particles and the dimension varies from 1 to about 10 μm. Besides a better adhesion of the PA6 domains to the matrix could be noticed in spite of the presence of particles with a very large diameter. The similar blends obtained by a two steps reactive blending show a reduced size of the dispersed phase with respect to the blends obtained by the one-step processing. Migration phenomena of the functionalizing reagents towards the polyamide phase during the one-step reactive processing could be responsible for the formation of large amount of functionalized (and branched) nylon chains and thus producing a lower content of graft copolymers (EPM-*g*-PA6) able to stabilize the interface.

In the case of 20/80 EPM/PA6 blends a notable reduction of the dimension of the dispersed phase (the polyolefin, EPM) has been observed for all the blends analysed by SEM microscopy (Fig. 10). The results can be explained on the basis of a

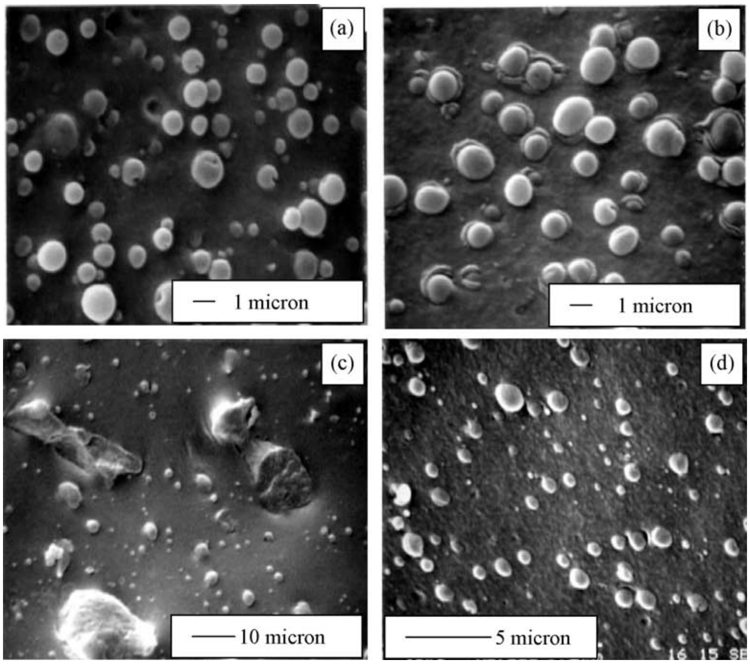


Fig. 9. SEM images of cryogenically broken surfaces of BLref1 (a), BL3 (b), BL9 (c) and BLref2 blends.

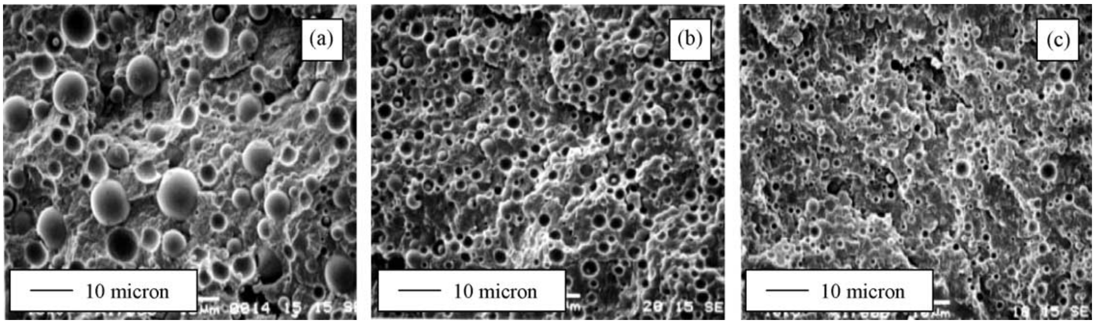


Fig. 10. SEM images of the cryogenically broken surfaces of BLref1b (a), BL14 (b) and BL15 (c) blends.

substantially higher efficiency in the EPM-*g*-PA6 copolymer formation (for examples for blends BL15 and BL16 the toluene extractable polyolefin fraction is ≤ 1 wt%) [35].

In pseudoductile matrix blends, as in the case of PA6/EPM 80/20 wt/wt blends, a tough-brittle transition occurs at a critical particle size [36–39] which increases with the increasing of the rubber fraction and is related to the distance between the particles. The critical surface-to-surface interparticle distance τ_c is independent of particle size and rubber fraction, and is characteristic of a plastic matrix. Hence a PA6-rubber blend is tough when the interparticle distance is smaller than τ_c.

The dispersed phase diameter value of about 1 μm, obtained by using both DEM and MAH in the blend BL16 allows to calculate an inter-particle distance τ value by the equation $\tau = d[(\pi/6\phi_r)^{1/3} - 1]$, where ϕ_r is the rubber volume fraction and d is the particle diameter. The inter-particle distance of 0.38 μm allows predicting good impact properties for this blend [39,40].

Some PA6/EPM blends with a PA6 matrix were produced in a twin screw extruder with $L/D = 40$ and screw diameter of 35 mm at a temperature of 230 °C. The DEM, MAH and DCP were fed into the extruder in the amount of 0.65, 0.14 and 0.035% by weight (with respect to the polymer mixture weight). In the comparative two steps process a functionalized EPM was used with a MFI at 230 °C and 2.16 kg of 1.3 and FD = 1.1% by weight. The mechanical tests were then performed on injection moulded specimen.

The impact properties of the one-step blends (containing different polymers EPM/PA6 ratios) are improved with respect to pure PA6 and the Izod impact strength increases with the increasing of EPM content (Fig. 11). Modulus and impact

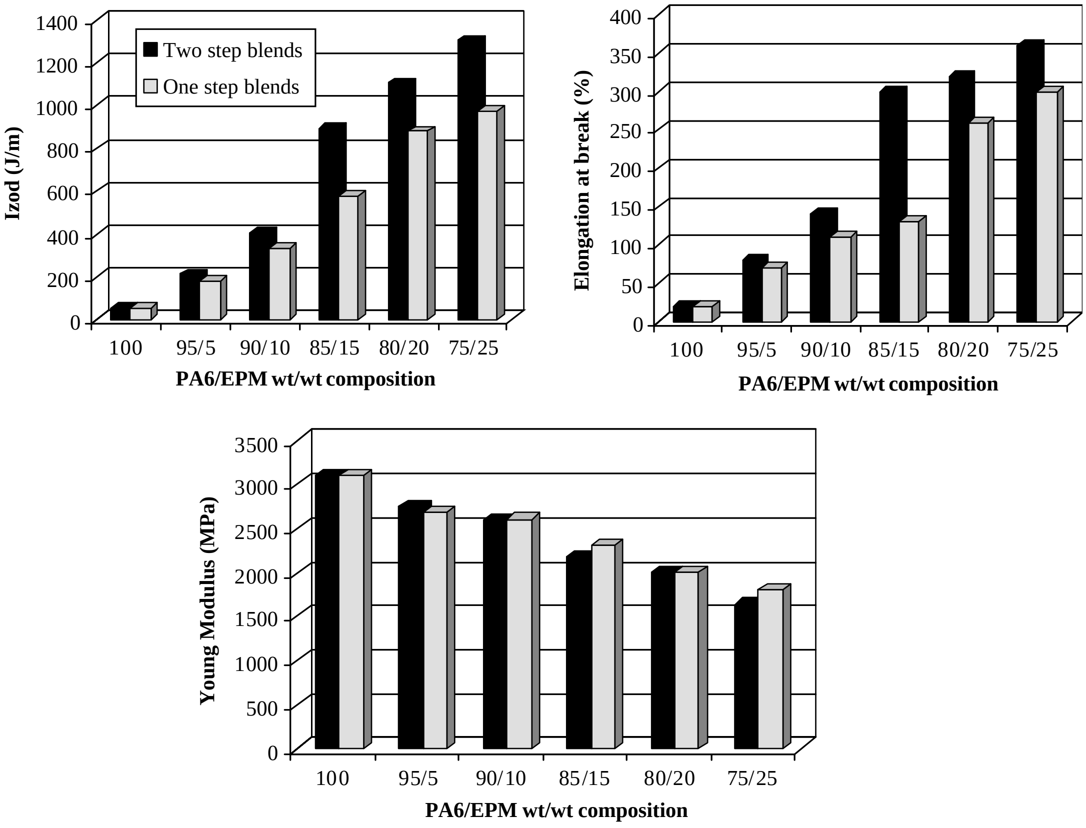


Fig. 11. Mechanical properties of the one-step and two-step blends: (a) Izod impact strength; (b) elongation at break; (c) Young modulus.

strength values are comparable with those obtained in the case of materials produced by two step ones.

A similar result was observed for elongation at break, a parameter that depends strongly on interfacial adhesion [41], that is on the amount of formed grafted copolymer. The best results in terms of elongation were collected for PA6 content higher than 75% by wt thus confirming the morphology evidences. These preliminary tests carried out on samples from extrusion testify that good mechanical properties can be obtained by using the advantageous one-step methodology in particular for PA6 rich compositions that can be used as high impact and shock resistant materials.

4. Final remarks

In the present work the one-step reactive blending process of EPM/PA6 (20/80 and 80/20 wt/wt) mixtures in the presence of maleates and peroxide was investigated. The occurrence of functionalization reactions onto both the polymers located in different phases was observed and related to the graft-copolymer formation. The morphology and properties of the prepared blends were analysed and compared to the two steps process.

On the whole the results evidenced that the one step process produced blends different from that obtained by the two steps process in terms of macromolecular structure and also morphology. Indeed in the former case carried out by addition of the functionalizing reagents to the molten EPM/PA6 blends, collected results indicated the formation of at least three different new polymer products, namely: the functionalized EPM, the modified PA6, and the graft EPM-PA6 copolymers.

A very simplified reaction mechanism (Scheme 1) can be proposed based on the functionalization reaction starting with the formation of primary radicals (1) which generate the macroradicals (3) and (4) probably by hydrogen abstraction from polyolefin and polyamide chains. The functionalized EPM (EPM-*g*-M) is formed by reaction of the macroradicals with the unsaturated monomers following by transfer reaction to produce again macroradicals (5). The functionalization process through macroradicals (6) similar to this described for the polyolefin produces a polyamide characterized by the presence of ester or anhydride groups grafted onto backbone (PA6*-*g*-M). PA6 is also subjected to the degradation process (2) giving (PA6*). The condensation reaction (7) between the end amino groups and the unsaturated ester or anhydride monomers can produce an end-functionalized polyamide (PA6*-M). A similar condensation reaction (8) between the end amino groups and the anhydride succinic groups grafted onto backbone of polyamide produces a branched polyamide (PA6*-*g*-PA6*). The same polymeric product can be formed by the macroradical polyamide reaction (9) with PA6*-M. The graft copolymers, EPM-*g*-PA6* is formed by polyolefin macroradical reaction with PA6*-M (10) and (11) or condensation reaction between the end amino groups of polyamide chains and the grafted groups onto polyolefin chains (12).

The observed functionalization degree showed that the grafting process of the polyamide (reaction (6) and (7)) cannot be considered as secondary reactions and is probably favoured by the larger affinity of polar molecules (like as DEM and MA) toward the polar polymer phase.

The level of reciprocal grafting (by reactions (10)–(12)) is particularly improved in the presence of MAH, probably more reactive at the interface (even if the reactivity of DEM in similar reactions is proved and reported in literature for two steps reactive blending) [22]. This could signify that an efficient reactive system involves condensation reaction (like (12)) and could be really induced in the presence of functional reactive monomer but needs the presence of grafted polyolefin at the interface thus suggesting the use of functional low molecular reagents more interactive with the apolar phase.

The thermal and morphology analysis showed significant improvement of the compatibilityby using both the functionalizing monomers although the presence of a large amount of functionalized/branched polyamide renders the one-step process more complex and difficult to control.

In polyamide matrix blends the one step process seems promising to obtain toughened polyamide material. Anyway the mechanical performances of the one step blends are slightly worse than those obtained by the two step process. The data reported here provide new information about the molecular structure of the products obtained in the compatibilization one step process of PO with PA. To achieve a better control of the process, functionalizing reagents more selective for the polyolefin phase, on the basis of chemical affinity or reactivity, will be tested in due course.

Appendix A

Different EPM/PA6 80/20 and 20/80 by weight blends containing a determined amount of polydiethyl fumarate (PDEF) [27] were produced in the Brabender mixer (Table A1).

The obtained mechanical blends were hot-press moulded and a FT-IR spectrum was recorded. The area of the 1736 cm^{-1} band (A1 due to the grafted carbonyl groups stretching) and the area of the 1460 cm^{-1} band (A2 CH_2 bending) for EPM/PA6 80/20 blends or the area of the 720–699 cm^{-1} band (CH_2 rocking and NH wagging) for EPM/PA6 20/80 blends were calculated and the corresponding ratios A_1/A_2 were reported versus the FD values determined on the basis of the mixture compositions.

For each sample three different films were prepared and consequently three different values for A_1/A_2 ratio were determined. By defining $X=A_1/A_2$ the expression of s_m (standard deviation) is:

$$s_\mathrm{m}=\sqrt{\frac{\sum_{i=1}^{N}[X_i-\bar{X}]^2}{N(N-1)}} \qquad \text{(A1)}$$

where $\bar{X}$ = medium area ratio and N is the number of area ratio

Table A1
Compositions of EPM/PA6/PDEF blends, corresponding FD and A_1/A_2 ratio values

Samples	EPM (g)	PA6 (g)	PDEF (g)	FD[a] (mol%)	A_1/A_2 medium value	s_m[b]
BLref1a	16	4	–	0	0.0728	0.004
Mix1	16	4	0.38	0.404	0.1784	0.026
Mix2	16	4	0.79	0.807	0.2357	0.008
Mix3	16	4	0.91	0.955	0.3220	0.049
Mix4	16	4	1.14	1.197	0.3773	0.010
Mix5	16	4	1.52	1.600	0.4439	0.050
Mix6	16	4	1.92	2.001	0.5332	0.049

[a] Corresponding to the content of PDEF.

[b] Standard deviation for A_1/A_2 values (Appendix A).

values determined. For the blends used to perform the calibration $N=3$ because three films have been analysed.

The lines equation $FD=A+BX$ as resulted by the fitting procedure were:

$$FD = -0.373 + 4.353X \text{ for EPM/PA6 80/20 blends}$$

$$FD = -0.214 + 5.487X \text{ for EPM/PA6 20/80 blends}$$

By calculating the A_1/A_2 ratio values of functionalized blends on the basis of the calibration curve it was possible to determine the FD values. Again the determination of A_1/A_2 ratios was performed onto three different spectra derived from three films for each sample.

s_{FD} values reported in Table 2 have been calculated considering that:

$$FD = A + BX = f(A,B,X) \tag{A2}$$

The variance expression is:

$$s_{FD}^2 = \left(\frac{df}{dA}\right)^2 s_A^2 + \left(\frac{df}{dB}\right)^2 s_B^2 + \left(\frac{df}{dX}\right)^2 s_m^2 \tag{A3}$$

By inserting the correct values of derivative expressions and A and B errors as s_A and s_B (derived by a fitting procedure) the following expression has been obtained:

$$s_{FD} = \left[0.00263 + 0.0218X^2 + 18.9510 s_m^2\right]^{1/2}$$

$$s_{FD} = \left[0.00298 + 0.0079X^2 + 30.1112 s_m^2\right]^{1/2}$$

The s_{FD} values are generally limited to the second decimal figure and by increasing the X value (which corresponds to high FD values) the error increased, but it depends also on the s_m parameter which is directly affected by a certain unhomogeneity of the mixtures due to the presence of immiscible polymers.

Appendix B

The functionalization degree for samples characterized by the presence of different grafted groups have been derived from a deconvolution methodology already applied to EPM samples functionalized with both maleic anhydride and diethyl maleate [24,26]. In these cases it is possible to evaluate the FD values derived from different groups: the FD values related to the grafted ester groups (FD_{DEM}) has been determined by considering again the ratio between the area of the band at 1736 cm^{-1} (calculated after deconvolution) and at 1460 cm^{-1} by the following equation:

$$FD_{DEM} = \frac{\varepsilon_{1460}}{\varepsilon_{DES}} \frac{A_{DES}}{A_{1460}} \tag{B1}$$

A_{DES}, 1736 cm^{-1} band area (νC=O of diethyl succinate); A_{1460}, 1460 cm^{-1} band area (bending CH_2); ε_{DES}, integral molar absorptivity coefficient for 1736 cm^{-1} band; ε_{1460}, integral molar absorptivity coefficient for 1460 cm^{-1}band.

The error has been calculated by the following equation:

$$s_{FDDEM} = \left[\left(\frac{\varepsilon_{1460}}{\varepsilon_{DES}} \frac{1}{A}\right)^2 s_{ADES}^2 + \left(-\frac{\varepsilon_{1460}}{\varepsilon_{DES}} \frac{A_{DES}}{A_{1460}^2}\right)^2 s_{A1460}^2\right]^{1/2} \tag{B2}$$

by considering that $s_{A1460}^2 \ll s_{ADES}^2$, the equation could be written as:

$$s_{FDDEM} = \left[\left(\frac{\varepsilon_{1460}}{\varepsilon_{DES}} \frac{1}{A}\right)^2 s_{ADES}^2\right]^{1/2} \tag{B3}$$

The determination of the FD values related to the grafting of MAH is more complex due to the presence of different carbonyl groups derived from maleic anhydride (as reported in Fig. 4) and required a deconvolution approach [24].

FD_{MAH},due to succinic anhydride (SAH) and succinic acid (SA) groups, can be written [18] as:

$$FD_{(MAH)} = \frac{\varepsilon_{1460}}{\varepsilon_{SA}} \frac{A_{SA}}{A_{1460}} + \frac{\varepsilon_{1460}}{\varepsilon_{SAH}} \frac{1}{A_{1460}} \sum_{1}^{4} A_{SAH\,i} \tag{B4}$$

ε_{SA}, molar absorptivity coefficient for 1717 cm^{-1} band; ε_{SAH}, integral molar absorptivity coefficient for succinic anhydride bands; A_{SA}, 1717 cm^{-1} band area; A_{SAHi}, SAH band areas.

As above the error could be calculated by the following equation:

$$s_{\mathrm{FD(MAH)}} = \left[\left(\frac{\varepsilon_{1460}}{\varepsilon_{\mathrm{SA}}} \frac{1}{A_{1460}} \right)^2 s^2_{\mathrm{ASA}} + \left(\frac{\varepsilon_{1460}}{\varepsilon_{\mathrm{SAH}}} \frac{1}{A_{1460}} \right)^2 \sum_1^4 s^2_{i\mathrm{SAH}} \right]^{1/2} \tag{B5}$$

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