

Ternary nylon-6/rubber/modified rubber blends: Effect of the mixing procedure on morphology, mechanical and impact properties

S. Cimmino, F. Coppola, L. D'Orazio, R. Greco,* G. Maglio,
M. Malinconico, C. Mancarella, E. Martuscelli and G. Ragosta

*Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, 80072 Arco Felice,
Napoli, Italy*

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Ternary polyamide-based blends have been prepared by adding to nylon-6 (PA6) an ethylene-propylene random copolymer (EPM) and the same EPM functionalized by inserting onto its backbone maleic anhydride groups (EPM-*g*-SA). Two kinds of processing have been used: (a) one-step mixing in which the three components were simultaneously introduced in the mixer; (b) two-step mixing in which the two rubbers EPM and EPM-*g*-SA were separately premixed before the final mixing with PA6. Also binary PA6/EPM-*g*-SA blends have been prepared to compare their properties with those of the ternary one.

Mechanical tensile characterization at room temperature and impact Izod tests at different temperatures as well as a morphological analysis of smoothed samples have been performed on all the blends. It has been shown by a model reaction that both in binary and ternary blends an EPM-*g*-PA6 graft copolymer is formed, which acts as an interfacial agent between the rubbery dispersed phase and the polyamide matrix. The blends obtained by the one-step mixing showed a gross morphology and a very poor impact resistance, whereas the ones prepared by the two-step mixing exhibited very fine morphologies and excellent impact performances. In addition, as shown at least in the case of one ternary blend, there seems to be good morphological stability of these materials after a second processing. This has been attributed to the influence of the interfacial agent formed during the melt mixing of the two premixed rubbers with PA6.

(Keywords: polyamides; blends; graft copolymer; morphology; mechanical properties; impact resistance)

INTRODUCTION

Some high-tonnage semicrystalline polymers, such as isotactic polypropylene and polyamides, show limitations in their end use because of weak impact resistance particularly below their glass transition temperature (T_g)^{1,2}. The performance of these materials may be improved by adding to them a certain amount (about 20 wt %) of a rubbery component with a much lower T_g , just as practised in the case of purely amorphous glassy polymers³. During impact the presence of the rubber particles is thought to generate high local stress concentrations. This induces a multiple craze irradiation and stopping throughout the material which helps to avoid catastrophic crack failures. In this way microscopic local yielding is able to dissipate most of the impact energy^{3,4}. The rubber particles must be finely and homogeneously dispersed in the matrix and also well adhered to it in order to be effective. Such a result can be achieved by the addition of a third component to the previously considered binary blend; namely a suitable copolymer having its sequences identical to or chemically compatible with each of the molecular chains of the two major components. The third component acts as an 'interfacial agent' producing a fine rubber dispersion and improving the adhesion of the rubber particles to the

matrix⁴⁻¹⁰. A further benefit can be obtained by the addition of the copolymer: a certain stabilization of the overall morphology during all the industrial processes the material must undergo. Such a feature should give constancy to the properties of the blends in all these steps.

Several examples dealing with nylon-6 (PA6) and nylon-6,6 (PA66)/polyolefin systems have been reported in patents¹¹⁻¹⁵. The materials are generally melt blended and graft copolymers or networks are formed by means of radical initiators or directly by mechanical degradation, with an appreciable improvement of the impact resistance of the polyamides. Ide and Hasegawa¹⁶ have studied the PA6/isotactic polypropylene (iPP) system to which an isotactic polypropylene (functionalized by insertion of anhydride groups onto the chain) had been added. During the melt mixing the anhydride groups react with nylon amino end groups to yield an iPP/PA6 graft copolymer. A similar approach has been followed by Braun and Eisenlohr¹⁷ on nylon-6/high-density polyethylene blends. In both cases the results were very promising.

In previous work¹⁸ an amorphous ethylene-propylene random copolymer (EPM) has been used by us. The modification was accomplished by solution grafting of maleic anhydride molecules promoted by radical initiators. The resulting EPM-*g*-succinic anhydride (EPM-*g*-SA) and EPM were used to obtain binary PA6/EPM or PA6/EPM-*g*-SA and ternary

* To whom correspondence should be addressed.

PA6/EPM/EPM-*g*-SA blends by melt mixing. The formation of an EPM-*g*-PA6 graft copolymer was assumed, since no solvent was suitable to separate blend components completely and to isolate the graft copolymer. However, indirect evidence of its formation could be provided on the basis of a model reaction between EPM-*g*-SA and aliphatic amines leading to amidic or imidic linkages according to the reaction temperature¹⁸. Only the impact properties of the binary PA6/EPM-*g*-SA initially containing 20 or 30% of EPM-*g*-SA were found to be very satisfactory, whereas the ternary blends showed lower impact performances.

In the present paper our efforts have been devoted to property improvements of these ternary PA6/EPM/EPM-*g*-SA blends. In particular the influence of melt mixing procedure and of composition on the blend morphology and hence on its impact resistance have been thoroughly investigated. In fact, two mixing techniques have been used:

(a) one-step mixing, in which all the components PA6, EPM and EPM-*g*-SA were simultaneously introduced in the Brabender-like apparatus;

(b) two-step mixing, in which EPM and EPM-*g*-SA were premixed in the same apparatus before the final mixing with PA6.

The two mixing procedures are conceptually different. In the former, in fact, the mixing of the components and the grafting reaction start simultaneously and the two processes can strongly interfere along the whole process. In the latter the mixing of the two rubbers EPM and EPM-*g*-SA is separately accomplished and the reactants are only successively brought together. In this way the grafting reaction can occur in a more regular and uniform fashion. Only in the case when the time of reaction is much longer than the mixing time are the two procedures equivalent in practice.

Also binary PA6/EPM-*g*-SA blends were studied to provide a meaningful comparison with the morphology and properties of the ternary ones. The results obtained in the previous work¹⁸, in fact, could not be used for this purpose since the PA6 matrix used was different, as mentioned in the section on Experimental materials.

EXPERIMENTAL

Materials

The polyamide-6 (PA6) used in this work (Sniamid ASN27/S produced by SNIA Viscosa, having a number-average molecular weight (M_n) of 2.3×10^4) was different from that utilized in a previous work¹⁸, which was a commercial product also containing about 1% of TiO₂.

The ethylene-propylene random copolymer (EPM) was Dutral Co/054 supplied by Montedison Spa, having a weight-average molecular weight (M_w) of 1.80×10^5 , an ethylene content (C_2) of 60 mol% and a glass transition temperature (T_g) of -60°C .

Before use the polyamide was kept under vacuum at 60°C for 48 h to eliminate the water content stored during industrial washing.

The EPM-*g*-SA with a graft content of maleic anhydride of 2.7 in weight was prepared following the same procedure as already described elsewhere¹⁸.

Blend preparation

One-step mixing. All the binary and ternary blends were prepared in a Brabender-like apparatus (Rheocord E.C.

of Haake Inc.) by simultaneous melt mixing of all the components at a temperature of $260 \pm 3^\circ\text{C}$ with a mixing time of 20 min and at a roller rotation speed of 32 r.p.m.

Two-step mixing. This procedure was used only for ternary blends. First EPM and EPM-*g*-SA were premixed in the same Rheocord at $130 \pm 2^\circ\text{C}$ for 10 min at 32 r.p.m. Secondly the rubber mixture obtained was melt mixed with PA6 under the same operating conditions as listed in the above paragraph.

The blend C* (80/15/5) obtained in this way was processed again in the Brabender-like apparatus in conditions (265°C and 64 r.p.m.) different from those mentioned in the above paragraph. This second treatment was made to check, at least in one case, the morphological stability of these systems.

Blend compositions

All the initial blend compositions are reported in Table 1.

Specimen preparation

The materials obtained by both mixing procedures were compression moulded in a heated press (Wabash Hydraulic Press) at a temperature of $260 \pm 5^\circ\text{C}$ and a pressure of $240 \pm 20 \text{ kg cm}^{-2}$. In this way it was possible to obtain 1 mm to 3 mm thick sheets, from which dumbbell-shaped specimens for mechanical tensile measurements and parallelepipedal specimens ($12.7 \times 50 \times 3 \text{ mm}^3$) to perform Izod impact tests were obtained respectively by means of a hollow punch and of a milling machine. A 2 mm deep notch having a radius of curvature at the tip of 0.25 mm was made on impact specimens by a sliding machine to overcome the influence of all other material defects on fracture initiation.

Techniques

Mechanical tensile tests. Classical stress-strain curves were obtained by an Instron machine (model 1122) at room temperature and a cross-head speed of 20 mm min^{-1} . Moduli, stress and elongation at yield and at rupture were calculated from such curves on an average of 10 specimens.

Izod impact tests. The energy necessary to break semi-beam cantilever specimens was detected by a Ceast fracture pendulum at a given temperature. The test temperature was changed by means of a home-made liquid-nitrogen apparatus. Therefore, curves of the resilience as a function of the test temperature were

Table 1 Initial blend composition

Blend code: PA6/EPM/EPM- <i>g</i> -SA	PA6 (wt %)	EPM (wt %)	EPM- <i>g</i> -SA (wt %)	Code ^a
100/0/0	100	0	0	A
80/10/10	80	10	10	B
80/15/5	80	15	5	C
80/20/0	80	20	0	D
80/0/20	80	0	20	E
70/0/30	70	0	30	F
80/10/10	80	10	10	B*
80/15/5	80	15	5	C*
80/18/2	80	18	2	G*

^a The asterisks mark the ternary blends obtained by the two-step mixing procedure

obtained for all the blends. Mainly two variables can be defined by such curves:

(a) the temperature T_i of the beginning of the brittle-ductile transition (see Figure 1), obtained from the intersection of the linear extrapolation of the resilience value of R at very low temperature (AB) and the straight line relative to the upturned portion of the curve (CD);

(b) the R value of the plateau at low temperatures below T_i .

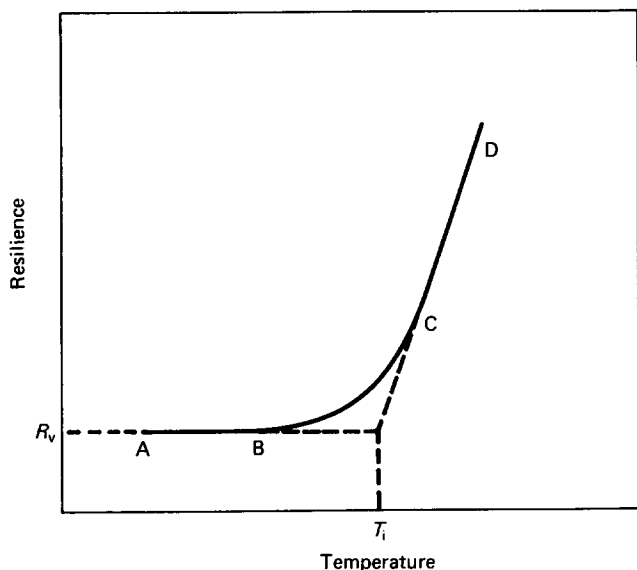


Figure 1 Typical resilience versus temperature curve for a semicrystalline polymer

Morphological observations by SEM. The compression-moulded specimens were microtomed by means of an LKB ultramicrotome (LKB Ultramicrotome III) and metallized by polaron sputtering. The microtomed surfaces were then observed by a scanning electron microscope (SEM 501 Philips) at different magnifications.

Specimen conditioning

The polyamide properties are very strongly dependent on their water content, since water acts as a plasticizer, lowering the glass transition temperature. Therefore all the specimens were water conditioned before testing, using the following procedure. The samples were kept in hot water at $90 \pm 1^\circ\text{C}$ for a period of time depending on the thickness of the specimen (1 h per 1 mm of thickness). Then they were taken out, dried on the surface and put in a sealed polyethylene envelope for 5 days. In this way a water content of 3.5 wt% of their own weight was obtained, which corresponds to the equilibrium absorption in standard conditions (at 20°C and 65% relative humidity). Conditioning at 90°C rather than at room temperature was chosen because the latter would have been highly time-consuming.

RESULTS AND DISCUSSION

Mechanical tensile properties and morphology

Stress-strain curves for binary and ternary blends are reported in Figure 2, all referred to that of pure PA6, which shows the typical behaviour of a semicrystalline

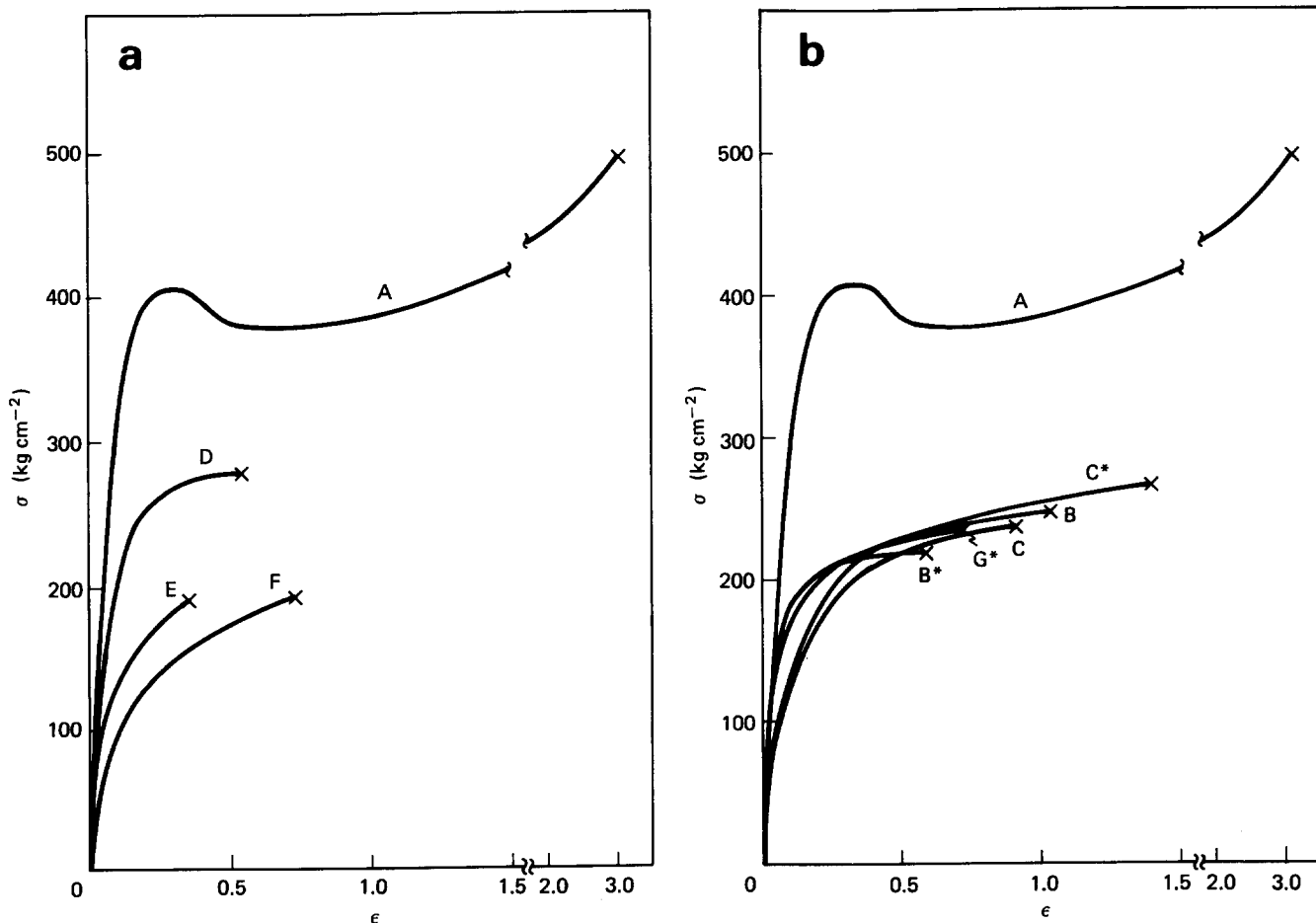


Figure 2 Stress-strain curves for (a) binary and (b) ternary blends referred to PA6 homopolymer behaviour. Codes and compositions as indicated in Table 1

polymer, with a yield point, a cold-drawing region and fibre rupture (curve A). The modulus E , the stress σ_y , and the elongation ϵ_y at yield, the strength σ_b and the elongation ϵ_b at break and the blend code are all reported as a function of composition in Table 2.

Curve D (Figure 2a), relative to the PA6/EPM (80/20) binary blend, shows a modulus E that is 4.5 kg cm^{-2} lower than that of PA6 (6.0 kg cm^{-2}). This decrease in modulus is due to the rubber contribution, whose modulus is about three decades smaller than that of the PA6 matrix. The blends can be placed in order of decreasing modulus: the two-step mixing ternary blends (Figure 2b) containing 10% and 5% of EPM-*g*-SA (curves B* and C* respectively) both exhibit an E value of about 3.4 kg cm^{-2} ; the corresponding ternary blends obtained by one-step mixing (curves B and C respectively) show a 2.9 kg cm^{-2} value; the E value of the remaining ternary mixture, containing only 2% of EPM-*g*-SA, is slightly lower (2.6 kg cm^{-2}); and finally the binary blends PA6/EPM-*g*-SA (curves E and F), containing 20% and 30% of the functionalized rubber, show values of 2.5 and 2.1 kg cm^{-2} respectively.

The blends containing various amounts of EPM-*g*-SA and 20% of total rubber all have very close E values (ranging from 2.5 to 3.4 kg cm^{-2}) which are lower than that of the PA6/EPM (80/20). This finding can be tentatively attributed to the effect of the graft copolymer EPM-*g*-SA-*g*-PA6 on the existence of interfacial zones between the PA6 matrix and the rubbery dispersed particles, in which there is probably an increase in free volume. This effect can also explain the decrease in modulus of such alloys with respect to the PA6/EPM blend containing the same amount of total rubber (20 wt %) but no EPM-*g*-SA, and therefore no interfacial zones. The slight differences between blends B, C, E, B*, C* and G* can be ascribed to different morphological features (subsequently discussed). The lowest E value (2.1 kg cm^{-2}), that of blend F, can be attributed to its higher rubber content (30%) with respect to that of the previously considered blends (20%).

A parameter that seems to be more interesting as a source of structural information is the elongation at break ϵ_b , as this expresses the capability of the material to be plastically deformed, which in turn depends on the overall structure and morphology of the system. In Figures 2a and 2b, as well as in Table 2, it is possible to note that for all blends there is a more or less sharp reduction of ϵ_b with respect to the PA6 performance ($\epsilon_b = 2.5$). PA6 is a semicrystalline polymer undergoing a classical spherulitic-fibrous morphological transformation by means of diffuse or localized cold drawing (according to

temperature and rate of deformation used during the testing) and therefore behaves very plastically. The addition of rubber and functionalized rubber can strongly modify the system. Two main reasons can be invoked to explain the reduction in ϵ_b for the blends:

(1) 'hindrance' of the free EPM rubber particles to cold drawing of the matrix, leading to an unstable flow which causes premature rupture of the specimen;

(2) a 'network' effect all over the system induced by the presence of EPM-*g*-SA-*g*-PA6, which, acting as an interfacial agent between dispersed and continuous phases, renders the system more or less interconnected and therefore less capable of flowing. These two causes can work either separately or simultaneously depending on the initial blend composition as well as on the mixing procedure.

In the case of the PA6/EPM (80/20) blend only the first effect will be effective and the very low ϵ_b value (~ 0.5) is due to the presence of very large particles with a poor adhesion to the matrix, as shown by SEM observations (Figures 10a and 10b). Also the lowering of the strength σ_b with respect to PA6 can be due to the presence of such particles. In fact the external load will induce around the particles very high stress concentrations with subsequent local yielding at an overall stress lower than in the case of PA6 homopolymer. This hypothesis is strongly confirmed by a stress-whitening effect observed on the blend specimens, indicating a diffuse craze formation. However, since there is no adhesion of the rubber particles to the matrix, only craze initiation will occur whereas craze termination will not. Therefore the crazes, developing perpendicular to the elongation direction, will easily coalesce into macroscopic cracks, leading to premature failure of the specimen soon after the beginning of cold drawing.

If one compares the behaviour of one-step mixing ternary blends with that of blend D, the following observations can be made:

(a) ϵ_b is larger (0.9);

(b) stress-strain curves show a smoother change in slope, indicating that at equal overall stresses the material yields more easily;

(c) a more intense stress-whitening effect is observed, indicating more effective craze formation;

(d) SEM micrographs show particles of smaller size, and furthermore some of the rubbery domains seem to show a certain adhesion to the matrix; however, their size distribution is still very large (cf. Figures 4, 5 and 10).

As the amount of total rubber is the same as for blend D, the increase in ductility and adhesion can only be attributed to substitution of part of the EPM by EPM-*g*-

Table 2 Moduli, stress and elongation at yield and at breakage of binary and ternary blends as a function of initial blend composition

Curve code	Composition: PA6/EPM/EPM- <i>g</i> -SA	$E \times 10^{-3}$ (kg cm ⁻²)	$\sigma_y \times 10^{-2}$ (kg cm ⁻²)	ϵ_y	$\sigma_b \times 10^{-2}$ (kg cm ⁻²)	ϵ_b
A	100/0/0	6.0 ± 0.5	4.1 ± 0.2	0.3 ± 0.02	5.6 ± 0.4	2.5 ± 0.3
B	80/10/10	2.9 ± 0.5	—	—	2.5 ± 0.2	0.9 ± 0.2
C	80/15/5	2.0 ± 0.2	—	—	2.9 ± 0.1	0.9 ± 0.1
B*	80/10/10	3.5 ± 0.4	—	—	2.2 ± 0.2	0.6 ± 0.1
C*	80/15/5	3.3 ± 0.2	—	—	2.7 ± 0.3	1.4 ± 0.2
D	80/20/0	4.5 ± 0.2	—	—	2.8 ± 0.1	0.5 ± 0.1
E	80/0/20	2.5 ± 0.2	—	—	1.9 ± 0.2	0.3 ± 0.1
F	70/0/30	2.1 ± 0.1	—	—	1.9 ± 0.3	0.7 ± 0.1
G*	80/18/2	2.6 ± 0.2	—	—	2.3 ± 0.2	0.7 ± 0.2

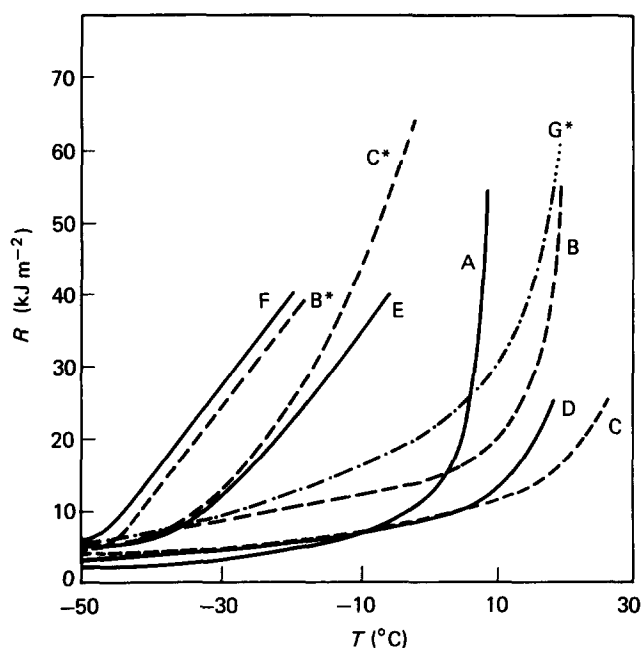


Figure 3 Izod resilience R as a function of test temperatures for PA6, binary and ternary blends, whose composition, R_v and T_i values are indicated in the table:

Code	Composition: PA6/EPM/EPM- <i>g</i> -SA	R_v (kJ m^{-2})	T_i ($^{\circ}\text{C}$) ^a
A	100/0/0	2.0	0
B	80/10/10	6.5	10
C	80/15/5	4.0	16
B*	80/10/10	6.4	-45
C*	80/15/5	5.0	-35
D	80/20/0	2.5	10
E	80/0/20	4.5	-37
F	70/0/30	6.5	-47
G*	80/18/2	6.4	9

^aError $\pm 5^{\circ}\text{C}$

SA in the blends. In fact, assuming the formation of an EPM-*g*-SA-*g*-PA6 graft copolymer during mixing this will act as an emulsifier. In other words, it will be segregated at the interface between some EPM particles and the PA6 matrix, plasticizing such a region. In this way the local stress at yield is lowered around such particles and this leads to an increase in the efficiency of the termination of crazes, radiating from each particle, in front of the neighbouring ones. In conclusion, the lowering of ϵ_b with respect to PA6 is due mainly to the 'hindrance' effect and the increase with regard to blend D to an augmented efficiency of multicraze phenomenon due to some partial (even though not homogeneous) action of the graft copolymer as an interfacial agent. Therefore no appreciable overall 'network' effect seems to be effective in this case.

Considering now the two-step mixing blend B*, compared with the one-step mixing blend B of the same composition, one can observe:

- (a) ϵ_b is lower (0.6);
- (b) the shape of the stress-strain curve is very similar;
- (c) no stress-whitening effect is observed in this case;
- (d) SEM micrographs (Figure 6) show a very homogeneous morphology with a very fine texture (particle sizes $\approx 0.1 \mu\text{m}$).

From the above considerations it appears that the EPM-*g*-SA-*g*-PA6 is very finely dispersed into the matrix, fully exploiting its role as an interfacial agent. Therefore the very small particles adhere strongly to the matrix, making the system well interconnected. This will decrease the macroscopic extensibility of the material.

It is interesting at this point to understand why a change in the mixing procedure has led to such a different result. When all three components (EPM, EPM-*g*-SA and PA6) are simultaneously mixed, the grafting reaction starts before the two rubbers can be mixed together. Therefore the reaction does not proceed homogeneously

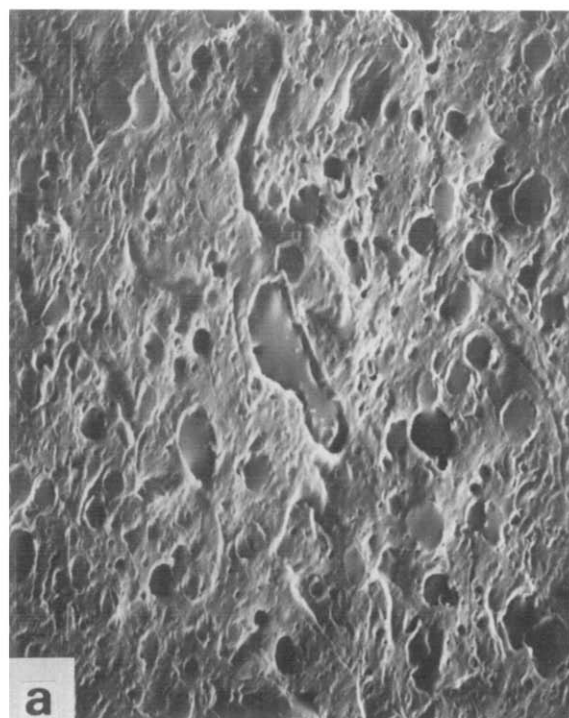


Figure 4 SEM micrographs of a microtomed surface of ternary blend B (80/10/10): (a) low magnification ($640\times$); (b) high magnification ($5000\times$)

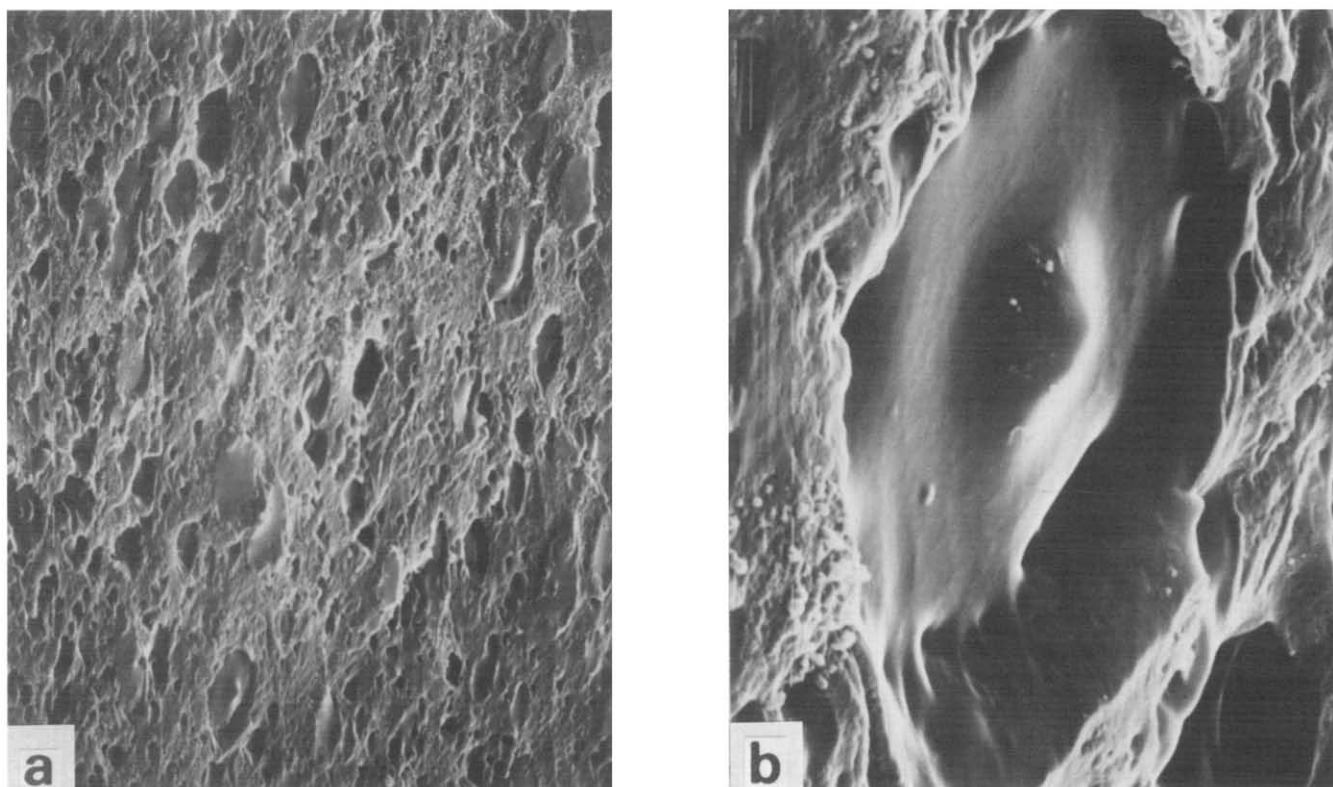


Figure 5 SEM micrographs of a microtomed surface of ternary blend C (80/15/5): (a) low magnification (640 \times); (b) high magnification (5000 \times)

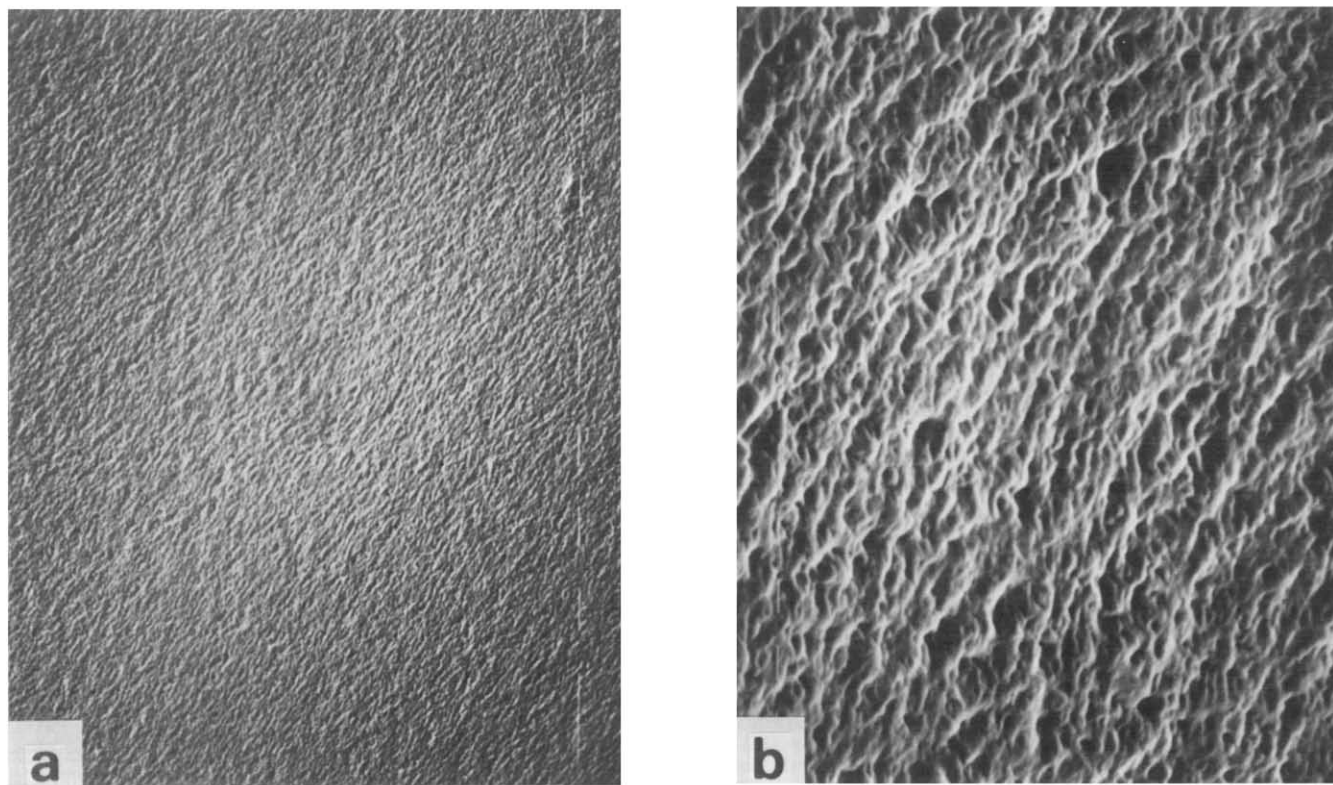


Figure 6 SEM micrographs of a microtomed surface of ternary blend B* (80/10/10): (a) low magnification (640 \times); (b) high magnification (5000 \times)

leading to a chaotic morphology in which particles free or linked to the matrix by EPM-*g*-SA-*g*-PA6 will coexist. The result is the very large distribution size as observed in Figure 4. In contrast, when EPM and EPM-*g*-SA have been premixed, the reaction with PA6 will occur regularly

on the rubber surface, continuously renewed by the tearing due to shear forces. The results will be the completion of the reaction and a continuous size reduction of the particles during mixing. The effect of decreasing the EPM-*g*-SA content but still using the two-

step mixing can lead to some different features. In fact, comparing blend C* with blend B*, one can note that:

- (a) ϵ_b is much larger (1.4);
- (b) the shape of the stress-strain curves are very similar;
- (c) almost no stress-whitening effect is present in this case;
- (d) SEM micrographs (Figure 7) show very fine morphology but with a particle size distribution (the mean particle size being larger than for B* blend).

The observations suggest that a good exploitation of EPM-*g*-SA-*g*-PA6 as an interfacial agent has been achieved, but, differently from the previous case, the 'network' effect is less effective than for blend B* as the copolymer content is lower. Moreover, a higher extensibility is obtained without any craze formation. The only possible explanation for such features seems to be a predominant shear yielding mechanism, favoured by a certain lower degree of interconnection and by a different particle and interparticle size distribution. This topology allows for a larger cold drawing of the matrix up to rupture than in the case of blend B*, whose structure is much tighter.

By further decreasing the copolymer content in blend G*, still obtained by a two-step mixing (2% of EPM-*g*-SA), the behaviour comes back closer to one-step mixing blends B and C. In fact ϵ_b is equal to 0.7 and a stress-whitening effect is present. These two results indicate that the EPM particles reacquire their individuality and hence a multicraze mechanism is acting again.

Finally going to the binary blend E which contains a very high amount of EPM-*g*-SA and no EPM, ϵ_b reduces to 0.3 since the system becomes even more strongly interconnected than in the case of blend B*. Also the morphological analysis (Figure 8) shows similar overall

features to blend B*, indicating that the two blends behave very similarly, with some minor differences. The results seem to suggest that only part of EPM-*g*-SA reacts to form the graft copolymer with PA6 whereas the remainder plays the same role as the EPM particles in ternary blends. Of course it is difficult quantitatively to assess how much EPM-*g*-SA has reacted and if the mechanisms are really identical, as one would infer from the corresponding morphologies, which seem to be qualitatively similar (cf. Figures 6 and 8).

Finally for the binary sample F containing 30% of the functionalized EPM the observed modulus decrease and slight ϵ_b increase (0.7) with respect to blend E are both very likely due to its higher rubber content, yielding a coarser grain with respect to the previous case (Figure 9).

Impact properties and morphology

The resilience R obtained by Izod tests as a function of temperature is reported in Figure 3, for PA6 homopolymer and all binary and ternary blends. The curve symbol, the composition, the R value at -45°C , R_v , and the beginning of the brittle-ductile transition T_i are also listed. The PA6 homopolymer exhibits a very low R_v value (2 kJ m^{-2}) and a transition temperature T_i of 0°C . The one-step mixing blends B and C show a certain improvement in R_v but a worsening with respect to T_i (10°C and 16°C respectively). This behaviour is in agreement with SEM micrographs (Figures 4 and 5) of microtomed surfaces at low ($640\times$) and high magnification ($5000\times$). There are indeed very large and irregularly shaped domains ($10\text{--}50 \mu\text{m}$) with a broad size distribution and a poor adhesion to the matrix. For the blends of the same composition obtained by two-step mixing, the impact properties change very strongly as evidenced by curves B* and C*. This is probably due to

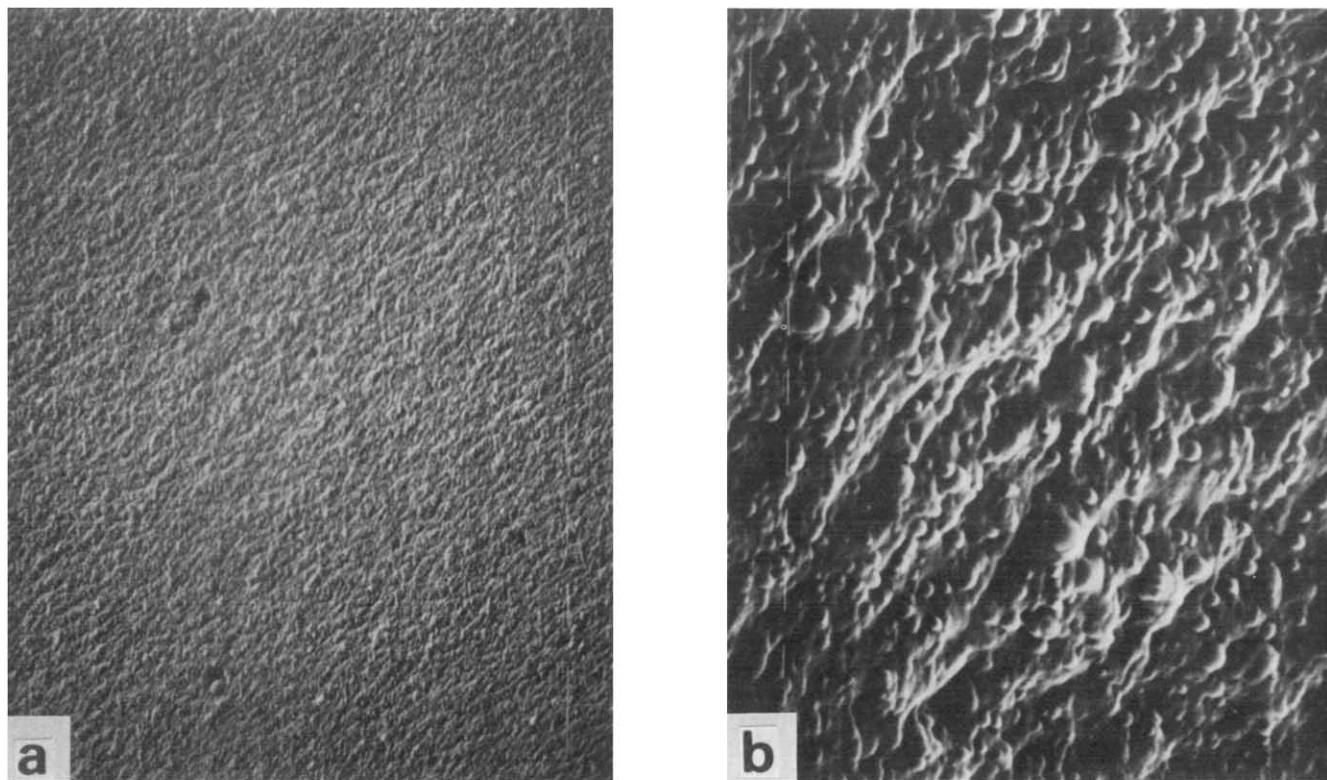


Figure 7 SEM micrographs of a microtomed surface of ternary blend C* (80/15/5): (a) low magnification ($640\times$); (b) high magnification ($5000\times$)

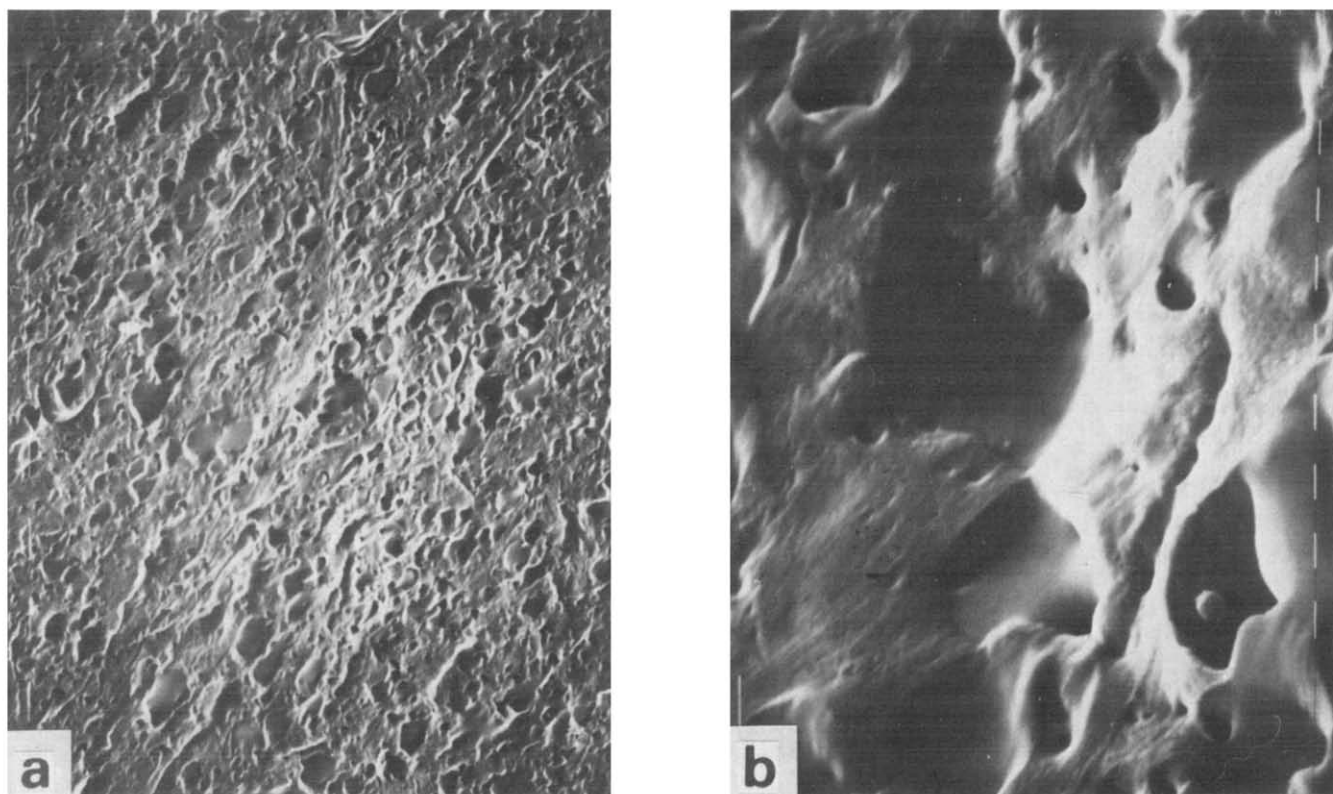


Figure 8 SEM micrographs of a microtomed surface of binary blend E (80/0/20): (a) low magnification (640 \times); (b) high magnification (5000 \times)

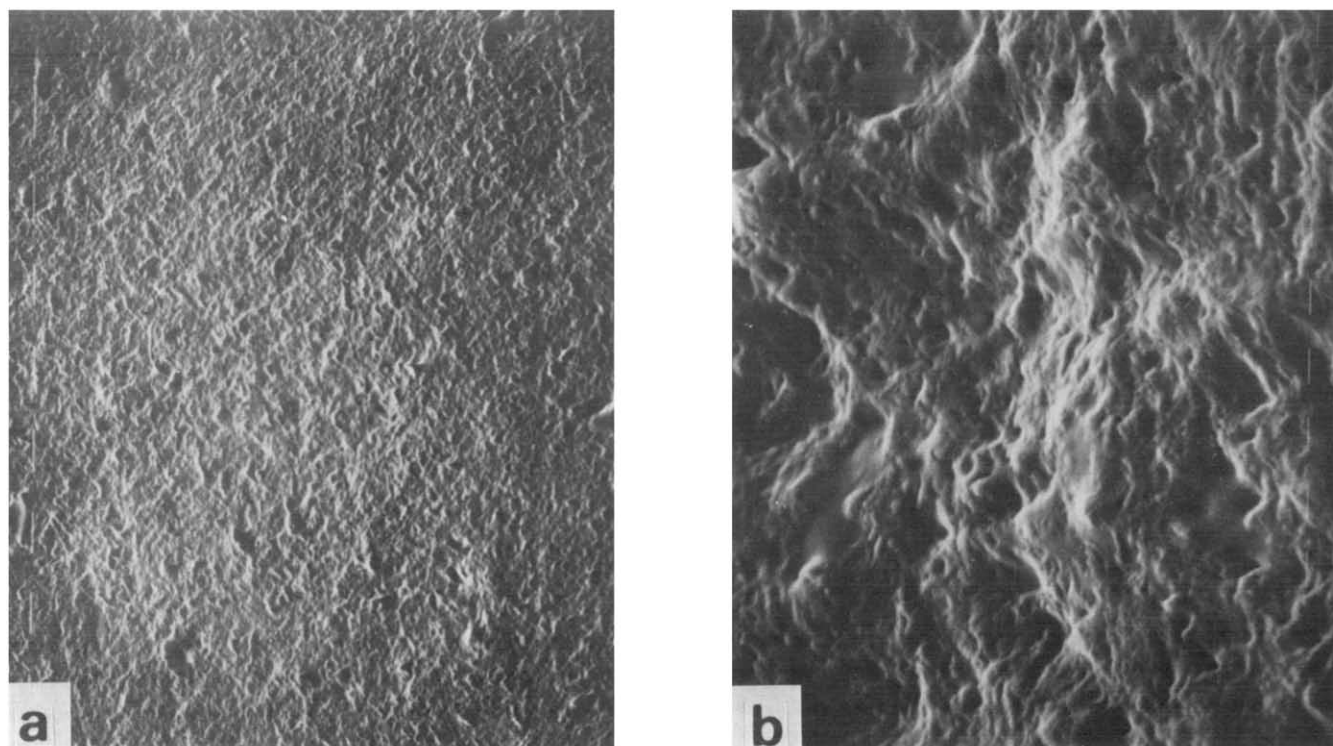


Figure 9 SEM micrographs of a microtomed surface of binary blend F (70/0/30): (a) low magnification (640 \times); (b) high magnification (5000 \times)

the anhydride groups of EPM-*g*-SA, which are very finely dispersed in the EPM rubber. Therefore, the grafting reaction with EPM-*g*-SA-*g*-PA6 formation can occur more regularly, giving rise to a very homogeneous texture.

Such an effect on the morphology is demonstrated by SEM micrographs (Figures 6 and 7). In fact the grain is

very fine in both cases. Furthermore, that corresponding to the blend B*, having a relatively higher modified rubber content, is finer than that of the blend C*. Such a finding has already been discussed and confirmed by the mechanical tensile properties. An analogous improvement in the impact properties had previously been obtained¹⁸, confirmed in this work, only using a much

higher amount of EPM-*g*-SA as shown by curves E (blend with 20 wt % of such a component) and F (with 30% of the same modified rubber). As it is possible to observe from Figure 3, blends E and C* and F and B* show a very similar trend, respectively. Furthermore, it is to be underlined that F contains 30% of total rubber whereas B* only 20%. This can lead to the same conclusion previously reported in this paper, i.e. that for these binary blends only a certain amount of EPM-*g*-SA would react, whereas the remainder would act only as a rubber soft phase. This seems to be confirmed also by SEM micrographs (Figures 8 and 9) where it is possible to observe that the grain of blend E is coarser than the corresponding ternary C* blend and that of F is even coarser than that of B*.

The particular efficiency of the two-step mixing procedure is also demonstrated by the comparison of blend D impact properties containing 20% of unmodified EPM with those relative to the G* blend having the same percentage of total rubber but 2% EPM-*g*-SA. As it is possible to see, with such a small amount of modified rubber the resilience-temperature curve shows a large improvement. This effect can be well understood if one compares the corresponding morphological features. In fact, as shown from SEM micrographs (Figures 10 and 11) when modified rubber is not present, large particles with no adhesion to the PA6 matrix can be observed (Figure 10). By adding only 2% of the functionalized rubber, a good homogeneity is already achieved (even though the texture is coarser than in the case of greater amounts of EPM-*g*-SA (Figures 6 and 7)).

CONCLUDING REMARKS

The results obtained in the case of the binary blend

confirm the findings of a previous work for which considerable amounts (20–30%) of modified rubber must be used to obtain a toughened polyamide at low temperatures. Such large quantities imply high costs since the modified rubber is obtainable by a long and complex solution process involving large solvent quantities¹⁸. Therefore an interesting result has been achieved by working on ternary blends in which a great proportion of EPR-*g*-SA (50–75%) is replaced by pure EPR, which is a commercial low-cost rubber. The goal has been achieved by using a two-step procedure in which the mixing of the rubbers has been separated by the successive grafting reaction in bulk with PA6. This gave the possibility of realizing very fine and homogeneous morphologies suitable to enhance strongly the impact resistance of these blends. Both features improve more and more with increasing EPM-*g*-SA content (cf. Figures 6, 7 and 11) but already with a 5% blend C* (80/15/5) the polyamide exhibits a behaviour comparable to that of the binary blend with a 20% content blend (80/20/0). This achievement is important not only from a practical point of view but also from a scientific one. The two-step procedure in fact can be applied conceptually to all the cases when mixing proceeds in parallel with a fast chemical reaction. A further preliminary result of the influence of the graft copolymer EPR-*g*-PA6 on the morphological stabilization of these systems after successive processing has been shown in the case of blend C* (cf. Figures 7 and 12). This is very important for complex materials which must be shaped successively (i.e. in injection-moulded items).

Work is in progress, however, to investigate more systematically such an effect with respect to the type of graft used (number and length of branches) and to the blend composition.

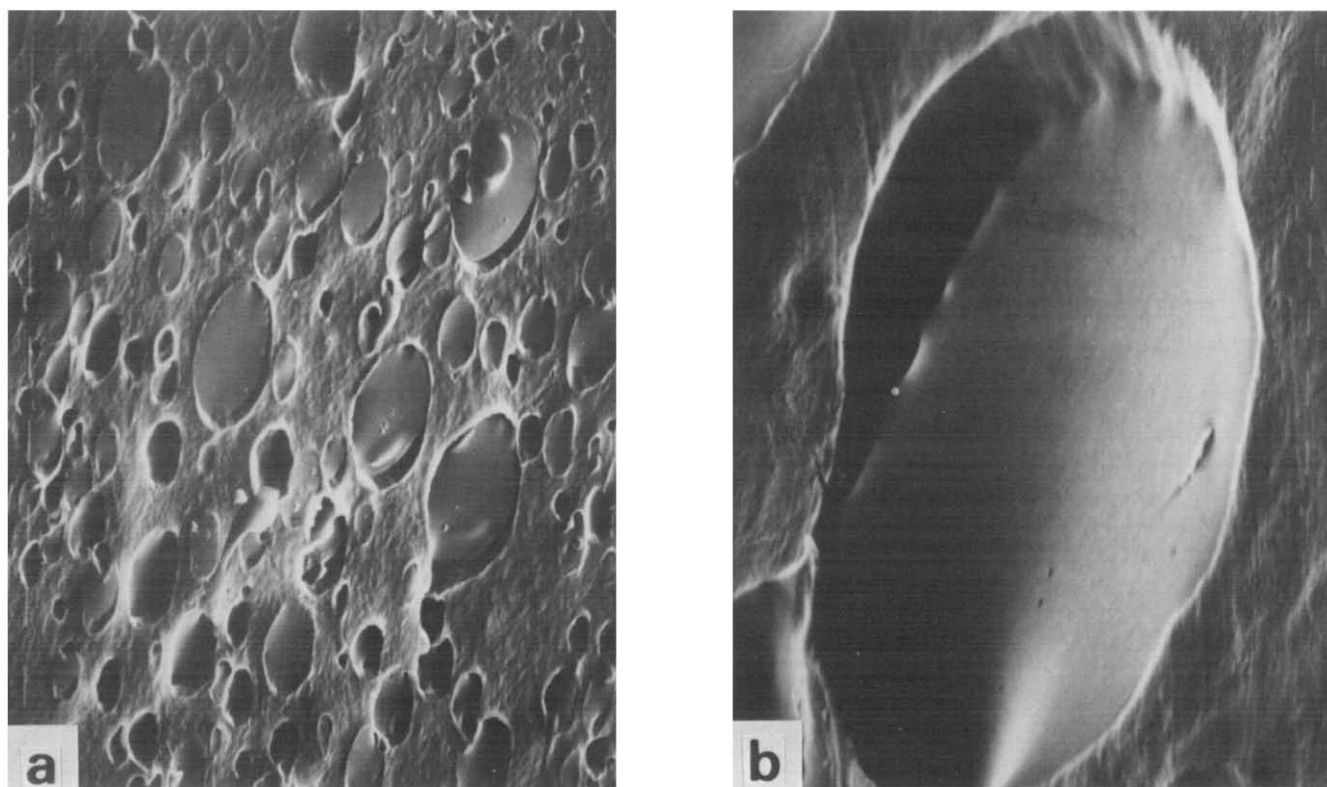


Figure 10 SEM micrographs of a microtomed surface of binary blend D (80/20/0): (a) low magnification (640 ×); (b) high magnification (5000 ×)

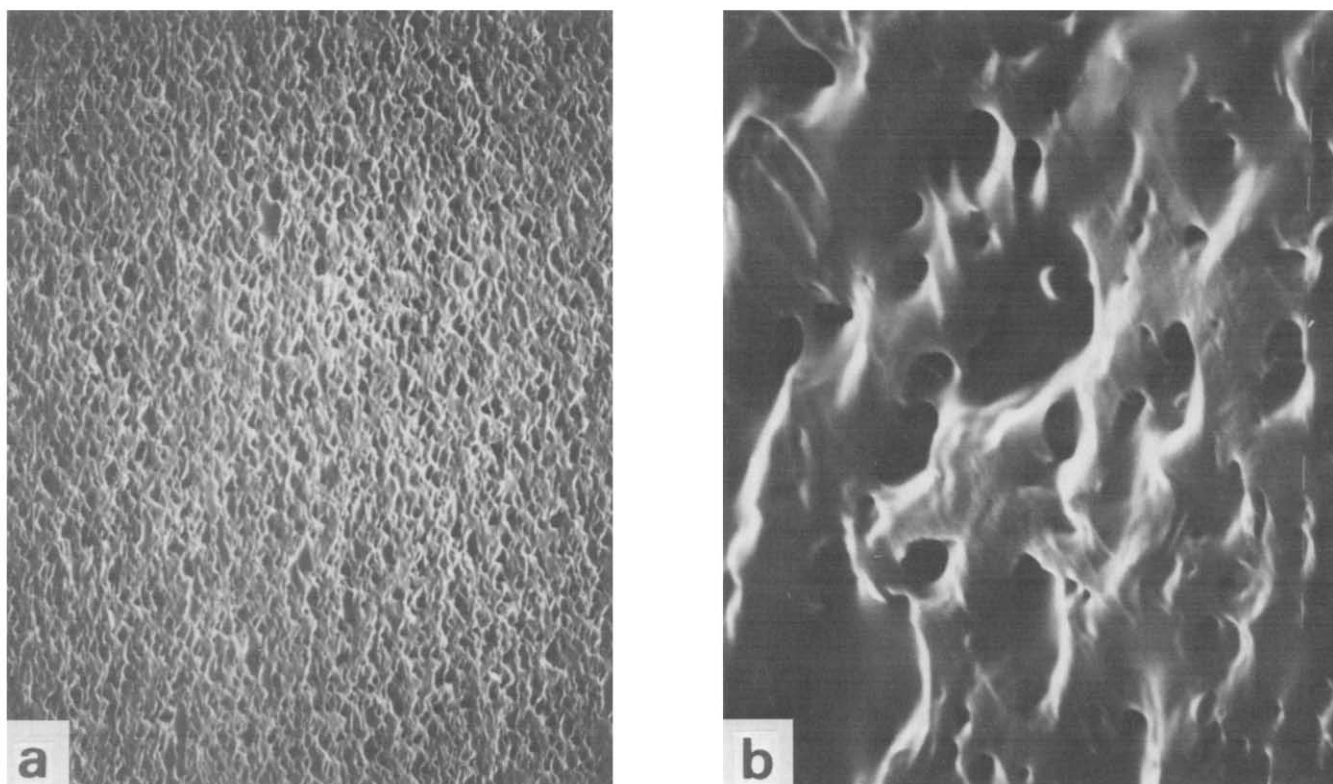


Figure 11 SEM micrographs of microtomed surface of ternary blend G* (80/18/2): (a) low magnification (640 \times); (b) high magnification (5000 \times)

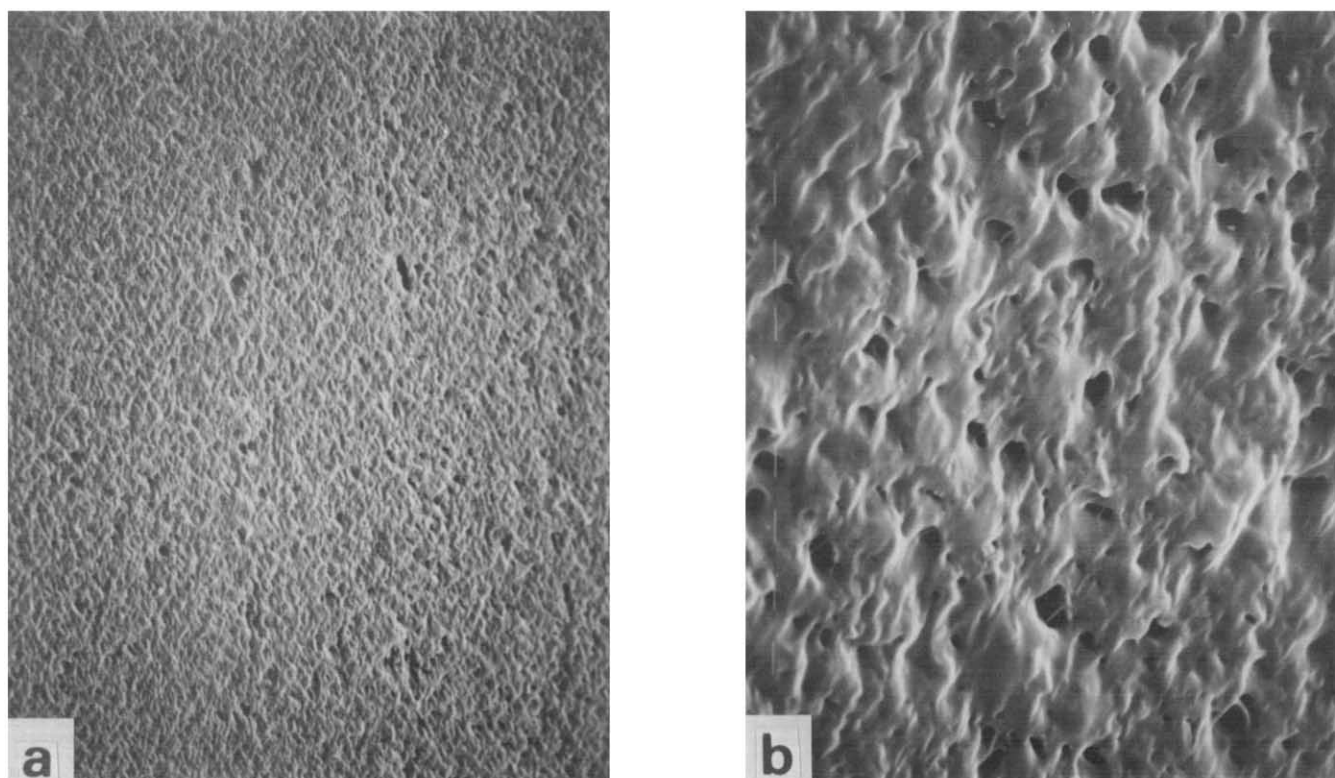


Figure 12 SEM micrographs of microtomed surface of ternary blend C* (80/15/5) processed a second time in the Rheocord at 26°C and 64 r.p.m.: (a) low magnification (640 \times); (b) high magnification (5000 \times)

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