Isotactic polypropylene/hydrogenated oligo(cyclopentadiene) blends: 2. Tensile stress–strain and morphological behaviour of annealed samples

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(Received 18 May 1992; revised 16 March 1993)

Mechanical tensile tests and morphological analyses were carried out on samples of isotactic polypropylene/hydrogenated oligo(cyclopentadiene) (iPP/HOCP) blends. The blends were obtained by melt mixing in a Brabender-like apparatus. Sheets of such blends were prepared by moulding the material under pressure, quenching in iced water and then annealing them in an oven at 140°C under vacuum for 24 h. Stress–strain tensile tests, previously obtained at room temperature, were performed at higher temperatures (80°C and 100°C). Morphology observations were performed by scanning electron microscopy after treatment of the blends with two different etching solvents (n-heptane and chloroform) at their boiling temperatures for various times in order to dissolve the HOCP component. An acid solution with a strong oxidizing action was used as well. In all the investigated blends (from pure iPP to up to 80% HOCP in the blend) the iPP molecules provide the material interconnection, as evidenced by fibre formation. The transition from ductile to brittle in the mechanical behaviour depends on temperature and composition.

(Keywords: polypropylene; oligo(cyclopentadiene); hydrogenated; blends; stress–strain; morphology)

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most diffuse semicrystalline polymers[1]. Its fundamental characteristics are easy processing, relatively low cost and large applicability. For these reasons, iPP has been widely studied both as a homopolymer and as a component of blends. For instance, an interesting improvement of its impact strength at room temperature or below can be obtained by adding a rubbery component to iPP. Therefore a great deal of work has recently been carried out on such blends[2–8].

The aim of these studies was to understand the influence of the different elastomer components (such as polyisobutylene or ethylene–propylene random copolymers) on the morphology, crystallization and melting behaviour of iPP. In fact, it was shown that the matrix characteristics can be changed by the presence of rubber, which influences directly the crystallization. Therefore the system consists of a semicrystalline matrix and a rubbery dispersed phase. The rubbery phase represents the reinforcing agent that improves the low impact strength of iPP at low temperatures.

In the present work a quite different type of additive was used to increase the iPP modulus. The component used was an amorphous oligomer, hydrogenated oligo(cyclopentadiene) (HOCP), whose glass transition temperature is higher than that of iPP.

Blends of iPP and HOCP have been studied in previous works in the composition range up to 50% by weight HOCP[9–14]. In particular, some properties of isothermally crystallized samples were thoroughly investigated. An analysis of the crystallization and thermal behaviour of thin films showed that the spherulitic growth rate, the equilibrium melting temperature and the overall crystallization rate of iPP were depressed by the addition of HOCP. The glass transition temperature increased with HOCP concentration in agreement with Fox's equation[9]. No segregation phenomenon of HOCP was observed. In addition, from small-angle X-ray scattering it was possible to observe an increase in the long period with the addition of HOCP while the lamellar thickness did not change[10]. From these results it was supposed that below the crystallization temperature of iPP (solid state), HOCP and uncrystallized iPP molecules form a homogeneous amorphous phase incorporated mainly in the interlamellar regions. Further study of the influence of different annealing processes on the phase structure showed that the presence of the HOCP molecules in the interlamellar regions caused a loss of thickening tendency in the crystalline lamellae due to annealing[11]. Mechanical tensile tests, performed at room temperature, showed that iPP is reinforced (higher modulus and yield stress) by the addition of HOCP[12]. This behaviour was attributed to the high T_g of HOCP and to the particular phase structure after crystallization of iPP. From some of the above results it was suggested that iPP and HOCP are miscible in the melt and in the amorphous regions in the solid state.

Finally, in the first paper of this series[13], a thermal characterization and dynamic mechanical tests were performed on samples, first quenched in iced water and

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0032-3861/93/245073-07

then annealed at 140°C for 24 h, in a composition range (0–80% HOCP by weight) larger than the one previously investigated. In particular, from the changes of the shapes of the modulus *versus* temperature curves, an interesting model was proposed: the concentration of HOCP in the interlamellar zones was supposed to vary along the interlamellar gap. Only a concentration gradient, in fact, going from zero HOCP content (at pure iPP near to the crystallites) to a high HOCP value (in the middles of the interlamellar zones) could explain the observed behaviour.

The aim of the present work was to obtain further information about the morphology and mechanical properties of the previously obtained iPP/HOCP blends. Mechanical tensile tests at 80°C and 100°C and morphological analyses by scanning electron microscopy (SEM) on smoothed and etched surfaces were carried out.

EXPERIMENTAL

Materials

Isotactic polypropylene, a commercial sample (Moplen T305) produced by Montedison ($\bar{M}_w = 3 \times 10^5$), and a hydrogenated oligo(cyclopentadiene) (Escor 5120) produced by Esso Chemical Co. ($\bar{M}_w = 630$) were the materials used in this work.

Blend and specimen preparation

Binary blends were prepared by melt mixing the materials in a Brabender-like apparatus (mixer 600 of HAAKE Inc.) at 200°C. The weight mixing ratios of iPP/HOCP were 100/0, 90/10, 80/20, 70/30, 50/50, 40/60, 30/70 and 20/80.

Compression-moulded sheets of 1.5 mm thickness were prepared on a heated hydraulic press (Wabash). The material, between two Teflon sheets, was heated at 200°C and kept for 10 min between the plates, without any applied pressure, to allow for complete melting. After this period a pressure of 10 MPa was applied for 5 min. Then the pressure was released and the samples were first quenched in iced water and then annealed in an oven under vacuum at 140°C for 24 h. The aim of the annealing was to avoid changes of the material structures during the temperature sweep of the mechanical tests.

Dumb-bell-shaped specimens (5.0 cm total length, 0.9 cm dumb-bell width, $0.12 \times 0.38\ \mathrm{cm}^2$ gauge section and 2.4 cm gauge length) were cut and used for mechanical tensile measurements.

Mechanical tensile tests

Stress–strain curves were obtained on an Instron machine (model 1122) at a constant crosshead speed of $10\ \mathrm{mm\ min}^{-1}$ at temperatures of 80°C and 100°C. Young's modulus E, which is a low strain property of the material, and the yield stress S_y were calculated from the stress–strain curves.

Morphological analysis

Smoothed surfaces of binary blends were etched first by chloroform at its boiling temperature ($T_b = 62$°C) for 4 h. However, this temperature seemed too low to be able to dissolve the HOCP in blends at high HOCP content. Therefore n-heptane (with $T_b = 98$°C) was used. Both the solvents were chosen because of their capability of selectively dissolving the HOCP phase and leaving unchanged the other phase.

Also a different kind of etching agent, having a strong oxidizing effect on both the amorphous iPP and HOCP, was used with the aim of obtaining information on the crystalline regions of the iPP. The oxidant was made in two steps: (i) concentrated sulfuric acid (97% by weight) was diluted with water in the ratio 1/4; (ii) CrO_3 was then added to the stirred solution at 80°C to obtain a saturated solution. In this case the samples were etched for 1 h.

All the etched samples were finally coated with a golden palladium alloy and observed by a scanning electron microscope (Philips SEM 501).

With n-heptane an extraction time of 30 min was used initially and, since the extraction was very limited, times up to 5 h were tried. However, very little difference was observed between the extraction at 30 min and that obtained after 5 h.

RESULTS AND DISCUSSION

Mechanical tensile tests

Typical stress–strain curves of pure iPP and iPP/HOCP blend specimens tested at temperatures of 80°C and 100°C are reported in *Figures 1* and *2*, respectively.

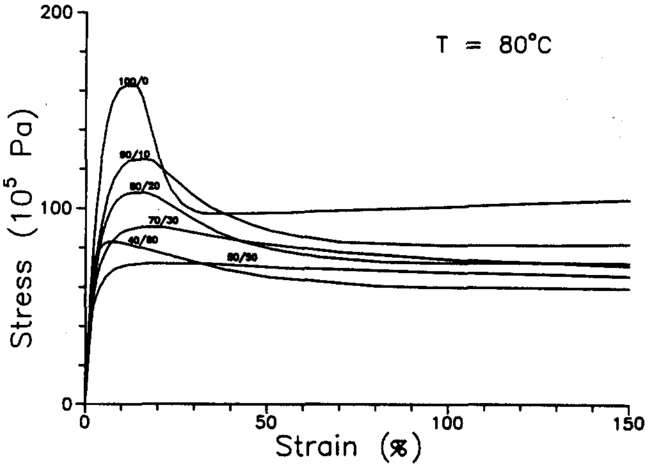

Figure 1 Stress–strain curves at 80°C for the different iPP/HOCP blends (indicated beside each curve)

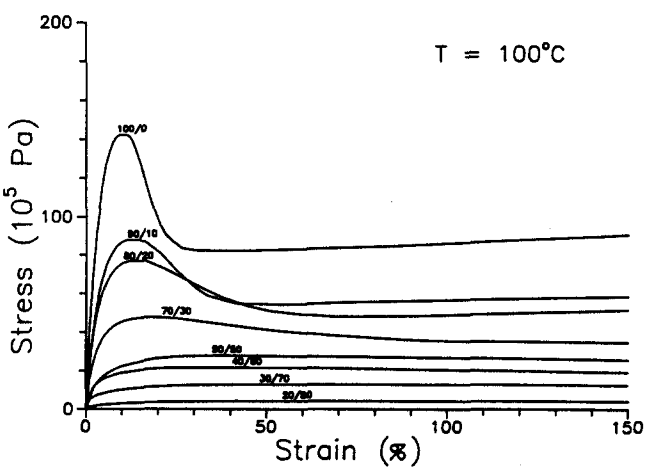

Figure 2 Stress–strain curves at 100°C for the different iPP/HOCP blends (indicated beside each curve)

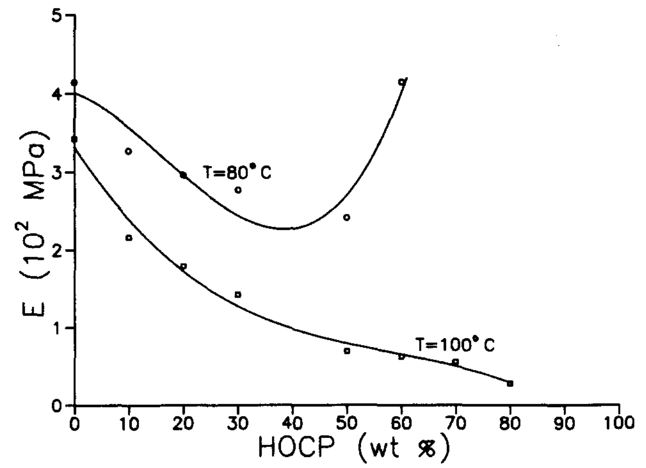

Figure 3 Young's modulus as a function of HOCP content at 80°C and 100°C

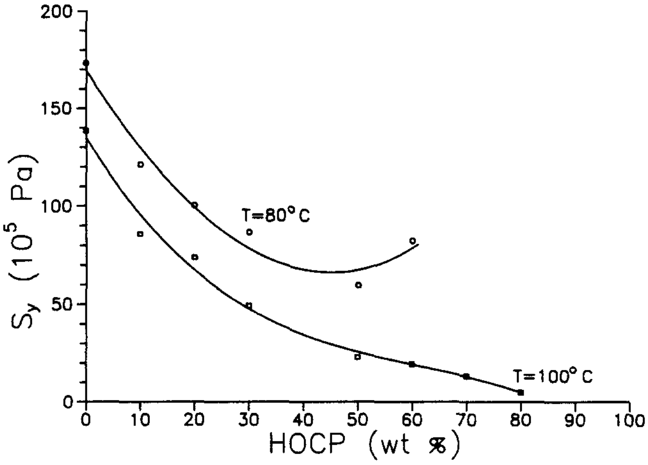

Figure 4 Yield stress as a function of HOCP content at 80°C and 100°C

At 80°C, the moduli E and the yield stresses S_y (measured at the peak position) decrease with increasing HOCP content up to 50%; a further enhancement of 10% determines an upward turn of the curves.

At 100°C, E and S_y decrease in all the investigated specimens. The quantitative values of E and S_y, as a function of blend composition, are given in *Figures 3* and *4*, respectively.

The observed behaviour is due to the following reasons: (i) as the HOCP is added to iPP the iPP crystallinity is lowered[13], therefore both the moduli and the yield stresses must decrease; and (ii) on the other hand, adding more and more HOCP to iPP determines a T_g enhancement in the amorphous regions of the blends. With respect to mechanical properties these represent two competing effects, since the first tends to decrease and the second to increase the material rigidity. Hence, at room temperature[12], only blend specimens having an HOCP content below 20% were able to be transformed into fibres (at higher HOCP amounts the specimens underwent brittle ruptures). At 80°C this ability was acquired also by blend samples with an HOCP content encompassing the range from 20% up to 60% (beyond this value again a brittle failure occurred). Finally, at 100°C over all the investigated range (0–80%) the specimens were transformed into fibres. This possibility would have been especially unexpected at an HOCP content higher than 70%, since the iPP dilution in such cases is very high. However, this effect relies on the iPP molecular weight, which seems to be sufficiently high to allow for entanglements to be efficient even in a relatively diluted system. In such a way the stretched, entangled molecules are able to sustain the load during the plastic elongation and allow for fibre formation.

Another interesting observation is that not only were E and S_y changed but the entire mechanical behaviour (as shown by the whole curve) was different for the diverse compositions. In fact, as the yield stress is lowered the

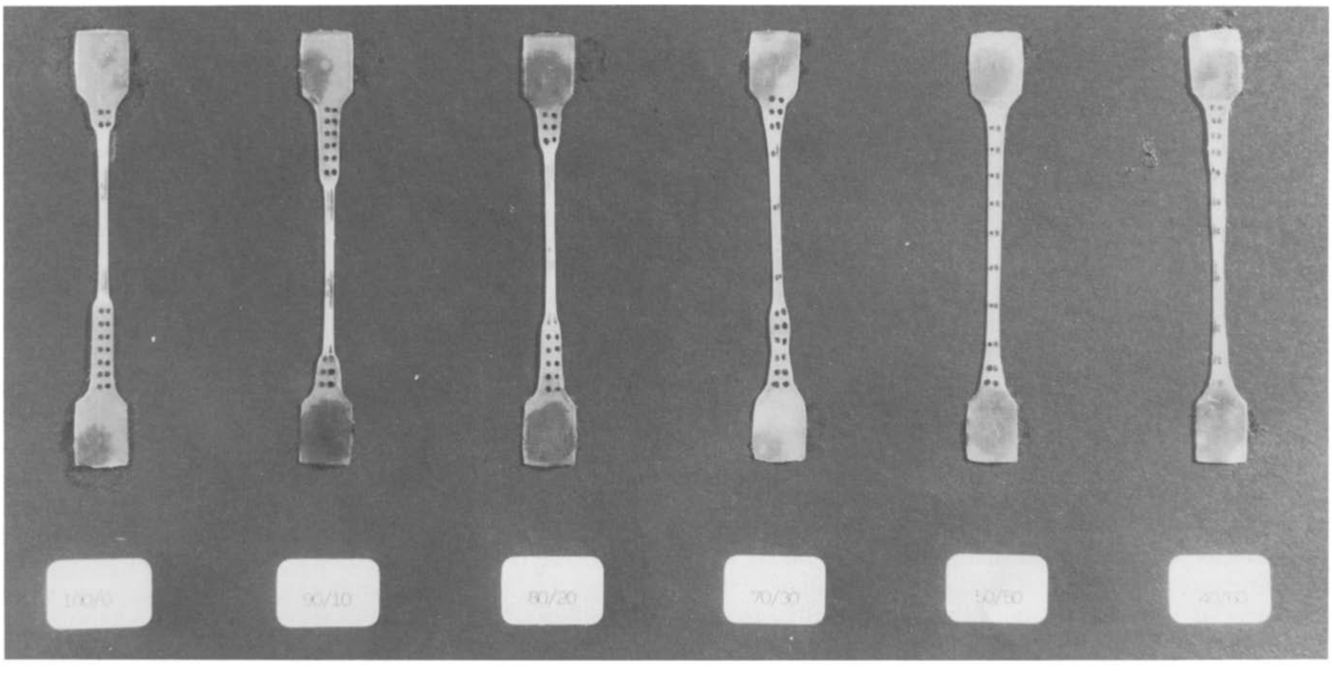

Figure 5 Photograph of iPP/HOCP samples (as indicated) elongated at 100°C

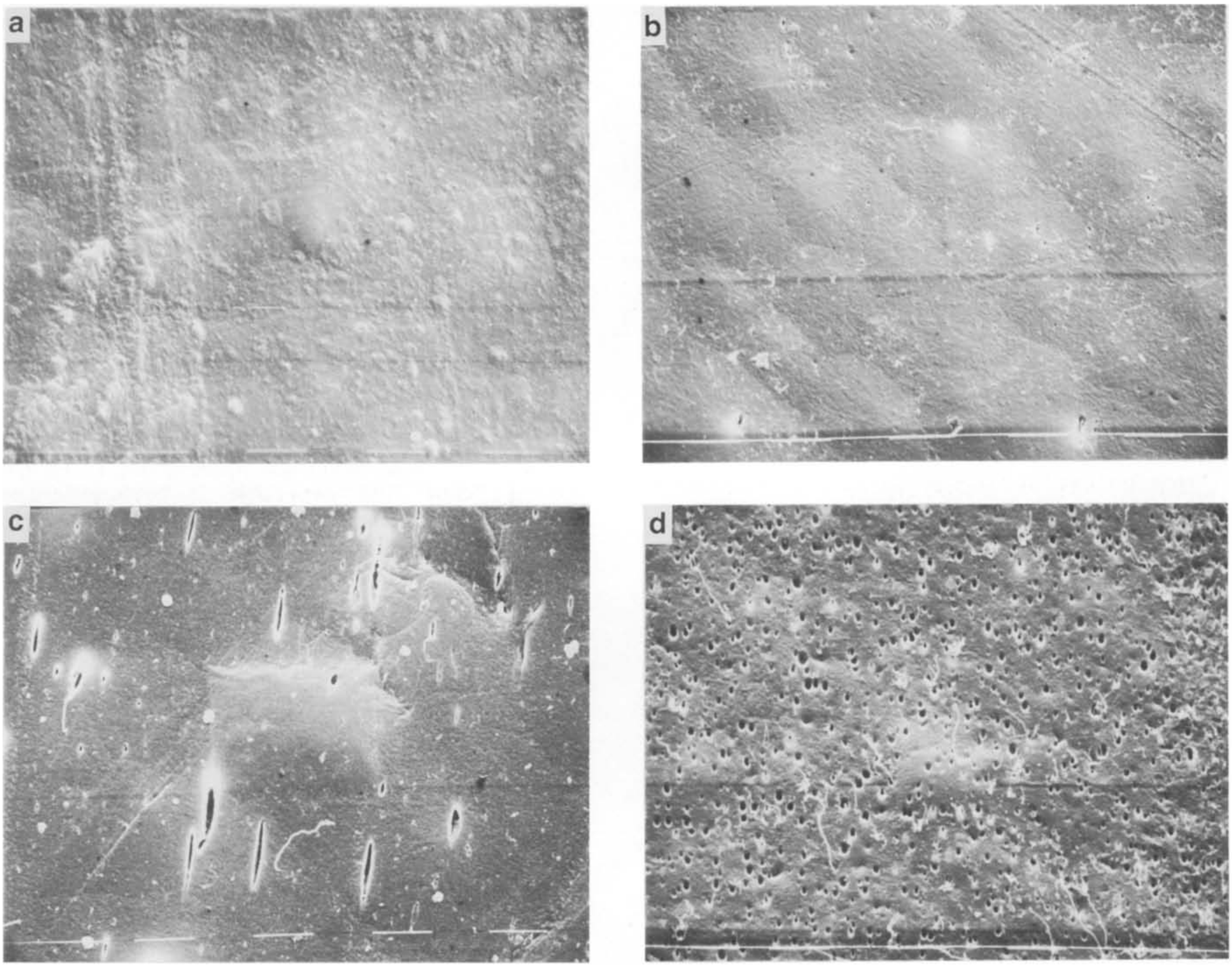

Figure 6 SEM micrographs (× 1250) of smoothed surfaces etched by n-heptane for the different blend compositions: (a) 100/0; (b) 90/10; (c) 80/20; (d) 70/30 (figure continued on next page)

elongation at yield increases with increasing HOCP content. This means that the neck, formed just after the yield peak, becomes less and less sharp and the relative zone of the specimen becomes larger and larger (see *Figure 5*). Therefore the sample deformation becomes more and more diffuse and homogeneous along the whole gauge length, as shown by the points that were drawn on the specimens to monitor their local elongation. This trend is continued and enhanced up to the blends containing 50% HOCP, for which the yield peak has completely disappeared. This is due to a further decrease of the overall iPP crystallinity and to a T_g value which is still lower than the testing temperature. This causes a homogeneous deformation, as shown in *Figure 5*, and a classical rubbery behaviour, as evidenced in *Figure 1*.

When the HOCP content is further increased to 60% the yield peak (*Figure 1*) and the neck formation (*Figure 5*) reappear but the curve has a different trend from those for HOCP contents less than 50%. The elongation at yield is, in fact, lower, the peak sharper and the stress at yield higher than that for the 50% blend. This effect is due to the T_g increase with the blend composition up to a value which is comparable with the testing temperature. Of course, the yield mechanism is somewhat different here from that of the other blends, where mainly a crystalline morphological transformation from a spherulitic structure to a fibrillar one is occurring and the amorphous regions are all of a rubbery consistency. Here most of the energy must be spent to overcome the frictional resistance in the amorphous zones of the sample which have entered the T_g range, and only a minor part is utilized to disrupt the residual crystallite spherulitic structure (here the total crystallinity is reduced to about 20%[13]).

Morphological analyses

Photographs of the surfaces etched by n-heptane for the different blend compositions are shown in *Figure 6*. Starting from pure iPP it is possible to note that the surface of the homopolymer is not attacked by the solvent. With increasing HOCP content some holes are obtained. However, up to 70% HOCP content the extracted HOCP seems to be too low with respect to the nominal content value. It is to be noted that a pure HOCP chip was easily dissolved in a few minutes in boiling n-heptane. A previous etching attempt had been made with boiling chloroform, but in this case an analogous result was obtained. In fact, a comparison of the morphology on

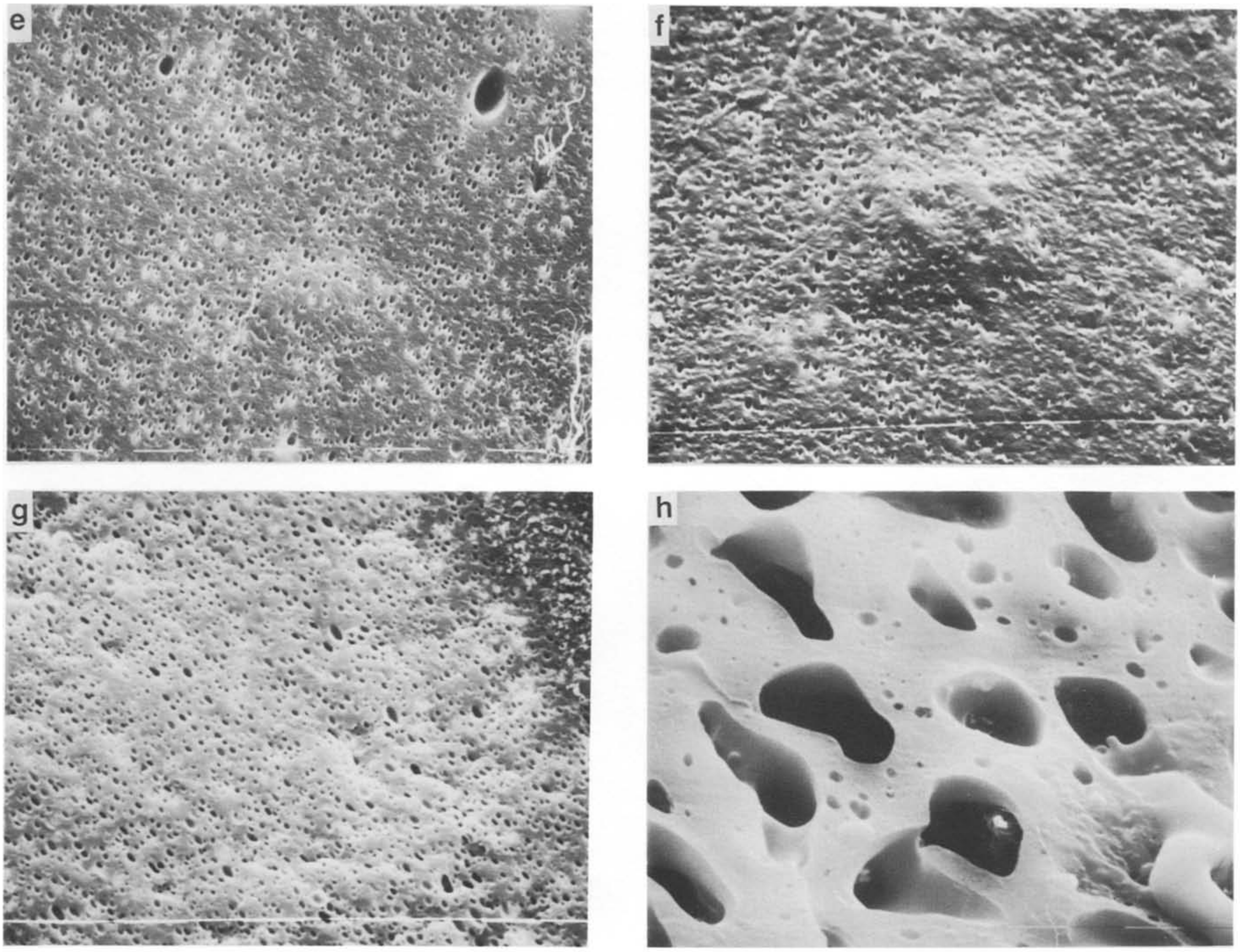

Figure 6 *continued* SEM micrographs (× 1250) of smoothed surfaces etched by n-heptane for the different blend compositions: (e) 50/50; (f) 40/60; (g) 30/70; (h) 20/80

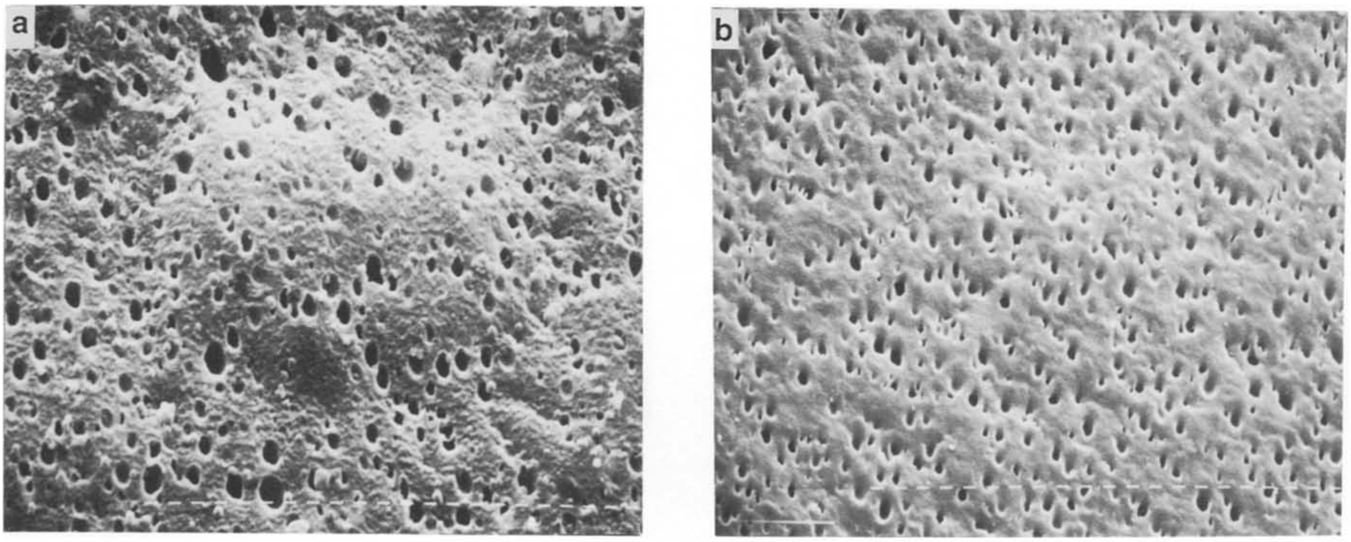

Figure 7 SEM micrographs (× 2500) of smoothed surfaces of the 50/50 blend etched by (a) n-heptane and (b) chloroform

the same blend (50/50) shows no significant differences for the two solvents (see *Figures 7a* and *7b*). Only at a very high HOCP content (*Figure 6h*) are the holes much larger, owing to the increased HOCP content. The change to n-heptane, having a higher boiling point (98°C) than chloroform (62°C), was made to overcome the difficulty of solvent penetration into the glassy regions, formed by a mixture of iPP and HOCP, but no significant results were obtained. Some tentative explanations are as follows.

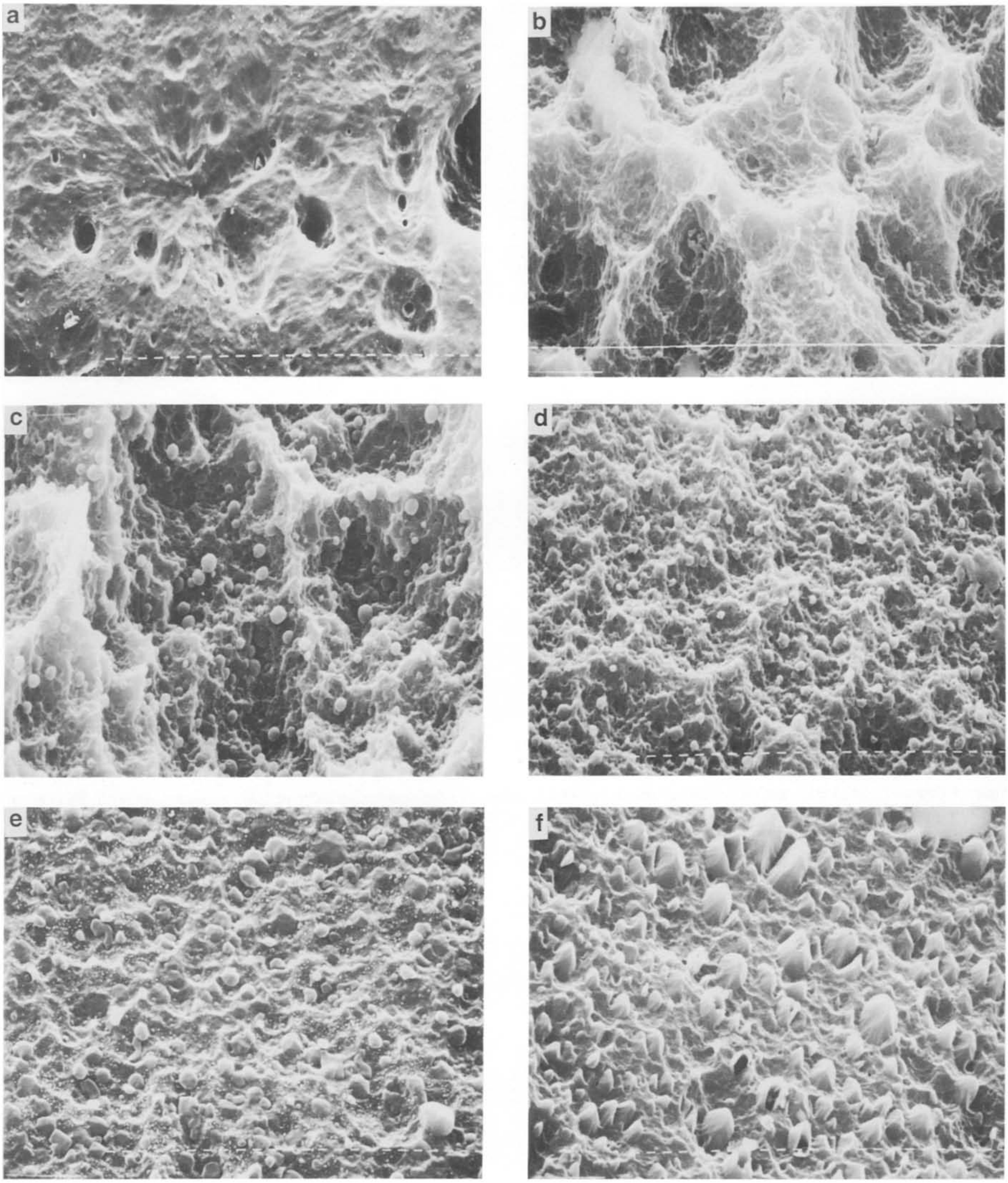

Figure 8 SEM micrographs (× 2500) of smoothed surfaces etched by the H_2SO_4/CrO_3 solution for the different blend compositions: (a) 100/0; (b) 80/20; (c) 70/30; (d) 50/50; (e) 40/60; (f) 30/70

(i) The easy dissolution of small, pure HOCP particles in a few minutes, mentioned above, occurred in a large amount of solvent and with very strong stirring. On the contrary, when the HOCP was intimately mixed with iPP and this mixture was tightly constrained between two crystalline lamellae, the HOCP extraction became rather difficult and even long etching times did not improve the situation.

(ii) As already mentioned[13], in the interlamellar regions, where the iPP/HOCP mixture is constrained, there is a concentration gradient. Therefore, since the maximum HOCP concentrations are in the middles of these regions, here the T_g is very close to the HOCP value (>100°C, as measured by a two-plate viscometer). Hence in these zones, which in other cases would be the most accessible to solvent penetration, both the boiling temperatures of the solvents used were somewhat insufficient to achieve efficient HOCP extraction.

Only at a very high HOCP content (80%) does the solvent penetration become a little more effective owing, perhaps, to a less tight iPP structure. However, the extraction is still very limited in comparison to the very large HOCP amount, showing that in this case also there is an iPP contribution to the system interconnection. This finding is in agreement with the mechanical stress–strain behaviour which shows the possibility of fibre making, even at the highest HOCP content.

A third etching agent was tried, namely the H_2SO_4/CrO_3 solution mentioned earlier. Since the solution is very aggressive towards the rubbery amorphous regions, irrespective of their chemical nature, the aim was to investigate the crystalline structure of iPP. Micrographs of the etched surfaces are shown in *Figure 8*. Starting with iPP, a small spherulite can be observed with some holes, but the surface does not appear to be strongly etched. The situation changes for the 80/20 blend where most of the surface has been destroyed, possibly leaving behind part of the supporting crystalline structure having removed most of the iPP/HOCP rubbery amorphous mixture. Analogous behaviour is observed for the 70/30 blend, which also shows some spherical particles. With increasing HOCP content the etching extent diminishes and the particles increase in size and tend to lose their spherical aspect. Probably these are iPP/HOCP domains that have been etched all around but become more and more difficult to oxidize since, also in this case, the etching temperature (80°C) still finds a glassy amorphous material with an increasing T_g.

CONCLUDING REMARKS

Morphological analyses and stress–strain behaviour have been extended to higher HOCP contents (above 50% by weight) and to higher temperatures (80°C and 100°C) than those detailed in previous papers[9–12]. The mechanical behaviour, at temperatures other than room temperature, shows that the iPP provides the internal system connection even at very high HOCP contents. This yields further evidence of the miscibility of the two components in the amorphous regions in all the investigated blends.

From the morphology it was possible to infer that the iPP keeps the HOCP in a tight structure. In fact, very good solvents for HOCP, like n-heptane and chloroform, were able to extract only a small portion of the HOCP even after long extraction times. This was probably due to the etching temperatures (62°C for chloroform and 98°C for n-heptane) being too low in comparison to the T_g of the mixture contained in the interlamellar regions.

A further attempt at etching the smoothed surfaces, made with a strong oxidizing agent, was able only partially to show the supporting crystalline structure. This also seemed to be due to the etching temperature being lower than the T_g of the mixture in the interlamellar gaps.

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