Rubber modification of polyamide 6 during caprolactam polymerization: influence of composition and functionalization degree of rubber

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Rubber-modified polyamides 6 (PA 6) were obtained directly during the hydrolytic polymerization of ε-caprolactam (CL). An ethylene–propylene elastomer (EPR) and dibutyl succinate grafted EPRs (EPR-g-DBS) were used as rubbery components to yield binary PA 6/EPR-g-DBS and ternary PA 6/EPR/EPR-g-DBS blends having about 20% by weight of total rubber. Model reactions and selective extractions of the blends indicated that (EPR-g-DBS)-g-PA 6 copolymers are formed during the CL polymerization. The influence of the grafting degree of EPR-g-DBS and, for ternary blends, of the weight ratio EPR/EPR-g-DBS on the morphology and on the impact properties of the blends was also investigated. A finer and more homogeneous dispersion of rubbery domains has been found for binary blends, while ternary blends exhibit a quasi-bimodal distribution of rubbery domains. The impact properties of ternary blends are enhanced with the increase of the relative amount of functionalized rubber. The dependence of the morphological features and of the impact properties on the functionalization degree is more complex. Straightforward correlations between mode and state of dispersion of rubber domains and impact properties were not found.

(Keywords: polyamide 6; functionalized rubber; polyamide blends; toughening)

INTRODUCTION

In a previous paper[1] we reported the preparation and characterization of rubber-modified polyamides 6 (PA6) by hydrolytic polymerization of ε-caprolactam (CL) either in the presence of an amorphous ethylene–propylene copolymer (EPR) modified by grafting of succinic anhydride (binary blends PA6/EPR-g-SA) or in the presence of both EPR and EPR-g-SA (PA 6/EPR/EPR-g-SA ternary blends).

The main practical result obtained was an improvement of the impact strength of PA 6, and a dependence of the morphology on the blend composition was observed. A close relation between impact behaviour and the mode and state of dispersion of the rubbery component in the matrix was also emphasized. However, attempts to prepare binary or ternary blends containing high amounts of EPR-g-SA (more than 10% w/w) failed because of the high reactivity of the grafted anhydride groups towards $-NH_2$ end groups of growing polyamide chains. As a consequence of the formation of highly grafted EPR chains, the polymerization mixture was too viscous to be efficiently stirred during the hydrolytic process, thus decreasing the degree of dispersion of the rubber phase attainable.

On the basis of these results and considering that ester groups exhibit a lower reactivity towards amine groups, a more efficient stirring of the reaction mixture and, consequently, a finer dispersion of the rubbery particles in the polyamide matrix could be expected if an EPR modified by grafting ester groups is used as a functionalized rubbery component.

In the present paper we report the preparation and characterization of rubber-modified PA 6 obtained directly during the hydrolytic polymerization of CL in the presence of EPR modified by grafting dibutyl succinate groups, EPR-g-DBS.

The aims of this investigation were: (*a*) to set up the experimental conditions of the CL polymerization in the presence of EPR-g-DBS; (*b*) to shed some light on the chemistry involved in the blend preparation and (*c*) to find and to analyse correlations between composition, functionalization degree of the rubber used, mode and state of dispersion of rubbery components as well as impact behaviour of the blends.

EXPERIMENTAL

Materials

The amorphous ethylene–propylene copolymer (EPR) used was Dutral CO54 (ethylene content, 67 mol%; $\bar{M}_w = 1.8 \times 10^5$), kindly supplied by Dutral S.p.A., and was used as received. Dibutyl succinate (DBS) was purified by distillation at reduced pressure. Caprolactam (CL), aminocaproic acid (ACA) and tridecylamine (TDA) were used without further purification.

The solvents used, when required, were purified according to standard procedures. EPR-g-dibutyl

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succinate (EPR-g-DBS) having 0.6, 2.0, 4.6 and 6.0 wt% of grafted DBS were prepared according to the reported procedure[2].

Techniques

Infra-red analyses of polymers were made on solution cast films by using a Perkin–Elmer 257 spectrophotometer. Low molecular weight products were analysed as Nujol mull. Gas chromatographic analyses were made with a Perkin–Elmer 3B apparatus. An SE 30 steel column (4 m high and 4 mm diameter) was used at 70°C.

Polymerization of caprolactam in the presence of dibutyl succinate

A mixture of CL (45.0 g, 0.398 mol), ACA (5.0 g, 0.038 mol) and DBS (2.00 g, 0.0086 mol) was poured into a cylindrical vial equipped with mechanical stirrer and a side arm for the distillation of volatile products. The vial was repeatedly degassed and filled with pure nitrogen. The polymerization was made at 260°C for 4 h. Volatile products were distilled through the side arm and consisted mainly of butanol, as revealed by gas-chromatographic analysis. The polymerization product was dissolved in formic acid, precipitated with an acetone/water mixture, repeatedly washed with acetone and dried at 60°C under vacuum; $\eta_{\mathrm{inh}} = 0.37$ dl/g in *m*-cresol at 25°C ($c = 0.5$ g/dl).

Reaction of EPR-g-DBS with tridecylamine

Two grams of EPR-g-DBS containing 5.3% by weight of grafted DBS (0.46 mmol of DBS) and 1.84 g (9.2 mmol) of tridecylamine (amine/ester molar ratio, 10/1) were heated at 260°C for 4 h in a 50 ml flask under a nitrogen atmosphere. Then the reaction mixture was dissolved in 50 ml of xylene and poured into 250 ml of acetone. The precipitated polymer product was washed repeatedly with acetone and dried in a vacuum oven at 60°C. Results of infra-red analysis were: 3300 cm^{-1} (s), 1770 cm^{-1} (w), 1738 cm^{-1} (w), 1700 cm^{-1} (s).

Typical procedure for a binary blend preparation

A mixture of 76.0 g (0.67 mol) of CL, 4.0 g (0.031 mol) of ACA and 20.0 g of EPR-g-DBS containing 2.0 wt% of DBS was poured into a cylindrical vial equipped with mechanical stirrer and a side arm for vacuum application or nitrogen inlet. The vial was repeatedly degassed, filled with pure nitrogen and immersed in an oil bath. The temperature of the oil was raised to 260°C within 30 min. The polymerization was achieved under vigorous stirring and a slow nitrogen stream. As the reaction progressed, an increase of the viscosity of the molten phase and of dispersion degree of the rubbery phase were observed. The polymerization was run for 3.5 h at atmospheric pressure and additionally for 30 min at reduced pressure (2 mmHg). After cooling, the crude reaction product was recovered, finely milled and extracted with methanol in a Soxhlet apparatus for 24 h. The mass of soluble products was 16.0 g (*ca.* 20% of the overall CL + ACA used).

Specimen preparation and conditioning

The blends obtained during CL polymerization were compression moulded in a heated press (Wabash hydraulic press) at a temperature of 260 ± 5°C and a pressure of 240 ± 20 kgf/cm^2 to obtain sheets 1 mm and 3 mm thick. The former were used to get dumb-bell-shaped specimens for mechanical tensile tests. The latter were used to make parallelepipedal notched specimens (50 mm x 13 mm x 3 mm) to use for Izod impact tests. A 2 mm deep notch having a radius of curvature at tip of 0.25 mm was made on the specimens by a sliding machine to overcome the influence of all other material defects during impact. Before mechanical and impact measurements the specimens were conditioned in water at 90°C to obtain the same amount of absorbed water (about 3% by weight). The procedure is reported in other works[4].

Mechanical tensile tests

Typical stress–strain curves were obtained by an Instron machine (Model no. 1122) at room temperature and a cross-head speed of 20 mm/min. Moduli and stress at rupture were calculated from such curves determined on an average of eight specimens.

Izod impact tests

The energy necessary to break notched Izod specimens was detected by a Ceast fracture pendulum at two different temperatures (−25°C and −10°C). The temperature was changed by means of a liquid-nitrogen cooling apparatus made in our laboratory.

Analysis by scanning electron microscopy

Before studies by electron microscopy, samples of binary and ternary blends were faced in an ultramicrotome LKB ((Ultramicrotome III) at room temperature, followed by coating with gold–palladium. Alternatively, for a better resolution of the state of dispersion of the rubbery component, an etching technique was developed. Microtome-faced surfaces of blends were exposed for 30 min to boiling xylene vapours, preferentially to remove the rubbery component, and subsequently prepared for SEM examination.

RESULTS AND DISCUSSION

Blend preparation

The preparation of the EPR-g-DBS samples, each with different amounts of grafted DBS, was accomplished in solution according to the procedure reported in reference 2. The hydrolytic polymerization of ε-caprolactam in the presence both of functionalized EPR and of a mixture of EPR and EPR-g-DBS was initiated by ε-aminocaproic acid and made under experimental conditions analogous to those used in previous work[1] (i.e. 260°C, 4 h) under vigorous stirring in a nitrogen atmosphere. The total amount of rubber in the feeding was kept constant to a value of 20% by weight since previous investigations showed that a blend composition of PA 6/total rubber close to 80/20 by weight represents a good compromise between good toughening improvement and reasonable values of tensile modulus.

To evaluate in a semi-quantitative way the reactivity of ester groups toward primary amine groups and the influence of this reaction on the molecular weight of the PA 6 prepared, a set of reactions involving low molecular weight compounds bearing ester or amine groups was preliminarily investigated. Furthermore, the products isolated from these 'model reactions' are easily characterized and provided us with useful information on

Table 1 Hydrolytic polymerization of ε-caprolactam in the presence of dibutyl succinate[a]

Code	CL (mol × 10^{-3})	ACA (mol × 10^{-3})	DBS (mol × 10^{-3})	$\frac{\text{ACA}}{\text{DBS}}$	$\frac{\text{CL}}{\text{DBS}}$	Inherent viscosity[b] (dl g^{-1})	$\bar{M}_n$ (g mol^{-1} × 10^{-3})[c]
PA 6	400	18	0	–	–	1.30	23.0 ± 0.5
DBS1	397	20	1.4	14.3	284	1.14	19.0 ± 0.4
DBS2	402	18	3.7	4.9	109	0.58	7.0 ± 0.2
DBS3	398	38	8.6	4.4	46	0.37	3.5 ± 0.1

[a] Reaction temperature: 260°C, reaction time: 4 h
[b] In *m*-cresol at 25°C; $c = 0.50$ g dl^{-1}
[c] Calculated by using the equation of reference 3

some aspects of the chemistry involved in the blend preparation.

Hydrolytic polymerization of ε-caprolactam in the presence of dibutyl succinate. Polymerization reactions of caprolactam were made in the presence of different amounts of dibutyl succinate. The polyamides 6 obtained were purified according to conventional procedures; their inherent viscosities were measured and approximate $\bar{M}_n$ values were calculated by using the empirical relation[3]:

$$\bar{M}_n = 15\,600\eta_{\mathrm{inh}}^{1.49}$$

The results are summarized in *Table 1* and show a decrease of the molecular weight by decreasing the CL/DBS molar ratio. This behaviour could be expected as a consequence of a stoichiometric imbalance of –COOH and $-NH_2$ end groups caused by the reaction between ester groups of DBS and the amino end groups of growing PA 6 chains. The occurrence of this reaction was confirmed by the presence of *n*-butanol in the volatile products evolved during the polymerization. Molecular weights, high enough for practial uses, may therefore be reached when the CL/DBS molar ratio is kept close to 2.5×10^2–3.0×10^2. For a blend containing 20 wt% of EPR-g-DBS (DBS = 3 wt%), it is possible to calculate, from the data of *Table 1*, that M_n values close to 19×10^3 g mol^{-1} may be foreseen for the polyamidic matrix, provided that grafted ester groups have a reactivity similar to that of free succinate groups and that the presence of the rubber phase does not influence the polymerization rate.

Reaction of EPR-g-DBS with tridecylamine. The reactivity of the succinate groups towards primary amines and the nature of the reaction products were investigated by reacting pure dibutyl succinate and tridecylamine (TDA). The reaction was effected in the absence of solvent at 260°C for 4 h, with use of an excess of amine. The isolated reaction product shows the well known amide bands at 3300 cm^{-1}, 1640 cm^{-1} and 1545 cm^{-1} in the i.r. spectrum while the C=O ester stretching band at 1738 cm^{-1} is absent, thus indicating that only tridecyl succindiamide is formed. EPR-g-DBS was also treated with TDA in similar reaction conditions. Two different $-NH_2$/–COOR molar ratios (10/1 and 2/1) were used. Two sets of reactions were accordingly made, with various reaction times in the range 30–360 min. Analysis of the recovered volatile products formed during the reaction showed the presence of butanol as the main component. The extent of the reaction was followed by i.r. analysis made on thin films of the recovered polymer, by which means the gradual disappearance of the band at 1738 cm^{-1} and the simultaneous growth of a doublet at 1700 cm^{-1} (s) and 1770 cm^{-1} (w), attributable to a cyclic imide group, were observed. Plots of *R*, defined as the absorbance ratio of the 1738 cm^{-1} and 1700 cm^{-1} absorptions, against time, for both sets of reactions, are reported in *Figure 1*. It is shown that a higher excess of amine groups increases the amount of the reacted ester groups at a given time and that after 240 min *R* reaches, for both curves, a limiting value that changes only slightly after an additional 120 min. Compared with previous results on the reactivity of grafted anhydride groups[1,4,5], these results indicate that grafted ester groups have a markedly lower reactivity towards amino groups by comparison with those of the anhydride groups. Moreover, probably a fraction of grafted ester groups does not react because of the fact that in an heterogeneous reaction, only a fraction of ester groups is accessible to the $-NH_2$ groups.

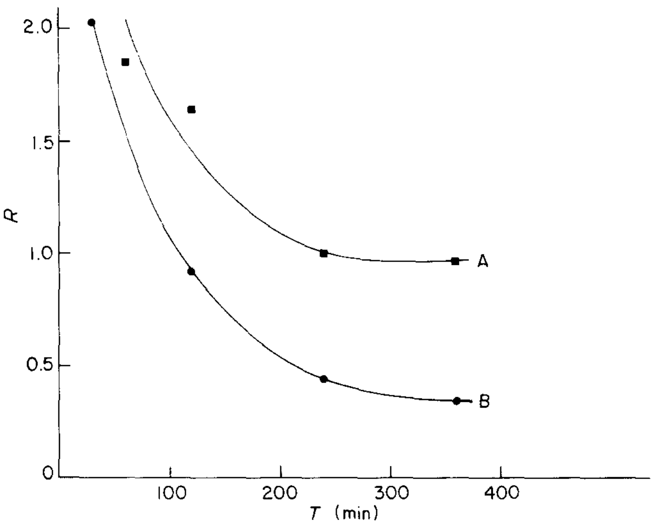
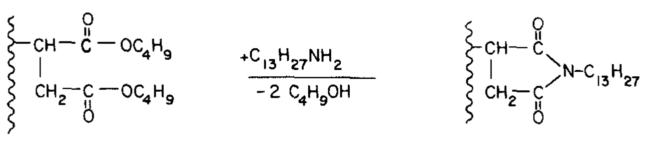
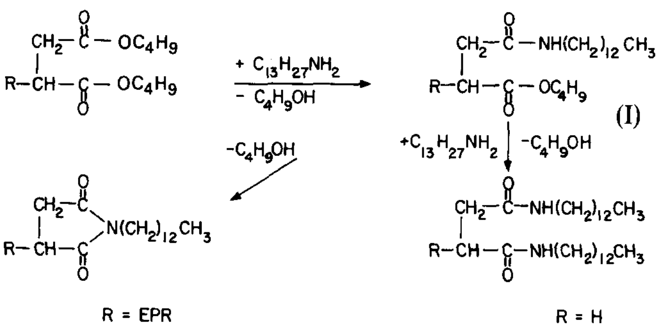


Figure 1 Dependence of the 1738 cm^{-1}:1770 cm^{-1} absorbance ratio, *R*, on time for the reaction of EPR-g-DBS with TDA. Molar ratio TDA/DBS: ■, 2/1; ●, 10/1

It is worthwhile remarking that the chemical and spectroscopic evidence indicates the occurrence of the following reaction:



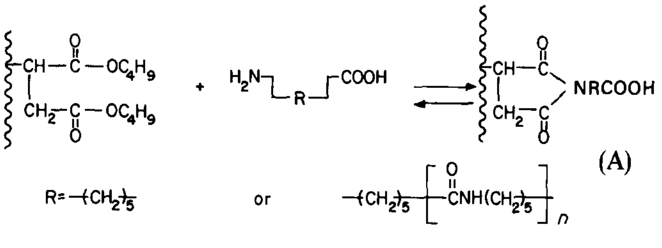
thus suggesting that the presence of the macromolecular chains preferentially leads to the formation of a cyclic imide, while a diamide was obtained for free DBS, as shown before. The following scheme reports the proposed reaction patterns, when free and grafted DBS are used respectively:



Structure (I) shows a hypothetical intermediate that can give rise to a cyclic imide if DBS is grafted onto EPR or to a diamide if free DBS is involved in the reaction.

Polymerization of ε-caprolactam in the presence of EPR rubbers. Binary PA 6/EPR-g-DBS and ternary PA 6/EPR/EPR-g-DBS blends with a general composition PA 6/total rubber close to 80/20 were prepared by using EPR-g-DBS bearing 0.6, 2.0, 4.6 and 6.0 wt% of DBS. A binary PA 6/EPR blend was also prepared for comparison purposes. Experimental conditions close to those used in the industrial process of hydrolytic polymerization of ε-caprolactam were used, and the polymerization was made according to the reported procedure[1], with the use of aminocaproic acid (ACA) as initiator. The starting materials, CL, ACA and EPR and/or EPR-g-DBS, were all mixed together in a vial previously degassed and vigorously stirred at 260°C for 4 h. The prepared blends, after grinding, were extracted by methanol to remove unreacted CL and cyclic oligomers. The products recovered from methanol consisted of about 20 wt% of CL + ACA in the feed.

In addition to the well known equilibria occurring in the hydrolytic polymerization of CL 6, the presence of EPR-g-DBS in the reaction mixture can give rise to the equilibrium:



(A) is subsequently involved in a condensation step with growing PA 6 chains forming (EPR-g-DBS)-g-PA 6 graft copolymer species, their composition and structure depending on the functionalization degree of EPR and on the molecular weight of the grafted polyamide chains. It is worth noting that, unlike the analogous reaction used to prepare binary blends with 20 wt% of EPR-g-SA, in the present case the reaction mixtures allow efficient stirring throughout the 4 h required for polymerization. This behaviour may be accounted for by the lower reactivity of the succinate groups with respect to the anhydride group, as shown before, and consequently by the lower number of PA 6 grafted chains in the former case. It has also been observed that during the preparation of the binary PA 6/EPR-g-DBS blends a fine dispersion of the rubber component occurs within the first 2 h of the process, whereas, for ternary blends, more than 3 h are required and, under the same reaction conditions, the higher the EPR-g-DBS/EPR ratio, the faster dispersion is reached.

EPR-g-DBS/EPR ratios of 3.0, 1.0 and 0.33 were used in the formulation of the ternary blends to investigate the dependence of the morphology of the blends either on the composition or on the chemical structure of the different grafted copolymers (EPR-g-DBS)-g-PA 6 formed. All of the blends prepared and investigated are reported in *Table 2* together with the code, the composition after methanol

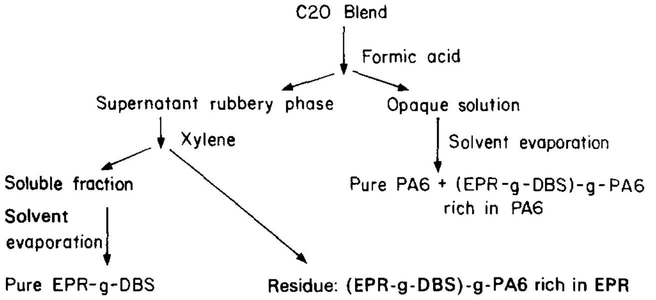
Table 2 Characterization of PA 6 and of the prepared binary PA 6/EPR and PA 6/EPR-g-DBS blends and ternary PA 6/EPR/EPR-g-DBS blends

Code	Grafting degree of EPR-g-DBS (wt%)	Intrinsic[a] viscosity of EPR-g-DBS (dl g^{-1})	Feed composition CL/EPR/EPR-g-DBS (wt%)	Methanol soluble fraction (wt% on CL + ACA)	Blend composition CL/EPR/EPR-g-DBS (wt%)	Inherent[b] viscosity of PA 6 (dl g^{-1})
PA 6	–	–	100/0/0	20.3	100/0/0	1.3
PA 6/EPR	–	–	80/20/0	22.0	74/26/0	1.0
A5	0.6	1.54	80/15/5	15.0	77/17/6	–
B5	2.0	–	80/15/5	18.7	76/18/6	–
C5	4.5	–	80/15/5	18.7	76/18/6	–
D5	6.0	0.90	80/15/5	20.0	76/18/6	–
A10	0.6	1.54	80/10/10	18.7	76/12/12	–
B10	2.0	–	80/10/10	17.5	76/12/12	1.0
C10	4.5	–	80/10/10	25.0	75/12.5/12.5	1.1
D10	6.5	–	80/10/10	20.0	76/12/12	1.1
A15	0.8	1.57	80/5/15	16.2	77/6/17	–
B15	1.8	1.24	80/5/15	17.5	77/6/17	–
C15	4.8	0.96	80/5/15	20.0	76/6/18	–
D15	5.6	0.89	80/5/15	20.0	76/6/18	–
A20	0.6	1.54	80/0/20	17.5	77/0/23	–
B20	2.0	–	80/0/20	20.0	76/0/24	1.0
C20	4.6	0.96	80/0/20	17.5	77/0/23	0.9
D20	5.6	0.89	80/0/20	18.7	76.5/0/23.5	–

[a] In tetrahydronaphtalene at 135°C
[b] In *m*-cresol at 25°C, $c = 0.50$ g dl^{-1}

extraction and the inherent viscosity of the PA 6 recovered by treatment with formic acid.

Blend analysis. An analysis of the blends prepared was made on B20, C20 and D20 binary blends and B10, C10 and D5 ternary blends by selective extraction of the components by two different solvents. By treatment with formic acid, emulsions were obtained in every case, thus clearly revealing the emulsifying effect of (EPR-g-DBS)-g-PA 6 formed. A complete phase separation could also not be reached after several weeks, and more or less opaque solutions, according to the content of EPR-g-DBS used, were obtained with a supernatant rubbery phase. As an example, we report the procedure followed on the C20 blend and illustrated below.



A sample of this blend was treated with formic acid. A supernatant rubbery phase was separated and the opaque formic acid solution was evaporated and the recovered product characterized by i.r. analysis. It mostly consists of PA 6, as indicated by the pattern of the spectrum, almost identical to that of pure PA 6. A very weak absorption at 1738 cm^{-1} shows, however, the presence of small amounts of ester groups. These findings suggest that the formic acid phase contains mainly pure PA 6 and that the suspended fine particles most likely consist of (EPR-g-DBS)-g-PA 6 copolymers with a composition rich in polyamide, but also bearing unreacted ester groups on the EPR chains. A rough evaluation of $\bar{M}_n$ of the polyamide recovered from formic acid solution, attained by using the previously reported relation between the measured inherent viscosity and $\bar{M}_n$, led to a value close to 13 000. The isolated supernatant rubbery phase represents 80 wt% of the initial rubber in the feed. Successive treatment of the rubber with xylene reveals that it is almost 65% soluble. Infra-red analysis of the soluble part shows that this consists of pure EPR-g-DBS, whereas the residue shows absorptions both at 1640 cm^{-1} and at 1738 cm^{-1}, characteristic of amide and ester groups respectively. Reasonably, this product, insoluble both in xylene and formic acid, consists of (EPR-g-DBS)-g-PA 6 graft copolymers rich in EPR. These results indicate that only about 50% of the initial EPR-g-DBS used in the feed have reacted during the polymerization of the

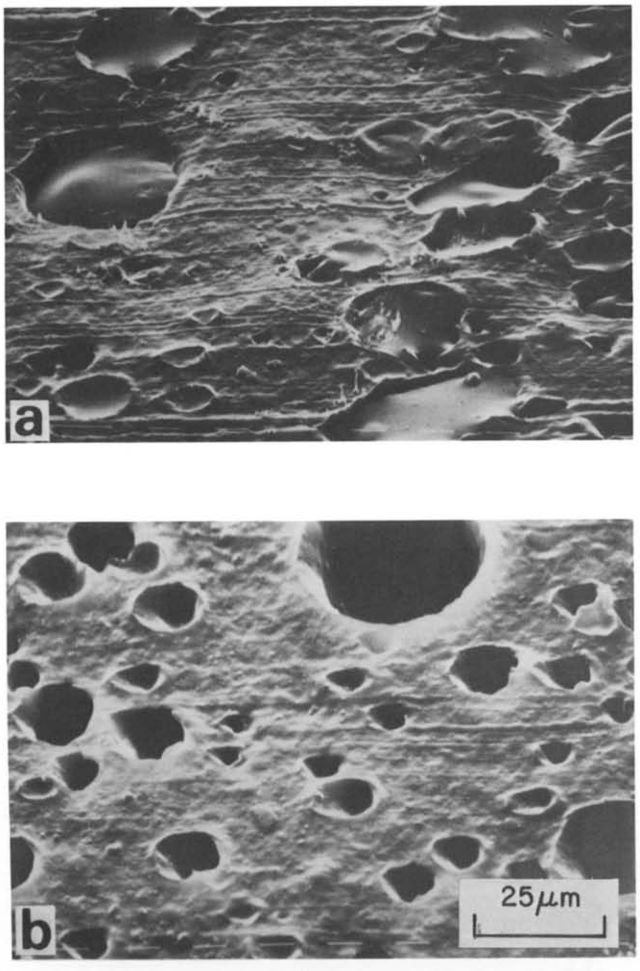


Figure 2 SEM micrographs of smoothed surfaces of binary PA 6/EPR 90/10 blend: (a) before etching 640 × ; (b) after etching 640 ×

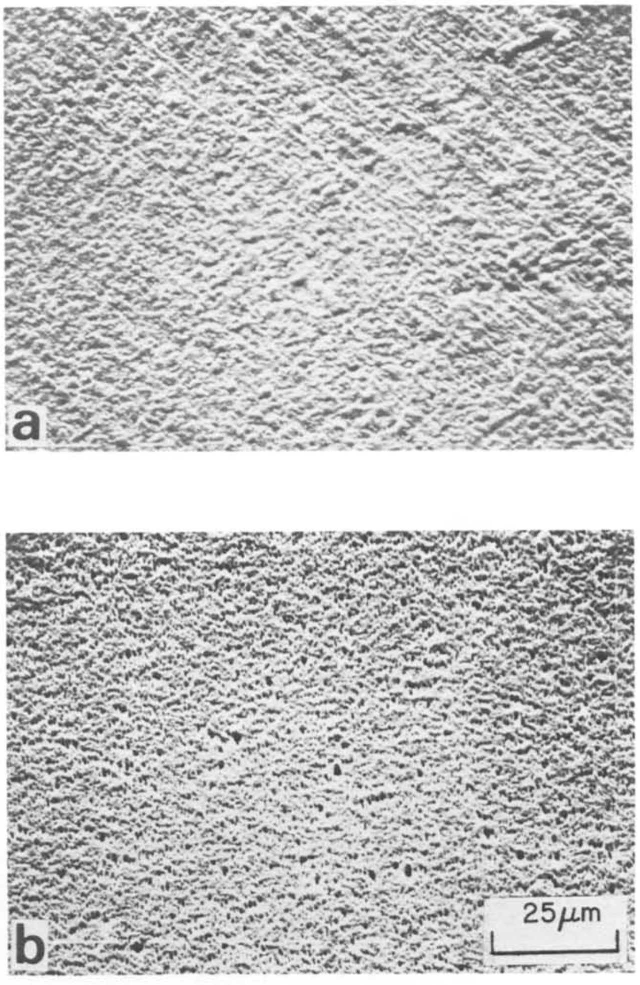


Figure 3 SEM micrographs of smoothed surfaces of B20 blend: (a) before etching 640 × ; (b) after etching 640 ×

caprolactam and that at a given grafting degree a wide range of composition of (EPR-g-DBS)-g-PA 6 graft copolymer was obtained.

Mode and state of dispersion of rubbery components

Scanning electron microscopy has proved to be a valuable technique for a careful inspection of the overall morphology of rubber-modified PA 6. Specimen surfaces were smoothed by using an ultramicrotome and analysed either as obtained or after exposure to xylene vapours (see the Experimental section). The latter technique proves to be very useful for resolving the morphology of blends, especially for specimens with a high degree of interconnection between the different phases. Surface s.e.m. micrographs (before and after etching) related to binary and ternary blends are reported in *Figure 2, 3* and *4*. The removal of the rubbery phase (consisting of EPR and/or unreacted EPR-g-DBS) shows the morphological features, particularly for the B20 blend, where the dispersed phase is intimately interconnected to the matrix.

Micrographs of smoothed surfaces of blends, after etching, arranged at increasing weight ratio (M) of functionalized EPR-g-DBS rubber over total rubber content are shown in *Figures 5–8*. The figures refer to values for the degree of functionalization of EPR-g-DBS of 0.6, 2, 4.6 and 6, respectively. The mode of dispersion of the rubber in the ternary blends, as clearly revealed by etching, consists mainly of spherical domains whose dimensions range from about 1 μm to more than 50 μm (see, as an example, blend D10). The SEM investigation, made mainly on etched smoothed surfaces, leads to the following observations.

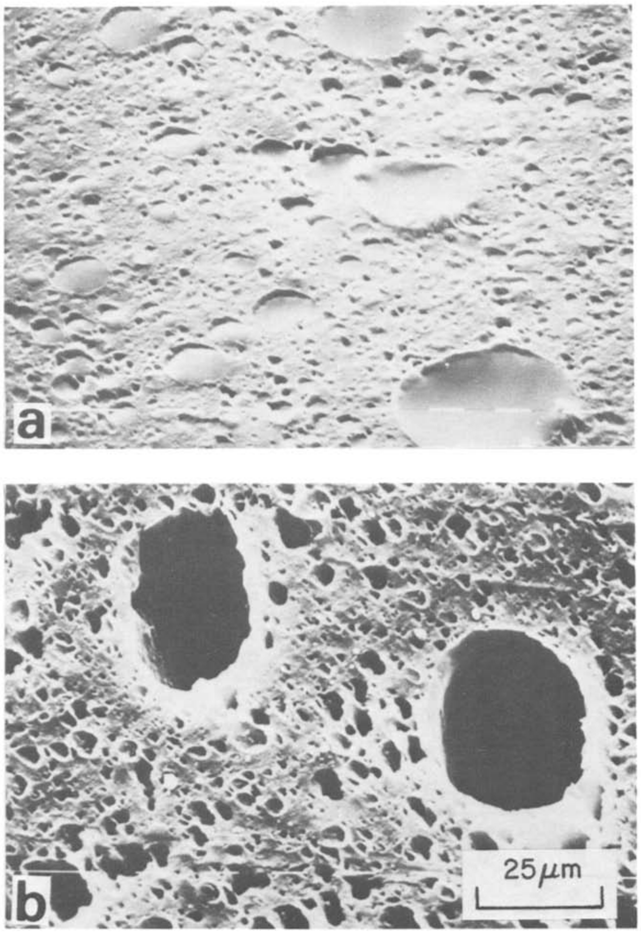


Figure 4 SEM micrographs of smoothed surfaces of C5 blend: (a) before etching 640 × ; (b) after etching 640 ×

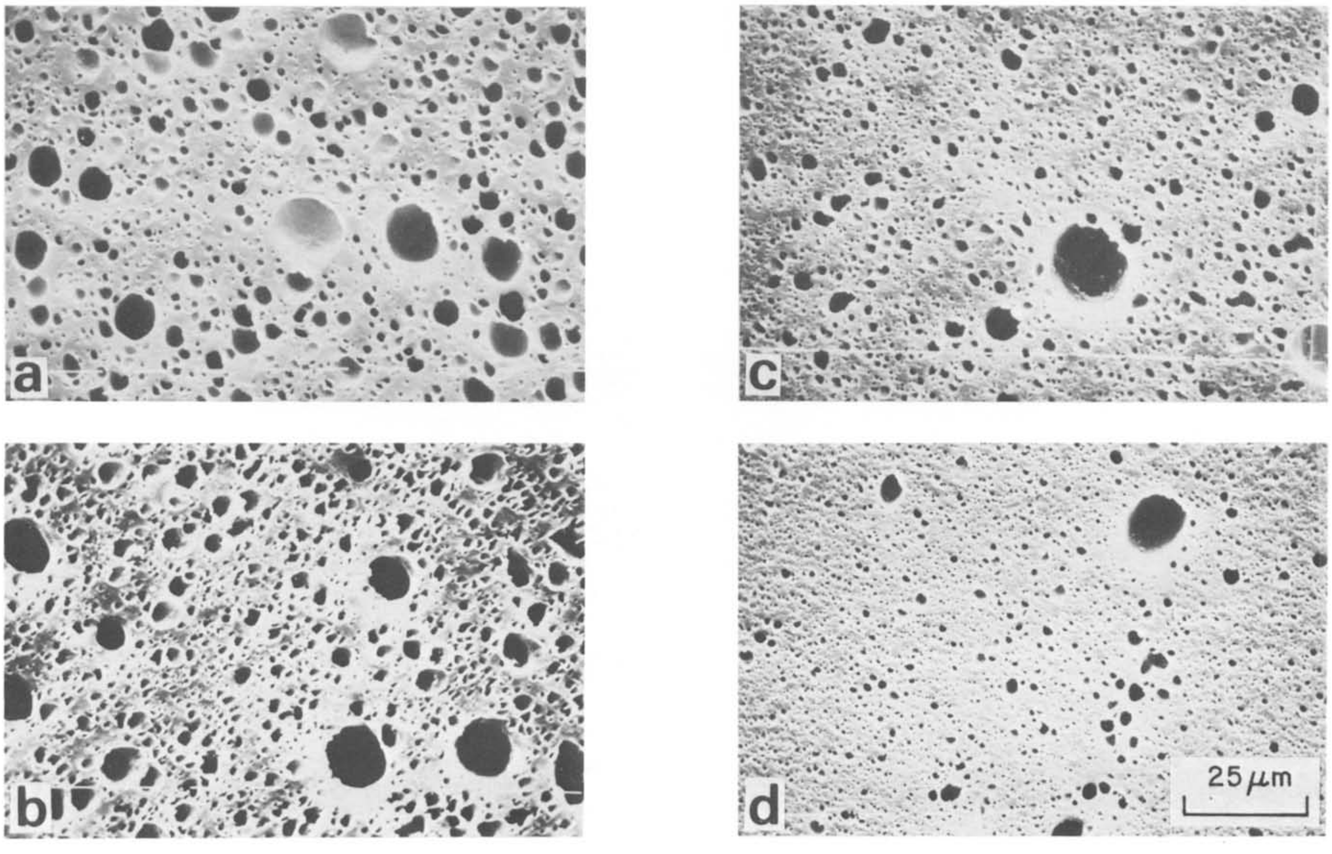


Figure 5 SEM micrographs of smoothed surfaces of A-coded samples after etching. Blends: (a) 80/15/5; (b) 80/5/15; (c) 80/10/10; (d) 80/0/20

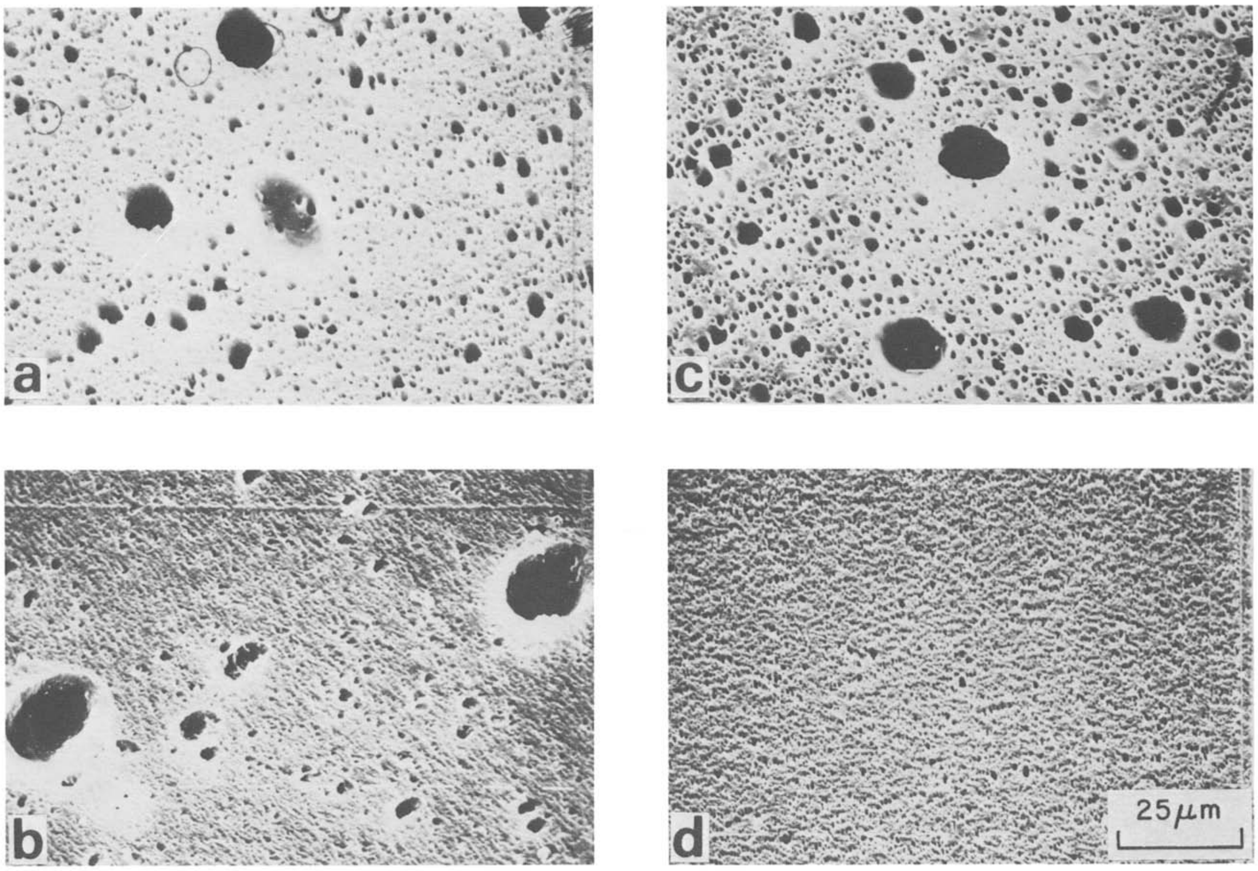


Figure 6 SEM micrographs of smoothed surfaces of B-coded samples after etching. Blends (a) 80/15/5; (b) 80/5/15; (c) 80/10/10; (d) 80/0/20

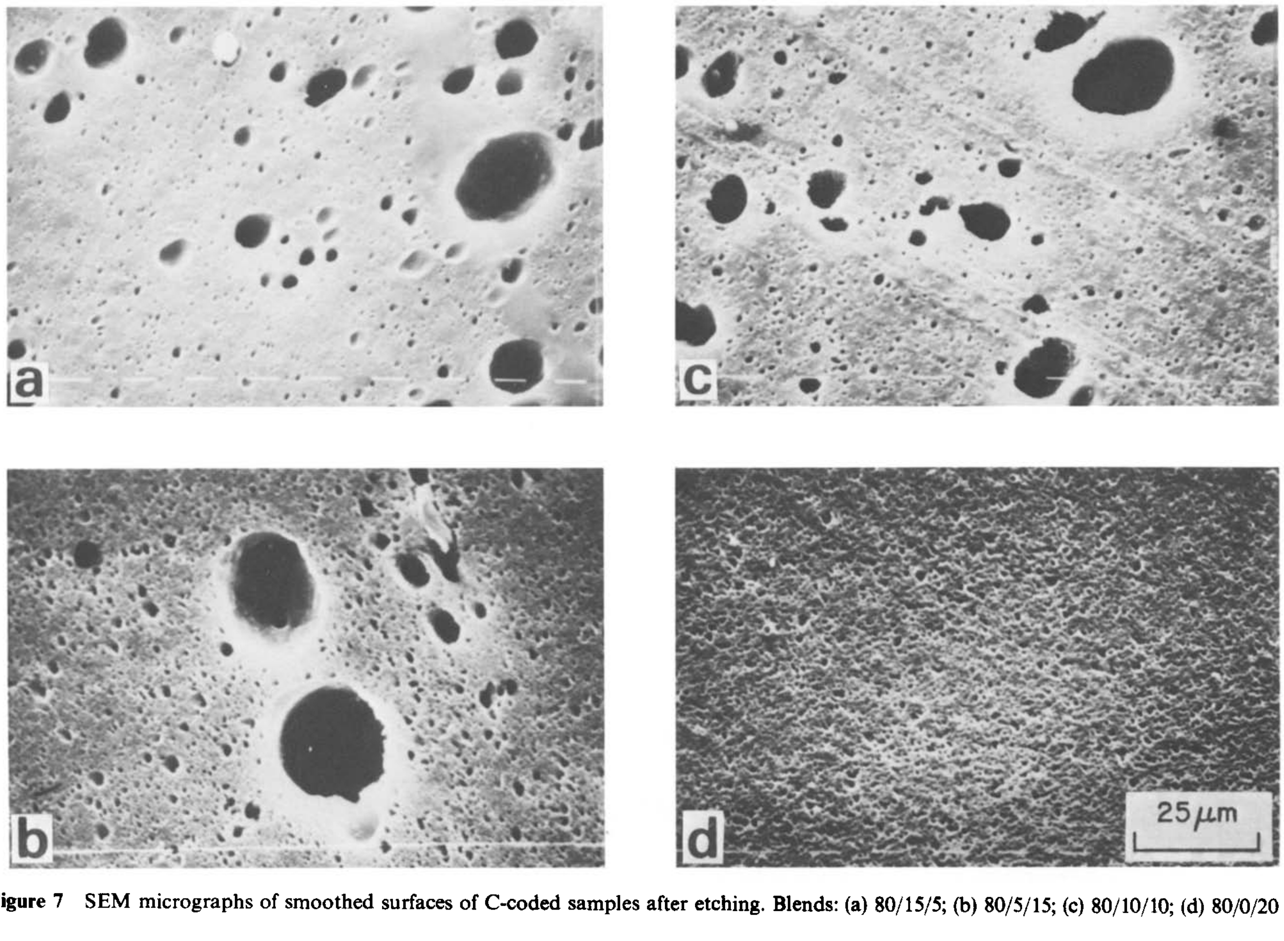


Figure 7 SEM micrographs of smoothed surfaces of C-coded samples after etching. Blends: (a) 80/15/5; (b) 80/5/15; (c) 80/10/10; (d) 80/0/20

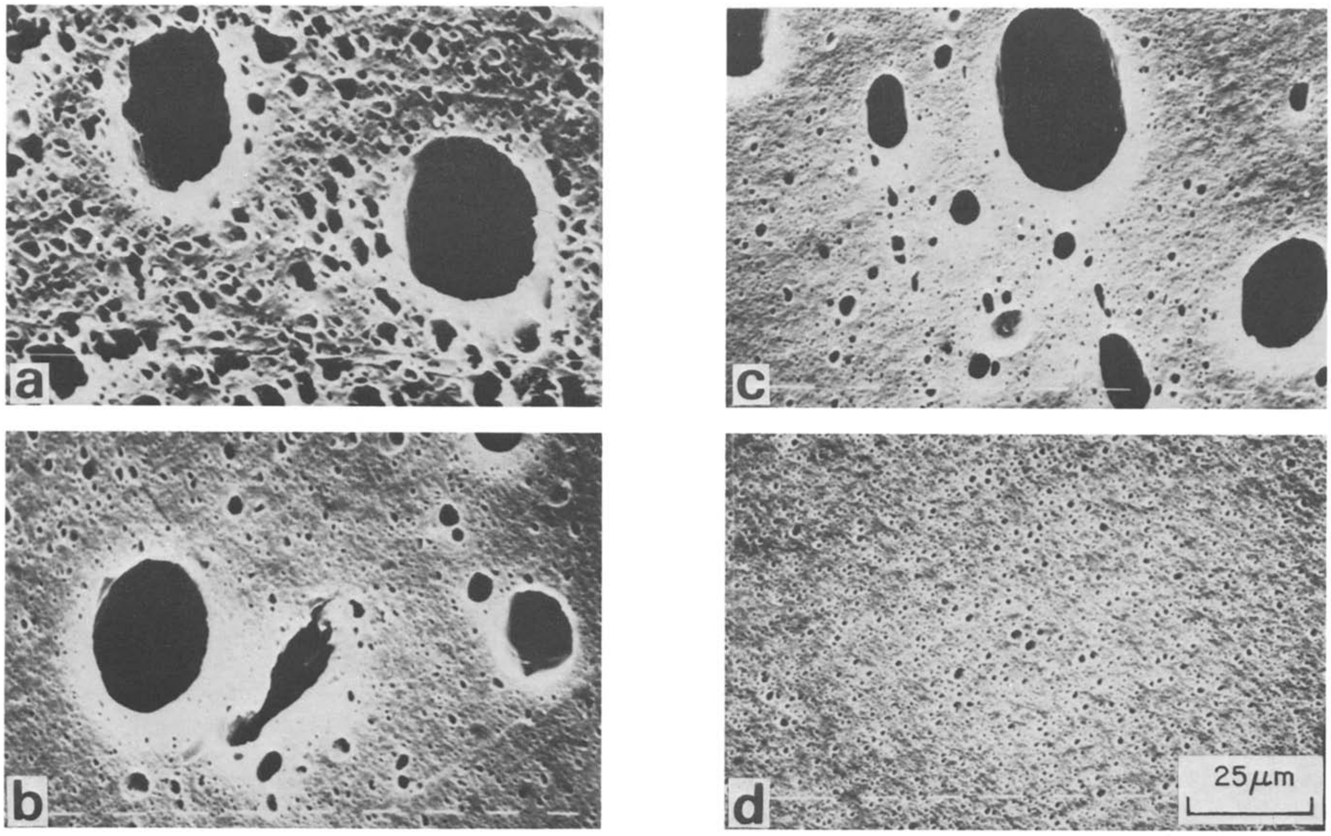


Figure 8 SEM micrographs of smoothed surfaces of D-coded samples after etching. Blends: (a) 80/15/5; (b) 80/5/15; (c) 80/10/10; (d) 80/0/20

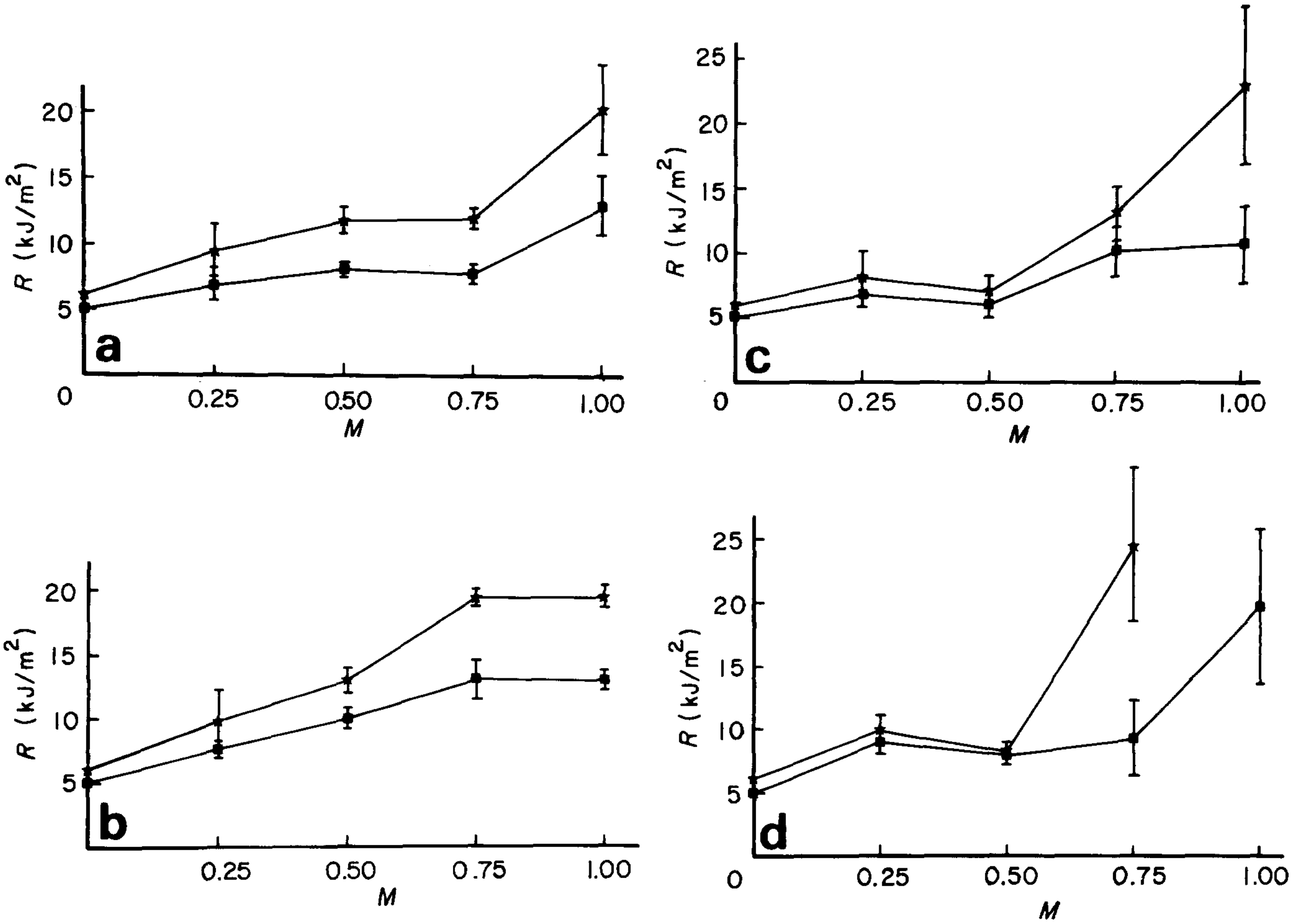


Figure 9 Impact resistance (R) of binary and ternary blends at increasing ratio M (functionalized rubber/total rubber) at two different temperatures: ★, −10°C; ■, −25°C. Grafting degree: (a) 0.6% (b) 2.0% (c) 4.6% (d) 6.0%

(i) Ternary PA 6/EPR/EPR-g-DBS blends show a quasi-bimodal mode of dispersion of rubbery components; domains with a size distribution around 1 μm coexist with very large domains (more than 50 μm across). This bimodal morphology seems to be more accentuated in ternary blends containing EPR-g-DBS with higher grafting degree (G). Moreover, increasing M for a given G of EPR-g-DBS, the number of domains per unit area with a diameter larger than 10 μm diminishes, whereas the number of smaller sized domains increases (see *Figures 5* and *8*).

(ii) Binary PA 6/EPR-g-DBS blends show a very fine texture, even though sporadic medium-sized domains are observed for A20 blends prepared from the EPR-g-DBS with lowest G (see *Figures 5d, 6d, 7d* and *8d*).

It emerges from the above that the mode and state of dispersion of rubbery components, especially for ternary blends, is strongly dependent not only on the composition, but also on the G value of the EPR-g-DBS used. The type of morphology observed in ternary blends is probably related to the fact that at the early stages of CL polymerization several different processes, often in competition with each other, are effective. Among them the most important are: (a) the dispersion of free EPR and EPR-g-DBS in the reaction mixture (CL, oligomers and PA 6 molecules); (b) the possible preferential mixing of EPR-g-DBS and EPR; (c) the reaction of EPR-g-DBS with PA 6 oligomers to form (EPR-g-DBS)-g-PA 6 graft copolymer molecules; (d) the dispersion of (EPR-g-DBS)-g-PA 6 into the rubbery phase; (e) the dispersion of (EPR-g-DBS)-g-PA 6 into the PA 6 phase.

The relative rate and weight of each of these processes will be influenced by composition, viscosity and G of functionalized rubber. It is likely that when the G value is higher, processes (c) and (e) prevail over the others, and consequently only part of EPR will be efficiently made compatible with PA 6, because not all the rubber has the chance to be in contact with both PA 6 and (EPR-g-DBS)-g-PA 6 molecules. This would explain why in ternary blends containing EPR-g-DBS with higher G one observes, together with a fine dispersion of rubbery particles, the presence of very large domains likely to contain EPR and unreacted EPR-g-DBS.

The small particles derive from the fraction of EPR and/or EPR-g-DBS that during the mixing had the chance of being emulsified with PA 6 by (EPR-g-DBS)-g-PA 6 graft copolymers, while the large particles consist mainly of rubber that had not been made compatible. For PA 6/EPR-g-DBS binary blends, where there is no free EPR to be emulsified, the anomalous behaviour of the A20 blend could be explained by considering thelow G value of EPR-g-DBS (0.6%) and the low reactivity of the ester group. The molecules of (EPR-g-DBS)-g-PA 6 graft copolymer formed during the polymerization, having therefore few PA 6 grafts per EPR chain, will be unable to emulsify all the unreacted EPR-g-DBS.

Impact properties

The Izod impact strength, R, measured at two different testing temperatures (−25°C and −10°C), is shown as a function of the weight ratio M, at constant G in *Figure 9* for binary and ternary blends. From the trend of the curves it emerges that generally R increases with the increase of M: binary PA 6/EPR-g-DBS blends ($M = 1$) being characterized by the highest impact-strength values.

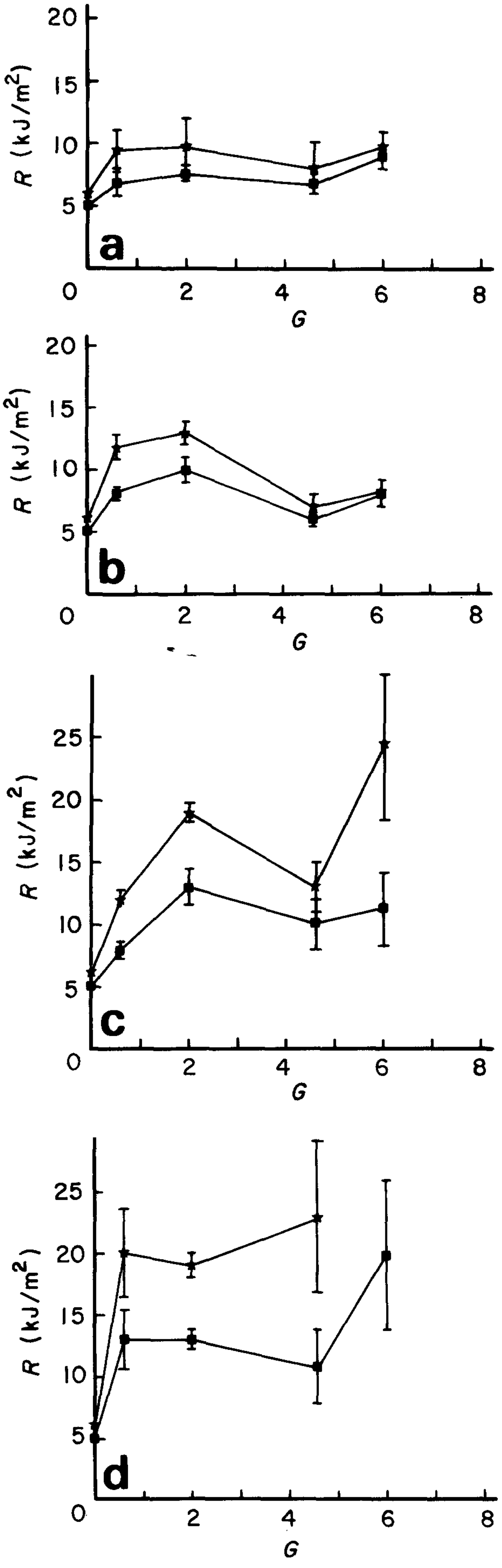


Figure 10 Impact resistance (R) of binary and ternary blends at increasing grafting degree (G) at two different temperatures: ★, T = −10°C; ■, T = −25°C. (a) M = 0.25, (b) 0.50, (c) 0.75, (d) 1.0

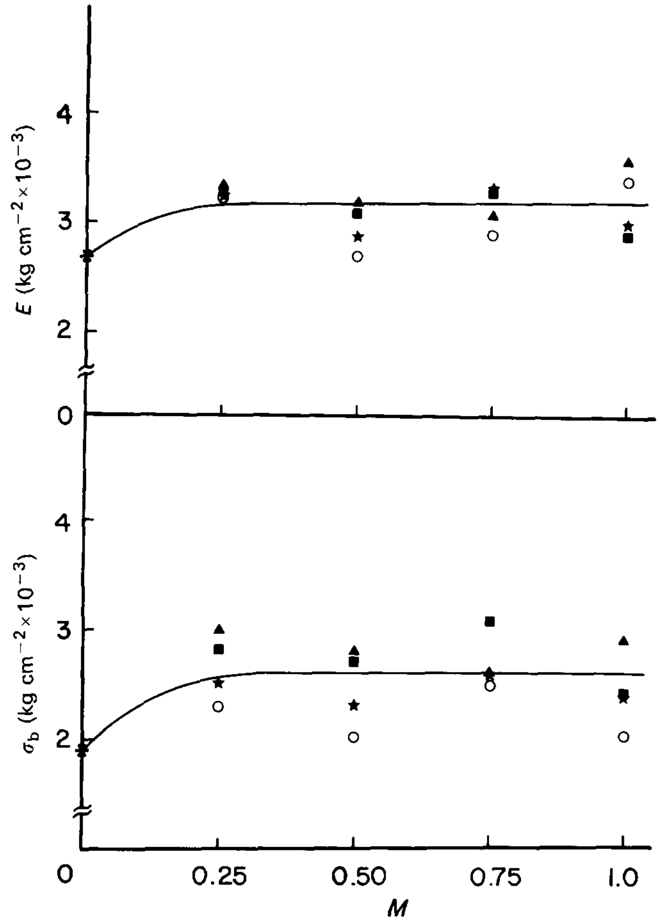


Figure 11 Elastic modulus (E) and breaking resistance (σ_b) for binary and ternary blends at increasing ratio M. EPR-g-DBS grafting degree: ▲, 0.6%; ■, 2.0%; ○, 4.6%; ★, 6.0%; *, 0%

It must be pointed out that no complete rupture of the specimens was observed for the blend D20 at −10°C.

As shown by *Figure 10*, the effect of the grafting degree of EPR-g-DBS on R is dependent on the composition of the blends. For ternary blends with the lowest *M* values (80/15/5 blends; see *Figure 10a*) *R* seems to be scarcely dependent upon *G*. These blends show an impact behaviour only slightly better than that of the corresponding PA 6/EPR (80/20) binary blend. For 80/10/10 ternary blends a maximum is observed in *R* for *G* values of about 2. A more complicated trend is shown by the curves *R* against *G* for ternary blends with higher *M*. Together with the maximum, a minimum at higher *G* values is observed (see *Figure 10c, d*).

In binary PA 6/EPR-g-DBS (80/20) blends, high *R* values are found at the lowest *G* value; as a matter of fact a small variation of *R* is shown when *G* ranges from 0.6 to 4.5. At −25°C the largest value of *R* is attained for a value for *G* of 6.

The fact that binary PA 6/EPR-g-DBS blends generally exhibit, at least at the temperatures investigated, the highest *R* values may probably be related to the small size and rather sharp distribution of dimensions of particles dispersed in the matrix of such materials (see *Figures 5d, 6d, 7d* and *8d*). Nevertheless, especially for ternary blends, the dependence of impact behaviour on composition and *G* for rubber cannot be simply interpreted in terms of mode and state of dispersion of rubbery components as it emerges from the morphological analysis.

The fact that a fine texture is not the only condition to give a better impact behaviour is demonstrated by the observation that for a grafting degree of 2 the binary PA 6/EPR-g-DBS (80/20) blends have practically the same *R* values of the ternary PA 6/EPR/EPR-g-DBS (80/5/15) blend, which shows a completely different morphology characterized by a quasi-bimodal distribution of dispersed domains (compare with *Figure 6c, d*).

At the same time it may be noted that D-type blends with composition 80/10/10 and 80/5/15 seem to have almost the same overal morphology (compare *Figure 8b, c*) and are characterized by a rather different impact behaviour (see *Figure 5d*). The dependence of some mechanical parameters obtained by tensile tests, such as modulus ($\bar{E}$) and ultimate strength σ_b on M for different grafting degrees is shown in *Figure 11*.

It may be observed that in the limit of experimental errors, these quantities are practically almost independent of the grafting degree, though the mode and state of dispersion of particles is different from one blend to another. This result, together with the observed impact behaviour of binary and ternary blends, leads to the conclusion that the mechanical response of a rubber-modified PA 6 must be the outcome of the combination of several factors, generally composition dependent. The type of phase structure, as detected by SEM morphological analysis, is one of these factors; others, such as size and distribution of dimensions of spherulites, lamella thickness and structure of interlamellar and interspherulite regions related to the PA 6 matrix, according to the findings of Martuscelli *et al.*[7] could play an important role in determining the final properties of blend materials.

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