JOURNAL OF MATERIALS SCIENCE 23 (1988) 4525-4533

Injection-moulded sepiolite-filled polypropylene: mechanical properties and dimensional stability

E. MORALES*, J. R. WHITE
Department of Metallurgy and Engineering Materials, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK

Sepiolite, a clay mineral, has been compounded with polypropylene to produce a range of materials with filler contents 10, 25 and 40 wt %. The compounds have been found to process easily by injection-moulding and their mechanical properties have been measured in this form after various ageing treatments including storage at low temperature, and annealing. Although their mechanical properties and shrinkage behaviour are slightly inferior to those of equivalent compounds in which talc is used as a filler, they appear to have better dimensional stability at elevated temperatures and this, coupled with the low cost of sepiolite, indicates that this material has commercial potential.

1. Introduction

The use of polypropylene injection-moulding compounds has expanded significantly in recent years, the most popular reinforcement fillers being short glass fibres, chalk, mica and talc. Glass fibre-filled grades generally give the highest strengths and stiffnesses, but are more prone to warpage than particulate-filled grades. A mixture of glass fibres plus a particulate filler is sometimes used to improve dimensional stability. For applications for which the highest stiffnesses and strengths are not required, particulate-filled compounds have the advantages of having even less tendency to distort and of being easy to mould and relatively cheap.

The properties of the moulded product depend on the nature of the filler, its concentration, and the moulding conditions. The most important characteristics of the filler are its size and shape, its ability to act as a nucleating agent for crystallization and its ability to adhere to the matrix resin. If the filler particle has a large aspect ratio, it tends to orient in the flowing melt during the moulding operation. The opportunities to reorient during solidification in the mould after flow ceases are limited and considerable orientation remains in the moulded product. Several studies have been made of the orientation distribution of short glass fibres used as reinforcement in polypropylene [1-4]. Sections through moulded bars display a stratified appearance, with the fibres in some layers having a strong axial orientation and in others having transverse orientation; the boundary between adjacent layers is normally quite sharp. Platelet-like fillers such as mica and talc also show orientation, but there is less information in the literature about their orientation distribution than for the glass-filled materials. Moulding conditions can be expected to influence the orientation distribution but no detailed understanding of this has yet been developed despite its importance, though some progress has been made with modelling behaviour in simple shapes [5-8]. The presence of preferred orientation in the reinforcing filler will, of course cause the properties to be anisotropic.

Filler particles often act as crystallization nuclei, and if they are present in sufficient concentration the high nucleation density results in a small spherulite size in the final solid. The filler particles may alter completely the crystal morphology. For example, in the case of a fibrous filler, if crystals nucleate close together along the fibre they quickly impinge, leaving the radial direction as the only direction for further growth. The consequent morphology is described as transcrystalline. Fibrous fillers may enhance the flow-induced orientation of the polypropylene molecules, or, perhaps more correctly and more significantly, may help to ensure that it is retained during cooling. This effect may have a more important influence over nucleation than the surface interaction at the polymer–filler interface in some composites [9, 10], though the adhesion between the polymer and filler will almost certainly influence the extent of molecular orientation relaxation during the critical period after mould filling has been completed and before solidification commences. Thus if coupling agents are used to increase the adhesion between polymer and filler, their effect may not simply be to inhibit fibre pull-out through the improved adhesion. There may be in addition modification of the crystal morphology that may in turn modify properties. It has been suggested that enhanced nucleation of polypropylene crystals on mica results in greater shrinkage in the resin (caused by greater crystallinity), which then increases the frictional forces during fibre pull-out when the moulding is fractured [11]. It should be noted that some

---

* *Present address*: Instituto de Ciencia y Tecnologia de Polimeros (CSIC), c/Juan de la Cierva, 3, 28006 Madrid, Spain.

0022-2461/88 $03.00 + .12

TABLE I Physical properties of the sepiolite

Hardness (Mohs)	2 to 2.5
Specific surface (BET)	160 to 170 $m^2 g^{-1}$
Density	2100 $kg m^{-3}$
Granulometry	
$> 44 \mu m$	Trace
$> 10 \mu m$	10%
$> 5 \mu m$	7%
$< 5 \mu m$	83%

treatments can lower the nucleating activity of the filler [12].

In the studies described here sepiolite, a clay mineral, is examined as a filler for injection-moulding grades of polypropylene. Sepiolite is a hydrated magnesium silicate with the ideal compositional formula $Si_{12} Mg_8O_{30} (OH)_4(H_2O)_4 \cdot 8H_2O$ [13]. It has a fibrous morphology with non-continuous octahedric layers, with open channels extended longitudinally in the fibre direction, and it has a large concentration of hydroxyl groups arranged in comb-like fashion along the edges of the octahedron. These provide the sites for surface structure modification through various organic reactions, permitting a range of surface activities to be produced and tailored to a range of applications. This, together with the high natural abundance and low cost of sepiolite, provided the motivation for examining it as a potential filler for polypropylene moulding compounds. In previous studies polypropylene–sepiolite compounds have been made, and studied in compression-moulded form. The mechanical properties of the compounds have been measured as a function of composition and the effect of different surface treatments has been investigated [14, 15]. The structure of the "interphase" region within the polypropylene, immediately adjacent to the filler, has been studied as part of an investigation into the role of this region in controlling the properties of the compounds [16–18]. The mechanical properties (stiffness, strength, toughness) of the sepiolite-filled compression moulding were found generally to be superior to those measured with talc-filled grades with which they may be expected to compete if made available commercially [19].

The purpose of the work described here was to evaluate sepiolite-filled polypropylene as an injection-moulding material. Compounds with sepiolite loadings of 10, 25 and 40 wt % were made and their properties compared with commercially available talc-filled polypropylene with the same filler levels.

2. Experimental procedure

2.1. Materials and specimen production

The test materials utilized were polypropylene (PP) (ICI HWM 25), talc-filled polypropylene based on the same polymer (ICI 22T40H) and sepiolite, supplied by Steetley Minerals Ltd in micronized form. The main physical properties of the sepiolite are shown in Table I.

A compound containing 40 wt % of sepiolite was made by mixing in a rolling mill at 190° C, then granulated. Some of this material was diluted to form compounds containing 10 and 25% sepiolite, respectively, by tumble-mixing with more polypropylene granules, then passed through a single-screw extruder and regranulated. Some of the 40% material was also passed through the extruder undiluted to complete the mixing process. Talc-filled compounds with 10 and 25 wt % filler were made from the 40% filled compound (22T4OH) in a similar way. Samples of unfilled and 40% talc-filled polypropylene were subjected to the same extrusion procedure to reduce the processing contribution to subsequent measurements upon which comparisons were to be made. The extruder barrel was kept at 220° C and the die at 200° C for all batches of material.

Samples were injection-moulded into ASTM D638 tensile test bars 190 mm long with gauge length cross section ~12.7 mm × 3.2 mm on a Butler–Smith 100/60 reciprocating screw machine with a 26 mm diameter screw. The mould cavity was end-gated, the nozzle temperature 200° C, the barrel temperature (2 zones) 200/220° C, injection pressure 161 MPa and mould temperature 35° C.

The specimens produced from each material were divided into four batches as follows:

(i) Tested approximately two hours after moulding, and referred to hereafter as "as-moulded".

(ii) Stored at ~20° C for one month before testing.

(iii) Stored in a deep-freeze cabinet at −80° C for one month before testing.

(iv) Stored at ~20° C for one month and then annealed at 120° C for 6 h before testing.

2.2. Mechanical testing

Uniaxial tensile tests were conducted on an Instron 1193 machine using a crosshead speed of 20 mm min^{-1}. Young's modulus values were determined using an extensometer and a crosshead speed of 0.5 mm min^{-1} and are presented as the tangent modulus at zero strain. Three-point bend tests were carried out on an Instron 1193 machine using a span length of 65 mm and a crosshead speed of 20 mm min^{-1}.

Impact tests were conducted on a Daventest Izod impact machine using test pieces extracted from the tensile bars. The ends of the bar were sawn off, leaving the central 63.5 mm of the gauge length. Tests were then carried out on samples according to a standard procedure (BS 2782, Part 3, Method 350) for specimens of dimensions 12.7 mm × 3.2 mm, using a Type A notch (2 mm deep with 45° entrance angle and 0.25 mm tip radius) cut across the bar thickness by using a broaching tool just before testing.

2.3. Shrinkage tests

Selected specimens were placed in an air oven at elevated temperature for varying periods (44 h at 100° C, 24 h at 120° C, 16 h at 140° C, 2 h at 160° C) in order to examine the shrinkage characteristics of the mouldings. The mould shrinkage was also determined by comparing the dimensions of the mouldings with those of the mould cavity.

2.4. Scanning electron microscopy

Fracture surfaces of samples broken under uniaxial tension were gold-coated and inspected in the SEM

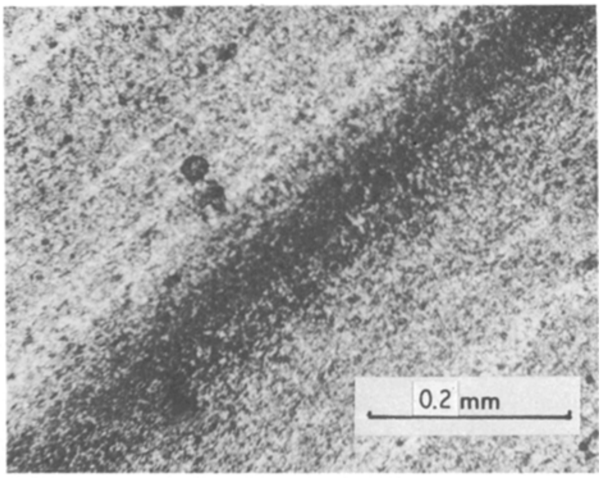

Figure 1 Polarized light micrograph of microtome section cut perpendicular to the flow direction in a bar moulded from polypropylene–10% sepiolite. The dark region in the middle of the field of view coincides with the centre of the moulding.

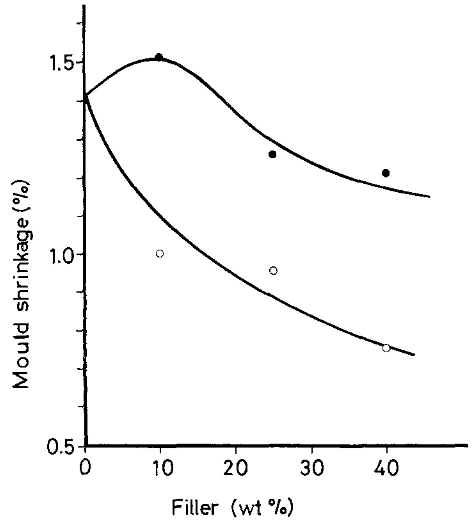

Figure 2 Moulding shrinkage in the flow direction as a function of filler content for (●) sepiolite-reinforced and (○) talc-reinforced polypropylene.

(Jeol JSM-T20). Specimens were viewed using the secondary electron image with an accelerating potential of 20 kV; at the magnification used, the different materials showed reasonable stability in the electron beam.

3. Results

3.1. Moulding properties

Sepiolite-filled polypropylene has not been injection-moulded before to our knowledge. It moulded easily, under conditions suitable for moulding polypropylene containing other fillers with similar loadings, and appeared to have an equally large operating window. The surface finish of the mouldings was good, but the general appearance was unattractive because of the colour, a handicap shared with polypropylenes containing other fillers.

Despite its fibrous morphology, sepiolite appears as ellipsoidal aggregates under the electron microscope. They were well dispersed throughout the moulded bars, though they appeared to be present in slightly higher concentration near to the centre of the specimen when viewing along the moulding direction (Fig. 1).

3.2. Mechanical testing

The results obtained for the mechanical properties of the compounds under study are summarized in Table II to IV and show that Young's modulus increases with filler content, whereas the effect on the tensile strength is not so clear. The values obtained for the Young's modulus with talc-filled grades are higher than those obtained with sepiolite-filled compounds of similar composition, except for the samples treated at high temperature. The tensile strength is fairly similar for all materials after annealing at 120° C but a large variation is observed at all other conditions. After ageing at $-80°$ C the value obtained with 40% talc loading is much lower (22 MN m^{-2}) than all of the others (in the range 27 to 30 MN m^{-2}). This material also recorded the lowest value (19 MN m^{-2}) in the as-moulded state, though in this case low values were also recorded for sepiolite compounds containing filler levels of 25% (20 MN m^{-2}) and 40% (23 MN m^{-2}). After ageing at room temperature most compounds increased in strength, the exception being those with 10% filler.

The flexural modulus also increases with filler concentration, showing, as a general rule, higher values for the talc-filled compounds than for the sepiolite-filled ones. Compounds containing sepiolite as filler show better behaviour in the as-moulded form, whereas the best values for the talc-filled compounds were obtained with the aged samples.

Thus, in most of the conditions tested, talc-filled compounds show better properties than those containing sepiolite, reversing the ranking obtained with compression-moulding compounds [19]. This we believe can be interpreted as a result of orientation of the talc particles during the injection-moulding process, a result of their high aspect ratio, whereas

TABLE II Mechanical properties: uniaxial tension test

Sample	As-moulded		Aged 20° C		Aged $-80°$ C		Aged 20° C, annealed 6 h 120° C	
	Modulus (GN m^{-2})	Strength (MN m^{-2})	Modulus (GN m^{-2})	Strength (MN m^{-2})	Modulus (GN m^{-2})	Strength (MN m^{-2})	Modulus (GN m^{-2})	Strength (MN m^{-2})
PP	1.0	29	1.0	30	1.0	29	1.0	32
PP-Sep 10	1.3	29	1.3	26	1.2	29	1.4	31
PP-Sep 25	1.5	20	2.5	30	2.1	29	2.1	28
PP-Sep 40	2.3	23	3.4	28	2.5	27	2.8	27
PP-Talc 10	1.4	33	1.9	32	1.7	30	1.6	32
PP-Talc 25	2.1	28	3.0	33	2.1	30	1.9	33
PP-Talc 40	3.2	19	5.2	32	2.6	22	2.1	32

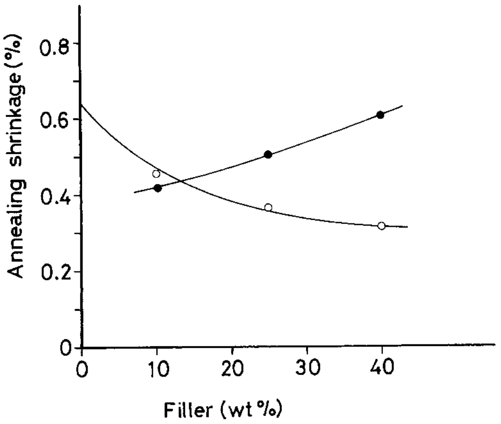

Figure 3 Annealing shrinkage in the flow direction as a function of filler content for (●) sepiolite-reinforced and (○) talc-reinforced polypropylene. The heat treatment for all specimens was 24 h at 120° C.

the same degree of orientation did not occur in the case of the sepiolite particles. This may in turn cause differences in the morphology of the polypropylene phase in the compounds containing different fillers. We shall return to this topic later.

The impact strength was found to decrease when the level of filler was increased, and again lower values were obtained with the polypropylene–sepiolite compounds than with the talc-filled grades. The samples aged at room temperature show a decrease in the impact strength, whereas high values were obtained for the samples aged at room temperature and then annealed at 120° C.

3.3. Shrinkage tests

3.3.1. Mould shrinkage

Mould shrinkage was measured in the flow direction after the moulded material had been allowed to remain for 48 h at 20° C. The following formula was used:

$$\text{Mould shrinkage } (\%) = 100\left(\frac{L_0 - L}{L_0}\right) \quad (1)$$

where L is the length of the bar at this time and L_0 is the length of the mould cavity [20].

The results obtained for samples aged 3 months at room temperature before measuring (Fig. 2) show that mould shrinkage decreased with the talc-filled compounds when the level of filler was increased, whereas for the sepiolite filled compounds an increase in the mould shrinkage was observed at low filler concentrations. The mould shrinkage obtained with the sepiolite-filled compounds was higher than that obtained with the talc-filled ones at all the concentrations studied.

3.3.2. Annealing shrinkage

An annealing shrinkage percentage was calculated by measuring the length L_a of the bar after it had been treated in an oven at a specified temperature for a specified time and then left at 20° C for at least 24 h. The following formula was employed:

$$\text{Annealing shrinkage } (\%) = 100\left(\frac{L - L_a}{L}\right) \quad (2)$$

where L is the length before the thermal treatment. Annealing shrinkage for the polypropylene–talc compounds decreased when the level of filler was increased, but the opposite effect was observed with the polypropylene-sepiolite compounds (Table V, Fig. 3).

3.4. Scanning electron microscopy

The fracture surfaces show the skin–core morphologies (Figs 4 to 6), as well as the alignment of the talc particles in the flow direction (Fig. 7). In addition, there is indication of good adhesion between sepiolite

TABLE III Mechanical properties: three-point bending test

Sample	As-moulded		Aged 20° C		Aged −80° C		Aged 20° C, annealed 6 h 120° C	
	Modulus ($GN\,m^{-2}$)	Strength ($MN\,m^{-2}$)	Modulus ($GN\,m^{-2}$)	Strength ($MN\,m^{-2}$)	Modulus ($GN\,m^{-2}$)	Strength ($MN\,m^{-2}$)	Modulus ($GN\,m^{-2}$)	Strength ($MN\,m^{-2}$)
PP	1.3	57	1.4	62	1.3	54	1.3	58
PP-Sep 10	1.5	60	1.8	65	1.4	59	1.6	64
PP-Sep 25	2.7	65	2.6	72	2.3	68	2.5	70
PP-Sep 40	2.9	66	3.1	70	2.7	66	3.0	66
PP-Talc 10	1.6	46	2.1	68	1.8	63	1.9	68
PP-Talc 25	2.1	49	3.0	72	2.6	67	2.4	71
PP-Talc 40	3.0	50	4.3	77	3.6	58	3.4	74

TABLE IV Mechanical properties: impact strength

Sample	Impact strength ($kJ\,m^{-2}$)			
	As-moulded	Aged 20° C	Aged −80° C	Aged 20° C, annealed 6 h 120° C
PP	3.7	3.6	4.3	7.2
PP-Sep 10	2.9	2.9	3.3	3.8
PP-Sep 25	2.1	1.4	1.8	2.0
PP-Sep 40	1.4	1.2	1.3	1.3
PP-Talc 10	4.1	2.8	3.3	5.9
PP-Talc 25	3.4	2.2	2.3	4.5
PP-Talc 40	2.8	2.0	2.2	3.1

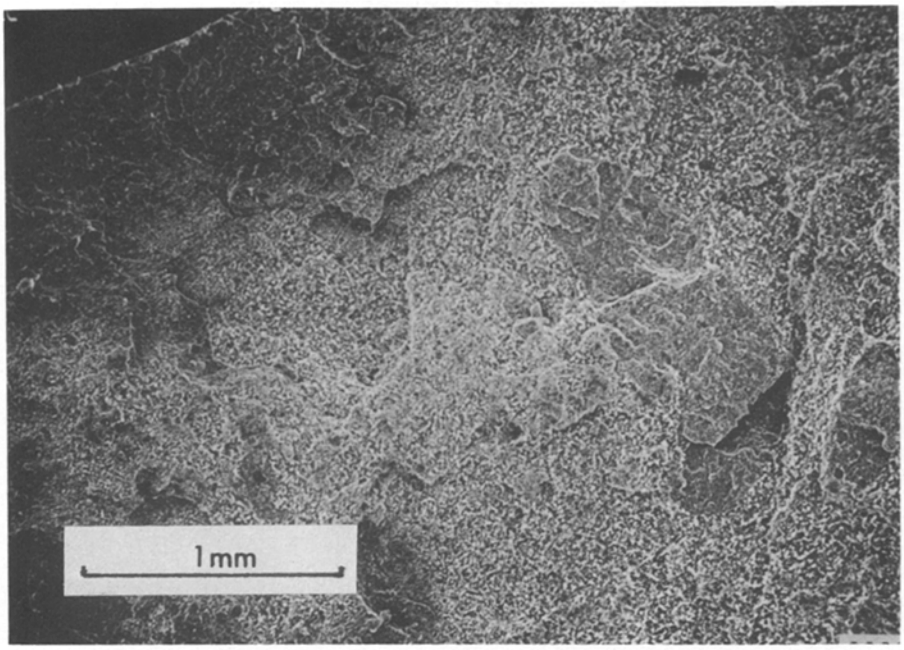

Figure 4 Skin–core morphology revealed in the fracture surface of polypropylene–40% sepiolite injection-moulding.

and polypropylene (Fig. 8), whereas adhesion is not evident in the case of the talc-filled compounds in which the talc particles have broken away cleanly from the polypropylene matrix during fracture (Fig. 9). Fibrillation occurs in the core and is more pronounced with lower filler levels (compare Figs 5 and 6). Fibrillation is not evident on low-magnification inspection of annealed samples (Fig. 10).

4. Discussion

Talc-filled polypropylene was found to have better mechanical properties than sepiolite-filled polypropylene of similar composition when in injection-moulded form. This effect is attributed to the orientation of the talc particles during the moulding process, as was evident in the scanning electron micrographs. Orientation parallel to the flow direction provides reinforcement in the bar axis direction and can be expected to improve uniaxial tensile properties measured in this direction, and bending and impact properties when tested by the methods used in this study. Sepiolite particles are much more nearly equiaxed and do not provide significant orientation-related reinforcement.

The results shows that the talc-filled grades required a considerable ageing time to develop their best properties. This in itself is not a serious handicap, for in most circumstances the transportation and shelf-time between moulding the article and utilizing it would comfortably exceed this, but is does indicate that substantial changes are occurring in the first few hours of the life of the moulding, and these may not be easy to control. Furthermore, if the moulded article is to be part of a complex assembly which is put together in the factory in which it is made, it might hamper efficient production if a storage time had to be allowed for before assembly. The sepiolite-filled materials show much less sensitivity to ageing. This is

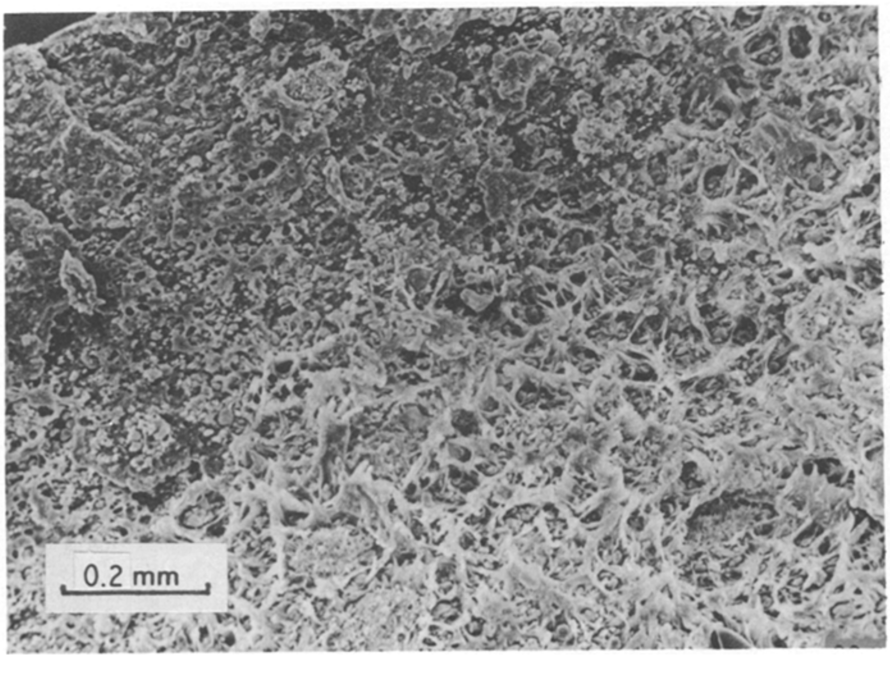

Figure 5 Skin–core morphology in polypropylene–25% sepiolite compound.

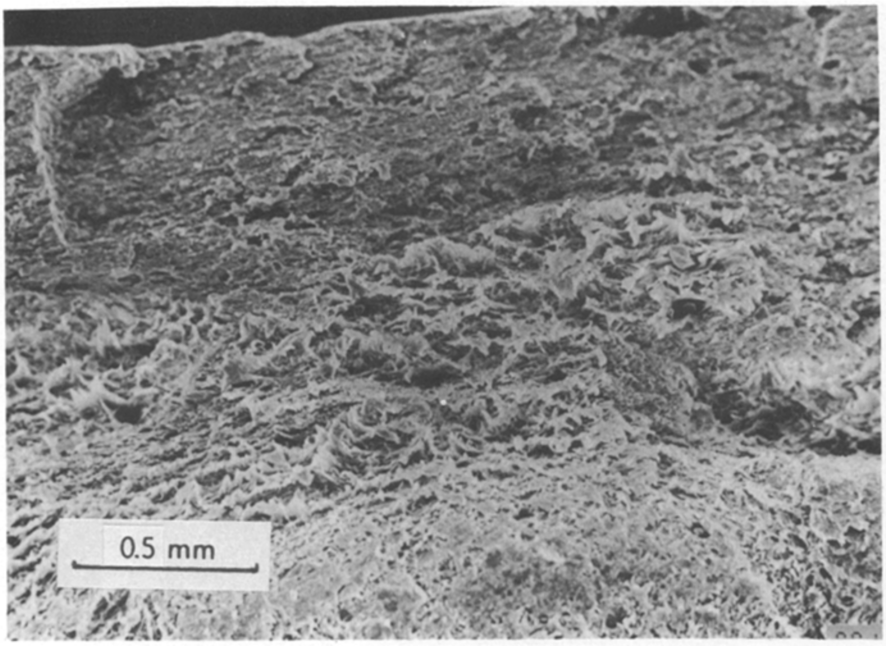

Figure 6 Skin–core morphology in polypropylene–40% talc compound.

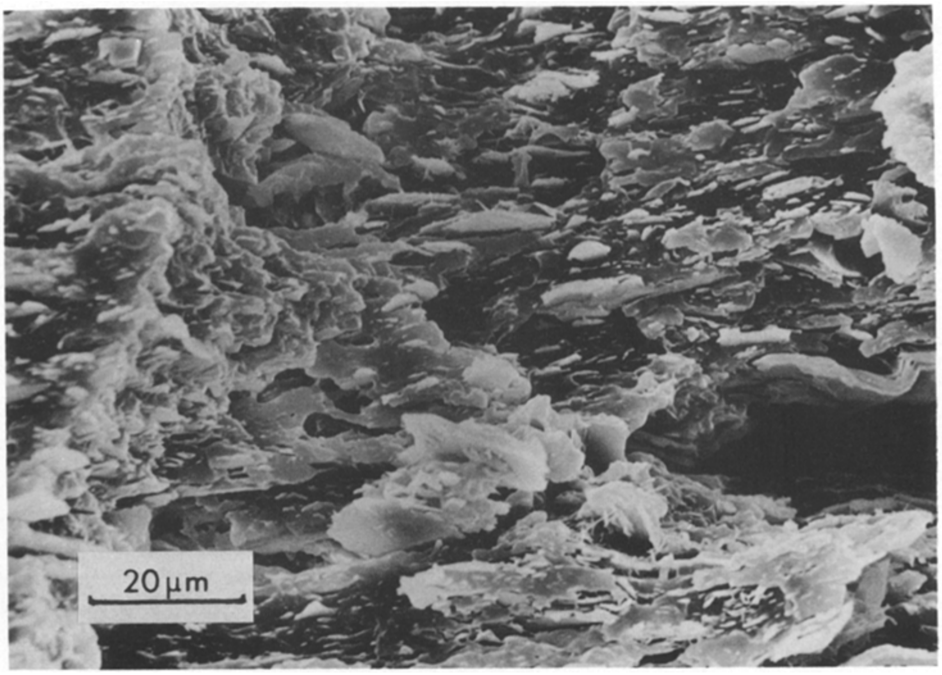

Figure 7 Fracture surface from the skin region of polypropylene–40% talc compound, showing talc particles predominantly edge-on and lying parallel to the surface of the moulding (horizontal, not in view).

probably because sepiolite is a more potent nucleating agent than talc, so that immediately after the moulding cycle has finished crystallization is more nearly complete in the sepiolite-filled materials than in the talc-filled one. Further crystallization, continuing over a period of several hours or days, is the most likely explanation for the substantial property changes observed with the talc-filled grades. The flexural strength in the as-moulded form of talc-filled polypropylenes was below that of the equivalent sepiolite-filled materials, but after ageing the talc-filled materials gave better results.

Differences in ageing have also been observed with measurements of residual stress distribution in bars taken from the batches of moulding upon which the work reported in this paper was conducted [21]. The

TABLE V Annealing shrinkage in the moulding direction

Sample	Shrinkage (%)			
	44 h, 100° C	24 h, 120° C	16 h, 140° C	2 h, 160° C
PP	0.21	0.63	0.66	0.83
PP-Sep 10	0.33	0.42	0.13	0.71
PP-Sep 25	0.51	0.50	0.61	0.85
PP-Sep 40	0.59	0.60	0.84	0.82
PP-Talc 10	0.55	0.45	0.62	0.94
PP-Talc 25	0.25	0.36	0.59	0.78
PP-Talc 40	0.20	0.31	0.46	0.86

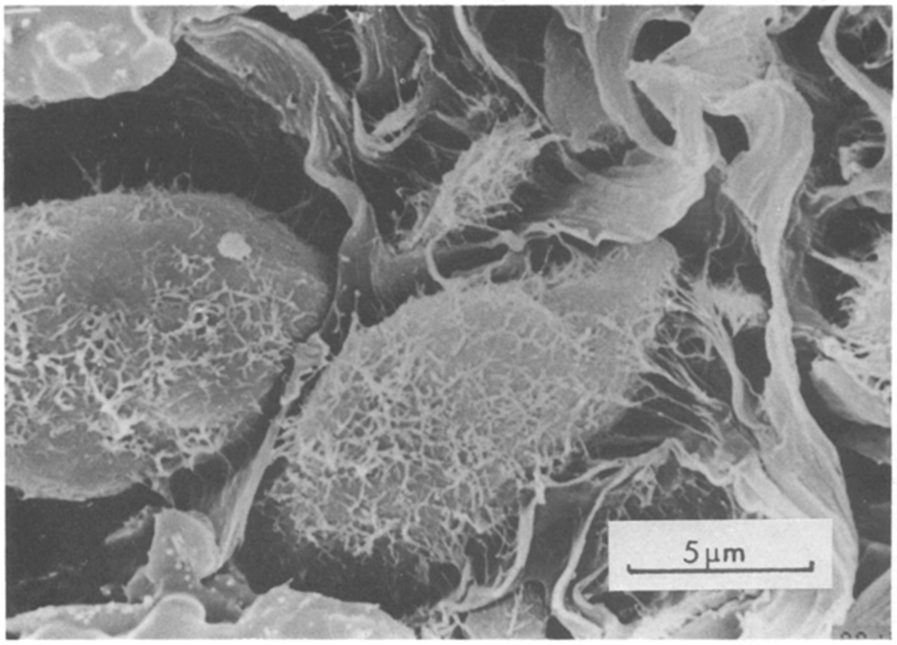

Figure 8 Sepiolite particles on fracture surface of polypropylene–40% sepiolite moulding, showing adhesive connections to the surrounding polymer.

stress distributions and the changes that occur in them on ageing are more complex with talc-filled grades than with those containing sepiolite, and can be expected to cause the talc-filled grades to be more prone to post-moulding distortion.

Despite several attempts to investigate the influence of residual stresses on fracture, the relationship has not been demonstrated clearly. This is because most actions taken to alter the residual stress level will also alter such important characteristics as molecular orientation and free volume, both of which can themselves be expected to have a marked influence on fracture. In as-moulded form most injection-mouldings possess tensile residual stress in the interior and compressive stresses near to the surface [22–24]. This is generally expected to be beneficial because it will tend to inhibit crack growth from a surface flaw, probably the most common type of field failure. In a notched impact test this is no longer the case, however, for the notch will usually penetrate the region near the surface that is in compression. In the impact tests conducted in the present work the root of the notch is in a region that is tensile over a substantial, centrally located fraction of its length, but is in a compressive region near to its edges (Fig. 11). On stressing the specimen (as during the test) the most severe conditions are experienced near the centre, in the plane strain region [25, 26]. Thus the presence of pre-existing tensile residual stresses here will enhance failure, reducing the fracture energy. Conversely, annealing was found to reverse the sense of the residual stresses [21] and if compressive stresses are present in the centre, this will reduce the potency of the bending deformation during the notched impact test and will result in higher energy dissipation.

Although residual tensile stresses are present near the surface these are apparently not sufficient to cause the part to fail in a brittle fashion nor to modify

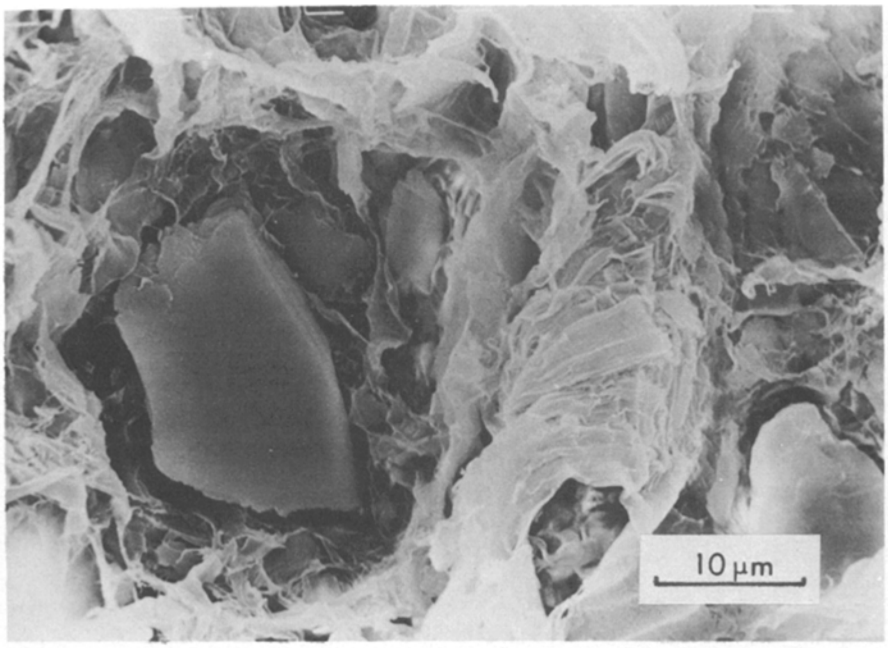

Figure 9 Talc particles exposed by fracture in polypropylene–40% talc moulding, showing no evidence of adhesion to the surrounding polymer.

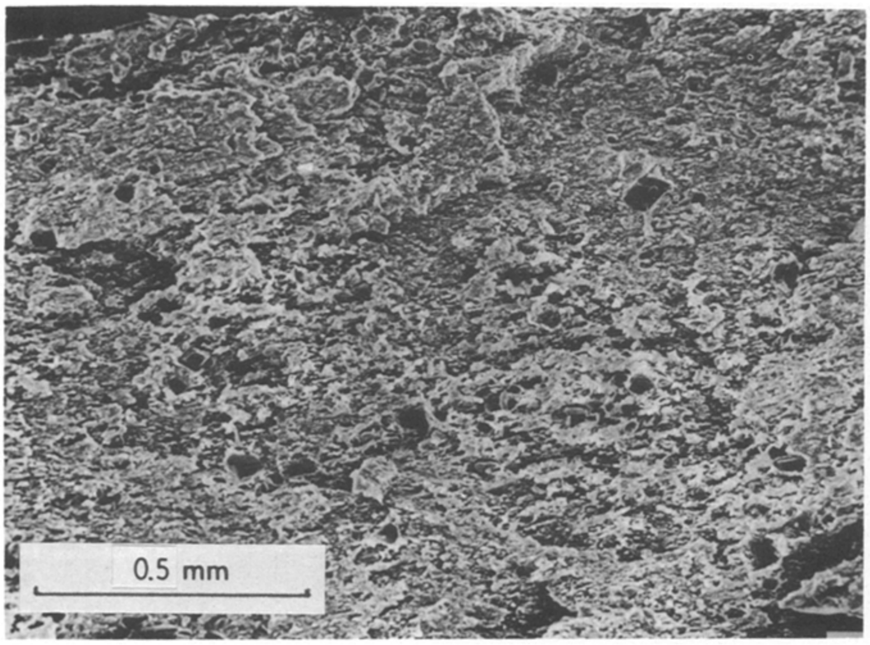

Figure 10 Fracture surface of polypropylene–40% talc specimen that had been annealed before testing.

the overall failure mechanism during these tests. Thus there may be a correlation between the impact tests results and residual stresses, but it must be remembered that annealing may also cause a change in crystallinity and/or a change in orientation, and possibly, a change in the packing within the non-crystalline phase. Any of these changes might also change the fracture behaviour, and the apparent correlation with changes in residual stress distribution cannot be taken as proof that there is a connection.

The shrinkage data seem to indicate some superiority of the talc-filled grades over the sepiolite-filled materials, but these simple tests may disguise a tendency for non-uniform shrinkage that is more prevalent in the talc-filled materials. The annealing shrinkage is less sensitive to temperature in the sepiolite compounds than in the talc compounds so that, if properly allowed for when dimensioning the mould cavity, sepiolite-filled polypropylene should produce articles which retain their dimensions more consistently over a range of elevated temperatures than corresponding talc-filled grades.

5. Conclusions

The studies presented here show that sepiolite can be used as a reinforcement in polypropylene compounds. They have good moulding properties and the dark brown colour is no worse than that obtained with other particulate-filled polypropylene compounds of this kind. The mechanical properties are much better than for the unfilled material, especially the flexural modulus and strength. The enhancement is not as high as in the case of talc-filled polypropylene, but the properties are adequate for many applications, and the cost reduction is, of course, beneficial too.

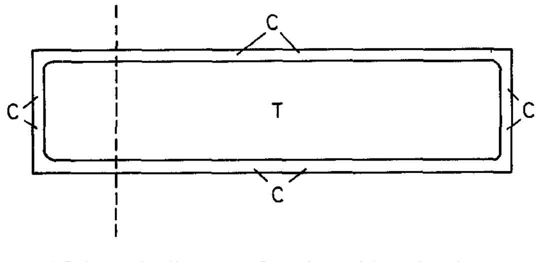

Figure 11 Schematic diagram of section of bar showing the most common location of tensile stresses (T) and compressive stresses (C) in the bar axis direction. The broken line indicates the position of the notch root used for impact tests.

The impact strength decreases as a result of the introduction of rigid particles into the polymer matrix. This can be improved by adding to the compound an impact modifier, but this may decrease other mechanical properties.

Although sepiolite-filled polypropylene compounds showed greater mould shrinkage and annealing shrinkage than equivalent talc-filled grades, they should be less prone to post-moulding dimensional changes. Their overall shrinkage is in line with values quoted for commercial grades of filled polypropylene [27].

Acknowledgements

E. Morales is grateful to the Consejo Superior de Investigaciones Cientificas, Spain, for the provision of a postdoctoral fellowship. We also wish to thank ICI, Wilton for the provision of the polypropylene and talc-filled compound, and Steetley Minerals Ltd, Worksop, for supplying the sepiolite.

References

1. P. F. BRIGHT, R. J. CROWSON and M. J. FOLKES, *J. Mater. Sci.* **13** (1978) 2497.
2. P. F. BRIGHT and M. W. DARLINGTON, *Plast. Rubb. Proc. Applics* **1** (1981) 139.
3. M. W. DARLINGTON and P. L. McGINLEY, *J. Mater. Sci.* **10** (1975) 906.
4. M. W. DARLINGTON, P. L. McGINLEY and G. R. SMITH, *ibid.* **11** (1976) 877.
5. M. J. FOLKES and D. KELLS, *Plast. Rubb. Proc. Applics* **5** (1985) 125.
6. F. J. LOCKETT, *Plast. Rubb. Process* **5** (1980) 85.
7. J. C. MALZAHN and J. M. SCHULTZ, *Compos. Sci. Tech.* **25** (1986) 187.
8. S. F. XAVIER, D. TYAGI and A. MISRA, *Polym. Compos.* **3** (1982) 88.

9. D. CAMPBELL and M. M. QAYYUM, *J. Polym. Sci., Polym. Phys. Edn* **18** (1980) 83.
10. D. CAMPBELL and J. R. WHITE, *Angew. Makromol. Chem.* **122** (1984) 61.
11. A. GARTON, S. W. KIM and D. M. WILES, *J. Polym. Sci., Polym. Lett. Edn* **20** (1982) 273.
12. T. KOWALEWSKI and A. GALESKI, *J. Appl. Polym. Sci.* **32** (1986) 2919.
13. K. BRAUNER and A. PRESINGER, *Mineralog. Petrogr.* **6** (1956) 120.
14. J. L. ACOSTA, E. MORALES, M. C. OJEDA and A. LINARES, *J. Mater. Sci.* **21** (1986) 725.
15. *Idem, Angew. Makromol. Chem.* **138** (1986) 103.
16. J. L. ACOSTA, M. C. OJEDA, E. MORALES and A. LINARES, *J. Appl. Polym. Sci.* **31** (1986) 1869.
17. *Idem, ibid.* **32** (1986) 4119.
18. A LINARES, E. MORALES, M. C. OJEDA and J. L. ACOSTA, *Angew. Makromol. Chem.* **147** (1987) 41.
19. J. L. ACOSTA, J. P. VIGO, M. C. OJEDA and A. LINARES, *Rev. Plast. Mod.* **354** (1985) 735.
20. M. FUJIYAMA and S. KIMURA, *Kobunshi Ronbunshu* **32** (1975) 581 (English Edn **4** (1975) 764) in press.
21. E. MORALES and J. R. WHITE, *J. Mater. Sci.*
22. B. HAWORTH, C. S. HINDLE, G. J. SANDILANDS and J. R. WHITE, *Plast. Rubb. Proc. Applics* **2** (1982) 59.
23. A. I. ISAYEV and D. L. CROUTHAMEL, *Polym. Plast. Technol. Eng.* **3** (1984) 177.
24. J. R. WHITE, *Polym. Test* **4** (1984) 165.
25. J. G. WILLIAMS, "Stress Analysis of Polymers" (Ellis Horwood, Chichester, 1980).
26. *Idem*, "Fracture Mechanics of Polymers" (Ellis Horwood, Chichester, 1984).
27. ICI Procom Technical Service, Data Summary PM 63 (1986)

Received 4 November 1987
and accepted 1 March 1988