Addition of ethylene-*co*-vinyl acetate rubber during caprolactam polymerization:
1. Synthesis and preliminary morphological characterization

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Blends of polyamide-6 and ethylene-*co*-vinyl acetate (EVA) random copolymers were prepared by the addition of EVA during the hydrolytic polymerization of caprolactam: non-functionalized EVA copolymers and those functionalized by succinic anhydride were used. It was found that vinyl acetate groups influence the polymerization kinetics of caprolactam and the degree of dispersion of the rubber particles in the polyamide matrix. The results of infra-red, thermal and morphological analyses were interpreted on the basis of the formation of grafted (ethylene-*co*-vinyl acetate)-*g*-polyamide-6 molecules, even in the absence of grafted succinic anhydride molecules on the backbone chains of EVA.

(Keywords: polyamide-6; ethylene-*co*-vinyl acetate; hydrolytic polymerization; caprolactam; synthesis; characterization)

INTRODUCTION

The toughening of polyamide-6 (PA6) by the addition of modified ethylene–propylene elastomers, (ethylene–propylene rubber)-*g*-succinic anhydride (EPR-*g*-SA), has been widely explored in our Institute. Two main routes, both based on reactive blending procedures, have been followed: (a) melt mixing of components[1]; (b) the formation of blends during caprolactam (CL) polymerization[2]. This second route allows the one-step preparation of the blend. Simultaneously, the dispersion of the rubbery component may be relatively fine and the interfacial adhesion strong. The analysis of blends prepared by this 'synthetic' route shows that only part of the functionalized rubber molecules are able to react, through the grafted succinic anhydride groups, with the amino end-groups of growing polyamide-6 chains, giving rise to the formation of (EPR-*g*-SA)-*g*-PA6 graft copolymers[2]. Most of the functionalized groups segregate inside spherical rubber particles and have no chance to come into contact with the end-groups of the polyamide chains. The segregation can be ascribed to the apolar nature of the polyolefinic backbone, dispersed in a polar medium with growing polyamide chains.

This limitation cannot be overcome by increasing the content of grafted groups, as this will lead to a decrease in the mechanical properties of the resulting blend, because of extensive crosslinking of the matrix[2] due to the high probability of reaction of the terminal groups of PA6 chains with functional groups grafted on the rubber.

Studies have been reported[3,4] in which polar rubbers have been dissolved in molten CL followed by the anionic polymerization of the monomer to PA6. However, the nitrile rubbers used in these studies cannot be used in the hydrolytic polymerization of CL due to the high temperature (260°C) needed. Nevertheless, the principle of increasing the affinity between the polymerizing matrix and the dispersed phase by incorporating a polar rubber is rather interesting. Among the polar rubbers, only saturated polymers should be suitable for the hydrolytic polymerization of CL.

This paper describes an attempt to synthesize toughened polyamide-6 by using saturated ethylene-*co*-vinyl acetate (EVA) random copolymers. Compared with the use of EPR copolymers[2], EVA copolymers are expected to be more 'miscible' with CL oligomers, due to the presence of the vinyl acetate comonomer. Blends have been prepared using EVA copolymers with different vinyl acetate content, both non-functionalized and functionalized with a constant degree of grafting of succinic anhydride groups. The blends were characterized by solvent extraction, infra-red analysis, calorimetry and scanning electron microscopy.

EXPERIMENTAL

Materials

The poly(ethylene-*co*-vinyl acetate) copolymers (EVA), kindly supplied by DuPont, are coded EVA20, EVA30 and EVA40. They contain respectively 20, 27.5 and 42.5 wt% of vinyl acetate and were used as received. The acetate content was obtained by i.r. calibration on the 1720–1730 cm^{-1} absorption of the carbonyl stretch.

Caprolactam (CL), aminocaproic acid (ACA), maleic anhydride (MA) and benzoyl peroxide (BPO) are Fluka analytical-grade products and were used without further purification.

The solvents used, when required, were purified according to standard procedures.

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Preparation of EVA-g-succinic anhydride (EVA-g-SA)

In a flask equipped with a nitrogen inlet and a condenser, 5 g of EVA20 were dissolved in 100 ml of xylene at 135°C. After dissolution, 3.23 g (33 mmol) of MA and a xylene solution containing 1.92 g (7.9 mmol) of BPO were added under vigorous stirring. After 1 h the reaction was stopped and the polymeric product was coagulated and repeatedly washed in acetone, and finally dried in a vacuum oven for 24 h at 50°C.

Evaluation of grafting degree

The amount of grafted SA groups was determined by potentiometric titration. The experimental procedure consists of the reaction of EVA-*g*-SA with *N*,*N*-dimethylethylenediamine, according to a previously reported method[5] and the subsequent titration of the tertiary amino groups of the EVA-*g*-(*N*,*N*-dimethylaminoethyl succinimide). The polymer (0.3 g) was dissolved in 50 ml of *o*-dichlorobenzene/ethanol 9/1 (v/v) and the solution was titrated with 0.02 M HCl in *o*-dichlorobenzene/ethanol 9/1 (v/v).

Techniques

The titration of amino groups was carried out using a Metrohm AG-CH 9100 Herisau potentiometer equipped with a processor for the analysis of the collected data. An Ag/AgCl electrode in a saturated solution of LiCl in isopropanol was used as reference electrode.

The i.r. spectra were obtained by using a Nicolet 5DXB *FT*i.r. spectrophotometer at 4 cm^{-1} resolution (60 scans collected).

The viscosity measurements of extracted polyamide-6 were performed at 25°C with a Cannon Ubbelohde viscometer. Concentrations of about 0.5 g dl^{-1} in *m*-cresol were used.

Polymerization of caprolactam in presence of acetic acid (LMW PA6)

A mixture of 50 g (0.44 mol) of CL and 2.7 g (0.021 mol) of ACA was poured into a cylindrical vial equipped with a mechanical stirrer and a side arm for the distillation of volatile products. The vial was repeatedly degassed and filled with pure nitrogen. The polymerization temperature was 260°C. After 2 h, 2.7 g (0.046 mol) of acetic acid were added and the polymerization continued for 2 h more. After cooling, the crude reaction product was recovered, finely ground and extracted with boiling methanol in a Soxhlet apparatus for 24 h.

Typical procedure for a binary blend preparation

A mixture of 50 g (0.44 mol) of CL and 2.7 g (0.021 mol) of ACA 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, filled with pure nitrogen and immersed in an oil bath thermostated at 260°C. After 2 h, 13.16 g of EVA20-*g*-SA (1 wt% of grafted anhydride), corresponding to 20 wt% of total blend composition, were added and the reaction continued for a further 2 h with vigorous stirring. As the reaction progressed, an increase of the viscosity of the molten reaction mixture was observed. After cooling, the crude reaction product was recovered, finely milled and extracted with boiling methanol in a Soxhlet apparatus for 24 h. The amount of MeOH extractables was *ca.* 34 wt% of the overall CL + ACA used. Before compression moulding, the MeOH-treated blend was dried under vacuum at 130°C for 24 h.

The compositions of all prepared blends as obtained after MeOH extraction are reported in *Table 1*. In this table the codes are as follows: the letters 'F' and 'M' stand for 'functionalized' and 'mechanical', i.e. blends in which, respectively, EVA-*g*-SA and EVA have been used. The first two numbers, 20, 30 or 40, indicate the vinyl acetate content of the used EVA, while the last two numbers, 10 or 20, account for the percentage of EVA in the feed. As an example: F3020 indicates a blend having 20 wt% of EVA30-*g*-SA.

Specimen preparation

The blends obtained during CL polymerization were compression moulded in a heated press at a temperature

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

Code	Grafting degree of EVA-*g*-SA (wt%)	Feed composition CL/EVA/EVA-*g*-SA (wt%)	Methanol soluble fraction (wt% on CL + ACA)	Blend composition[a], PA6/EVA/EVA-*g*-SA (wt%)	Inherent viscosity of PA6[b] (dl g^{-1})	$\bar{M}_n$ (g mol^{-1})
LMW PA6		100/0/0		100/0/0	0.176	1 200
F2010	1	90/0/10	18.8	88/0/12	–	–
F2020	1	80/0/20	34.0	73/0/27	0.623	7 700
M2010	–	90/10/0	23.0	87/13/0	0.906	13 400
M2020	–	80/20/0	32.0	75/25/0	0.316	2 800
F3010	1	90/0/10	21.0	86/0/14	0.565	6 800
F3020	1	80/0/20	18.7	77/0/23	0.655	8 300
M3010	–	90/10/0	23.0	88/12/0	0.708	9 300
M3020	–	80/20/0	32.0	74/26/0	0.385	3 800
F4010	1	90/0/10	29.0	88/0/12	0.608	7 400
F4020	1	80/0/20	34.3	75/0/25	0.471	5 100
M4010	–	90/10/0	14.0	90/10/0	0.481	5 200
M4020	–	80/20/0	19.5	77/23/0	0.455	4 800

[a] As obtained by subtracting the methanol-soluble fraction from the lactamic phase

[b] The PA6 homopolymer recovered by formic acid extraction of the blends

of 240°C and at load of 20 tons for 7 min (2 min without load and 5 min at maximum load) to obtain sheets 3 mm thick.

Analysis by scanning electron microscopy

The compression-moulded samples were cut into bars of dimensions $60 \times 6.0 \times 3.0\,\mathrm{mm}^3$. The surfaces of the bars were smoothed with a Reichert–Jung cryotome model 1150-Autocut. The microtomed surfaces of all the samples were exposed for 20 min to boiling chlorobenzene vapour (except M2020 and M4020, where 10 min exposure time was used) for selective removal of the rubbery phase. The samples obtained were examined by a scanning electron microscope (SEM 501 Philips) after coating with Au–Pd alloy.

Thermal analysis

Differential thermal analysis was carried out by using a Mettler TA 3000 differential scanning calorimeter operating under N_2 atmosphere. This apparatus is equipped with a control and programming unit (microprocessor TC-10) and a calorimetric cell (DSC-30), which allows scans from -170 to 600°C.

The scan speed used was $10^\circ\mathrm{C\,min}^{-1}$ in heating and cooling experiments. The data shown refer to second-run experiments (i.e. heating, cooling and reheating).

RESULTS AND DISCUSSION

Blend preparation

All of the blends prepared together with their codes and the inherent viscosity of the polyamide-6 (PA6), recovered by formic acid extraction, are reported in *Table 1* (for explanation of codes and composition, see 'Experimental' section). The last column shows the approximate number-average molecular weight (M_n), obtained by using the empirical relation[6]:

$$M_n = 15\,600\eta_{\mathrm{inh}}^{1.49}$$

For comparative purposes, a homopolyamide obtained in the presence of stoichiometric amounts of acetic acid (LMW PA6) is reported and characterized.

Previous studies[2] showed that, in the rubber modification of PA6 by using EPR copolymers, a certain number of factors must be considered in order to obtain an optimum balance of properties in a reactive blending process, in which the resin matrix is polymerized in the presence of a pre-formed functionalized rubber. These factors include the following:

(1) The optimum grafting degree of the functionalized rubber depends on the reactivity of the grafted groups[2,7]. When, as in the case of succinic anhydride, the grafted groups are highly reactive towards the functional groups of the matrix, their concentration must be kept relatively low, in order to avoid extensive crosslinking of the rubber with the polymer matrix. In the present work we have chosen 1 wt% of anhydride, which is close to the grafting degree found suitable in the case of EPR/PA6 blends[2].

(2) The polymerization time (t_p) at which the rubber is added plays a major role in determining the final mode and state of dispersion of the rubber in the PA6 matrix. In fact, the reaction between the rubber and the polymerizing PA6 matrix occurs at the interface in the heterogeneous mixture of the two components. It is unlikely, therefore, that a grafted polyamide chain can continue to grow, as it will be segregated with the dispersed phase. For this reason, it is better to have a t_p sufficiently long in order to graft longer PA6 chains onto the reactive rubber. On the other hand, if t_p is too long, the viscosity of the reacting medium is very high, and the dispersion of the rubber will be very poor. A good balance between these two opposing effects indicates that a t_p of about 2 h is required, as assumed in a previous study[2]. By this time, the molecular weight of PA6 has already reached 16 000, which is 80% of the final value as obtained in a test polymerization[2].

(3) The vinyl acetate (VA) content in EVA copolymers can influence the degree of dispersion attainable between EVA and growing PA6 chains. In the present study we have used EVA copolymers with three different VA contents, namely 20, 27.5 and 42.5 wt%.

Before starting a detailed analysis of *Table 1*, it is worth noting that the quantitative extraction with methanol and formic acid, effected in order to recover respectively polycaprolactam oligomers and pure homopolymer from the blends, becomes more and more difficult as the VA content and the EVA content increase in the blends. This is due to the increasing polarity of the EVA copolymers, which become more soluble in the solvent of PA6. In view of this consideration, more precise correlations are possible for those blends having 10 and 20 wt% of EVA with lower contents of VA.

In the subsequent discussion we will concentrate our attention more on the lines of *Table 1* concerning the blends with EVA at 20 and 30 wt% of VA. Furthermore, as far as the F2010 blend is concerned, sedimentation of the rubbery phase upon formic acid extraction did not occur even after several weeks. The reason why this phenomenon has occurred is not quite clear, but, as a consequence, a PA6 fraction, free of EVA and other copolymeric fractions, was not recovered. Consequently the data on inherent viscosity and M_n for that blend are missing.

General features, common to all the blends shown in *Table 1*, are the large amount of methanol-soluble fraction and the low molecular weight of PA6. In our previous paper[2], it was shown that the addition of ethylene–propylene rubber grafted with SA groups during the polymerization of CL always causes an increase in the amount of MeOH extractables. This increase is attributed to the role of the grafted SA groups acting as monofunctional terminators for the CL polymerization, as suggested by other reported data[8]. In the case of EVA-*g*-SA, the same effect can be assumed (see *Scheme 1*) and results in the grafting of PA6 chains, which are unlikely to react further with CL, as the carboxyl end-group is relatively unreactive towards the cyclic monomer.

PA6 grafted chains could only grow by reacting with amino end-groups of polymerizing PA6 chains. Nevertheless, this last reaction is highly unfavoured by the heterogeneity of the system.

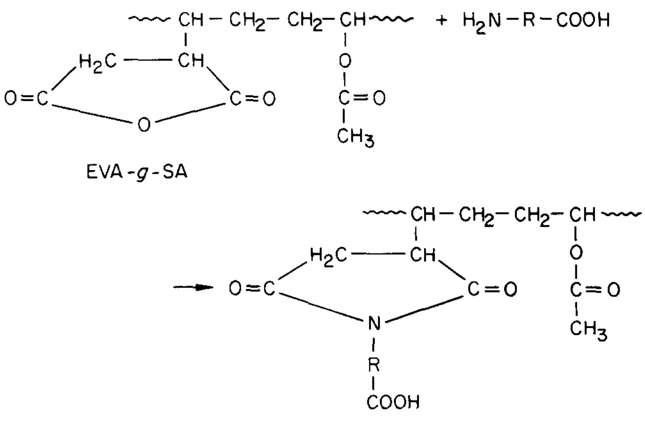
Furthermore, it must be explained why the molecular weight of the final PA6 after 4 h of polymerization is always less than the molecular weight of the same PA6 at the time the rubber is added, i.e. after 2 h of polymerization. These effects were not found in the case of polymerization in the presence of EPR. A tentative explanation is reported in *Scheme 2*.

Reaction (1): The vinyl acetate of EVA can react with the amino end-groups of growing PA6 chains in a way similar to that reported in *Scheme 1* for succinic anhydride groups. This will slow down the molecular-weight increase of PA6.

Reaction (*2*): The vinyl alcohol, produced in reaction (1), according to literature data[9], can cause a decrease in the molecular weight of PA6 via a cleavage of the amide linkage.

Reaction (*3*): Vinyl alcohol groups can also be produced by high-temperature saponification of vinyl acetate (see reaction (3a))[10], with production of acetic acid. This latter is able either to react with amino end-groups of growing PA6 chains (see reaction (3b)) or to break the amide linkage, causing a further decrease of molecular weight (see reaction (3c)). To check the occurrence of reactions (3b) and (3c), acetic acid, in an amount corresponding to the acetate content of blend M3020, was added after 2 h of t_p to PA6 in a test experiment. The resulting values of inherent viscosity and molecular weight are reported in *Table 1*, under the code LMW PA6. It is evident that the molecular weight is well below the molecular weight of a PA6 after 2 h t_p (16 000 g mol^{-1}).

Scheme 1



where R = polyamide chain

Some other relevant features are shown by *Table 1*:

(a) For mechanical blends at low content of EVA (cf. M2010, M3010 and M4010) M_n decreases as VA content increases. The reverse occurs when the EVA content is 20 wt% (see M2020, M3020 and M4020).

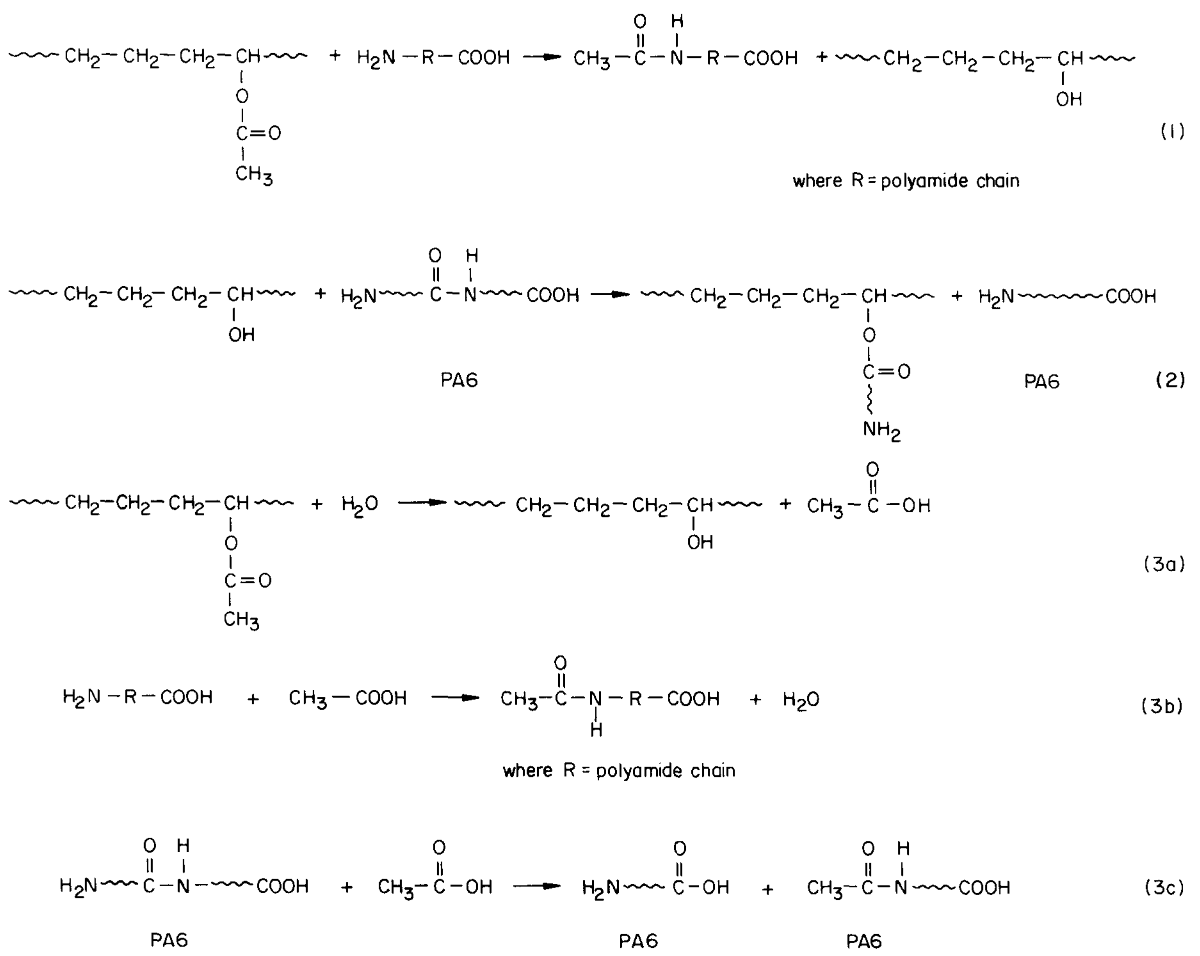
(b) M_n decreases, too, when the content of EVA in the mechanical blends increases from 10 to 20 wt%.

(c) In F3010 and F4010, M_n values are almost constant, while on going from F3020 to F4020 there is a clearer decrease in the M_n values and consequently an increase in the extractables. More contradictory is the comparison of 'F' blends at 10 and 20 wt% of EVA content. In fact, from F3010 to F3020 there is an M_n increase, whereas it decreases from F4010 to F4020.

(d) A comparison between functionalized and mechanical blends at 20 wt% rubber content shows that the PA6 recovered from 'F' blends always has a higher M_n than the corresponding 'M' blends.

Features (a) and (b) can be rationalized on the basis

Scheme 2



of the negative influence of VA groups on the polymerization reaction, as shown in *Scheme 2* and particularly reactions (1) and (3b). More difficult to explain is why the molecular weights increase in the mechanical blends at 20 wt% of EVA content, increasing the VA content. Nevertheless, M_n values of 2800 and 3800 are so low as to render unreliable a quantitative comparison of them.

A possible explanation of observations (c) and (d) may be found in the more polar nature of EVA copolymers compared with EPR copolymers. As a matter of fact, in the case of PA6/EPR blends obtained during caprolactam polymerization in the presence of EPR-*g*-SA molecules[2], the high polarity of SA molecules grafted onto the non-polar polyolefinic backbone leads to the movement of these molecules out of the rubbery domains, favouring their interaction with the PA6 end-groups. This leads in turn to a noticeable negative influence of anhydride molecules on the molecular weight of PA6 homopolymer. On the contrary, it is conceivable to assume that the polar nature of EVA polymers will stabilize a strong interaction between SA and acetate groups. In view of this effect the SA molecules will be segregated inside the rubbery phase together with several acetate groups and both will have a smaller negative influence on the attainable M_n of the matrix polymer. This explains the behaviour reported in comment (d), and also the contradictory trend shown in (c) can be at least partly accounted for.

Blend characterization

The procedures used to separate and characterize the components of PA6/EVA blends were exactly the same as those reported for PA6/EPR[2]. The separation procedure involves dispersion in formic acid of a weighed amount of ground sample (after MeOH extraction) followed by seeding of the resulting emulsion in a separating funnel. After several days (sometimes weeks), a supernatant white phase separates, while the remaining solution is normally constituted by an opalescent upper phase and a clear bottom one. In the case of PA6/functionalized EPR blends, analysis of the different phases gave some indications on their composition. In particular, the supernatant phase, analysed by i.r. spectroscopy, showed only bands characteristic of the unreacted rubber, which was a large proportion of the original rubber used. This led to the conclusion that most of the rubber, inside dispersed particles, does not react with PA6 chains. The compatibilizing efficiency was ascribed essentially to a few grafted chains of the type (EPR-*g*-SA)-*g*-PA6, which constitute the opalescent intermediate phase in the formic acid test. The same test, carried out on mechanical PA6/EPR blends, gave a top supernatant phase and no opalescent intermediate phase; the top phase was shown to be pure EPR. In the present case,the i.r. analysis of the top supernatant phase gives responses different from PA6/EPR blends. In particular, in *Figures 1* and *2*, the i.r. spectra of supernatant phases of mechanical blends M4020 and M3020 are reported. As can be seen, in both spectra the absorption bands characteristic of PA6 are evident (3297, 1637 and 1546 cm^{-1}). There is no way to distinguish between grafted PA6 chains or homopolyamide mechanically dispersed in the rubbery phase by i.r. methods. Nevertheless, the low molecular weight of homopolyamide recovered from the blends indicates a strong solubility of PA6 in formic acid, so it is difficult to believe that the PA6 found in the spectra of the supernatant rubbery phase can be unreacted mechanically dispersed polymer.

In conclusion it is possible that reaction (2) of *Scheme 2* can occur, leading to the formation of EVA-*g*-PA6 grafted copolymer.

Thermal analysis

In *Table 2* the observed melting temperature (T'_m), as

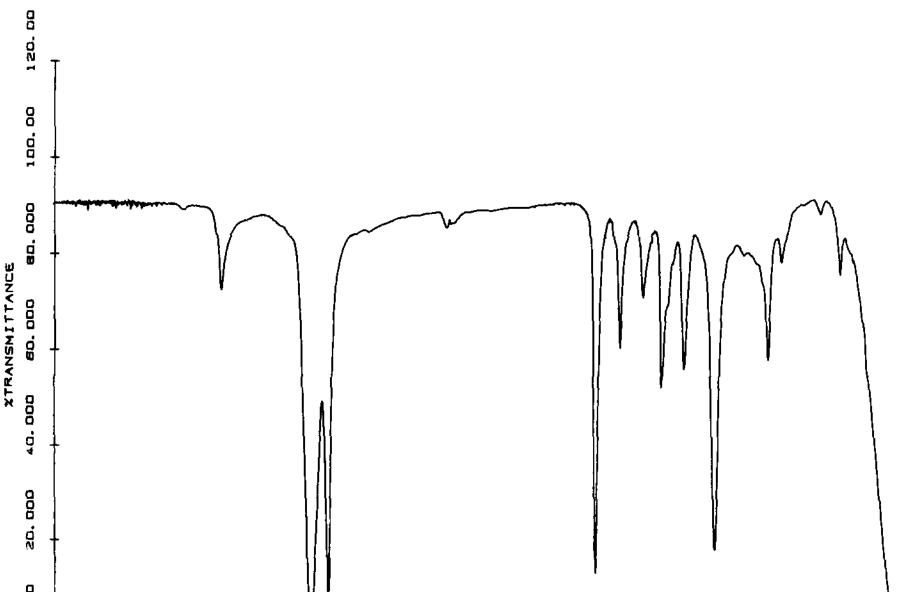


Figure 1 *FT*i.r. spectrum of rubbery supernatant phase of M4020 blend obtained from formic acid extraction (xylene casting onto KBr disc)

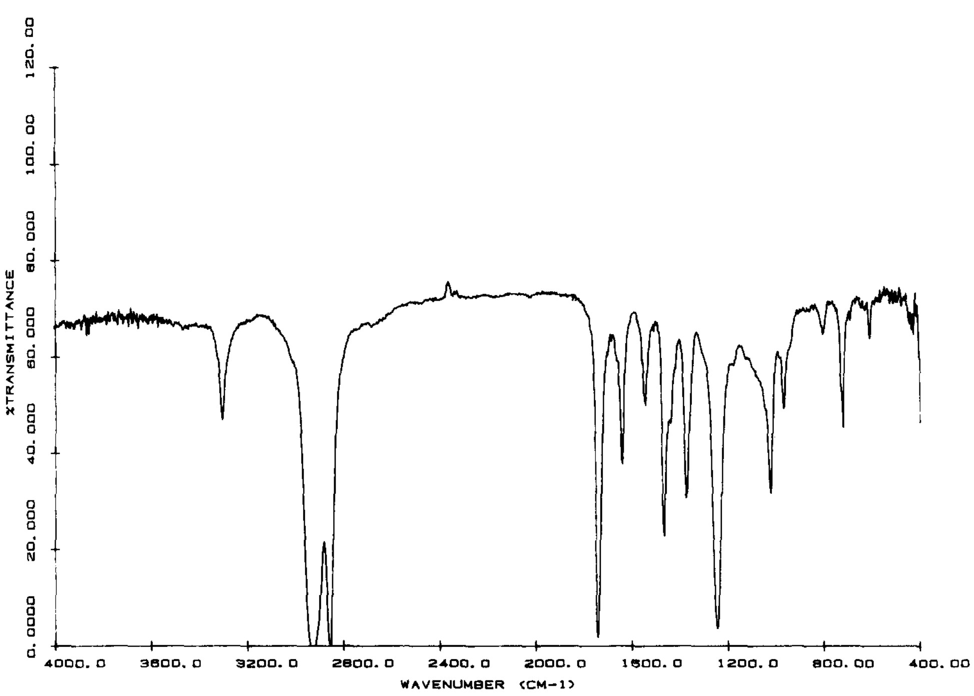


Figure 2 *FT*i.r. spectrum of rubbery supernatant phase of M3020 blend obtained from formic acid extraction (xylene casting onto KBr disc)

Table 2 Thermal analysis of commercial PA6, of low-molecular-weight PA6 (LMW PA6), of prepared binary blends and of PA6 extracted from the blends

Sample	T'_{m} (°C)	T_{c} (°C)
PA6[a]	219	173
LMW PA6	212	186
F2020	220	187
Polyamide extr. from F2020	220	188
M2020	220	185
Polyamide extr. from M2020	218	192
F3020	220	189
Polyamide extr. from F3020	220	191
M3020	218	186
Polyamide extr. from M3020	218	192
F4020	222	184
Polyamide extr. from F4020	219	191
M4020	219	191
Polyamide extr. from M4020	217	189

[a] Commercial sample obtained from SNIA Tecnopolimeri S.p.A.

Table 3 Melting temperatures T'_{m} (°C) of commercial PA6, of low-molecular-weight PA6 (LMW PA6), of starting EVA copolymers and of formic acid extractables

Sample	Blend	PA6[a]	Rubber[b]
F2020	220	220	81 (220)
M2020	220	218	87 (220)
F3020	220	220 ($\sim$80)[e]	–
M3020	218	218	75 (219)
F4020	222	219	–
M4020	219	217	41 (219)
PA6[c]	219	–	–
LMW PA6	212	–	–
EVA20[d]	88	–	–
EVA30[d]	56	–	–
EVA40[d]	55	–	–

[a] Extracted by formic acid

[b] Insoluble fraction from formic acid extraction of blend (supernatant phase)

[c] Commercial sample obtained from SNIA Tecnopolimeri S.p.A.

[d] Starting rubber

[e] Melting peak of EVA copolymer (see text for explanation)

measured from the second d.s.c. run, and the crystallization temperature (T_{c}) obtained in non-isothermal experiments are reported for the prepared blends and the recovered PA6. It is preferable to refer to the second-run melting, as in the first run two melting peaks are sometimes present, which always merge into one peak in a second run[11]. It can be observed that the T_{c} of blends are always higher than that of plain commercial PA6. This observation indicates that the PA6 in blends is probably more nucleated. For comparative purposes the T'_{m} and T_{c} values of a commercial PA6 are also reported.

In *Table 3* the d.s.c. melting temperatures, corresponding to all the phases obtained by formic acid extraction of the blends, are reported. For comparison, the T'_{m} of commercial PA6 and the starting EVA rubbers are also reported. Unfortunately, complete recovery of components was possible only for the F2020 and M2020 blends, while at higher VA content, only the mechanical blends gave a supernatant rubbery phase suitable to be recovered. For a better understanding of the values reported in *Table 3*, in *Figure 3* the d.s.c. curve of the starting EVA20, together with the curve for a commercial PA6 sample, is reported, while in *Figure 4* the d.s.c. curves of the rubbers extracted from F2020 and M2020 are shown. It must be noted that in the d.s.c. curves of the supernatant rubbery phases a sharp high-temperature endothermic peak is always observed, characteristic of the melting of a polyamide phase (the values are reported in parentheses in *Table 3*). On the contrary, in the case of the d.s.c. curve of material soluble in formic acid, only the endothermic peak of PA6 is normally observed, with no evidence of EVA melting peaks. Nevertheless, in the

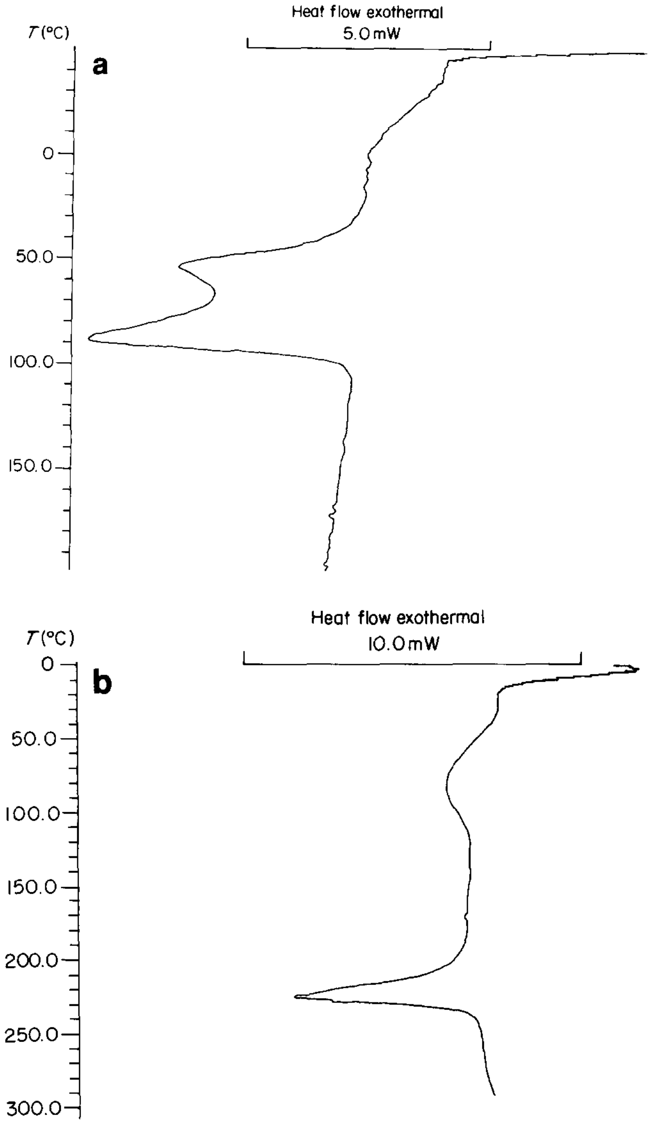


Figure 3 D.s.c. first-run melting endotherm of: (a) starting EVA20 copolymer and (b) a commercial PA6 sample

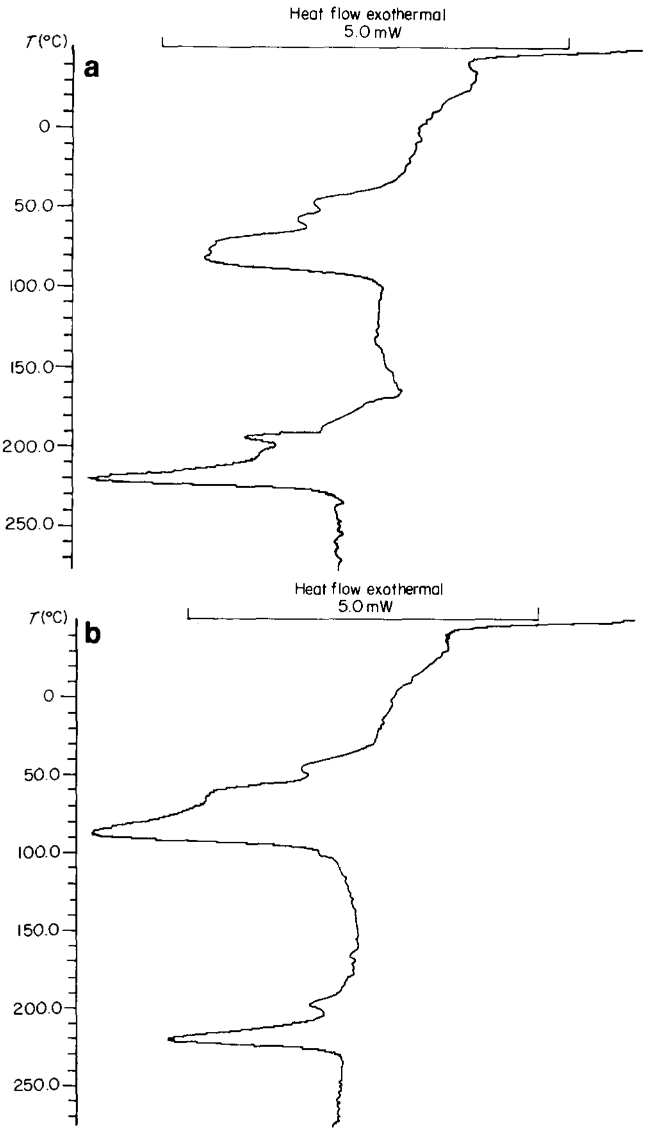


Figure 4 D.s.c. first-run melting endotherm of: (a) rubber extracted from F2020 and (b) rubber extracted from M2020

case of F3020 blend a peak at low temperature, visible in the first-run experiment, characteristic of the fusion of EVA, is evident in the d.s.c. curve of extracted PA6. This is shown in *Figure 5* together with the two peaks of PA6 (see 'Experimental' section for further details).

The thermal analysis reported above gives us further evidence that graft copolymers EVA-*g*-PA6 or (EVA-*g*-SA)-*g*-PA6 do form during caprolactam polymerization, as already suggested in the previous paragraph.

Morphological characterization

The SEM micrographs of blends F2020, M2020, F3020, M3020, F4020 and M4020 are shown in *Figures 6*, *7* and *8*. Analysis was carried out on the surfaces of blends, after smoothing and etching with chlorobenzene vapour. This technique allows selective extraction of the rubbery phase, leaving the polyamide phase unaffected. From the SEM analysis of the blend surfaces, the following features emerge.

'M' type blends. The rubber is segregated into spherical domains, represented by the cavities left after solvent extraction, whose dimensions are on average around 15 μm. Such an average diameter is much less than the

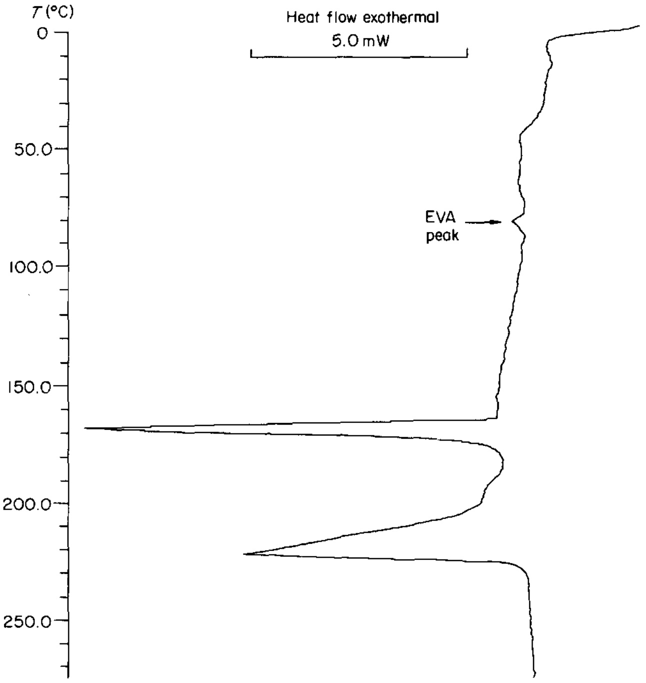
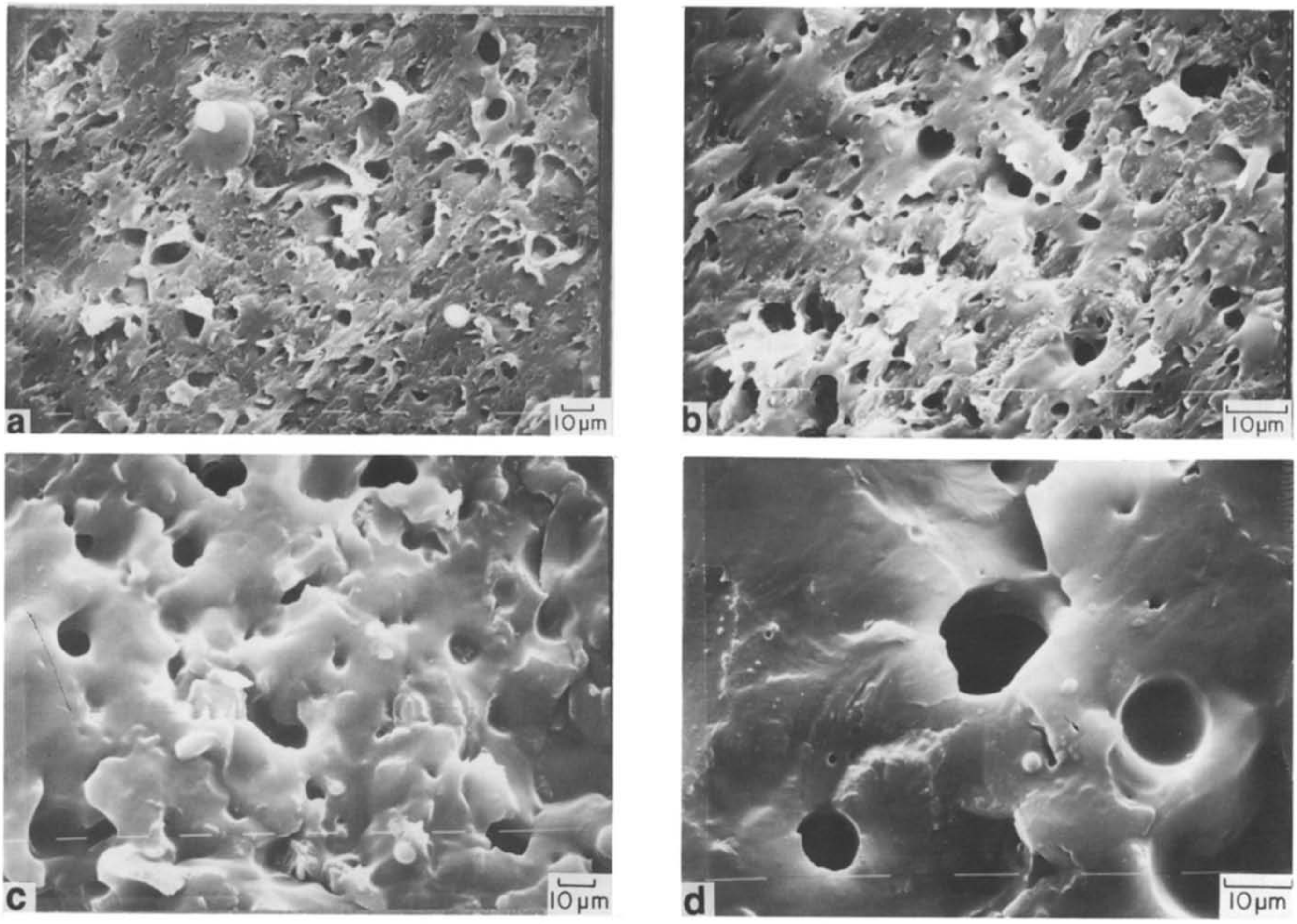


Figure 5 D.s.c. melting endotherm of PA6 obtained from formic acid dissolution of F3020



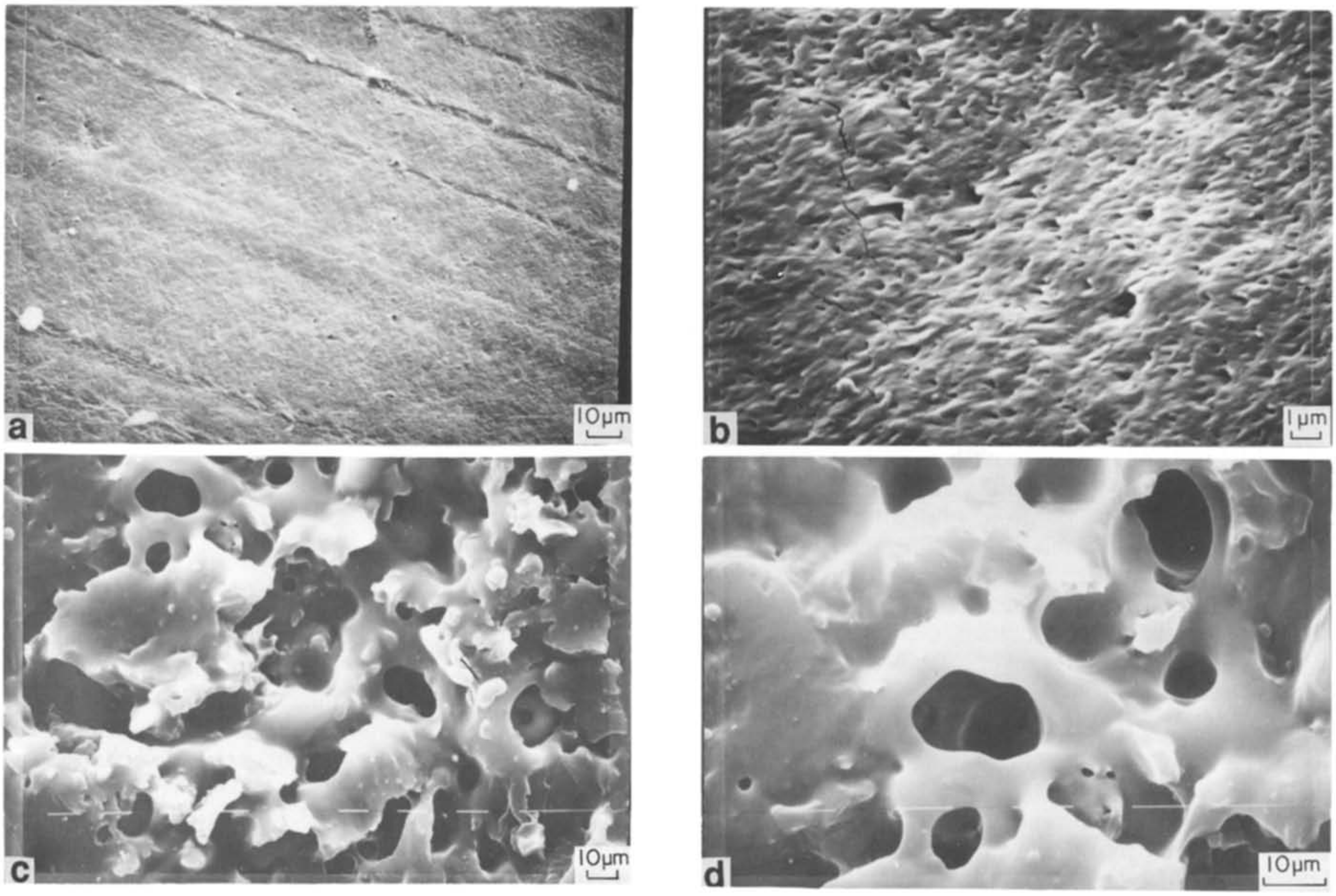


Figure 7 SEM micrographs of smoothed surfaces after etching of F3020 and M3020 blends: (a) F3020; (b) F3020; (c) M3020; (d) M3020

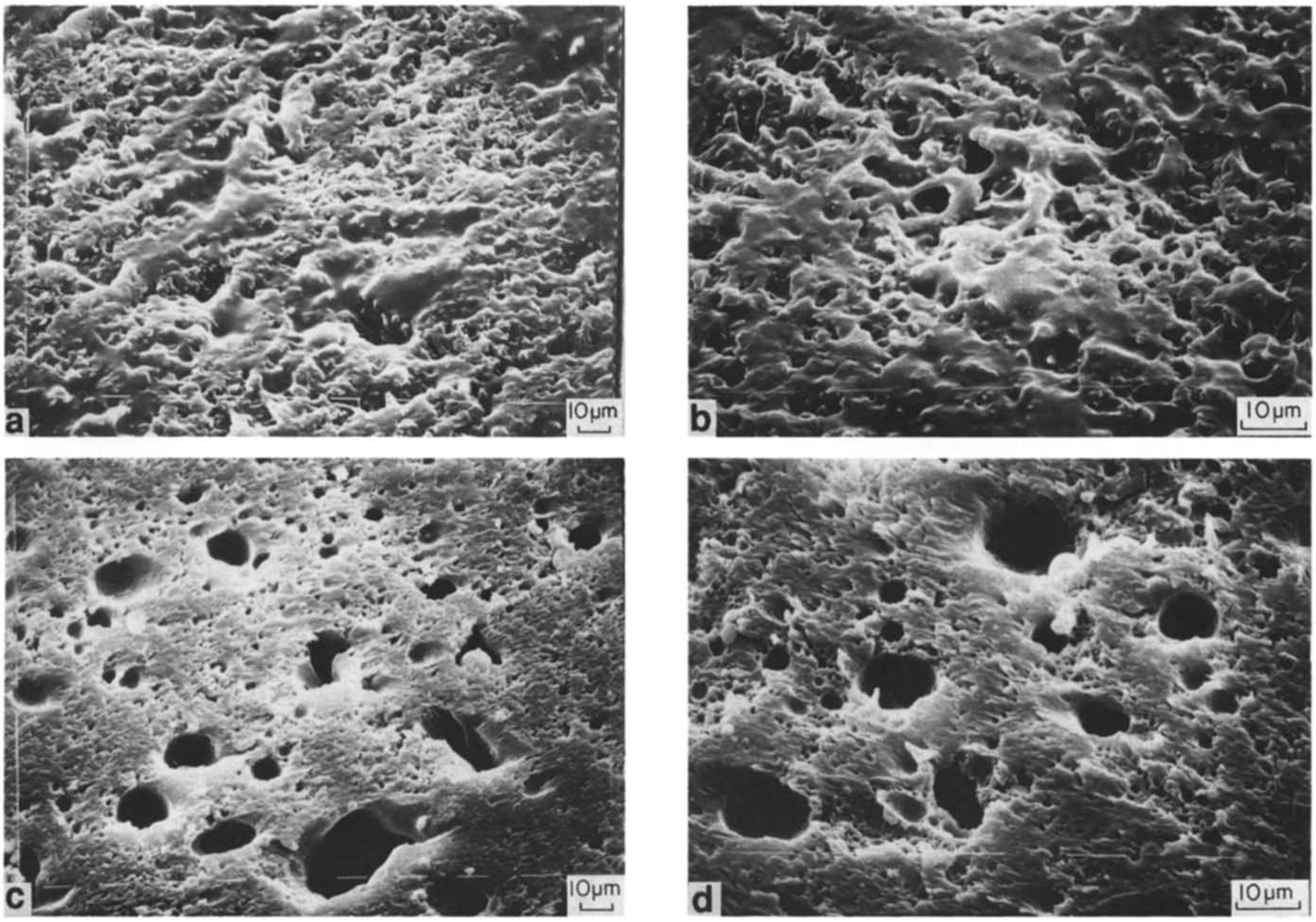


Figure 8 SEM micrographs of smoothed surfaces after etching of F4020 and M4020 blends: (a) F4020; (b) F4020; (c) M4020; (d) M4020

average found in the PA6/EPR blends[7], around 30 μm. This can be at least partly attributed to the higher polarity of EVA copolymers, compared with EPR copolymers, which when blended with the relatively highly polar PA6 may reduce the tendency of the rubbery phase to coalesce. There is slight evidence of spherical domains very small in size (1 μm or less), not extracted by chlorobenzene vapour (see particularly *Figures 6d* and *7d*), never found in the case of PA6/EPR blends[7]. On the basis of our previous spectroscopic and calorimetric evidence on the formation of graft copolymers EVA-*g*-PA6, we can assume that these domains might be due to the presence of such graft copolymers, unextractable by solvent.

In the case of M4020 blend (see *Figures 8c* and *8d*), there is clear evidence of a 'bimodal' distribution of the rubbery phase, as domains of 20 μm or more coexist with domains much smaller, around 2 μm. The presence of very fine particles can be due to the larger extent of reaction between EVA and PA6, as the VA content of EVA40 is the highest among the employed EVA copolymers.

'F' type blends. The average dimensions of the rubbery phase, between 0.2 μm in F3020 (see *Figure 7b*) and 4 μm in F2020 and F4020 (see *Figures 6b* and *8b*), are lower than that found in 'M' type blends. This can be at least partly explained by the higher molecular weight of the PA6 in the 'F' blends at 20 wt% of rubber content, if compared with the corresponding 'M' blends. The molecular weight of the matrix plays an important role as it determines the viscosity of the medium in which the rubbery particles are dispersed. If the viscosity is too low, as for the 'M' blends, the shear forces acting on the surface of the rubbery particles are not sufficient to break the domains into smaller spheres. Also, the increased polarity introduced by the anhydride groups can play a role in the same direction. The best results in terms of degree of dispersion of the rubbery phase seem to be obtained for the F3020 blend. Once again, a large number of small unextracted spherical domains are evident, particularly in F2020 and F4020 blends (see *Figures 6b* and *8b*).

CONCLUSIONS

The rubber modification of PA6 by using saturated EVA copolymers either unmodified or upon grafting with SA molecules effected concurrently with caprolactam polymerization turns out to be a very complex process where different chemical reactions may coexist or interfere with that of PA6 polymerization. The VA comonomer of EVA interferes with caprolactam polymerization, causing a decrease in the molecular weight of the PA6 if compared with the molecular weight of the PA6 at the time the rubber is added. Several reaction paths can be drawn in order to explain such an effect: among them, the high-temperature saponification of the acetic groups with production of acetic acid and subsequent depolymerization of polycaprolactam chains is the most important, as revealed by a model experiment. There is some clear evidence about the formation of graft copolymers EVA-*g*-PA6 already in the absence of SA groups, which are known to be able to produce such grafted copolymers. The presence of anhydride groups causes a finer dispersion of EVA in PA6, as revealed by SEM analysis. The most regular distribution of the rubbery component is observed in the case of blends containing functionalized EVA copolymer with 30% of vinyl acetate along the chain. The low molecular weight of PA6 is an obstacle to the use of such blends as mouldable toughened plastics. In fact, for PA6-based technopolymers the molecular weight of PA6 is around 20 000. Nevertheless, work is in progress to study the possibility of adding these blends as miscible plasticizers in high-molecular-weight PA6 or PA6-based blends.

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