

Polycarbonate/acrylonitrile-butadiene-styrene blends: 1. Complementary etching techniques for morphology observations

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Blends of bisphenol A polycarbonate (PC) and acrylonitrile-butadiene-styrene copolymer (ABS) were prepared in a Brabender-like apparatus and compression moulded in a press. Specimen surfaces, smoothed by a microtome, were etched by two different agents: (1) an aqueous solution of NaOH capable of hydrolysing the PC alone; (2) an aqueous solution of acids capable of oxidizing the ABS alone. The simultaneous utilization of both methods yielded complementary information on the blend morphology.

(Keywords: polycarbonate; acrylonitrile-butadiene-styrene; blend; morphology; etching)

INTRODUCTION

Blends of bisphenol A polycarbonate (PC) and acrylonitrile-butadiene-styrene copolymer (ABS) have been commercial products for some time¹. The two components provide complementary improvements: PC contributes to good mechanical and thermal properties, whereas ABS contributes to processability, economy and more reliable notch impact resistance. A number of patents concerning these blends have been issued in the past, but scientific knowledge about their behaviour is still limited owing to the complexity of the system. The blends consist, in fact, of four polymeric species and of three phases, having a morphology depending on a variety of factors: molecular characteristics of the components, ABS composition, blend composition, rheological properties, processing conditions, thermal treatments and so on. Their excellent properties therefore necessitate a better understanding of the relationships between processability, morphology and performance of this material.

The present work is the first of a series of papers in which we try to obtain a deeper insight into PC/ABS blend behaviour by means of a systematic analysis. Particularly, we report here on two different methods of etching. The first one utilizes a basic NaOH solution, which is capable of hydrolysing the PC alone on smoothed blend surfaces. The second one, in contrast, utilizes a strong acid solution to etch the ABS alone on surfaces of the same blends. The two agents turn out to be very suitable for successive accurate morphological observations by scanning electron microscopy (SEM).

In subsequent papers of this series, the processability,

thermal behaviour, tensile properties and impact performance of these blends will be analysed. Also, blends made with the same PC but with ABS having different compositions will be analysed and discussed.

EXPERIMENTAL

Materials

The PC used (a u.v.-stabilized polymer having a melt flow index $MFI = 11$ g/10 min measured at 300°C under 1.2 kg according to ASTM D1238) and the ABS used (a copolymer having a $MFI = 18$ g/10 min measured at 220°C under 10 kg according to ASTM D1238) are both commercial products of Enichem Tecnoresine, with the tradenames of Sinvet 223 and Sinkral M122, respectively.

Before blending, the materials were dried in a vacuum oven at 100°C for 24 h in order to avoid PC degradation and defects in the samples.

Blend preparation

All the blends were prepared by melt mixing in a Brabender-like apparatus (Rheocord EC, Haake Inc.) at a temperature of $220 \pm 3^\circ\text{C}$ and at a roller speed of 32 rpm. The blends so obtained were coded as follows: PC-90, PC-80, PC-75, PC-70, PC-60, PC-50, PC-40, PC-20, PC-10 (where the numbers indicate the weight percentage of PC in the blend).

Specimen preparation

The blends from the mixer were compression moulded in a heated press at a temperature of 220°C and a pressure of 200 kg cm^{-2} in order to obtain 3.5 mm thick sheets. Small bars ($60 \times 6 \times 3.5 \text{ mm}^3$) were cut from the sheets and their cross-section (for a few specimens also their longitudinal section) was smoothed by a microtome. The purpose was to prepare suitable surfaces for successive etchings as described below.

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Table 1 Etching times (min) as a function of blend composition for base (1) and for acid (2) solutions

| | PC-90 | PC-80 | PC-75 | PC-70 | PC-60 | PC-50 | PC-40 | PC-20 | PC-10 |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| (1) | 20 | 20 | 20 | 20 | 30 | 30 | 40 | 40 | 40 |
| (2) | 6 | 6 | 6 | 6 | 5 | 5 | 5 | 4 | 4 |

Etching techniques

Method 1. Organophilic or aqueous bases can cause rapid hydrolysis of PC, whereas ABS is very stable in their presence. This was first reported by Eastmond², who used an aqueous solution of KOH (30% w/v) to etch smooth surfaces of multiphase systems containing PC. For low PC content in an ABS matrix, the solution worked rather well. But when PC was the matrix, as soon as it was hydrolysed, the dispersed ABS domains were removed from their original positions and some of them were lost, giving rise to an altered view of the internal morphology. The problem, however, could be overcome by limiting the extent of PC hydrolysis on the surface by a trial-and-error procedure. In fact, for each blend composition, it was necessary to optimize the etching time in order to obtain satisfactory phase contrast without losing the original morphology (see *Table 1*). An aqueous solution of NaOH (30% w/v) was used, at a constant temperature of 105°C, instead of KOH.

Method 2. PC, which is easily hydrolysed in a strong basic solution, is, in contrast, very stable when it is immersed in aqueous solutions of strong oxidizing organic or inorganic acids. ABS, on the other hand, has the opposite behaviour: it is not attacked by bases but is easily oxidized by acids. Therefore, an acidic solution, made of 5 g of CrO₃, 120 ml of H₂SO₄ and 30 ml of H₂O, was used as the etching agent for ABS in our system, at 80°C and for different times as reported in *Table 1*. In fact, in this case also, it was necessary to find an optimum etching time when the ABS was the matrix (in PC-40, PC-20, PC-10 blends) in order to preserve the original morphology of the dispersed PC phase.

The above-illustrated methods 1 and 2 are therefore complementary for morphological observations in PC/ABS blends. In both cases, after etching, the specimen surface was washed with hot water. The washing time was found to be a very important factor to reveal different morphological features. Therefore, at the beginning, the specimens were washed only for 5 min, and then later for 20 min, so obtaining complementary information in the two cases.

Morphology observations

The smoothed and etched specimens were coated with Au/Pd alloy before SEM observations. The SEM used in this work was a Philips EM 502 and the acceleration voltage was 30 kV.

RESULTS AND DISCUSSION

The morphology of PC/ABS blends was investigated in previous papers by several techniques. Osmic acid and RuO₄ were used, for instance, to stain the polybutadiene (PB) contained in the ABS^{3,4}. The observations were made by transmission electron microscopy (TEM): the contrast between PC and ABS phases was rather poor, the reason being the relative densities of the two polymers

(PC = 1.2, ABS = 1.04–1.06). By staining the PB, the densities become closer, and this can decrease the contrast between the PC and the ABS.

In another case simple observations by scanning electron microscopy were effected on surfaces of cryogenically fractured specimens; the result was unsatisfactory, in this case also, owing to poor phase contrast^{5–8}.

Bucknall and others^{9,10} etched the PB in samples of pure ABS by an aqueous solution of sulfuric, phosphoric and chromic acids; etching was followed by a two-stage replica process. The technique was suitable to reveal fine features of the internal structure in composite rubber particles as well as details of orientation in injection-moulding specimens and of crazes and shear bands induced in the material by mechanical deformation. However, the method was quite sophisticated and complex, and required particular skill.

Eastmond and others² used an aqueous solution of a strong base to hydrolyse the PC phase in solution-cast films of PC/PS (polystyrene) and PC/SAN (styrene-acrylonitrile copolymer) blends. The contrast obtained in this case was quite good, but the authors suggested the use of this technique preferably only in the case where the PC was the dispersed phase in a matrix of a different polymer, like SAN or PS.

For our PC/ABS blends, we decided to perform two kinds of etches (see the 'Experimental' section) in order to get a satisfactory contrast between the two phases. At the same time, this procedure gave the possibility of a cross-check of the observed specimen morphology.

In *Figure 1* surface photographs of a PC-70 specimen, first smoothed and then etched by NaOH solution (30% w/v) at a temperature of 105°C, are shown. The micrographs in *Figures 1a* and *1b* are relative to the same etching time (5 min) but have different magnifications (originally 320× and 1250× respectively). It is clear that in 5 min the PC was only lightly hydrolysed by the NaOH solution and the observed ABS particles were those cut in the middle by the microtome during the smoothing of the blend surface (in fact, they appear to be flattened). *Figures 1c* and *1d*, having the same magnifications as those used for *Figures 1a* and *1b*, correspond to a longer etching time (10 min). In this case only some of the flat ABS particles, sitting on the surface, have been taken out by the PC etching, whereas most of them still remain in their original positions (in *Figure 1d* a few holes are observable where the ABS particles were located).

After 20 min (*Figure 1e*) the first layer of the ABS particles has been completely swept away and the internal morphology of the material is revealed. After 40 min (*Figure 1f*) the etching is too long and hydrolysis proceeds in an irregular way in the different zones underneath the smoothed surface. In fact, as already suggested by Eastmond², most of the ABS particles were etched away at different levels of depth together with the hydrolysed PC, giving rise to a very rough and irregular

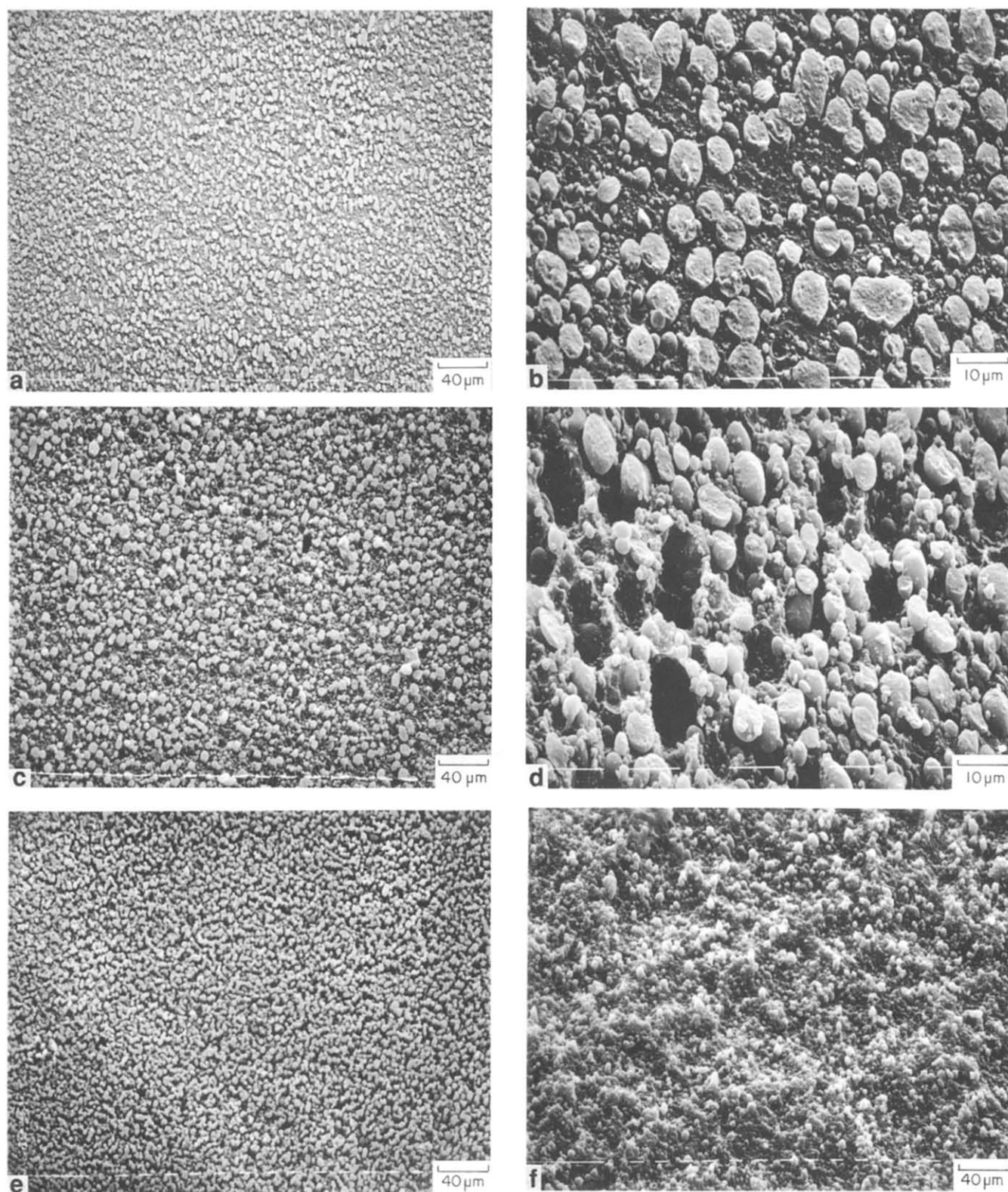


Figure 1 SEM micrographs of smoothed surfaces of a PC-70 blend etched by an aqueous NaOH solution for different times (and observed at two diverse magnifications): (a) 5 min (originally 320 \times); (b) 5 min (originally 1250 \times); (c) 10 min (320 \times); (d) 10 min (1250 \times); (e) 20 min (320 \times); (f) 40 min (320 \times)

morphology. Therefore, a time of 20 min seemed to be the most suitable to etch away only the first layer of the ABS particles and to reveal, in this manner, the real morphology of this blend specimen.

It must be recalled that the optimum etching time is a function of the blend composition (see *Table 1*).

The surfaces of blend specimens PC-90, PC-80, PC-75,

PC-70, PC-60, PC-50, PC-40, PC-20 and PC-10, etched by the NaOH solution and washed by water for 5 min, are shown in *Figures 2a* to *2i* respectively. In all cases a two-phase structure is present with various morphological features formed during the processing and the moulding of the materials. There is a size increase of the ABS domains on going from PC-90 (*Figure 2a*) to PC-70

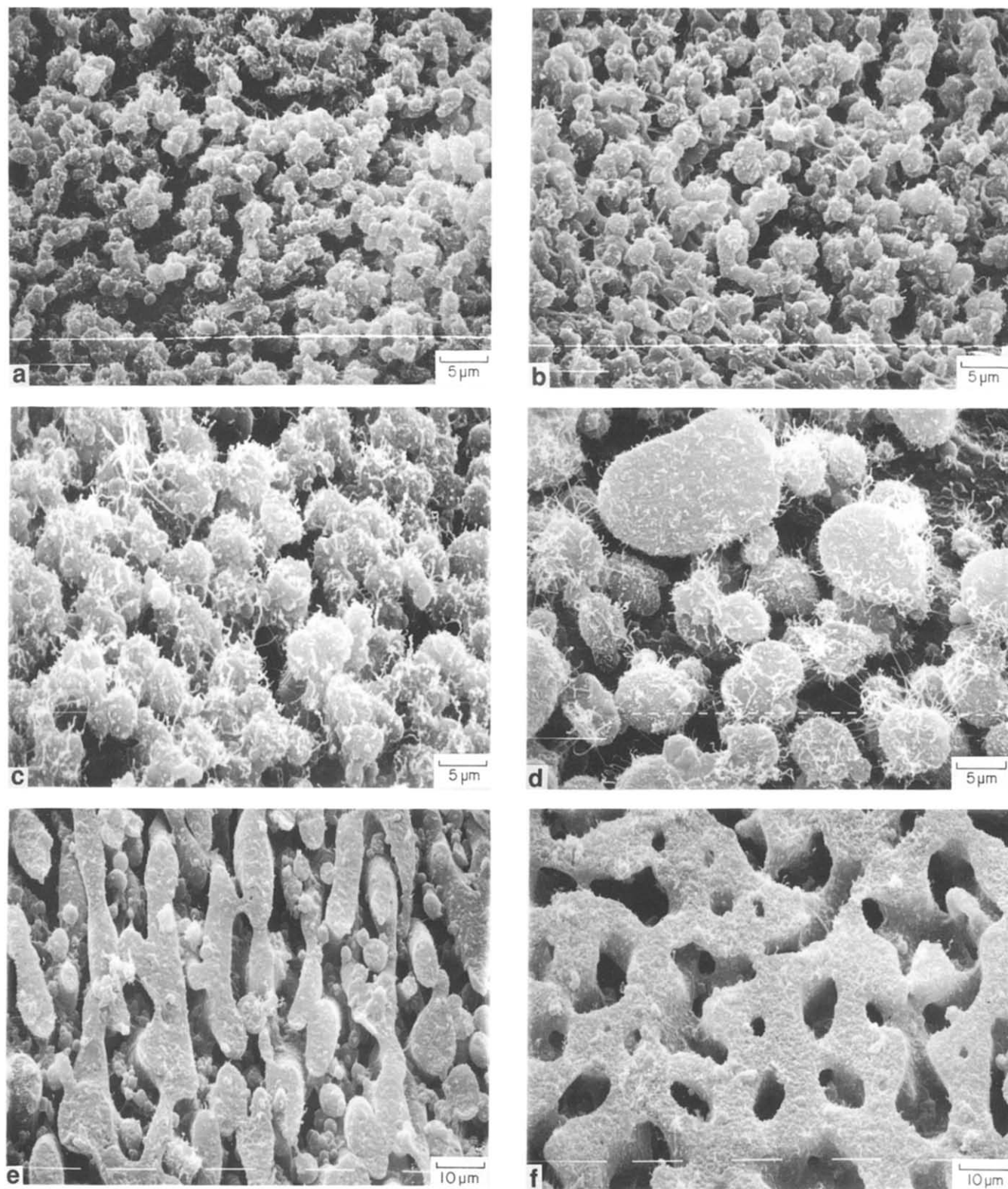


Figure 2 SEM micrographs of smoothed surfaces of PC/ABS blends, etched by an aqueous NaOH solution for different times as indicated in Table 1: (a) PC-90; (b) PC-80; (c) PC-75; (d) PC-70; (e) PC-60; (f) PC-50; (figure continued on next page)

(Figure 2d). The domain distribution seems to be rather narrow, especially for the first three blends (PC-90, PC-80 and PC-75; Figures 2a, 2b and 2c, respectively), but the domains are not randomly dispersed in the matrix. It is to be underlined that all the ABS domains are covered with a fine down of residual PC. This effect is due to the low washing time used in this case after the

etching process. The PC-70 exhibits a broad size distribution, probably due to a coalescence effect of the ABS particles with increasing amount of ABS. An ABS continuous phase starts to appear in the PC-60 blend (Figure 2e), even though ABS dispersed domains are still present. This would imply that phase inversion is starting to occur, and this becomes even more evident with a

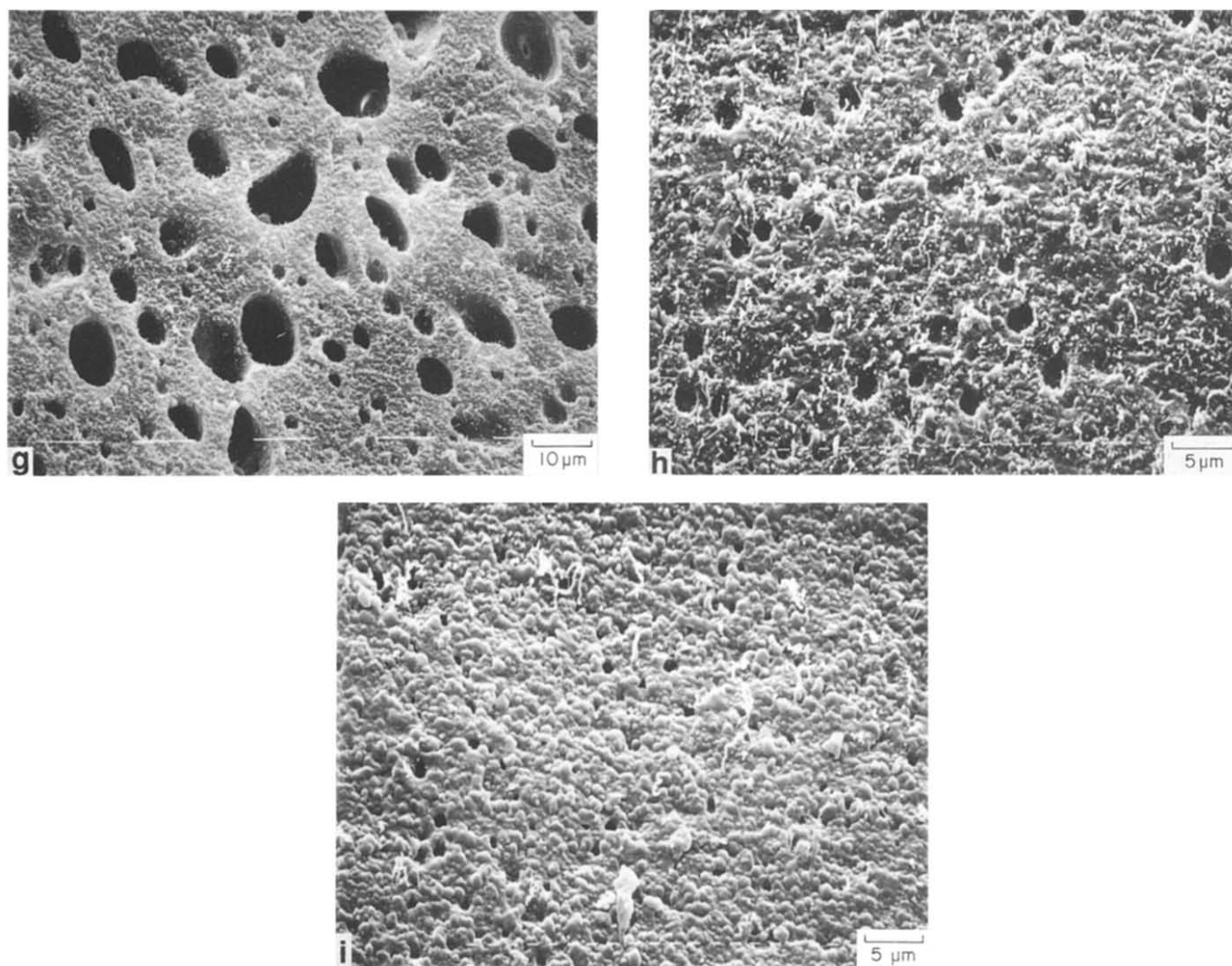


Figure 2 continued (g) PC-40; (h) PC-20; (i) PC-10

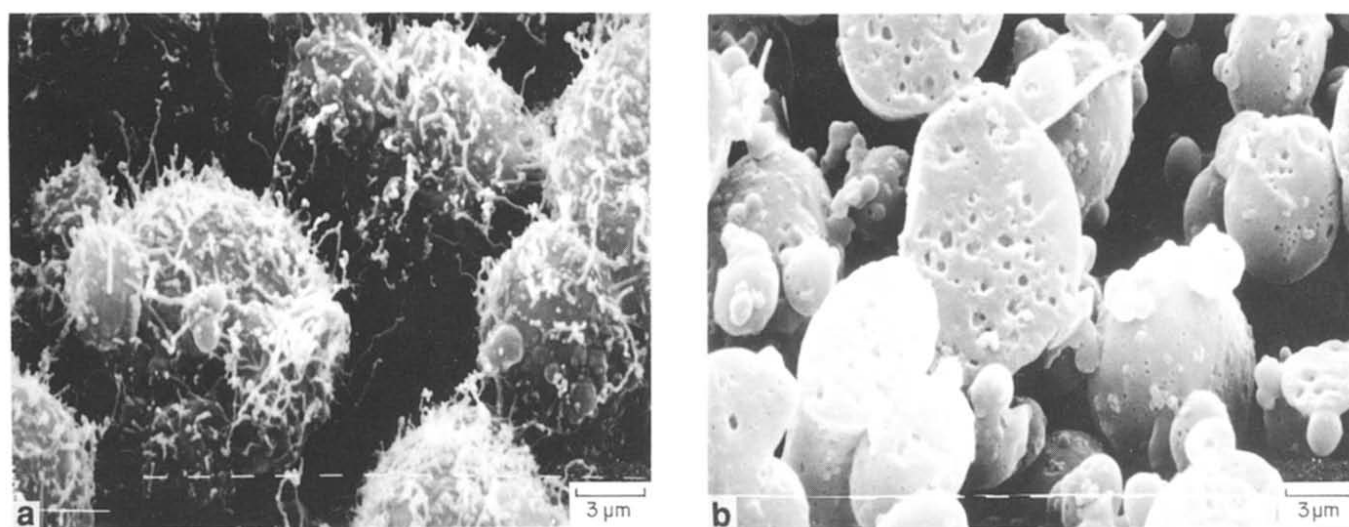


Figure 3 SEM micrographs of smoothed surfaces of PC-70, etched by an aqueous NaOH solution for 20 min and washed with hot water for different times: (a) 5 min, (b) 20 min

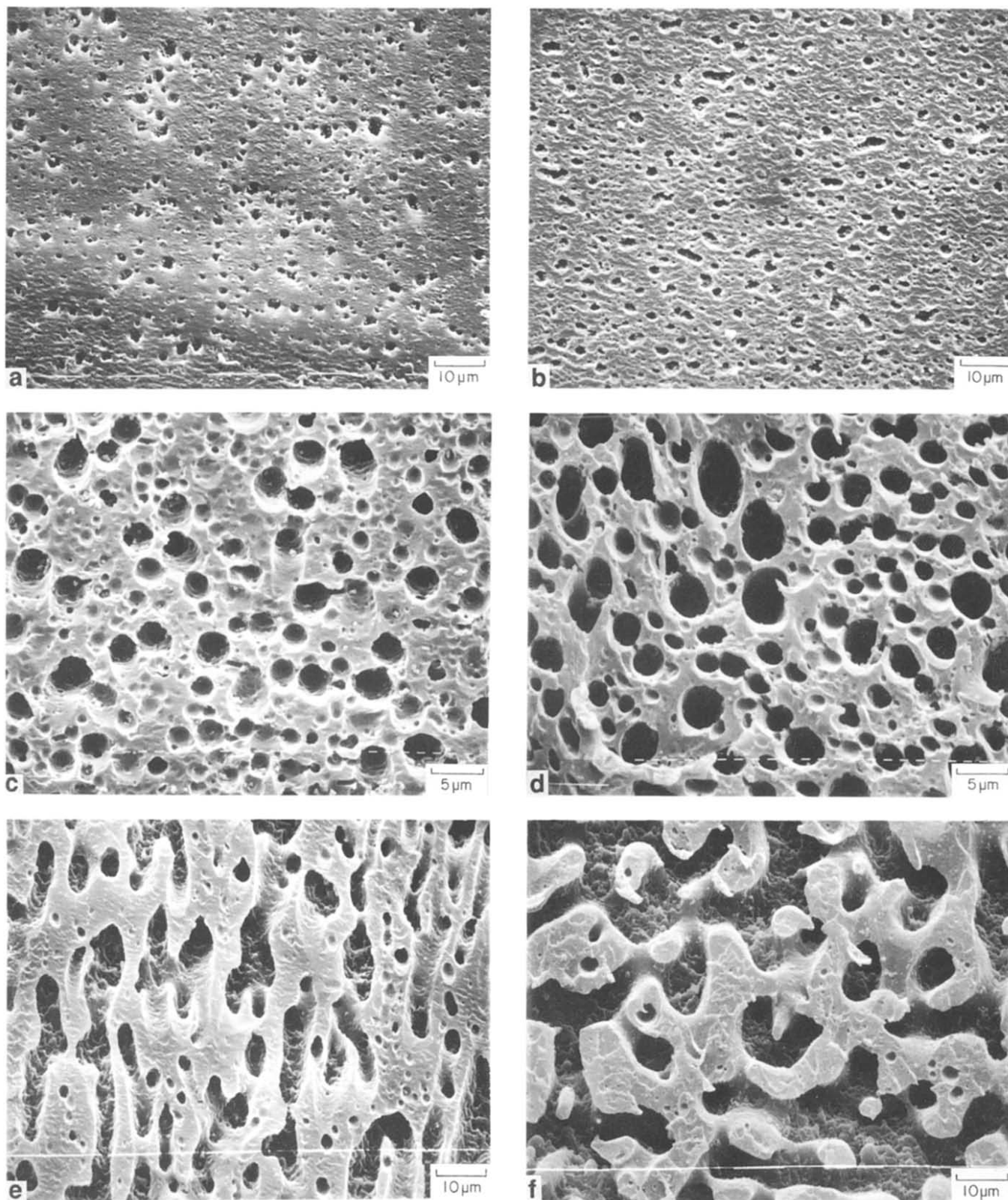


Figure 4 SEM micrographs of smoothed surfaces of PC/ABS blends etched by an aqueous acid solution (see 'Experimental' section) for different times as indicated in *Table 1*: (a) PC-90; (b) PC-80; (c) PC-75; (d) PC-70; (e) PC-60; (f) PC-50; (figure continued on next page)

further ABS increase (PC-50, *Figure 2f*) where the PC domains begin to be isolated in the ABS matrix. At higher ABS contents (from PC-40, *Figure 2g*), the basic solution leaves holes in the ABS matrix, corresponding to PC domains; the holes are smaller the lower the PC content in the blend. This interpretation will be confirmed also by the rheological behaviour described elsewhere¹¹. For

pure ABS no holes are observed, confirming that the copolymer is not attacked by the basic solution.

Two micrographs for a PC-70 specimen etched as the ones already shown in *Figure 2* but washed with hot water for different times are presented in *Figures 3a* (5 min) and *3b* (20 min) respectively. It is evident, by comparison between *Figures 3a* and *3b*, that for the latter

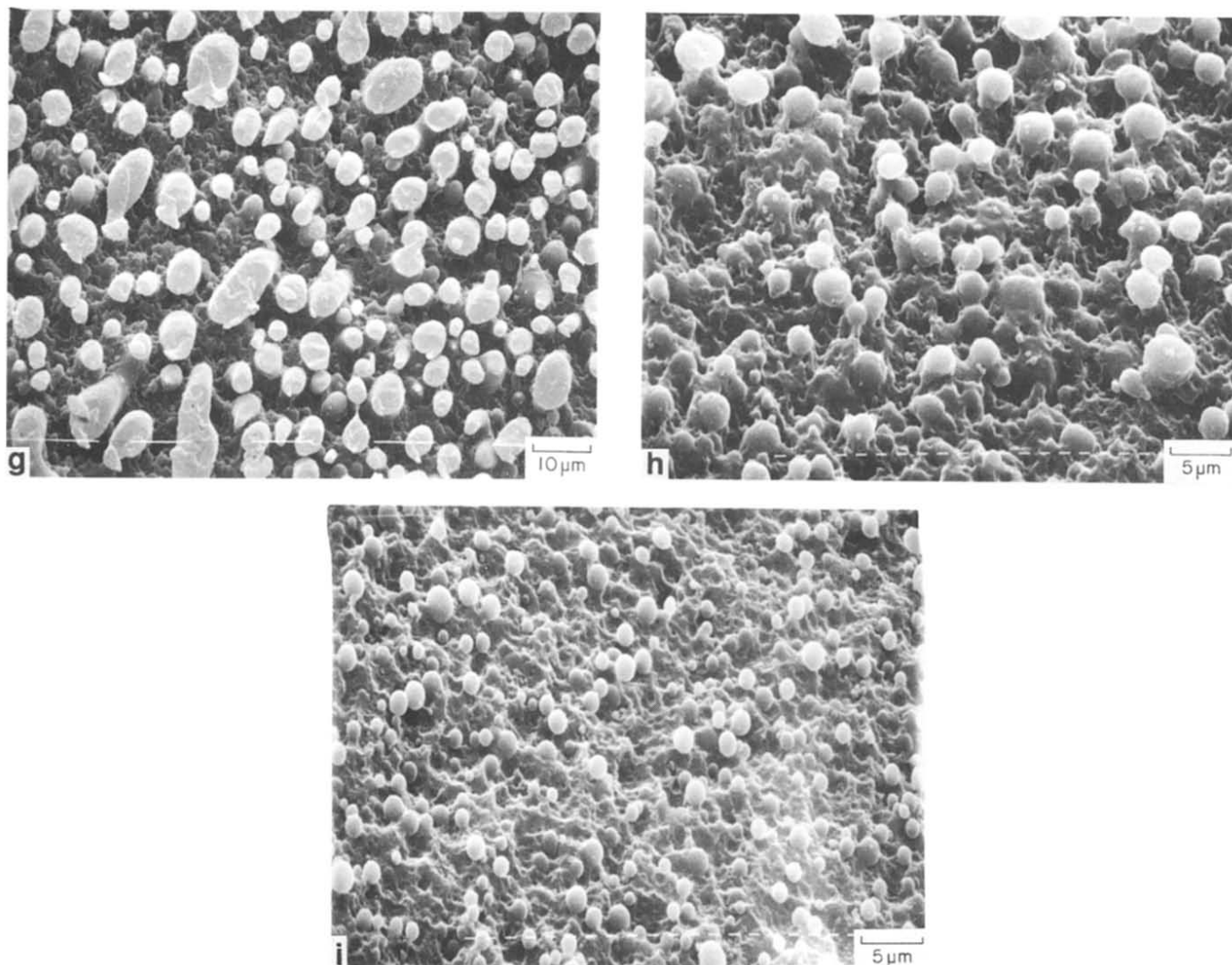


Figure 4 continued (g) PC-40; (h) PC-20; (i) PC-10

the washing time used was sufficient to sweep away all the PC down. Therefore fine details of the morphology, previously masked by the PC down, are now observable: the ABS particles show on their surface tiny holes and other microstructures, which make the interactions between the two phases somewhat more intimate. In other words, not only is the contact surface area between the two components very much increased by the existence of these superstructures with respect to the case of smooth particles, but also the reciprocal protrusions tend to resist mechanical forces transmitted from the matrix to the dispersed domains. Therefore, during mechanical deformation of the matrix, the dispersed phase can be accordingly deformed, increasing the energy dissipated by the system.

Passing to the etching obtained by the acid solution, the surfaces relative to all the blends are shown in Figure 4. Here the observed holes in PC-90, PC-80, PC-75 and PC-70 are left by the ABS dispersed domains (Figures 4a to 4d). The ABS particles lie on the same plane and therefore these micrographs are suitable for a more quantitative analysis than those of Figure 2. Figure 4e confirms the coalescence of the ABS particles as the ABS content reaches 40%, with the formation of very large domains accompanied by small spherical ones. Co-continuous phases are formed at 50% of ABS (Figure

4f), cylindrical domains are formed at 60% of ABS (Figure 4g) and spherical particles at higher ABS contents, the smaller the lower the amount of dispersed phase. With respect to the surfaces treated with the basic solution, it is possible here to see clearly the shape of the PC domains and to compare these with the corresponding holes left by the previous etching.

To obtain a three-dimensional image of the domains, the surfaces of two different sections of a PC-60 blend are presented in Figure 5. One (Figure 5a) is a cross-section of the compression-moulded slab whereas the other one (Figure 5b) is a section cut perpendicularly to it. The same has been done for the PC-40 blend (Figures 6a and 6b). In the first case the PC exhibits a lamellar structure, whereas in the second one cylindrical domains are observable.

Both the techniques used provide clear pictures and fine morphological features of the blends. This knowledge will be very useful for the interpretation of the results obtained in the other papers of this series.

CONCLUDING REMARKS

Two etching methods using different agents have been presented in this paper: the first one, using an aqueous base solution, is very suitable for selectively hydrolysing

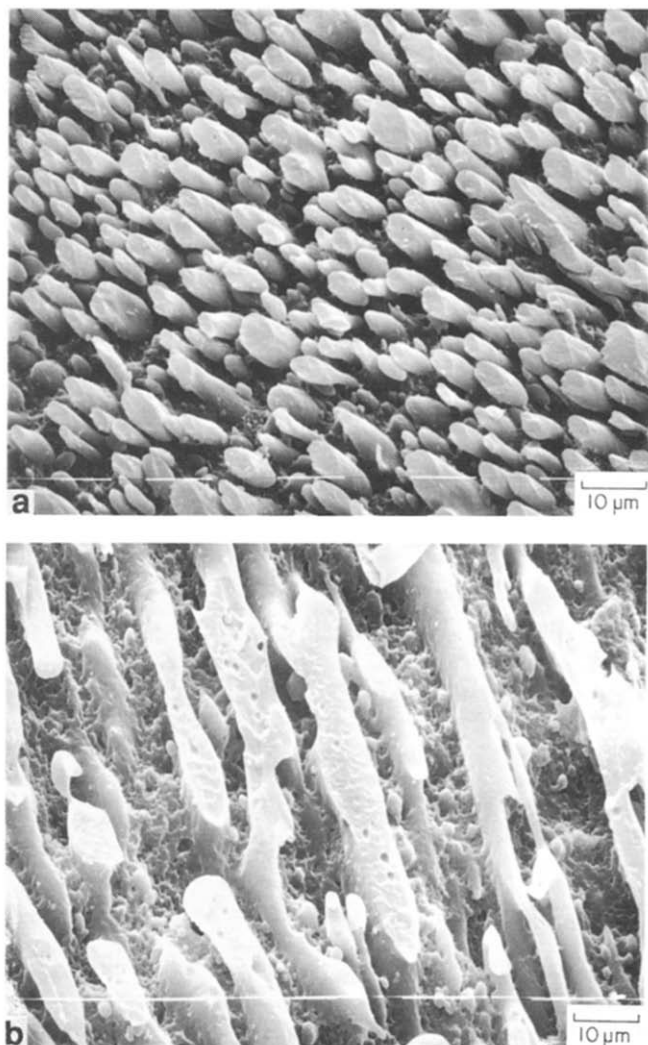


Figure 5 SEM micrographs of smoothed surfaces of a PC-60 blend etched by an aqueous acid solution (see 'Experimental' section) for 5 min: two cross-sections perpendicular to each other, showing the lamellar structure of the PC domains

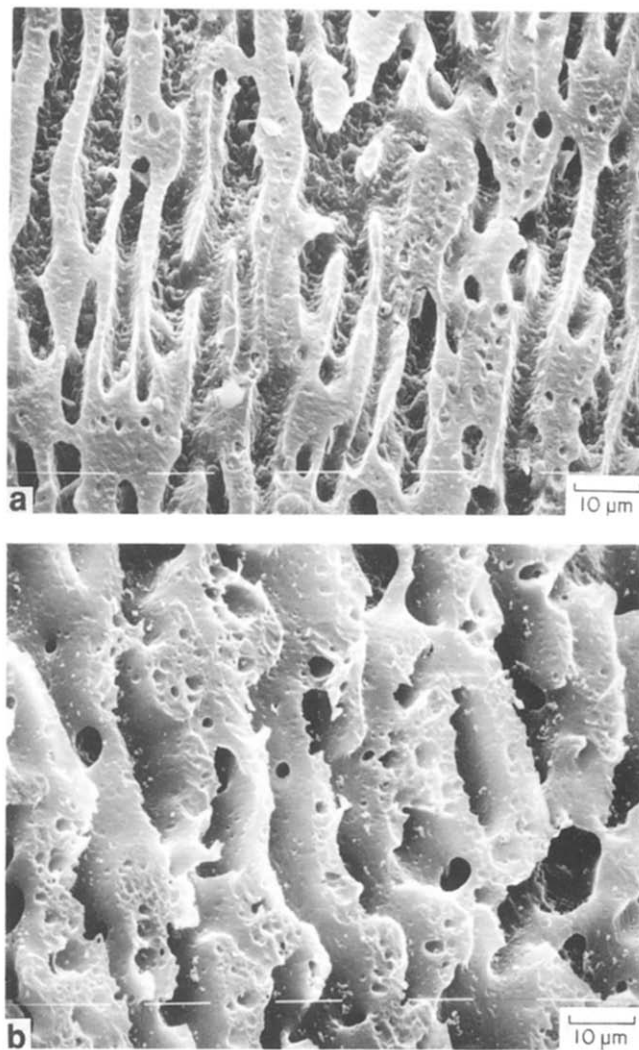


Figure 6 SEM micrographs of smoothed surfaces of a PC-40 blend etched by an aqueous acid solution (see 'Experimental' section) for 5 min: two cross-sections perpendicular to each other, showing the cylindrical structure of the PC domains

the PC; the second one, using a strong oxidizing acid solution, is able to oxidize the ABS selectively.

The simultaneous use of both methods provides a cross-check of the fine morphological features present in both the phases and, as will be shown in subsequent papers, of the features induced by mechanical and impact deformations and/or fracture.

The proposed methods, up to now used separately, are rather easy to apply, even though a certain amount of care must be used, especially in the cases when the component to be etched is the matrix. In such a case an optimum etching time must be found by a trial-and-error procedure for each blend composition in order to reveal the internal morphology of the specimen for each of the two techniques.

The washing time can be used to reveal particular features of the morphology as well.

Work is in progress to analyse the processing of these blends as well as their mechanical behaviour at low deformation rates in tensile tests on unnotched specimens and at high deformation rates in flexural tests on sharply notched specimens.

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