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Reactive compatibilization of aliphatic polyamides with functionalized polyethylenes

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The grafting efficiency on different nylons (6, 11, 12, 6,10 and 6,12) of ethylene–glycidyl methacrylate copolymer (PE-*g*-GMA) and ethylene–ethyl acrylate copolymer at a composition of 85/15, when melt-mixed under optimum conditions, was investigated. Two of these nylons, 6 and 11, were selected to be studied in the complete composition range. Using techniques like dynamic mechanical analysis, tensile testing, differential scanning calorimetry, scanning electron microscopy and Fourier transform infra-red spectroscopy (*FT*i.r.) for the characterization of the blends, it was shown that the most efficient grafting occurred in the case of nylon 11/PE-*g*-GMA blends. The formation of a copolymer was confirmed by extraction experiments. The existence of both polymers in the isolated copolymers was proved by *FT*i.r. and thermal analysis. Overall, the concept of the compatibilization of the polyamide–polyethylene system was confirmed in the case of nylon 11/HDPE compatibilized by PE-*g*-GMA copolymer. © 1996 Elsevier Science Ltd.

(Keywords: nylons; ethylene/glycidyl methacrylate copolymers; blends)

INTRODUCTION

The continuous growth in the use of plastic materials has been combined with an increasing concern about the environmental problems caused by their disposal. So, recycled polymers may gain significance in terms of low cost feed stocks for developing new high performance blend products[1].

In order to develop high performance blends from recycled polymers we need effective methods for compatibilization and toughening of these blends. An interesting approach is to create copolymers that could be used as compatibilizers on immiscible pairs of polymers by an *in situ* formation of a copolymer through an interfacial chemical reaction between properly selected functional polymers.

Among different recycled polymers, polyolefins and polyamides are of significant importance. Polyamides have attracted much attention as a reactive component, because of the free amine and/or carboxylic acid end groups and the amide groups in the backbone. Although the compatibilization of the blends polypropylene–polyamides has been extensively studied, using mainly maleic anhydride functionalized copolymers[2-10], less effort has been given to the system polyethylenes–polyamides[11-13].

Most of the possible reactions which lead to reactive blending in polyamides have been summarized by Xanthos[14] and Xanthos and Dagli[15]. Additionally, copolymers containing epoxy groups have also been used as reactive partners of hydroxy-terminated polymers[16]. Such reactions can take place in the case of amino or amide containing copolymers in analogy with the epoxy resins.

In the present work a comparative study on the reactive blending of various polyamides with ethylene–glycidyl methacrylate copolymer (PE-*g*-GMA) and ethylene–ethylacrylate copolymer (PEEA)[17] at the 85/15 composition was performed. Blends were subjected to tensile testing, extraction experiments and scanning electron microscopy (SEM). Two of the previous systems, those of nylon 6/PE-*g*-GMA and of nylon 11/PE-*g*-GMA were furthermore studied in the complete composition range and examined using dynamic mechanical analysis (d.m.a.), tensile testing, differential scanning calorimetry (d.s.c.), SEM and Fourier transform infra-red spectroscopy (*FT*i.r.). Finally, the concept of the compatibilization of the polyamide–polyethylene system was examined in the case of nylon 11/HDPE compatibilized by PE-*g*-GMA copolymer.

EXPERIMENTAL

Materials and specimen preparation

Nylons 6, 11 and 6,10, were obtained from BDH and nylons 12 and 6,12 from Ega-Chemie KG. PEEA with 18% (w/w) ethylacrylate was obtained from Aldrich (Europe) while PE-*g*-GMA copolymer (Lotader 8840) was from Atochem Co. (France). All materials were dried in a vacuum oven at 60°C for 48 h to remove sorbed water before processing.

Blends were prepared by melt-mixing in a stainless steel home-made batch mixer, consisting of a cylindrical rotor, rotating into a thermostated cylindrical cup at

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about 100 rpm. The base of the rotor was tapered into a flat cone (*ca* 2°). Mixing was carried out under a blanket of inert gas (Ar) and the maximum amount produced per batch was *ca* 10 g. Temperature and blending time (in the case of nylon 6) were varied to obtain improved ultimate tensile properties, i.e. elongation at break ε_b (see *Figure 1*). Optimum mixing conditions were determined to be 230°C and a mixing time of 15 min. Blending experiments were repeated at least twice to ensure that the blending procedure was reproducible.

Compositions prepared under these conditions were 85/15 nylon/PEEA and nylon/PE-*g*-GMA for the various nylons and 85/15, 75/25, 50/50 and 25/75 for the system of nylon 6/PE-*g*-GMA as well as 85/15, 75/25 and 50/50 for the system of Nylon 11/PE-*g*-GMA. Films were made by compression moulding between Teflon sheets at 250°C and 70 kg cm^{-2}, pressure release and quenching to 0°C.

Apparatus and procedures

Extraction experiments were performed in boiling toluene for 4 h in order to remove the unreacted ethylene copolymers. The films after the extraction were dried in a vacuum oven at 100°C for 24 h. The nylon 6/PE-*g*-GMA films were further treated with formic acid at room temperature for 24 h to remove the ungrafted nylon 6. The insoluble fraction was filtered, washed with formic acid and methanol, and dried at 100°C for 24 h *in vacuo*. In the case of nylon 11/PE-*g*-GMA samples were subjected to Soxhlet extraction with dimethylacetamide (DMAc) for 24 h and dried under the same conditions.

The SEM was carried out with a Jeol model JSM-5200 instrument. Cryofractured and etched surfaces were examined at a tilt angle of 30°.

The d.s.c. measurements were carried out in an inert atmosphere using a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was carried out with an indium standard. The sample weight was *ca* 10 mg and the heating rate was 20°C min^{-1}. The samples were heated up to 250°C, quenched to −80°C followed by heating to 250°C. The second heating scan was recorded.

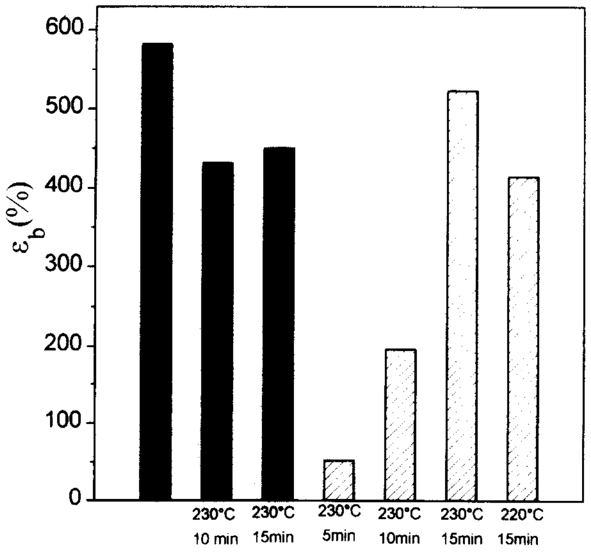


Figure 1 Optimization of mixing conditions: (■) nylon 6; (▒) nylon 6/PE-*g*-GMA (85/15); (▨) nylon 6/PEEA (85/15)

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester type T5001 and film strips with dimensions 4.0 × 0.65 × 0.025 cm. Data reported were obtained at a crosshead speed of 10 cm min^{-1}.

The d.m.a. data, loss tangent (tan δ) and complex modulus $|E^*|$ were obtained at 110 Hz using a direct-reading viscoelastometer (Rheovibron model DDV II-C). Specimen dimensions were 3.0 × 0.20 × 0.02 cm.

The *FT*i.r. spectra were obtained using a Perkin-Elmer 1600 spectrometer.

RESULTS AND DISCUSSION

*Comparison of the reactivity of PE-*g*-GMA and PEEA towards various nylons*

The reactivity of the studied nylons (6, 11, 12, 6,10, 6,12) to the polyethylene modified with epoxy groups (PE-*g*-GMA) was compared with that of the same nylons to (PEEA) copolymer at a composition of 85/15. The comparison was based on the tensile properties of the blends as these, especially ε_b, are very sensitive to blend component adhesion strength or partial miscibility at the interface of blend components in phase separated systems and are routinely used to evaluate the degree of compatibilization in polymer alloys[18,19]. Ultimate properties σ_b, ε_b and yield strength σ_y of these blends are summarized in *Table 1*. In the case of nylons 6 and 12, both blends have lower σ_y and σ_b. On the other hand, for nylon 11, the σ_b value remains the same as for the pure material for the blend with PE-*g*-GMA, while for the blend with PEEA we observe a small reduction. Finally, for the blends of nylons 6,10 and 6,12, σ_y increases while σ_b decreases for the former and remains at the same level for the latter. All show good elongation at break (ε_b), as shown in *Figure 2* and specifically the blends with PE-*g*-GMA show ε_b values comparative to the ones of the pure nylons (the minimum values are observed in the blends of Nylons 6 and 6,12). In the cases of nylons 11, 12 and 6,10, PE-*g*-GMA appears to be more reactive while for nylons 6 and 6,12 both copolymers are comparable.

Morphological examination by means of SEM was performed to the cryofractured surfaces of the blends and the micrographs are shown in *Figure 3*. Examination

Table 1 Tensile properties of the pure polymers and the binary blends prepared

Sample	σ_y (MPa)	σ_b (MPa)	ε_b (%)
Nylon 6	35 ± 4	72 ± 7	583 ± 72
Nylon 11	29 ± 2	41 ± 5	477 ± 72
Nylon 12	26 ± 2	47 ± 4	551 ± 50
Nylon 6,10	13 ± 1	51 ± 7	592 ± 58
Nylon 6,12	12 ± 1	33 ± 4	470 ± 28
Nylon 6/PEEA (85/15)	23 ± 1	49 ± 6	524 ± 61
Nylon 11/PEEA (85/15)	22 ± 1	30 ± 3	317 ± 49
Nylon 12/PEEA (85/15)	15 ± 1	24 ± 2	359 ± 47
Nylon 6,10/PEEA (85/15)	17 ± 1	29 ± 3	377 ± 24
Nylon 6,12/PEEA (85/15)	20 ± 1	28 ± 2	318 ± 92
Nylon 6/PE-*g*-GMA (85/15)	22 ± 3	40 ± 5	451 ± 111
Nylon 11/PE-*g*-GMA (85/15)	22 ± 2	41 ± 4	531 ± 54
Nylon 12/PE-*g*-GMA (85/15)	21 ± 1	37 ± 4	488 ± 48
Nylon 6,10/PE-*g*-GMA (85/15)	11 ± 1	37 ± 4	572 ± 81
Nylon 6,12/PE-*g*-GMA (85/15)	21 ± 1	31 ± 2	347 ± 80

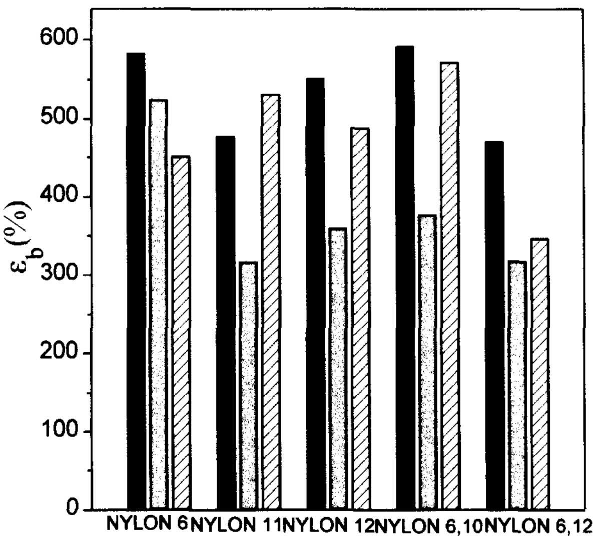


Figure 2 Elogation at break, ε_b(%), of the blends of PEEA or PE-*g*-GMA with various nylons: (■) nylon(s); (▒) nylon(s)/PEEA (85/15); (▨) nylon(s)/PE-*g*-GMA (85/15)

of *Figure 3* shows a ductile type of fracture. In all cases a tough type of fracture with particles dislodged from the matrix is observed, suggesting a fine dispersion and strong incorporation of PE-*g*-GMA into the nylon matrix.

To complete the above comparison, extraction experiments with boiling toluene were performed in order to remove the unbonded polyethylene copolymer, and the results are recorded in *Table 2*. Although the extracted blends contained 15% of PE-*g*-GMA only 1–2% PE-*g*-GMA was extracted, indicating a very effective grafting between the two polymers in all cases.

Comparison of the grafting of PEEA on to the various nylons with that on to the PET matrix[20] has shown in the latter case a lower grafting efficiency as the removable amount of the polyethylene copolymer was higher.

Based on the above results two nylons were selected to be studied with PE-*g*-GMA in the complete composition range; nylon 6 in order to compare the results with those

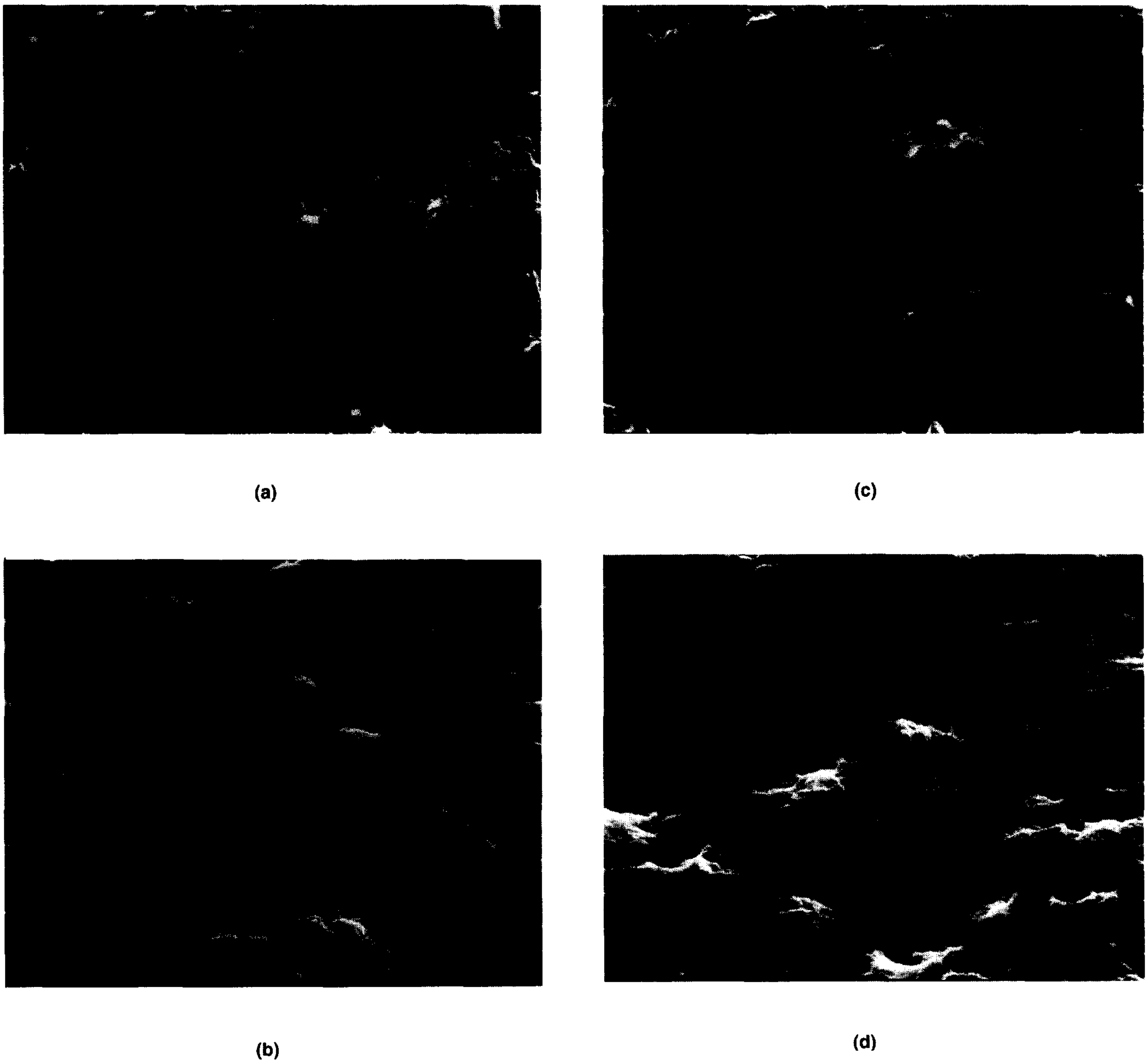


Figure 3 Scanning electron micrographs of cryofractured surfaces of blends (85/15): (a) nylon 11/PE-*g*-GMA; (b) nylon 12/PE-*g*-GMA; (c) nylon 6,10/PE-*g*-GMA; (d) nylon 6,12/PE-*g*-GMA

of previous work on nylon 6/PEEA[17], and nylon 11, which seems to be the most effectively compatibilized by PE-*g*-GMA.

*Reactive blending of Nylon 6 and Nylon 11 with PE-*g*-GMA*

Tensile testing. *Table 3* gives the tensile properties in terms of ultimate strength and elongation, σ_b and ε_b, respectively, and energy to tensile failure, E_b, of nylon 6, nylon 11 and PE-*g*-GMA as well as of their blends prepared at the indicated compositions under optimum conditions. For the case of nylon 6/PE-*g*-GMA at low PE-*g*-GMA contents (up to 25 wt%), blends show good mechanical properties although some reduction is seen. At high PE-*g*-GMA contents, ductility is high since PE-*g*-GMA becomes the matrix. A minimum in mechanical properties is obtained at the intermediate composition (50/50) at which matrix inversion probably occurs. The picture for the case of nylon 11/PE-*g*-GMA blends is different. The σ_b values remain constant at the σ_b level of nylon 11 at all examined compositions, while ultimate elongation, ε_b, which is more sensitive to compatibilization, increases on increasing the PE-*g*-GMA content. It should be noted that even in the 50/50 composition a σ_b value equal to that of nylon 11 was taken while the ε_b value is well above that of nylon 11. This can be explained by the fact that PE-*g*-GMA and nylon 11 are semi-compatible, because of the long segment of methylene units in the main chain of nylon 11, which allows better melt-mixing of the two components and a more effective reaction than the one between PE-*g*-GMA and nylon 6. This is further supported by the results of d.m.a., as will be discussed later, and by the values of the energy to tensile failure, E_b, of these blends, which are similar or even enhanced for the system of nylon 11/PE-*g*-GMA, but significantly lowered in the nylon 6/PE-*g*-GMA system than for the pure components. The comparative results for the two systems referring to ultimate strength and elongation, σ_b and ε_b, respectively, are presented in *Figure 4*. The observed good mechanical properties can be attributed to the interpolymer reactions, which lead to grafting at the interface of nylon 6/PE-*g*-GMA or nylon 11/PE-*g*-GMA (*Scheme 1*).

Table 2 Weight reduction of the blends after the extraction in hot toluene

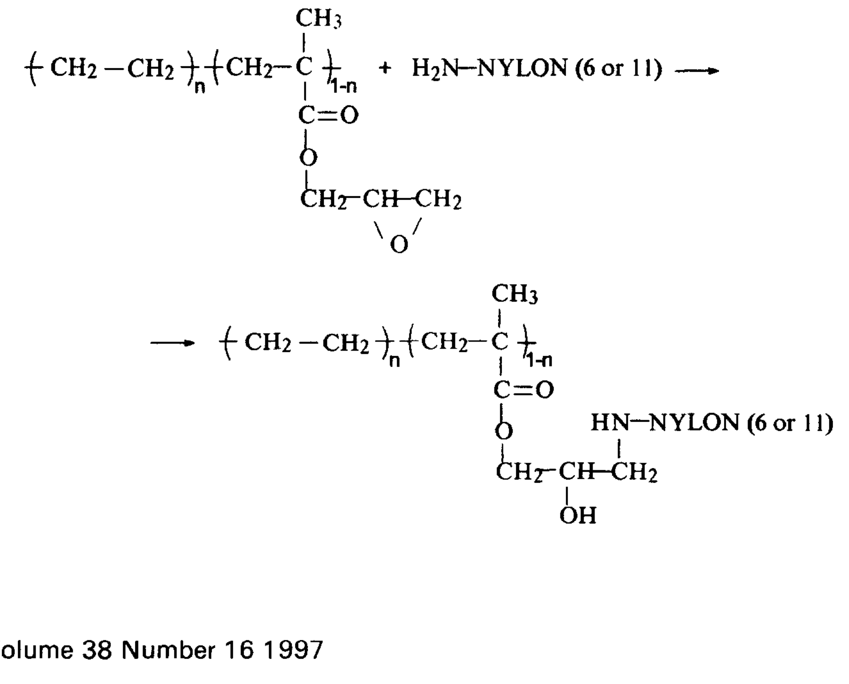
Blend	Weight reduction (%)
Nylon 6/PE-*g*-GMA (85/15)	1.1
Nylon 12/PE-*g*-GMA (85/15)	1.6
Nylon 6,10/PE-*g*-GMA (85/15)	1.1
Nylon 6,12/PE-*g*-GMA (85/15)	1.0
Nylon 11/PE-*g*-GMA (85/15)	1.3
Nylon 11/PE-*g*-GMA (75/25)	2.0
Nylon 11/PE-*g*-GMA (50/50)	5.0

Dynamic mechanical properties. The dynamic viscoelastic spectra of the quenched (0°C) pure blend components are shown in *Figures 5* and *6* in terms of the temperature dependence of the loss E'' and storage E' modulus for the nylon 6/PE-*g*-GMA and nylon 11/PE-*g*-GMA, respectively.

The main relaxation of nylon 6 in its blends does not show any noticeable shift (*Figure 5*) and its secondary sub-ambient temperature relaxation seems to be superimposed by the β relaxation of PE-*g*-GMA. So it is not clear whether there is any shift in β relaxations or not.

The main relaxation of nylon 11 associated with T_g is located at *ca* 62°C (α) while the secondary sub-ambient temperature relaxation is detected at −42°C (*Figure 6*). As shown in *Table 4*, there is a systematic shift of the nylon 11 (α) and (β) and of the PE-*g*-GMA (β) relaxations towards each other with increasing compatibilizer content. For the 50/50 composition, the α is reduced from 62 to 55°C and the β of nylon 11 is shifted from −42 to −38°C while the β of PE-*g*-GMA shifts from −8 to −1°C. These suggest a limited miscibility of the two phases, which becomes higher on increasing the PE-*g*-GMA content.

Thermal properties. The melting temperatures (T_m) of nylon 6, nylon 11 and PE-*g*-GMA in their blends are presented in *Table 5*. nylon 11 does not show any noticeable depression, but nylon 6 on the contrary presents a detectable T_m depression that increases on increasing the PE-*g*-GMA content. The annealed samples were examined in order to evaluate whether this depression was due to thermodynamical or morphological effects[21,22].



Scheme 1

Table 3 Tensile properties of blends

Blends of nylon/PE-*g*-GMA	Nylon 6			Nylon 11		
	σ_b(MPa)	ε_b(%)	E_b(J cm^{-3})	σ_b(MPa)	ε_b(%)	E_b(J cm^{-3})
100/0	72 ± 7	583 ± 72	192	41 ± 5	477 ± 72	135
85/15	40 ± 5	451 ± 111	140	41 ± 4	531 ± 54	148
75/25	41 ± 3	462 ± 66	116	39 ± 4	557 ± 59	148
50/50	13 ± 1	132 ± 36	14	38 ± 2	599 ± 24	135
25/75	11 ± 1	190 ± 20	17	—	—	—
0/100	15 ± 1	755 ± 41	75	15 ± 1	755 ± 41	75

The data obtained showed no depression after annealing at 150°C for 2 h; thus, the observed composition dependence of T_m is attributed to morphological factors. Regarding the PE-*g*-GMA component there is a significant T_m depression, which, in the case of nylon 11/PE-*g*-GMA blends, is higher. In both cases the T_m values obtained were independent of composition. The crystallinity of nylons 6 and 11 in their blends does not vary with blend composition while the crystallinity of PE-*g*-GMA seems to increase on increasing its content.

Morphology. Cryofractured surfaces of all blends showed a homogeneous ductile type of fracture with particles dislodged from the matrix. In all cases the nylon matrix undergoes extensive yielding which is not dependent on the composition.

It is known from the literature[23] that the addition of a strong adhering rubber to a nylon (nylon 6,6) matrix increases the toughness variously up to a factor of about 60. Among the criterions of a good component adhesion is the particle size of the rubber whose diameter should

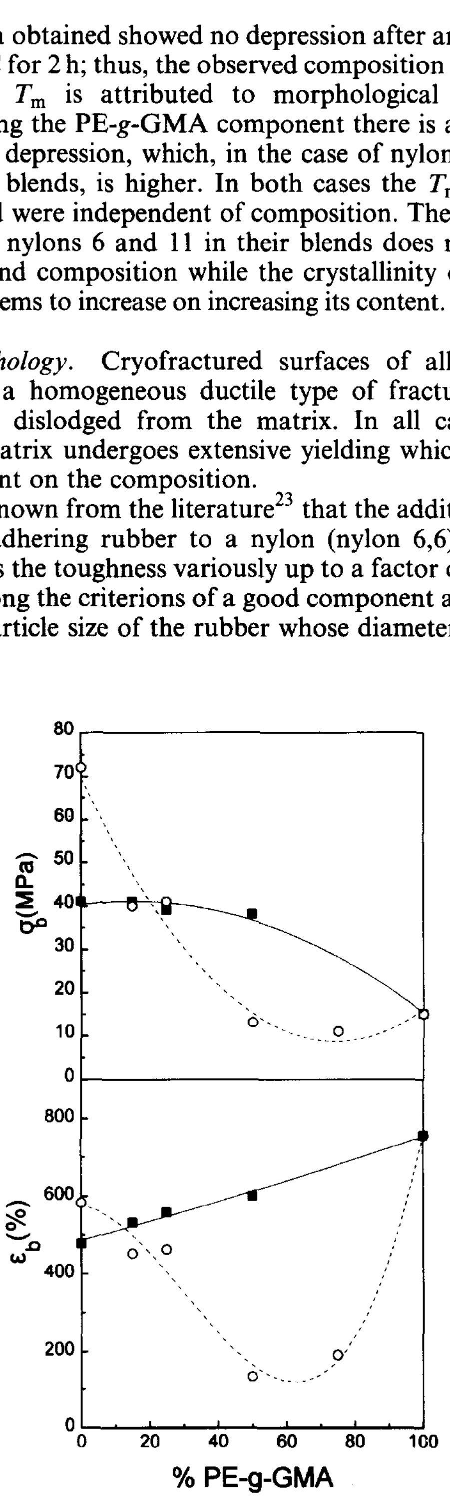


Figure 4 Composition dependence of ultimate properties of (○) nylon 6/PE-*g*-GMA and (■) nylon 11/PE-*g*-GMA blend

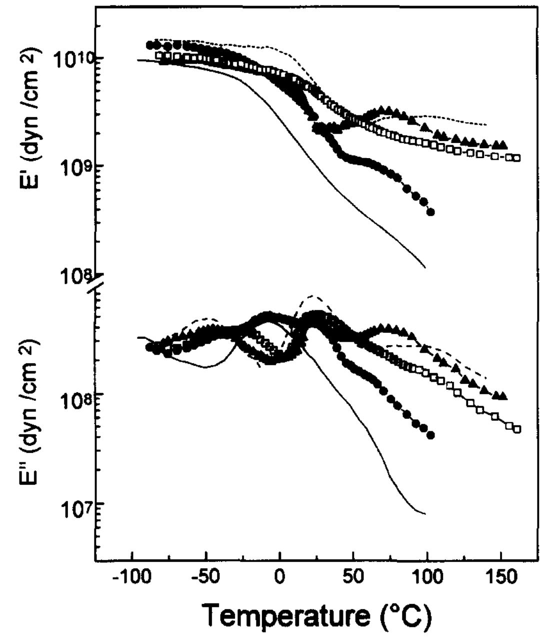


Figure 5 Temperature dependence of the storage and loss modulus of nylon 6/PE-*g*-GMA blends: (·····) 100–0; (▲) 85/15; (□) 75/25; (●) 50/50; (——) 0–100

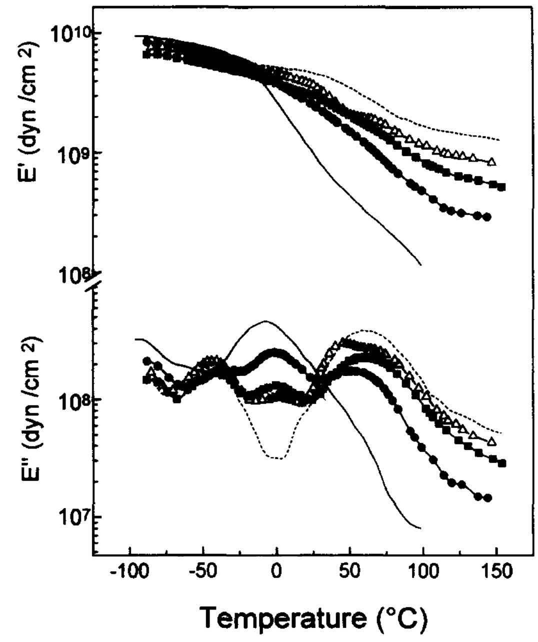


Figure 6 Temperature dependence of the storage and loss modulus of nylon 11/PE-*g*-GMA blends: (·····) 100–0; (△) 85/15; (■) 75/25; (●) 50/50; (——) 0–100

Table 4 Viscoelastic transitions (E''_{max} in °C) of blends

Blends of nylon 11/PE-*g*-GMA	Nylon 11		PE-*g*-GMA
	β	α	(β)
100/0	−42	62	–
85/15	−41	–[a]	1
75/25	−40	60	0
50/50	−38	55	−1
0/100	–	–	−8

[a] Double peak

Table 5 Thermal properties (T_m in °C)

Blends of nylon/PE-*g*-GMA	Nylon 6		Nylon 11	
	Nylon	PE-*g*-GMA	Nylon	PE-*g*-GMA
100/0	218		187	
85/15	217	106	187	102
75/25	216	107	187	102
75/25[a]	218	108	–	–
50/50	214	107	185	102
50/50[a]	–	–	182	102
25/75	212	106		–
0/100	—	112	–	112

[a] Isolated copolymer

be around 1 μm for blends with rubber contents up to 25%. *Figure 7* shows the micrographs of the surfaces of nylon 11/PE-*g*-GMA blends etched with boiling toluene. In all compositions examined small 'holes' are visible after the extraction, which, however, do not exceed 1 μm diameter for the 85/15 and 75/25 blends, a fact in agreement with the above parameters required for toughening of nylon.

Extraction experiments and copolymer characterization

The grafting efficiency of PE-*g*-GMA on to nylon 6 or 11 was further evaluated by extraction experiments. In all cases the unreacted ethylene copolymer was removed first with hot toluene. The results for nylons 6 and 11 blends, summarized in *Table 2*, show that a very low amount of the PE-*g*-GMA was removed using this particular procedure. Two blends were selected for isolation of the copolymers formed; nylon 6/PE-*g*-GMA (75/25) and nylon 11/PE-*g*-GMA (50/50). The unbonded nylon was dissolved in formic acid at room temperature in the case of nylon 6/PE-*g*-GMA blend, while Soxhlet extraction in DMAc was used for the nylon 11/PE-*g*-GMA blend. The remaining copolymers were characterized by *FT*i.r. and d.s.c., while mechanical analysis was used for the characterization of the nylon 11/PE-*g*-GMA blend. The results obtained by *FT*i.r. are shown in *Figure 8*. In both cases the isolated copolymers, besides the absorption due to the polyamides, contain a carbonyl absorption at 1732 cm^{-1} which certifies the presence of PE-*g*-GMA.

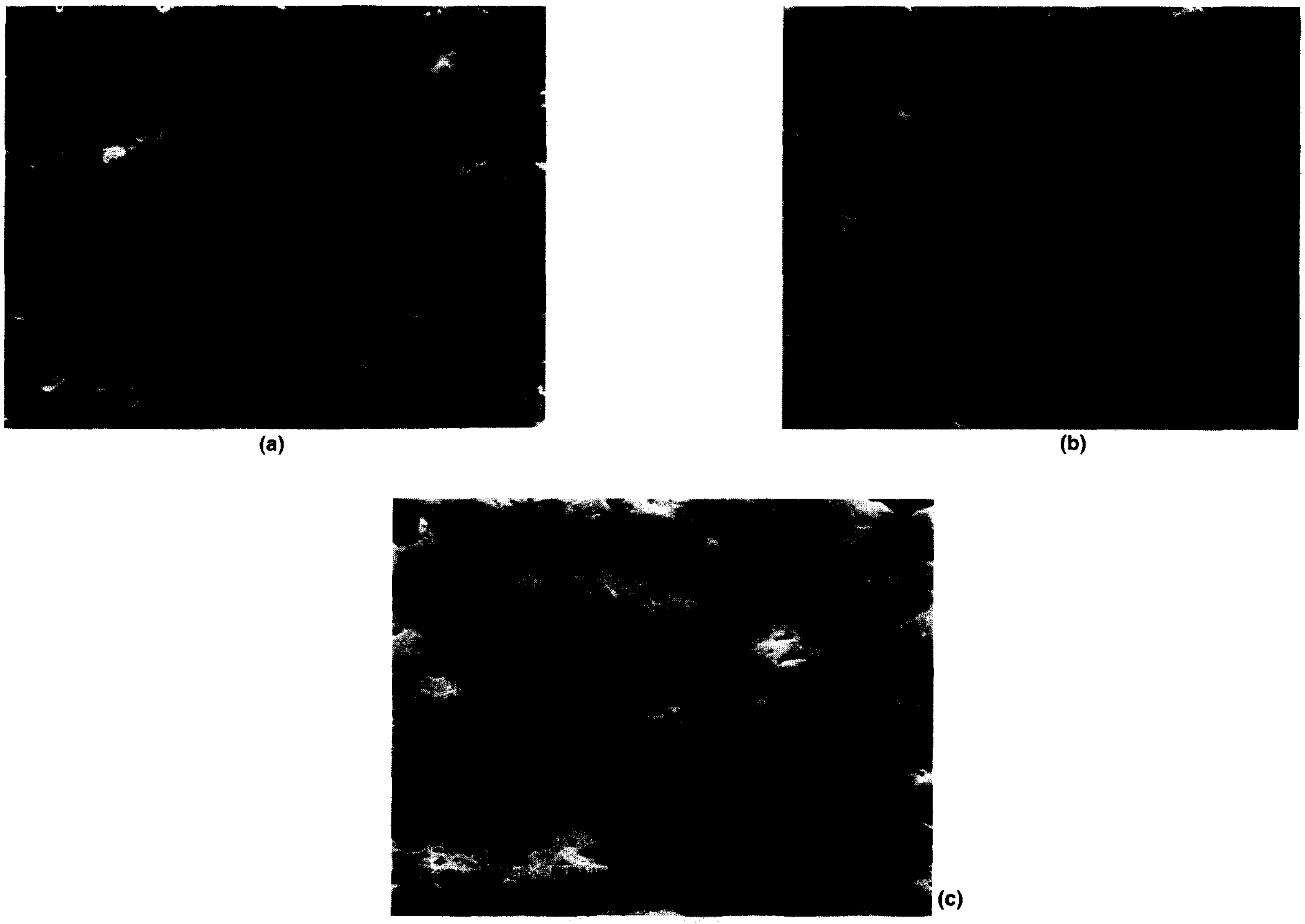


Figure 7 Scanning electron micrographs of nylon 11/PE-*g*-GMA blends selectively etched in boiling toluene: (a) 85/15; (b) 75/25; (c) 50/50

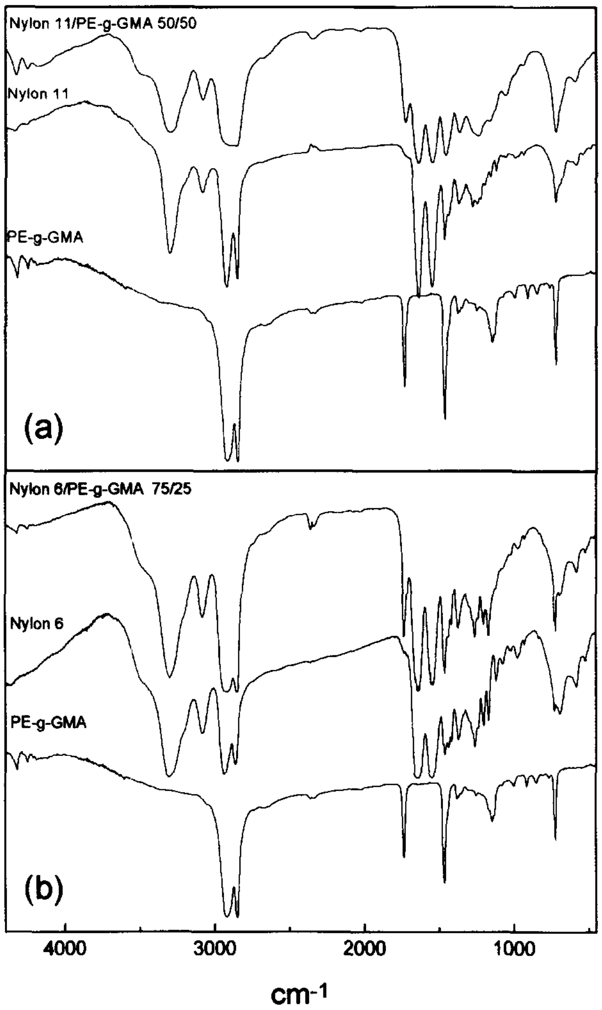


Figure 8 *FT*i.r. spectra of the copolymers derived from (a) nylon 11/PE-*g*-GMA (50/50) and (b) nylon 6/PE-*g*-GMA (75/25) blends, compared with those of the pure polymers

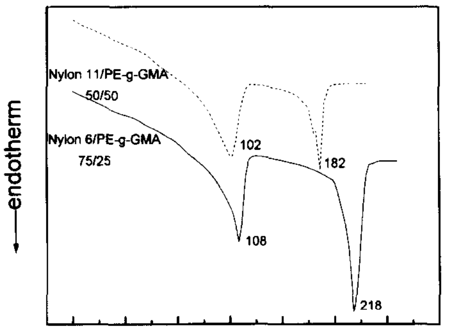


Figure 9 D.s.c. thermograms of the copolymers derived from (·····) nylon 11/PE-*g*-GMA 50/50 and (——) nylon 6/PE-*g*-GMA (75/25) blends

The presence of both of the constituent polymers in the isolated copolymers is also confirmed by the d.s.c. thermograms (*Figure 9*), where in both cases the two characteristic endotherms are observed. For the nylon 6 blend the situation before and after the extraction is the same, meaning that the T_m of nylon 6 remains unshifted while the T_m of PE-*g*-GMA shows a small displacement to lower temperatures (108°C) instead of 112°C for the pure PE-*g*-GMA. For the nylon 11/PE-*g*-GMA copolymer, there is an additional depression of the nylon 11 melting temperature, from 187°C for the pure component to 185°C in the blend and to 182°C in the copolymer. For the same copolymer, the PE-*g*-GMA component shows a shift in T_m from 112°C for the pure PE-*g*-GMA to 102°C in the blend as well as in the copolymer. Since the amount of the PE-*g*-GMA removed by the extraction process is very low, it is reasonable to expect the same T_m for the PE-*g*-GMA portion in the copolymer. nylon 6 does not present any T_m shift in its blend so we do not expect any shift in the formed copolymer either. On the contrary, nylon 11 shows a detectable T_m depression in its blend, and the amount removed during the extraction is higher than that of PE-*g*-GMA, thus explaining the additional T_m depression observed.

Finally, d.m.a. was performed in the case of nylon 11 copolymer. The results in terms of E'' are presented in *Figure 10* in comparison with the analogous spectra of the pure components and the blend before the extraction. The shift in the transitions of the two polymers towards each other in the copolymer confirms the existence of some interactions between the two components.

As was mentioned in the Introduction, the copolymers formed by this reactive processing can be used as compatibilizers for the system polyamide/polyethylene. While this work was in progress a similar attempt on compatibilization of nylon 6/HDPE by PE-*g*-GMA copolymer in a twin extruder appeared[12]. Our work also included the compatibilization of a nylon 11/HDPE system, but the results are not given in this publication. However, it may be reported that for the system of nylon 11/HDPE/PE-*g*-GMA for the composition of 20/60/20, σ_b and ε_b were, respectively, 21 ± 2 MPa and 665 ± 41% while for the incompatible pair of nylon 11/HDPE for the same ratio (25/75), σ_b and ε_b were 16 ± 2 MPa and 11 ± 1%.

The above results show the effective grafting of the various polyamides with functionalized polyethylenes and the consequent effective compatibilization of polyamide/polyethylene blends. Since the type of mixer

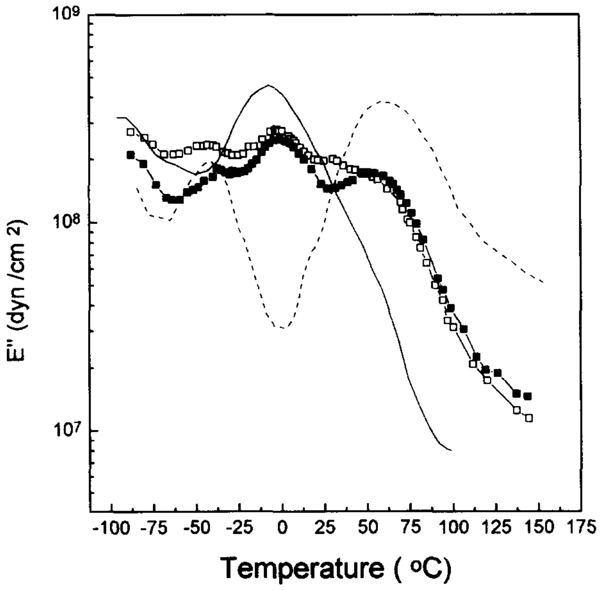


Figure 10 Temperature dependence of the loss modulus of the copolymer derived from the nylon 11/PE-*g*-GMA (50/50) blend: (·····) nylon 11; (——) PE-*g*-GMA; (■) blend; (□) copolymer

greatly affects the quality of the mixture produced, there is the possibility that these results can be further enhanced by using a more effective industrial mixer.

CONCLUSIONS

Reactive compatibilization of various nylons with functionalized polyethylenes having ester or epoxy groups can be performed at elevated temperature and prolonged mixing time. The mechanical properties of the blends with high polyamide content are comparable with those of the pure materials or are even better. Morphological examination of the same blends showed that the polyethylene particles dispersed in the polyamide matrix were less than 1 μm diameter, which is required for supertoughening of nylons.

The grafting efficiency was further checked by a combination of extraction experiments with *FT*i.r. spectroscopy and thermal analysis. The isolated copolymers had characteristic absorptions of both polyamide and ethylene components. In the case of nylon 11/PE-*g*-GMA blends the observed mutual displacement of the main transitions in mechanical analysis supports the semi-compatible nature of this system.

Finally, the concept of the compatibilization of various polyamides with polyethylenes was checked in the case of nylon 11/HDPE, using PE-*g*-GMA as compatibilizer, with promising results.

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