Comminuted thermoset recyclate as a reinforcing filler for thermoplastics

Part I *Characterisation of recyclate feedstocks*

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This, and a subsequent paper consider the re-use of thermoset recyclate as a functional filler for polypropylene. Emphasis is given in this communication to characterisation of feedstocks produced by size-reducing dough moulding compound (DMC) and woven glass phenolic laminate (GWP). The physical properties of these microcomposite particulates have been analysed to determine their size, morphology, structural integrity and thermal stability at polypropylene melt processing temperatures. The DMC recyclate was found to have a glass fibre content of 26^w/o, with fibres up to 10 mm retained in the comminuted particulates. The material is stable up to ∼220°C. The GWP, however comprised 79^w/o of woven glass platelets which are largely preserved in the size-reduced recyclate. The material is thermally stable up to 290°C. © *2001 Kluwer Academic Publishers*

1. Introduction

Much of the published work on thermoset recycling discusses polyester-based sheet and dough moulding compositions (SMC and DMC). In this connection, three main recycling technologies have been considered, involving granulation, incineration and chemical recovery of the polymer matrix [1–6].

Granulation, or comminution, is often a preferred technique [7–9] as the entire material is re-used, and in principle, can be repeatedly recycled. In contrast, only the polymer fraction, which may be as low as 30 wt%, is recovered by incineration [6, 10] and chemical processes [6, 11–13], where typically the inorganic residue, containing the fibre reinforcement and fillers, is either landfilled or used as a low grade aggregate [8].

Size-reduced thermoset recyclate is often used as a filler replacement in the parent composite. The commitment to this route is demonstrated by the formation of dedicated SMC and DMC recycling plants during the early 1990's, including ERCOM in Germany [7, 8, 14–16] and until recently, Phoenix in Canada [17]. These schemes are based on reducing waste to manageable, palm sized, pieces at the component manufacturing stage. This is comminuted, usually by hammer milling, and classified into a range of particle and fibre rich fractions. The recyclate is then either returned to the processor or sold as feedstock.

With size-reduced recyclate, high levels of mixed/contaminated waste (∼90 wt%) can be treated with binders. If the source of this waste is known, then the material can be compression moulded to produce novel medium specification materials. For example, foam/GRP sandwich panels have been recycled to produce a lightweight wood/plastic substitute [18] and reinforced polyurethane has been reclaimed for use as thermally insulating floor panels [19].

With highly contaminated waste, the recyclate/binder can be mixed with aggregate and cast as a cement substitute, to produce products such as fire resistant panels, railway sleepers and park benches [20, 21].

Although, little work has been published on the influence of granulation technique on recyclate characteristics, a combination of shredding and impact milling seems to be the most frequently adopted approach [22–24]. Shredding is used to reduce the waste components into manageable sized pieces, whilst impact milling produces the recyclate feedstock. For example, hammer milling in combination with a range of classifiers can yield several grades of material, varying from fine particulates to long (∼20 mm) monofilaments. With impact milling techniques however, throughput and economics of comminution depend strongly on the final material size required [25].

The majority of research published on re-use of thermoset composites has investigated the feasibility of incorporating the recyclate back into the parent composite [2, 24–28]. In general, this work considers the recyclate as a replacement for particulate fillers and has shown that satisfactory material, with loadings up to 25 wt%, can be manufactured with minimal alteration to resin formulation [27]. These recyclate composites may have slightly inferior properties when compared to their virgin counterparts [29]. The observed reduction in performance is attributed to a lack of interfacial bonding between reinforcement and matrix, with the angular and coarser recyclate particulates acting as stress raisers [2, 24, 25]. At loading levels above 30 wt%, processing often becomes problematic, resulting in

unacceptable composite properties. This can be accounted for by adsorption of resin onto the recyclate, leading to large changes in rheological behaviour [25, 27].

Bledzki *et al*. [24] have investigated the dynamic mechanical properties of recyclate filled composites. They showed that the addition of DMC and SMC recyclate into virgin material leads to a decline in fatigue characteristics, arising from enhanced crack initiation and growth. Structural analysis showed that this behaviour was caused by cracks within the recyclate particles and by poor interfacial bonding between the recyclate and host matrix.

Jutte and Graham [25] have incorporated thermoset recyclate into thermoplastics matrices, suggesting that a combination of shredding and granulation is preferable for recyclate production. Recyclate was processed by dry blending with polypropylene (PP) granules, prior to compounding in a reciprocating-screw extruder. They identified that a high back pressure caused fibre-bundle degradation with dispersion of fibres into clumps and that a melt index of greater than seven was necessary to achieve satisfactory recyclate wet-out. The mechanical properties of the moulded parts were reported to be inferior to virgin materials and formulation optimisation together with treatment of the recyclate with coupling agent, was recommended.

Chen *et al*. [23] carried out a similar investigation, incorporating ground glass-reinforced polyester resin composite into polypropylene, polyamide-6, polybutylene terephthalate and polycarbonate. They also showed that mechanical properties were generally superior to the unfilled virgin polymers, apart from a decrease in elongation at break and impact strength, but inferior to commercially available short fibre-reinforced thermoplastics. This was attributed to the shorter fibre length in the recyclate composite and poor interfacial bonding between fibres and matrix. They suggested that attrition during melt compounding may be the determining factor controlling the final fibre length.

The use of stabilisers and treatments has been assessed by Godlewski [22], who added SMC recyclate into polypropylene. In this work, the SMC was hammer milled to generate particulates containing fibre lengths of between 2 and 10 mm. These were pre-blended with PP pellets, talc and melt stabilisers, then compounded in a twin-screw extruder. Promotion of interfacial bonding of fibres to the matrix was found to increase mechanical properties.

This paper considers the re-use of recyclate feedstock, produced from dough moulding compound (DMC) and woven glass reinforced phenolic (GWP). Waste products from these materials have been size-reduced to yield a high proportion of fibre-particulate bundles. Hammer milling was selected for this purpose, since it is a high impact process, which exploits the limited impact performance of thermoset composites and as mentioned above, is the most commonly used commercial size reduction technique. Recyclate characterisation has been carried out, not only to determine the physical properties of the initial feedstocks and their structural integrity, but also to establish how they will behave at elevated temperatures during melt processing with thermoplastics.

2. Experimental
2.1. Recyclate materials
Two thermoset composites were selected for investigation, a polyester dough moulding compound (DMC) and a woven glass phenolic laminate (GWP). These materials have extremes in formulation and composite performance and are considered representative of many high volume thermoset composites available, based on phenolic and polyester resins.

The polyester composition was derived from an electrical housing, with an open box structure and 5 mm wall thickness. It contained a relatively low loading (22 wt%) of short randomly oriented glass fibres. Subsequent analysis revealed a filler content of 9% calcium carbonate and 42% aluminium hydroxide fire retardant.

A 7 mm thick woven glass phenolic laminate was also investigated. This was supplied in sheet form and contained a high loading ($\sim$80 wt%) of continuous, highly aligned E-glass fibres. This waste material had been manufactured via a prepreg route using hexamine cured phenolic novolak.

2.2. Comminution of recyclate feedstock
Size reduction of the thermoset composite components into feedstock was carried out in three stages. Initially the components were cut using a band-saw into smaller pieces (approximately 10 cm × 20 cm). These were then broken down in a Hosokawa Micron Alpine 40/32 Ha hammer mill fitted with a 20 mm round hole screen. Finally this material was further reduced in size using a smaller Alpine 25MZ hammer mill with a 4 mm round hole screen.

The recyclate was classified by passing through a 0.5 mm sieve to remove the finer material with the coarser particles retained for use in this investigation.

2.3. Physical characterisation of recyclate feedstock
With the DMC material, characterisation of the recyclate feedstock was complicated by the presence of both fibrous and particulate fractions.

2.3.1. Particle size distribution
The particle size distribution of the feedstocks were determined by dry-sieving the recyclate samples, following previously reported procedures. A stack of six sieves with decreasing sizes ranging from 3.35 to 0.15 mm were selected. Samples were agitated for 10 minutes, then the mass of recyclate collected on each sieve was weighed and weight fractions used to calculate the particle size distribution. For this purpose the fibres were considered as particulates.

2.3.2. Fibre length distribution
Image analysis was used to provide a direct measure of fibre length. This technique has been studied in-depth by Sawyer [30], who identified that good dispersion

of the fibres is paramount for achieving accurate measurement, with automatic image analysis systems. A manual Optimax VIDS II system was used and dispersion of the fibres in light oil was found to be adequate for achieving acceptable fibre dispersion and a uniform suspension of monofilaments.

The fibres were extracted from the thermoset composites by ashing at 450°C for 18 h. The particulate fillers in the DMC recyclate give a complex residue, comprising a mixture of glass fibres, calcium carbonate and alumina (derived from aluminium hydroxide). This composition was simplified by dissolving the calcium carbonate in dilute hydrochloric acid and taking measurements on the resultant dispersion of fibres and alumina.

Five hundred fibres were measured for each sample and the results processed to obtain the mean weighted fibre length and the fibre length distribution. Use of a weighted average fibre length has been applied in this study since this emphasises the contribution made by the longer fibres to the reinforcing efficiency of thermoplastics composites.

2.4. Thermal analysis

Thermogravimetric analysis (TGA) was used to characterise the thermal stability of the thermoset recyclate feedstock materials.

Measurements were carried out in triplicate on a Perkin Elmer TGS-2 instrument, using 6–8 mg samples and a gas flow rate of 50 cc/min. A heating rate of 10°C/min was used and weight loss measured as a function of increasing temperature. Under isothermal conditions, the samples were ramped to temperature at 160°C/min and the weight loss measured at specified dwell times.

Some measurements were also undertaken using a Perkin Elmer DSC7 differential scanning calorimeter, where samples were sealed in aluminium pans and heated in a nitrogen atmosphere at a rate of 10°C/min.

2.5. Mechanical properties of thermoset recyclate

The tensile properties of the thermoset recyclate materials were determined before comminution following procedures given in BS 2782 method 320E. However, with the DMC material, the gauge length used was 40 mm shorter than that recommended due to the limited amount of flat material available. Aluminium end tabs (1.5 mm thick) were bonded to the specimens using room temperature curing epoxy resin.

The flexural properties of the recyclate materials were evaluated by the three point bend test method according to BS2782 Part 3. Test coupons 100 mm long and 10 mm wide were used with a span:thickness ratio of 20. This relates to a 85 mm span for the DMC and 52 mm for the GWP materials. The samples were loaded at a rate of 5 mm/min and the displacement measured using a 25 mm gauge length extensometer positioned under the load roller.

Vickers hardness of the recyclate materials was determined using a 5 kg load mass. Ten readings were taken normal to the laminate/component external surfaces.

Material toughness was measured using a Ceast Torino impact test machine in accordance with BS 2782 Part 3. Tests were carried out on Type 1 specimens (80 mm × 10 mm × 4 mm) cut from the gauge length of a moulded test bar. These were notched with a single edgewise Type A notch; 2 mm deep with a 0.25 mm notch tip radius. Impact strength determination was carried out 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.

Mechanical tests were undertaken at 23°C, after heating specimens to various temperatures to simulate the effects of melt processing on structural integrity of the recylates.

2.6. Microscopic characterisation

Both optical and scanning electron microscopy were used to charcterise the physical form of the recyclate feedstock materials. For SEM analysis, samples were first splutter coated with gold and examined under a Cambridge Stereoscan 250 microscope.

3. Results and discussion
3.1. Characterisation of comminuted materials

Visual inspection of the DMC recyclate revealed that the structural characteristics of the parent material were retained in both the 20 mm and 4 mm feedstocks. The recyclate contained predominantly fibre-particulate bundles (Fig. 1), with the majority of fibres being encapsulated in polyester resin matrix.

Particle size analysis of the 3 mm recyclate (Fig. 2) reveals large particles, with 69% of the recyclate being greater than 1 mm. This compares to a maximum particle size of 40 μm for traditional fillers, and as such, might be expected to exert a significant influence on the performance of the recyclate in thermoplastics composites. In this regard, it is well documented that the stress concentrating effect of larger particles can lead to a reduction in strength [24, 25]. However, with thermoset recyclate fillers the feedstock particle size distribution is not necessarily representative of that obtained in the ultimate composite, since as mentioned earlier, size reduction continues to occur during melt processing. Furthermore, the recyclate filler is a micro-composite in its own right and is expected to behave differently to traditional monolithic fillers.

The wide range of fibre lengths present in the feedstock, from <0.1 mm to >10 mm, leads to complications in characterising the fibre length distribution, the smaller fibres becoming difficult to measure at the magnifications required to view the longer ones. Consequently, the particle size distribution has been used only as an indication of the fibre length distribution. This leads to an underestimate of true fibre length, as particulates/fibres with high aspect ratios can pass through screen sizes much smaller than their length.

Microscopic examination of the comminuted recyclate has revealed that the recyclate particulates are covered in a thin layer of fine powder, electrostatically
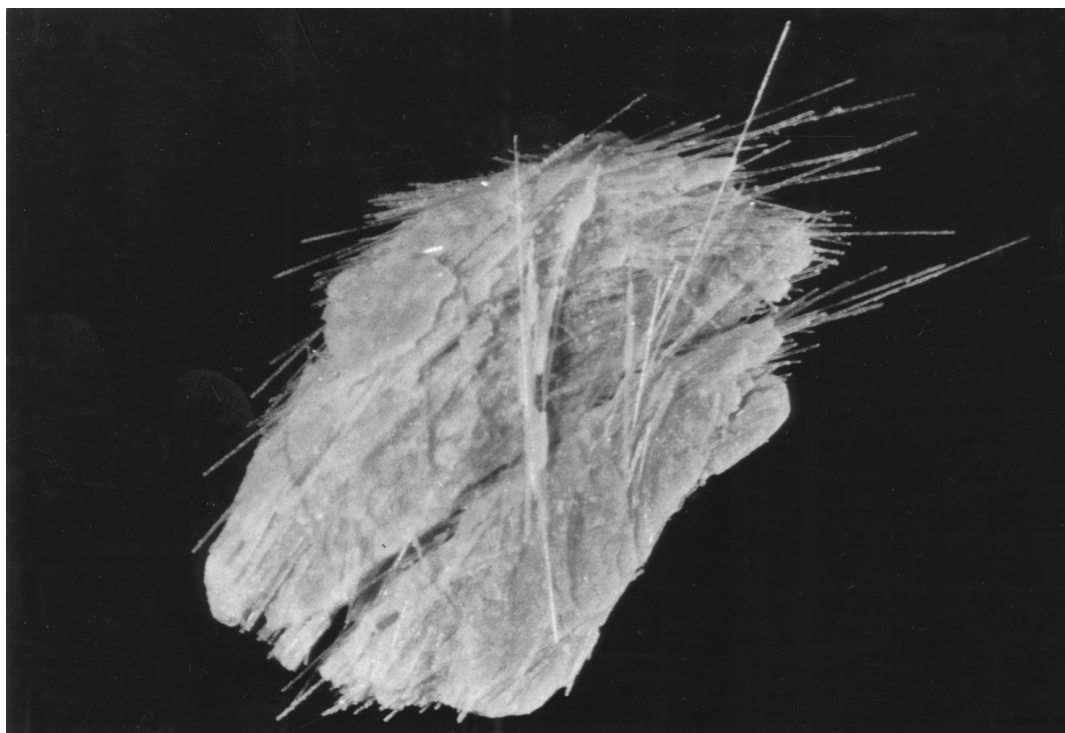
2mm

Figure 1 DMC recyclate fibre-particulate bundle.

adhering to their surface. Closer inspection of the DMC feedstock shows that fibres protruding from the particulates are relatively clean, with small amounts of matrix material remaining bonded to their surfaces (Fig. 3). It is also apparent that substantial fibre attrition has occurred.

It is likely that the presence of residual matrix material on the fibre surfaces will reduce the efficiency of any treatment system applied. Similarly surface particulates not only prevent treatment of the underlying fibre, but also, have a poor load transfer capability.

Visual examination of the hammer milled GWP recyclate revealed extensive interply delamination due to low interlayer shear strength in this composite.

The particle size distribution of the 4 mm GWP recyclate is given in Fig. 2. Again, the large particle size is apparent, with 50% of the recyclate being greater than 0.6 mm. A large proportion of this recyclate was in the form of fibre tows (Fig. 4) and woven platelets (Fig. 5), with the fibres remaining encapsulated in phenolic resin. Typically, these platelets were one or two plies thick.

Microscopic analysis of the recyclate surface shows that these recyclate particulates are again covered in a thin layer of fine powder and that some of the resin rich regions, within the weave pattern, are cracked. Closer inspection of the GWP platelets confirms that the woven ply structure is relatively intact, with a few cracks running parallel to the fibre tows (Fig. 6). As with the DMC feedstock, fragments of resin remain bonded to the fibre surfaces and the exposed fibres remain as intact bundles.
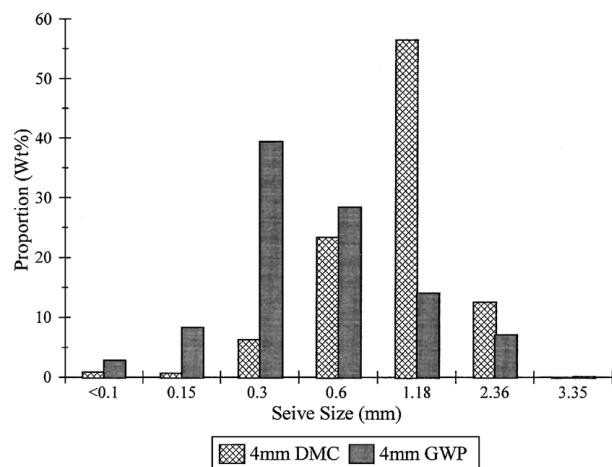
3.2. Thermal properties of recyclate materials
3.2.1. Thermal analysis of DMC recyclate
Fig. 7 shows that the DMC recyclate exhibits four weight loss stages, with derivative peaks at $295°$, $350°$, $470°$ and $710°C$. It is concluded that the peak at $295°C$ corresponds to decomposition of ATH, and those at $350°$ and $470°C$ result from degradation of the polyester matrix. The peak arising from a weight loss at $710°C$ is attributed to $CaCO_3$ calcination.

DSC can be used to resolve the ATH disassociation reaction from polyester degradation and has been evaluated using virgin ATH and the polyester matrix material. This reveals that dissociation of ATH exhibits a large endotherm between 220 and $380°C$, in contrast to the polyester resin which exhibits no endotherm,
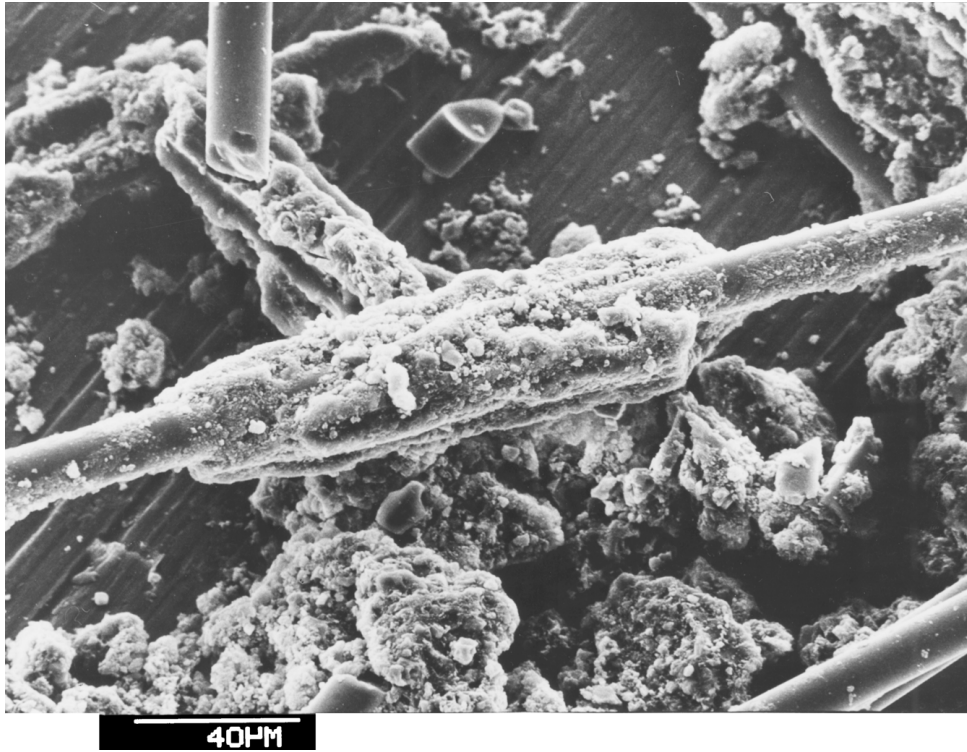

Figure 2 Particle size distribution of 4 mm DMC and GWP feedstocks.

Figure 3 DMC monofilament showing bonded matrix fragment and particulates.


2mm

Figure 4 Fibre tows in 4 mm GWP feedstock.

although, thermal degradation of the polyester causes a slight increase in the base line above 275°C.

The fibre and filler loading levels in the DMC feedstock can be determined using a combination of TGA and DSC analysis procedures which have been described elsewhere [31]. This reveals a composition for the DMC recyclate used in this study of: 26 wt% polyester resin, 42 wt% ATH, 9% CaCO$_3$ and 22% glass fibre. Moisture and residual monomer account for the remaining 1%.

Characterisation of the DMC constituents revealed that both the polyester and ATH components degrade
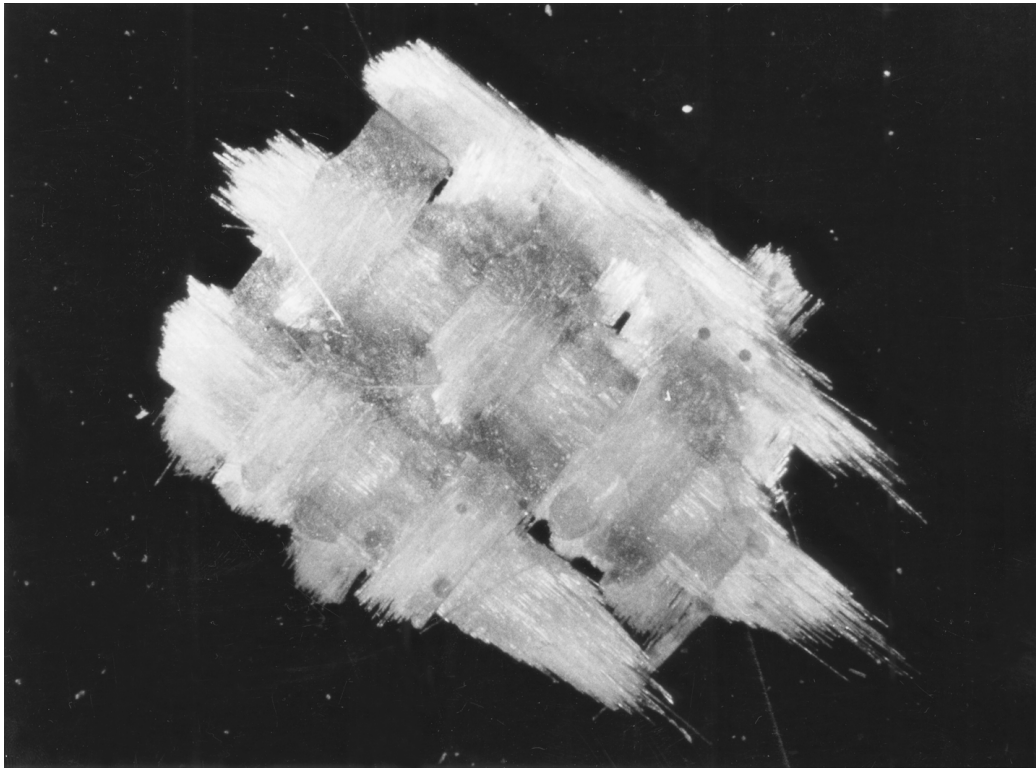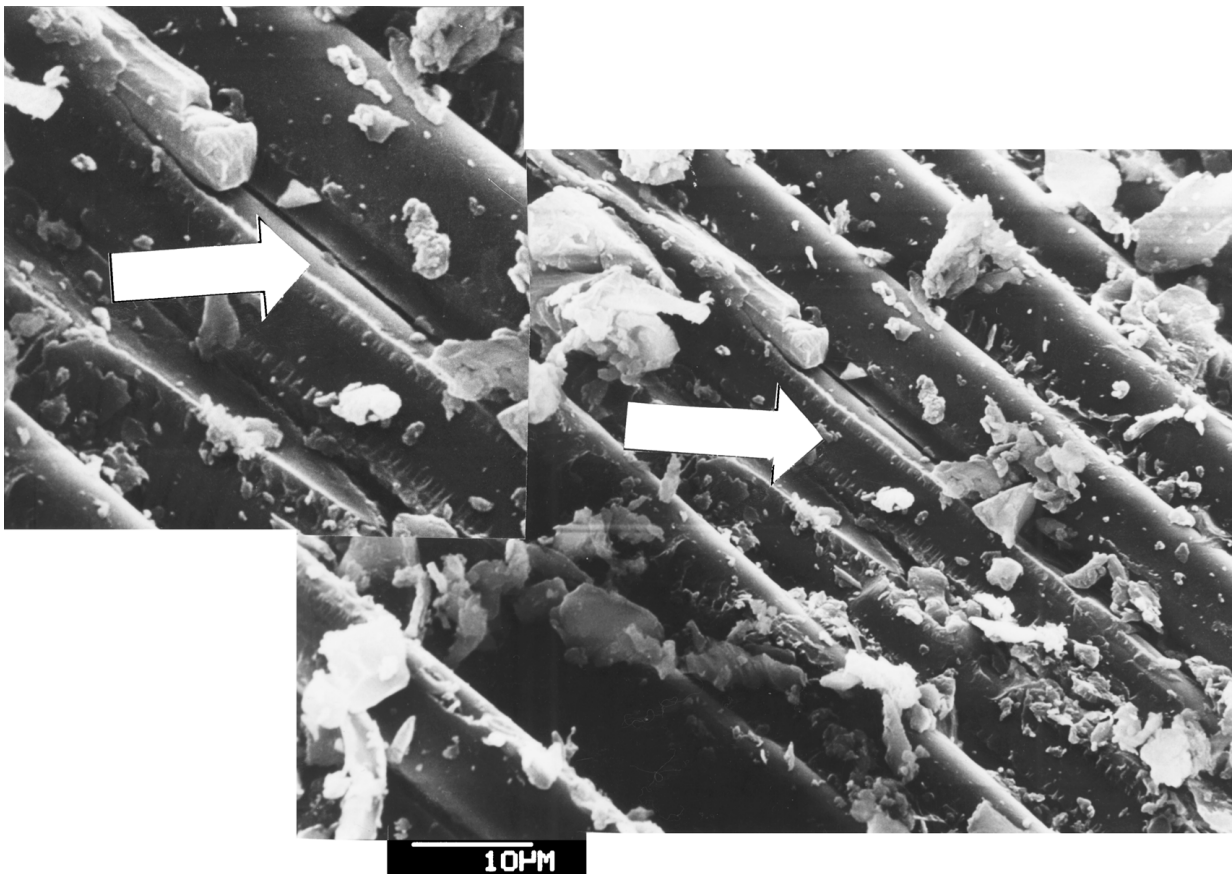
1mm

Figure 5 Woven platelet in 4 mm GWP feedstock.

10μM

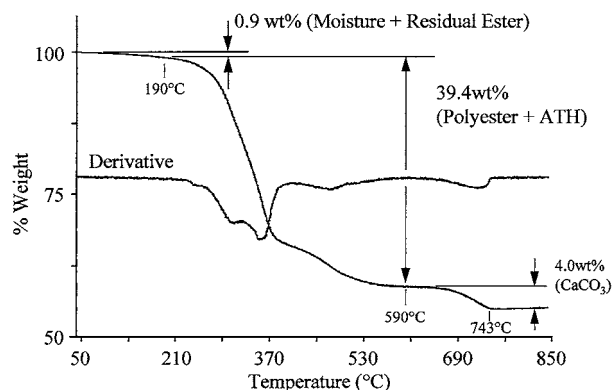*Figure 6* Surface of 4 mm GWP platelet showing cracks running parallel to fibres.

Figure 7 TGA thermogram of DMC recyclate feedstock.

Figure 9 The influence of processing temperature on DMC feedstock thermal stability.

at typical thermoplastics processing temperatures, polyester degradation beginning at 115°C and ATH at 220°C.

This degradation may have a significant influence on the mechanical performance of the recyclate composites. In particular, as inferred earlier, decomposition during melt compounding may facilitate break up of the recyclate, reducing the maximum particle size in the final composite. Furthermore, the evolution of volatiles may also inhibit interfacial bonding to the matrix and degradation by-products may reduce the integrity of the host matrix.

The level of degradation is expected to depend, not only on the composition and processing temperature, but also, on particle size and processing environment. These latter two factors vary during the recycling process, the environment changing from oxidative to non-oxidative and size reduction occurring as material passes through the process.

The influence of these effects on thermal stability of the 4 mm feedstock has been investigated using isothermal TGA, at a twenty minute dwell time. Two dwell temperatures, 220° and 290°C, were selected to cover the range used to process most common thermoplastics.

Before investigating the DMC recyclate, the stability of the base polyester matrix and ATH filler were studied. In each case both materials were dried in the TGA apparatus by dwelling at 120°C for 20 min, prior to ramping to the isothermal temperature.

Fig. 8 reveals that ATH can be regarded as relatively stable at 220°C, exhibiting a 3.8% weight loss over
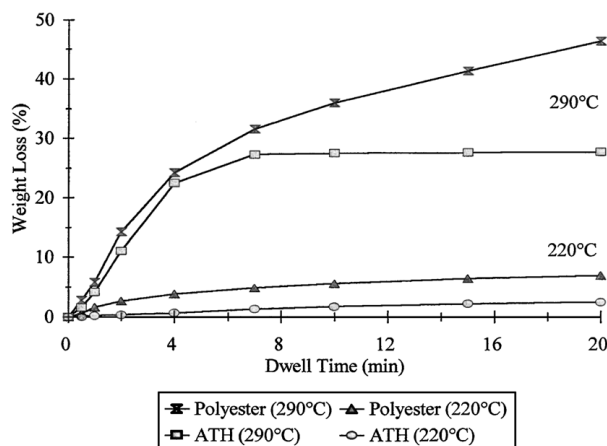

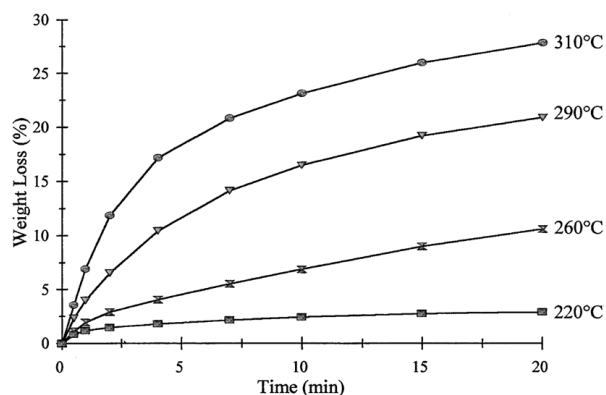Figure 8 Isothermal TGA of ATH and the DMC polyester matrix.

20 min. However, at 290°C weight loss is rapid and has reached its equilibrium value, of 29 wt%, within four minutes. This stabilisation is due to the conversion of ATH into alumina and monohydrate going to completion. Continuation of the isotherm up to 20 minutes results in little/no further weight loss, the temperature being too low to convert the monohydrate to alumina.

Corresponding thermograms for the polyester matrix system show that this is less stable than ATH. The weight loss at 220°C stabilises at 9.9% after 20 min, whilst at 290°C it is still rising to 47.7%.

There are two further areas of interest relating to the thermal stability of the DMC feedstock, the total amount of degradation that occurs during processing and the relative contributions of the ATH and polyester components to the overall weight loss. The first has been determined by isothermal TGA at a range of dwell temperatures and, the second, by measuring the extent of ATH disassociation, using combined TGA and DSC analysis.

Fig. 9 reveals that recyclate degradation progressively increases with exposure temperature. Visual inspection of the recyclate showed that, at 220°C the material appeared to be unaffected, at 260°C and 290°C the surface had changed to a light brown colour, whereas at 310°C the colour darkened and the material had a crumbly texture, indicative of extensive matrix degradation and loss of strength.

The relative contributions of the ATH and polyester components to DMC degradation were also investigated by isothermal analysis using dried materials. Drying was accompanied by a weight loss of 0.8%, caused by evolution of absorbed moisture and residual monomer. The contribution of ATH to degradation has been determined by measuring the amount of unconverted ATH after various dwell times (1, 2, 4, 7, 10 and 20 min) using DSC. The results are summarised in Table I.

At 220°C most of the initial loss (up to 4 min) is caused by degradation of polyester. However, as the isotherm progresses disassociation of the ATH increases, which above 10 min, accounts for about a third of the weight loss.

In contrast, at 290°C DMC recyclate degradation is dominated by ATH decomposition, which accounts for 80% of the weight loss. Figs 8 and 9 reveal that disassociation is nearing completion after 10 min, with

TABLE I Thermal stability of DM recyclate: Contribution of ATH and polyester to overall degradation

| Dwell Time (min)	220°C Isothermal			290°C Isothermal		
	DMC (wt% loss)	% ATH	% Polyester	DMC (wt% loss)	% ATH	% Polyester
1	0.5	1.7	97.5	3.3	80.0	19.2
2	0.8	10.1	89.1	6.1	87.9	11.3
4	1.1	12.9	86.3	10.6	87.8	11.4
10	1.6	33.3	65.9	16.4	80.8	18.4
20	2.1	34.2	65.0	20.1	71.3	27.9

Figure 10 The influence of processing atmosphere on thermal stability of DMC recyclate.

Figure 11 DSC analysis of GWP feedstock initial weight loss.

its associated weight loss stabilising at 13%. This behaviour is similar to that observed in the pure ATH sample and implies that full conversion to alumina will occur during processing at these temperatures. This could be particularly significant if processing with water sensitive matrices (such as polyamides and PET), as a recyclate loading level of 30 wt% will release ~4 wt% of water during processing.

Previously described thermal analysis determinations have been carried out on the 4 mm feedstock in an oxidative atmosphere (air). This is representative of the initial processing conditions, when the recyclate is fed into the extruder. However, as identified in the preliminary trials, size reduction continues during processing and air is excluded as the recyclate is encapsulated by the melt. Both of these effects are expected to influence thermal stability of the recyclate.

The influence of particle size on the rate of degradation has been evaluated by isothermal TGA analysis on a finer grade of recyclate, with maximum particle size <0.5 mm.

It is clear that the rate of degradation increases as the particle size decreases (Table II). At both temperatures the smaller particle size, <0.5 mm, exhibits an increase in weight loss of between 33% and 42%. This implies that degradation will become more severe as the recyclate travels through the extruder.

The effect of processing environment on recyclate stability has been evaluated by carrying out isothermal TGAs using oxidative (air) and non-oxidative (nitrogen) atmospheres. Fig. 10 shows that an inert atmosphere reduces the extent of degradation at the higher temperature studied (200°C), where weight loss is reduced to around 65% after 20 minutes. This is due to a reduction in the decomposition rate of the polyester, for which the peak degradation temperature is raised from 350° to 380°C.

3.2.2. Thermal properties of GWP recyclate
TGA demonstrates that the GWP recyclate has much greater thermal stability than the DMC feedstock. Two

TABLE II Effect of recyclate particulate size on DMC feedstock thermal degradation (isothermal TGA)

	% Weight Loss (after 20 min)		% Increase in Weight Loss
	>0.5 mm	<0.5 mm	
220°C	2.3	3.1	35
290°C	23.0	32.7	42
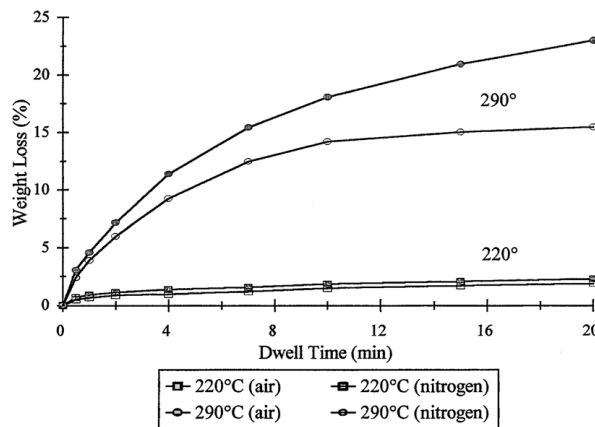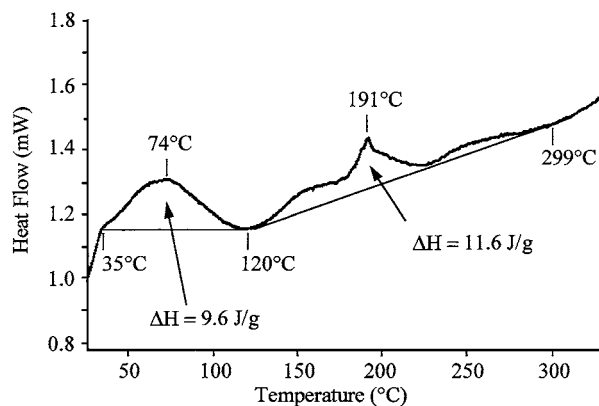
principal weight losses were found. The first, (~2.3%), occurs between ambient and 280°C. The second, (19%), takes place between 350° and 600°C and represents the bulk phenolic resin degrading. The remaining inorganic residue, 79 wt%, comprises glass fibres. This result is consistent with previous reports that phenolics are stable up to 300°C, with a small loss (1–2 wt%) being caused by evolution of adsorbed moisture and residual monomers, with the main decomposition reactions occurring between 300° and 800°C [32].

Investigation of the initial weight loss, using DSC, revealed a two stage mechanism, with peaks at 74°C and 191°C (see Fig. 11). The relative contributions of these have been determined by undertaking a sixteen hour isothermal TGA at 90°C. This drove the first mechanism to completion and accounted for a weight loss of 1.2%. A subsequent dynamic TGA scan (at a heating rate of 10°C/min) confirmed that the second mechanism accounted for the remaining loss of 1.1%, occurring between 120°C and 245°C.

The first stage in the mechanism is believed to be caused by evolution of residual monomers (phenols and fomaldehyde) and adsorbed moisture. The relative amounts of these has been determined by drying a sample for 16 hrs at 90°C. The moisture was then reintroduced by conditioning for 8 weeks at 22°C and 50%RH, using an undried sample as a control. The subsequent dynamic TGA scan identified an initial weight loss and hence, a moisture content of 0.7 wt%. The remaining
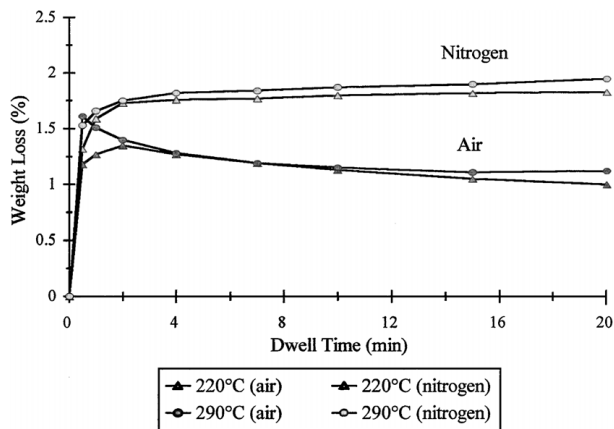
Figure 12 Thermal stability of GWP feedstock in inert and oxidising atmospheres.

TABLE III Mechanical properties of DMC and GWP laminates

		DMC		GWP	
	Orientation	Mean	SD	Mean	SD
Vickers Hardness Number	-	30.6	1.0	79.5	10.7
Notched Charpy Toughness (kJ/m^2)	Parallel	22.6	9.8	87.4	8.8
Tensile Modulus (GPa)	0°	20.9	0.9	41.5	3.1
	90°	17.0	1.2	-	-
Tensile Strength (MPa)	0°	46.1	2.1	319.4	24.2
	90°	29.6	1.8	-	-
Elongation @ Peak (%)	0°	1.5	0.2	7.4	0.5
	90°	1.1	0.3	-	-

0.5 wt% of the initial weight loss being attributed to residual monomeric volatiles.

The second endotherm in Fig. 11 is attributed to the phenolic curing reaction going to completion. The ether links, which are characteristic of phenolics cured at ~140°C, undergoing condensation reactions with the phenolic hydroxyl groups forming water and polymeric quinone methides. This water by-product accounts for the second weight loss measured during the TGA scan and accounts for 1.1 wt%. This finding agrees with the findings of Whitehouse *et al.* [32], who report that this reaction occurs between 170° and 200°C.

Isothermal TGA of the GWP recyclate, in both air and nitrogen, indicates a greater stability than the DMC feedstock. Weight losses of, 1.6% in air and 1.9% in nitrogen were measured at both temperatures studied (Fig. 12). It is significant that the majority of these losses occurred whilst the samples were ramping to temperature. This confirms that the bulk phenolic is not degrading and that, as discussed above, the losses observed are caused by the evolution of residual monomers, adsorbed moisture and the cure reaction going to completion.

Fig. 12 also reveals that the samples heated in air gained mass as the isotherm proceeded. In contrast, the nitrogen samples stabilised at 1.9% weight loss. According to the work of Conley [33], this weight gain is caused by oxidation of the phenolic methyl bridges with the formation of hydrogen peroxide. At higher temperatures this peroxide structure undergoes decomposition to form a protective char.

These results confirm that the GWP recyclate is stable at commonly used thermoplastics processing temperatures. The evolution of moisture, residual monomers and completion of the cure reaction, leading to a small weight loss, of less than 2%. As for the DMC recyclate, the release of a small amount of water can be expected to promote degradation of moisture sensitive thermoplastics.

3.3. Structural integrity of recyclate composites

When adding fillers to thermoplastics, the mechanical performance of the composite is dependent on the intrinsic properties of the filler. Hence the mechanical properties of the DMC and GWP composites are of particular interest. These have been measured using test coupons cut from flat sections on the original mouldings. As initial tests revealed a significant level of preferred fibre orientation, properties were measured in both the 0° and 90° directions. These results are summarised in Table III.

Comparing the properties of the two materials studied, it is apparent that the GWP has a much greater structural integrity and is therefore expected to provide a greater level of reinforcement when added to thermoplastics. One disadvantage of this higher integrity is an increase in hardness, which may result in a greater level of abrasion and wear to the extruder during compounding.

Having established above that the recyclate undergoes thermal degradation during processing, it is important to determine what influence this has on the integrity of the feedstocks. This is expected to influence both the extent of size reduction during processing, and ultimately the performance of the composite to which it is added.

Since the extent of degradation will depend on the surface:volume ratio of the sample, it is difficult to reproduce the degradation seen by a recyclate particulate, in a test coupon. As a consequence, a comparative method has been carried out, using a three point bend test. This methodology has been chosen as the measured performance is dominated by the outer specimen surfaces. In addition, this test is also a good measure of overall performance, subjecting the material to tension, compression and shear.

The test pieces were thermally aged, in air, for 20 min at 220°C and 290°C. The dwell was started after a dummy test piece, containing an embedded thermocouple, had reached the required temperature.

With DMC, weight losses of 1.2% and 10.4% were measured at 220° and 290°C, which represent the losses seen by the 4 mm feedstock after a 3 min dwell time. Visual examination of the coupons revealed a slight discoloration at 220°C. In contrast, the coupons aged at 290°C showed significant signs of degradation, the exposed surfaces turning dark brown and cracks, 5 mm to 10 mm long, forming on the cut edges parallel to the test coupon length.

The flexural results (Table IV) reveal that little or no loss in structural integrity of DMC occurs at 220°C. However, at 290°C the reduction in performance is

TABLE IV Effect of thermal aging on the structural integrity of DMC and GWP

		Weight Loss (%)	Flexural Modulus		Flexural Strength		Failure Mode
			(GPa)	SD	(MPa)	SD	
DMC	Ambient	-	14.3	0.64	94.1	3.2	Tensile
	220°C	1.2	13.7	0.28	91.1	14.4	Tensile
	290°C	10.4	10.2	0.91	52.3	5.4	Tensile
GWP	Ambient	-	30.9	1.9	562.8	12.3	Tensile
	220°C	1.2	26.7	0.6	388.4	35.1	Shear
	290°C	2.0	26.0	1.2	351.1	13.7	Shear

significant, the strength being reduced to 56% and the modulus to 71% of the untreated values. This implies that the integrity of the DMC will be retained when it is added to polypropylene, but not when added to polyamides which are normally processed at higher melt temperatures.

Aging the GWP flexural test coupons for twenty minutes resulted in a weight loss of 1.3% at 220°C and 1.6% at 290°C. Unlike the DMC materials these losses are comparable to those exhibited by the recyclate feedstocks during isothermal TGA. This good level of agreement is due to the weight losses being caused by the evolution of moisture and residual monomers and, not degradation of the bulk resin.

Examination of the test coupons after thermal treatment revealed colour changes similar to those seen with the recyclate feedstocks and blistering just under the testpiece surfaces. These blisters are believed to have formed by the entrapment of water vapour, caused by the phenol condensation reaction going to completion. This problem is common when curing phenolic composites.

Flexural test results for GWP (Table IV) demonstrate that aging at either temperature used leads to a similar loss in performance, the strength being reduced to 65% and the modulus to 85%. This behaviour is accompanied by a change in failure mode, from tensile to shear; indicating a reduction in interlaminar shear strength. This is attributed to blister formation, rather than degradation of the phenolic resin; the aging temperatures being below the main phenolic degradation onset temperature of 350°C.

The main conclusion from these results is that the GWP recyclate will be stable at polyamide, as well as polypropylene, melt processing temperatures. However, the release of small amounts of water vapour (~1.8 wt%), due to absorbed moisture and the cure reaction going to completion, may restrict usage in water sensitive matrices. The associated reduction in interlaminar shear strength, caused by the formation of blisters, is expected to assist in the break up of multiply platelets during processing, without reducing the overall integrity of the recyclate.

4. Conclusions

In terms of recycling, there are three main observations to note from the characterisation studies. The first is that primary size reduction by hammer milling retains the structural integrity of the reinforcing fibres. This is critical if the reinforcing potential of the recyclate is to be realised. Secondly, the nature of the feedstock particulates depends on the level and form of the reinforcement in the parent thermoset. Finally, both grades of recyclate release a small amount of water during thermal aging, restricting their use as a filler, in the as-produced state, to thermoplastics that are not sensitive to water.

The structure of the parent material was retained. The recyclate contained fibre-particulate bundles, with the fibres remaining encased in matrix material. The structural integrity of the fibres is preserved, with fibres up to 10 mm being retained and 69% of the recyclate particulates are greater than 1 mm in diameter.

At 220°C recyclate degradation is limited, exhibiting a 2.3% weight loss and little loss in structural integrity. However, at 290°C degradation is severe with ATH disassociation going to completion within 10 min. The evolution of water accounts for 80% of the weight loss (~23 wt%). This reflected by a 30–50% reduction in flexural properties.

The level of degradation increased with ATH content, processing temperature, a reduction in recyclate particle size and the presence of an oxygen environment.

Characterisation of the GWP laminates confirmed a composition of 79 wt% woven glass, 19 wt% phenolic resin and 2 wt% volatiles. Size reduction, by hammer milling, was found to exploit the poor interlaminar shear strength of the material. The woven glass fibres dominated the nature of the recyclate. The thermoset composite broke down into woven fibre platelets and fibre tows, with the fibres being protected by phenolic resin. 50 wt% of the particles were greater than 0.6 mm in diameter. The recyclate was thermally stable at both 220° and 290°C, evolution of water and residual monomers accounting for the observed weight loss of 1–2%. The formation of blisters, during thermal aging, reduced the interlaminar shear strength of the material. This was expected to aid the breakdown of large particulates during compounding without reducing the integrity of the recyclate.

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