JOURNAL OF MATERIALS SCIENCE **36** (2001) 2977–2990

Comminuted thermoset recyclate as a reinforcing filler for thermoplastics

Part II *Structure—property effects in polypropylene compositions*

C. E. BREAM, P. R. HORNSBY
Wolfson Centre for Materials Processing, Brunel University,
Uxbridge, Middlesex, UB8 3PH, UK

Well characterised dough moulding compound (DMC) and woven glass fibre-reinforced phenolic (GWP) recyclate fillers have been investigated as reinforcements for polypropylene. Consideration is given to the use of treatment systems to enhance fibre-matrix interfacial bonding and mechanical properties. Using a combination of grafted polymer and coupling agent, significant increases in recyclate/polypropylene composite properties are possible, the levels obtained critically depending on glass fibre content. The role of the recyclate particles in initiating failure is discussed, as is the influence of compounding route on recyclate integrity and molecular mass changes to the host polymer matrix. © *2001 Kluwer Academic Publishers*

1. Introduction

Characterisation of dough moulding compound (DMC) and glass woven phenolic (GWP) thermoset recyclate feedstocks was considered in an earlier communication [1]. These systems had very different forms and levels of glass fibre reinforcement and resin thermal stabilities, which are expected to influence their reinforcing potential, in addition to their behaviour during melt processing with thermoplastics.

This paper considers the application of these well-characterised thermoset recyclate fillers as reinforcements for polypropylene. Particular emphasis is given to the use of treatments to enhance fibre-matrix interfacial bonding and hence mechanical properties and to the influence of the compounding route on recyclate integrity and stability of the host polymer matrix.

2. Experimental

2.1. Materials

2.1.1. Fillers and matrix material

Fibre-reinforced dough moulding compound and woven glass reinforced phenolic resin composites, both derived from manufacturing waste, were used after suitable comminution. Size reduction and characterisation procedures were described in a previous communication [1].

Some polypropylene compositions contained only calcium carbonate (Fordacal 10-Fordamin Co) for use as a particulate control. This grade is 99.4% pure and has a density of 2710 kg m^{-3} and a mean particle size of 10 μm [2].

A commercial grade of glass-reinforced polypropylene (BASF Procom GC30S401) was also selected for comparison. This in an elastomer-modified material containing 30 wt% of coupled short glass fibres.

A heterophasic form of polypropylene copolymer (Stammylan P 56M10-DSM) was chosen as the matrix material. This is a rubber toughened grade containing a 10% dispersion of EPR particles with a melt flow index of 6.2 dg/min (2.16 kg, 230°C).

2.1.2. Treatment system

A two-component treatment package was used to promote recyclate/matrix interfacial bonding. This comprised functionalised polypropylene in combination with an organofunctional silane.

Maleic anhydride functionalised polypropylene (Exxcelor PO 1015 Exxon) was selected as the copolymer, containing 0.4 wt% of chain grafted maleic anhydride. This had a melt flow rate of 22 dg/min (190°C, 1.2 kg).

The silane coupling agent (VS142—OSI Specialities) comprised a 40% solution of a gamma-aminopropyltriethoxy silane ($H_2N(CH_2)_3Si(OC_2H_5)_3$).

For some of the work the silane was supplied in masterbatch form (Comadd DSPP25-A1100—Brugg Compound). This was prepared from porous polymer granules impregnated with 25 wt% gamma-aminopropyltriethoxy silane by tumble blending, with capillary action controlling the uptake and dispersion of the silane.

FTIR analysis of this carrier polymer suggested that it was a blend of polypropylene and ethylene-vinyl acetate copolymer. The melt flow index of the impregnated granules was found to be 6.4 g/10 min (230°C, 2.16 kg).

2.2. Preparation and processing of polypropylene/recyclate compositions

Compounding was undertaken using a 40 mm screw diameter co-rotating twin-screw extruder.

The thermoplastics matrix was added at the intake zone, using a volumetric single screw feeder. The recyclate feedstock was added either at the intake zone, after tumble blending with the matrix granules, or by down-stream feeding into the melt, using a K-Tron Soder twin screw feeder. In some experiments silane coupling agent was drip-fed directly into the extruder via a feed port at 0.3 L (where L is the overall length of the screw), using a burette. The resulting compound was die-formed into strands, cooled in a waterbath, then pelletised.

The compounded materials were dried in a hot air circulating oven for 8 h at 80°C, then moulded into tensile test bars (BS 2782: Method 322, test piece 1A) using a Demag D150 NCIII-K injection moulding machine fitted with a 45 mm diameter general purpose screw.

2.3. Characterisation of compositions

The characteristics of the recyclate feedstocks used were reported in an earlier communication [1]. However it is important to note that during compounding the thermoset reinforcement undergoes further comminution. This leads to a change in both its particle shape and size distribution in the ultimate compound.

The recyclate loading in the filled thermoplastic materials was confirmed by ashing samples cut from the central sections of tensile test bars. These were heated at 850°C for 4 hours to burn off the polymer and ensure that the calcium carbonate filler had fully calcined, leaving a residue containing glass fibres, alumina and calcium oxide. After cooling to below 100°C, the ashed samples were placed in a desiccator to restrict the uptake of moisture. After 24 hours these were weighed and their inorganic content determined. Allowance was made for the loss in weight associated with the conversion of calcium carbonate and aluminium hydroxide to their oxide forms.

Fibre-length distribution was measured in compound granules and in injection moulded material using previously reported ashing and image analysis procedures [1].

The melt flow index of the filled and unfilled materials was evaluated in accordance with BS 2782: Method 720A. Measurements were performed at 230°C using a 2.1 mm diameter die and a 2.16 kg load.

Molecular weight measurements were undertaken by gel permeation chromatography (GPC) at RAPRA Technology Ltd using 1,2-dichlorobenzene solvent. The accuracy of this technique was estimated to be ±5%.

2.4. Determination of mechanical properties

Tensile properties were measured according to BS 2782 Method 320C using a cross-head speed of 5 mm/min. Before testing, injection moulded samples were conditioned at 50%RH (23°C) for a minimum of 48 hrs prior to testing. An average of ten measurements was taken.

Modulus measurements were carried out using a 50 mm gauge length extensometer at a test rate of 1 mm/min. Modulus was determined from the initial gradient of the stress/strain graph. The one exception to these test conditions was for the elongation at break for the unfilled materials. As these coupons did not fracture at 5 mm/min, the test rate was increased to 100 mm/min once the materials had started to neck.

Material toughness was measured using a Ceast Torino impact test machine in accordance with BS 2782 Method 359. Tests were carried out on Type 1 notched Charpy specimens (80 mm × 10 mm × 4 mm) cut from the gauge length of moulded test bars. These were notched with a single edgewise type A notch (2 mm deep with a 0.25 mm notch base radius). Impact strength determination was undertaken on ten samples using a span of 62 mm and a 2J hammer, dropped from an angle of 150°. For the GWP laminate a Type 2 specimen was used, with a 52 mm span and a 4J hammer. As for the tensile and modulus determinations test specimens were conditioned in the test environment for a minimum of 48 h prior to testing.

2.5. Microstructural characterisation

The microstructure of the recyclate composites was examined using a combination of light and electron microscopy. Optical samples were examined directly from fractured tensile pieces, whilst for SEM, samples were first sputter coated with gold to form a conductive layer.

Some analysis was also carried out on samples which had been fractured at temperatures below the brittle-ductile transition temperature for the material, by immersing the test sample in liquid nitrogen for five minutes.

The dispersion of the recyclate particulates in the polypropylene composites was evaluated by cutting longitudinal and transverse sections, taken from the centre of the gauge length of test specimens. These were then ground and polished to 1 μm.

The dispersion of the EPR elastomeric phase in the polypropylene matrix was examined by etching in boiling *n*-heptane for 90 seconds.

3. Results and discussion

3.1. Influence of compounding procedure on fibre length distribution

Preliminary trials showed that a significant level of fibre attrition occurred during processing, with 90% arising during the compounding stage. This is in agreement with the findings of Franzen *et al.* [3], who report that the degree of fibre breakage can be reduced by feeding the fibres directly into the melt. This removes polymer granule—fibre interactions, which have been identified as the primary cause of fibre breakage.

DMC recyclate was selected in order to study the effects of fibre attrition during compounding, since it has a lower strength than GWP and was expected to show greater difference between primary intake addition and melt feeding. The effect of feed position on fibre breakage was assessed by measuring fibre length distributions after both compounding and moulding stages.

It should be noted that commercially, short fibre reinforced thermoplastics are normally produced by downstream feeding of the fibres into the melt at around 0.75 L. This can lead to a 20% increase in the number and 45% increase in the weight average fibre lengths [3]. In these trials, the 0.3 L feed position was selected, as recyclate size reduction, as well as fibre wet-out and dispersion, were requirements during compounding, necessitating a longer residence time in the extruder.

It was observed that relative to primary intake feeding, melt feeding led to a small increase in fibre length, the number average increasing by 7% and the weight average by 3%. However, injection moulding limited the benefit obtained by melt feeding, reducing the number average to 244 μm and the weight average to 350 μm. This result is unexpected and suggests that recyclate-granule interaction is not the primary fibre breakage mechanism.

Wolf has identified the mechanisms of fibre breakage in long fibre thermoplastics during injection moulding [4]. One of the claimed benefits of long fibre reinforced thermoplastics is that a proportion of the fibre bundles remain intact during processing. This protects the fibres from attrition in the melt and leads to a significant number of fibres remaining at the high end of the distribution. Similar behaviour might be expected from the thermoset recyclate materials, with the thermoset resin providing protection for the fibres.

In the initial stages of processing, damage arises from granules being squeezed between the screw flight and the edge of the intake zone and by granule-granule interactions, resulting in a reduction in granule length by ≥50% [4].

However analysis of the PP/DMC fibre length distributions suggests that fibres are broken by the shear forces generated at the barrel wall, the flight-barrel clearance and the screw root. These mechanisms are reported to dominate under the high stress conditions used in these trials, leading to fibre length distributions similar to short fibre materials. This is confirmed in Fig. 1, which shows the fibre length distributions for the two recyclate materials are very similar to moulded short glass fibre-reinforced polypropylene.

Fig. 1 also shows that for the PP/GWP composition long fibres have been retained in the moulded material, leading to a 10% increase in the weighted average fibre length over the commercial short fibre variant. However, inspection revealed fewer recyclate bundles are retained in the moulded PP/DMC, than in the PP/GWP material.

This difference in degree of attrition between the two filler variants is considered to originate from the inherent characteristics of the recyclates. In this regard, three aspects are particularly significant; the fibre loading level, the physical nature of the reinforcement and the thermal stability of the thermoset.

As discussed later, thermal degradation and loss in strength of the recyclates is minimal at polypropylene processing temperatures and is expected to have only limited effect on the integrity of these feedstocks. Considering the physical form of the materials, the GWP feedstock is predominately made up of fibre tows. These have a high aspect ratio and contain densely packed fibres aligned parallel to the 'granule' axis. Hence these can be considered similar to long

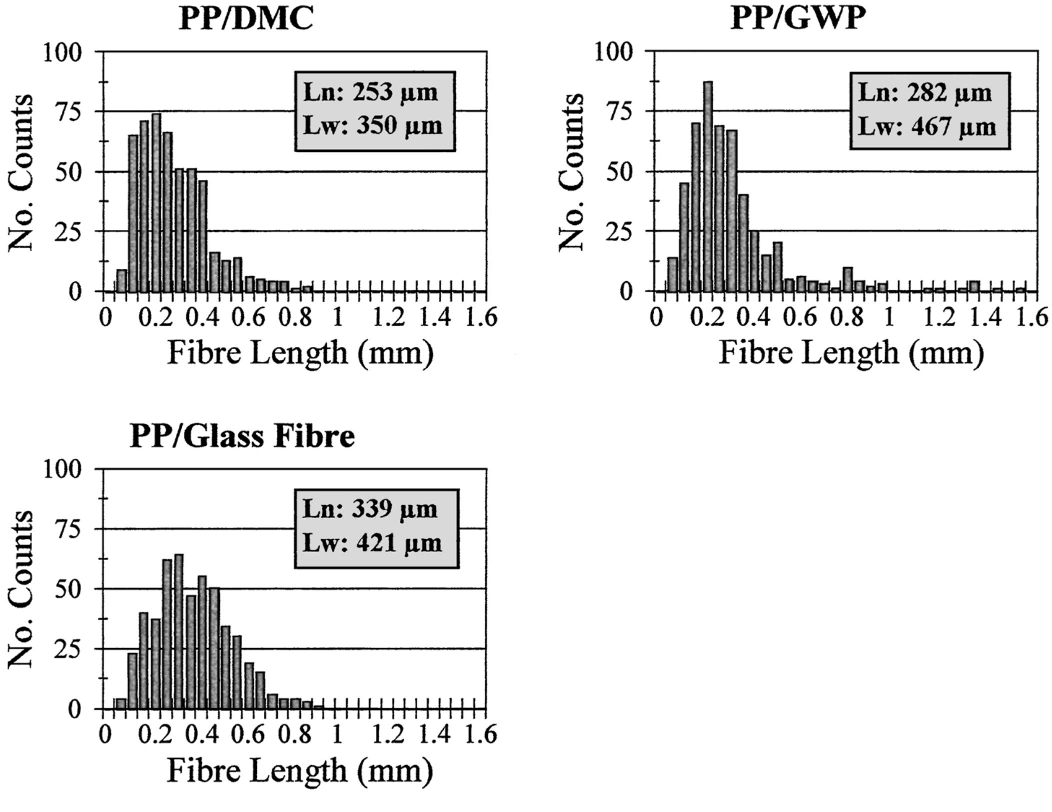


Figure 1 Influence of recyclate type on fibre length distribution (Ln—number average length; Lw—weight average length).

TABLE I Influence of compounding and recyclate on the molecular weight of the polypropylene matrix

	MFI (g/10 min)	Mw Mean	Mw SD	Mn Mean	Mn SD	Poly-dispersity
PP (as received)	6.8	458,500	7,200	32,600	3,600	14.2
PP (compounded)	10.8	324,500	5,200	30,500	800	10.6
PP/$CaCO_3$	15.7	262,400	2,600	26,600	2,800	10.0
PP/DMC	8.6	383,600	5,100	33,100	1,200	11.6
PP/GWP	3.5	480,500	1,100	32,500	2,000	14.8

fibre-reinforced thermoplastics granules. In contrast, the DMC feedstock is more like short fibre-reinforced thermoplastics, containing shorter randomly orientated fibres. The lower fibre loading and random dispersion of the DMC fibres, results in particulates with a lower structural integrity, which are more prone to breakage.

Considering these differences in recyclate performance, the similarity between the observed fibre length distributions is surprising, the DMC material exhibiting 87% of the GWP's mean fibre length (number average). It is likely that the high shear condition experienced in the twin-screw extruder dominate the size reduction process, overriding more subtle differences in recyclate characteristics highlighted above.

3.2. Influence of recyclate on polypropylene stability

Previous analysis of the thermal stability of the recyclate materials revealed that both materials were relatively stable at the processing temperature used for polypropylene (∼220°C). The GWP exhibited a 2% weight loss caused by the evolution of moisture and residual monomers [1]. The DMC yielded a slightly higher weight loss (3%), caused by disassociation of the ATH and degradation of the polyester.

The extent of polypropylene degradation has been determined by measuring changes in the melt flow rate and the molecular weight distribution of the polymer.

It is apparent from Table I that passage through the extruder with and without the incorporation of calcium carbonate filler causes a significant level of degradation. This molecular breakdown is also reflected by an increase in melt flow rate, the reduction in chain length reducing molecular entanglement and melt viscosity. Examination of the molecular weight distributions revealed that the majority of the reduction is caused by degradation of molecules at the high end of the distribution. This degradation mechanism has not been investigated, but is believed to thermally induced, being particularly pronounced in the case of the filled composition, where higher shear stresses are developed in the melt.

However, the addition of the recyclate materials leads to unexpected behaviour (Table I), the DMC exhibiting a higher molecular weight and a broader distribution than the $CaCO_3$-filled material, giving comparable results to the unfilled compounded polypropylene. More significantly however, processed polypropylene containing GWP recyclate leads to a retention of the molecular weight distribution to a level seen in the unprocessed matrix. This implies that the recyclate fillers are stabilising the host matrix.

TABLE II Influence of melt compounding and the addition of recyclate on the stability of the polypropylene matrix

	Degradation Onset Temperature (°C) Mean	SD
PP (as received)	241.0	1.3
PP (compounded)	223.8	3.8
PP/$CaCO_3$	226.3	0.7
PP/GWP	243.2	1.6

This hypothesis is supported by an increase in the degradation onset temperature, measured by TGA. The GWP filled material (PP/GWP) exhibiting a comparable onset temperature to the uncompounded matrix and a 15°C increase over the $CaCO_3$ filled and unfilled materials (Table II). The onset temperature of the DMC filled material (PP/DMC) could not be evaluated, as degradation of the DMC above 190°C masked the polypropylene onset temperature (∼220°C).

The stabilisation effect with DMC recyclate is attributed to evolution of water vapour and degradation by-products from the recyclate additives. These volatiles lead to 'foaming' of the melt and result in a reduction in melt and granule densities. This is reflected in the high level of porosity in the compounded granules relative to the $CaCO_3$-filled material, which was pore-free. Foaming has two effects; firstly, a reduced melt density lowers the shear forces generated in the melt and, secondly; the porous granules reduce the injection moulding residence time, from ∼18 min for a fully dense granule, to ∼10 min for the recyclate granules. Both of these factors reduce the heat and shear history of the material and hence, reduce the levels of degradation.

Results for the GWP-containing material suggest a second stabilisation mechanism may exist. In this regard it is shown that quinone methide and related products are formed during the initial stages of phenolic degradation, which are particularly effective at deactivating the alkyl radicals that initiate degradation of polypropylene [5]. The formation of these reactive structures is responsible for the colour change seen on heating above 140°C, giving phenolics their characteristic yellow-brown colour.

3.3. Filler-matrix interfacial bonding

It is apparent from Fig. 2 that, in the absence of treatment, there is no apparent interfacial bonding formed between the recyclates and polypropylene matrix. Accordingly, means for introducing adhesion were

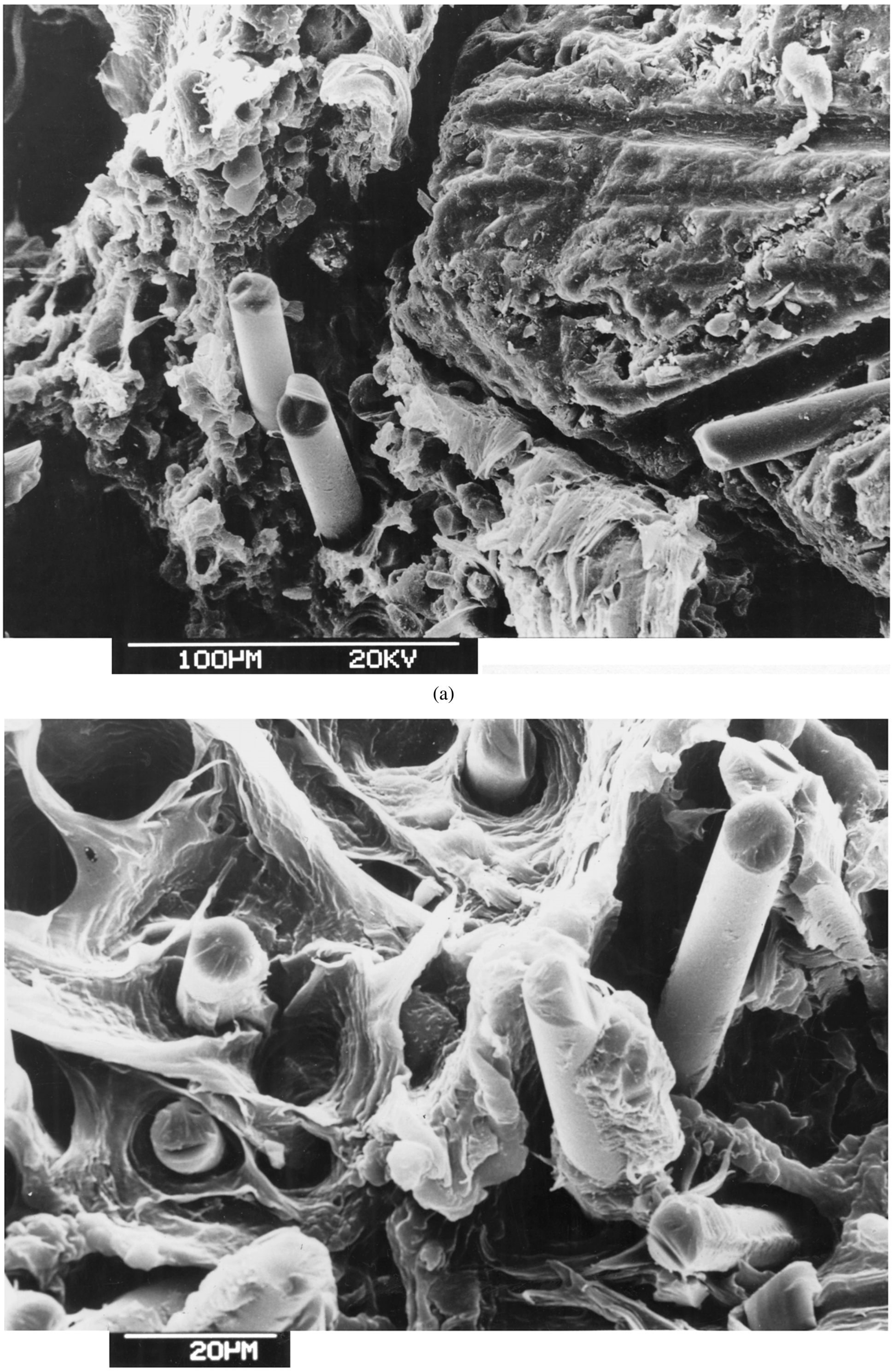


Figure 2 Scanning electron micrographs showing no recyclate matrix interfacial bonding (a) PP/DMC, (b) PP/GWP.

investigated using combinations of aminosilane surface treatment and maleic anhydride matrix modification.

Traditionally, coupling agents are applied to fillers by surface coating prior to compounding. However, with thermoset recyclate, a progressive reduction in particle size occurs during compounding, which creates new and therefore untreated surfaces, potentially leading to uneven treatment and a reduction in composite performance. Consequently, alternative treatment strategies were investigated involving drip feed of the coupling agent directly into the polymer melt and use of a silane masterbatch combined in the polypropylene/recyclate composition.

These two techniques are essentially the same, the coupling agent being dispersed throughout the matrix, enabling treatment of new surfaces as they form. The main differences being the presence of EVA in the masterbatch carrier granule and the nature of the coupling agent. The silane used for drip treatment was prehydrolysed, whilst in the masterbatch, this was not the case.

The main draw-backs of adding the treatment to the melt are that higher levels are required and alcohol and water by-products are formed during processing. However, since both recyclate materials have been found to release water at thermoplastics processing temperatures, the evolution of by-products from the treatment system is not expected to have a pronounced additional effect on processing characteristics, or on mechanical performance of the composite.

The relative effects of these application techniques was established using the DMC recyclate at a 30 wt% filler loading level. Treatment levels of 20 wt% functionalised polypropylene (based on unmodified polypropylene) and 5 wt% silane treatment (based on filler), were selected to be on the high side, to ensure that any interactions could be detected. In the masterbatch experiments, a filler treatment level (5 wt% silane) was obtained by adding 8.4 wt% masterbatch to the matrix. Recyclate loading levels achieved were verified by determining the inorganic content of the materials to ensure that comparable loadings had been obtained. (i.e. between 29 wt% and 31.5 wt% of recyclate).

The performance of the treatment system was assessed, principally, by analysing the tensile strength of the composites, this property being directly related to the interfacial bond strength. Looking at the treatment components in isolation (Fig. 3), it is apparent that use of silane coupling agent leads to little or no strength enhancement, whilst inclusion of functionalised polypropylene results in a 33% increase over the untreated DMC material. However, when used in combination, a strength increase of up to 47% occurs, the extent of improvement depending on the application procedure used.

These changes are reflected in the stress-strain characteristics for these materials (Fig. 4) and the nature of their fracture surfaces. The untreated and coupled materials exhibited matrix yielding, with no sign of bonding to either the fibres or particulates (Fig. 2a). In contrast, the grafted (PPg) and grafted-coupled (PPgc) materials showed brittle fracture, with encapsulation of the pulled-out fibres. These changes are evident in Fig. 5a, with the formation of interfacial bonding inhibiting matrix yielding and reducing strain to failure.

Similar characteristics were achieved with untreated and treated GWP filled material (compare Figs 2b and 5b).

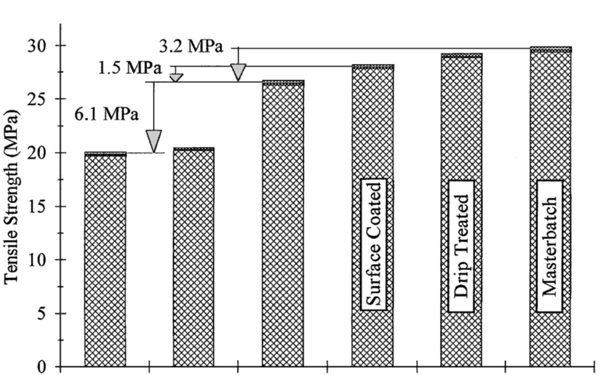


Figure 3 Influence of treatment system and application technique on the tensile strength of PP/DMC: 30 wt% recyclate, 20 wt% grafting and 5 wt% coupling agent. Treatment: c: coupled, g: grafted, gc: grafted-coupled. Treatment technique: sc: surface coated, dt: drip treated, mb: masterbatch.

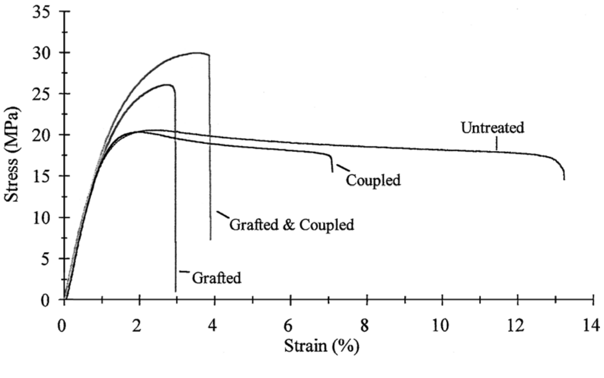


Figure 4 Influence of treatment system on stress–strain characteristics of unmodified and treated forms of PP/DMC recyclate.

3.4. Mechanical properties of recyclate-filled polypropylene composites

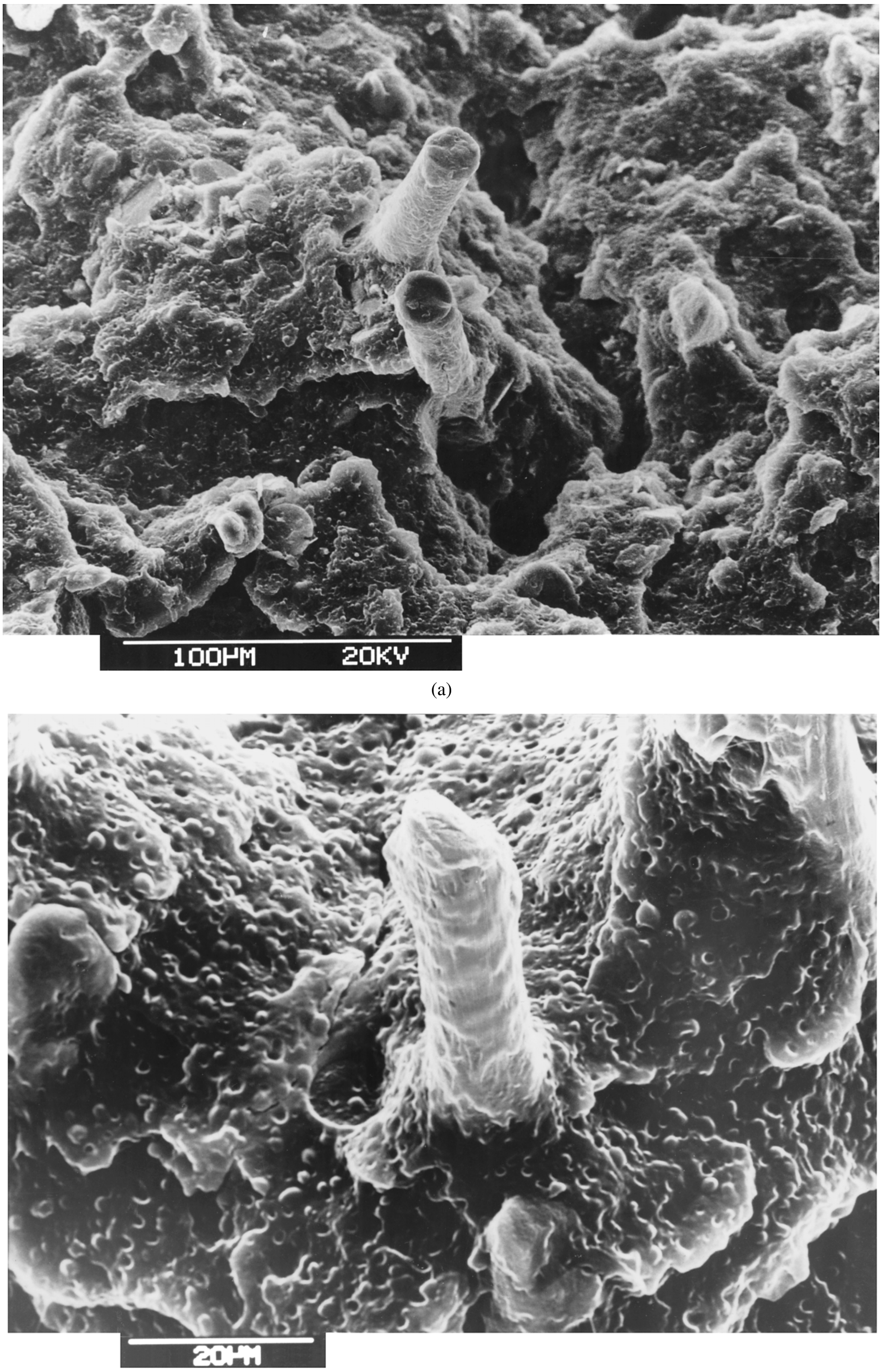
The effect of recyclate type on composite properties was compared in both treated and untreated compositions, in addition to unfilled polypropylene, $CaCO_3$-filled and glass fibre-filled polypropylene controls (Fig. 6). When considering these results it is important to take account of the fact that the GWP recyclate contained 79 wt% and the DMC only 22 wt% of glass fibres. Hence at a 30 wt% recyclate loading this relates to a glass content of 24 wt% for the PP/GWP and 7 wt% for the PP/DMC materials, whereas the calcium carbonate and short glass fibre-reinforced control materials each contained 30 wt% of additive.

Due to their relatively low glass fibre content, results for the DMC filled composites are comparable to those for compositions containing particulate filler. However there are differences in the particle size distributions in the moulded composites, in particular the presence of large particulates (1–2 mm) in the recyclate materials.

It is well documented [6, 7] that an increase in particle size reduces the stress at which dewetting occurs, causing a reduction in mechanical performance. As expected, this behaviour is observed when comparing the $CaCO_3$ and untreated DMC filled materials. The DMC exhibits a 65% reduction in the elongation at break and a 24% reduction in toughness. However, this is not reflected in their respective strength and modulus properties, the DMC achieving the same strength and a 30% increase in tensile modulus relative to the $CaCO_3$-filled material. This implies that the recyclate is behaving more than just a particulate filler, with some of the reinforcing potential of the fibres being realised.

This reinforcing efficiency is increased further by the application of the treatment system. The promotion of interfacial bonding leading to a 50% increase in strength and a 70% decrease in elongation at break. Similar effects are observed with the $CaCO_3$ material, but at a lower level, the treatment increasing the strength and reducing the elongation by only 30%. This suggests that in the recyclate the treatment system promotes bonding, both to the DMC particulates, and also to the reinforcing fibres.

The toughness of particulate filled thermoplastics commonly increases with the development of the interfacial bonding at the filler-matrix interface. This was observed with the $CaCO_3$ filled material, which



(a)

(b)

Figure 5 The effects of treatment system on: (a) PP_{gc}/DMC tensile fracture surface, (b) PP_{gc}/GWP tensile fracture surface.

exhibited a 24% increase in notched Charpy toughness. In contrast however, the DMC material showed no improvement, and only exhibited 75% of the toughness for untreated $CaCO_3$. This behaviour is believed to be caused by the size and limited strength of the DMC particles.

In contrast to the DMC material, polypropylene composites incorporating GWP have a much higher glass content (24 wt%), which is closer to the glass filled control at 30 wt%. This is reflected in the results shown in Fig. 6, which reveals that the treated GWP material lies between the performance of the $CaCO_3$ and glass filled controls. In fact, the untreated GWP outperforms both the treated and untreated particulate filler, in all ways. This confirms that with this recyclate much of the reinforcing efficiency of the fibres is being recovered. Promotion of interfacial bonding further enhances the performance of the recyclate, achieving 72% of the strength and 83% of the toughness of the glass fibre-reinforced control.

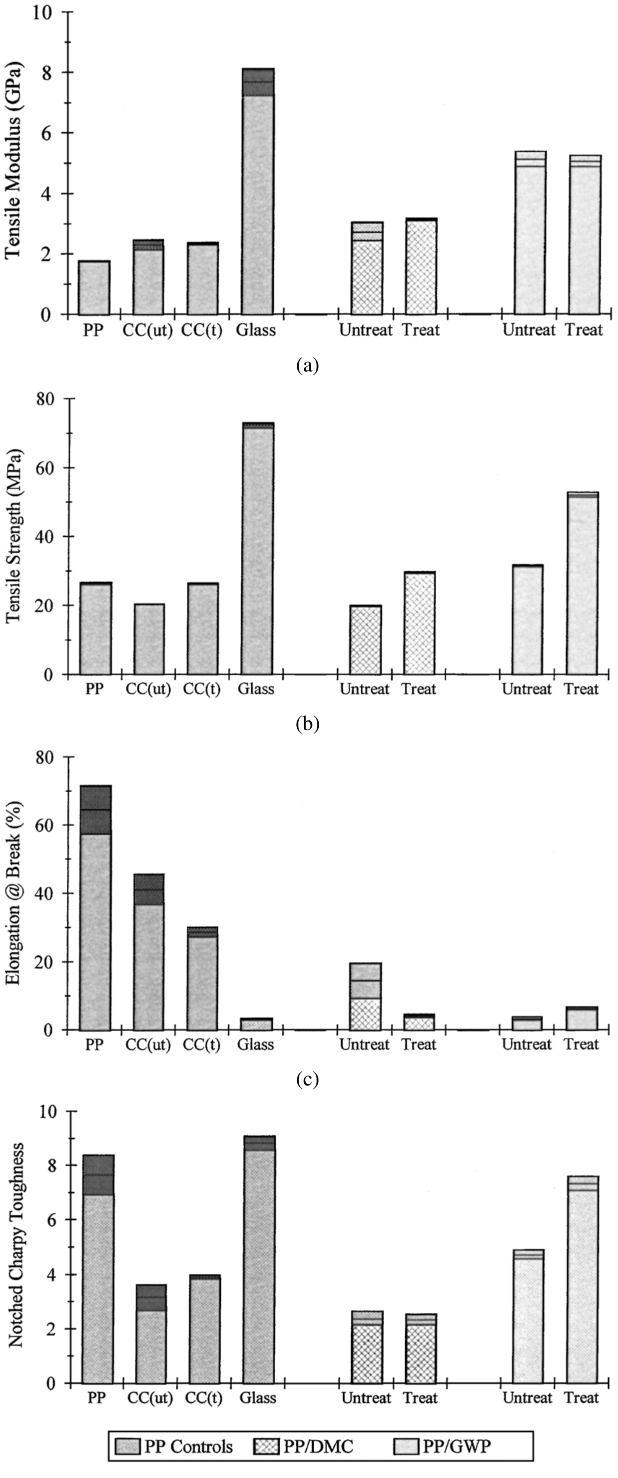


Figure 6 Mechanical properties of polypropylene compositions containing DMC and GWP recyclates, calcium carbonate and short glass fibre-reinforcements. Compositions contain 30 wt% recyclate, glass fibre or filler. (CC(ut): 30 wt% untreated calcium carbonate, CC(t): 30 wt% treated calcium carbonate. Glass: commercial short glass fibre reinforced PP).

3.5. Composite failure mechanisms

To establish the influence of the recyclate particulates on the final composite performance, it is helpful to identify whether they initiate failure and how they interact with propagating cracks. This has been investigated by observing crack initiation and crack growth mechanisms.

Crack initiation has been determined by cryogenic tensile fracture, below the glass transition temperature of the materials. This was achieved by immersing specimens in liquid nitrogen prior to testing. At these temperatures, brittle failure occurs and the fracture surfaces exhibit ridges radiating from the fracture centre. This identifies the crack initiation site and enables the source of failure to be established.

The growth mechanism has been evaluated by inserting a sharp crack in the material, and monitoring how it propagates under load. For this purpose, a 1 mm edgewise Charpy notch was machined in the centre of a tensile test piece, prior to loading to failure under ambient conditions. The sharpness of the notch was assured by also running a razor blade along the notch tip.

3.5.1. DMC recyclate

The low glass fibre content of the DMC composition limits the reinforcing potential of this recyclate, causing it to function more like a particulate than a fibrous filler. The influence of particle size on the mechanical performance of polymer composites has been investigated by Vollenberg and Heikens [8]. They identified, that the strength, stiffness and the stress at which dewetting occurs, are all reduced by an increase in filler particle size, in a system with no matrix-filler interaction. This implies that composite performance is dependent on the maximum particle size of the filler and hence, for a recyclate filler, on the level of feedstock size reduction achieved during processing.

As identified earlier, a high level of recyclate size reduction occurs during processing. However, despite this, a few large particulates, 0.5 mm to 1 mm in diameter, are retained in the final composite. Brittle fracture can result in a fracture surface with 'hackles' radiating from such a particulate (Fig. 7), suggesting that the particulate is the primary stress raiser and is acting as the crack initiator. However, closer inspection of the fracture reveals that the particle initiating failure has also undergone brittle failure (Fig. 8). Furthermore, it is apparent that the cracks formed can be filled with matrix material. For example, the fracture surface seen in Fig. 9 exhibits 'veins' of yielded material running through the particle. Since this is a composite material in its own right, the formation of intra-particle cracks may result from, either the mechanical properties of the DMC recyclate being inherently lower than the recyclate composite, and/or the possibility that the DMC particulates are damaged during the compounding process.

Earlier evaluation of the parent composite from which the recyclate had been obtained, revealed that the mechanical properties were anisotropic, exhibiting a 46.1 MPa longitudinal and a 29.6 MPa transverse tensile strength [1]. This compares to a tensile strength of 29.7 MPa for the treated PP/DMC composite. These results indicate that the transverse tensile strength of the parent DMC composite is reached and, that particulates aligned normal to the load direction can be expected to undergo failure.

A second factor concerns the influence of size reduction and thermal ageing on DMC properties. In terms of thermal ageing, it has previously been shown that at 220°C, thermal degradation is limited, promoting no significant reduction in structural integrity [1].

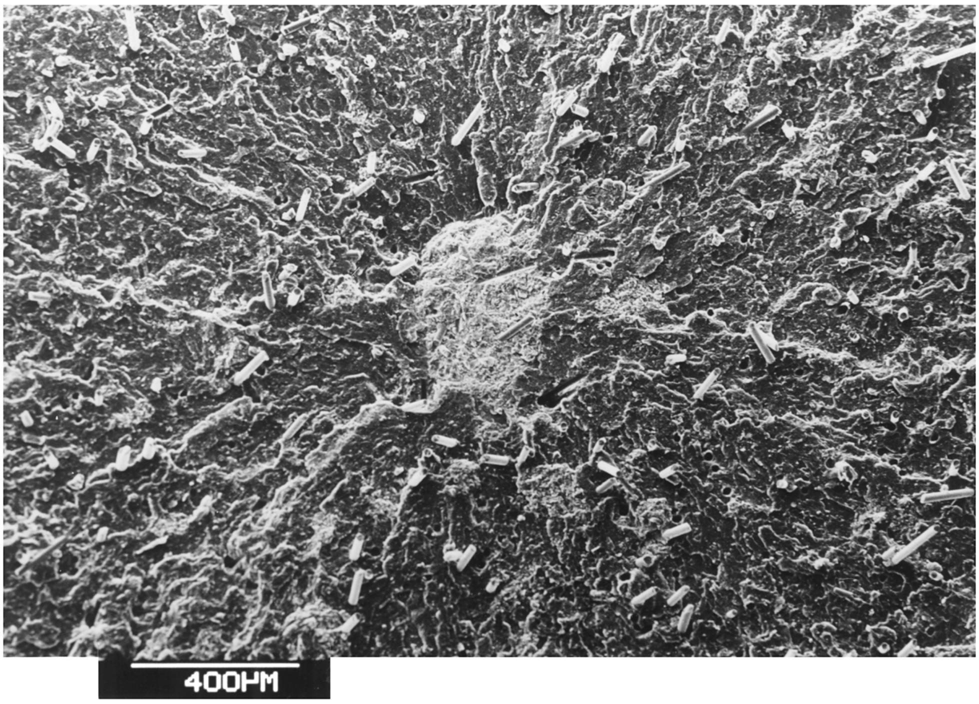


Figure 7 Failure initiation from large DMC recyclate particle in PP/DMC composite (cryogenic fracture surface).

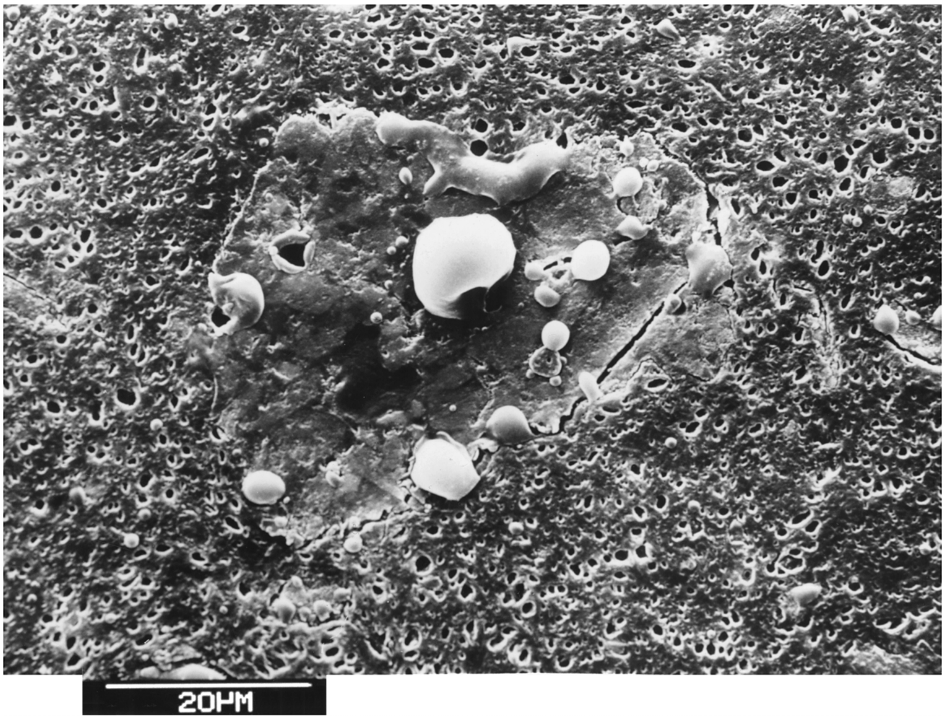


Figure 8 Internal crack in DMC particulate (PPgc/DMC composite, polished and heptane etched).

However, the effect of size reduction, by particulate-particulate, particulate-extruder and particulate-melt interactions, is less clear. Two conflicting mechanisms occur. Firstly, particulate fracture is expected to take place along lines of weakness. Secondly, these interactions may also promote the formation of new cracks, leading to a reduction in performance. In this connection, Schiebisch [9] and Bledzki [10], who investigated the recycling of granulated SMC back into the host composite, have identified that the presence of cracked recyclate particulates may act as failure initiators.

Observation of crack growth has been carried out on both the untreated and treated matrix systems. For the untreated material, the crack propagated by ductile failure across the entire surface. The matrix was seen to yield and cavitate around the DMC particulates and fibres (Fig. 10), demonstrating that the interface offers the least resistance to crack growth and that little or no interfacial bonding has been achieved. It was also noticeable that the particulates were almost fully encapsulated in elastomeric material, suggesting that the elastomer to polypropylene interaction is the weak link.

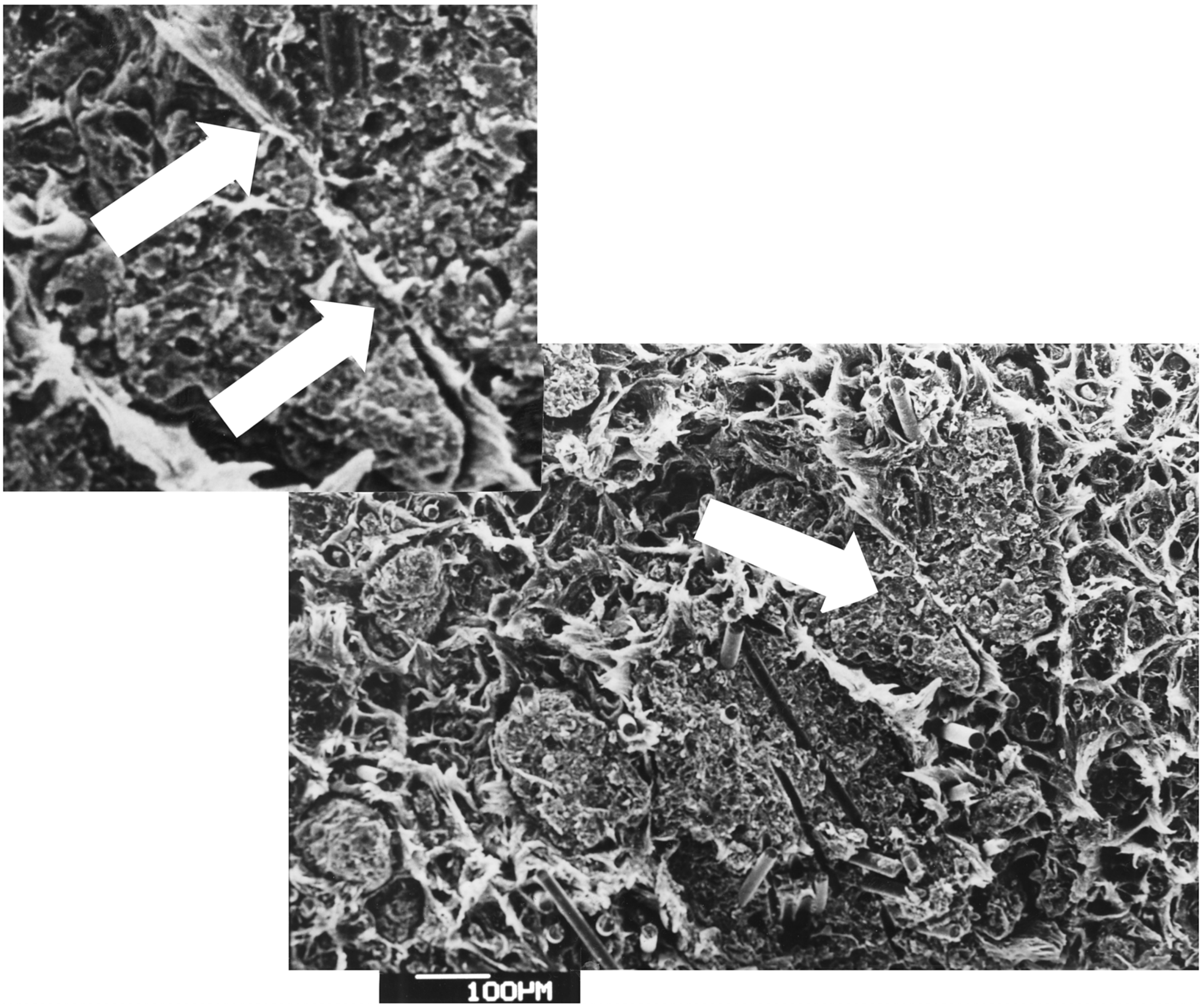


Figure 9 Cracked DMC particulate in PP_{gc}/DMC composite showing evidence of matrix penetration into recyclate cracks and matrix yielding (shown in inset).

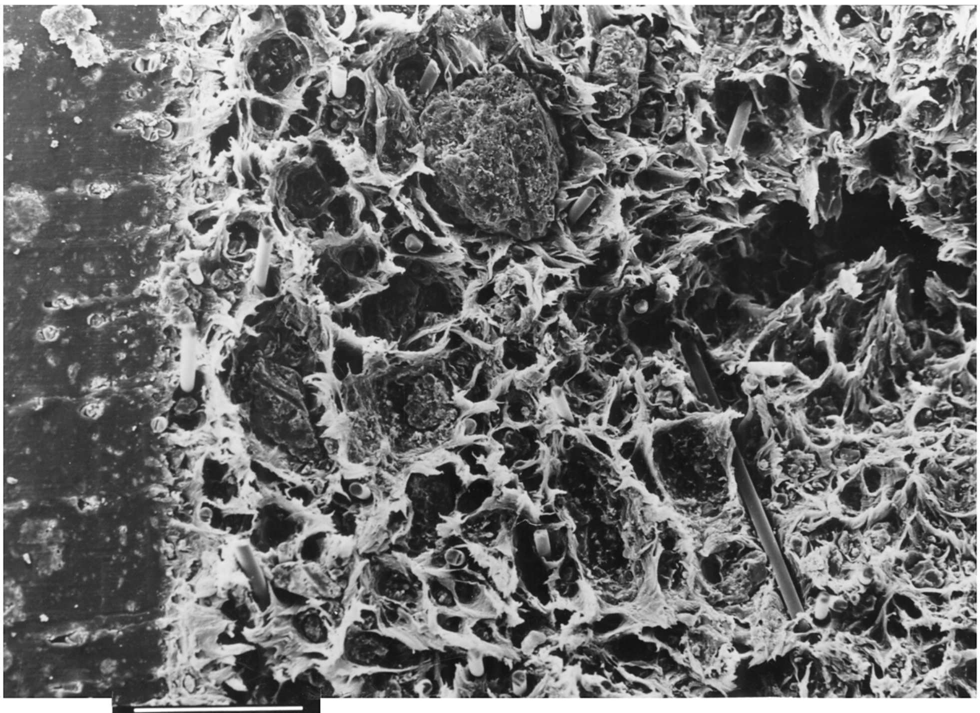
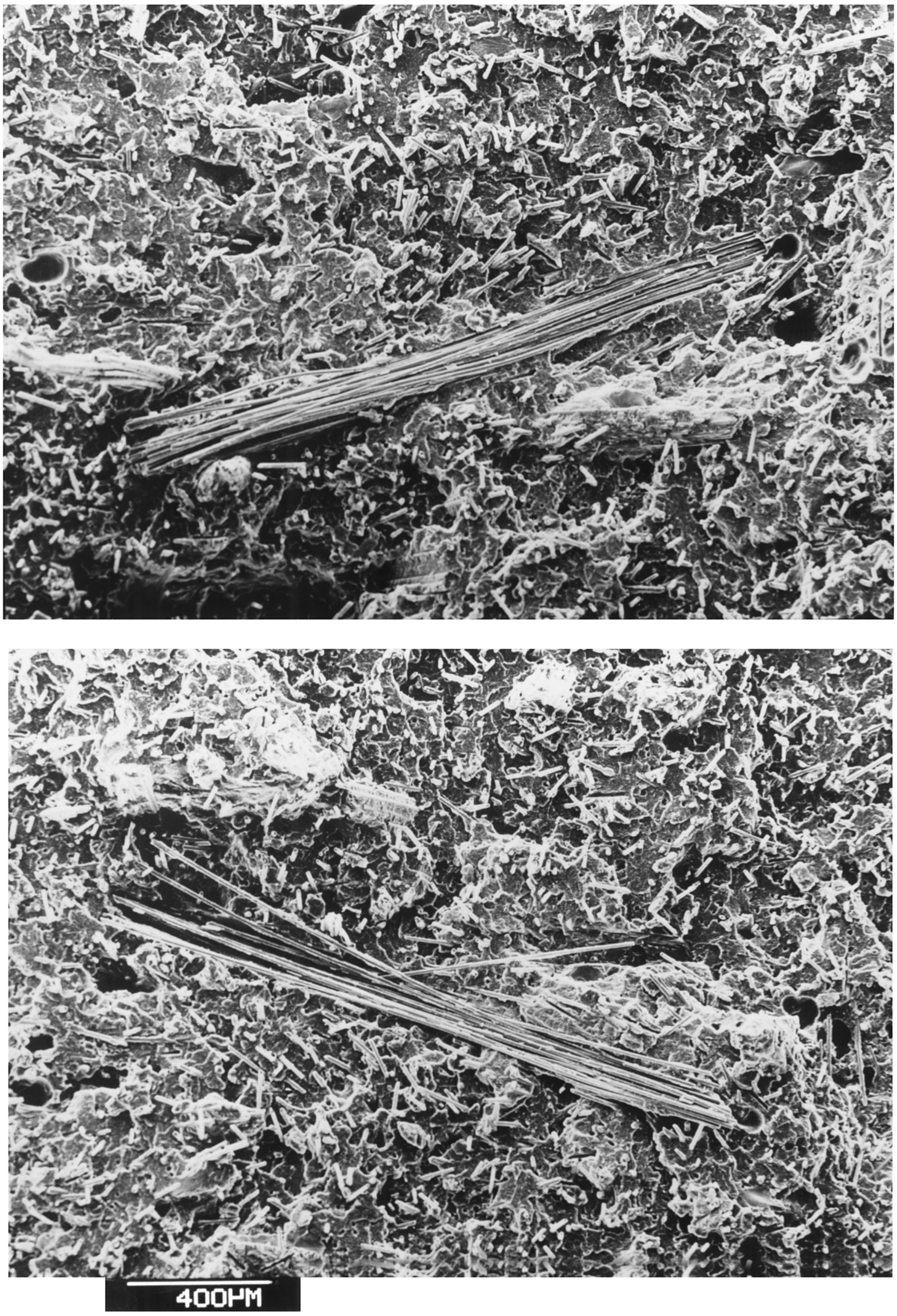


Figure 10 Ductile crack propagation in untreated PP/DMC composite (notched tensile test, with notch shown on left).

Crack growth in the treated material initially developed in a similar way to the untreated composite, with shear yielding, dewetting and no evidence of interfacial bonding. Closer inspection revealed that little elastomer phase was present on the particulates, confirming that the treatment system is preventing rubber encapsulation. The absence of bonding to the fibres and particulates suggest that the interfacial bond strength is still being exceeded in this area. Part way through however, the failure mode changed to brittle. This was caused by the reduction in cross section leading to an effective increase in loading rate, causing the composite to go through its ductile/brittle transition. The fracture surface revealed bonding to both particulates and fibres and no sign of particulate fracture. This implies that the interfacial bonding is offering greater resistance to crack propagation, than the matrix.

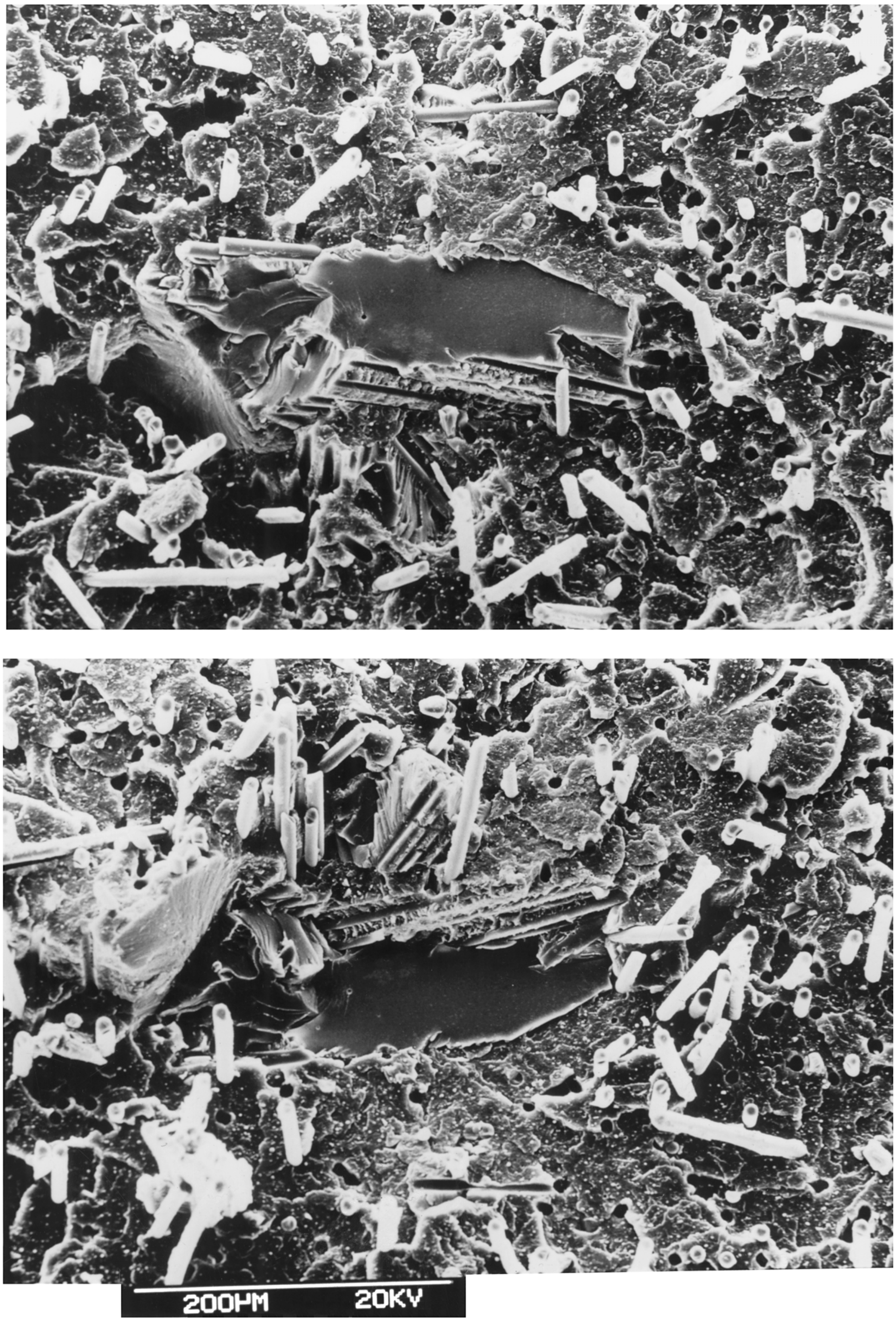
3.5.2. GWP recyclate

Similarly, to the DMC recyclate, a high level particle size reduction continues to occur during compounding and moulding, with GWP-containing materials although a few large platelets, greater than 1 mm, remain in the composite. Cryogenic fracture of the materials again demonstrated that failure can initiate from these larger inclusions. Inspection of the fracture surfaces suggested that failure is initiated by one, or a combination of, brittle failure of large resin rich particulates, transverse tensile failure of fibre bundles (Fig. 11a) and/or large platelets (Fig. 11b) acting as stress raisers.



(a)

Figure 11 Initiation of failure in untreated PP/GWP composites (a) fractured fibre tow, (b) fractured resin particulate. (*Continued.*)



(b)

Figure 11 (*Continued.*)

The first two mechanisms are expected to dominate, as these are believed to originate from cracks within the recyclate feedstock. Inspection of the hammer-milled feedstock indicated the presence of such cracks, running parallel to the fibre tows [1]. Further examination of the moulded test coupons confirms that these defects are retained in the recyclate composite (Fig. 12). If these cracked fibre tows and resin particulates align perpendicular to the applied stress, they will offer little resistance to crack growth and act as failure initiators.

In the case of large platelets, the orientation of the inclusion is not significant as the bidirectional nature of the fibre reinforcement prevents crack growth. In the absence of the first two mechanisms, a third type of failure initiation may occur, characterised by the pull-out of the platelets. These platelets do not appear to fracture having a higher structural integrity.

Crack propagation in the untreated material occurred by ductile failure across the entire surface, the matrix de-wetting and cavitating around the GWP platelets and fibres (Fig. 13). As with the untreated DMC material this suggests that the interface offers the least resistance to crack growth and that little or no interfacial bonding has been achieved.

Crack growth in the treated material initially developed in a similar way to the untreated composite.

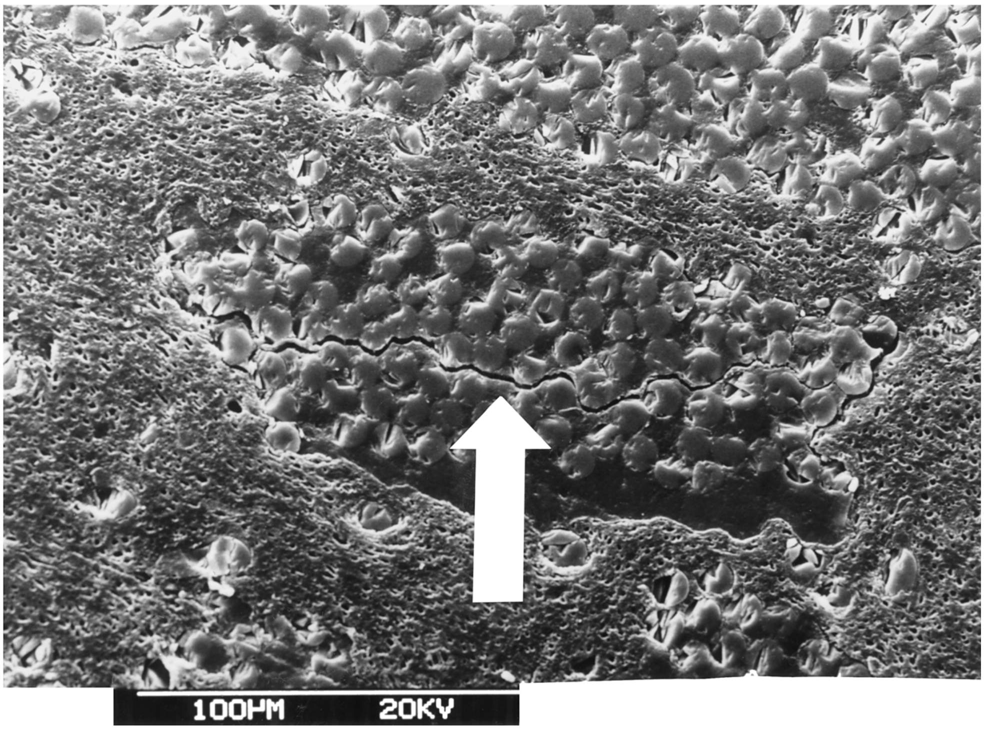


Figure 12 Crack in GWP fibre tow in PP/GWP test specimen (polished and etched).

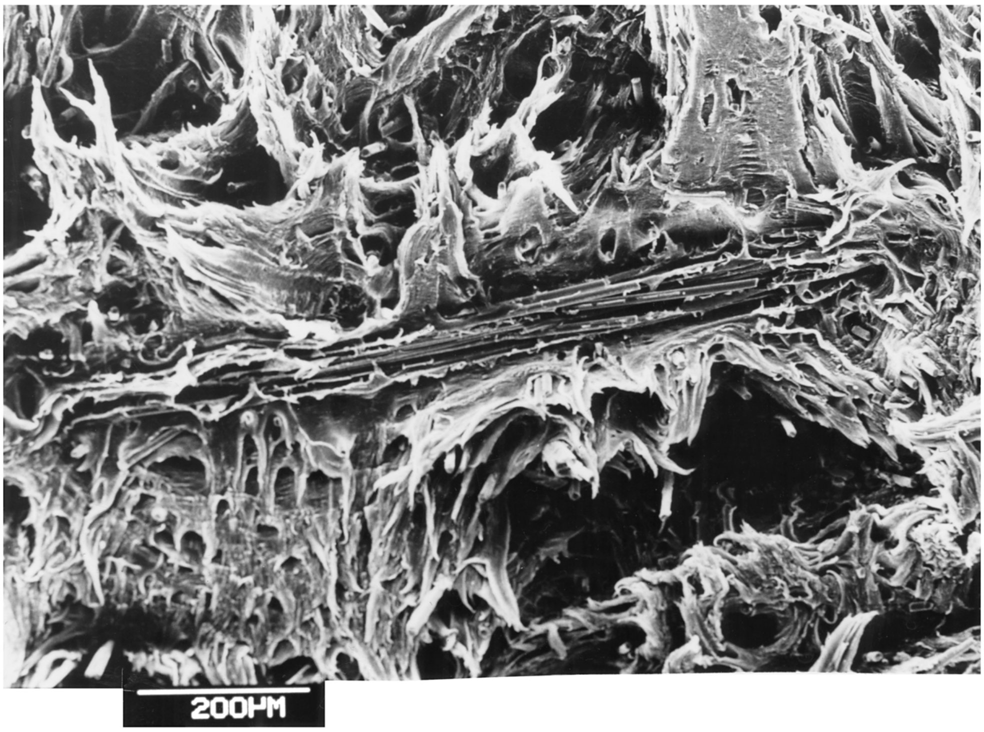


Figure 13 Matrix de-wetting and cavitation around GWP fibre tow in untreated PP/GWP.

However, as with the treated DMC material, the failure mode changes to brittle as the cross sectional area decreases. This brittle fracture surface revealed bonding to both particulates and fibres and no evidence of particulate fracture.

4. Conclusions

Size reduction during compounding is dominated by the generation of shear forces in the melt. Consequently, melt feeding of the recyclate offers little or no benefit over primary intake feeding.

Both the DMC and GWP recyclates have comparable fibre length distributions to commercial short glass fibre-reinforced material.

The higher structural integrity of the GWP recyclate leads to a higher retention of large particulates in the moulded thermoplastic composite. The fibre tows, encapsulated in thermoset resin behave in a similar manner to long fibre reinforced thermoplastics.

Evolution of volatiles, due to thermal degradation of the recyclate, leads to foaming of the melt and a reduction in the level of degradation in the host matrix.

Quinone methides produced during the degradation of the phenolic GWP recyclate, function as a polypropylene melt stabiliser.

A combination of grafting and coupling agent promotes matrix-recyclate interfacial bonding, enabling recovery of the reinforcing ability of the glass fibres.

Increases in composite strength of between 45 and 65% have been achieved using 20 wt% grafting and 5 wt% coupling levels.

Observation of the failure mechanism of the recyclate composites has confirmed that the large recyclate particulates are initiating failure, promoting ductile crack propagation in the matrix. In the untreated matrix these particulates act as stress concentrators; initiating dewetting and cavitation. However, the treated materials behave differently; failure initiating from particulate fracture. In the case of the DMC recyclate; failure occurs by rupture of the DMC. With GWP the higher structural integrity of the recyclate limits the level of particulate fracture, cracks initiating failure in the fibre tows and resin rich particulates.

Acknowledgements

The authors are grateful to the following organisations for their support of this work undertaken through the EPSRC/DTI LINK Structural Composites Programme: Alcan Chemicals, DSM Resins (UK), Balmoral Group, BIP Plastics, British Plastics Federation, Cray Valley, Croxton and Garry, Dow Europe, Filon Products, Ford Motor Company, Jaguar Cars, GKN Technology, Laminated Profiles, Owens Corning, Fiberglas, Permali, Rover Group and Scott Bader. Collaboration with the University of Nottingham is also acknowledged.

References

1. C. E. BREAM and P. R. HORNSBY, *J. Mater. Sci.* **36** (2000).
2. C. E. BREAM, Ph.D. thesis, Brunel University, 1998.
3. B. FRANZEN, C. KLASON, J. KUBAT and T. KITANO, *Composites* **20**(1) (1989) 65.
4. H. J. WOLF, *Polymer Composites* **15**(4) (1994).
5. T. HENMAN, in "Developments in Polymer Stabilisation," edited by G. Scott (Applied Science, London, 1979) Ch. 2.
6. K. MITSUISHI, S. KODAM and H. KAWASAKI, *Polymer Engineering and Science* **25**(17) (1985) 1069.
7. J. VARGA and J. KARGER-KOCSIS, *Composites Science and Technology* **48** (1993) 191.
8. P. VOLLENBERG and D. HEIKENS, *Composites Interfaces* (1986).
9. J. SCHIEBISCH and G. EHRENSTEIN, Society of Plastics Industry 49th Annual Conferences, 7–9 February, 1994.
10. A. K. BLEDZKI, K. KUREK and CH. BARTH, *Kunststoffe German Plastics* **82** (1992) 1093.

Received 20 April
and accepted 26 December 2000