Rubber modification of polyamide-6 effected concurrently with caprolactam polymerization: influence of blending conditions and degree of grafting of rubber

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Blends of polyamide-6 and functionalized ethylene–propylene rubber (EPR) copolymers were obtained concurrently with the hydrolytic polymerization of caprolactam. It was found that both the degree of grafting of EPR and the time at which the rubber is added during the polymerization reaction of caprolactam play an important role in determining the mode and state of dispersion of the rubbery component and thus the impact behaviour of the material.

(Keywords: blending; rubber; polyamide-6; caprolactam)

INTRODUCTION

Methods to obtain rubber-modified polyamide-6 (PA6) with improved impact behaviour were described in previous papers[1–6]. Such methods consist of the right formulation of binary and/or ternary blends containing as rubbery component an ethylene–propylene rubber (EPR) random copolymer and/or a suitable functionalized EPR. The functionalization of EPR was performed by means of homogeneous grafting reactions of unsaturated molecules such as maleic anhydride, to form EPR-*g*-succinic anhydride (EPR-*g*-SA), and dibutyl maleate, to form EPR-*g*-dibutyl succinate (EPR-*g*-DBS)[7].

Two routes have been followed to prepare the blends:

(1) concurrently with caprolactam polymerization;

(2) melt mixing in a Haake Brabender-like apparatus. In this case the ternary alloys were obtained by two different procedures: (a) all the components were introduced at one time in the mixer (single-step mode); (b) the two rubbers were premixed separately before final mixing with PA6 (double-step mode).

Mechanical tensile tests at room temperature and Izod impact tests at various temperatures on notched specimens have been performed as well as morphological analysis on smooth and/or etched samples of all blends. Very high impact properties have been achieved for binary blends containing EPR functionalized by routes (1) and (2) and for ternary PA6/EPR/EPR-*g*-SA blends by route (2b). The results have been related to the mode and state of dispersion of the rubber[8], to the degree of grafting of the EPR and to the blending procedures used. The influence of rubbery components on the structure and crystallization behaviour of the PA6 matrix has also been investigated[9].

The features observed in PA6/EPR-*g*-SA (EPR-*g*-DBS) and PA6/EPR/EPR-*g*-SA (EPR-*g*-DBS) blends were interpreted by assuming that during mixing a graft copolymer, able to act as an interfacial and emulsifying agent, is formed between the functionalized EPR rubber and PA6. In the case of blends with EPR-*g*-SA, this graft copolymer (EPR-*g*-SA)-*g*-PA6 is obtained by means of a heat-induced condensation between the carboxylic groups of EPR-*g*-SA molecules and the $-NH_2$ end groups of polyamide molecules. The morphology observed in the case of PA6/EPR/EPR-*g*-SA ternary blends is accounted for if it is assumed that the graft copolymer partially acts as an 'interfacial agent' (improving adhesion between the matrix and the dispersed phase, and decreasing the average dimension of the EPR rubber domains) and partially forms much smaller domains very rich in (EPR-*g*-SA)-*g*-PA6 strongly adherent to the matrix[1–6,8].

The influence of the degree of grafting (*DG*) of EPR-*g*-SA on the morphology and the tensile and impact properties of binary and ternary blends prepared by melt mixing has been investigated[6]. Finer and more homogeneous dispersions of the rubbery domains and better impact properties are obtained with increasing degree of grafting of the EPR in the blends. At equal *DG* values and for the composition used, the binary PA6/EPR-*g*-SA alloys show a better behaviour than the ternary ones. These results are related to the presence of an (EPR-*g*-SA)-*g*-PA6 graft copolymer formed during melt mixing, which acts as an interfacial and emulsifying agent.

Attempts to prepare binary or ternary blends by route (1) containing high amounts of EPR-*g*-SA (more than 10% w/w) failed for two reasons: the high reactivity of the grafted anhydride towards $-NH_2$ of growing PA6 chains, and the relatively high degree of grafting of the EPR-*g*-SA used (3% by weight of succinic groups)[2,3]. As a consequence, highly grafted EPR chains are formed from the beginning of the polymerization of caprolactam, producing an abrupt increase in the viscosity of the mixture. Such blends are then too viscous to be stirred efficiently. In order to investigate 80/20 PA6(EPR+

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Table 1 Characterization of PA6 and of the prepared binary PA6/EPR and PA6/EPR-*g*-SA blends

Code	*DG* (%)	*PT*[a] (min)	Extractable in MeOH (%)	Composition (%)	
				PA6	EPR-*g*-SA
A	—	—	13.5		[b]
B	0	0	—		[c]
C_0	0.7	0	37.5	71.4	28.6
C_{40}	0.7	40	27.5	74.4	25.6
C_{120}	0.7	120	17.8	76.8	23.2
D_0	1.4	0	42.3	69.7	30.3
D_{40}	1.4	40	29.7	73.4	26.3
D_{120}	1.4	120	22.2	75.7	24.3

[a] See text for definition
[b] Pure PA6
[c] PA6/EPR 77.5/22.5 binary blend

modified EPR) blends, in which the amount of modified EPR ranged from 0 to 100% of the total rubber content, by route (1), it was necessary to use EPR-*g*-DBS[4]. In fact, because of the relatively low reactivity of the ester groups towards $-NH_2$ groups of growing PA6 chains, it was possible to prepare blends with higher EPR-*g*-DBS content, and to study the influence of different degrees of grafting on the morphology and properties of the blends.

In the present paper we have developed a modification of route (1). Such a modification is based mainly on the fact that the functionalized rubber (EPR-*g*-SA) is added not at the beginning of the polymerization reaction of caprolactam but after selected times. This allows us to study the influence of the molecular mass of preformed PA6 chains on the structure of the (EPR-*g*-SA)-*g*-PA6 graft copolymer, on the mode and state of dispersion of the rubbery component in the final blends and thus on its properties. Only binary PA6/EPR-*g*-SA blends with an 80/20 (w/w) composition were investigated.

In order to avoid problems arising from too high degrees of grafting of the rubbery phase, which lead to gelation of the polymerizing mixture[2,3], we decided to limit our investigation to a low degree of functionalization of EPR-*g*-SA. So two functionalized rubbers, differing in degrees of grafting (0.7 and 1.4 wt% of grafted groups), were used in the preparation of the blends.

EXPERIMENTAL

Materials

The amorhous ethylene–propylene rubber (EPR) random copolymer (commercial name Dutral Co054, ethylene content 67 mol%, $M_w = 1.8 \times 10^5$ amu), kindly supplied by Dutral SpA, was used as received. Maleic anhydride was a reagent-grade product (RPE) from Carlo Erba. Caprolactam (CL) and aminocaproic acid (ACA) were Fluka reagent-grade products. The solvents, when required, were purified according to standard procedures.

Succinic-anhydride-grafted EPRs (EPR-*g*-SA) having 0.7 and 1.4 wt% of grafted groups were prepared according to a procedure previously reported by us[7].

Techniques

The i.r. spectra were obtained with a Nicolet DxB *FT*i.r. spectrophotometer at 4 cm^{-1} resolution (32 scans collected).

Viscosity measurements of polyamide-6 samples were performed with a Cannon–Ubbelohde viscosimeter at $T = 25°C$ in *m*-cresol ($c = 0.5$ g dl^{-1}).

Typical procedure for a binary blend preparation

Here we report the preparation of the blend coded as 'C_{40}' in *Table 1*. A mixture of 76.0 g (0.67 mol) of CL and 4.0 g (0.31 mol) of ACA was poured into a round-bottomed four-necked flanged flask equipped with vacuum inlet, N_2 inlet and mechanical stirrer. The flask was repeatedly degassed, filled with pure nitrogen and immersed in an oil bath thermostatted to 260°C. The polymerization was carried out for 40 min under atmospheric pressure. Then 20.0 g of finely ground EPR-*g*-SA containing 0.7 wt% of SA were rapidly added to the molten mixture. The polymerization was continued under vigorous mechanical stirring (around 600 rpm) for 200 min.

Upon cooling, the crude reaction product was recovered, finely ground and extracted with boiling methanol (MeOH) to remove unreacted monomer and lower oligomers in a Soxhlet apparatus for 24 h. The amount of MeOH extractables was ~27.5% of the overall CL+ACA used. Before testing, the MeOH-treated blend was dried under high vacuum at 130°C for 24 h.

After MeOH extraction, the compositions of all the prepared blends have been recalculated and are reported in *Table 1*. In this table, the codes are as follows: A is pure polyamide-6 (PA6); B is a binary PA6/EPR blend; C are blends with EPR-*g*-SA at 0.7% degree of grafting; and D are blends with EPR-*g*-SA at 1.4% degree of grafting. The subscript numbers (0, 40 and 120) indicate the time of polymerization at which the rubber was added (polymerization time *PT*).

Specimen preparation

The blends obtained concurrently with synthesis were compression moulded in a heated press at 260°C and a pressure of 240 kg cm^{-2} to obtain sheets 3 mm thick. Successive samples of $60 \times 6.0 \times 3.0$ mm^3 were cut and notched at the middle of their length as follows: first, a blunt notch was produced using a machine with a 'V'-shaped tool and then a sharp notch 0.2 mm deep was made by a razor blade fixed on a micrometer apparatus. The final value of notch depth was measured after fracture by using an optical microscope.

Impact fracture measurement

Charpy impact tests were carried out at an impact speed of 1 m s^{-1} by using a CEAST fracture pendulum. Samples with a notch depth-to-width ratio of 0.3 and a test span of 48 mm were fractured at various temperatures ranging from −50 to 20°C. The temperature was changed by means of a home-made liquid-nitrogen apparatus. Curves of impact strength as a function of test temperature were obtained for all the blends investigated. Prior to testing, the specimens were dried under vacuum at 90°C for 10 h.

Morphological analysis

Microtomed surfaces of all the blends investigated were exposed for 20 min to boiling xylene vapour and subsequently examined in a scanning electron microscope (Philips SEM 501) after coating with gold–palladium

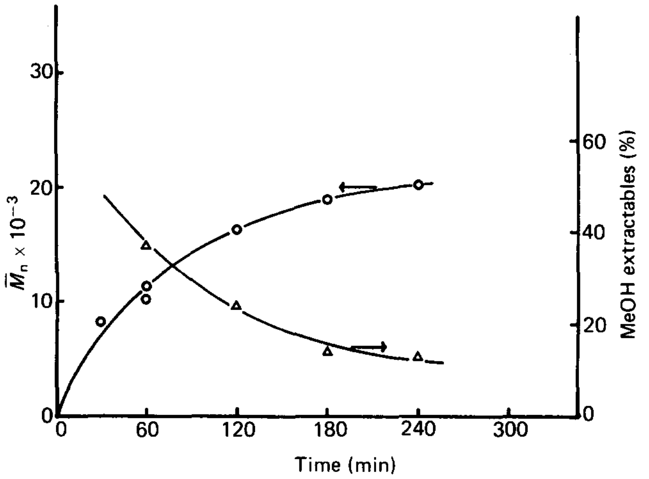


Figure 1 M_n of plain PA6 (○) and MeOH extractables (△) as functions of the polymerization time

alloy. It was observed that the xylene selectively dissolved the rubbery phase, leaving the PA6 matrix undissolved.

RESULTS AND DISCUSSION

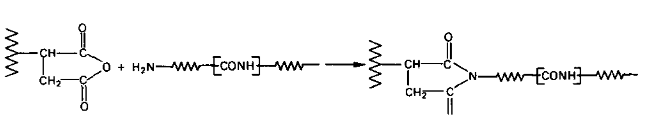
Rubber addition and kinetics of PA6 polymerization

All the blends prepared and investigated in the present paper are reported in *Table 1* (see 'Experimental' section for explanation of codes and compositions). The M_n values of the PA6 obtained are reported as a function of the polymerization time, together with the values of the MeOH extractable fractions, in *Figure 1*. It can be seen that the largest increase in the molecular weight is obtained during the first 2 h of polymerization, when the polycaprolactam reaches an M_n value of about 16000, 80% of the final value (around 20000). In order to study the influence of the degree of polymerization on the morphology and mechanical properties of the final blend, the rubber was added to the reacting mixture after different times of polymerization (*PT*), namely 0, 40 and 120 min.

The choice of 120 min as the limiting time of rubber addition has been made on the basis of the following two considerations:

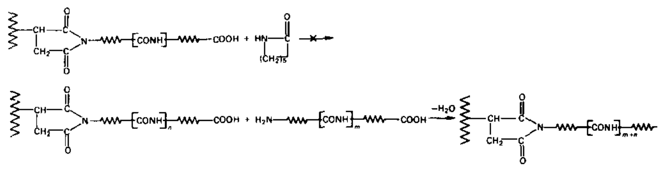
(1) The viscosity of the reacting medium for times exceeding 120 min becomes too high to ensure intimate mixing of the rubber inside the polymerizing matrix, at least with our single-blade stirrer. More efficient mixers (i.e. a Brabender-like apparatus) would be necessary as we reach conditions closer to the melt mixing of high-molecular-weight polymers.

(2) On the basis of our previous work[10] we know that a reaction occurs between groups grafted onto EPR and growing PA6 chains, which leads to the formation of an imidic linkage:



From the stoichiometry of this reaction it happens that, for $M_n = 16000$ and an EPR-*g*-SA at 1.4% by weight of anhydride, the amount of residual amino end groups is almost equal to the amount of anhydride groups. For longer *PT*, the further decrease in the amino end groups will leave a useless excess of anhydride groups in the system.

The influence of *PT* on the MeOH extractables for C and D type blends is shown in *Figure 2*. It can be seen that the addition of grafted EPR increases the amount of extractables. This effect is more pronounced when the EPR-*g*-SA is added at the beginning of the polymerization reaction and when the degree of grafting of EPR is larger. Such behaviour can be explained on the basis of the following consideration: EPR-*g*-SA may be considered as a monofunctional terminator of polymerization and it is known in the literature that similar molecules lead to a decrease in the equilibrium conversion and in the molecular weight of the resulting homo-PA6[11]. Furthermore, once a growing PA6 chain has reacted with the anhydride group of EPR-*g*-SA, it can continue its growth only via the –COOH end group. Such a group is known to be much less reactive than an amino group towards addition to cyclic caprolactam, and it can only condense with the amino end group of a second growing polycaprolactam chain:



The effect of this will be a decrease of the M_n of the grafted PA6 chains with respect to the homo-PA6.

Another effect that must be taken into account is the influence of the rubber on the 'viscosity' of the polymerizing medium. It was observed in fact that:

(1) The addition of the rubber always leads to a more viscous final polymeric melt.

(2) The increase in viscosity is more marked when the rubber is added at high *PT*.

(3) No differences were found between the two sets of experiments carried out with rubbers at different degrees of grafting.

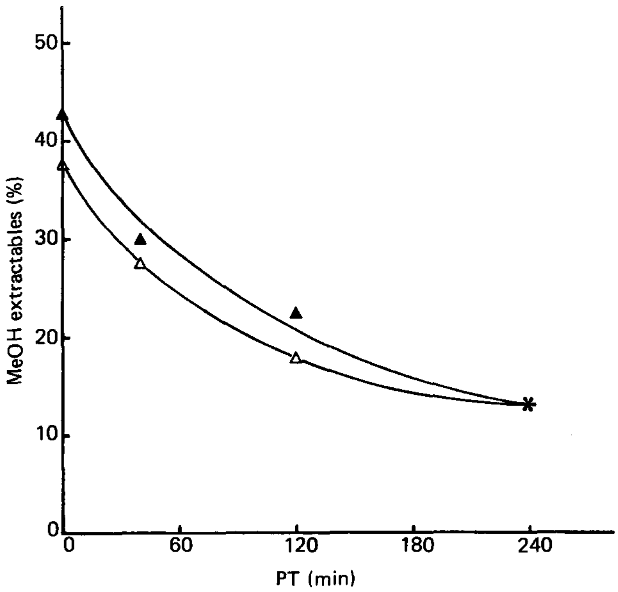


Figure 2 MeOH extractables as a function of *PT*: (▲) PA6/EPR-*g*-SA ($DG = 1.4\%$) blends; (△) PA6/EPR-*g*-SA ($DG = 0.7\%$) blends; (*) plain PA6

(4) Increase in the stirrer speed has a negative effect on the efficiency of mixing, as the polymeric melt tends to climb the stirrer shaft. On the contrary, we found it useful to decrease the stirrer speed in the last hour of polymerization, at least for blends with $PT = 2$ h.

Blend analysis

In a previous paper[4] we described a method of characterization of PA6/EPR-*g*-SA blends based on selective alternate solvent extractions. A similar approach (see *Figure 3*) was followed in the present work. Finely ground samples of blends were treated overnight with formic acid to remove all the homo-PA6. The resulting emulsion was left to stand in a separatory funnel for the time necessary to give a stable phase separation (this usually takes from a few days to several weeks). At this point, the supernatant solid phase was collected, washed with formic acid, coagulated with methanol, dried and weighed. Afterwards, this sample was treated with xylene to eliminate and to weigh the rubbery fraction that did not react with polyamide-6. What remains, if anything, should likely be practically pure graft copolymer, (EPR-*g*-SA)-*g*-PA6. It must be pointed out that the formic acid solution is never transparent, even after weeks, suggesting that some graft copolymer having longer PA6 chains does not give sediment from formic acid.

The results of HCOOH and xylene extractions, together with the final blend composition (i.e. after MeOH treatment), are reported in *Table 2*. From the data it can be concluded that:

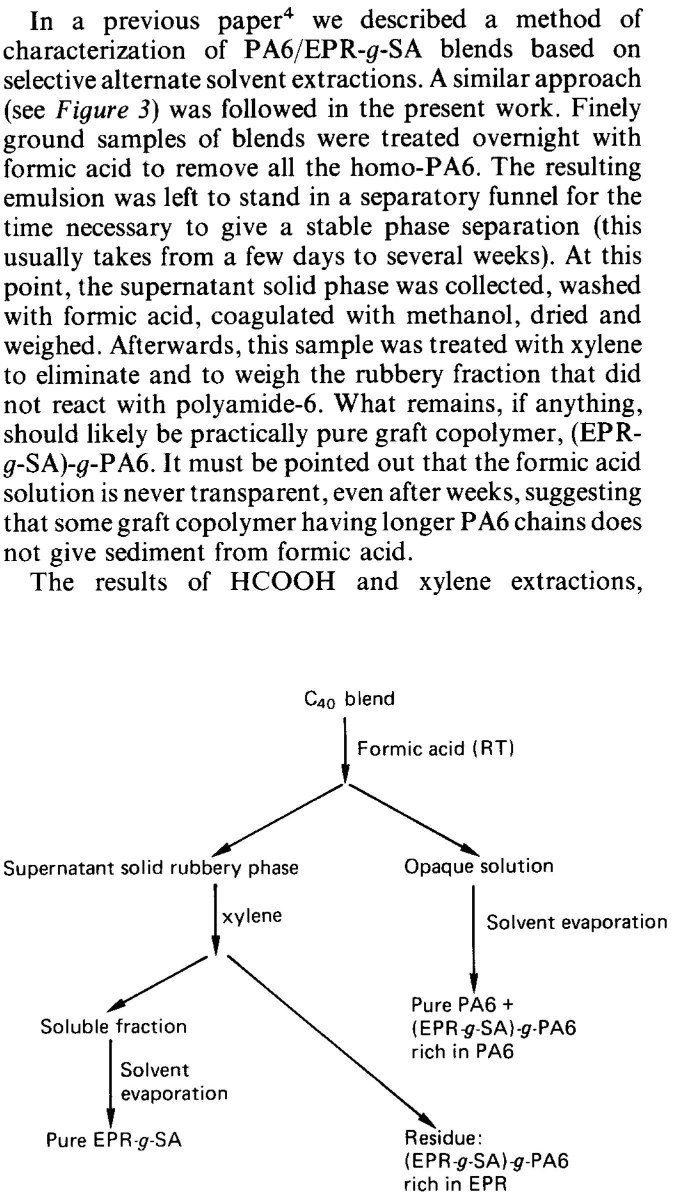


Figure 3 Steps in the selective extractions of blend C_{40} with formic acid and xylene

(1) For the blends coded C containing the rubber with lower degree of grafting, the residue of HCOOH extraction, that is the rubbery phase, is always less than the initial rubber. A similar effect is not found in the blends coded D.

(2) For the series coded C, the C_{120} shows the lowest amount of HCOOH residue.

A possible explanation of such experimental evidence is as follows. The reaction between anhydride groups and growing PA6 chains will cause the formation of a shell of reacted rubber around a core of unreacted EPR-*g*-SA. To allow an extensive reaction of the core, such a shell should be 'soft' and the droplet should break down under shear into smaller spheres. When the degree of grafting is too high, the shell formed is quite tough and the stirring is less able to break the emulsion. In contrast, at a lower degree of grafting, the shell is breakable and the grafting reaction can continue during the polymerization. From the above, we can conclude that for the blends coded C, we always have the formation of relatively high amounts of grafted (EPR-*g*-SA)-*g*-PA6 molecules, which upon HCOOH extraction remain inside the polyamide phase.

Such an effect is more evident for the C_{120} blend, where the length of grafted PA6 chains is similar to that of homo-PA6.

Further support for this explanation is given by the last columns of *Table 2*, where we report the xylene extraction of the residue from HCOOH extraction (owing to the small amount of recovered material, it was not always possible to carry out gravimetric analysis). In the case of blends C, we suppose that the preliminary HCOOH extraction removes all the (EPR-*g*-SA)-*g*-PA6 molecules very rich in PA6, which constitute the outer shell of the dispersed phase, and leaves as a residue the core of the particles, mainly made up of less reacted rubber with few PA6 chains on it. Thus, the residue of HCOOH extraction of blends C should be very soluble in xylene, as we actually found (see last columns of *Table 2*). It must be pointed out that the residue of xylene extraction shows, on d.s.c. analysis, the existence of a PA6 crystalline phase. On the contrary, the preliminary HCOOH extraction in the case of blends D should be unable to remove all the (EPR-*g*-SA)-*g*-PA6 from the outer shell of the particles, as many of the grafted molecules are highly and tightly entangled with each other and with the core of the domains, owing to the higher degree of grafting. Such an outer shell, rich in short PA6 chains, is also insoluble in

Table 2 Characterization of the prepared blends by selective solvent extraction

	Composition (%)		HCOOH extraction (%)		Xylene extraction[a] (%)	
Code	PA6	EPR-*g*-SA	Extract	Residue	Extract	Residue
B		[b]	73	25		—
C_0	71.4	28.6	77	22	—	24
C_{40}	74.4	25.6	78	22	60	39
C_{120}	76.8	23.2	86	11	—	45
D_0	69.7	30.3	68	30	26	70
D_{40}	73.7	26.3	72	27	22	75
D_{120}	75.7	24.3	76	20	27	68

[a] Xylene extraction was carried out on the residue of HCOOH extraction
[b] PA6/EPR 77.5/22.5 binary blend

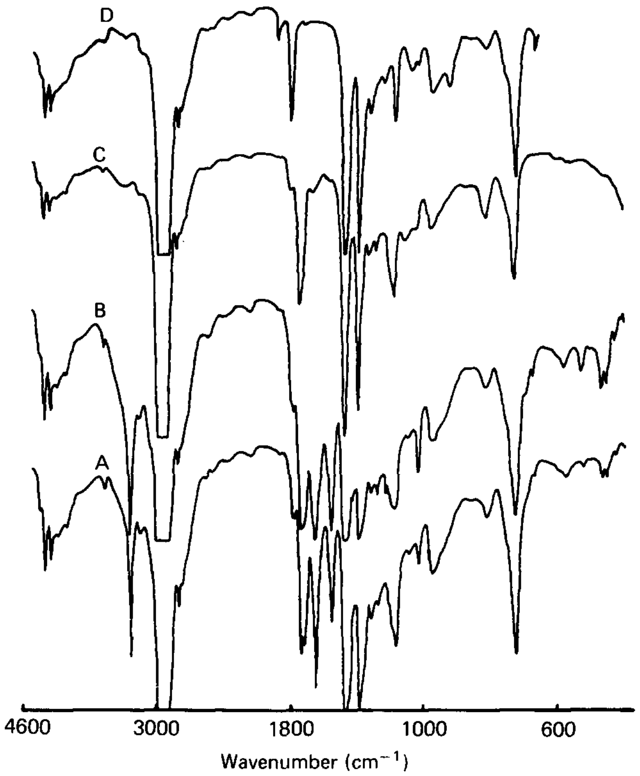


Figure 4 I.r. spectra of the extracted fractions of the blend C_{40}: (A) HCOOH residue; (B) xylene-insoluble fraction of the HCOOH residue; (C) xylene-soluble fraction of the HCOOH residue; (D) pure EPR-*g*-SA (see scheme in *Figure 3*)

xylene, as evidenced by the large residue after xylene extraction. Furthermore, the residue after xylene extraction, in this case, does not show evidence of a crystalline phase, supporting the idea that those chains are very short.

FTi.r. characterization

The spectra corresponding to the blend C_{40} at different steps of extraction (see *Figure 3*), together with the spectrum of pure EPR-*g*-SA, are reported in *Figures 4* and *5* respectively. It is evident that in the HCOOH residue are present the absorptions of EPR-*g*-SA and PA6 (see 2500–3500 cm^{-1} region). Furthermore, we can note, in the carbonyl stretching region, the 'amide I' and 'amide II' band (1640–1545 cm^{-1}) together with a group of three bands (1709, 1728 and 1778 cm^{-1}) whose attribution is somewhat difficult: the 1728 cm^{-1} band could be due to the esterification of part of the residual succinic anhydride groups following the methanol extraction, the band at 1778 cm^{-1} being the symmetric stretching of anhydride. The 1709 cm^{-1} band could either be considered as the acidic moiety of the said hemi-ester or, together with the 1778 cm^{-1} band, it might be the imide symmetric and asymmetric stretching.

A similar analysis, carried out on the residues of xylene extractions on C_{40} and D_{40} blends (see *Figure 3*) is reported in *Figure 6*. It can be seen that the spectra always show the presence of amidic linkages together with bands corresponding to the polyolefinic backbone. Such amidic groups seem to be more evident in the case of the blends coded C, as a result of the presence of few long PA6 molecules instead of the shorter, even more frequent, chains likely to occur inside the D series.

Morphological investigation

Scanning electron micrographs of microtomed and etched surfaces of all investigated blends are shown in *Figures 7–9*. The PA6/EPR blend (*Figure 7*) exhibits the morphology typical of an incompatible system. The rubber is segregated in very large spherically shaped domains, whose dimensions range from 20 μm to more than 100 μm. Furthermore, the walls of the left cavities are very smooth, indicating no adhesion to the PA6 matrix.

As EPR is substituted by EPR-*g*-SA, a strong

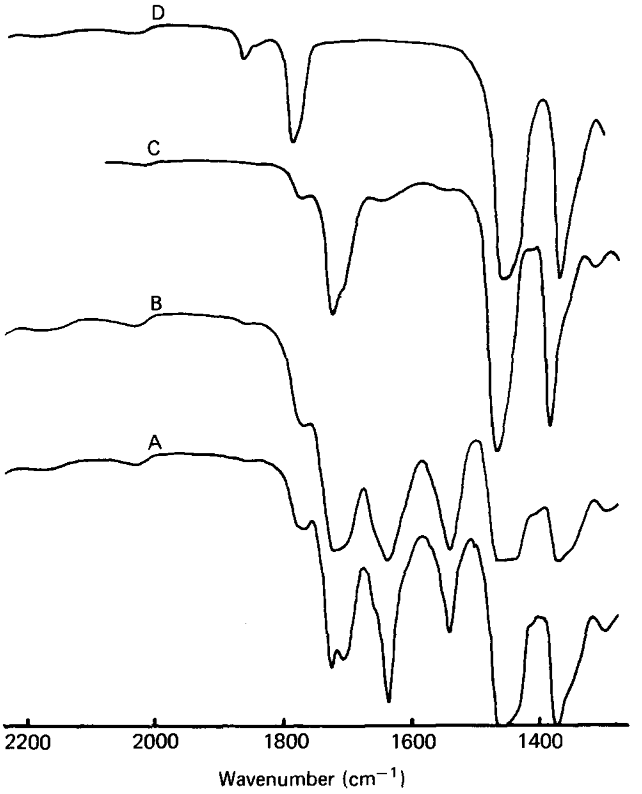


Figure 5 Carbonyl stretching region of the i.r. spectra shown in *Figure 4*

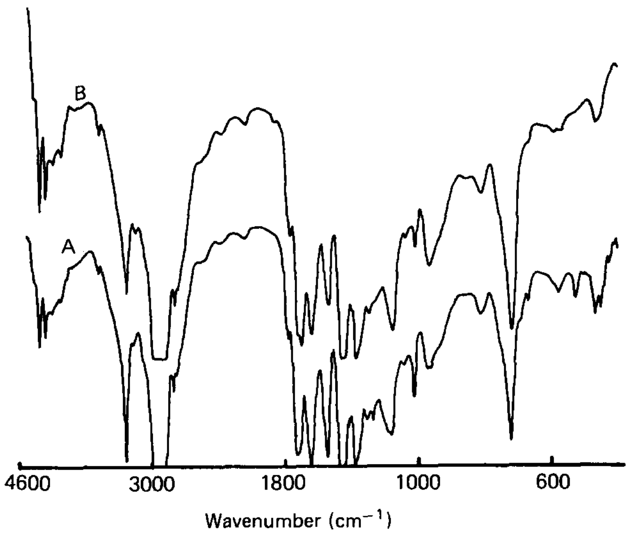


Figure 6 I.r. spectra of the xylene-insoluble fraction of the HCOOH residue for the blends with $PT=40$ min: (A) C_{40} blend; (B) D_{40} blend

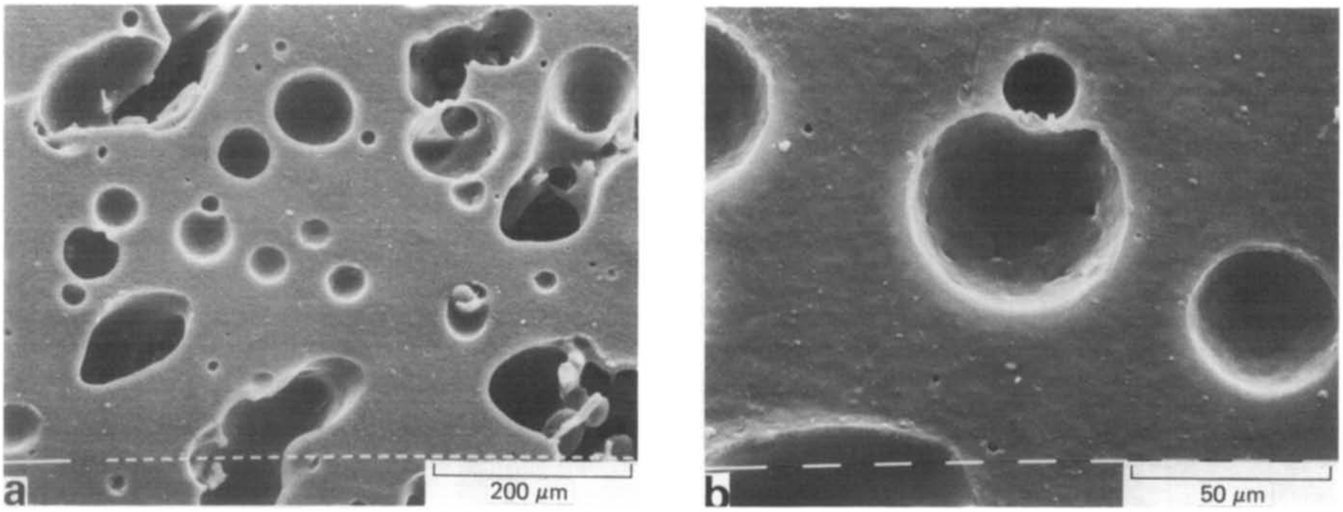


Figure 7 SEM micrographs of a microtomed surface of a hydrolytic PA6/EPR (80/20) binary blend after etching

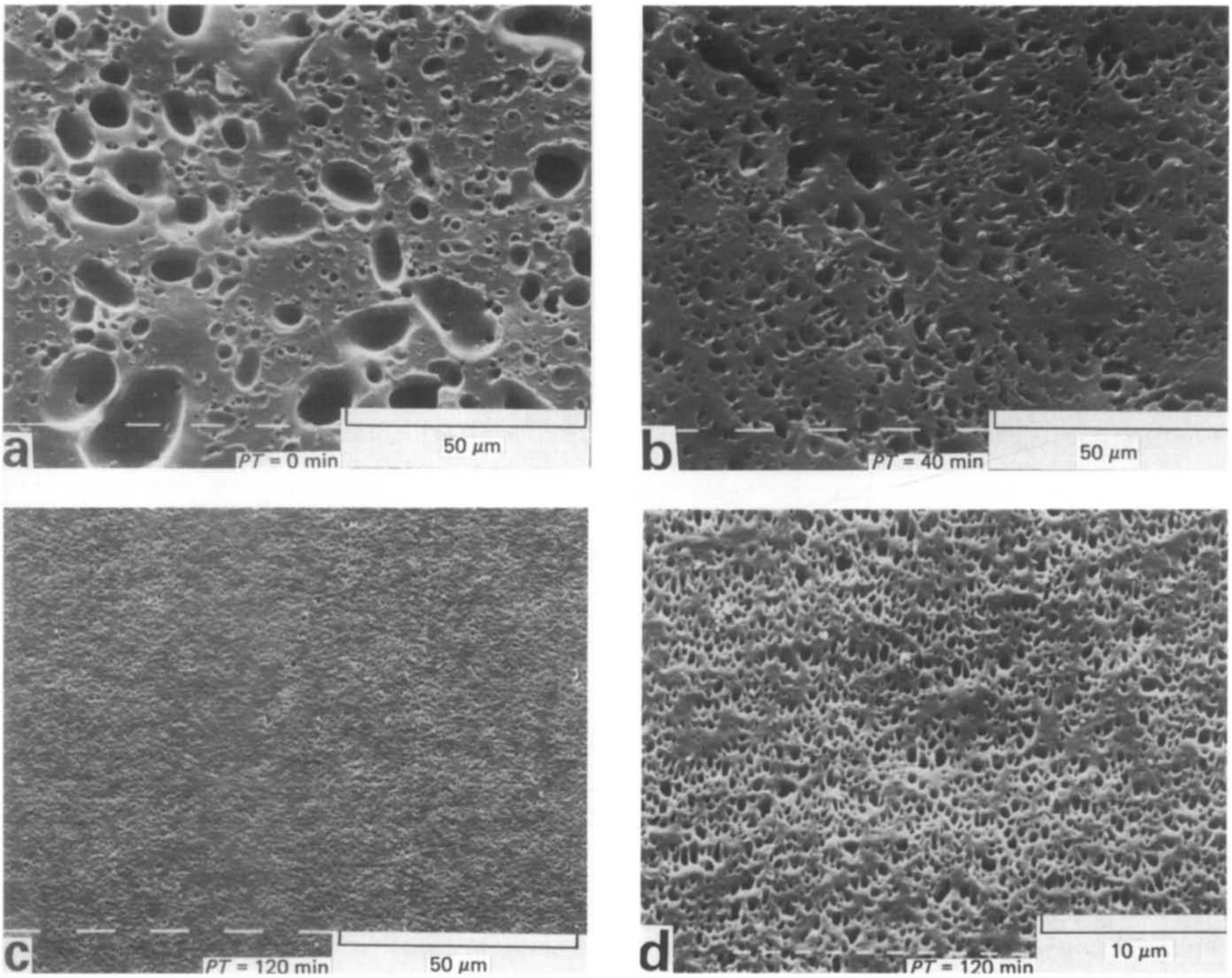


Figure 8 SEM micrographs of microtomed surfaces of hydrolytic PA6/EPR-*g*-SA (80/20) binary blends after etching (degree of grafting $DG = 0.7\%$ and *PT* as indicated)

modification in the mode and state of the dispersion of the rubber component is achieved. The extent of such an effect, as shown by *Figures 8* and *9*, is dependent on the degree of grafting (*DG*) of the EPR-*g*-SA used and on the stage of reaction at which the rubber was added to the reacting mixture (*PT*). From an inspection of *Figures 8* and *9* it emerges that:

(1) The dimensions of etched domains relative to the blends containing EPR-*g*-SA with $DG = 0.7\%$ are much lower than those of the blend containing unmodified EPR

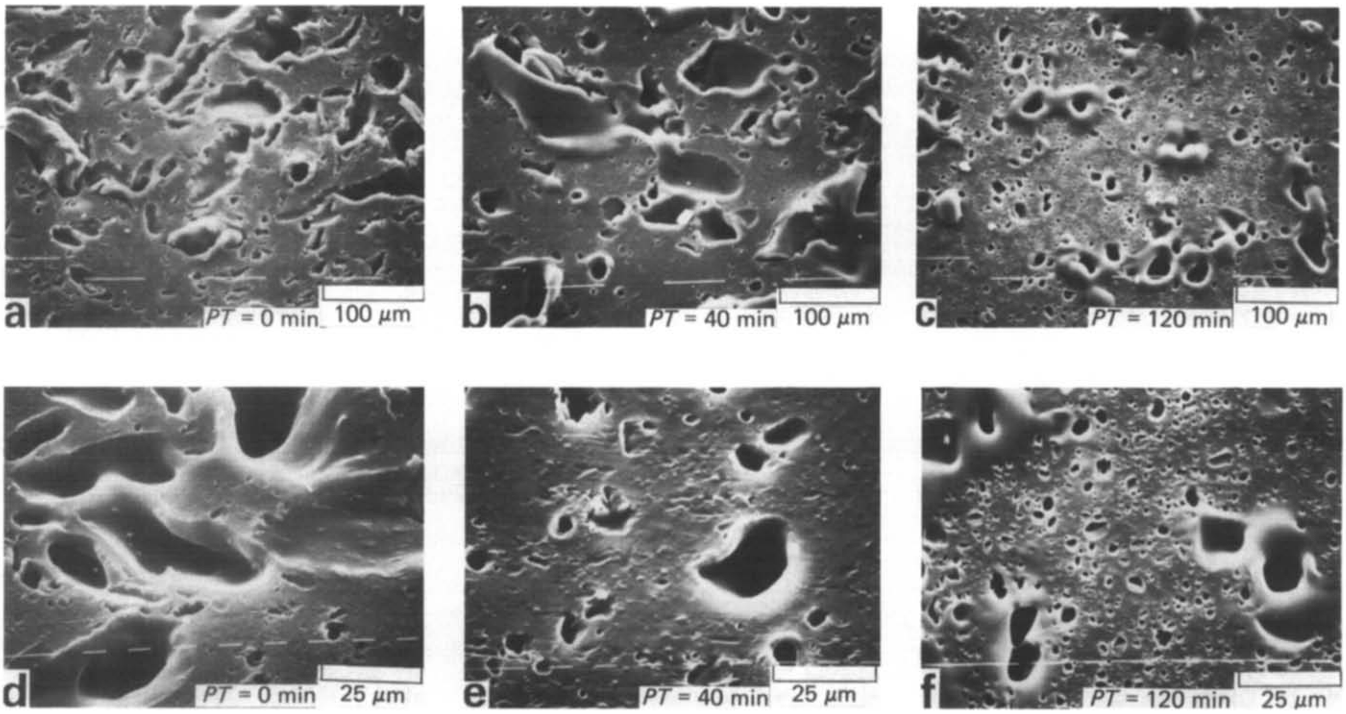


Figure 9 SEM micrographs of microtomed surfaces of hydrolytic PA6/EPR-*g*-SA (80/20) binary blends after etching (degree of grafting $DG = 1.4\%$ and PT as indicated)

(compare *Figures* 7 and *8*). Moreover by increasing PT the average dimensions of such domains decrease, leading to a very fine and homogeneous texture. In fact, for the blend obtained with the highest PT, particles less than 1 μm are present (*Figures 8c* or *8d*).

The above observation can be accounted for by assuming that during the process of blend preparation part of the EPR-*g*-SA is involved in the formation of (EPR-*g*-SA)-*g*-PA6 graft copolymer, which can act as an emulsifier and/or interfacial agent. The effectiveness of such a copolymer will be the greater the higher the molecular weight of the grafted polyamide chains. Thus an increase in PT leads to blends with a finer dispersion and an improved interfacial adhesion because the graft copolymer formed has segments of molecular weight comparable to those of the PA6 homopolymers.

(2) A very irregular distribution of rubbery phase is observed in the case of D blends (see *Figure 9*). Tiny domains ($\sim 1\,\mu$m) coexist with medium size ($\sim 10\,\mu$m) and very large ones (50–100 μm). Some of them are only partially dissolved by the boiling xylene vapour. This quasi-bimodal morphology, however, seems to be more evident in D_0 and D_{40} blends (*Figures 9a* and *9b*). In fact, with increasing PT the number of large domains tends to diminish, whereas the number of smaller sized domains increases (*Figure 9c*). Such an effect, as already mentioned, is due to an improved action of the formed (EPR-*g*-SA)-*g*-PA6 graft copolymer, whose PA6 length branches become more and more compatible with PA6 matrix.

It is interesting at this point to understand why a change in the degree of grafting of the EPR-*g*-SA produces such a marked effect on the overall morphology of the resulting blends. For this purpose, two aspects must be taken into account: the grafting reaction and the efficiency of mixing during the polymerization process. When the DG of EPR-*g*-SA is low, the overall reactivity towards the growing PA6 chains is relatively low. Therefore, the grafting reaction may occur gradually on the rubber surface continuously renewed by the shearing forces induced by stirring. This allows the achievement of good mixing and dispersion of the rubbery component. The results will be the completion of the reaction and a continuous size reduction of the particles by the emulsifying action of the grafted copolymer, as evidenced in *Figure 8*. On the contrary, at higher DG the reactivity of EPR-*g*-SA increases and therefore the grafting reaction starts very rapidly, giving rise on the rubber surface to a graft copolymer rich in PA6 chains. The presence of such highly grafted (EPR-*g*-SA)-*g*-PA6 chains, strongly anchored to the growing PA6 matrix, enhances the viscosity of the mixture. This will decrease more and more the ability of the stirring apparatus to get a satisfactory dispersion. Consequently all the anhydride groups within the grafted EPR-*g*-SA particles are lost with respect to the emulsifying action. Thus the efficiency of the graft copolymer, formed under such conditions, will be much lower if compared to that obtained in the previous case, and therefore a coarser morphology with larger and irregular domains is achieved.

Impact properties of blends

The Charpy impact strengths (R) of PA6 homopolymer and of blends C and D as a function of temperature are reported in *Figure 10*. As can be seen, R of pure PA6 (curve A) remains constant at very low values, over the whole investigated temperature range. The corresponding fracture surface shows the appearance typical of a brittle material. A similar trend with R values slightly lower is observed for the PA6/EPR blend (curve B). Such behaviour is in agreement with the morphology of this blend in which large domains with a broad size distribution and no adhesion to the matrix are present.

Passing to the PA6/EPR-*g*-SA blends containing

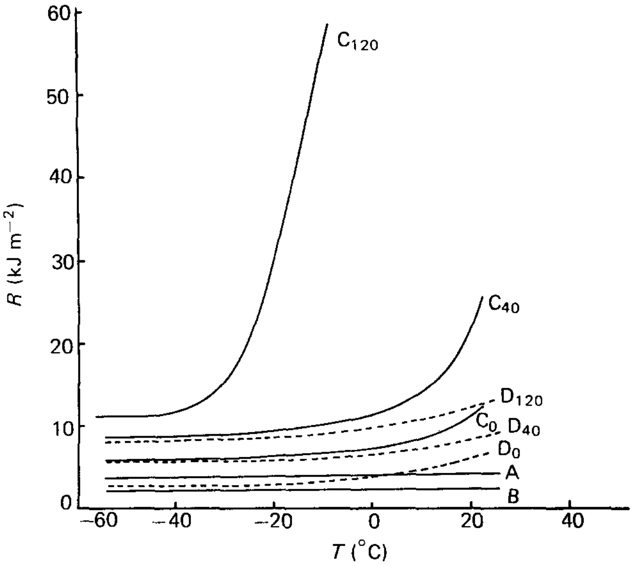


Figure 10 Charpy resilience (R) as a function of test temperature for PA6 homopolymer and for binary PA6/EPR and PA6/EPR-*g*-SA blends. Curves are as follows:

Code	Composition	*GD* (%)	*PT* (min)
A	PA6	—	—
B	PA6/EPR (80/20)	—	—
C_0	PA6/EPR-*g*-SA (80/20)	0.7	0
C_{40}	PA6/EPR-*g*-SA (80/20)	0.7	40
C_{120}	PA6/EPR-*g*-SA (80/20)	0.7	120
D_0	PA6/EPR-*g*-SA (80/20)	1.4	0
D_{40}	PA6/EPR-*g*-SA (80/20)	1.4	40
D_{120}	PA6/EPR-*g*-SA (80/20)	1.4	120

rubber with a *DG* of 0.7% (curves C) a large improvement in the impact performance is observed with respect to PA6. The extent of this effect is higher the greater the time of polymerization at which the rubber is added. Furthermore, the curve of R against temperature shows a clear transition from a brittle to a ductile mode of fracture along the test temperatures. The blend with code C_{120} shows the lowest brittle–ductile transition temperature together with the best impact behaviour. It is interesting to observe that the zone around the notch tip of specimens broken at temperatures around the transition starts to present a stress-whitening phenomenon. This effect, due to multicraze formation, is more pronounced for high values of *PT* and test temperature. The blends containing EPR-*g*-SA with *DG* of 1.4% exhibit, at equal values of *PT*, lower impact performance than blends C (compare curves C and D in *Figure 10*).

The impact behaviour observed in the case of blends C and D is certainly related to the mode and state of dispersion of the rubbery component in the final material. The blend characterized by more fine regular and homogeneous morphology exhibits the best impact behaviour (blend C_{120}). Thus it may be concluded that, when the blends are prepared concurrently with the hydrolytic polymerization of caprolactam, factors such as degree of grafting of the rubber and the time of polymerization at which the rubber is added to the reaction mixture play a decisive role in determining the end properties of the modified PA6. The chemical structure of the (EPR-*g*-SA)-*g*-PA6 graft copolymer formed during the blending and polymerization process and the viscosity of the reactive mixture, in fact, depend on such factors. When the degree of grafting of EPR-*g*-SA used is relatively low and especially at higher values of *PT*, (EPR-*g*-SA)-*g*-PA6 copolymer is likely characterized by PA6 segments whose length is comparable to those of plain PA6. Such a copolymer will have a higher capability to act as emulsifier and compatibilizing agent between the PA6 matrix and the unreacted molecules of EPR-*g*-SA.

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