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High-rate fracture toughness of polypropylene-based, hybrid, particulate composites

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The high-rate fracture behaviour of two hybrid, particulate, composite systems consisting of a polypropylene matrix, containing both inclusions of ethylene–propylene rubber and particles of talc or calcium carbonate, was investigated by varying the formulation of the dispersed phase. Depending on the behaviour of the different materials, linear elastic or elasto-plastic fracture mechanics was applied to determine their fracture resistance. It was found that, for certain compositions, the hybridization of the secondary phase produces synergistic effects with respect to the corresponding binary systems.

1. Introduction

An important recent development in polymeric materials concerns the preparation of hybrid particulate composites obtained by incorporating both rubbery and inorganic particles into a polymeric matrix. By the correct addition of both types of secondary phase it is possible to obtain, with a given matrix, a variety of materials with targeted and optimal performances for the specific requirements of different applications.

Basically, the addition of the elastomeric phase enhances the material toughness, whereas the addition of inorganic fillers increases the material stiffness and, moreover, can offer other advantages such as a reduction in cost, a good surface appearance and improved processing behaviour. However, it has been found that the incorporation of rigid fillers into brittle matrices can also produce a significant toughening effect [1–11].

The toughening mechanisms activated by the rubber particles have been envisaged in multiple crazing and/or shear-yielding deformations, as well as in rubber-particle cavitation, depending on the system considered (see for example [12–17]), whereas, in the case of rigid particulate fillers in brittle matrices, the toughening effect has been mainly ascribed to a crack-pinning mechanism [4]. In some hybrid particulate composites, under some circumstances, synergism can be obtained with several toughening mechanisms operating simultaneously and the composites have impressive mechanical properties [18–20].

In the present work, the high-rate fracture behaviour of two particulate hybrid systems consisting of a polypropylene (PP) matrix filled with particles of ethylene-co-propylene rubber (EPR) and of talc or calcium carbonate ($CaCO_3$) were studied for different ratios. This research was aimed at identifying the formulations that give optimal impact-fracture resistance without impairing the material stiffness. Depending on the fracture behaviour of the different composites examined, linear–elastic or elasto-plastic fracture mechanics methods were applied in high-rate tests, although conventional characterization of the impact-fracture behaviour of the materials was also performed.

2. Experimental procedure

The materials examined can be classified as follows: (a) base system, PP homopolymer; (b) binary systems, PP modified with EPR, and PP with the addition of talc or $CaCO_3$; and (c) ternary systems, PP with the addition of both EPR and talc, or $CaCO_3$. All the heterophasic materials were obtained by mechanical blending of the components.

The volume fraction of the dispersed phases was varied up to 0.18 for the inorganic fillers, whereas, it was varied up to 0.36 and 0.50 for the rubbery inclusions in the binary and ternary systems, respectively.

The formulations considered are shown in the ternary diagram in Fig. 1, with talc as the inorganic filler. Roughly the same formulations were considered for the case of $CaCO_3$ rigid inclusions.

The values of some main physical properties of these materials are given in Table I.

All the materials were supplied by Himont Italia SpA (Ferrara (I)) in the form of injection-moulded, 3.5 mm thick, dumbell specimens [21], from which SE(B) specimens with thickness $B = 3.5$ mm, width $W = 12.7$ mm and span $S = 50$ mm, for fracture tests were cut out. Single-edged sharp notches were made in the samples by sawing with a razor blade, which had a tip of about 15 μm radius, to a depth of about 6.4 mm (the notch-depth-to-specimen-width ratio was approximately $a/W = 0.5$).

High-rate fracture tests were performed by an instrumented impact pendulum made by CEAST SpA

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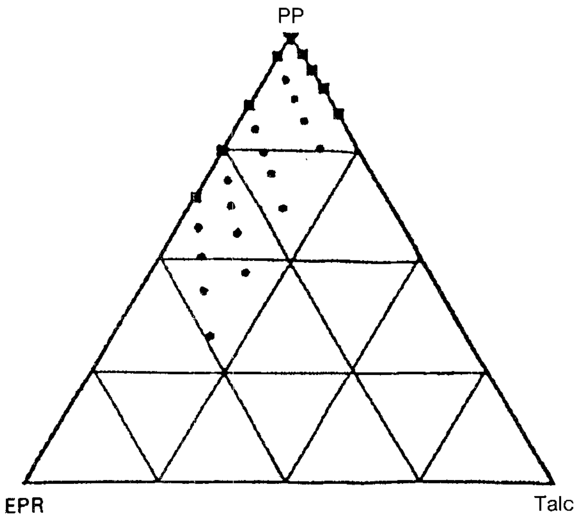

Figure 1 Compositions of the hybrid particulate composite systems consisting of PP–EPR talc.

TABLE I The main physical characteristics of the component materials

Characteristics	PP	EPR	Talc	$CaCO_3$
Density (kg m^{-3})	910	870	2720	2780
Particle size (μm)	–	0.1–2	2–10	0.5–12
Aspect ratio	–	~ 1	~ 12	~ 1

(Turin (I)), which enabled a force versus time curve to be recorded during the test. The data could then be processed in order to obtain other parameters, such as the energy, the displacement and the velocity, as a function of time.

Depending on the fracture behaviour of the material examined, linear–elastic or elasto-plastic fracture-mechanics tests were carried out to determine the fracture resistance (G_{Ic} or J_{Ic}, respectively), according to the respective ASTM standards [22, 23]. In the following, the fracture resistance is denoted by G_{Id} or by J_{Id} to indicate the dynamic-fracture resistance since the tests were performed at high-rate, although any possible dynamic effects have been ignored in the analysis of the results.

J-testing was performed by using a multispecimen technique [23] in which the tests were stopped at different degrees of displacement. A steel screw, connected to the frame of the instrument by means of a rigid steel plate, placed close to the anvils of the specimens, enabled movement backwards and forwards of a stopper, very precisely. Thus, by suitably adjusting the position of this stopper, it was possible to arrest the hammer of the pendulum at different displacements of the specimens. Compared with other procedures [24–26], this device has the advantage of avoiding direct strokes of the tup against the stopper, which could damage the transducers inside the tup itself.

As an example, Fig. 2 gives plots of force and energy versus time, for a test stopped at a given displacement of the sample. The time-to-arrest of the striker is clearly detected by the onset of wide-amplitude oscillations due to the vibrations induced in the transducers when the striker is stopped.

All the fracture tests were performed at room temperature at an impact speed of about 1.8 m s^{-1}.

Tensile tests were also carried out using an Instron machine at room temperature and at a cross-head rate of 10 mm min^{-1}, in order to measure the Young's modulus and the yield stress of the materials. The value of the yield stress at the high rate, when needed to draw the blunting line according to the J-testing procedure [23], was determined by extrapolating the yield-stress data obtained at low rates between 10^{-2} and 10^{3} mm min^{-1}.

3. Results and discussion

For the three binary systems considered, the values of the Young's modulus, E, are shown in Fig. 3 as a function of the volume percentage of the dispersed phase. As expected, the Young's modulus increases or

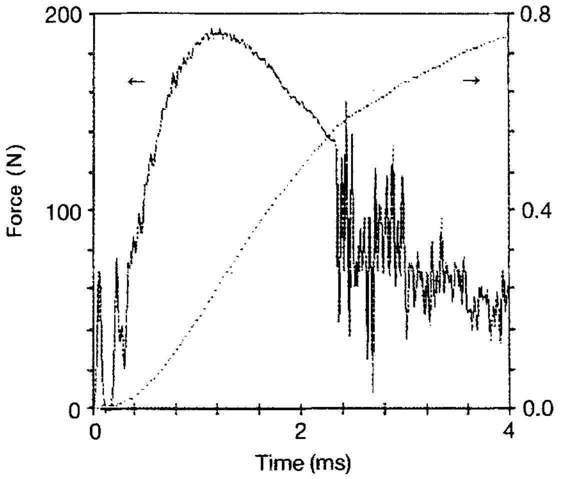

Figure 2 A typical force versus time curve for a ductile sample during an impact test which was stopped at a given specimen displacement.

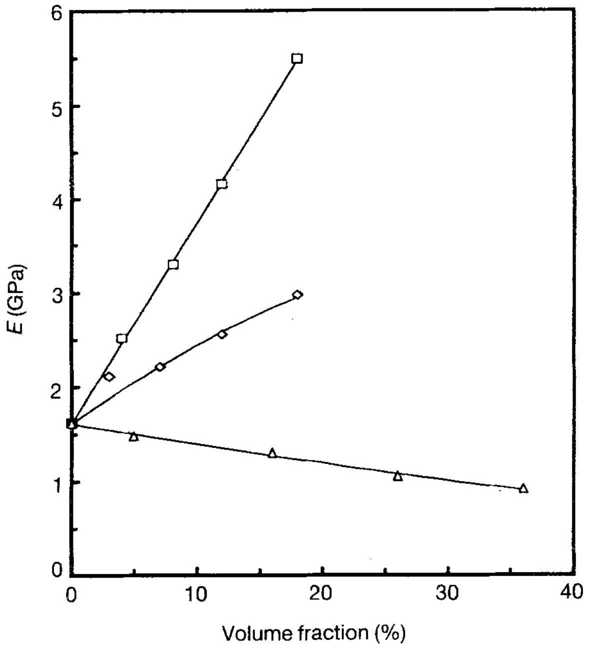

Figure 3 Tensile elastic modulus of the binary systems, at room temperature and at a displacement rate of 10 mm min^{-1}, as a function of the dispersed phase: (□) talc, (◇) $CaCO_3$ and (△) EPR.

decreases monotonically with increases in the content of the secondary phase, depending on whether it is rigid or soft. However, the addition of talc appears to be more effective than addition of calcium carbonate in improving the material stiffness. For instance, at 10 vol % of filler, the increase of the elastic modulus of the composite, compared with that of pure PP, is about 34 and 58% for calcium carbonate and talc, respectively. This effect can be attributed mainly to the stiffness of talc (~ 170 GPa) being higher than that of $CaCO_3$ (~ 35 GPa).

Fig. 4a and b show, for the ternary systems, the behaviour of the Young's modulus, E_c, normalized with respect to the Young's modulus of the PP matrix, E_m, as a function of the rubber volume percentage with different contents of talc and $CaCO_3$ respectively. In both cases, whatever the rigid filler content, the addition of the elastomeric phase causes the elastic modulus to decrease. Moreover, the greater effectiveness of talc compared with $CaCO_3$ in improving the material stiffness is still evident in the hybrid systems.

For the binary systems, the values of the yield stress, σ_y, are given, as a function of the volume percentage of the secondary phase, in Fig. 5, which shows that the addition of EPR, as well as of $CaCO_3$, to PP produces a monotonic decrease in the yield stress, whereas the latter increases slightly when talc is added to a level that appears to be independent of the talc content, at least within the range of talc contents considered. This effect was also observed by other authors [27] and has been attributed to the different shape ratio between the particles of $CaCO_3$ and talc. The former are almost spherical, whereas the latter are lamellar in shape and, in our samples, were found to be oriented along the drawing direction.

For the ternary systems, the values of the yield stress, σ_{yc}, normalized with respect to the value of the yield stress of the PP matrix, σ_{ym}, are given in Fig. 6a and b as a function of the percentage volume of the elastomeric phase for different contents of talc and $CaCO_3$, respectively. These results show that σ_{yc} decreases monotonically with the increase in rubber content for both types of heterophasic system considered. In addition, at a fixed rubber content, σ_{yc} appears to be practically unaffected by the presence of talc, whereas it is clearly affected by the $CaCO_3$ fraction up to about 30 vol % rubber.

The results for the high-rate fracture resistance, G_{Id}, for the binary systems containing rigid fillers are plotted in Fig. 7 against the percentage volume of the

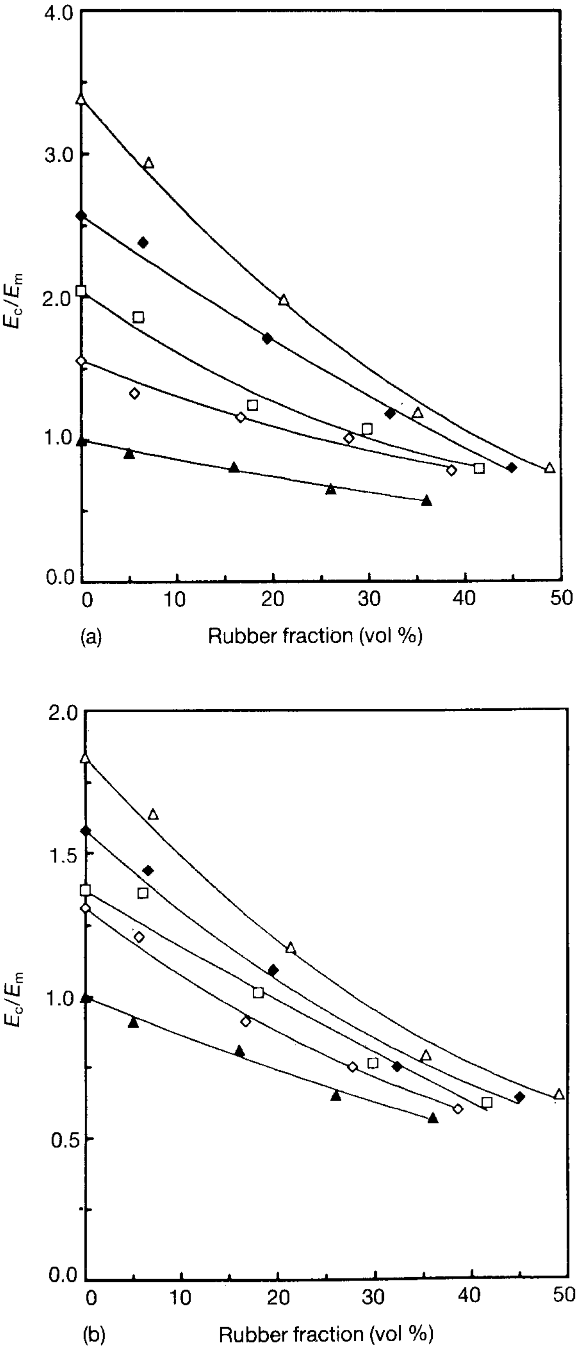

Figure 4 Tensile elastic modulus of the ternary systems, normalized with respect to that of the PP matrix, at room temperature and at a displacement rate of 10 mm min^{-1}, as a function of the rubber content with rigid inclusions (▲) 0, (◇) 4, (□) 8, (◆) 12 and (△) 18 vol % of: (a) talc and (b) $CaCO_3$.

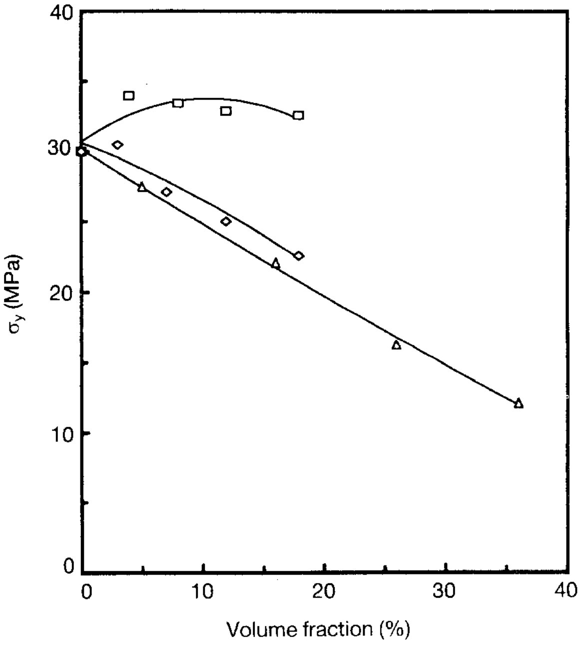

Figure 5 Tensile yield stress of the binary systems, at room temperature and at a displacement rate of 10 mm min^{-1}, as a function of the dispersed phase: (□) talc, (◇) $CaCO_3$ and (△) EPR.

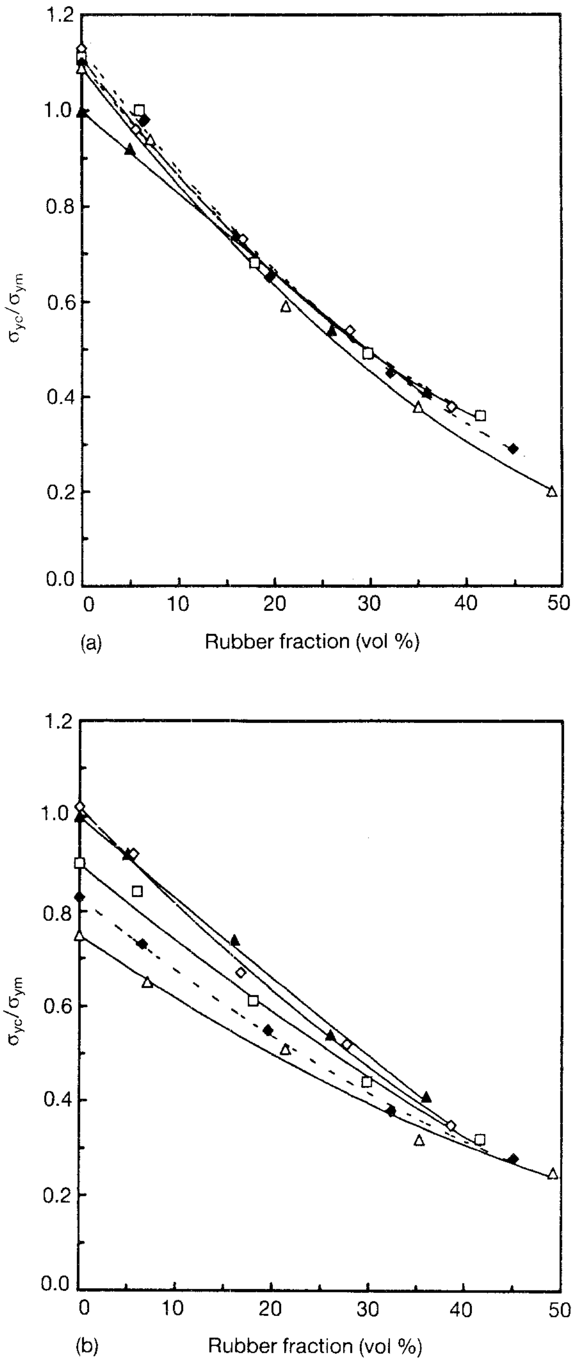

Figure 6 Tensile yield stress of the ternary systems, normalized with respect to that of the PP matrix, at room temperature and at a displacement rate of 10 mm min^{-1}, as a function of rubber content with rigid inclusions (▲) 0, (◇) 4, (□) 8, (◆) 12 and (△) 18 vol % of: (a) talc and (b) $CaCO_3$.

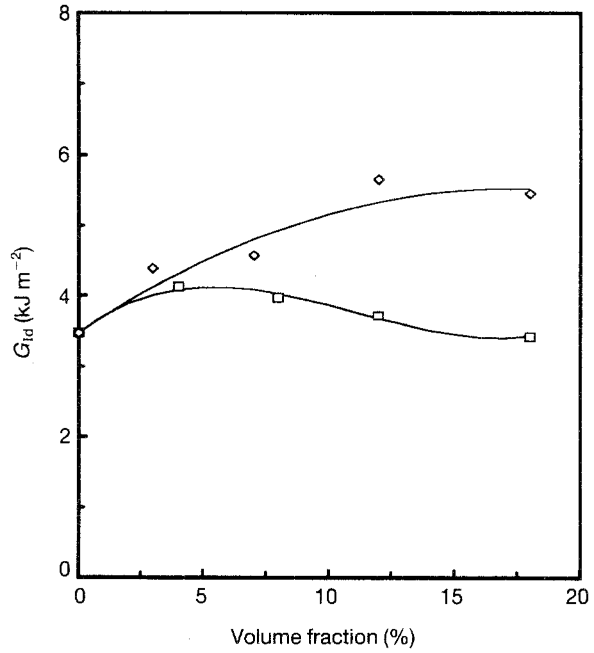

Figure 7 High-rate fracture resistance, G_{Id}, of the systems containing rigid inclusions as a function of the volume fraction of the filler: (□) talc and (◇) $CaCO_3$.

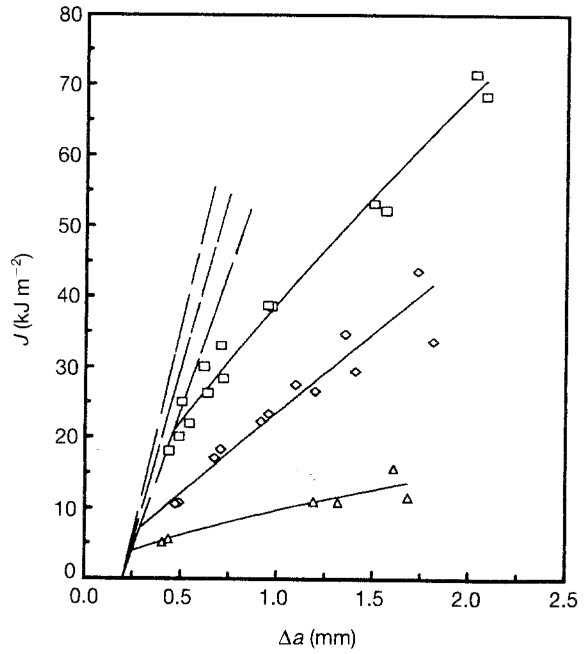

Figure 8 (——) High-rate J_R -curves of samples of rubber-modified PP with different rubber contents: (△) 16, (◇) 26 and (□) 36 vol %. (---) The respective blunting lines at an offset of 0.2 mm.

dispersed phase. It can be observed that G_{Id} increases with the amount of $CaCO_3$ inclusions in the range of compositions explored, while G_{Id} shows only a small increase with increases in the talc content in the matrix upto a maximum value at about 5 vol % of talc. We have not yet performed any specific, systematic investigation into the mechanisms responsible for these effects.

Because of the high ductility of the systems consisting of PP with EPR added, the high-rate fracture resistance of these materials needed to be evaluated from their respective J-resistance (J_R) curves, such as those shown in Fig. 8 for samples with different rubber contents. According to the standard procedure [23], the fracture resistance at initiation, J_{Id}, is evaluated at the intersection of the J_R-curve with the straight line parallel to the blunting line at an offset of 0.2 mm. It is clear that by increasing the rubber content J_{Id} increases, and the J_R-curves become steeper, indicating that both fracture initiation and propagation require increasing amounts of energy in order to occur.

The slope of the J_R-curve, $\mathrm{d}J/\mathrm{d}a$, evaluated at $J = J_{Id}$, is assumed here to be a parameter that to some extent characterizes the resistance of the material to the onset of crack propagation, although it is not an intrinsic property of the material, depending, as it does, on the geometry [28].

For the rubber-modified PP samples, the values of J_{Id} and $(dJ/da)_{J=J_{Id}}$ are plotted as a function of the rubber content in Fig. 9a and b, respectively. In Fig. 9, the points between parentheses, relating to the sample with the highest rubber content, must be considered to be overestimated, since the specimen size requirements for the correct determination of the J_R-curve [23] are not met. In any case, it was found that, in our testing conditions, the addition of rubber to PP affects the resistance to fracture initiation for rubber contents higher than about 16 vol %, whereas resistance to crack propagation is improved for rubber contents higher than 5 vol %.

Since the ternary systems considered both consist of a high number of materials with different compositions, and the procedure to determine the J_R-curve is laborious and time-consuming, we made a preliminary approach to the study of the impact fracture of these materials by means of more conventional tests. Measurements were carried out on the total energy, U_{tot}, needed to fracture the SE(B) specimens completely, and on the energy up to the maximum on the load–time curve obtained during the test, U_{max}, (both U_{tot} and U_{max} were normalized with respect to the ligament area of the specimen). Both these parameters were considered meaningful since, when the fracture behaviour is ductile, U_{max} could be assumed to be to some extent representative of the energy necessary to initiate fracture, whereas U_{tot} mainly

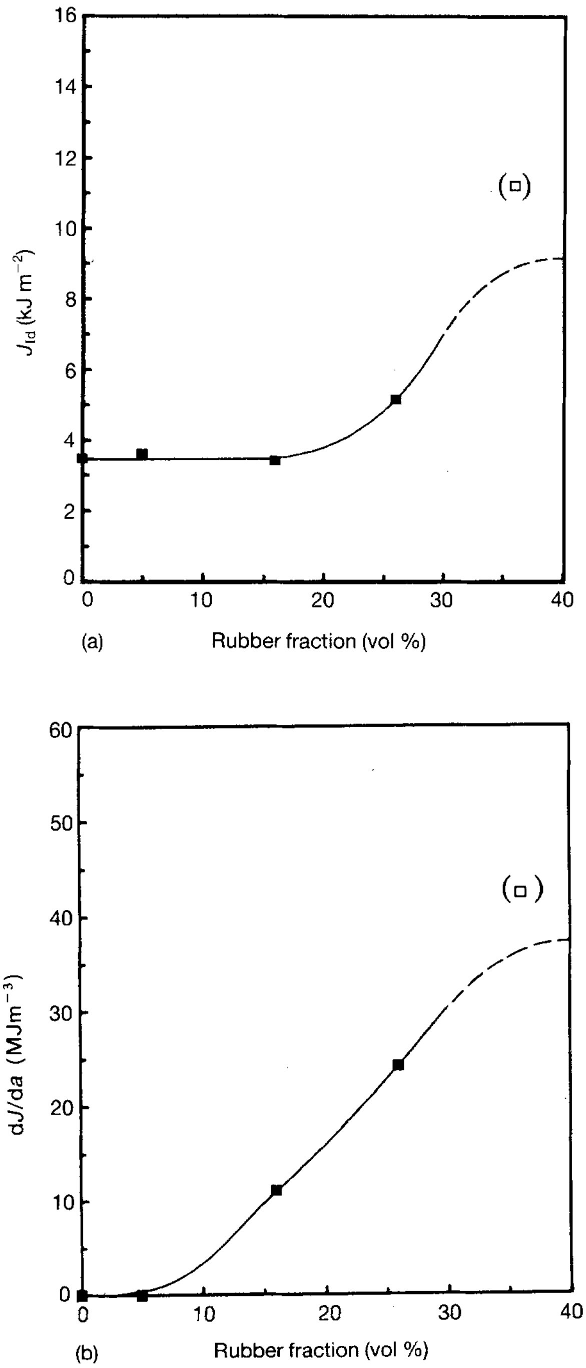

Figure 9 (a) High-rate fracture resistance at fracture initiation, J_{Id}; and (b) dJ/da, evaluated at $J = J_{Id}$, for samples of rubber-modified PP as a function of rubber content.

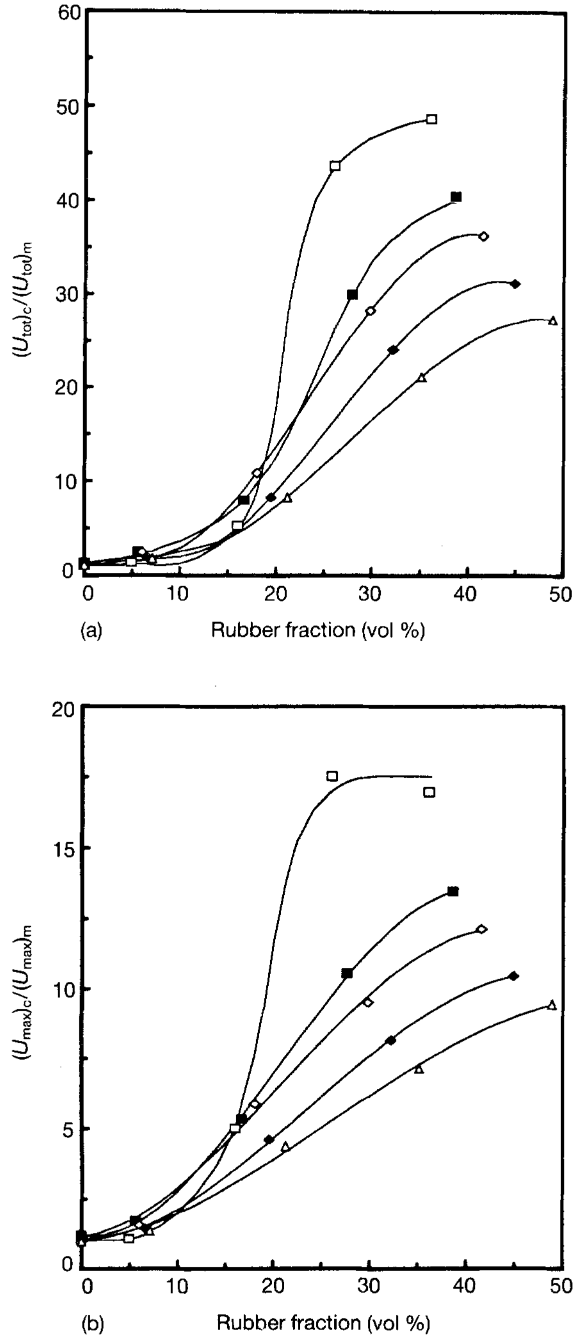

Figure 10 (a) Total energy to fracture and (b) energy up to the maximum load, evaluated in high-rate tests and normalized with respect to the corresponding values of the matrix, for the ternary system PP + EPR + talc, as a function of rubber content for different amounts of talc inclusions: (□) 0, (■) 4, (◇) 8, (◆) 12 and (△) 18 vol %.

represents the energy needed to produce crack propagation up to complete fracture of the specimen.

For the hybrid composites consisting of PP with the addition of talc and EPR, Fig. 10a and b show, respectively, the results of U_{tot} and U_{max}, both normalized by the corresponding values of pure PP, as a function of the rubber volume percentage in the composite at different talc contents. The results show that, with high rubber contents (greater than about 20 vol %), the addition of the rigid phase causes both U_{tot} and U_{max} to decrease, which clearly indicates that the ductility of these systems is impaired. With low rubber contents (less than about 20 vol %) the crossing of the curves relating to the different amounts of talc added to the composite reveals that, for given rubber contents, neither U_{tot} nor U_{max} exhibit monotonic behaviour with increasing talc percentages. This result can be better observed in the cross-plots of Fig. 10a and b in Fig. 11a and b, respectively. These indicate that, with rubber contents of 5 and 16 vol %, both U_{tot} and U_{max} show a broad maximum with about 4 vol % of talc inclusions.

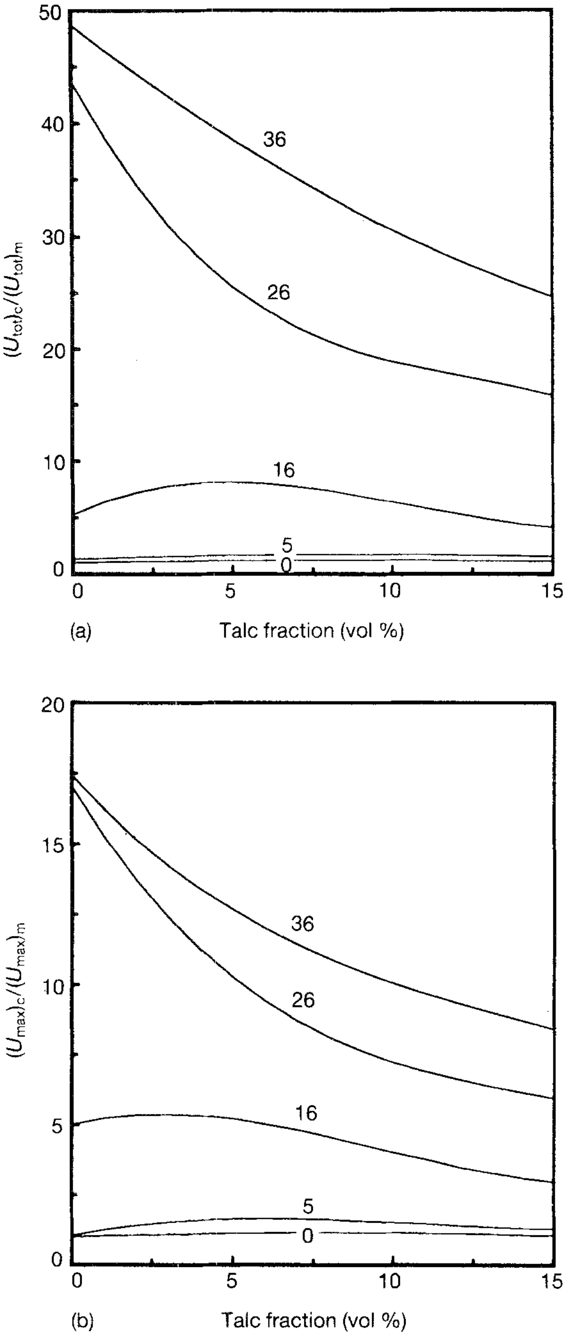

Figure 11 Cross-plots of the diagrams in Fig. 10a and b. The numbers give the rubber percentages.

Very similar results were also obtained for the systems consisting of PP with the addition of EPR and $CaCO_3$.

This investigation therefore shows that, in certain ranges of compositions, the hybridization of the secondary phase produces optimization of the impact-fracture properties compared with the corresponding binary systems.

Finally, for the material whose composition corresponds to the maximum of both U_{tot} and U_{max} in Fig. 11a and b (PP + 16 vol % EPR + 4 vol % talc), the J_R-curve was also determined. This curve, and that relating to the sample of PP with 16 vol % EPR added, are shown in Fig. 12. Hence, the values of J_{Id} and $(dJ/da)_{J=J_{Id}}$ for such materials, as well as the value of G_{Id} relating to the sample constituted by PP + 4 vol % talc are reported in Table II. The comparison of these data definitely proves that, for the ternary system considered, the resistance both to fracture initiation and to propagation is greater than in the corresponding binary systems.

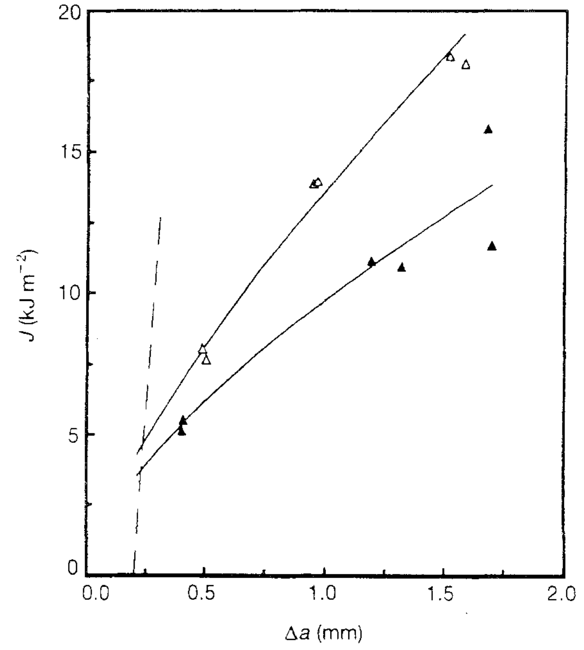

Figure 12 J_R-curves for the two samples constituted by: (▲) PP + 16 vol % EPR and (△) PP + 16 vol % EPR + 4 vol % talc.

TABLE II Fracture-mechanics data for a hybrid composite and the corresponding binary systems

Materials	J_{Id} (kJ m^{-2})	$(dJ/da)_{J=J_{Id}}$ (MJ m^{-3})
PP + 16% EPR + 4% talc	4.7	14.6
PP + 16% EPR	2.7	10.0
PP + 4% talc	4.1[a]	–

[a] Value of G_{Id}.

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References

1. D. C. PHILLIPS and B. HARRIS, in "Polymer engineering composites", edited by M. O. W. Richardson (Applied Science, London, 1977).
2. A. J. KINLOCH and R. J. YOUNG, in "Fracture behaviour of polymers" (Applied Science, London, 1983).
3. C. B. BUCKNALL, *Adv. Polym. Sci.* **27** (1978) 121.
4. F. F. LANGE and K. C. RADFORD, *J. Mater. Sci.* **6** (1971) 1197.
5. A. G. EVANS, *Phil. Mag.* **26** (1972) 1327.
6. A. C. MOLONEY, H. H. KAUSCH and H. R. STEIGER, *J. Mater. Sci.* **18** (1983) 208.
7. L. J. BROUTMAN and S. SAHU, *Mater. Sci. Engng* **8** (1971) 98.
8. P. K. MALLICK and L. J. BROUTMAN, *ibid.* **18** (1975) 63.
9. R. J. JOUNG and P. W. R. BEAUMONT, *J. Mater. Sci.* **12** (1977) 684.
10. J. SPANOUDAKIS and R. J. JOUNG, *ibid.* **19** (1984) 473.
11. *Idem., ibid.* **19** (1984) 487.
12. C. B. BUCKNALL, in "Toughened plastics" (Applied Science, London, 1977).
13. H. BREUER, F. HAAF and J. STABENOW, *J. Macromol. Sci. Phys.* **14** (1977) 387.
14. R. A. PEARSON and A. YEE, *J. Mater Sci.* **21** (1986) 2475.
15. *Idem., ibid.* **21** (1986) 2462.
16. C. B. BUCKNALL, in Proceedings of the Benibana International Symposium on how to improve the toughness of polymers and composites?, Yamagata University, October 8–11, 1990 (Yamagata (J), 1990) p. 30.
17. A. YEE, *ibid.* p. 4.
18. A. J. KINLOCK, D. L. MAXWELL and R. J. JOUNG, *J. Mater. Sci. Lett.* **3** (1984) 9.
19. *Idem., J. Mater. Sci.* **20** (1985) 9.
20. *Idem., J. Mater. Sci. Lett.* **4** (1985) 1276.
21. ASTM Designation D638-84: Standard Test Method for Tensile Properties of Plastics (type I) (American Society for Testing Materials, Philadelphia, Pennsylvania, 1984)
22. ASTM Designation E399: Standard Test Method for Plane-strain Fracture Toughness of Metallic Materials. (American Society for Testing Materials, Philadelphia, Pennsylvania, 1990)
23. ASTM Designation E813-87: Standard Test Method for J_{Ic}, a Measure of Fracture Toughness. (American Society for Testing Materials, Philadelphia, Pennsylvania, 1987).
24. W. L. SERVER, in "Elastic plastic fracture", ASTM-STP 668 (American Society for Testing Materials, Philadelphia, Pennsylvania, 1979).
25. A. SAVADORI, M. BRAMUZZO and C. MAREGA, *Polym. Testing* **4** (1984) 73.
26. A. SAVADORI, *ibid.* **5** (1985) 209.
27. G. LEVITA, A. LAZZERI, A. MARCHETTI and G. L. GUERRINI, *Mater. Engng* **1** (1989) 215.
28. As quoted in T. Ricco and A. Pavan, *Ang. Makr. Chem.* **201** (1992) 23.

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