Effect of Structure of Functionalizing Molecules on the Inter-Macromolecular Reactions and Blending of Poly(ethylene-*co*-propylene) (EPM) with Poly(6-aminohexanoic Acid) (PA6)

by **Elisa Passaglia**[a]), **Maria-Beatrice Coltelli**[b]), and **Francesco Ciardelli***[a])[b])

[a]) CNR-ICCOM Pisa Section, Department of Chemistry and Industrial Chemistry, via Risorgimento 35, I-56121 Pisa

[b]) PolyLab-INFM, c/o Department of Chemistry and Industrial Chemistry University of Pisa, via Risorgimento 35, I-56126 Pisa

Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

Two different functionalizing systems, *i.e.*, monohexadecyl maleate (= hexadecyl hydrogen (2*Z*)-but-2-enedioate) in the presence of dicumyl peroxide (= bis(1-methyl-1-phenylethyl) peroxide) or 4-carboxybenzenesulfonazide (= 4-(azidosulfonyl)benzoic acid), were used in distinct experiments to perform in a one-step procedure the formation of a EPM–PA6 graft copolymer, necessary to obtain a compatibilized blend, from a molten mixture of ethylene–propylene copolymer (EPM) and polyamide 6 (PA6). The characterization of the graft polymer by selective solvent extraction of the blends and the subsequent IR and NMR analysis of the various fractions established the occurrence of functionalization reactions preferentially onto the polyolefin with both reagents. Also the formation in good yield of graft copolymers at the phases interface was observed. Moreover, the morphology and thermal characterizations of the blends by means of SEM and DSC analyses were used to evaluate the compatibilization extent in comparison with blends obtained by the conventional two-step procedure or by the one-step procedure with commercial maleic acid derivatives.

Introduction. – The one-step reactive blending of mixtures of polyolefins and polyamides was for the first time employed by *Lambla* and co-workers [1–3] for blending low-density polyethylene (LDPE) or high-density polyethylene (HDPE) with polyamide 11 (PA11) by treatment with various peroxides alone or in the presence of maleic anhydride (MA), reagents that were used in low concentration to prevent or hinder secondary reactions. The removal of the ungrafted maleic anhydride favored the interchain reactions involving MA-grafted polyolefin macromolecules and the terminal NH_2 groups of the polyamide [4][5]. These reactions are essential to achieve the compatibility necessary for the modulation of final properties [6][7].

Recently we obtained compatibilized blends of ethylene–propylene copolymer (EPM) and polyamide-6 (PA6) by performing the reaction in the presence of peroxide and a mixture of maleic anhydride/diethyl maleate (DEM) of different composition [8] with the concomitant functionalization of polyamide and formation of branched polyamide. The functionalization degree of the polyamide phase was generally very high (reaching up to 15 mol-%), favored by a larger affinity of polar DEM and MA toward the polar polymer phase. The grafting between the two polymers was affected by the extent of the polyamide branching, which consumed the functionalizing monomers [9].

In an attempt to limit PA6 functionalization and branching, we now report the one-step reactive blending of EPM and PA6 by using new functionalizing monomers having better affinity for or selectivity to react with the polyolefin.

Monohexadecyl maleate (=hexadecyl hydrogen (2*Z*)-but-2-enedioate; MEM, *Fig. 1*) was used in the former case concerning affinity since it is characterized by a long aliphatic chain providing high affinity for the polyolefin phase. Its reactivity towards the terminal NH_2 groups of PA6 was, on the other side, demonstrated to be similar to MA and DEM [10].

Monohexadecyl maleate (MEM)

4-(Azidosulfonyl)benzoic acid (ASBA)

Fig. 1. *Functionalizing monomers MEM and ASBA*

For the latter process concerning selectivity, 4-(azidosulfonyl)benzoic acid (ASBA; *Fig. 1*) was studied as grafting molecule, as it preferentially reacts by insertion into the C−H of tertiary C-atoms [11] present in EPM, but not in PA6. It can be used without peroxides, often responsible of secondary crosslinking reactions or thermo-oxidative degradation [12]. Moreover, the presence of a potentially reactive carboxylic group makes it suitable for the reaction with terminal NH_2 groups of PA6.

Results and Discussion. – *One-Step Functionalization with MEM and Dicumyl Peroxide.* MEM and dicumyl peroxide (=bis(1-methyl-1-phenylethyl) peroxide; DCP) were used in different molar ratios for the blending of EPM/PA6 at 230°. The torque behavior during the mixing and in particular the end values (*Table 1*) seemed to be depending on the MEM/DCP ratio; the torque value decreased with increasing MEM due to the plasticizer effect and minor incidence of inter-chain reactions.

The IR spectrum (film; *Fig. 2*) of the acetone-extraction residue (from BLemi1 to BLemi3) showed the absorption bands characteristic of both the polymers and a very complex outline in the carbonyl-stretching region. The band at 1707 cm^{-1} due to acid groups and the band at 1730 cm^{-1} due to ester groups are both present as in the functionalizing monomer MEM. The bands at 1775 and 1865 cm^{-1} can be attributed to the asymmetrical and symmetrical stretching, respectively, of a grafted cyclic anhydride-function (succinic anhydride), formed by a cyclization reaction at high temperature [10] (*Fig. 3*).

The 1700–1900 cm^{-1} range of the IR spectrum was analyzed by a deconvolution approach [8][13]. In this case, we considered four bands due to the grafted groups and one due to the partial overlapping with the amide-I band (1640 cm^{-1}). All the areas related to the bands of different functional groups were calculated, and a relative trend of the functionalization degree was evaluated by comparing the area ratios with a reference band at 1460 cm^{-1} (bending $-CH_2$). Moreover, a rough estimate of the functionalization degree (FD) was calculated on the basis of integral absorptivity values (ε)

Table 1. *Starting Composition of One-Step Reactive-Blending Runs of EPM with PA6*

Run	Functionalizing reagents [mol-%]	MEM/DCP [mol-ratio]	Final torque [N·m]
BL00	none	–	3.2
BLemi1	MEM (1.04), DCP (0.07)	15	2.6
BLemi2	MEM (1.04), DCP (0.14)	7.5	2.6
BLemi3	MEM (2.08), DCP (0.07)	30	1.8
BLemi4	MEM (2.08), DCP (0.23)	9	3.4
BLemi1TS[a])	–		5.5
BLsz1	ASBA (0.4)		3.1
BLsz2[b])	ASBA (0.34)		3.2
BLsz3[b])	ASBA (0.34)		3.3
BLszTS[a])	–		3.1

[a]) Two-steps blends produced by blending with *Nylon 6* the previously functionalized EPM samples (with MEM and DCP for BLemiTS and with ASBA for BLszTS). [b]) Added Na_2SO_4: 0.5 wt-% for BLsz2 and 1 wt-% for BLsz3.

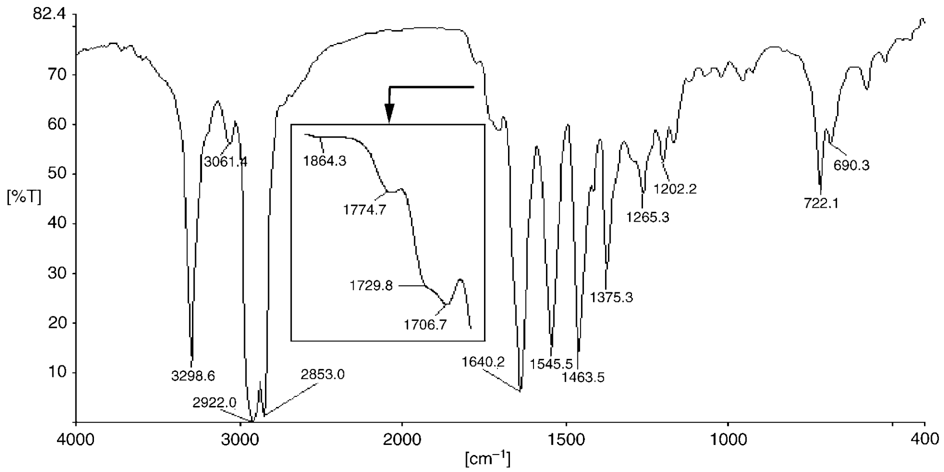


Fig. 2. *IR Spectrum of BLemi1 after extraction with acetone*

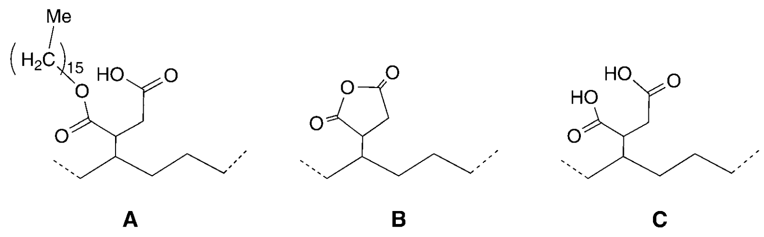


Fig. 3. *Grafted functional groups derived from MEM*

obtained for the C=O stretching of grafted groups at 1707, 1730, and 1780 cm^{-1} [14], and the polymer band at 1460 cm^{-1} [8] (*Table 2*).

Table 2. *Functionalization Degree of EPM/PA6 Blends Obtained by One-Step Runs with MEM/DCP*

Run	Feed composition [mol-%])	A_{1707}/A_{1460}	A_{1730}/A_{1460}	A_{1780}/A_{1460}	FD [mol-%][a])
BLemi1	MEM (1.04), DCP (0.07)	0.302	0.177	0.079	0.37
BLemi2	MEM (1.04), DCP (0.14)	0.227	0.382	0.205	0.53
BLemi3	MEM (2.08), DCP (0.07)	0.215	0.386	0.027	0.45
BLemi4	MEM (2.08), DCP (0.23)	0.433	1.088	0.444	1.32

[a]) Number of grafted MEM groups per 100 monomer units calculated on the basis of the blend compositions.

The ratio A_{1730}/A_{1460} due to ester groups was doubled when the peroxide feed concentration was even doubled, by keeping constant the amount of fed MEM. Under the same conditions, the ratio A_{1780}/A_{1460} due to grafted anhydride groups was more than doubled (see, *e.g.*, BLemi1 *vs.* BLemi2). Probably during blending, MEM was converted into the more reactive maleic anhydride prior to the grafting [15] [16]. However, the approximated FD was higher for lower MEM/DCP ratios (obtained by increasing the amount of DCP at constant amount of MEM), in agreement with results obtained for polyolefins [13] [17–20].

The successive selective extraction of the BLemi1 product with formic acid and heptane allowed us to separate the unreacted PA6 (*Fig. 4*) and the unreacted EPM (*Fig. 5*) from a final residue. This final residue was characterized by intense IR bands of either EPM and polyamide PA6 (*Fig. 5*), thus confirming the occurrence of the intermacromolecular reaction between the two polymers to a larger extent than that obtained for the mechanical mixture (BL00, *Table 3*).

Table 3. *Selective Acetone, Formic Acid, and Heptane Extractions of the Blends from the One-step Runs.* n.d. = not determined.

Run	Acetone-extract fraction [wt-%]	Formic acid extract fraction [wt-%]	Heptane-extract fraction [wt-%]	Residue [wt-%]
BL00	0.7	19.6	76.0	1.5
BLemi1	5.4	16.6	45.5	32.5
BLemi2	5.3	16.2	n.d.	n.d.
BLemi3	8.8	17.8	n.d.	n.d.
BLsz1	1.1	17.7	60.2	21.0

The copolymer composition was evaluated on the basis of the mass balance, and it contained 88 wt-% of EPM and the 12 wt-% of polyamide according to the probable formation of long EPM chains with shorter PA6 grafting. The extracted-polyamide fractions showed a higher concentration of COOH than terminal NH_2 groups confirming the reaction of NH_2 with the grafted or ungrafted MEM derivatives, as observed for maleic anhydride and its mixture with DEM in case of EPM/PA6 blends [8] or PA6 [9] (*Table 4*).

The ^{1}H-NMR spectrum of the formic acid extract fraction (PA6) of BLemi1 showed the presence of weak signals at δ 4.15, 1.2, and 0.8 (*Fig. 6*), and the ^{13}C-NMR spectrum

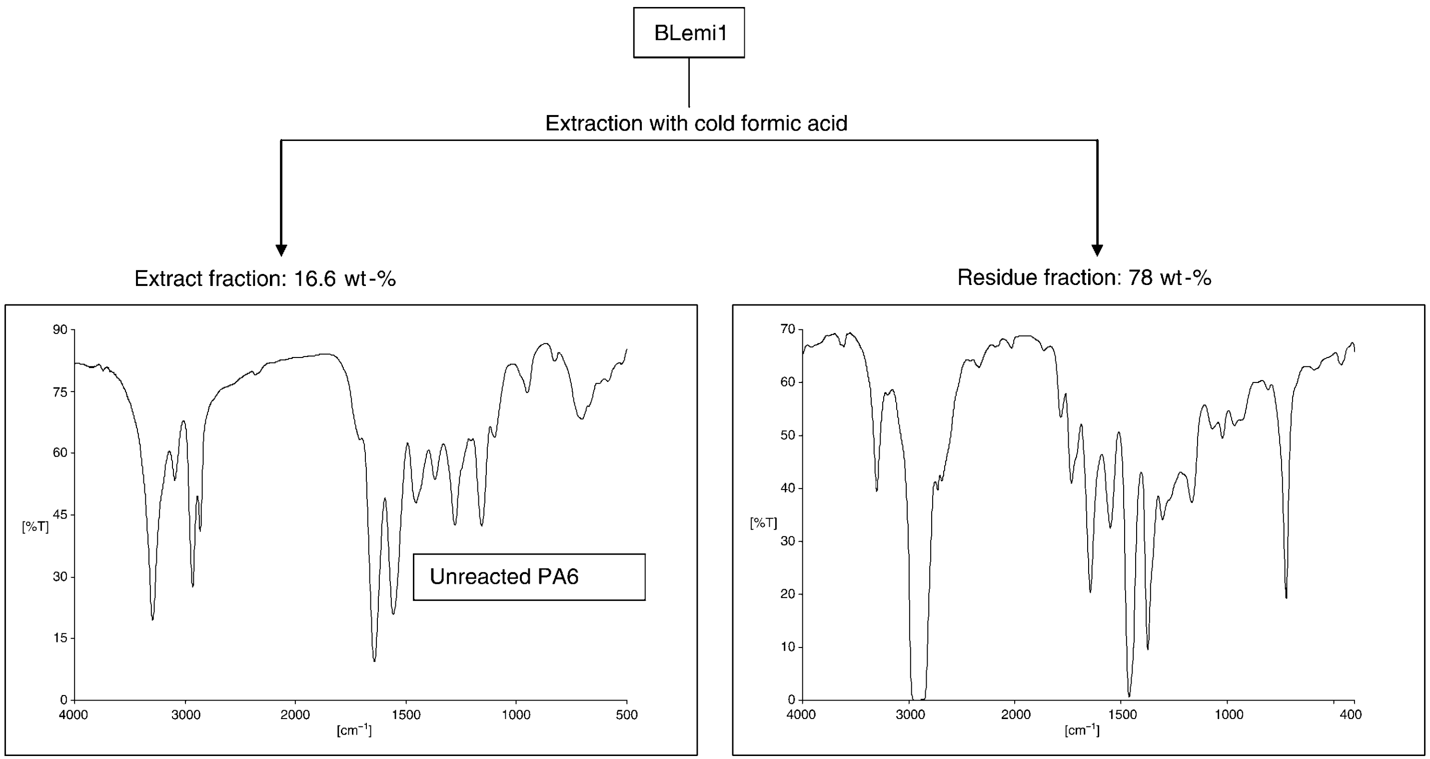


Fig. 4. *IR Spectra of the extract* (PA6) *and residue fractions after the formic acid extraction of BLemi1*

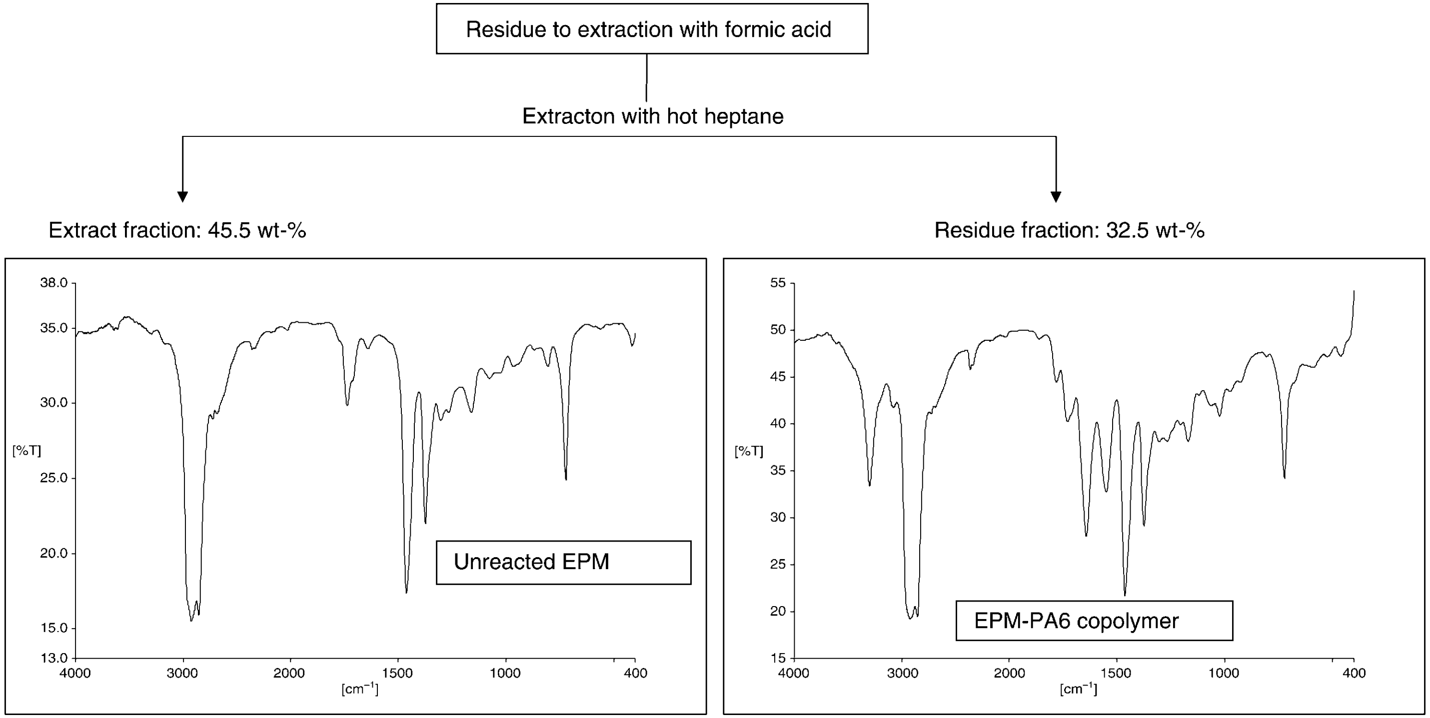


Fig. 5. *IR Spectra of heptane extraction of the residue fraction obtained by the formic acid extraction of BLemi1* (see *Fig. 4*)

Table 4. *Titration Results of the Formic Acid Extract Fraction* (unreacted PA6 fraction) *of some One-Step Blends*

	PA6[a])	BL00	BLemi1	BLemi2	BLsz1
COOH groups [10^{-3} equiv./kg]	50	110	328	196	240
NH_2 groups [10^{-3} equiv./kg]	51	155	24	12	218

[a]) PA6 is the pure polyamide 6.

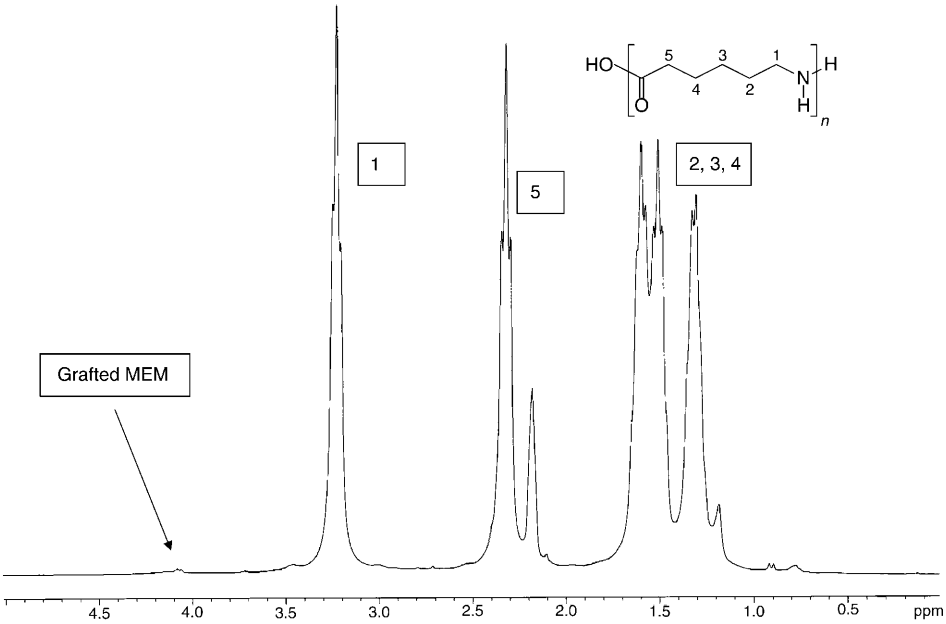


Fig. 6. *^{1}H-NMR Spectrum of the formic acid extract fraction* (PA6) *of BLemi1*

displayed several weak signals in the range δ 27–31 due to the long aliphatic chain (*Fig. 7*) as expected for grafted MEM. The functionalization degree was *ca.* 2.5 mol-%.

The morphological analysis of samples produced by the above-described one-step procedure showed that the size of dispersed phase is comparable with that of samples produced by the two-steps methodology (*Fig. 8*), and better than that of samples produced by the one-step methodology with DEM as monomer. Some differences can be noticed by changing the feed conditions. For example, the highest dispersed-phase diameter and the highest diameter dispersion were characteristic for BLemi2, *i.e.*, for the blend with the highest DCP/MEM ratio. However, the general trend confirmed that the use of MEM as functionalizing monomer seems to be very attractive for the one-step process. Indeed, its better solubility in the apolar phase gives preferential functionalization of EPM (*Scheme*, path *a*) rather than the polyamide, thus avoiding the branching of the latter [9] and leading to an easier control of the morphological

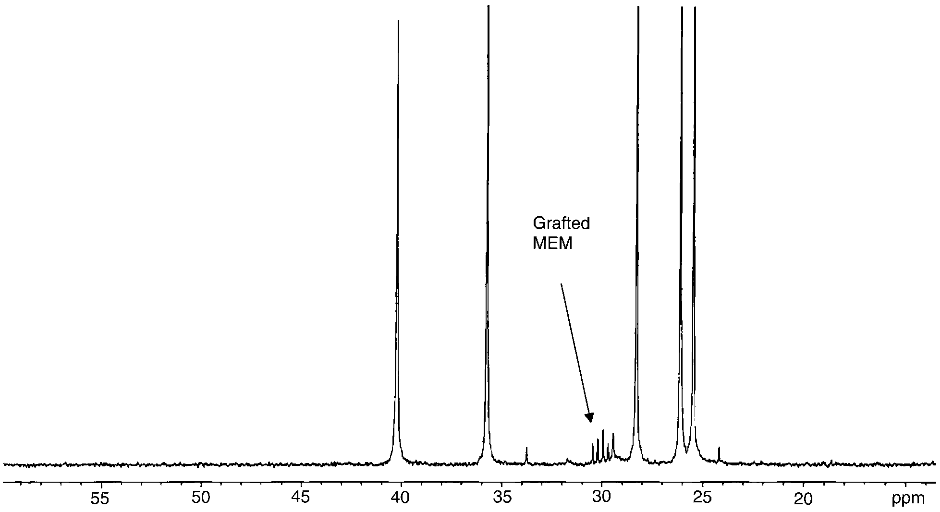


Fig. 7. *^{13}C-NMR Spectrum of the formic acid extract fraction* (PA6) *of BLemi1*

characteristics of the final blend similar to those obtained by the two-step procedure [21–23].

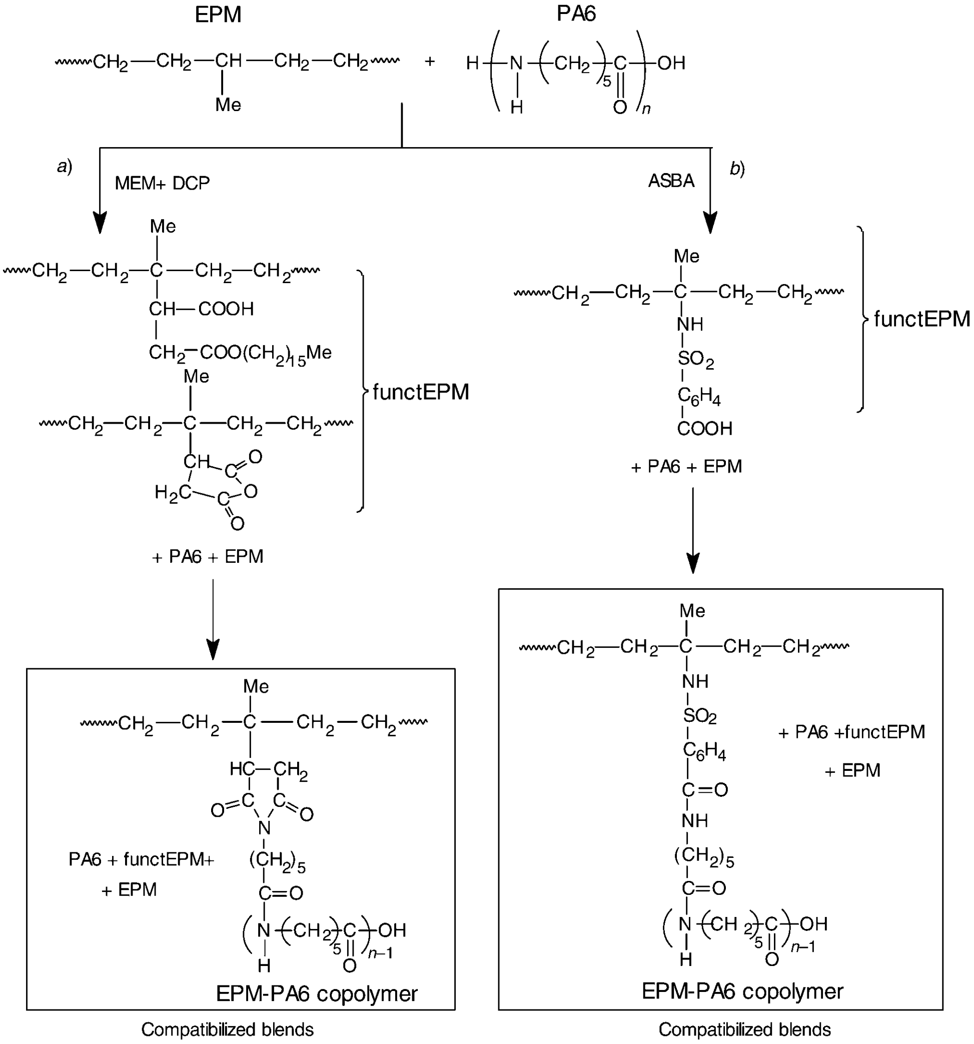
One-step Functionalization with ASBA. The possibility to functionalize polyolefins with ASBA [11] was highlighted by processing the EPM copolymer with the monomer to yield the grafted sample used to produce the two-step blend (BLszTS, *Table 1*). The presence of grafted $NHSO_2C_6H_4COOH$ groups at the polyolefin chain could be evidenced by the strong IR absorption band at 1702 cm^{-1} (*Fig. 9*) of an EPM sample treated with ASBA and extracted with hot acetone. At the same time, the treatment of PA6 with ASBA did not produce a functionalized polyamide, as shown by IR analysis (*Fig. 10*), thus confirming the preferential reactivity of ASBA towards macromolecules containing tertiary C-atoms such as the ethylene-propylene copolymers.

The blends obtained by the one-step procedure starting with EPM/PA6 and ASBA (BLsz1 to BLsz3 in *Table 1*) were first extracted with acetone, and then successively with formic acid and heptane: a consistent amount of residue fraction containing both polymer bands evidenced the formation of grafted EPM-PA6 copolymer (*Fig. 11* and *Scheme*, path *b*).

From the mass balance, the composition of the copolymer was calculated as being *ca.* 84 wt-% of EPM and 16 wt-% of polyamide. In fact, the titration results obtained with the formic acid extract fraction of BLsz1 confirmed the occurrence of a certain extent of degradation and agreed with a $\overline{M_n}$ of the polyamide of *ca.* 4600 Dalton (*Table 4*); on the basis of this data, we suppose that, on average, two chains of PA6 are grafted onto one chain of EPM.

DSC (Differential scanning calorimetry) analysis (*Table 5*) indicated a weak decrease of the enthalpy and crystallization temperature for blend BLsz1, in agreement with a better compatibility as compared to the reference blend [21]. In the presence of Na_2SO_4 (runs Blsz2 and BLsz3), used to improve the yield of copolymer by condensation (*Scheme*, path *b*), a further decreasing of the crystallization temperature was

Scheme. *Reactions Occurring in the One-Step Compatibilization Procedure of PA6 and EPM Performed with MEM and DCP and with ASBA*



observed, while the crystallization enthalpy was increased. This last result is probably related to the lowering of the molecular mass of the polyamide during the blending.

The morphology of the blends, compatibilized with ASBA either by the one-step or two-steps procedure, is quite similar and comparable (*Fig. 12*) in terms of size of dispersed phase (*ca.* 2–3 μm). However, an improved adhesion can be observed for BLszTS with respect to BLsz1 characterized by the presence of holes indicating the detachment of PA6 spheres during the fracture. Slightly better morphology seemed to be reached by using Na_2SO_4 as additive, as showed by the reduced dimension of dis-

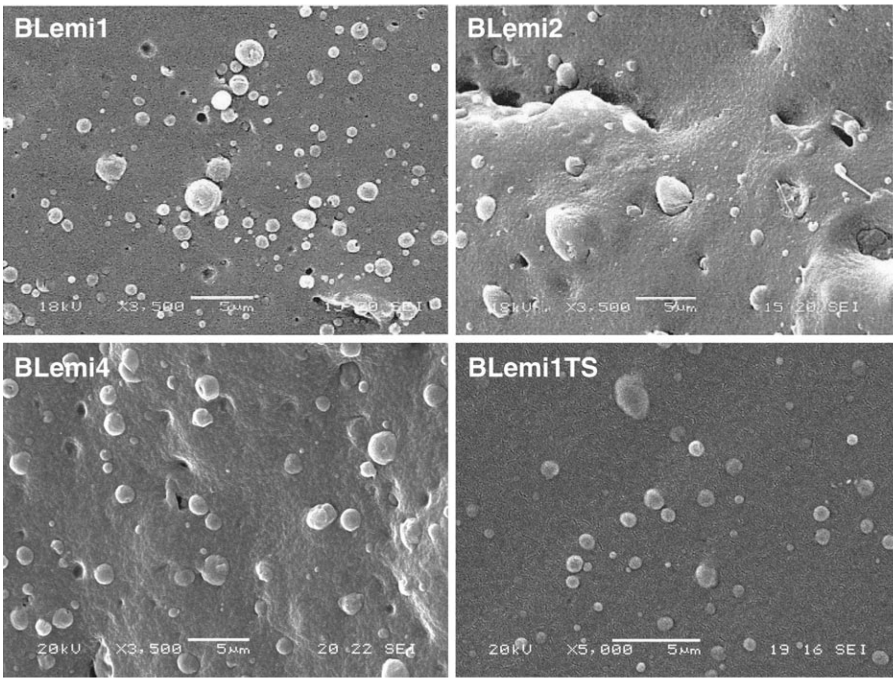


Fig. 8. *Scanning electron microscopy* (SEM) *analysis of one-step- and two-steps-produced EPM/PA6 blends, prepared by using MEM and DCP.* Magnification: BLemi1, BLemi2, BLemi4, ×3500; BLemi1TS, ×5000.

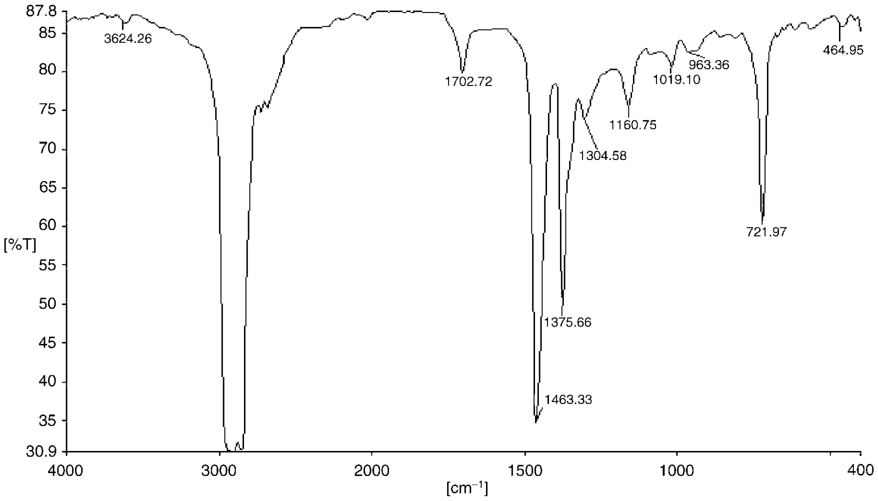


Fig. 9. *IR Spectrum of EPM functionalized with ASBA*

persed phase that was more adhered to the matrix; this result partially confirms the data obtained by DSC measurements.

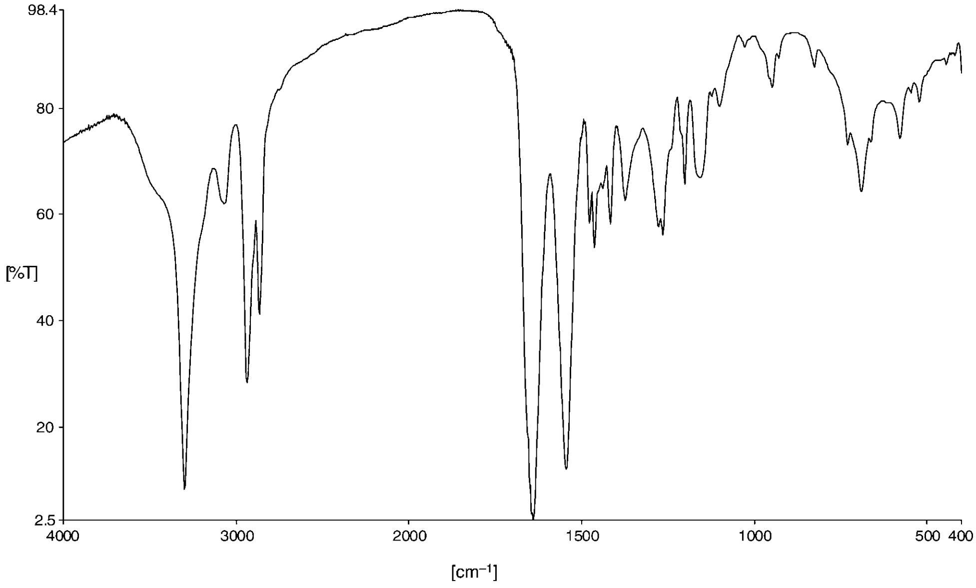


Fig. 10. *IR Spectrum of PA6 after treatment with ASBA and washing with acetone*

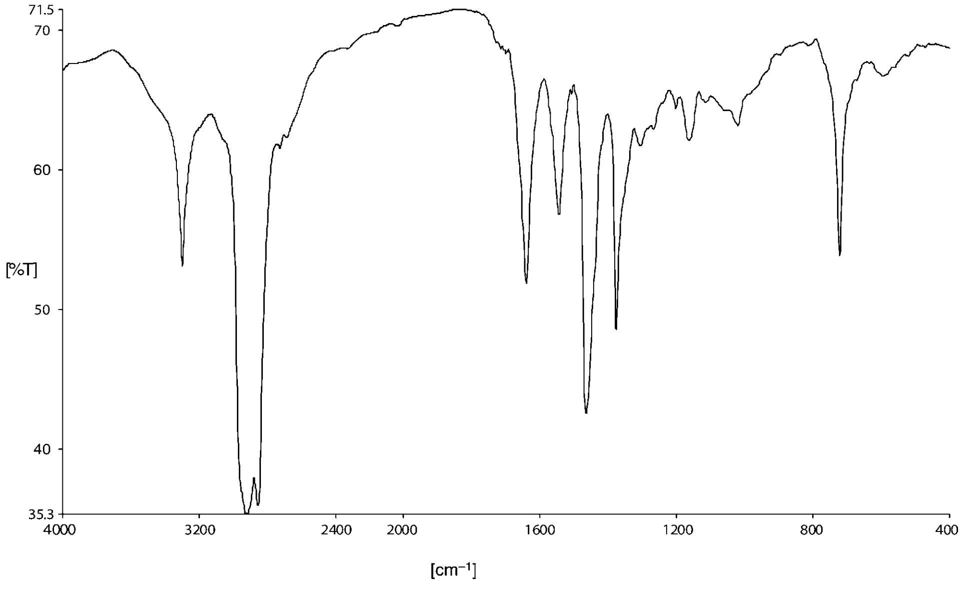


Fig. 11. *IR Spectrum of the residue fraction after solvent extractions of the one-step-produced BLsz1 blend*

Conclusions. – The one-step reactive processing to produce compatibilized EPM/PA6 blends was successfully performed by using two different kinds of functional

Table 5. *DSC Data of ASBA-Functionalized Blends*[a])

Blend	T_m [°]	ΔH_m [J/g]	T_c [°]	ΔH_c [J/g]
BL00	220	11.1	175.0, 100.0[b])	−4.1, −3.0[b])
BLsz1	213.3	12.1	172.7, 94.7[b])	−3.5, −3[b])
BLsz2	213.7	10.3	168.7	−6.5
BLsz3	212.3	11.1	169.0	−8
BLszTS	221.0	12	181.3, 97.7[b])	−4.4, −2.1[b])

[a]) T_m = PA6 melting temperature; ΔH_m = PA6 melting enthalpy; T_c = PA6 crystallization temperature; ΔH_c = PA6 crystallization enthalpy. The enthalpy values were normalized with respect to the PA6 amount in the blends. [b]) Two different crystallization peaks were observed for these samples.

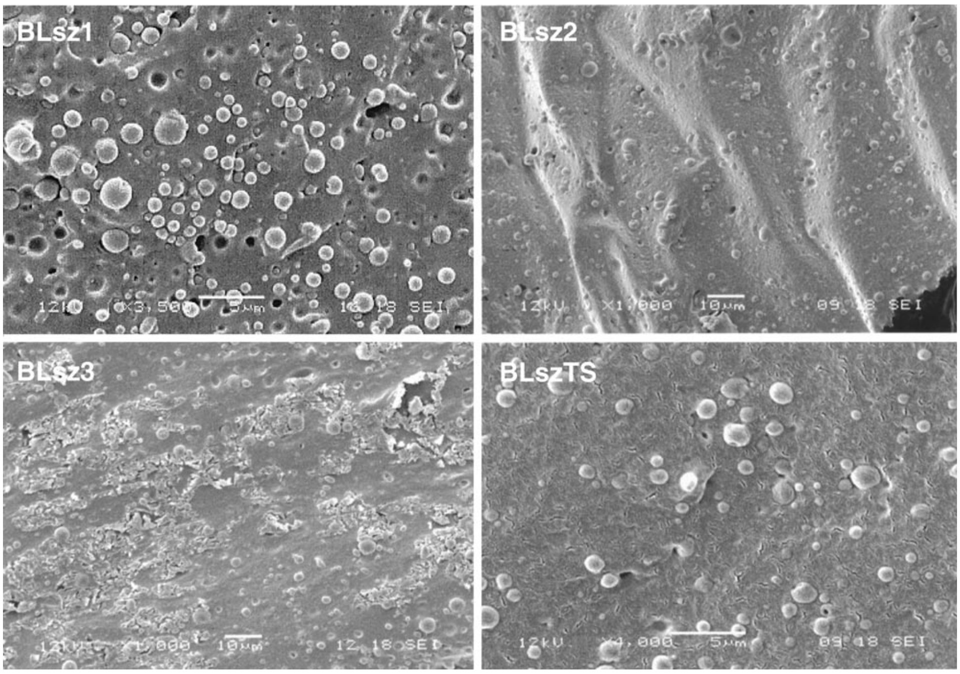


Fig. 12. *Scanning electron microscopy* (SEM) *analysis of one-step- and two-steps-produced blends obtained by using ASBA as functionalizing reagent.* Magnification: BLsz1–BLsz3, ×3500; BLszTS, ×5000.

reagents able to limit side processes such as preferential functionalization and branching of nylon.

The first kind was based on a mixture of monohexadecyl maleate (MEM) and dicumyl peroxide (DCP), which, thanks to the long aliphatic residue of MEM, has a better affinity toward the polyolefin phase, thus favoring the grafting of EPM. At the same time, the formation of different grafted reactive functionalities at the polyolefin macromolecules granted the production of an appreciable amount of EPM–PA6 copolymer necessary for the compatibilization.

The second kind was based on 4-(azidosulfonyl)benzoic acid (ASBA) as functionalizing reagent. The selective reactivity of ASBA towards the tertiary C−H moieties of EPM allowed again the selective grafting of functional groups at the EPM chains and improved the formation of grafted copolymer EPM–PA6, thus favoring the production of a finely dispersed blend. In both cases, the EPM–PA6 copolymer characterization indicated the preferential formation of a structure with long polyolefin chains with short grafted polyamide chains.

The use of MEM/DCP or ASBA allows one to obtain selectively a polyolefin primary functionalization, thus increasing the yield of the EPM–PA6 copolymer at the interface. The effectiveness of the one-step process is then improved yielding compatibilized materials having morphological properties comparable with those obtained with the more expensive and time-consuming two-steps procedure.

The authors would like to express their thanks to Dr. *Marco Rubertà* for his contribution to the experimental work.

Experimental Part

Materials. Monohexadecyl maleate (MEM; kindly supplied by *EniChem*), 4-(azidosulfonyl)benzoic acid (=4-carboxybenzenesulfonazide; ASBA, *Aldrich*), and dicumyl peroxide (DCP, *Aldrich*) were used without further purification. Polyamide 6 (*Ultramid-BASF*) was characterized by $\overline{M_n}$ 20000 D. EPM-CO-O34 (22.7 wt-% propylene), supplied by *Enichem Elastomeri*, was characterized by a *Mooney* viscosity (100°) of 40–48, $\overline{M_w}$ 138000 D, and $\overline{M_n}$ 55200 D.

Reactive Blending. One-step-functionalization runs were performed at 230° in a *Brabender* plastograph mixer equipped with a 30-ml mixing chamber, at a rate of 30 rpm. An EPM/PA6 mixture 80:20 (*w*/*w*; 20 g) was introduced into the mixer, and the functionalizing reagent(s) was (were) added after the torque stabilization (*Table 1*). The blending was carried out for 10 min and then stopped.

Characterization. The blends were first extracted with boiling acetone to remove oligomers, unreacted monomers, and peroxide-decomposition products. For a few blends, the residual fraction was extracted with formic acid to remove unreacted polyamide 6, and with hot heptane to remove unreacted EPM. Extractions with formic acid were carried out for 20 d substituting fresh solvent each 3 d. This procedure was chosen after having extracted a reference EPM/PA6 blend, produced without any low-molecular-weight chemicals (*Table 3*).

IR Spectra: *Perkin-Elmer-1760-X-FT* IR spectrometer; film samples, obtained with a *PM 20/20* press (22 MPa pressure at 230° for 5 min). NMR Spectra: *Varian-Gemini-200* spectrometer at 200 (^{1}H) and 50 (^{13}C) MHz; *ca.* 35-mg samples dissolved in DCOOD; ^{13}C-NMR: totally decoupled, 0.4 s delay.

The titrations of terminal NH_2 and COOH groups of polyamide samples were carried out with a visual method dissolving *ca.* 1 g of sample in 70 ml of benzyl alcohol at 150° under a N_2 flow (*Table 4*). After addition of MeOH/H_2O 2:1 (*v*/*v*; 20 ml), the resulting soln. was titrated with 0.02N KOH in ethylene glycol (this soln. was daily standardized against 0.0196N HCl) by using phenolphthalein as a visual indicator to determine the concentration of the COOH groups. Similarly, the concentration of the NH_2 groups was determined by titration with 0.0196N HCl and bromophenol blue as indicator. The concentration of the terminal groups was calculated, taking into account the blank contribution, with *Eqn. 1*, where [Tgroups] = terminal-groups concentration in 10^{-3} equiv./kg, ml_s = amount of ml of titrating solution to titrate sample, ml_b = amount of ml of titrating solution to titrate blank, T = titrating-solution concentration (mol/l), and m_{PA6} = sample mass in g.

$$[\mathrm{Tgroups}] = \frac{(ml_s - ml_b) \cdot T}{m_{PA6}} \cdot 1000 \qquad (1)$$

Standard DSC thermal analysis was carried out with a *Perkin-Elmer-DSC7* differential scanning calorimeter equipped with a *CC7* device for low temp. The temp. range was 20–250° and the scanning rate 10°/min. Calibrations were made by using In and Zn as references. Scanning electron microscopy (SEM) was performed on samples cryogenically fractured after immersion in liq. N_2 with a *Jeol-JSM-T-300* instrument.

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Received February 7, 2006