JOURNAL OF MATERIALS SCIENCE **24** (1989) 3235–3244

Mechanical and high speed fracture properties of polypropylene and hydrogenated poly(cyclopentadiene) blends

V. DI LIELLO, E. MARTUSCELLI, G. RAGOSTA
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del C.N.R, 80072 Arco Felice, Naples, Italy

P. BUZIO
FIAP, S.p.A., 22078 Turate, Como, Italy

Mechanical tensile tests and fracture mechanics analysis at high speed were carried out on specimens of isotactic polypropylene (PP)–hydrogenated poly(cyclopentadiene) (HPCP) blends obtained under different crystallization conditions. In addition a morphological investigation of the fractured surfaces by means of scanning electron microscopy was also performed. Improved low strain properties (modulus and yield stress) were found by the addition of HPCP to PP for both quenched and highly crystallized materials. This effect is enhanced when the quenched samples undergo a further heat treatment such as annealing. The fracture toughness parameters (G_c and K_c) decrease with increasing amounts of HPCP in the blend. The annealing improves the toughness of quenched samples enhancing G_c and K_c while it has no effect on samples crystallized at high temperature. All the above mechanical and fracture results were explained at the molecular level in terms of the interconnection existing in the material which depends on the crystallization conditions, annealing and blend composition.

1. Introduction

Easy processing, large applicability and relative low cost of isotactic polypropylene (PP), has in the past, stimulated an extensive amount of research especially to improve some unfavourable properties such as poor impact strength at low temperature or at high loading rate. This goal has been achieved by blending PP with suitable rubbers or by *in situ* polymerization of the rubber component. Therefore, many studies have been carried out on such blends with the main purpose of investigating how the composition and the mode and state of dispersion of the rubbery second phase affect the mechanical and/or the impact properties of PP [1–6].

Martuscelli *et al.* [7, 8] previously reported the results of an investigation concerning the study of the thermal and crystallization behaviour as well as the phase structure of the melt and in the solid state below T_c of isotactic (PP–hydrogenated polycyclopentadiene (HPCP) blends. It was found that (i) the spherulitic growth rate, the overall crystallization rate and the equilibrium melting temperature of PP were depressed following the addition of HPCP, (ii) there was a single composition-dependent glass transition temperature and, (iii) that the long spacing, that is the average distances between the barycentre of two PP adjacent crystalline lamellae, increases with the HPCP content in the blend.

From these and other findings it was possible to conclude that HPCP and PP are compatible in the melt. Furthermore in the solid state, that is below the crystallization temperature of PP, HPCP and uncrystallized molecules of PP form an homogeneous phase located mainly in the interlamellar regions [7, 8]. In this paper we have investigated the dependence of different heat treatments such as crystallization conditions and annealing on mechanical tensile properties and on high speed fracture toughness of the PP–HPCP blend. The aim of the research is to correlate the mechanical properties and the fracture parameters of such blends with the different microstructures and morphology obtained in order to provide useful information on the mechanisms through which the various structural parameters control the growth and propagation of cracks. For this purpose the high speed fracture data has been analysed using the approach of linear elastic fracture mechanics (LEFM) whose parameters as previously reported [9–10], are particularly suitable for monitoring morphological and structural changes in the material. Furthermore a fractographic analysis has been performed by means of scanning electron microscopy.

2. Experimental procedure

2.1. Material and blend preparation

Materials used in this study included a commercial isotactic polypropylene (PP), Moplen T305 produced by Montedison with a weight-average molecular weight (M_w) of 300 000 and an hydrogenated amorphous poly(cyclopentadiene) (HPCP), Escorer 5120 produced

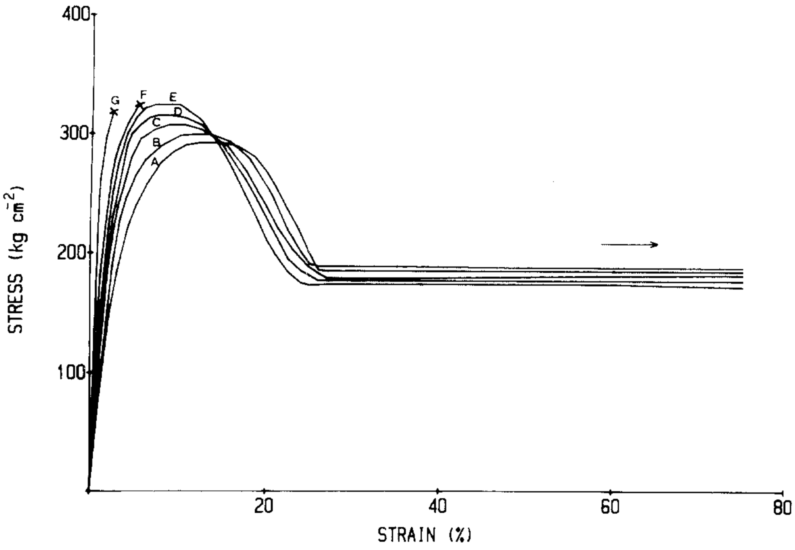

Figure 1 Typical stress–strain curves for quenched PP–HPCP blends at different HPCP percentages: A, 0%; B, 5%; C, 10%; D, 15%; E, 20%; F, 30%; G, 50%.

by Esso Chemical Co. with a M_w of 630 and a glassy transition temperature (T_g) of about 65° C. Binary PP–HPCP blends with weight ratios of 95 : 5, 90 : 10, 85 : 15, 80 : 20. 70 : 30 and 50 : 50 were obtained by melt mixing the polymers in a extruder at 200° C.

2.2. Specimen preparation

From the blended samples, 1.5 and 4.0 mm thick sheets were obtained by compression moulding in a heated press. The samples were heated at 200° C and kept for 10 min between the plates, without any applied pressure, allowing 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 crystallized as follows (i) quenched in water at room temperature, (ii) immersed in a thermostated bath and kept at 135° C for 5 h. Some of the samples thus crystallized were annealed in an oven at 140° C under vacuum for 24 h.

The 1.5 mm thick sheets were used to obtain dumbbell shaped specimens for mechanical tensile measurements whereas from 4.0 mm sheets rectangular specimens $60 \times 6.0 \times 4.0\,\mathrm{mm}^3$ were cut for performing Charpy impact tests. Prior to impact tests the specimens were notched as follows: first a blunt notch was produced using a machine with a V-shaped tool and then a sharp notch of 0.2 mm deep was made by a razor blade fixed to a micrometric apparatus. The final value of notch depth was measured after fracture by using an optical microscope.

2.3. Mechanical tensile tests

Stress–strain curves were obtained by an Instron machine (Model 1122) at room temperature and at a cross-head speed of $10\,\mathrm{mm\,min^{-1}}$. Moduli, stress and elongation at yield and at rupture were calculated from such curves on an average of about 10 specimens.

2.4. Charpy impact tests

Fracture tests were carried out on a Charpy Instrumented Pendulum (Ceast Autographic Pendulum MK2), at an impact speed of $1\,\mathrm{m\,sec^{-1}}$. Samples with a notch depth to width ratio of 0.3 and span test of 48 mm were fractured at room temperature. The relative curves of energy and load plotted against time or displacement were recorded.

2.5. Fracture toughness parameters

The impact data were analysed according to the concepts of linear elastic fracture mechanics (LEFM). From this approach two parameters can be determined which describe accurately the conditions for the onset of crack growth in the material [11]. One is the stress intensity factor, K, a parameter that determines the distribution of stress ahead of the crack tip. The fracture occurs when K achieves a critical value K_c given by

$$K_c = \sigma \gamma a^{1/2} \tag{1}$$

where σ is the nominal stress at the onset of crack propagation, a the initial crack length and γ is a calibration factor depending on the specimen geometry. For single cracked bent specimens, γ is given by Brown and Srawley [12].

The other parameter is the critical strain energy release rate, G_c, which represents the energy necessary to initiate the crack propagation. This can be expressed in terms of fracture energy by means of the equation

$$G_c = U/B\Phi W \tag{2}$$

where U is the fracture energy corrected from the kinetic energy contribution, B and W the thickness and width of the specimen, respectively, and Φ a calibration factor which depends on the length of crack and size of the sample. The values of Φ were taken by Plati and Williams [13].

2.5. Fractography analysis

Fracture surfaces of notched specimens were examined by using a scanning electron microscope (SEM), after coating the broken surfaces with a thin layer of gold–palladium alloy.

3. Results and discussion

3.1. Mechanical tensile properties

Nominal stress–strain curves for quenched samples of pure PP and PP–HPCP blends containing various amount of HPCP are reported in Fig. 1. For blend

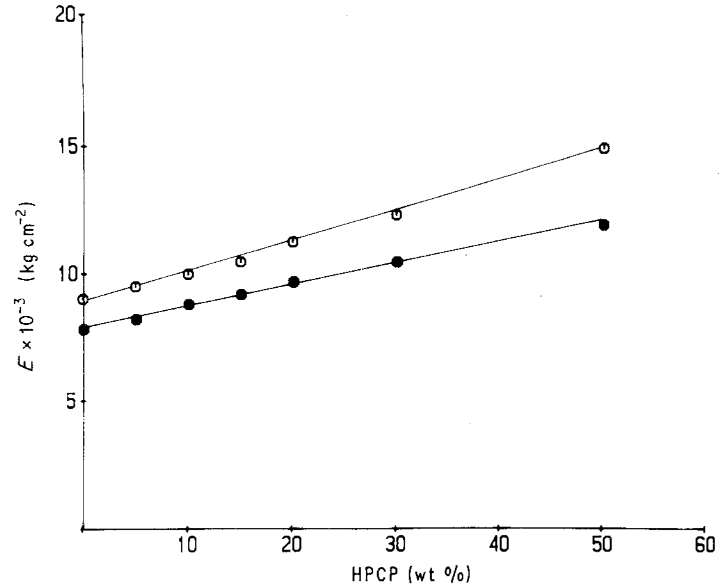

Figure 2 Young's modulus, E, as a function of HPCP content for PP–HPCP blends: ●, quenched samples; ○, quenched and annealed samples.

compositions up to 80:20 the deformation mode is very similar to the PP homopolymer. In fact, all the materials exhibit a sharp yielding point which is followed by necking, full cold-drawing and fibre rupture. A visual observation during the tensile testing reveals the formation of macroscopic shear bands on the surface of the specimens after the upper yield point. In contrast with these features blends with HPCP content equal or higher than 30% show a brittle behaviour with failure occurring before necking. In this case the presence of a little number of crack-like features (crazes) along the gauge section of the samples are visible.

The parameters calculated from the above mentioned stress–strain curves are plotted in Figs 2, 3 and 4 as a function of composition. The Young's modulus, E which is a low strain property of the material, increases linearly with increasing HPCP content. A similar trend is observed for the yield stress, σ_y. On the contrary the elongation at yield, ε_y, as well as the strength, σ_r and elongation at break, ε_r, relative to the blends with a ductile behaviour show a linear decrease enhancing the amount of HPCP. The ultimate parameters of blends with a brittle behaviour are not reported since they are not comparable with the previous ones, for which the rupture always occurred after fibre formation. From the results described above an interesting feature emerges. The tensile properties do not seem to show any abrupt change in the composition range investigated. The mechanical tensile behaviour of PP–HPCP blends can be explained if the findings of Martuscelli *et al.* [7, 8] are taken into consideration. In fact as the amount of the amorphous high-T_g component (HPCP) increases, the glass transition of the corresponding blends is shifted towards higher values (see Table I). Therefore, the ductile or the brittle mode of failure shown in Fig. 1 depends mainly if the T_g of the blend is above or below the testing temperature. For HPCP content no greater than 20%, the amorphous phase is still in a rubbery state and hence the material can be deformed plastically. Conversely at higher HPCP concentrations the amorphous phase becomes much less compliant to flow since the resulting T_g is close to the testing temperature and consequently the material shows brittle behaviour. However, the modification of PP by the HPCP addition in all the cases produces an improvement in the modulus and yield stress values. This

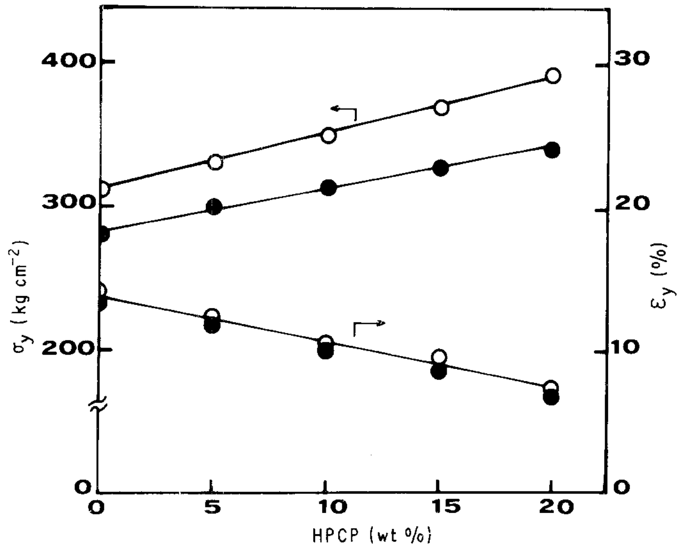

Figure 3 Yield strength, σ_y, and elongation at yield, ε_y, for PP–HPCP blends as a function of HPCP content. ●, quenched samples; ○, quenched and annealed samples.

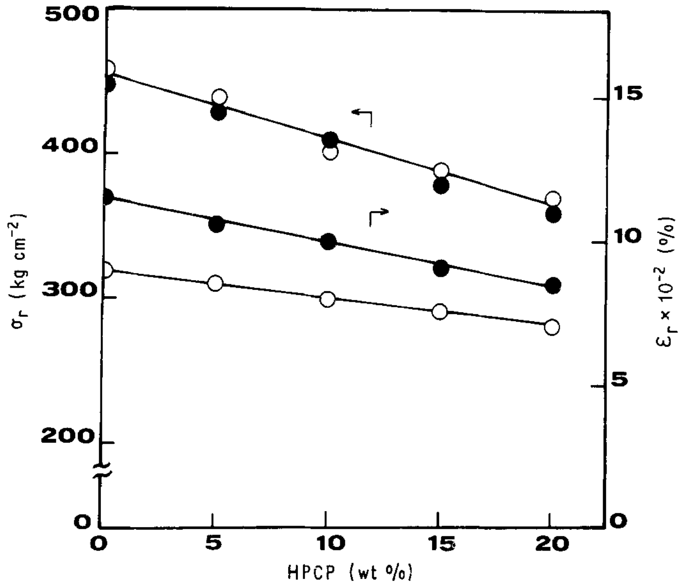

Figure 4 Ultimate strength, σ_r, and elongation at break, ε_r, for PP–HPCP blends as a function of HPCP content. ●, quenched samples; ○, quenched and annealed samples.

reinforcing effect as to be expected is followed by a worsening in the ultimate properties. However, what is interesting to note by the experimental data is that, at least for blends containing up to 20% of HPCP, the reduction in end-properties is very restricted so it may not reflect a serious material limitation especially when cold-drawing is a required part of manufacture.

The mechanical tensile behaviour of PP–HPCP blends after an annealing treatment is shown in Fig. 5. It can be seen that the annealing does not change the basic shape of the stress–strain curves. On the contrary it affects properties such as modulus, yield stress and elongation at break as reported in Figs 2, 3 and 4. A comparison of these parameters with those of unannealed samples shows that, the annealed materials exhibit greater E and σ_y values and lower ε_r values, while almost identical ε_y and σ_r values are detected for both the sets of samples. A plausible explanation of the above results arises from the fact that, during annealing a partial melting recrystallization process take place. Therefore, in addition to lamellar thickening, a rearrangement of uncrystallized material into the amorphous zones occurs. This may cause mainly for the blends variations in the composition of the amorphous phase which becomes more rich in HPCP, enhancing its glassiness. On the other hand the further crystallizations as well as the molecular rearrangements of PP chains into the interspherulitic and intraspherulitic zones induced by annealing, should also produce materials with a higher degree of interconnection with respect to the unannealed ones. Therefore, in the light of these considerations it appears that the observed better low strain properties such as E and σ_y of annealed samples, can be attributed to an increased stiffness (crystallinity and/or glassiness increase) and to an enhanced difficulty in deforming materials more interwoven because the level of tensile stress for a fixed strain is increased.

The influence of crystallization conditions on the characteristics of tensile deformation and mechanical properties of these materials is now presented. Stress–strain curves for pure PP and PP–HPCP blends crystallized at temperature of 135° C are shown in Fig. 6. All the samples fail in a brittle manner at low elongation and without yielding. This trend is completely opposite to that observed for specimens having the same composition but crystallized by quenching (see Fig. 1). The different behaviour arises from the different structures formed under the diverse

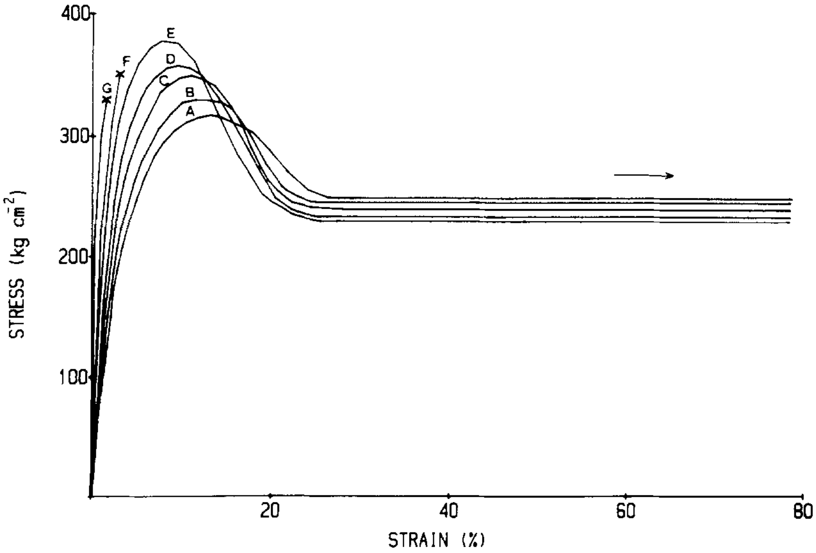

Figure 5 Typical stress–strain curves for quenched and annealed PP–HPCP blends at different HPCP percentages: A, %; B, 5%; C, 10%, D, 15%; E, 20%; F, 30%; G, 50%.

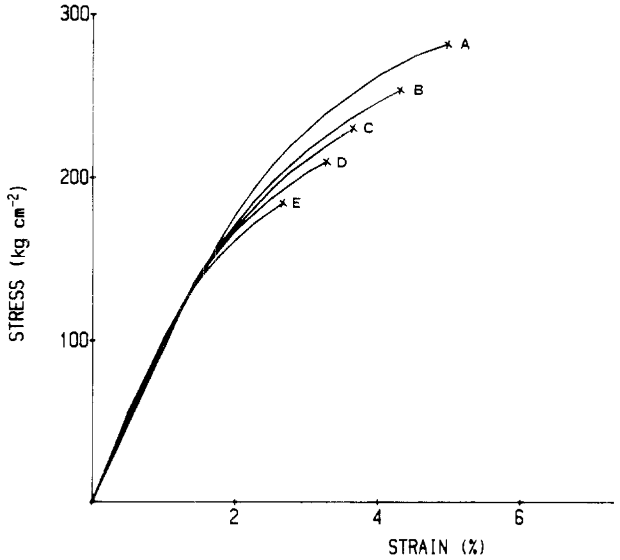

Figure 6 Typical stress–strain curves at different HPCP percentages for PP–HPCP blends crystallized at 135° C. A, 0%; B, 5%; C, 10%; D, 15%; E, 20%.

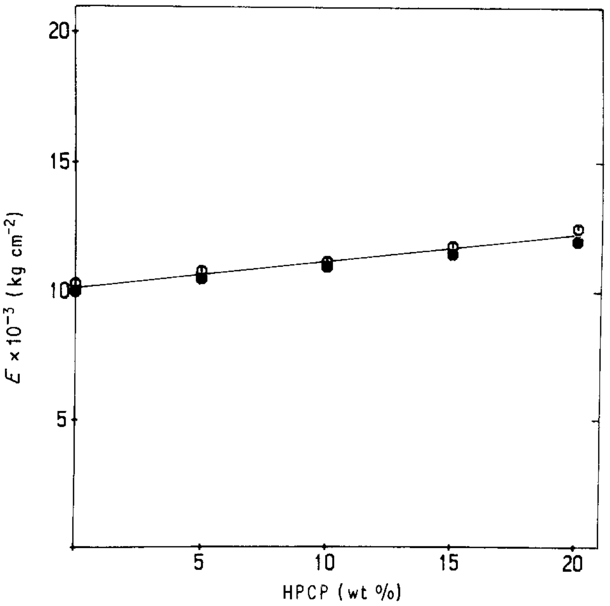

Figure 7 Young's modulus, E, as a function of HPCP content for PP–HPCP blends crystallized at 135° C. ●, unannealed samples; ○, annealed samples.

crystallization conditions and especially depends on the nature of the amorphous phase bridging the crystallites.

For quenched samples the crystallization process occurs very rapidly so that the chains can retain almost entirely the original entanglement network existing in the melt. Therefore, many non-crystallized molecules provide a strong connection between crystalline lamellae within spherulites but also between spherulites. These tie-chains act as local transducers of load among lamellae and spherulites so the overall material yields. As a consequence, the sample may exhibit the full spectrum of a ductile deformation. Conversely for specimens crystallized at high T_c, since the crystallization rate is very low, most of the very mobile molecules are able to disentangle from each other and to migrate towards the crystalline substrate. This creates a rather poor interconnection within the material because only very few tie-molecules are left to bridge the crystallites. Therefore, when an external load is applied the interspherulitic links are insufficient to carry the stress between spherulites and a brittle fracture at the spherulite boundaries without yielding is the net result. Furthermore it must be pointed out that the distribution and the arrangement of amorphous HPCP phase into the PP matrix can be greatly affected by the crystallization conditions. We should expect, as matter of fact, that the phase structure, following the crystallization of PP, may be strongly influenced by the rate of crystallization.

Returning to the mechanical properties results of the highly crystallized samples, as reported in Figs 7 and 8, a slight linear enhancement in the modulus followed by a lowering in end-properties is observed with increasing HPCP content. Such behaviour can be explained according to the above considerations. In fact, with respect to the modulus, the presence of amorphous glassy material (HPCP) likely in the interlamellar regions [7, 8] should affect the stiffness of the crystal-amorphous layers. Therefore, the reason for the increasing modulus with HPCP content may be related to an increased stiffness of the amorphous intervening layers. Instead, for the lowering in the ultimate properties, the controlling factor most probably is a reduction in the number of tie-chains that connect adjacent spherulites. In fact, since a tensile force between spherulites can be transferred only by

TABLE I Glassy transition temperature T_g, by differential scanning calorimetry measurements of PP, HPCP and their blends

Blend composition PP–HPCP (wt %)	T_g (° C)
100:0	−14
90:10	−8
80:20	−3
70:30	+5
50:50	+19
20:80	+45
0:100	+65

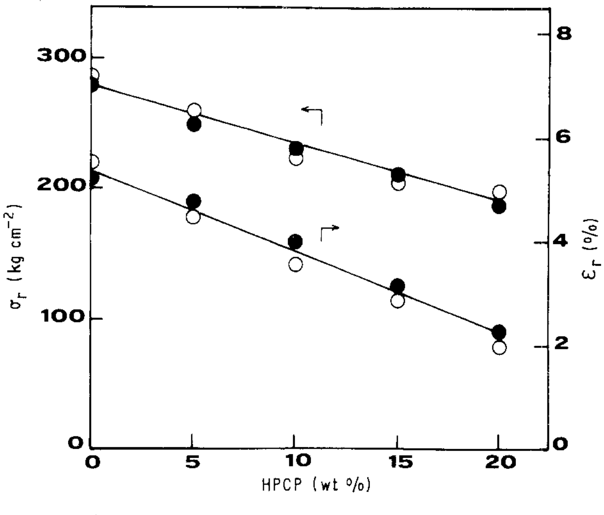

Figure 8 Ultimate strength, σ_r, and elongation at break, ε_r, as a function of HPCP content for PP–HPCP blends crystallized at 135° C. ●, unannealed samples; ○, annealed samples.

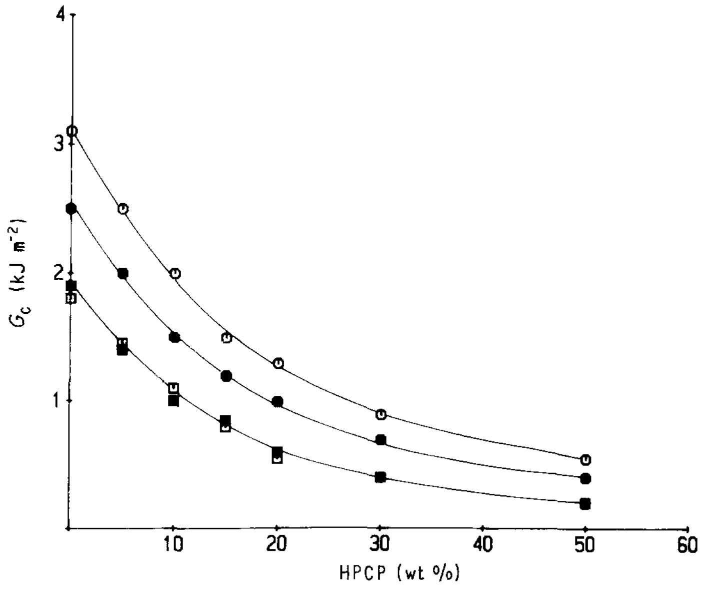

Figure 9 Critical strain energy release rate, G_c, as a function of HPCP content for PP–HPCP blends: ●, quenched samples; ○, quenched and annealed samples, □, samples crystallized at 135° C; ■, samples crystallized at 135° C and annealed.

tie-chains, if the density of tie-chains decreases with enhancing HPCP, the load becomes concentrated at increasingly fewer sites, producing larger stress concentrations. Thus a more brittle fracture at lower stress levels occurs.

Finally as shown in Figs 7 and 8 for the blends crystallized at high T_c, the annealing has little or no effect on the mechanical properties. This can be attributed to the fact that the samples are kept at the crystallization temperature (135° C) for a period of time that is beyond the necessary crystallization times. Therefore, after the complete crystallization the samples are annealed for several hours at a temperature which is very close to the annealing temperature. This leads to a very stable material and hence no further substantial structural changes can be obtained by successive heat treatments.

3.2. Impact fracture toughness and fractographic analysis

The critical strain energy release rate, G_c, and the critical stress intensity factor, K_c, calculated according to Equations 1 and 2 are reported as a function of blend composition in Figs 9 and 10 respectively. From the two kinds of plots it is possible to make the following observations. For all the thermal histories examined G_c and K_c follow a quite similar trend with composition. Namely G_c and K_c decrease with increasing the amount of HPCP in the blend. However the parameter G_c seems to be more sensitive to the HPCP addition. The quenched samples exhibit, in all the range of composition investigated, G_c and K_c values much higher than those of the samples crystallized at 135° C. The annealing improves the toughness of quenched samples enhancing G_c and K_c while it has no affect on the samples crystallized at 135° C.

On the basis of the above results it could be deduced that, different morphologies obtained by imposing diverse heat treatments as well as the amount of HPCP, opposed various resistances to the crack propagation. Therefore, it seemed promising to investigate how morphological characteristics and composition influence the formation and growth of cracks in the material in order to find a correlation with the macroscopic fracture toughness parameters. For this purpose a fractographic analysis was made by means of scanning electron microscopy.

Electron micrographs of fractured surfaces taken

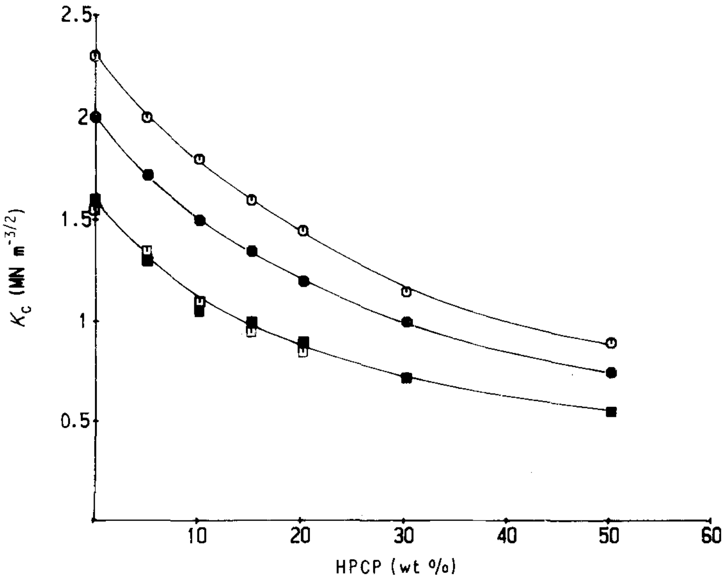

Figure 10 Critical stress intensity factor, K_c, as a function of HPCP content for PP–HPCP blends: ●, quenched samples; ○, quenched and annealed samples; □, samples crystallized at 135° C; ■, samples crystallized at 135° C and annealed.

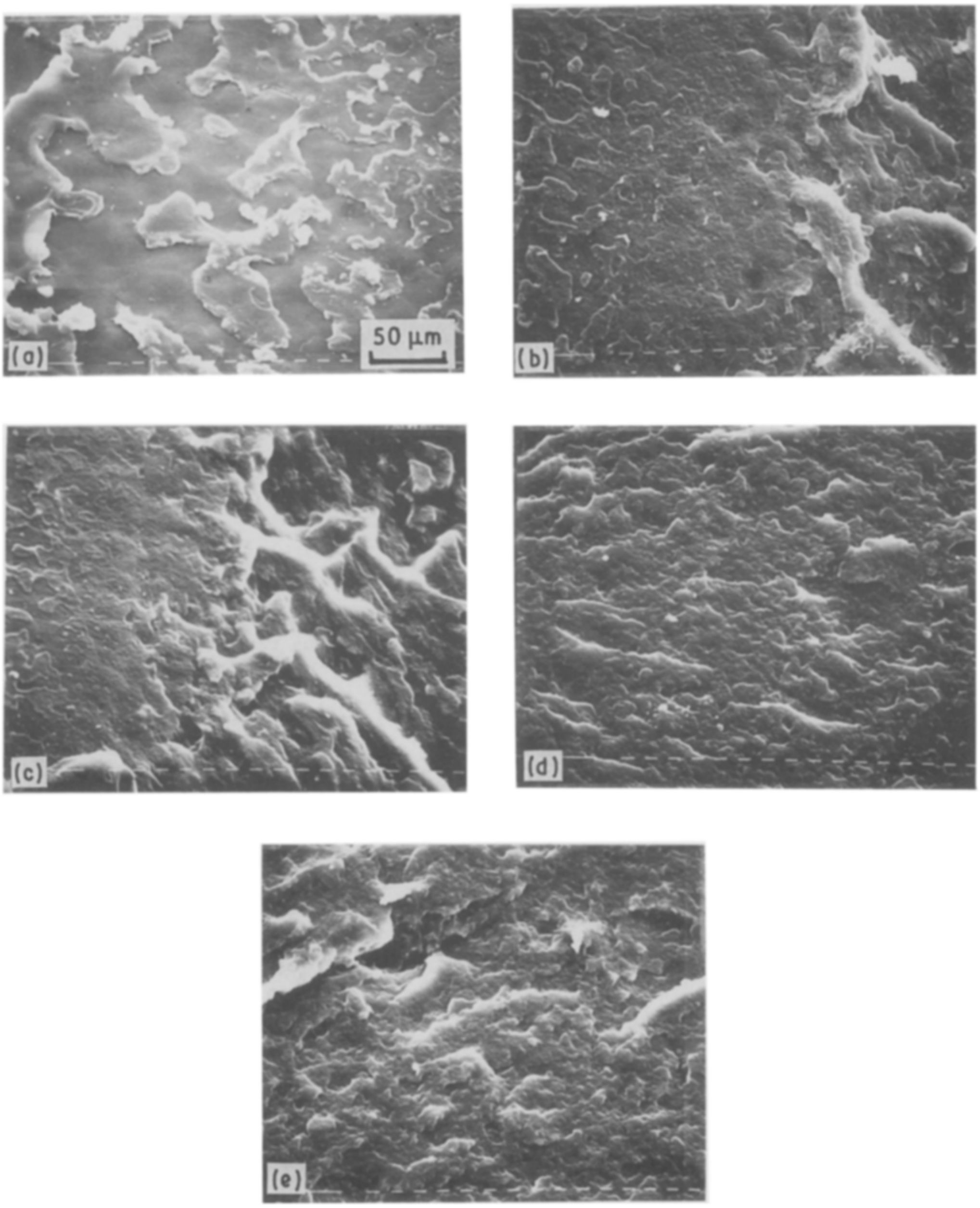

Figure 11 Scanning electron micrographs of fractured surfaces of quenched PP–HPCP blends at different HPCP percentage: (a) 0%; (b) 10%; (c) 20%: (d) 30%; (e) 50%. (The notch tip is situated on the left-hand side of micrographs.)

near the notch tip of quenched samples are shown in Fig. 11. As can be seen for pure PP a very large region plastically deformed with morphological features similar to the mirror area of the amorphous glassy polymer is visible [14, 15]. When HPCP is added, the area of the region decreases markedly (see left hand side of Figs 11b and c) and at high HPCP content the fracture surface becomes almost completely brittle (see Figs 11d and e). The presence of "patch" patterns or "mackerel" on the fracture surface of PP and blends with low HPCP concentrations suggests, according to previous work [10], that the onset of crack propagation is preceded by crazing. The formation and growth of such crazes can be well explained in terms of the tie-molecular concept. In fact, as already mentioned, the quenching treatment provides a fine spherulitic microstructure with a high level of connectivity in both crystallites and spherulites regions. This leads to a material which is able to bear the stress concentrations and hence crazes may develop within interspherulitic and intraspherulitic zones. Furthermore if the degree of interconnection in both areas is sufficiently high, as in the case of pure PP, the crazes formed in one of these zones still have enough strength to cause further crazing in their neighbourhood before they break down. Therefore, massive crazing can be formed in front of the crack tip which can absorb a large amount of energy before the final fracture occurs. This process for the PP–HPCP blends is reduced as a result of the fact that the interspherulitic and intraspherulitic link density decreases by enhancing the amount of HPCP. In addition a worsening in the quality of the interlayered amorphous material where crazes nucleation first take place must be accounted for. Thus as the HPCP content increases, the tendency for craze formation and their stability are greatly decreased and hence lower fracture toughness values are achieved.

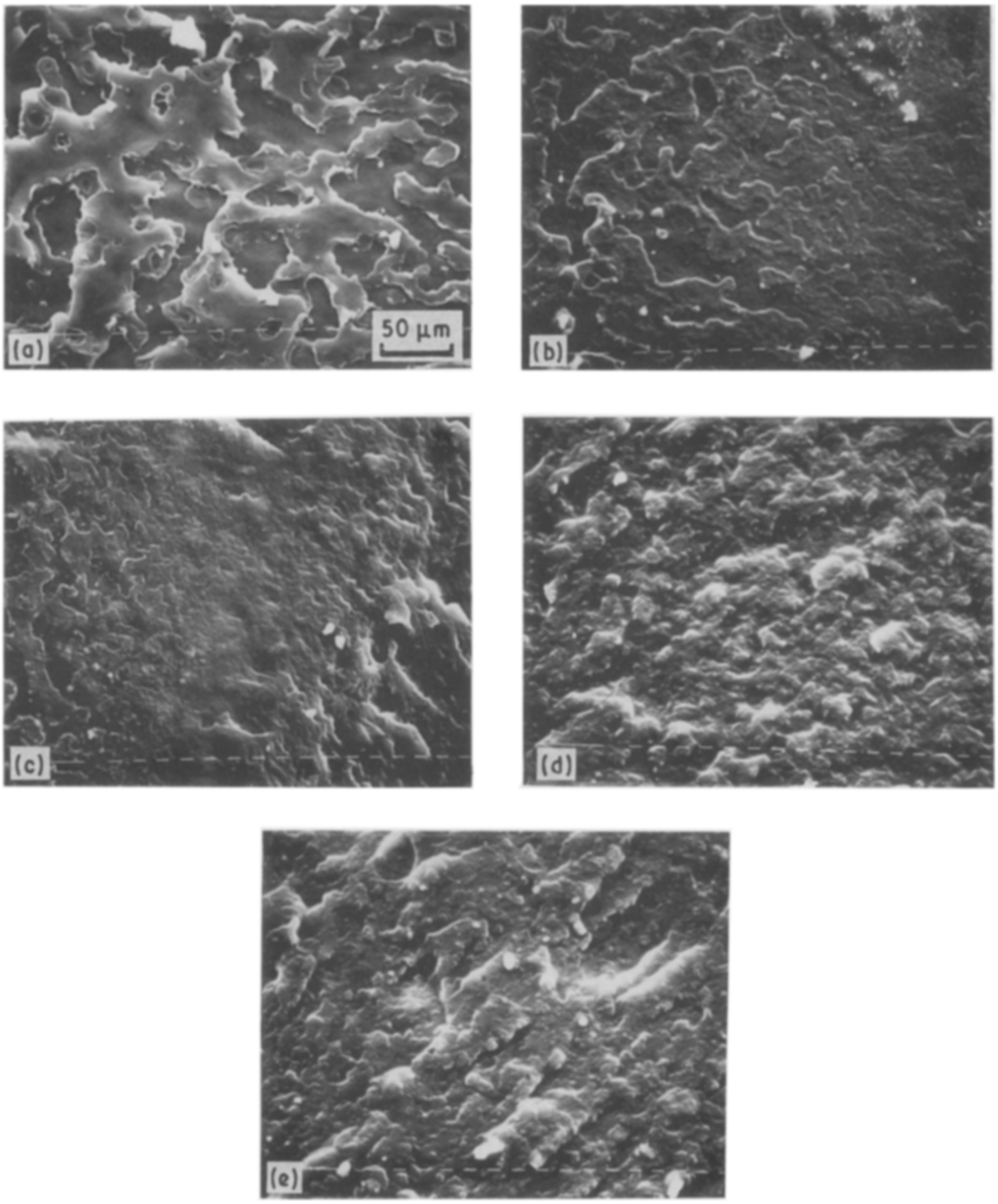

Figure 12 Scanning electron micrographs of fractured surfaces of quenched and annealed PP–HPCP blends at different HPCP percentages: (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e) 50%. (The notch tip is situated on the left-hand side of micrographs.)

Further evidence that the fracture process is essentially controlled by the interconnection within the material which in turn determines the craze structure, arises from the annealed and highly crystallized samples. Fig. 12 shows the fracture surfaces of annealed fine spherulitic materials. It can be seen that the area of region plastically deformed with "patch" patterns is larger than that of the annealed specimen (compare Fig. 11 with Fig. 12). This is due to the fact that the annealing renders the material more interconnected enhancing both interspherulitic and intraspherulitic links and the consequent greater craze stability and greater resistance to the crack propagation in both regions can be obtained. This leads to the observed better impact toughness values.

For samples crystallized at high temperature the SEM micrographs reported in Fig. 13 reveal for PP a plastic deformation in the form of crazes confined preferentially in the boundary zones, whereas most of the coarse spherulites are nearly undeformed. The amount of such a deformation tends to decrease as HPCP is added (see Figs 13b and c). It also appears that at concentrations of HPCP higher than 20% (Figs 13d and c), the morphology of the corresponding fracture surfaces results quite differently assuming a more brittle appearance with little or no evidence of undeformed spherulites. These features indicate that, in such materials the crack propagates essentially by cleavage of both interspherulitic and intraspherulitic regions.

All the above findings are related to the fact that, in this case, due to a very slow crystallization process, the spherulite boundaries are much less crack resistant than the inner zones because of the very few interspherulitic links. On this basis for pure PP, crazes may develop essentially at the interfaces between coarse spherulites, resulting in a boundary fracture, with a lower toughness value than that of the quenched sample. The resistance to this type of failure is further reduced when HPCP is added. The addition of HPCP

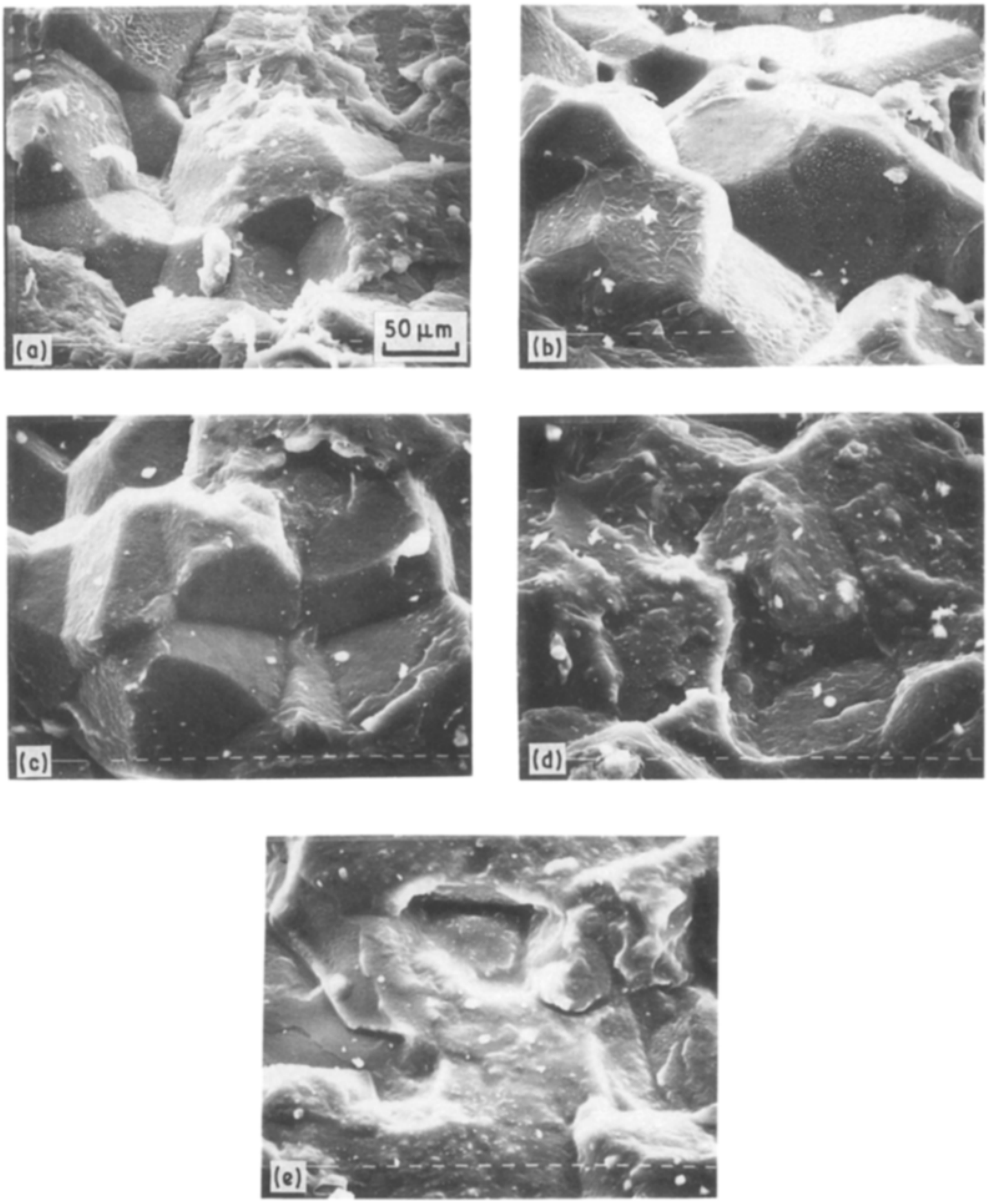

Figure 13 Scanning electron micrographs of fractured surfaces at different HPCP percentages for PP–HPCP blends crystallized at 135° C: (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e) 50%. (The notch tip is situated on the left-hand side of micrographs.)

enhances the weakness of the spherulite boundaries (the interspherulitic link density deceases) and at the same time it increases the stiffness of the interior zone of the spherulites. Both these effects make the growth of cracks between and also within spherulitic regions easier, leading to a complete interspherulitic fracture for blends containing a low amount of HPCP (no greater than 20%) and to a fracture of interspherulitic and intraspherulitic type for blends with high HPCP content.

4. Concluding remarks

In this paper it has been shown that crystallization conditions, thermal treatments and composition can strongly influence the structure and morphology of PP–HPCP blends and consequently their mechanical tensile behaviour as well as the fracture impact toughness. In particular from the results achieved the following conclusion can be drawn.

The tensile mechanical properties seem to confirm the existence of a high degree of PP–HPCP compatibility in the amorphous state. In fact, the modulus and the other tensile parameters change linearly with composition and are more or less proportional to the ratio of components as expected from a compatible blend.

The presence of HPCP enhances the tensile brittleness of both quenched and highly crystallized materials, and it improves the low strain properties like modulus and yield stress. This last effect is enhanced when the quenched samples undergo a further heat treatment such as annealing.

The fracture toughness parameters (G_c and K_c) which represent the resistence of the material prior to the crack propagation, decrease with increasing the amount of HPCP. The annealing enhances the fracture toughness of quenched samples whereas it has no effect on samples crystallized at high temperature.

For a given crystallization condition and thermal treatment the parameters G_c and K_c are enhanced with increasing tendency to craze formation which is the dominant mechanism of deformation in such materials.

Finally at molecular level the above mechanical and fracture results may be explained in terms of the interconnection existing in the material between lamellae, amorphous regions and spherulites.

Acknowledgement

This work has been partially supported by C.N.R. "Progetto Finalizzato Chimica Fime II".

References

1. E. MARTUSCELLI, C. SILVESTRE and L. BIANCHI, *Polymer* **24** (1983) 1458.
2. L. BIANCHI, S. CIMMINO, A. FORTE, R. GRECO, E. MARTUSCELLI, F. RIVA and C. SILVESTRE, *J. Mater. Sci.* **20** (1985) 895.
3. J. KARGER-KOCSIS, A. KALLO, A. SZAFNER, G. BODOR and Z. SENGAI, *Polymer* **20** (1979) 37.
4. F. C. STEHLING, S. C. HUFF, G. SPEED and J. WISSLER, *Appl. Polym. Sci.* **26** (1981) 2693.
5. F. COPPOLA, R. GRECO, E. MARTUSCELLI, H. W. KAMMER and C. KUMMERLOWE, *Polymer* **28** (1987) 47.
6. R. GRECO, C. MANCARELLA, E. MARTUSCELLI, G. RAGOSTA and JINGHUA YIN, *Polymer* **28** (1987) 1929.
7. E. MARTUSCELLI, C. SILVESTRE, M. CANETTI, C. De LALLA, A. BONFANTI and A. SEVES, *Polymer* in press.
8. E. MARTUSCELLI, M. CANETTI and A. SEVES, Submitted to *Polymer*.
9. F. COPPOLA, R. GRECO and G. RAGOSTA, *J. Mater. Sci.* **21** (1986) 1775.
10. R. GRECO and G. RAGOSTA, *J. Mater. Sci.* **23** (1988) 4171.
11. A. J. KINLOCH and R. J. YOUNG, "Fracture behaviour of polymers" (Applied Science, London, 1983).
12. W. F. BROWN and J. SRAWLEY, ASTM STP, 410 (American Society for Testing and Materials, Philadelphia, 1966) p. 13.
13. E. PLATI and J. G. WILLIAMS, *Polym. Eng. Sci.* **15** (1975) 470.
14. R. GRECO and G. RAGOSTA, *Plast. Rubber Proc. Appl.* 7 (1987) 163.
15. J. MURRAY and D. HULL, *J. Polym. Sci., Part 2,* **8** (1970) 583.

Received 7 July
and accepted 18 November 1988