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Enhanced fracture strain of polypropylene by incorporation of thermoplastic fibres

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The incorporation of continuous, uniaxial oriented, nylon and polyethylene terephthalate fibres into isotactic polypropylene leads to the expected increase in tensile strength as predicted by the rule of mixtures. The elongation to break, however, is found to be significantly in excess of those of the fibres and the matrix and increases with fibre volume fraction. The increase in ductility of the composites is attributed to decrease in spherulite size of the polypropylene and to restrained necking of the fibres due to transcrystalline growth at the fibre surface.

1. Introduction

It is well established that incorporation of high-modulus fibres into thermoplastics leads to significant increases in modulus of rigidity, tensile yield and fracture strength and heat distortion temperature [1–3]. The use of high modulus, brittle fibres usually leads to reduction in elongation to break and impact strengths of the composites are consequently low. The influence of fibres on impact strength is determined to a large extent by the nature and extent of interfacial bonding between the fibres and matrix and the consequent effect on the mechanisms of crack initiation and propagation. In general, it is found that using high-modulus brittle fibres, impact strengths are usually reduced for tough matrices whereas brittle materials show some improvement.

A number of workers have recently investigated the effects of incorporating high-strength thermoplastic fibres of relatively low-moduli into thermoplastic matrices. Kantz and Corneliussen [4–6] have reported that for isotactic polypropylene reinforced with up to 4% continuous nylon and polyester fibres the yield strength of the composites were almost twice that of the unreinforced polymer and that the elongation at yield occurred at, or near, the ultimate elongation of the fibres. The latter observation was stated to be due to restrained yielding in the matrix with necking occurring in the composites instantaneously at the onset of fibre rupture. The presence of the thermoplastic fibres in the polypropylene matrix was also shown to induce transcrystalline morphology radially from the fibres. Such modifications of matrix morphology lead to speculation as to their possible role in the deformation mechanism of the composites. Kantz and Corneliussen considered that the formation of transcrystalline growth led to improved adhesion of the fibres to the matrix and hence was partly responsible for the enhanced yielding in the composites. However, the composites exhibited marked increase in fracture toughness which was considered to be due to fibre debonding at a relatively weak interface, and the pull-out stress was found experimentally to be approximately two orders of magnitude lower than the yield strength of the composites.

The effects of incorporating short length thermoplastic fibres in thermoplastic matrices has also been investigated by Blumentritt *et al.* [7–9]. With increasing fibre content there was an increase in modulus and tensile strength and reduced elongation to break. For composites in which there was evidently limited adhesion between the fibres and matrix the composite properties were correspondingly reduced. For ductile matrix composites the ultimate elongation was reported to depend on the fracture strain of the reinforcement in a similar manner to that observed previously [7, 8], although the reported data do show composite fracture strains in excess of the measured elongation to break of the fibres. The variation in toughness of the composites with fibre volume fracture showed no general trends and possibly arose from the complexities in the mechanism of fracture. Scanning electron micrographs of fracture surfaces did show however, in agreement with Kantz *et al.* [5] that fibre pull-out was a major result of fracture and that little fibre fracture occurred [9].

The present work was undertaken with the aim of further understanding the effects of incorporating thermoplastic fibres into thermoplastic matrices. In particular, we were concerned to understand the effects of any changes in matrix morphology on the mechanical behaviour of the composites. Some preliminary work had shown that measurable changes in spherulitic growth did occur in polypropylene crystallized from the melt in the presence of nylon and terylene fibres. The present paper deals with the tensile behaviour of isotactic polypropylene reinforced with continuous fibres of high-tenacity nylon and terylene.

2. Experimental

The samples of isotactic polypropylene used in this work were supplied by ICI (Plastics Division) Limited and designated GX543M (injection moulding grade) and PXC8639 (a special powder premix designed for blending with glass fibres to give "coupled" glass-fibre reinforced polypropylene). Samples of 111 H and Nylon 114 high-tenacity fibres were also supplied by ICI (Fibres Division) Limited.

Some details of the materials are given in Table I. Continuous unidirectional fibre composites were prepared by winding the fibres around a rectangular metal frame. To facilitate good fibre matrix contact and more uniform fibre distribution thin moulded sheets of polypropylene were placed between successing windings. The assembled frame was heated in a laminating press to between 210 and 220° C and held at this temperature for 5 min under contact pressure. The pressure was raised to 4 MN m^{-2} for 1 min and the composite sheets then cooled to room temperature either at a rate of 25° C min^{-1} (water cooled) or at 1° C min^{-1} (air cooled).

TABLE I Properties of composite constituents

Material	1% Tensile Modulus (MN m^{-2})	Tensile Strength (MN m^{-2})	Elongation at Break (%)
Polypropylene GX543M	9.5	35	11.5
Polypropylene PXC8639	5.5	35	9
Terylene 111H (192 filaments/ bundle)	142	844	7.5
Nylon 114 (140 filaments/ bundle)	76	780	13.5

Standard tensile test specimens were prepared according to BS 2782, (1965), Pt 3, using a high speed router. Tensile tests were carried out at room temperature and at an extension rate of 2 cm min^{-1} (strain rate 6.66×10^{-3} sec^{-1}) on an Instron tensile testing machine. The % elongation was calculated on the basis of the initial gauge length and the final length of the test piece.

3. Results and discussion

The tensile properties of the materials used in this study are given in Table I, in the form of tensile strength, modulus and elongation at break. The values given for the fibres are those obtained in this work but are in close agreement with the manufacturer's data. The tensile modulus and elongation to break however are markedly dependent on strain rate, and the values given refer to an extension rate of 2 cm min^{-1}. The variation of tensile strength, and fracture strain for polypro-

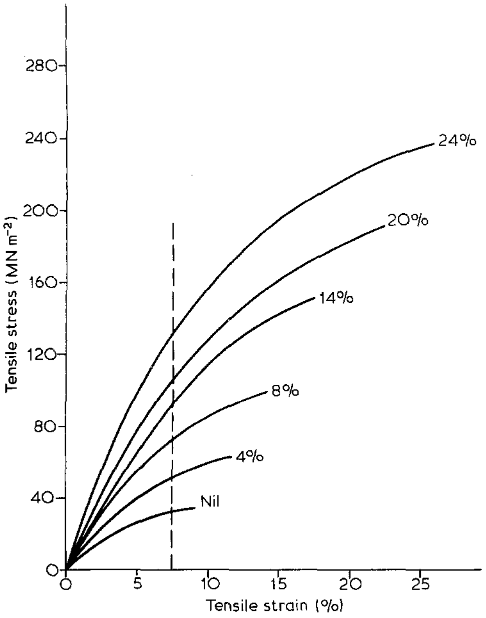

Figure 1 Tensile stress–strain behaviour of terylene (111H)/polypropylene (8639) composites as function of V_f.

TABLE II Tensile properties of continuous thermoplastic fibre reinforced polypropylene extension rate (2 cm min^{-1})

V_f (%)	Terylene 111H					
	GX543M			PXC8639		
	1% Secant Modulus* (MN m^{-2})	Fracture Stress* (MN m^{-2})	Fracture Strain (%)	1% Secant Modulus* ($\text{MN m}^{-2} \times 10^{-2}$)	Fracture Stress* (MN m^{-2})	Fracture Strain (%)
–	9	35	11.5	5	35	9.5
4	17 (15)	68 (66)	12.5	8 (11)	64 (64)	11.5
8	19 (20)	104 (99)	14	14 (21)	100 (99)	14
14	12 (28)	170 (150)	16	15 (24)	152 (150)	17
19	16 (35)	198 (188)	20	–	–	–
20	–	–	–	17 (32)	193 (196)	22
23	21 (40)	240 (220)	23	–	–	–
24	–	–	–	20 (38)	239 (229)	25.5

V_f (%)	Nylon 114					
	GX543			PXC8639		
	1% Secant Modulus* ($\text{MN m}^{-2} \times 10^{-2}$)	Fracture Stress* (MN m^{-2})	Fracture Strain (%)	1% Secant Modulus* ($\text{MN m}^{-2} \times 10^{-2}$)	Fracture Stress* (MN m^{-2})	Fracture Strain (%)
–	9	35	11.5	5	35	9.5
3	15 (11)	60 (59)	15	13 (7)	55 (56)	16
8	10 (15)	93 (94)	22.5	11 (11)	94 (94)	20
14	14 (19)	160 (137)	27.5	14 (15)	134 (137)	25
20	15 (23)	194 (183)	33	15 (19)	179 (183)	32
31	20 (31)	260 (265)	37.5	19 (27)	264 (265)	41

pylene composites as a function of volume fraction of nylon and polyester continuous fibres, V_f, are given in Table II and Figs. 1 to 4. The dashed lines in Figs. 1 to 4 indicate the maximum elongation at break for the fibres themselves.

As would be expected for continuous fibre composites the fracture stress increases with V_f in general agreement with the upper limit given by the rule of mixtures. The tensile modulus also increased with V_f but to a smaller extent than expected from the rule of mixtures. Of more significance in Table II are the observed values of fracture strain of the composites and their variation with V_f. For the four types of composite examined the fracture strain was substantially higher than those of the constituents and increased with V_f. A similar, although less pronounced, effect may be seen in the data of Blumentritt *et al.* [7, 8]. The variation of elongation at break with V_f is shown in Fig. 5, where it may be seen to approximate linear dependence up to values of V_f of approximately 25% beyond which increasing V_f has less effect. Spherulites were clearly evident in the microtomed sections of the composites viewed through crossed polarizers and although it did not prove possible to produce good quality micrographs, estimates of the average spherulite size were readily made, and shown to be dependent on V_f. In addition, transcrystalline regions mucleated at the fibre surfaces were evident in

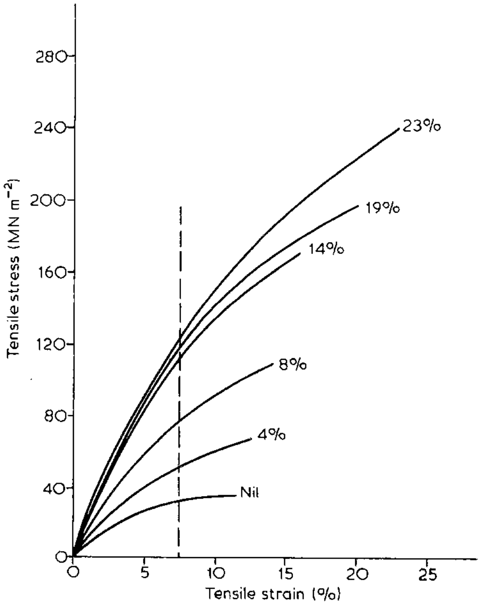

Figure 2 Tensile stress–strain behaviour of terylene (111H)/polypropylene (543H) composites as function of V_f.

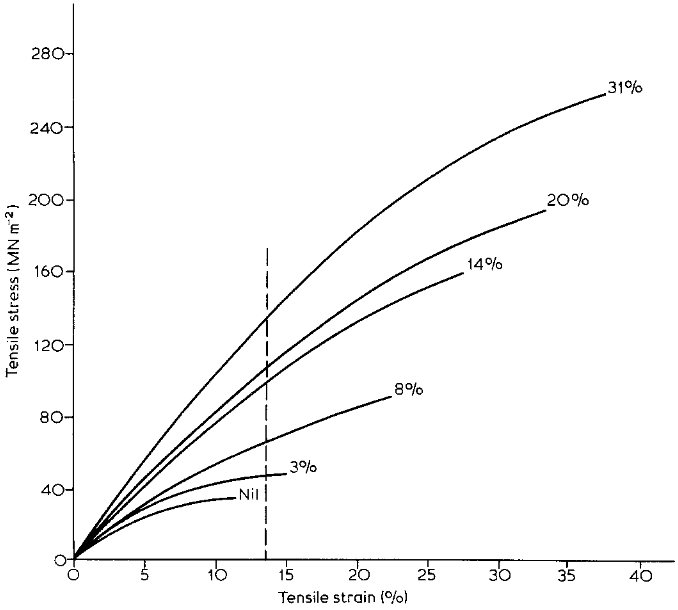

Figure 3 Tensile stress–strain behaviour of nylon (114)/polypropylene (543H) composites as function of V_f.

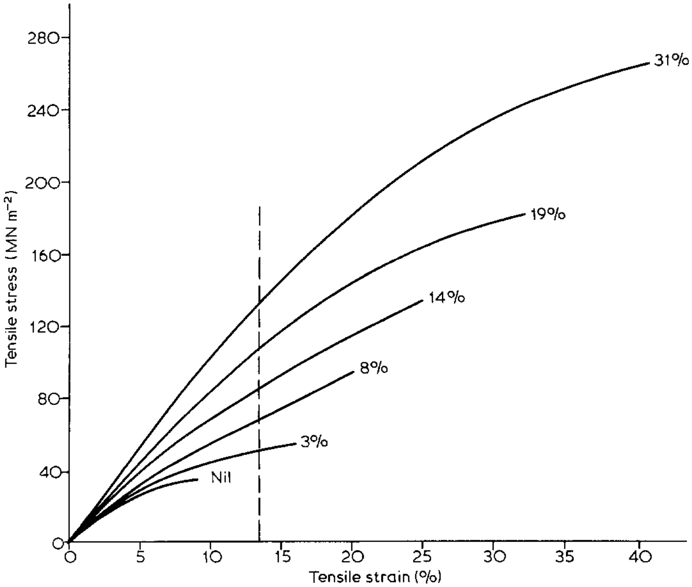

Figure 4 Tensile stress–strain behaviour of nylon (114)/polypropylene (8639) composites as function of V_f.

every case, Fig. 6. Data for 543M contained both Terylene 111 H and Nylon 114 are presented in Fig. 7. By plotting the data as a function of ultimate composite strain (Fig. 8) an approximate linear relationship is found to hold for Nylon reinforced composites. For Terylene 111 H the spherulite size levels off to a minimum radius at $V_f = 14\%$ although elongation at break continues to increase with increasing V_f. The small spherulite sizes present in 8639 prevented accurate assessment of the dependence of fracture strain and V_f on $\bar{R}$, although it may be said that increasing V_f leads to a corresponding decrease in $\bar{R}$. Chatterjee *et al.* [10–12] have recently published results of a study of nucleation rates of both substrate-induced transcrystalline and bulk spherulitic growth and have observed changes in the rates of bulk nucleation depending on the nature of substrate in contact with the polymer. The reason for the rate changes were not deduced, although effects of changes in supercooling cannot be discounted. The tensile behaviour of polypropylene and other semi-crystalline thermoplastics is dependent on the size of spherulites produced by crystallization from the melt which in turn is determined by the rate of cooling [13–15].

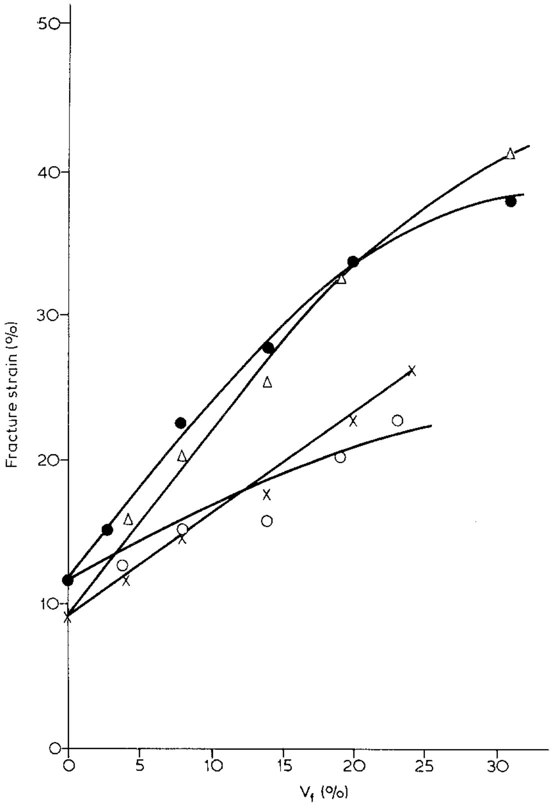

Figure 5 Variation of fracture strain with fibre volume fraction: Terylene/polypropylene 543H o; Terylene/polypropylene 8639 X; Nylon/polypropylene 543H •; Nylon/polypropylene 8639 Δ.

Recently it has been reported that for a grade of polypropylene (HMW25) (ICI Limited) changes in average sphurulite diameter, $\bar{R}$, brought about by changes in the rate of cooling from the melt led to marked changes in elongation at break [13], with the spherulite size decreasing as the fracture strain increased. Similar experiments carried out using 543M and 8639 polymers have shown similar, although less marked, effects (Table III).

The maximum elongation to break of the fibres may be seen from Table I to be respectively 7.5 and 13.5%, whereas for composites containing the respective fibres elongations of 24 and 41% were obtained. Since the fibres are subject to thermal treatment during fabrication of the composites, the treatment could have led to modification of the fibre properties resulting in increased ductility. Experiments to assess the effect of heating to the fabrication temperature were therefore carried out. The fibres were placed in a tube furnace at various temperatures under low tension, both in air and in a nitrogen atmosphere for 5 min, then allowed to cool to room temperature. The results from these experiments are presented in Table IV where it may be seen that the modulus of the fibres decreased following heat treatment consistent with earlier reports [16, 17]. The tensile strength also shows some decrease although this

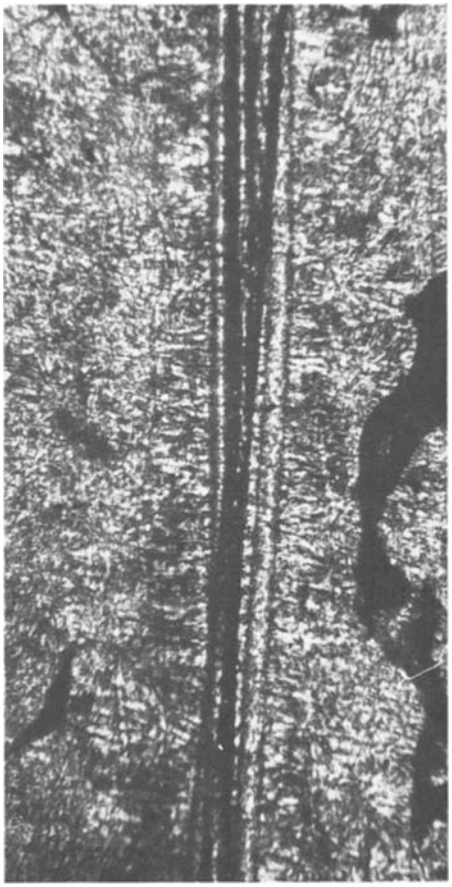

Figure 6 Optical micrograph showing transcrystalline growth at surface of terylene fibres in polypropylene 543H.

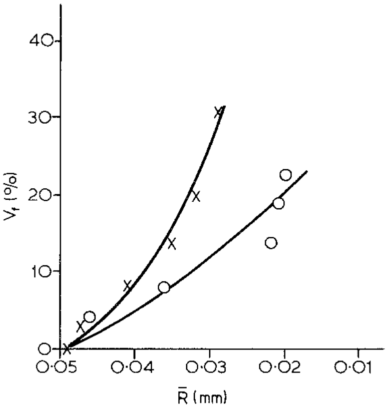

Figure 7 Variation of spherulite size with V_f: Terylene/polypropylene 543H o; Nylon/polypropylene 543H X.

TABLE III Effect of cooling rate on the properties of polypropylene (extension rate 2 cm min^{-1})

Type	1% Secant Modulus ($\text{MN m}^{-2} \times 10^{-2}$)	Tensile Strength (MN m^{-2})	Elongation at break (%)	Density (g cm^{-3})	Spherulite Radius (mm)
GX543M*	9	35	11.5	0.908	0.049
GX543M†	11	29	4.5	0.913	0.475
PXC8639*	5	35	9	0.909	very small
PXC8639†	6	30	5	0.910	small

*cooling rate 25° C min^{-1}
†cooling rate 1° C min^{-1}

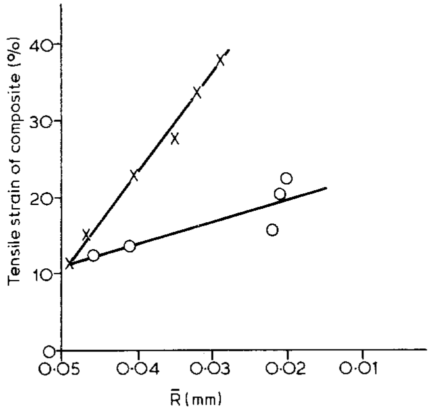

Figure 8 Variation of composite fracture strain with spherulite size: Terylene/polypropylene 543H ○; Nylon/polypropylene 543H ×.

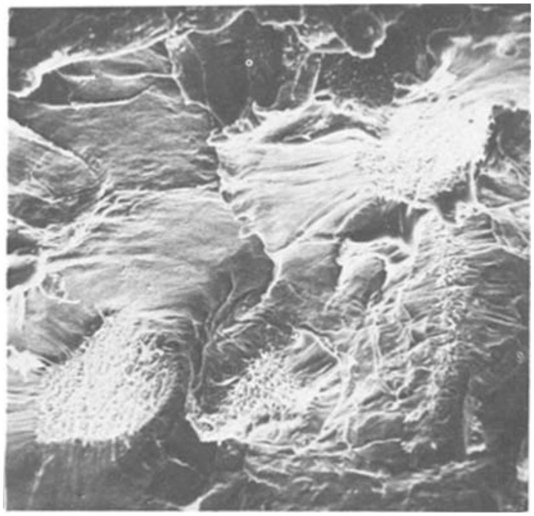

Figure 9 SEM of fractured surfaces of polypropylene 8639 (magnification × 192).

may be due in part to damage caused to the fibres during handling. Heat treatment of the fibres also produced a slight decrease in fracture strain. Reported effects of heat treatment of fibres show a diversity of effects [18] with fracture strain reported as decreasing [16], or that yarn ductility tended to increase [17]. The results of this work however show that heat treatment itself does not lead to any significant increase in fracture strain.

Scanning electron micrographs of fractured specimens are shown in Figs. 9 to 13. The fracture surfaces of the unreinforced 8639 and 543M polymers were significantly different, probably reflecting the large differences in spherulite size. Two distinct fracture regions are evident in 8639, the initiation region in which there is a large amount of plastic deformation, and a more extensive region of brittle fracture, Fig. 9. 543M appears to have undergone only very limited plastic flow with a greater tendency to inter-spherulitic brittle fracture, Fig. 10.

TABLE IV Effect of thermal treatment (under still air and N_2 atmosphere and low tension) on tensile properties of fibres

Temp (°C)	Terylene 111H			Nylon 114		
	1% Secant Modulus* ($\text{MN m}^{-2} \times 10^{-2}$)	Fracture Stress* (MN m^{-2})	Fracture Strain* (%)	1% Secant Modulus* ($\text{MN m}^{-2} \times 10^{-2}$)	Fracture Stress* (MN m^{-2})	Fracture Strain* (%)
20	142	844	7.5	77	780	13.5
200	107 (127)	820 (739)	7.9 (7.9)	50 (72)	719 (726)	12.7 (8.8)
210	107 (127)	799 (745)	7.2 (7.2)	50 (72)	719 (719)	12.3 (11.5)
220	107	752	7.2	50	719	12.0
230	107 (132)	752 (739)	7.4 (7.0)	46 (72)	706 (719)	12.0 (12.4)

*values in brackets are for heat treated samples under N_2 atmosphere.

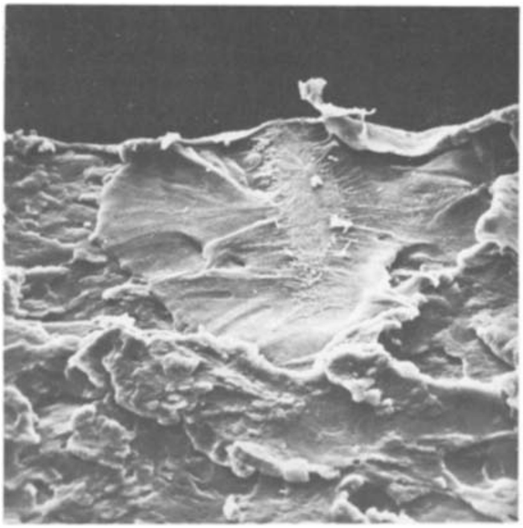

Figure 10 SEM of fractured surfaces of polypropylene 543M (magnification × 220).

Figure 12 SEM of fracture surface of fibre 24% terylene 11H/polypropylene 8639 composite (magnification × 2350).

Fracture of the original fibres appeared to occur by localized becking, probably at defect regions in the fibre, since the fracture occurred more or less in one plane without any drawing of the fibres away from the fracture surface.

In the composites the fracture surfaces in the region of the fibres undergo much greater plastic deformation compared to regions remote from the fibres where a brittle mode of failure is observed. As may be expected on the basis of spherulite size, the extent of plastic deformation is more evident in the 8639 composites, although Fig. 11 shows significant plastic deformation in 543M at high volume fractions. The enhanced ductility of the matrix in the region of the fibres we would suggest is a direct consequence both of the transcrystalline growth and of the decreased spherulite size in these regions. In regions remote from the fibres the decrease in spherulite size is less marked and consequently the fracture mechanism is not significantly altered.

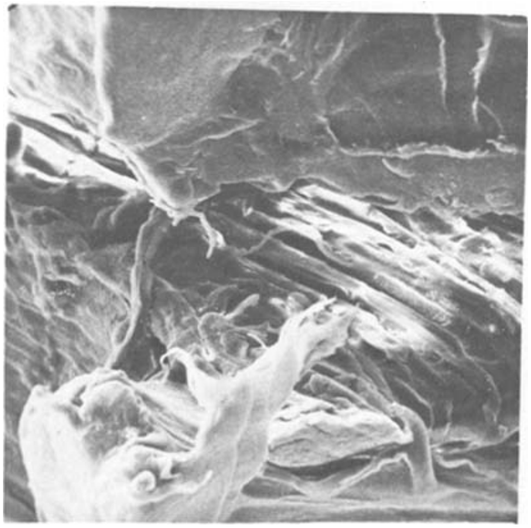

Figure 11 SEM of fracture surface of 23% terylene/polypropylene 543M composite in region of fibre pull-out (magnification × 215).

The fracture surfaces of the fibres in the composites show much greater plastic deformation compared to the broken original fibres (Fig. 12). In most cases the outer "skin" shows extensive deformation, whereas the centres of the fibres give the appearance of brittle fracture, reminiscent of cup and cone fracture of metals. Of particular significance is the deformation of the fibres away from the fracture surfaces, where extensive drawing of the fibres occurs, an effect not observed to any degree in fractured original fibres Fig. 13. It may be deduced from these observations that in the presence of the matrix the localized necking of the fibres which normally leads to premature failure of the fibres is restrained, and the strain is more uniformly distributed along the length of the fibres. The net effect is to postpone the incidence of fracture and thus increase the overall elongation to break. For laternal necking to occur this would require lateral extension of the transcrystalline regions, along the crystallographic a-axis. If one considers the expected mode of deformation of spherulite and transcrystalline structures it is

Figure 13 SEM of fibre surface from 24% terylene/polypropylene 543M composites (magnification × 560).

probable that separation of lamellae along the c-axis direction which is along the fibre axis for the transcrystalline regions, would occur more readily than disruption of the crystallites along the a-axis direction as would be required if necking of the fibres produced distortion of the transcrystalline regions.

4. Conclusion

The incorporation of continuous uniaxially oriented nylon and terylene fibres into isotactic polypropylene leads to a marked increase in elongation to break in addition to the expected increase in tensile strength and modulus. The increase in elongation is presumed to be due both to increased ductility of the matrix arising from decrease in spherulite size, and to restrained necking of the fibres due to the effect of transcrystalline growth on the surface of the fibres. The reason for the reduction in spherulite size has not been established and further work is underway in attempts to elucidate the mechanism.

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References

1. J. THERBERGE, D. ARKLES and R. ROBINSON, 29th Conference Reinforced Plastics and Composites Institute, SPI, 1974.
2. W. V. TITOW and B. J. LANHAM, "Reinforced Thermoplastics" (Applied Science Publishers, London, 1975). p. 54.
3. F. MANDY, *Plastics and Rubber* **1** (1976) 119.
4. M. R. KANTZ and R. D. CORNELIUSSEN, *J. Polymer. Sci. Polymer Letters* **11** (1973) 279.
5. *Idem, Polymer Preprints* **14** (1973) 447.
6. *Idem,* ACS, Div. of Organic Coatings and Plastic Chem., *Plast. Preprints* **2** 34 (Sept. 1974) 361.
7. B. F. BLUMENTRITT, B. T. VU and S. L. COOPER, *Polymer Eng. Sci.* **14** (1974) 663.
8. *Idem, ibid,* **15** (1975) 428.
9. *Idem, Composites* **6** (1975) 105.
10. A. M. CHATTERJEE, F. P. PRICE and S. NEWMAN, *J. Polymer Sci., Phys.* **13** (1975) 2369.
11. *Idem, ibid,* **13** (1975) 2385.
12. *Idem, ibid,* **13** (1975) 2391.
13. J. L. WAY, J. R. ATKINSON and J. NUTTING, *J. Mater. Sci.* **9** (1974) 293.
14. V. A. KARGIN, T. I. SOGOLOVA and L. I. NADAREISHVILI, *Polymer Sci. USSR* **6** (1954) 1404.
15. J. H. REINSHAGEN and R. W. DUNLAP, *J. Appl. Polymer Sci.* **20** (1976) 9.
16. M. P. W. WILSON, *Polymer* **15** (1974) 281.
17. D. C. PREVORSEK and J. P. SIBILIA, *J. Macromol. Soc. B.* **5** (1971) 617.
18. J. W. S. HEARLE, P. K. SEN GUPTA and A. MATTHEWS, *Fibre Sci. Technol.* **3** (1971) 167.

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