# Mechanical Recycling of Automotive Composites for Use as Reinforcement in Thermoset Composites

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# Abstract

The aim of this research was to investigate the potential use of recycled glass fibre composite materials as a replacement for virgin reinforcing materials in new thermoset composites. Specifically the closed-loop mechanical recycling of composites used heavily in the automotive sector known as dough and sheet moulding composites, DMC and SMC respectively, are investigated. The recycling of glass reinforced thermoset polymer composite materials has been an area of investigation for many years and composites used in the automotive industry are of particular interest due to legislative and social pressures on the industry.

The mechanical recycling process and then collection of useful fibrous grades of recycled materials, recyclate, by a novel air separation technique were investigated first. The properties of these recyclate fibres were characterised and compared directly with the properties of virgin glass fibres they were to be used to replace. Single fibre tensile tests were employed to compare the strengths of the fibres and single fibre pull-out tests were used to investigate the strength of the interface between the fibres and a polyester matrix. These tests showed the recyclate fibres to be weaker and have a poorer interface with the polyester matrix than the virgin glass fibres. Understanding the properties of the recyclate materials meant their reformulation into new composites could be carefully considered for the production of new high performance materials.

Two grades of the collected recyclate materials were then reformulated in to new DMC and SMC composites, replacing percentages of the virgin glass fibre reinforcement. The mechanical properties of the resulting manufactured composites were characterised throughout for direct comparison against one another and an unmodified control material, using both three-point flexural tests and Charpy impact tests. Through the modification of existing manufacturing techniques and the development of novel production equipment it has been possible to successfully manufacture both DMC and SMC composites with the recyclate materials used to replace virgin glass fibres. Virgin glass fibres have successfully been replaced by recyclate materials without disrupting standard production techniques and with minimal reduction of the mechanical properties of the resulting composites. As the loadings of recyclate materials used were greatly increased both the flexural and impact strengths were significantly degraded and it was found that chemical modification of the composite could be used to improve these formulations. It has been shown that the recyclate materials should be considered and treated as a distinct reinforcing ingredient, separately from the remaining virgin glass fibres.

# Publications

Some of the content of this thesis has been published during the course of the research:

J. Palmer, O.R. Ghita, L. Savage, K.E. Evans. *Successful closed-loop recycling of thermoset composites*. Composites Part A: Applied science and manufacturing, 2009. 40(4) p. 490-498.

J. Palmer, O.R. Ghita, L. Savage, K.E. Evans. *Recyclate fibres – matrix interface analysis for reuse in sheet moulding compounds (SMC)*. Proceedings of European Conference on Composite Materials (ECCM 13). 2008. Stockholm, Sweden.

J. Palmer, O.R. Ghita, L. Savage, K.E. Evans. *New automotive composites based on glass and carbon fibre recyclate*. Proceeding of International Conference for Composite Materials (ICCM 17). 2009. Edinburgh, UK.

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# Contents

# List of Figures

13

# List of Tables

# Nomenclature

| Symbol | Dimension | Description |
|--------|-----------|-------------|
| $V$ | (mm s$^{-1}$) | Cross head speed |
| $\varepsilon'$ | (s$^{-1}$) | Rate of applied strain |
| $l_s$ | (m) | Sample span |
| $h$ | (m) | Specimen thickness |
| $\sigma_F$ | (Pa) | Flexural stress |
| $F_{max}$ | (N) | Maximum force |
| b | (m) | Specimen width |
| s | (m) | Deflection |
| $E_F$ | (N m$^{-2}$) | Flexural modulus |
| $a_{cU}$ | (kJ m$^{-2}$) | Charpy impact strength |
| $W_b$ | J | Energy at break |
| $W_f$ | J | Frictional energy losses |
| $F_D$ | (N) | Drag force |
| $F_L$ | (N) | Lift force |
| $F_B$ | (N) | Buoyancy force |
| $C_D$ | - | Drag coefficient |
| $u$ | (m s$^{-1}$) | Velocity of particle relative to fluid |
| $A_p$ | (m$^2$) | Cross-sectional area of particle normal to the direction of the drag force |
| $\rho$ | (Kg m$^{-3}$) | Fluid density |
| $L_c$ | (N) | Load applied to composite |
| $L_m$ | (N) | Load applied to matrix |
| $L_f$ | (N) | Load applied to fibre |
| $A_f$ | (m$^2$) | Fibre surface area |
| $\sigma_c$ | (Pa) | Stress on composite |
| $\sigma_f$ | (Pa) | Stress on fibre |
| $\sigma_m$ | (Pa) | Stress on matrix |

| | | |
|---|---|---|
| $\sigma^*$ | (Pa) | Failure Stress |
| $V_f$ | - | Fibre volume fraction |
| $E_c$ | (N m$^{-2}$) | Composite Young's Modulus |
| $E_f$ | (N m$^{-2}$) | Fibre Young's modulus |
| $E_m$ | (N m$^{-2}$) | Matrix Young's modulus |
| $\varepsilon_f^*$ | - | Fibre failure strain |
| $\sigma_f^*$ | (Pa) | Fibre failure strength |
| $\varepsilon$ | - | Strain |
| $l$ | (m) | Fibre length |
| $x$ | (m) | Distance from fibre end |
| $r$ | (m) | Fibre radius |
| $\tau_{IF}$ | (Pa) | Interfacial shear stress |
| $R$ | (m) | Radius of matrix |
| $l_c$ | (m) | Critical fibre length |
| $P_f(\sigma_f)$ | - | Probability of fibre failure |
| $m$ | - | Weibull modulus or shape parameter |
| $\sigma$ | (Pa) | Stress |
| $\sigma_0$ | (Pa) | Weibull scale parameter |
| $l_0$ | (m) | Largest fibre length that contains only one flaw |
| $n$ | - | Number of data points |
| $i$ | - | Rank of a data point |
| $P_i$ | - | Probability of failure of $i$'th data point |
| $\langle\sigma\rangle$ | (Pa) | Average fracture stress |
| $\Gamma$ | - | The gamma function |
| $\tau_d$ | (Pa) | Critical value of interfacial shear stress above which debonding occurs |
| $L_d$ | (N) | Load at debonding |
| $l_e$ | (m) | Embedded fibre length |
| $\mu_m$ | (Pa) | Matrix shear modulus |

| | | |
|---|---|---|
| $G_i$ | (J m$^{-2}$) | Interfacial fracture toughness |
| $\nu_m$ | - | Matrix Poission's ratio |
| $\nu_f$ | - | Fibre Poission's ratio |
| z | (m) | Debonded fibre length |
| $q_o$ | (Pa) | Residual clamping stress |
| $\mu$ | - | Friction at interface |
| $\sigma_d$ | (Pa) | Maximum debond stress |
| $\sigma_i$ | (Pa) | Initiation of debonding stress |
| $\sigma_{fr}$ | (Pa) | Frictional pull-out stress |
| $l_{free}$ | (m) | Free fibre length |
| X | (m) | Extension |
| C | (m N$^{-1}$) | True fibre compliance |
| $C_a$ | (m N$^{-1}$) | Recorded fibre compliance |
| $C_s$ | (m N$^{-1}$) | System compliance |
| $d_f$ | (m) | Diameter of fibre |

# Chapter 1

## 1. Introduction

The overall aim of this research project was to investigate the closed-loop recycling of glass reinforced thermoset composites by mechanical recycling. In particular, to investigate the possibility of using these recycled materials to replace the virgin reinforcing fibres in new composite formulations. The specific types of composites investigated are those used extensively in the automotive sector, known as sheet moulding compounds (SMC) and dough moulding compounds (DMC). The automotive sector is under ever increasing legislative pressures to consider the sustainability and environmental impact of their products, from the production of $CO_2$ emissions to the disposal of vehicles at the end of their useful lives. Whilst composites such as SMCs and DMCs facilitate the reduction of $CO_2$ emissions produced by a vehicle, through weight savings, they are perceived as un-recyclable because of the thermosetting resins used.

The recycling of such composites has been an area of research for over twenty years, with thermal, chemical and mechanical methods of recycling all being considered [1], [2], [3] but few being applied commercially. This research focuses specifically on mechanically recycling of waste SMC automotive components with the aim of retaining the composites original reinforcing glass fibres, during the recycling process. These recycled fibrous materials are then to be utilised as reinforcing materials, to replace virgin reinforcing glass fibres, in new DMC and SMC composites. It is believed that such a recycling method will both fit the definitions of 'reuse' and 'recovery' as defined by legislation such as the end-of-life vehicle directive [4] and that by replacing the most expensive material ingredient in such composites, the reinforcing fibres, the process will be more commercially viable.

Firstly, by applying granulation methods discussed in previous investigations [5], this study starts with thorough investigation into the different material grades that can be produced and then separated from the ground waste materials. The most fibrous grades are identified and collected, by air classification, to be used as replacement for the virgin reinforcing fibres in new DMC and then SMC composites. The manufacturing

techniques and the reformulation methods used to incorporate these recyclate materials into the new composites are then investigated, to optimise the properties of the resulting composites. Mechanical testing experiments, in the form of Charpy impact and three-point flexural testing, are used to study the effect the recyclate materials and production methods used and to characterise and compare the resulting composites mechanical properties against one another and standard control materials.

As well as directly investigating the effect that these recyclate materials have on the mechanical properties of new composites, the individual properties of the recyclate fibres were also compared to those of individual virgin fibres. Single fibre tensile tests were used to characterise the fibre's average strengths and single fibre pull-out tests were performed to investigate the strength of the interface between fibres and a polyester resin matrix. This investigation was performed to provide possible insight into any differences observed in the mechanical properties of the composites manufactured using the different types of reinforcement.

## 1.1. Thesis Outline

The remainder of the thesis is split into the following chapters:

Chapter 2 is a literature review and starts by giving an introduction to the main drivers behind the need for research into the recycling of these composite materials, specifically from the perspective of the automotive industry. The properties, materials and manufacturing methods associated with both sheet and dough moulding compounds are then introduced. Finally the literature relating to the various methods of recycling such composites are summarised, with specific focus on the mechanical recycling research previously investigated.

Chapter 3 describes the experimental techniques used in the investigation. The purpose of the test and any relevant literature is discussed first, followed by the test method and finally the specific experimental set-up used for this investigation.

Chapter 4 explains the production and classification methods used to produce the recyclate materials for this investigation. The chapter moves from the raw material

selection, to the granulation process and then to classification of the recyclate grades. Each stage is investigated to optimise the processes for production of a fibrous recyclate, before moving to the next. Finally the shape and dimensions of the two chosen recyclate grades, to be trialled as reinforcement in new composites, are analysed and compared.

Chapter 5 is a direct comparison of the mechanical properties of the individual glass fibres recovered from the recyclate with the properties of the virgin fibres they are to replace. The role of glass fibres in composite materials and the relationship between the individual fibres and the overall composites properties is first introduced. Fibre strengths are then investigated by means of single fibre tensile tests and the interface between the different fibre types and virgin polyester resin is then also investigated by use of the single fibre pull-out test.

Chapter 6 uses both grades of fibrous recyclate to replace virgin glass fibres as reinforcement in new DMC formulations. Firstly the manufacturing conditions are investigated to optimise the DMC compounding process for the inclusion of recyclate materials. Then experiments are performed investigating the reformulation methods used, to facilitate the use of higher loadings of recyclate materials without further degrading the composite's mechanical properties. Finally a wetting agent is added to the formulation in an attempt to improve the performance of composites containing the very highest loadings of recyclate.

Chapter 7 investigated the potential of using recyclate to replace virgin glass fibres in new SMC composite formulations. The complex manufacturing techniques involved in SMC production required the design and implementation of new novel piece of machinery to allow the inclusion of recyclate materials as reinforcement. As well as investigating the mechanical properties of composites containing recyclate materials, formulations were put through industrial moulding and painting processes to investigate the feasibility of implementing the new technology on an industrial scale and to investigate any surface finish effects.

In Chapter 8 the results and conclusions from the previous results chapters are brought together and the success of the investigation discussed.

Finally in Chapter 9 suggestions for areas of potential future study are highlighted.

# Chapter 2

## 2. Literature Review

### 2.1. Composite Materials

A composite is an engineered material that consists of two or more different and distinct components. A wide variety of constituents can be combined, depending on their individual properties, to produce a material with specific characteristics. Most composites are typically based around two material components known as; a 'matrix' and a 'reinforcement'. The reinforcement is generally much stiffer and stronger than the matrix, typically being of fibres in either continuous or discontinuous form. The matrix is then used to bind the reinforcement in a desired orientation or shape, transfer load to the reinforcement and protect it from environmental damage. Filler materials are also commonly used in the manufacture of many composites for a range of reasons; from simply reducing the overall material cost to potentially enhance many of the physical properties of the composite, such as surface finish and reducing part shrinkage.

Polymer composite materials based on a thermosetting resin matrix and glass fibre reinforcement have been used in the automotive industry since the late 1950s and have seen continued growth in consumption ever since. One of the many drivers behind the increased application of polymer composites has been the ever increasing pressure on automotive manufacturers to produce more sustainable vehicles. The use of composites potentially allows the production of vehicles with greater fuel efficiency, through weight savings, and extended vehicle life, through increased durability, over vehicles made with traditional metal materials.

Despite their increasing popularity and the many potential benefits that these materials offer, there are factors which could potentially affect the future use of many polymer composites in the automotive sector, such as their perceived un-recyclability due to the thermosetting resins used.

## 2.2. Need to Recycle

### 2.2.1. General

The automotive industry is subject to a range of both legislative and social pressures demanding that the new vehicles produced have ever reduced emission of pollutants and increased fuel efficiencies. The introduction of new materials and manufacturing techniques has seen significant progress in these areas, such as the use of polymer composites which potentially allow substantial weight savings over components traditionally made from metals. However these advances provide other issues as the manufacturers are further required to consider the entire life-cycle of a vehicle, from sourced raw materials at manufacture to disposal at the end of its useful life. The reuse or recycling of composite materials is far more complicated than that of metals and threatens their future application in the automotive sector.

### 2.2.2. End-of-Life Vehicle Directive

Prior to the introduction of recent legislation the area of automotive recycling had predominantly been commercially driven, primarily through the sale of reusable parts such as gear boxes and starter motors etc, and with the other income streams from the recycling of metal components. The remaining materials were then generally land filled and the vehicle's last owner was responsible for its disposal and potentially liable for any relating costs.

New European legislation titled the 'End of Life Vehicle (ELV) Directive 2000/53/EC' [4] has been introduced, effective from January 2006, with the primary aim of reducing the amount of waste from automotive vehicles when they are scrapped. The Directive sets out to prevent waste from ELVs and instead promote greater reuse, recycling and recovery of their parts and materials. The targets set out in the Directive state that from 2006 a minimum of 85%, by weight, of an ELV should be recovered, with 80% of the vehicle being 'reused' and 'recycled', and from 2015 these targets will increase to 95% and 85% of the weight of the vehicle, respectively.

## 2.2.3. What does the ELV Directive Mean for Automotive Manufacturers?

Nine million tonnes of waste is generated from end-of-life automotive vehicles every year in Europe, and investigations into the effects of the ELV legislation have shown that it is not possible for the automotive manufactures to meet the required 85% recycling targets through metal recycling alone [6]. Metal components on average account for only 76% of a car's total weight with plastic materials account for the next largest fraction at 9%, as shown in Figure 2.1, and therefore they must be considered for recycling or reuse if the ELV targets are to be met. The main route for the disposal of ELV components which are not made of metal is currently landfill and, in a few cases, incineration [7], [8]. These methods of disposal do not meet the definitions of 'reuse' and/or 'recycling' according to the ELV Directive, therefore other disposal routes need to be found.
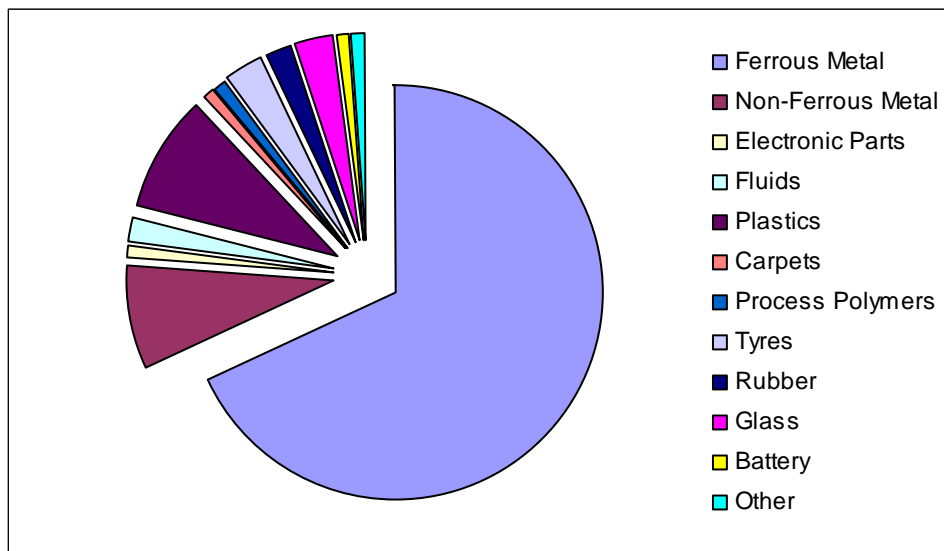


*Figure 2.1, Material Break-Down for an Average Passenger Vehicle in 2000 [6].*

Of the vast array of different polymer components that exist in automotive vehicles today, the ones that account for the greatest weight are those used to make large semi-structural components such as body panels. Two of the most common types of these composite materials are known as sheet moulding compounds (SMC) and dough moulding compounds (DMC) respectively [9].

## 2.3. Sheet and Dough Moulding Compounds

### 2.3.1. General

Sheet and dough moulding compounds, or composites, are the names given to a type of raw, fibre-reinforced and heavily filled thermoset polymer composite materials. SMC and DMC are parallel technologies which use similar combinations of resins, fillers, fibres and additives but are distinguished by the very different manufacturing processes used. In the automotive industry SMC and DMC are used to produce a range of interior and exterior automotive parts, such as deck lids, bumpers, grilles and battery casings as shown in Figure 2.2.
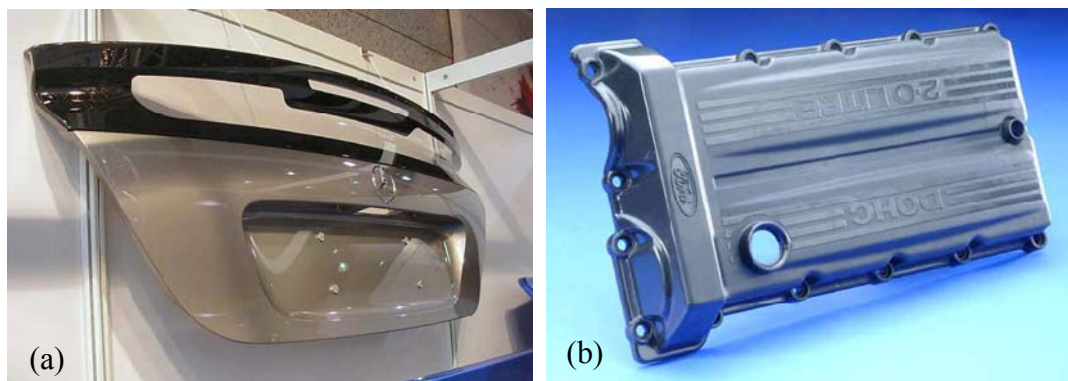


*Figure 2.2, Examples of Automotive SMC Components: (a) Mercedes Tailgate [10], (b) Engine Cover [11].*

It is estimated that 210,000 tonnes of SMC materials were produced in Europe in 2007, with 39% of the market for SMC being automotive, electrical being 39%, construction 16% and other markets representing the final 6% [12]. The use of shorter, randomly orientated reinforcing fibres in DMCs means that they typically have poorer mechanical properties than SMCs, and as a result are not as widely used, production of DMC materials in Europe during 2007 was in the region of 75,000 tonnes [12].

For brevity the material's properties and ingredients will simply be discussed in the context of SMC for the remainder of the chapter but they also apply to DMC materials, unless otherwise stated.

## 2.3.2. Material Properties

In the automotive sector SMCs are seeing increased growth and material selection over both steel and other competing polymer composites, such as those produced by injection moulding and hand lay-up, because of the unique combination of advantageous design and material properties they offer [13], [14]:

**Weight Reduction**

Glass fibre reinforced SMC composite mouldings can typically be 20-30% lighter than equivalent steel parts, potentially resulting in substantial fuel savings over the operational life of a vehicle.

**High Quality and Durable Finish**

Critically it is possible to achieve a Class-A surface finish when moulding SMC, equivalent to polished steel, as required for exterior automotive body panels. SMC composite body panels are also more resilient than metals so minor impacts are more easily dissipated, meaning they do not dent, and they are also more resist to corrosion by road salts and other corrosive environments to which automotive parts are typically exposed.

**Part Consolidation and Modular Assembly**

Several parts can be integrated into one SMC moulding, greatly reducing the number of sub-assembly stages otherwise required during the manufacture of equivalent metal parts, therefore reducing production costs. For example, parts such as aerial antenna or threads can be integrated directly into the moulding process and require no further processing stages.

**Customization and Design Freedom**

Tooling costs for SMC are substantially lower than for metal. This makes it easier for manufacturers to regularly produce the new designs that the market demands, and also suits the high-end of the automotive market where production volumes are much lower.

**Thermal Stability**

A major advantage of SMC, compared to thermoplastic based composites, is its dimensional stability. The coefficient of linear expansion for SMC is very similar to

those of steel and aluminium [15], which means a good interface fit with no gaps between panels in the winter and no buckling in the summer. This also means that exterior body parts can be painted at the high temperatures used for on-line painting of entire vehicles and they don't have to be processed separately.

## 2.4. Raw Materials and Manufacturing

### 2.4.1. Introduction

This research was based on investigating the use of materials recovered from recycled automotive SMC components as ingredients in new DMC and SMC materials. Both of these types of composite are made with very similar ingredients, however the production techniques used differ greatly. This chapter will provide an overview of the types of materials used, their roles within the formulations and the production methods used to produce both types of composite. The exact formulation of any SMC or DMC is dependent on the properties required of the final product, and there are an enormous range of possible material and additive combinations available.

### 2.4.2. SMC and DMC Material Ingredients

#### 2.4.2.1. General

Both of the formulations selected for this investigation, used as the controls and base formulations for the recyclate reformulations, were those of commercially produced composites and were provided by Menzolit UK. The SMC formulation provided was one commonly used for the manufacture of exterior automotive components, chosen for its combination of good mechanical properties and Class-A finish. The DMC formulation was one typically used to produce a range of compression moulded final products, including some smaller interior automotive components.

#### 2.4.2.2. Thermosetting Resin

A variety of thermoset resins can be used for the production of SMCs, such as epoxy or phenolics, however unsaturated polyester resins are the most commonly employed. Polyester resins are chosen because of their low cost, as they have excellent resistance to a range of both chemical and environmental degradations and it is possible to

pigment, fill and process the resin in liquid form, unlike many other thermosetting and thermoplastic resins.

The manufacture of a thermoset polyester matrix begins with the production of unsaturated polyester resin. These unsaturated molecules are produced by the condensation reaction known as polyesterification, the monomers used to make polyesters are diacids and glycols, Figure 2.3. The vast majority of the resins used in the SMC industry are based on maleic anhydride acids and ethylene or propylene glycols, with the possible addition of other chemicals such as orthophthalic or isophthalic acids to modify the chemical structure of the polymer chains [14]. The exact type of unsaturated polyester resin made can be formulated with different combinations of these chemicals depending on the required properties of the final composite part such as; part shrinkage, structural strength, Class-A finish.

The unsaturated polyester resins are typically dissolved in a reactive diluent, which is nearly always styrene in the case of the resins used for SMC manufacture. The styrene helps reduce the viscosity of the raw material, for ease of handling and improved wetting of the reinforcing fibres and during curing it facilitates the cross-linking of the polyester molecules.
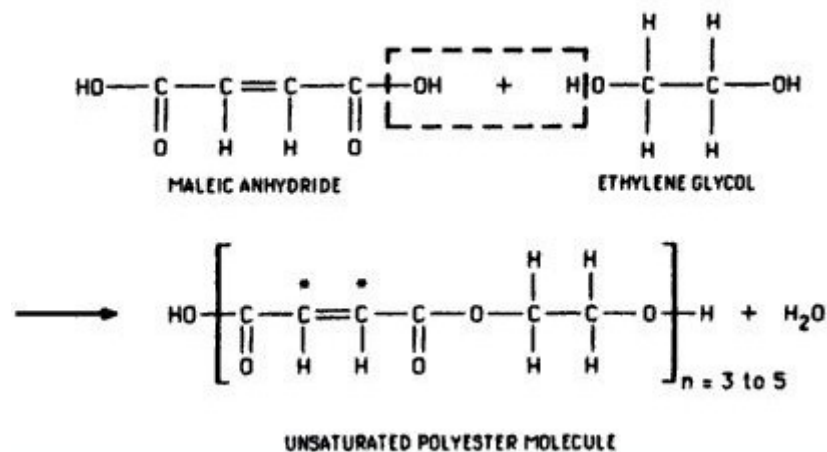


*Figure 2.3, Production of Unsaturated Polyester Molecules, (* Marks the Unsaturated Carbon Double Bonds) [16].*

### 2.4.2.3. Styrene

Styrene is not only used for its ability to act as viscosity reducer for the unsaturated polyester resins but it is also vital for transforming the resins into a solid polymer, during the cross-linking or cure. Styrene is almost exclusively the monomer used in production of SMC.

Once the cross-linking reaction has been initiated, during the moulding process, free radicals are produced at the carbon-carbon double bonds on both the polyester chains and the styrene. The styrene molecules react with these free radicals, in turn creating further new free radical which can then react with another styrene molecule or another polyester chain. These reactions results in the many polyester chains being bridged together and the continual creation of further free radicals, this continues until there are no more reactive sites. The net result is a 3D network of polyester chains bridged together by styrene molecules forming a solid thermoset polymer. The total content of styrene in the composite needs to be carefully controlled as increased quantities can result in higher peak exotherms during curing and can also result in reduced tensile and flexural strength of the final composite [17].
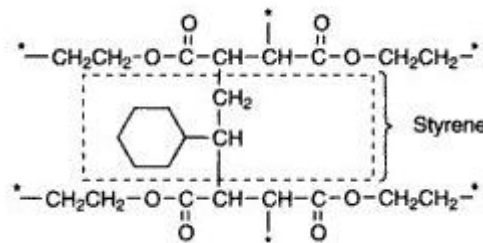


*Figure 2.4, Chemical Structure of Cross-Linking Process During Curing of Polyester Resin [18].*

### 2.4.2.4. Low-Profile Additive (LPA)

Thermoplastic additives are formulated in to SMC composites to reduce the polymerisation shrinkage and to improve the surface finish. Polyester resins show considerable amounts of shrinkage during cross-linking, potentially up to 7% [19], which can reduce the composite's ability to meet tight dimensional tolerances and the high quality surface finish required of many mouldings. The addition of certain thermoplastics has been found to compensate for this large volume shrinkage, though the exact mechanism of this process is still an area of investigation and debate. The

33

most common theories agree that phase separation of the polyester and the thermoplastic resins during cure and the creation of micro-voids in the cured resin both contribute to the effect [20], [21], [22]. Whilst the formation of these voids allows control of the shrinkage and improves surface finish, the composites mechanical properties are reduced as the level of LPA is increased [23]. Therefore controlled formulation must be used to strike careful balance between the desired properties of the final composite.

Only small amounts of these materials, typically 2-5% of the total formulation weight, are required to eliminate any shrinkage and produce a high quality surface finish [14]. Again there are a large number of possible materials available depending on the requirements of the composite being formulated, though typically vinyl acetate or polystyrene are used for SMC manufacture.

### 2.4.2.5. Initiator

Initiators are materials which thermally degrade to produce free radicals that in turn activate the double bonds in the styrene and the unsaturated polyester, thus initiating the cross-linking reaction, Figure 2.4. Their formulation can also be used to control the rate of reaction and therefore help to determine the cycle time of the moulding process. Typically peroxides are used as the initiator due to their low cost, though there are a vast number of initiators available and the exact choice of material is again dependant on the application of the final product, the resins used and the moulding conditions.

### 2.4.2.6. Inhibitor

The initiators used in SMC are typically unstable and will decompose with time, even at room temperature, slowly initiating the cross-linking reaction. To prevent premature cross-linking and help extend the materials shelf life some form of inhibitor is also included in the composite formulation. As the inhibitor acts to prevent the polymerisation of the resin, it can also be formulated to retard the rate of polymerisation and reduce the peak exotherm, during the actual moulding process.

### 2.4.2.7. Release Agent

Release agents are materials with low melting point which, during moulding, create a resin incompatible oily film at the composite – mould surface interface, which enables

easy detachment of the cured part from the mould. Typically calcium or zinc stearate are used as they have melting points of 150 $^{o}$C and 122 $^{o}$C respectively, allowing them to be used for curing conditions up to 165 $^{o}$C typical used for the moulding of SMC polyester components.

### 2.4.2.8. Thickener

The thickening process only takes place in SMC, not DMC, production but is an extremely important and carefully controlled process. The viscosity of the raw material must change over time, so that firstly the resin is able to completely 'wet-out' and impregnate the fibrous reinforcement during fabrication, but then become viscous enough so that it may be handled for distribution and forming into mould charges later. The viscosity of the final product must also allow the even flow of fibres and resin during the moulding process. Alkaline earth oxides or hydroxides, such as calcium oxide or magnesium hydroxide, are most commonly used for the thickening process. Formulation and control of the material's viscosity is a critical process and dependant on many factors, such as the type of resin, water content of formulation and compound filler level, so must be carefully controlled and monitored.

### 2.4.2.9. Reinforcing Fibres

Reinforcing fibres are primarily used in these composites to provide the material with improved mechanical properties and dimensional stability. Of the many reinforcing fibres available generally only glass fibres are used in the production of SMC, most commonly they are of the electrical grade, or 'E-glass'. E-glass fibres are chosen for their combination of good mechanical properties and low cost, though other grades of glass are sometimes used in specialist applications, such as the aerospace industry. The use of carbon fibres to reinforce SMC has been used occasionally, though generally for the low volume, high performance markets of the automotive industry, such as the Dodge Viper [24].

The glass fibres used are typically of very small diameters (10-20 μm) so many filaments are brought together in large numbers to form bundles known as 'rovings'. For SMC production the fibres can be in the form of chopped fibre rovings, continuous filament roving or chopped fibre mats, whilst DMC exclusively uses chopped fibre rovings.

### 2.4.2.10. Filler

Particulate mineral fillers are added to the composite to perform a wide range of functions, such as [13]:

- Reduce overall composite cost
- Control paste viscosity
- Decrease mould shrinkage
- Improve surface finish
- Increase composite modulus

The exact selection of the filler materials is based on balancing these properties for the desired application of the final composite e.g. for automotive exterior body panels the surface finish is considered extremely important and therefore very fine fillers, less than 5 μm average particle diameter, will typically be used. There are many possible types of filler materials available, which are often used in combination in the composite industry. Typically only calcium carbonate is used for SMC manufacture as it provides all of the required properties and comes in a wide range of grades. Small amounts of other 'functional' fillers maybe added to provide other specialist properties [14], e.g. alumia trihydrate can be added to provide flame retardant properties [1].

### 2.4.2.11. Wetting and Dispersion Agents

Chemicals which act as wetting and also dispersion agents are added to the resin at the early stages of manufacture and in order to ensure that the filler ingredients are thoroughly dispersed throughout the resin and that a good interface between resin and particulate components exists [25]. The addition of certain additives also allows higher loadings of filler and/or fibres to be achieved without adversely affecting the viscosity and quality of the final compound.

### 2.4.2.12. Pigment

Another advantage of SMCs is that it is possible for them to be coloured by pigmentation, reducing the need for the costly and polluting painting processes. Either a powder or a paste pigment may be used, though careful selection of the desired pigment

is required as they often contain chemicals which can affect the inhibition or the initiation of the cross-linking reaction.

None of the SMC or DMC formulations manufactured in this research were pigmented.

## 2.5. Sheet Moulding Compound

### 2.5.1. General

Sheet moulding compounds can be basically described as three phase composite materials consisting of; randomly orientated chopped glass fibres as the reinforcement, calcium carbonate powders as the filler and thermosetting resin as the matrix. The two major differences between SMC and DMC production are the chemical thickening process required for SMC and the way in which the reinforcing fibres are introduced during the manufacturing processes. SMC manufacture is a complex process and most modern SMC production facilities are fully automated and temperature controlled, allowing for continuous production if desired.

### 2.5.2. Formulation

As mentioned above, selection of the exact ingredients for any SMC formulation is entirely dependent on the critical properties required of the final product, whether they are physical appearance, mechanical strength or environmental resistance. The SMC used for this research was one formulated specifically to make automotive external body parts and the material ingredients having been chosen accordingly, an example of a typical SMC paste formulation with all ingredients except the glass fibres, is give in Table 2.1.

Whilst it is possible to produce SMC with continuous fibres, due to the lack of any abrasive manufacturing processes, the majority of applications use chopped fibres. For the majority of automotive SMC applications continuous glass fibre rovings are chopped to length, typically 25 mm, during the manufacturing process at a loading of between 50-70% of the formulation's total weight, with resin being 35-55% and filler being 40-70%.

## 2.5.3. Manufacturing

A schematic diagram of an SMC production line is shown in Figure 2.5 and each stage of the manufacturing process is described below. Firstly two separate batches of paste are mixed using all of the raw ingredients except for the reinforcing fibres:

- Paste Part A. The majority of the materials including the polyester resin, low profile additive, filler and other additives are all blended into one paste batch.
- Paste Part B. The other batch contains the thickening agent, some resin and any pigments all mixed in a styrene solution.

In the factory raw materials for each of the batches are pumped directly from storage to dosing containers where they are measured out by weight, according to the prescribed formulation, and then all pumped on to the required mixer for compounding. Immediately prior to being dispensed into the two doctor boxes on the SMC production line, batches of the two different parts of paste formulation, A and B, are thoroughly blended together at a controlled ratio (for the formulation in Table 2.1 that would be 15\1) and heated to $30^{o}$C, to initiate the thickening process.

| Part A | | Part B | |
|---|---|---|---|
| Ingredient | Weight % | Ingredient | Weight % |
| Polyester Resin | 17 | Styrene | 15 |
| Low-Profile Additive | 14 | Low-Profile Additive | 30 |
| Styrene | 2 | Thickener | 8 |
| Inhibitor | Trace | Colour Pigment | 1 |
| Initiator | 0.5 | Filler | 46 |
| Wetting Agent | 1 | | |
| Mould Release | 1.5 | | |
| Filler | 64 | | |
| Total | 100 | Total | 100 |

*Table 2.1, An Example of a Typical SMC Paste Formulation [14].*

Two rolls of a thermoplastic film are drawn through the SMC production line to act as carriers for the paste materials, as shown in Figure 2.6, and later they prevent the loss of styrene from the raw materials during storage. A layer of the paste, at a controlled constant thickness, coats the carrier films as they are pulled through the doctor boxes. Simultaneously, continuous filaments of glass fibres are fed from rovings to a cutting machine which chops them to the desired length at a constant rate. The chopped glass fibres fall randomly under gravity onto the bottom carrier film, now coated with a layer of the paste. The second carrier film with an identical paste layer is then sandwiched on top of these fibres, at $180^{o}$, and this sandwich goes through a system of compaction rollers to 'wet-out' the fibres and produce the final continuous sheet.

The precise control of the speed of the carrier film, the thickness of paste pulled through the doctor box and rate of the glass chopping all combine to determine the overall glass content of the final product, and can all be precisely adjusted to produce the desired composite properties.
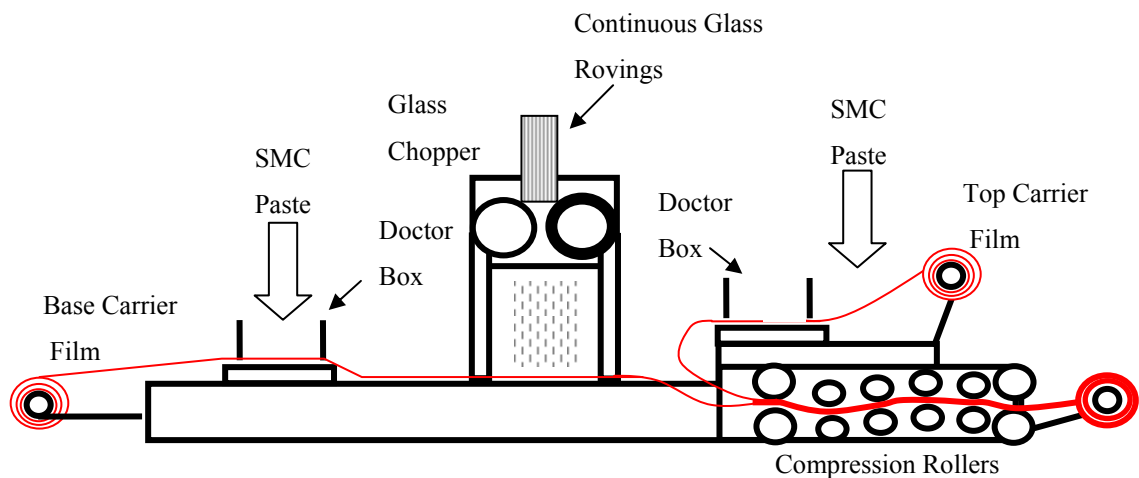


*Figure 2.5, Schematic Diagram of a Typical SMC Manufacture Production Line.*

After production the sheets are matured in a controlled environment, away from humidity and light, for between 2 and 7 days so that the paste can reach a sufficient viscosity to produce the final product, as shown in Figure 2.6, ready for handing and moulding. Once matured the material can be moulded immediately or stored in controlled conditions for up to another four weeks.
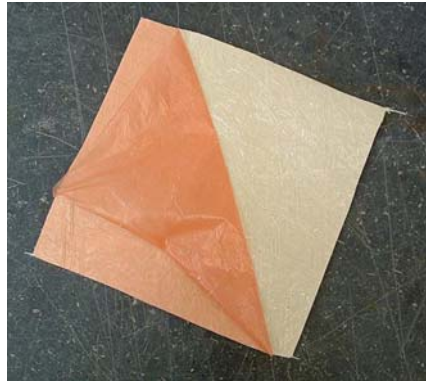
*Figure 2.6, Raw SMC Ply with Orange Thermoplastic Carrier Film.*

## 2.6. Dough Moulding Compound

### 2.6.1. General

Dough moulding compounds, also known as bulk moulding compounds (BMC), use very similar material ingredients to SMCs but are manufactured using a much simpler and less labour intensive process.

### 2.6.2. Formulation

In contrast to SMCs, DMCs typically use a much shorter reinforcing glass fibre (between 4 and 12 mm) and much lower percentages of reinforcement ~ 25% of the total formulation weight. They are instead generally more heavily filled, with between 50-80% of the formulation weight being filler materials and with the remaining 20-35% being the resin. The DMC formulation used in this research was provided by Menzolit UK, an example of a basic DMC formulation is given in Table 2.2.

| Ingredient | Weight % |
|---|---|
| Polyester Resin | 15 |
| Thermoplastic Resin | 5 |
| Inhibitor | Trace |
| Initiator | 0.4 |
| Release Agent | 1.6 |
| Filler | 63 |
| Fibre | 15 |
| Total | 100 |

*Table 2.2, Example of a Basic DMC Formulation [14].*

### 2.6.3. Manufacturing

DMC manufacture is done by batch production with three separate stages all performed in one high shear mixer [13], such as that in Figure 2.7.

1. Firstly all of the wet ingredients are blended together; resins, inhibitor, and initiator for a mixing time of around four minutes.
2. Then all of the remaining dry ingredients, except the glass fibres, are added to the wet ingredients already in the mixer and mixed for a further twenty minutes, to ensure that all materials are evenly and thoroughly dispersed.
3. Finally pre-chopped glass fibres are added to the paste in the mixer and it is all mixed for a further 4-5 minutes, to wet-out and disperse the fibres.
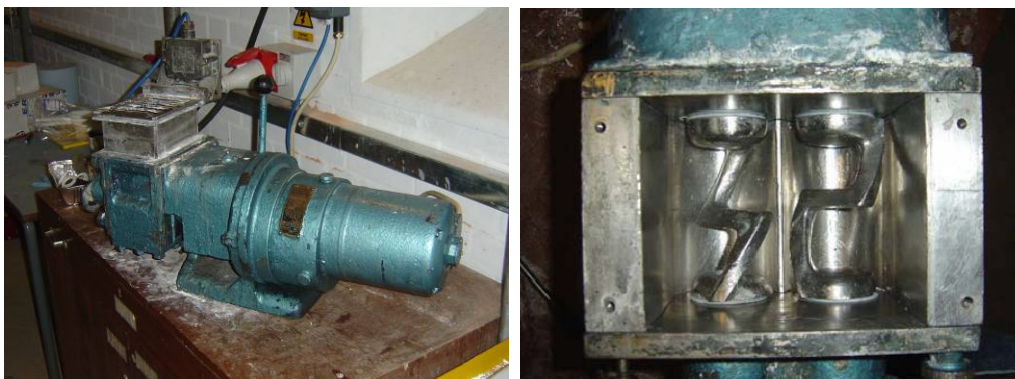


*Figure 2.7, The 'Z'-Blade DMC Mixer Used for this Research.*

After the mixing stages the finished raw compound, Figure 2.8, is discharged from the mixer and, as DMCs do not require any maturation time after compounding, may be moulded immediately or can be stored in controlled conditions for up to four weeks.



*Figure 2.8, Raw DMC Material.*

## 2.7. Previous Investigations into Recycling Thermoset Composites

### 2.7.1. General

There have been a range of investigations into the recycling of thermoset composites and especially SMCs over the past twenty years. A wide range of recycling routes have been considered, though they can generally be grouped in to the three main methods of; thermal, chemical and mechanical recycling. Figure 2.9 illustrates these different areas and the recycling processes grouped under each method.

**Recycling of Thermoset Composites**

```
Recycling of Thermoset
      Composites
```

Thermal → Combustion, Fluidised-bed, Pyrolysis
Chemical → Solvolysis
Mechanical → Filler Particle, Fibrous Particle

**Combustion**
Energy recovery, large residue due to low organic content

**Fluidised-bed**
Thermal degradation for recovery of fibres, filler and energy

**Pyrolysis**
Chemical decomposition for chemical, filler and fibre recovery

**Solvolysis**
Chemical degradation

**Filler Particle**
Fine granulation of all materials to act as filler

**Fibrous Particle**
Potential reinforcement from retained fibre length

*Figure 2.9, Previously Investigated Composite Recycling Methods [1].*

An overview of the methods previously investigated is discussed below.

## 2.7.2. Thermal Recycling Methods

### 2.7.2.1. General

There is an ever increased demand for energy around the world and the ELV Directive allows for up to 10% of the 95% 2015 target to be obtained from 'energy recovery' [4]. Several methods of recovering the energy from DMC and SMCs by thermal methods have been investigated by several different authors and are discussed below.

### 2.7.2.2. Energy Recovery or Incineration

All materials have a calorific value, so waste materials can potentially be combusted and energy recovered from the heat, e.g. by conversion to electricity. Composites such as SMC are, however, heavily loaded with non-organic ingredients such as fillers and glass fibres and the only organic material that will combust is the resin which typically only constitutes a maximum of up to 35% of the total formulation's weight. Mineral fillers such as calcium carbonate decompose at high temperatures, absorbing energy, and some SMC formulations even contain fire retardants. These factors therefore limit the amount of energy obtainable by incineration, estimated to approximately 6.7 MJ Kg$^{-1}$ for a typical SMC formulation [26]. In addition there is then a large amount of solid residue left over which requires further disposal. These residual materials are not useful

as fillers in new SMC or DMC materials as the temperatures involved convert the calcium carbonate filler into calcium oxide, which adversely affects the thickening process in virgin material production [27].

### 2.7.2.3. Fluidised-Bed

Another method of recycling composites by thermal degradation is the use of a fluidised-bed process, which has been applied to SMC and DMC recycling in several studies, [28], [29]. The primarily the aim of this research has been the recovery of the reinforcing fibres, as these are of potentially higher value as a recycled material than the filler and resin ingredients, both glass and carbon fibre reinforced composites have been investigated.

The method works by thermally decomposing chopped sections of composite in a bed of silica sand, which is heated and fluidised by air at around 450-500 $^{\circ}$C. The organic resin is thus volatilised and by a combination of attrition of the sand particles and then by transportation in the air stream, the filler and fibre particles are separated from the resin and can be collected as desired. The volatilised organic components may potentially be combusted for heat and energy recovery, whilst the filler and fibre particles could be re-used in new composites. When such recovered fibres were used as reinforcement in new DMC compounds by Kennerly et al [28] it was found that up to 50% replacement of the virgin fibres was possible, with minimal drop in the composites mechanical performance. The authors also suggested that processing at high temperatures would have remove any of the polyester compatible silane coating from the recovered fibres, therefore fibres were re-coated with a similar silane before compounding in a new DMC formulation. In spite of this re-coating no improvement in the resulting composite's mechanical properties, compared to those with the untreated fibres, were observed.

There are currently no commercial applications of this process in operation, with investigations being performed on relatively small scale models, and for the process to be economically viable it is estimated that at least 9,000 tonnes of composite would need to be processed per year [28].

### 2.7.2.4.    Pyrolysis

The pyrolysis process involves the degrading of a material with heat, into simpler molecules, in the absence of oxygen. This approach can be applied to polymer composite materials so that the resin matrix is broken down into simpler gas and liquid products, which can be recovered along with the separate reinforcing and filler materials to potentially be used in new composite materials.

There have been a number of investigations into the use of pyrolyisis as a means of processing scrap SMC [30], [26], [31], [32] at a range of temperatures and processing times. It has been shown that temperatures below 300 $^o$C do not allow the complete pyrolisation of the resin and at temperatures over 600 $^o$C an undesirable degradation of the inorganic matter is observed, as described by Torres et al.[26]. The gaseous and liquid products produced have been analysed further in several investigations as they could potentially be used to produce energy. The oily liquids have been found to have a calorific value of approximately 35 MJ $Kg^{-1}$, meaning they could be used as a source of fuel, however the gaseous materials were found to predominantly be made up of CaO and $CO_2$, with some $H_2$, $CH_4$ and other hydrocarbons present, resulting in a much lower calorific value at approximately 15 MJ $Kg^{-1}$ and meaning they are not particularly as useful as a fuel.

Several applications for the remaining solid residue have also been investigated, predominantly as a filler or reinforcement in new composite materials. The glass fibres have been recovered from the solid material, by sieving, and used to replace virgin fibres in DMC by Cunliffe et al. [32]. At both 25% and 100% replacements, by weight, the mechanical properties were significantly poorer than a control, though the part's surface finish was reported to still be good. Graham [33] investigated a similar fibre replacement process in DMC and again a reduction in all mechanical properties was observed at replacements as low as 10%. These reductions in mechanical properties when the recovered recyclate is used as reinforcement in DMC are likely due to the thermal degradation of the glass fibres at the high temperatures used which can reduce the strength of the fibres by up to 50% [29]. By grinding solid residue down to a fine powder the author was able to use it successfully as a replacement for filler in SMC, with slight improvements shown in the mechanical properties at a 20% replacement.

### 2.7.3. Chemical Recycling

#### 2.7.3.1.      General

Chemical recycling processes involve degrading the composite's polymer matrix into basic chemical substances which can then potentially be reused as fuel or in the manufacturing of new polymers. This process also potentially allows the recovery and reuse of any filler and/or reinforcing materials that may have also been in the composite.

#### 2.7.3.2.      Solvolysis

The solvolysis process aims to degrade the composite's polyester-styrene polymer network by reaction of the ester linkages. The process generally involves refluxing the composite material in a solvent, for various lengths of time depending on the chemicals involved and the amount of degradation desired. A vast range of solvents, such as potassium hydroxide, ethanol and acetone have been trialled by the authors Patel et al. [30] and Winter et al. [34] specifically for the recycling of SMC composites.

Both investigations were able to successfully extract the polyester resin from the filler and fibre components, with Winter et al. [34] recovering over 90% of the resin from the composite. Both authors found that to achieve acceptable levels of recovery with the investigated solvents the SMC had to first be ground to a fine powder, meaning that the recovered fibres were therefore not suitable for use as reinforcement in new composites. However Winter et al. was able to recycle larger pieces of SMC with ethanolamine as the solvent, and found that the clean recovered fibres could be used to replace up to 50% of the virgin fibres in DMC composites without affecting the compounding process or mechanical properties.

#### 2.7.3.3.      Hydrolysis

Hydrolysis is the chemical decomposition of a material by solvolysis, by reaction with water as the solvent. Laboratory investigations have shown that it is possible to degrade the SMC's polyester resin to liquid products almost identical to the commercial chemicals originally used in polyester manufacture [34]. Winter at al. also found that it was eventually possible, after several further stages of processing, to use the recovered filler and fibre materials to replace up to 50% of the equivalent materials in new DMCs without dramatically affecting their mechanical properties. However, acceptable levels

of degradation in less hydrolytic conditions are only possible when the composite is first ground to a fine powder [30], and in all cases large quantities of waste chemicals are produced which require further careful disposal.

## 2.7.4. Mechanical Recycling

### 2.7.4.1.    General

The principle of mechanical recycling revolves around the size reduction of the waste component for reincorporation into another material. There have been a large number of studies into the recycling of thermoset composites by mechanical, or particulate, recycling and this is the only recycling route that has been applied commercially to process waste SMCs, to date. However, the methods of size reduction and utilisation of the resulting materials, known as 'recyclate', have varied greatly throughout the literature. The SMC recyclate materials have been investigated as a potential ingredient in range of new materials, such as thermoplastics composites [35], [36] and concrete [37], however this research is only interested in the closed-loop recycling process and only past investigations using the recyclate to produce new SMC and DMC will be discussed further.

### 2.7.4.2.    Size Reduction

The effective re-use of recycled composites as ingredients in new materials relies on some process of size reduction. Automotive SMC parts can be in excess of 5 $m^2$ and therefore an initial cutting or shredding process is typically adopted, so that the composite is then small enough to be processed further with other machinery. It is then comminuted further to produce particles small enough to be incorporated in new composite formulations. There have been few in-depth investigations into the best method of reducing the shredded SMC to a processable size, but typically some form of impact grinding has been employed, utilising the resins brittle properties to reduce the amount of energy required to process it. Inoh et al. [5]  compared the recyclate produced by, and the economic implications of, several common granulation techniques, including roller, hammer and ball mills, deciding upon a screen-classifier type rotating hammer mill to produce recyclate for further investigation. Such equipment has commonly been employed in the other scientific studies [35], [38], [39] and also by

industrial scale operations such as the ERCOM and Mecelec, as it is cheap to set-up and most importantly the process preserves the original reinforcing fibre's length [38].

### 2.7.4.3.        Recyclate Classification

The exact characteristics of the recyclate are dependent on both the feedstock materials and the granulation techniques used. Recyclate is a complex, heterogeneous blend and combination of the resin, filler particles and reinforcing fibres, over a diverse range of sizes, in all shapes and aspect ratios. Generally only part of the produced recyclate will be desirable for reformulation into new compounds, e.g. if the recyclate is to be used to replace filler particles an average particle size of less than 10 μm normally is required, and therefore the larger particles in the recyclate will have to be separated off.

There is no official standard for the classification of recyclate and as a result all previous studies have implemented their own methods of grinding and classification, making their results very difficult to compare directly. However, the recyclate materials produced are generally defined as one of two different grades:

1. 'Coarse' grade materials consisting of the larger particles, typically bundles of glass fibres held together by resin, too large to be used as filler materials but with the potential to be used as reinforcement in new composites or be ground down again.
2. 'Fine' grade materials ground down to very fine particles for potential use as filler.

The equipment and methods used to classify the recyclate into these two groups have varied greatly throughout the previous research, with the most common and rather simplistic method being the use of sieve meshes. Particles larger than 0.5 mm have been considered as coarse 'fibre-length' recyclate and everything smaller fine 'filler-sized' [2], [35], or several stages of sieves have been used to separate particles with use of varying mesh sizes, 1 - 5.5 mm [40]. The shape and nature of the recyclate does not lend itself well to grading by dry sieving,  as the materials clump or 'fuzz-ball' together [41], [42] under the action of the sieves. These clumps contain a range of particles and fibres that would otherwise be classified by the following finer meshes, and as they build up on the mesh surface they prevent further materials from passing through. Sieving is also

not a practical method for separating fibrous materials such as glass fibres as there is no distinction between length and width, it is possible for a 10-20 mm long fibre to fall through finer meshes because of its very fine diameter [43]. In spite of these problems and the short comings of the sieving method no other equipment or methods have been investigated for the separation of these recyclate grades. Some investigations have not employed a post-granulation classification process at all but instead performed several stages of granulation with classifier screens of decreasing aperture size used to control the maximum particle size of each grade [39], [42].

### 2.7.4.4.    Physical Characterisation of Recyclate

In general particle size analysis of the recyclate grades has been defined by the sieving process employed to classify them, simply giving a maximum and minimum particle size range for a weight percentage of the recyclate, despite the discussed inaccuracies of this method for fibrous materials [42]. DeRosa et al. [44] attempted to measure the length of coarse particles under a microscope and found a range of particle sizes between 0.5 and 25 mm though they were unable to produce an accurate distribution due to the 'the extreme variety in the fibres'. Bream and Hornsby [35] attempted to separate the glass fibres from the other recyclate constituents and to then measure the fibre length distribution under a microscope. Again a large length distribution was observed making it difficult to accurately focus-on and distinguish between individual fibres for measurement, as a results only an indication of the fibre length distribution was recorded and given as being between <0.1 and >10 mm.

Given the diverse range of particles produced by any impact granulation process and the lack of homogeneity in the particles, it is very difficult to characterise each of the separated grades by their physical morphology and no surprise that no thorough investigation into this characteristic of the material has been performed.

### 2.7.4.5.    Recyclate Material Composition

The initial composition of the composite used to produce the recyclate may not be known and results of compositional and scanning electron microscopy (SEM) investigations by previous authors clearly show that the recyclate materials consists of a complex combination of the composite's original ingredients. The resin, filler and glass fibres remain adhered together to some extent in all of the particles grades [35], [45].

Therefore, for example, if an investigation plans to replace virgin reinforcing glass fibres with recyclate on a 1:1 basis by weight, the glass content of the resulting composite material will actually be reduced, as the recyclate grade is not 100% glass fibre. This effect has been highlighted by several investigations [45] though only taken into consideration by Bledzki et al. [38].

### 2.7.4.6. Composite Reformulation

The methods used to reformulate SMC and DMC composites to include the recyclate materials have varied greatly throughout previous investigations. The vast majority of work has focused on incorporating the recyclate into DMCs rather than SMCs, due to the simpler manufacturing process involved. Recyclate was predominantly used to replace the filler materials in the new composites due to the powdery nature of the recyclate produced by the granulation. Replacement of the filler materials has been successful in some investigation used in both SMC [5], [27] and DMC [38], [46], [42] without dramatically effecting the composites mechanical properties, however all attempts to replace reinforcing fibres with coarser recyclate materials have produced substantially weaker composites [42], [45].

## 2.7.5. Previous Research into Mechanical Recycling

### 2.7.5.1. General

Whilst there have been attempts to use the recyclate as an ingredient in composites based on other polymer matrices, such as polypropylene [35], [40], [36], [39], only the investigations which have attempted to introduce the recyclate into the parent thermoset composites will be discussed in-depth in the following section.

### 2.7.5.2. Industrial Recyclate Production

Several companies have set-up industrial operations to collect waste SMC for granulation, classification and then sale as a raw material [47]. The most documented companies are Phoenix Fibre Glass in Canada, which closed in 1996 due to a lack of demand for the material, and ERCOM which was formed from a German consortium of companies from the SMC industry as is still in operation. There are several other companies that have also been involved in this area around Europe: Mecelec and Valcor in France, Lorenz in Germany and Milijotek in Sweden.

Of the various companies that have produced recyclate only ERCOM's material has been investigated by in-depth scientific investigation. At their processing plant the granulation of the waste composite part is firstly performed, if necessary, using a shredder to reduce the larger components to a useable size. Then hammer mill granulators are used to produce the recyclate material. Air classifiers and cyclones are used at the first stage of classification to remove coarse particles and any contamination and then again at the next stage to separate the fine from the coarser materials and return the largest particles to the granulator for reprocessing [48]. Finally fine and fibrous grades of material are classified, as described in Table 2.3, using tumbler sieves.

| *Grade:* | P1 | P2 | P3 | F1 | F2 | F3 |
|---|---|---|---|---|---|---|
| **Grain Size (mm)** | <0.2 | 0.2-0.5 | >0.5 | <0.5 | 0.5-1.25 | >1.25 |
| **Fibre Length (mm)** | <0.25 | 0.25-0.3 | 3-15 | 0.5-3 | 3-6 | 6-20 |
| **Densty (kg/m^3)** | 650 | 300 | 160 | 600 | 450 | 260 |
| **Material (wt%)** | | | | | | |
| **Glass Fibre** | 45 | 47 | 47 | 42 | 53 | 46 |
| **Resin** | 41 | 35 | 36 | 36 | 33 | 30 |
| **Filler** | 14 | 18 | 17 | 22 | 14 | 24 |

*Table 2.3, ERCOM Recyclate Grades [3].*

The finer classified grades of ERCOM recyclate, labelled 'P', are the powdery in appearance and have therefore commonly been used to replace the filler materials used in SMC and DMC manufacture, such as calcium carbonate. Larger recyclate particles are classified into the three 'F' grades and because of their coarser particle sizes they are considered as potential reinforcing rather than filler grades.

### 2.7.5.3. Scientific Investigation

Bledzki et al. [38] produced recyclate materials by grinding waste SMC in a hammer mill granulator, and then separated it into different grades using a combination of air classifiers and sieves. No specific details of the air classification equipment or methods used are given, though the article's acknowledgments and future papers by the authors strongly suggest the recyclate came from the ERCOM processing plant. Three grades of fibrous recyclate named 'coarse', 'medium' and 'fine' were chosen for investigation.

These three fibrous grades were used in new DMC formulations at loadings of 5, 10 and 30% of the weight of the total formulation, whilst retaining the overall glass content of the formulation at 35%, by weight.  The flexural strength of all of the new DMCs were reduced, to between 90 and 60% of the values recorded for a standard control material, the fine materials showing the least variation with increased recyclate loading. The reductions in composite strengths were attributed to a poor bonding between the recyclate particles and the new resin matrix, as observed under a microscope. DMC materials containing the recyclate were also trialled in a full scale production mould, and were found to process as well as the standard materials. This is one of the few papers to suggest that SMC recyclate does not have to just be ground to a powder, but that there are other fractions available and that there is potential value in retaining coarser particles, which could potentially be used to provide reinforcement.

Further work by Bledzki et al. [46] compared use of SMC recyclate along with other recycled composite materials, such as printed circuit boards, as ingredients in new DMC and SMC composites. Grades from both of the waste materials were produced by ERCOM. Reformulation of new DMC was performed using grades F2 and P1, Table 2.3, added at loadings of 15 and 30% of the formulation, whilst the overall glass and filler contents were retained at 35% and 32% respectively, by weight of the total formulation. At the 15% replacement the DMCs with grades F2 and P1 of the SMC recyclate showed an increase in flexural strength and modulus, but a drop in tensile and impact strengths when compared to the standard reference material. All composites showed reductions, between 20-30%, in all mechanical properties; flexural, impact and tensile strength and flexural modulus at 30% loadings.

Two grades of the fine SMC recyclate materials, P1 and P2, were also used in the production of SMC. Recyclate could only used to make up a maximum of 10% of the total paste formulation's weight before its viscosity became too high to process effectively. All of the mechanical properties of the new SMCs compared well with those of the control material, with increases in the flexural strength and modulus observed. These improvements were attributed to the fine fibres in the recyclate filler which may have provided a certain degree of additional reinforcement.

Petterson and Nilsson [27] also used the recyclate materials produced by ERCOM, specifically filler grade P2 and fibre grade F1. The amount of recyclate added to the reformulations was initially determined by experimentation, to evaluate the maximum amount of recyclate that could be added such that the raw compound could still be processed in an identical manner to standard materials. Half of the calcium carbonate filler was removed from the SMC formulation, representing 37% of the total formulation, and replaced with an equal combination of P2 and F1 grades, which then only represented 10% of the total. Two DMC formulations were made with 100% of the calcium carbonate replaced by recyclate materials, one with grade F1 and the other with equal amounts of grades P2 and F1. Both SMC and DMC composites were produced without changes to the standard manufacturing processes. During moulding trials a delay in the curing reaction for materials containing recyclate was recorded, suggesting the reduction in thermal conductivity of the raw composites containing recyclate. The SMC materials produced had an improved flexural strength and only small drops in the flexural modulus and impact modulus, 88% and 97% of the control standard SMC respectively. Both DMC formulations, however, saw dramatic drops in mechanical performance with the combination of P2 and F1 producing slightly better results than that of the simply F1 formulation, with a flexural strength 59% and an impact strength 64% of the standard control DMC. The surface finishes of the moulded parts were inspected visually and the SMC panels containing recyclate could not be separated from the standard control materials, whilst the DMC panels were seen to have significantly reduced smoothness.

The observed improvement in the SMC properties may well have been due to the presence of glass fibres in the filler material, replicating results observed by Bledzki et al. Though no possible reasons are given for the dramatic drop in the DMC properties, they may have be due to the reformulation method used. When completely replacing the standard filler with the fine recyclate there was a resulting drop in composite's overall filler content, but these reformulations had to be used due to the observed resin absorption by the recyclate materials, affecting the paste's processability.


Inoh et al.'s [5] investigation considered the potential recycling of SMC recyclate from the perspective of establishing a commercial processing facility, starting with the equipment for shredding of waste materials though to the manufacture of new

composite materials including the produced recyclate as a raw ingredient. Firstly the different types of granulation equipment for the production of recyclate were compared. A rotating hammer mill type granulator was found to be the best processing equipment, for the production of a recyclate material that could be used in new composites, on the basis of economic efficiency and fibre length retention. The recyclate used for further DMC compounding and moulding trails was not further classified after the granulation process, a mean particle diameter of 40 μm was determined by the classifier screen used in the granulator. Initial investigations showed that use of the recyclate as filler caused large increases in the composite paste viscosity, as compared to calcium carbonate, therefore limiting the amount that could be effectively reformulated into the new composite. Addition of the recyclate into DMC was trialled with 50% of the weight formulation being recyclate, replacing 100% of the reinforcing fibres and 60% of the standard filler. The resulting DMC formulation showed large reductions in all mechanical properties, with the flexural and impact strengths reduced to 57% and 32% of the standard, respectively. Two batches of SMC were also made with the same recyclate material replacing standard filler materials. Reformulation was done at 10% and 20% of the total formulation weight, with slight adjustments made to the resin content to maintain the final paste viscosity. In comparison with a control material, both formulations of the SMC showed an improvement in the flexural and impact strengths and only slight reductions in the flexural modulus and surface quality.

Jutte and Graham [42] produced their own coarse 'fibre' and fine 'filler' grades of recyclate SMC using a rotating hammer mill type granulator with two different mesh sizes for the different grades, 3/8 inch and 3/16 inch respectively. Both of these materials were reintroduced into three different DMC formulations, six batches in total, for comparison with a standard DMC:

1. 5.8%wt of the total formulation was recyclate, replacing 10% of the virgin filler and 2.5% of the fibre.
2. 11.6%wt of the total formulation was recyclate, replacing 20% of the virgin filler and 5% of the fibre.
3. 70% wt of the total formulation was recyclate, replacing 100% of the virgin filler and 100% of the fibre materials.

Mechanical testing of the produced DMCs showed a drop in all of the mechanical properties for all composites, using both the 'fibre' and the 'filler' recyclates. The best results were obtained when the 'fibre' recyclate was used in formulation 1, giving a reduction in mechanical and impact strengths to 73% and 83% respectively, compared to the DMC control standard. Though no reasons for the drop in performance are discussed by the authors, such large drops are quite surprising given that only relatively small amounts of the reinforcement were being replaced. Fine filler materials were also separated from the above grades using a 0.0082 inch mesh sieve, for the replacement of calcium carbonate in SMC. Though no new composites were manufactured the resin absorption characteristics of the recyclate powder, in comparison with the standard calcium carbonate filler, were again investigated. It was found that double the standard levels of resin were required to retain a usable paste viscosity, similar to the observations of previous authors [5], [46].

Research by DeRosa et al. [45], [2] used recyclate materials provided by the industrial company Mecelec. The exact grades were not given, though the particle fibre length range was measured by the authors to be between 0.5 and 17 mm. The material content of the recyclate was first determined by thermo-gravimetric analysis and then acid digestion. Then a DMC reformulation was made based on these results, replacing 100% of the virgin fibres with recyclate whilst retaining the overall glass content of the formulation at 11.5% of the compound weight and adjustments were also made to the filler content to allow for the resin and filler materials in the recyclate. This was the only time that such a considered approach was applied when using the recyclate materials, despite being discussed by several previous authors. Batches of DMC were also made with different lengths of chopped virgin glass fibres (3.175, 6.35, 12.7 and 19 mm) to compare against the recyclate reinforced composite – in an attempt to quantify the reinforcing effectiveness of the recyclate in terms of an equivalent virgin fibre length. Finally blends of 70%wt virgin fibres and 30%wt recyclate fibres were used as the reinforcement; adjustments were also made to maintain 17% of the total DMC formulation glass fibres, by weight. Similar to the findings of the previous research by other authors all DMC formulations containing recyclate materials showed a drop in the mechanical performance, both flexural strength and modulus, in comparison with the

100% virgin fibre equivalent. The 100% recyclate reinforced DMC had properties only slightly better than those of a totally un-reinforced control material and did not compare closely with any of the reformulations using different virgin fibre length, suggesting the recyclate used had a very poor reinforcing potential.

Attempts were then made to improve the bond between the recyclate and DMC's polyester resin by surface treatment. The theory of the treating of the recyclate was to produce sites of reactive unsaturated ester, on the cured polyester resin materials in the recyclate grades, which could then be active in new cross-linking reactions with virgin resin. The surface treatment involved three stages, firstly by hydrolysis of the polyester matrix and then further reactions of the materials to create the desired fresh unsaturated bonds. After the treatment only a very slight increase in carbon-carbon bonds in the recyclate was found using Fourier Transform Infrared spectroscopy (FTIR). This was the first study to consider modifying the recyclate to improve its reinforcing potential, however no improvement in the mechanical performance of the resulting composite was achieved in comparison with untreated recyclate materials.

## 2.7.6. Discussion

Of all the investigated thermal recycling methods the fluidized-bed and pyrolysis processes appear the most promising as, in theory, they allow the recovery of all the composite material's original ingredients and/or the energy from the composite. However as with all thermal recycling methods, there results a significant reduction in the mechanical properties of the recovered materials, which limits their potential reuse as reinforcement or filler, and further investigations are required into possible applications or markets for these resulting products. The methods all require a large amount of initial energy input to reach the high temperatures required for successful processing. The use of thermal methods does not allow for a 'closed-loop' recycling route for SMC or DMC composites and only fits the definition of 'recovery' in the ELV Directive. This means that it can only account for 10% of the 95% 2015 ELV Directive target, and energy recovery is already applied for the recycling of other automotive components, such as tyres, so it is unlikely that it will be adopted for processing these materials also.

Lab scale investigations into the chemical recycling of SMC have been partially successful. However these processes require the use of a range of hazardous chemicals and often a large amount of heat, for long periods of time, to reach desired results. After recovery of the resin and fibre components there is typically also still a large amount of chemical waste, produced by the various processes involved, which then requires further disposal. As a result of these issues such methods of SMC recycling are not yet commercially viable.

More success has been observed in the mechanical recycling investigations by granulation of the waste SMC for replacement of filler materials in new composites. However, throughout the literature there has been little or no comparison between the methods by which recyclate SMC materials have been reformulated into either new SMCs or DMCs. These differences occur as a result of the variations in the granulation methods used, the type of classification procedure applied and method of reformulating the different grades back into new the composite, making it very difficult to compare any of the investigations directly.

The source of feed stock and the granulation methods used have varied throughout, however it is generally agreed that some form of impact granulation, typically a rotating hammer mill type granulator with a classifier screen, allows some of the original fibre length to be retained and is also the most economically viable process for the size reduction. The methods of classification and distinction between the different grades of recyclate, if they are classified at all, have also differed greatly throughout all previous studies. There is general agreement that there are two grades of particles in the recyclate that may potentially be separated off and used to replace either virgin filler or reinforcing materials, though there is no standard method of differentiating between the two. Classification of the recyclate materials is a very difficult problem due to the complexity and diversity of the materials produced, and as a result has generally been approached simplistically, if at all, by collection of the finest powder-like materials by dry sieving to be used as filler in a new composite.

Incorporating recyclate into new DMCs, as a filler or reinforcement, has generally always resulted in a drop in the composites tensile, flexural and impact properties and all studies have shown a trend towards further decreases in mechanical properties as the

quantity of recyclate used is increased. Reductions in the composite's properties have even been seen when the more fibrous 'reinforcing' grades have been used to replace standard fillers. Several authors have highlight that because recyclate consists of a blend of resin, filler and fibre a direct weight replacement for any of the raw ingredients by recyclate in a new composite is not truly accurate. DeRosa reported that nearly three times the weight of recyclate would have to be added for true replacement of virgin fibres to keep the overall glass content the same [45]. Other authors have continued with a simple 1:1 weight replacement, which naturally results in a reduction in the level of the reinforcement in the new composite and would have contributed to the drops in mechanical performance observed. Poor adhesion between the composite matrix and the recyclate particles has also been cited as a potential cause of the poorer mechanical properties but not investigated further.

There have been some successes when the finer recyclate grades were used to replace filler materials in SMC formulations, with the mechanical properties being comparable with those of a standard control formulation. However it has only been possible to replace a small quantity of the virgin filler materials, up to 20%, before the paste material becomes un-processable due to the resin absorption of the recyclate causing large viscosity increases. It has not been possible to use coarser grades of recyclate in the SMC production as the paste has to pass under the doctor box blades, a gap typically only 1.5 mm high, and it is feared that the coarser particles would cause clogging of the doctor box or even tears in the carrier film [42].

The authors have rarely considered the financial implications of the different reformulation methods and recyclate materials used. The vast majority of the mechanical recycling work has used the finer/filler grades of recyclate materials to replace the virgin filler materials. Typical filler ingredients used in SMC and DMC manufacture are very cheap raw materials whereas the reinforcing fibres used are the most expensive ingredient in the composite. For example calcium carbonate filler costs approximately 0.08 £/Kg and E-glass fibres cost around 0.75 £/Kg. If it is possible to recover the reinforcing materials in the recycled SMC cheaply enough and use them to replace the virgin reinforcing fibres, as well providing a recycling solution the process may also potentially allow the manufacturers to make a cost saving and make such a recycling process more commercially viable.

Few researchers have investigated the mechanical properties of the actual recyclate fibres, recovered from mechanical recycling, for direct comparison with the properties of virgin glass fibres they are to replace. The mechanical performance of a composite material, such as SMC, is inherently dependant on the properties of the reinforcing fibres, such as their strengths and interfacial properties with the polymer matrix. Differences between the properties of the recyclate fibres from those of the virgin glass fibres may provide insight into the mechanical properties of composites reinforced by such fibres.

# Chapter 3

## 3. Experimental Techniques

### 3.1. Introduction

The purpose of this chapter is to give details of all the experimental techniques used in this research. The purpose of the tests used and any relevant literature is discussed first, followed by descriptions of the apparatus and methods used to perform the experiments.

### 3.2. Recyclate Production

#### 3.2.1. Waste Materials

The waste materials used to produce the recyclate for this investigation were Aston Martin SMC front fender sections, provided by Mitras Automotive, as shown in Figure 3.1.



*Figure 3.1, SMC Front Fender Section for Granulation.*

They were moulded from an automotive, class-A surface finish, formulation and were supplied straight from the factory after the moulding process. Virgin SMC parts have been chosen over actual ELV components for simplicity, if it is possible to recycle this factory waste then further investigation can be performed on the use of actual ELV parts, which could potentially introduce further variables to the separation, chemistry and reformulation of the recyclate. The average age of an ELV in the UK is 14 years [49] and over this life-time the composite components are likely to have collected and

absorbed a range of contaminations such as; water, exhaust fumes, oils, road tar and salt etc. The vast majority of automotive exterior mouldings are also painted and have reinforcing ribs glued to them, to improve crash impact strengths and load bearing ability. Nearly all parts also include some form of metal fixings and screws for integration with the rest of the vehicle during assembly and may even have had electrical components moulded into them directly. The current method of automotive recycling generally involves the shredding of the entire vehicle rather than the dismantling of individual parts. The different materials in shredded product are then separated by a series of air, magnetic and water classifiers [8], each stage of which could potentially introduce other contaminants to the recyclate.

### 3.2.2. Granulation

Granulation was used to reduce the supplied waste SMC components to a particle size that could be used as an ingredient in new composite materials. The exact equipment and methods used to produce the recyclate materials are discussed in depth later in Chapter 4.

### 3.2.3. Classification

Not all of the materials produced by the granulation process are practical for use as reinforcement in new composites and therefore some classification stage is required to separate the materials of interest from the rest. The equipment and methods used to separate the different grades of recyclate materials are discussed in depth in Chapter 4, along with an analysis of the collected materials.

## 3.3. Recyclate Material Content

### 3.3.1. Introduction

As discussed in the literature review chapter the comminuted recyclate materials are a complex blend of the individual raw materials; the polyester matrix, the calcium carbonate filler and the glass fibre reinforcement. To analyse the effectiveness of the used classification method for the collection of the glass fibres in the recyclate, and to

later allow more accurate reformulation into new composites, it is desirable to know the exact composition of the different recyclate grades. This information can be established by investigating the weight percentages of the resin, filler and glass fibres in the different grades of recyclate, determined by a two stage process. Firstly a sample of the recyclate materials can be placed in a furnace to burn-off the resin materials and then these materials washed in dilute hydrochloric acid to dissolve the calcium carbonate filler materials and leave only the reinforcing fibres. Weighing the recyclate before and after each stage allows the weight percentages of each of the materials to be calculated.

Before this experiment can be performed it is important to determine the thermal stability of the material constituents in the composite, so that the correct thermal conditions can be used when determining the weight percentage of the resin materials, such properties can be established by thermo-gravimetric analysis (TGA).

### 3.3.2. Thermo-Gravimetric Analysis Method

A Netzsch TGA 209 [50] machine was used to measure the mass of a recyclate sample whilst subjecting it to a controlled heating profile in a controlled atmosphere. Individual samples of each of the matrix, filler and fibre materials used to make the waste SMC composites were supplied by Menzolit UK. All tests were performed in an atmosphere of air, replicating the atmospheric conditions to be used later in the furnace to burn off the resin, the gases were continually supplied to the closed TGA system at a controlled flow rate of 70 $cm^3$/min. Samples were mounted in to the machine in a crucible and the sample's mass determined by the TGA's internal balance, less the weight of the crucible. The samples were heated from 25 to 800 $^o$C at a controlled rate of 10 $^o$C/min and the mass of the sample monitored and recorded throughout. After the test the recorded results were analysed further using the Netzch TA software to determine the samples mass loss and the onset temperatures of these losses.

### 3.3.3. Burn Off and Acid Digestion Method

A ceramic crucible was first weighed on a set of digital scales, accurate to the nearest milligram, and then filled with a sample of the recyclate material and weighed again. This crucible was placed in a furnace that had been preheated to 650 $^o$C and left for one

hour, to burn off the resin materials. Once removed from the furnace and allowed to cool the crucible was weighed again before the remaining recyclate materials were transferred to a pre-weighed glass beaker. The weight of the beaker containing the recyclate materials was recorded and then dilute hydrochloric acid added to the beaker to dissolve the calcium carbonate filler. Acid was slowly added and the materials agitated until no further reaction occurred, the remaining fibres were then washed clean in water and then placed in an oven at 120 $^{o}$C for two hours, to dry. Once dry and allowed to cool the beaker was finally weighed again, the difference between the materials originally and the final weight of the dried fibres allows the weight of filler materials and the weight of fibres to be determined. This process was repeated five times for each of the recyclate grades, along with samples of the unclassified recyclate straight from the grinder, and the average percentage weights calculated.

## 3.4. Composite Manufacture

### 3.4.1. Raw Materials

Below is a tabulated overview of the raw material ingredients used in the manufacture of the SMC and DMC composites used throughout this research.

| | SMC | DMC |
|---|---|---|
| **Polyester Resin** | 1) Derived from maleic acid and standard glycols, dissolved in styrene<br>2) A saturated polyester dissolved in styrene | Derived from orthophthalic acid and standard glycols, dissolved in styrene |
| **Low-Profile Additive** | Liquid solution of polyvinyl acetate (PVCa), dissolved in styrene | Liquid solution of polyvinyl acetate (PVCa), dissolved in styrene |
| **Inhibitor** | p-benzoquinone | p-benzoquinone |
| **Initiator** | t-BUTYL peroxyester type organic peroxide | t-BUTYL peroxyester type organic peroxide |
| **Mould Release** | Calcium stearate | Zinc stearate |
| **Filler** | Calcium carbonate, average particle size of ≤5 μm | Calcium carbonate, average particle size of ≤10 μm |
| **Reinforcement** | E-glass fibre rovings cut to 25 mm lengths during manufacture | Pre-chopped E-glass fibre rovings of length 6 mm |
| **Thickener** | Magnesium oxide, in liquid form | N/A |
| **Wetting Agent** | Wetting and dispersion additive, BYK® W-996 | N/A |

*Table 3.4, Types of Raw Materials Used for SMC and DMC Composite Manufacture in this Investigation.*

## 3.4.2. DMC Manufacture

Dough moulding compounds have been manufactured throughout this research for the characterisation of composites containing recyclate materials. All DMC batches were manufactured using standard machinery and production equipment by following the processes described earlier in Section 2.6.3. Mixing was performed using a 2 litre capacity 'Z'-blade mixer, Figure 2.7, capable of producing 1.5 Kg of material per batch.

### 3.4.3. SMC Manufacture

Sheet moulding compounds have been manufactured with the inclusion of recyclate materials for comparison with standard SMC formulations. This investigation involved the design and implementation of unique production methods and therefore the equipment and the production methods used for the SMC manufacture in this research will be discussed fully in Chapter 7.

## 3.5. Composite Moulding

### 3.5.1. Introduction

Whilst the material formulations and manufacturing methods have been adjusted to accommodate the recyclate materials in the raw composite, the final cured parts for testing have been moulded, prepared and tested consistently by the same means throughout this investigation, for both the SMC and DMC.

Although it is possible to injection mould DMC formulations, many DMC and all SMC raw materials for automotive applications are cured by compression moulding. The compression moulding tool consists of a 'male' or 'cavity' part which is fixed to the top surface of the press, to produce the visible section of the moulding, and on the bottom of the press is the other section of the mould known as the 'female' or 'core', Figure 3.2. Mould tools are custom made for each desired part and as a result the curing process and conditions for each part will differ slightly, depending on the size and complexity of the moulding's shape.
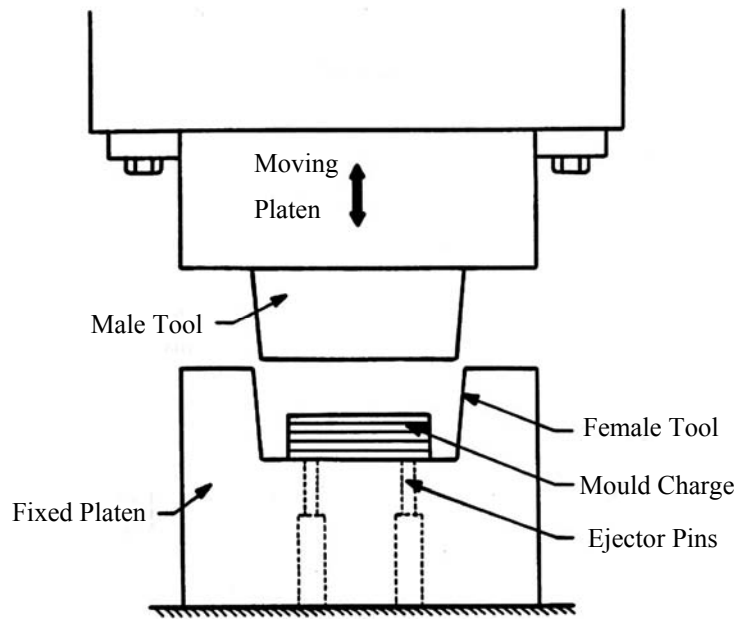
*Figure 3.2, Simple Compression Moulding Press [51].*

## 3.5.2. Moulding Method

Past investigations into the effect on the curing of DMC and SMCs incorporating recyclate materials have shown that there is a resulting delay in the start of the composite's cure reaction, caused by a reduction in the raw material's thermal conductivity [27]. However this does not affect the total cycle time required and the curing process is still complete after a typical moulding cycle of three minutes. All test panels for this investigation were therefore moulded under the same conditions as they would be in the commercial production environment:

1)  The mould tool was preheated to 145 $^o$C before the manufacturing process began, using the electrical cartridge heaters in the surfaces of the press.
2)  A charge was then prepared from the raw compound, typically weighing 375 g but dependant on the material used, such that a panel 3.6 mm thick would be formed – similar to the thickness of the original automotive components.
3)  The charge was placed in the centre of the mould and the press immediately closed, the materials were cured for three minutes at 145 $^o$C and pressure of 4.1 MPa.

4) After three minutes the mould was opened and the panel ejected from the tool with a pressurised air ejector pin situated in the centre of the female part of the mould tool.

5) Any flash around the edge of the moulded panel was removed using a razor blade, the panels were labelled according to the raw composite batch used and then left to cool on a flat surface.

### 3.5.3. Apparatus

Flat test panels were compression moulded in a steel mould, with a square cavity of dimensions 230 x 230 mm, fitted to a Bytec industrial heated press, both shown in Figure 3.3.
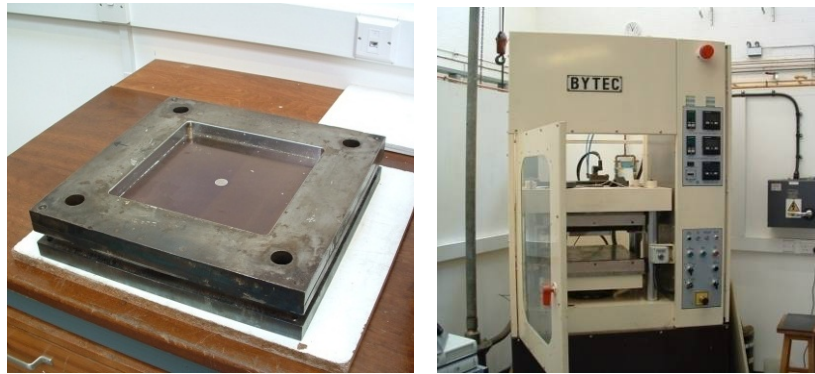


*Figure 3.3, The Mould Tool Cavity and Press used for Moulding Test Panels.*

## 3.6. Test Sample Preparation

### 3.6.1. Introduction

Automotive compression moulded SMC or DMC composite parts are often very complex shapes as they can incorporate several components that would otherwise require modular assembly if made from materials such as steel. Flow effects such as 'knit lines' or 'rippling' are known to be caused by complex mould geometries and poorly designed mould tools. For this investigation the parts moulded were simple flat rectangular panels so that specimens could be prepared from them for mechanical testing, and so that flow patterns would not be produced or affect the results from the specimens tested.

## 3.6.2. Method

From each different batch of raw DMC and SMC manufactured, four individual test panels were moulded and two of these then randomly selected for mechanical testing. All specimens were cut from these test panels in exactly the same way, using a band saw and according to a stencil pattern as shown in Figure 3.4. Previous investigations have shown that the orientation of the test specimens does not significantly influence the mechanical properties of SMC panels [15], [52]. Similar tests were performed for this investigation with test panels of SMC and DMC made of the standard formulations and moulded in the tool shown in Figure 3.3. The results of these tests are presented in Appendix A, no sample orientation effects were observed and for the remainder of the investigation two sets of four specimens were prepared for testing from each panel, at $90^{o}$ to one another, as shown in Figure 3.4. All flexural and impact samples were cut according to the specific geometries required of the relevant ISO testing standards. Using a cutting pattern ensured that the same regions of the test panels were consistently tested for every different composite formulation, and samples were labelled after cutting according to the pattern.
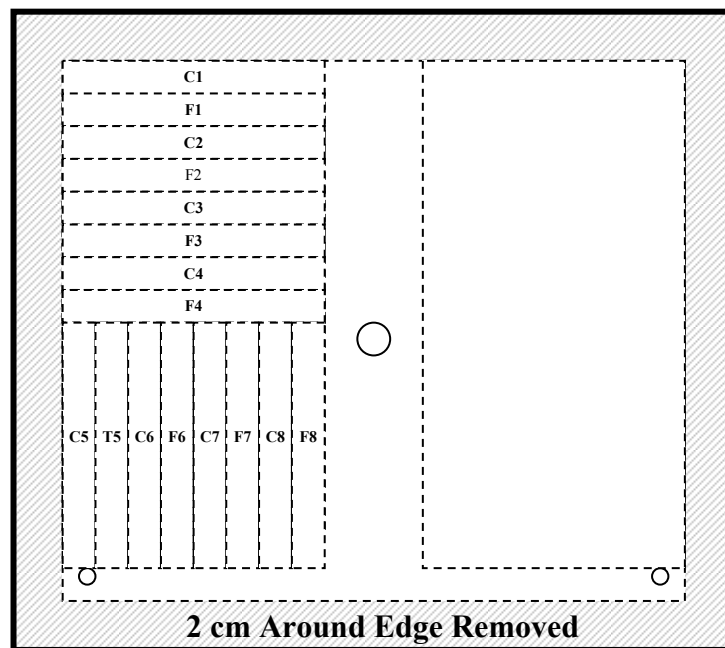


*Figure 3.4, Test Panel Cutting Stencil: F# - Specimen for Flexural Testing, C# - Specimen for Impact Testing.*
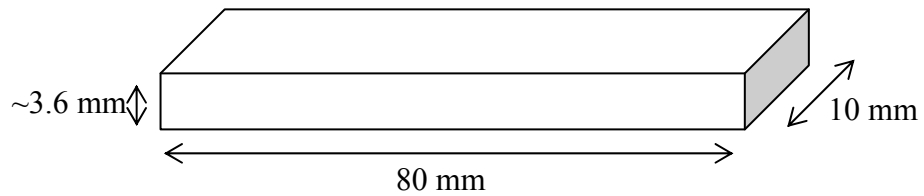
*Figure 3.5, Test Specimen Geometry.*

Samples were labelled immediately after being cut from each test panel to uniquely identify the batch of material they were from and what test they were to be used for.

## 3.7. Mechanical Characterisation

### 3.7.1. Introduction

A vast array of tests can be performed to characterise SMC and DMC materials depending on the requirements of the composite's end application, in accordance with specific ISO testing standards; such as water absorption, electrical conductivity and flammability etc. For the simple composite formulations provided for this research only the mechanical properties of the different composites were investigated, by three-point flexural and Charpy impact testing. The purpose of these tests was to allow direct comparison of the mechanical properties of the different DMC or SMC formulations and against one another and against standard materials, rather than in an attempt to tailor composites to the demands of any specific end application. All tests described below were used to characterise both the SMC and the DMC composites in this investigation, but are described in the context of SMC composites for brevity.

### 3.7.2. Flexural Testing

#### 3.7.2.1. Introduction

Three-point flexural testing is one of the most common test methods used to compare SMCs as it is a useful technique for evaluating the materials mechanical properties and much data can be collected from just one test. Flexural strength is a critical characteristic for many of the automotive applications of SMC and was used in this study to directly compare the different formulations against one and another and against a control material made of a standard formulation.

### 3.7.2.2. Experimental Apparatus

A Lloyd Instruments EZ-20 machine [53] was used for all tests with a 500 N load cell used to record the applied force and the deflection measured by the machine's internal extensometer. NEXYGEN™ PC software was used to record the test data for all specimens.



*Figure 3.6, Three-Point Testing Equipment and Sample Set-up.*

### 3.7.2.3. Experimental Technique

Three-point flexural testing was performed in accordance with the DIN EN ISO 14125 standard, at room temperature. Eight un-notched specimens were tested from each SMC panel, two panels from each SMC batch were investigated and two separate batches were made of each different formulation, resulting in 32 test specimens for each SMC formulation variation. All specimens from each of the individual formulations were tested on the same day under the same conditions.

Specimens were placed symmetrically between the two bottom supports, as shown in Figure 3.6, and tested until failure. Tests were recorded using the 'three-point bend' test method in the machine's software, with an initial pre-load of 5 N applied to each test specimen before the test, to ensure that it did not slip. The machine cross-head speed, $V$, for all test samples was calculated according to equation (3.1) from the test standard, for a sample strain rate, $\varepsilon'$, of 0.01.

$$V = \frac{\varepsilon' l_s^{\,2}}{6h} \qquad\qquad (3.1)$$

Where $l_s$ is the sample span and $h$ the thickness of the tested specimen.

### 3.7.2.4.    Calculations

The dimensions of all the test specimens were measured and recorded before testing using a micrometer. The force applied from the load cell, $F$, and deflection, $s$, of each sample from the machines internal extensometer were recorded throughout the test by the NEXYGEN™ software and the mode of failure was noted after each test. The recorded data was exported from the test PC and further calculations were performed in Microsoft EXCEL using the following equations, according to the test standard:

The maximum flexural strength, $\sigma_F^*$, calculated as:

$$\sigma_F^* = \frac{3F_{max}l_s}{2bh^2} \tag{3.2}$$

where $F_{max}$ is the maximum force recorded during the test, $h$ is the specimen's thickness and $b$ is the specimen's width.

The flexural modulus, $E_F$, calculated as:

$$E_F = \frac{l_s^3}{4bh^3}\left(\frac{\Delta F}{\Delta s}\right) \tag{3.3}$$

Where $s$ is the deflection of the specimen.

## 3.7.3. Charpy Impact Tests

### 3.7.3.1.    Introduction

The impact behaviour of composites is very important for structures that are employed in automotive applications, especially body and bumper sections [54] where dynamic and static loading of parts is common. Whilst the results from impact testing cannot be usefully transferred to the design of the final composite components, they do allow the

comparison of the failure modes and energy absorption capabilities of two or more formulations tested under identical impact conditions. Impact tests are commonly used to characterise composite materials and as well as providing these comparative values of impact strength, inspection of the resulting fracture surfaces can also provide an insight into the material's failure mechanisms. Several failure mechanisms are understood to dominate the fracture process in short fibre reinforced polymer composite materials [55], [56]:

1. Matrix deformation.
2. Matrix fracture.
3. Matrix/fibre interface effects such as matrix/fibre debonding and fibre pull out.
4. Fibre fracture.

Inspection of the tested impact specimens fracture surfaces could potentially provide insight into any different dominant fracture mechanisms for the different composite formulations.

For this investigation the impact resistance of the composites were evaluated using the Charpy impact tests.

### 3.7.3.2.      Experimental Apparatus

Charpy impact tests were carried out on un-notched specimens using a Ceast Resil Impactor Junior [57] with a non-instrumented impact head, Figure 3.7.
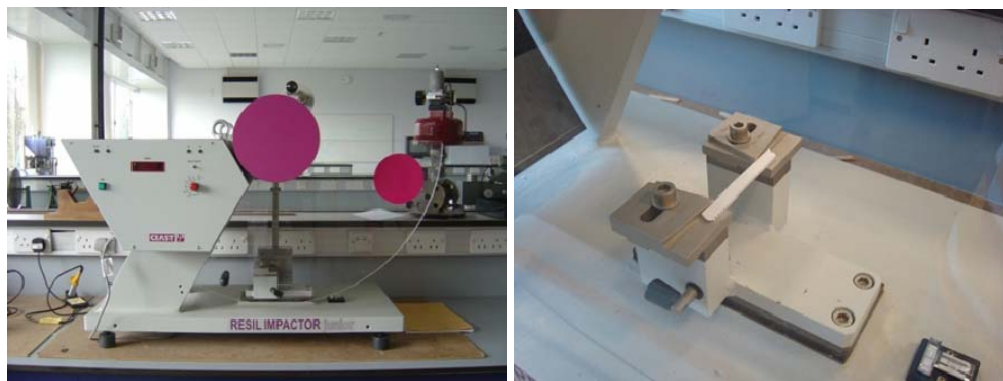


*Figure 3.7, Charpy Impact Test Machine and Specimen Set-up.*

### 3.7.3.3.　　　Experimental Technique

All specimens were prepared and tested according to DEN EN ISO 179-1 Standard, eight specimens were tested from each SMC panel, two panels from each SMC batch were investigated and two separate batches were made of each different formulation, resulting in a total of 32 test specimens for each SMC formulation variation. A non-instrumented pendulum type 4 J striking head was used for all DMC tests and a 15 J head was used for all SMC tests. Specimens were un-notched due to the low fracture strengths to be recorded and it has been shown that notching has negligible effect when testing fibre reinforced thermoset composites [58].

For each test the specimen's width, $b$, and thickness, $h$, were measured using a micrometer and recorded before the specimen was mounted symmetrically on the machine's supporting frame. A span of 62 mm was used and the sample aligned such that the striking head would impact it perpendicularly at its midpoint. Once the specimen was mounted the pendulum was released from its starting position and the specimen fractured, the energy exerted during the impact, $W_b$, was then recorded from the machines digital display. Before each set of tests the striking head was allow to fall freely, without impacting a specimen, so that any losses in the system due to friction could be recorded, $W_f$.

The Charpy impact strength, $a_{cU}$, for each sample was then calculated as the total energy absorbed by the specimen divided by its cross sectional area, using the following equation from the test standard:

$$a_{cU} = \frac{\left(W_b - W_f\right)}{b.h}.10^3 \qquad\qquad (3.4)$$

## 3.7.4. Statistical Analysis

Heterogeneous composites such as SMC and DMC are prone to high coefficients of variation in the results of mechanical testing specimens, [59], [60], [61], [62], [52]. Due to this scatter there is a resulting large standard deviation and the mean results of groups from independent tests may appear to be similar, when any differences between groups may merely have been caused by chance of an individual result differing greatly from

the majority of the test sample. Further analysis of the recorded test data from this investigation was used to determine whether or not the differences observed, or lack of, between results were due to changes between the material formulations or if they were in fact solely due to the random variation from uncontrollable factors, noise. Statistical analysis of the recorded results was performed using the 'analysis of variance' method, ANOVA, as it allows several different material formulations to be compared directly. Results from the statistical analysis are presented as tables showing the '*P*-values' determined by a post-hoc analysis of the ANOVA results, at a confidence level of 95%. These '*P*-values' are used to determine any significant differences between the different formulations, any value of $P<0.05$ indicates that the difference between values of the two compare means is significant, and not just a result of the natural variation, in the result tables the significant values are marked with an '*' for clarity. All statistical analysis was performed using statistical software (SPSS version 15, Statistical Package for Social Science; SPSS Inc, Chicago, Ill).

### 3.7.5. Scanning Electron Microscopy

#### 3.7.5.1.　　　General

Scanning electron microscopy (SEM) was used to image the recyclate materials and fracture surfaces of the DMC impact specimens at high magnifications, from x30 up to x3000 dependant on the material being inspected.

#### 3.7.5.2.　　　Apparatus

All specimens were non-conducting and therefore a 4 nm coating of gold was applied to all samples using a sputter coater. If samples were not coated they tended to 'charge' under the electron beam, which caused areas of brightness on the images and damaged the polymer in the composite causing unwanted visible defects. Images were taken using a Hitachi S-3200N [63] scanning electron microscope at an accelerating voltage of 25 keV and using the secondary electron detector.

#### 3.7.5.3.　　　Recyclate Powder

SEM was used to take images of the finest grades of recyclate where the particles were too small to be characterised under a microscope. The powder was sprinkled onto a

carbon tape, so that it was securely mounted when in the vacuum chamber, before gold splutter coating.

### 3.7.5.4. Fibres

Both virgin and recyclate fibres were imaged using the SEM, both to investigate the differences in surface finish and to measure their respective diameters. Samples were also mounted securely on carbon tape and gold coated, both individual fibre filament and bundles were imaged.

### 3.7.5.5. Impact Specimens

As discussed the fracture surface can help give an insight into the failure mechanisms in the composite and so samples from each of the tested batches were imaged. Previous investigations into the use of recyclate in DMC have suggested that a weak bonding between recyclate particles and the new matrix is a potential cause of weakness and the starting place of cracks during failure [44]. The fracture surfaces may also show areas of debonding between the recyclate at the matrix and give an indication of any flow or dispersion effects.

# Chapter 4

# 4. Recyclate Classification Results

## 4.1. Introduction

The purpose of this experimental and results chapter is to introduce the recyclate materials, their production from waste SMC materials by granulation, their classification into different grades and the characterisation of these grades. Each stage of the recyclate production process was investigated and conducted in-house so that it could be properly evaluated and then the processing conditions optimised for the desired results.

## 4.2. Granulation

### 4.2.1. Introduction

Thorough investigation into the many available granulation methods has shown that the most relevant equipment for industrial application and the retention of the composites reinforcing glass fibres, as desired for this research, to be a rotating hammer mill type granulator [5], [38]. The purpose of this section was to establish the best granulation conditions for the production of a recyclate material that could potentially be used as reinforcement in new composite materials, by preserving the original reinforcing glass fibres.

### 4.2.2. Method

Figure 4.1 below shows the working principle of a rotating hammer mill as used for this research. The materials to be granulated are fed through a feed chute at the top of the machine into the grinding chamber. Inside the grinding chamber are several hammer heads rotating at high velocity around a central axis, these hammers impact with the feed materials continually breaking them into smaller pieces. The feed materials remain in the granulation chamber, being continually broken down by the hammer heads, until they are small enough to pass through the apertures in the classifier screen at the base of the chamber and into a collection bin.
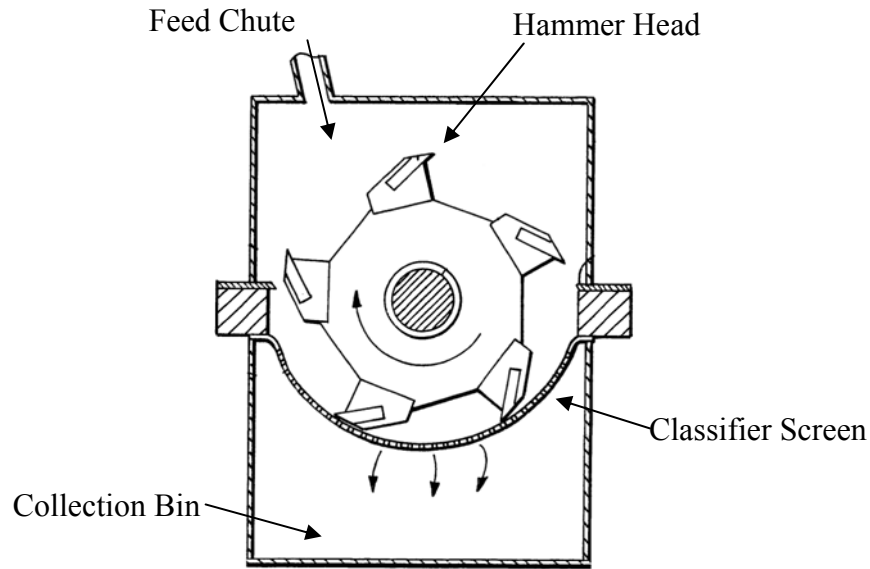
*Figure 4.1, Diagram of a Rotating Hammer-Mill Type Granulator [64].*

### 4.2.3. Experimental Technique

Trials were performed using a TRIA [65] rotating hammer mill type granulator to establish the granulation conditions best suited to producing a fibrous recyclate material, with the original long fibre length retained. Three different classifier screens were trialled in the granulator, having round apertures of 5, 8 and 10 mm respectively. After granulation the recyclate materials in the collection bin were visually inspected to establish which classifier screen had best produced a recyclate material that could potentially be used as reinforcement in new composites. The waste parts shown in Figure 3.1 were cut down to approximately 30 x 30 cm sections using a band saw before being fed into the granulator.

## 4.3. Results: Granulation Trials

To establish the best settings for granulation of the recyclate with the rotating hammer mill granulator three different classifier screens were trialled. The resulting recyclate products were inspected visually to identify the screen which produced the most fibrous recyclate, a material most suited to use as reinforcement in new composites. For inspection the collected materials were sprinkled over a black background, for contrast, and images were taken using a digital camera.
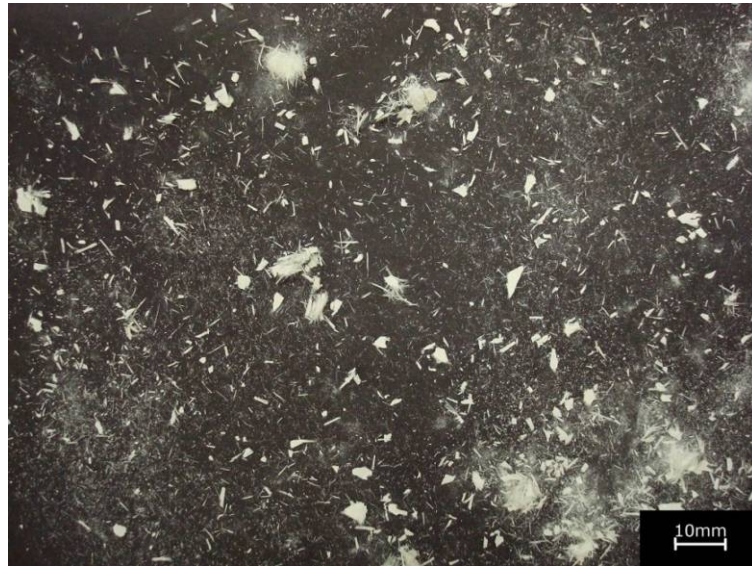
*Figure 4.2, Recyclate Produced with a 5 mm Classifier Screen Aperture.*

The use of a 5 mm aperture classifier screen resulted in a very fine recyclate material, shown in Figure 4.2, particles appear to predominantly be very small and powdery, including a number of rectangular shaped chips. Whilst there does appear to be a fibrous grade amongst these materials, the original fibre length of the virgin fibres (25 mm) does not appear to of been retained.



*Figure 4.3, Recyclate Produced with an 8 mm Classifier Screen Aperture.*

The use of an 8 mm aperture classifier screen produced a recyclate material which appears to be predominantly fibrous, with the glass fibres still in bundle form, Figure

4.3. There are a range of different shaped materials which appear fibrous, with high aspect ratios, along with some circular chips that would not be of any use and again some powdery materials.



*Figure 4.4, Recyclate Produced with a 10 mm Classifier Screen Aperture.*

The recyclate produced with a 10 mm classifier screen aperture, Figure 4.4, does not appear suitable for use as reinforcement, having not been properly broken down. The recyclate appears to be made predominantly of large chips of composite which are too large to be used as either filler or reinforcement.

## 4.3.1. Discussion

Visual inspection of the different granulated materials clearly demonstrates that the size of the classifier screen's apertures used in the granulator has a large effect on the type of recyclate produced, when processing SMC materials. Whilst all of the produced recyclates are a blend of particles of all shapes and sizes the materials produced with an 8 mm aperture appear to be the most suitable for consideration as a potential reinforcement in new composites. Further inspection and quantification of the shapes of these granulated materials is performed and presented in Section 4.6.

## 4.4. Classification: Recyclate Grades

### 4.4.1. Introduction

As discussed in Chapter 2 no standard method for classifying different grades of materials from SMC recyclate exists. The majority of scientific investigations have used the dry sieving method, despite its inaccuracies, and whilst industrial scale operations such as ERCOM and Pheonix Fiberglass have used some form of cyclone air classification in addition to the sieves in separating their grades of materials, no scientific evaluation of the processes have been performed. The purpose of this section was to investigate the use of air classification to find the most suitable settings for the classification of the fibrous particles from the ground recyclate.

### 4.4.2. Air Classification

#### 4.4.2.1.　　　Introduction

There are many different air classification methods and designs available which are used in a vast array of industries, from the mining to the agricultural industries, to classify all variety of particles.  For this investigation the method that appeared to be most suitable was the use of gravitational air classification, as it allows a large range of particle sizes to be classified and is commonly used for the de-dusting of mixtures [66]. In gravitational type air classifiers the particles pass through a rising current of air, which facilitates the separation of lighter and/or finer particles from the coarser, heavier material. Responsible for this separation are the force of gravity ($F_G$), the drag force ($F_D$) and the buoyancy or lift force ($F_L$), Figure 4.5. The overall net force on a particle will then be the difference between the net gravitational force, the difference between the weight of the particle and the buoyancy force, and the net drag force. If the net gravitational force is less than the drag force, then the particle will be carried upwards in the air current, else the gravitational force dominates and the particle falls through to the base of the classifier.
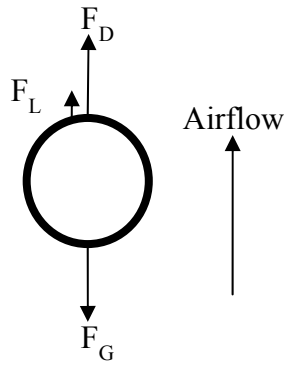
*Figure 4.5, Simple Force Balance Diagram for a Particle in an Airflow.*

### 4.4.2.2.  Zig-Zag Classification Method

The zig-zag classifier is a type of air cascade classifier, formed of several inclined rectangular pipes fixed together to produce a vertical channel with a 'zig-zag' appearance. The recyclate materials are fed into the separator two thirds of the way up the separation channel and then fall downwards under gravity. The separation airflow is blown upwards through the separation channel from the bottom to top. At each elbow in the channel the product has to pass through the airflow in order to fall onto the opposite wall.  The product crosses the airflow at approximately right angles and at each elbow a cross-flow separation takes place, Figure 4.6. Two grades of material are classified: commonly termed a fine and a coarse product. The fine product is carried upwards by the air current out of the classifier to be separated from the airflow by a cyclone, and then collected. The coarse product falls through the air stream in the channel and is eventually collected at the base of the machine. It is only possible to separate two grades of material at each classification run, if more than two grades of material are to be classified from the feed materials then the settings on the machine have to be adjusted after one stage of classification is complete and either the previously collected fine or coarse grade reprocessed as a new feed material.
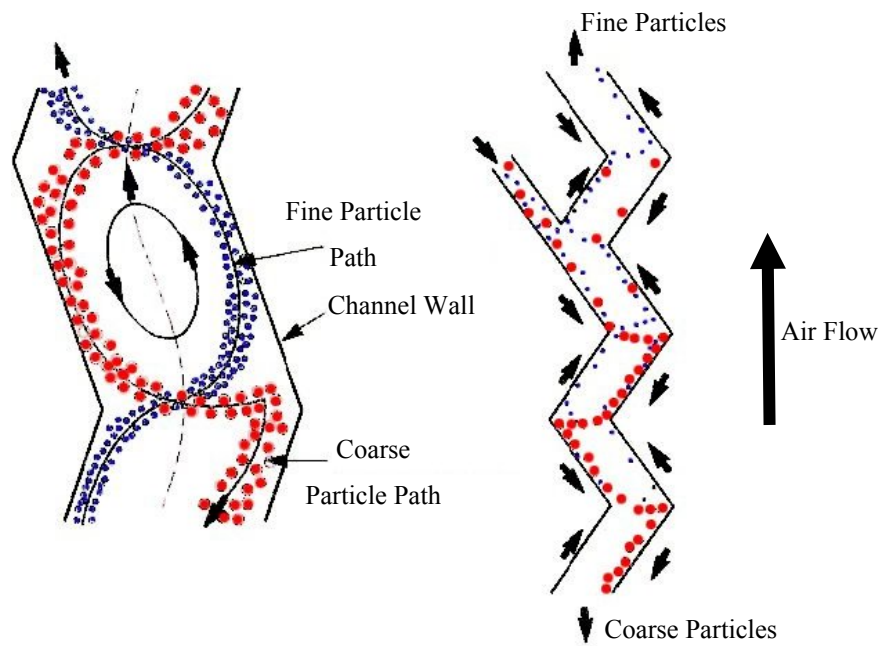
*Figure 4.6, Operating Principle of the Zig-Zag Classifier.*

The particles to be collected as the fine and coarse grade are determined by accurate control of the airflow drawn through the system by the fan. This is achieved by the careful adjustment of three valves located around the machine, the 'cyclone valve', 'sock valve' and 'fan slide valve', as shown in Figure 4.7.
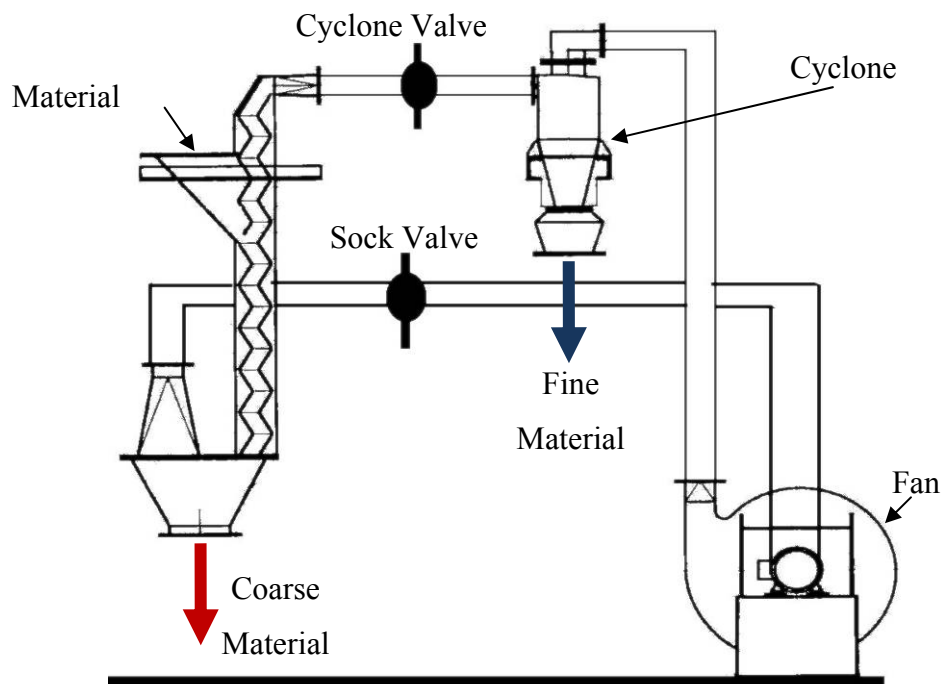


*Figure 4.7, Illustration of the Zig-Zag Classifier.*

The design of classification equipment for the separation of specific particles of different sizes and shapes depends upon the differences in their behaviour when subject to the action of the same airflow. From the balance diagram of such a falling particle shown in Figure 4.5, it is clear that the behaviour is dependent on a net gravitational force and a resistive force known as drag. For instance the drag force, $F_D$, experienced by a particle settling with uniform velocity in a fluid under Stokes flow conditions is given by [67]:

$$F_D = \frac{1}{2}\rho C_D u^2 A_p \qquad\qquad (4.1)$$

Where $A_p$ is the cross-sectional area of the particle normal to the direction of the drag force, $u$ is the velocity of the particle relative to the fluid, $\rho$ is the density of the fluid and $C_D$ is the drag coefficient.

The resistive drag force depends upon an experimentally determined value known as the drag coefficient. The typical method for solving the particle's final balance equation is to equate the particle in question to a regular shaped particle, such as an equivalent perfect sphere [67], for which many drag coefficients, in relation to the Reynolds number, are available in the literature. There are far fewer studies [68] into the behaviour of actual irregular shaped particles in the airflow, as the case is complicated by a number of factors; such as the orientation of the moving particle, which changes over time during the separation causing continual changes in the balance of the forces acting upon it [69] and the extreme variation of shape observed even in graded particle grades [70].

In the case of the chosen air classification equipment any predictive model is further complicated by several other factors, including; the many particle interactions which will constantly be changing the balance conditions [71], the turbulent nature of the imposed fluid flow on the particles and wall effects [72] as the fluid and the particles collide with the faces of the separation unit. Therefore the conditions for classification of the different materials in the recyclate were established empirically. Trials were performed on the ground recyclate materials by carefully adjusting the airflow through

the system with the valves and then feeding in the ground recyclate. The collected fine and coarse grades were visually inspected and if necessary reprocessed with different airflow settings to classify off further grades of material.

### 4.4.3. Results: Recyclate Classification

The recyclate is clearly a complex blend of many different particles of all shapes and sizes, however only those which could potentially be used as reinforcement are of interest for this research. Trials were performed using a Hosokawa Micron [73] ZZ-63x200 MZM zig-zag classifier to establish the settings and the number of processing steps required to separate off the desired grades, the final results are shown in Figure 4.8.

**Original Material**

**1. *Coarse:* 'Reprocess'**

**(28%wt)**



**Fine: Useful Materials**

**2. *Coarse:* 'Coarse Fibre'**

**(21%wt)**



**Fine: Filler and**

**Powder**

**3. *Coarse:* 'Fine Fibre'**

**( 21%wt)**



**4. *Fine:* 'Powder'**

**( 30%wt)**
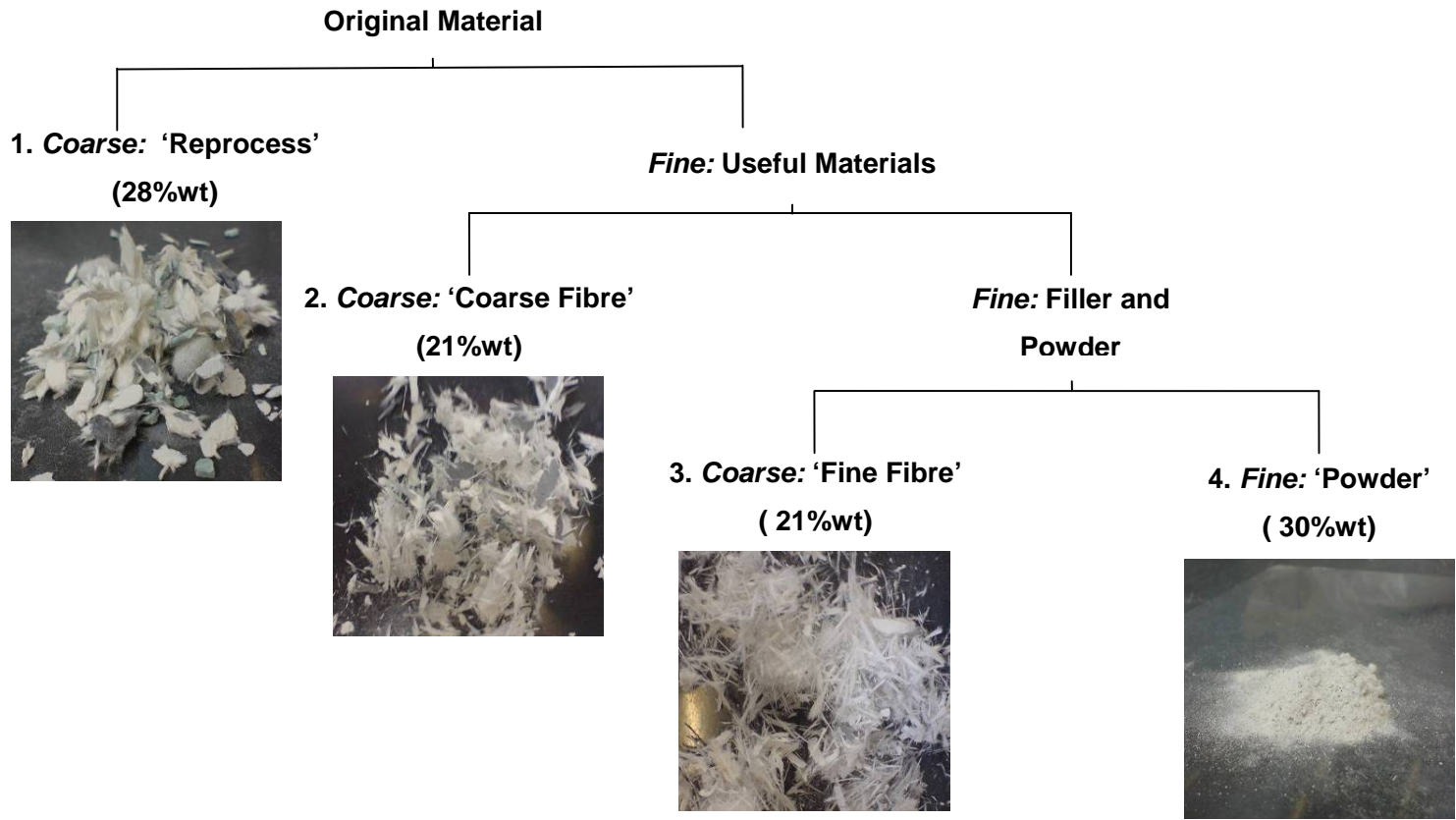


*Figure 4.8, The Three Stages of Zig-Zag Classification and the Resulting Recyclate Grades.*

Stage 1 of the classification was used to classify off the particles that were considered to be too large to be used as either filler or reinforcing materials, labelled 'Reprocess', which equalled 28% of the total recyclate by weight.

Adjusting the settings on the classifier, to slightly reduce the airflow and then re-processing the fine cut from Stage 1 of the classification allowed two further grades to be produced at Stage 2. This time the collected coarse grade, labelled 'Coarse Fibre', was a material considered useful for trials as a potential reinforcement in new composite materials, appearing to predominantly consist of glass bundles of fibres. A total of 21% of the original weight of recyclate was separated off at this stage.

Finally the fine cut from the second classification stage was re-processed again, with a further reduced airflow, to produce a final two grades of recyclate at Stage 3. The 'Fine Fibre' grade was another grade of materials to be trialled as reinforcement in new composites. It appears to be composed of both individual and finer bundles of glass fibres and was 21% of the original ground recyclate's total weight. The fine cut from this final classification stage was a very fine powdery material shown in Figure 4.9, labelled 'Powder'. It appears similar to that the type of material used as filler in the DMC and SMC composites manufacture in the previous investigations discussed in Chapter 2, and was 30% of the total recyclate weight.
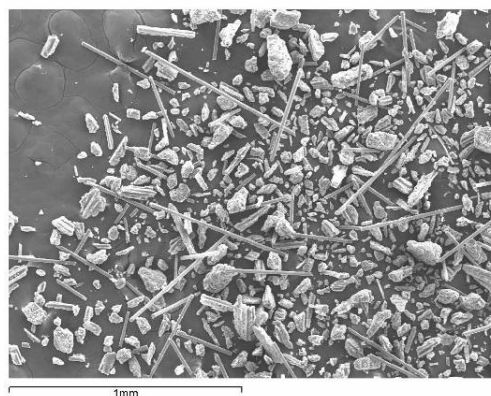


*Figure 4.9, SEM Image of the 'Powder' Grade of Recyclate.*

### 4.4.4. Discussion

These classification trials have resulted in two grades of materials that visually appear as if they could be used as reinforcement in the manufacture of new composites, a 'Coarse Fibre' and a 'Fine Fibre'. They appear to be fibrous and to contain many of the original glass fibres with some of their original fibre length retained. The other two grades separated during these trials are of no further use for this specific investigation, however, the 'Reprocess' grade could potentially be returned to the granulator to be broken down further and then classified again to obtain useful grades. The 'Powder' grade could potentially be used as filler materials, similar to the work performed in previous investigations as discussed in Chapter 2, so neither would necessarily be wasted.

For simplicity the 'Coarse Fibre' and 'Fine Fibre' recyclate grades will be referred to as just 'Coarse' and 'Fine' fibre recyclate respectively throughout the remainder of this thesis.

## 4.5.  Recyclate Material Content

### 4.5.1. Thermo-Gravimetric Analysis Results

The results recorded during the thermo-gravimetric testing are displayed in Figure 4.10, showing a plot of the three sample's masses as a function of the applied temperature. The calcium carbonate sample is shown to be thermally stable until an onset temperature of 713 $^{o}$C, after the onset the sample steadily thermally degrades, resulting in a 45% mass loss by 800 $^{o}$C.
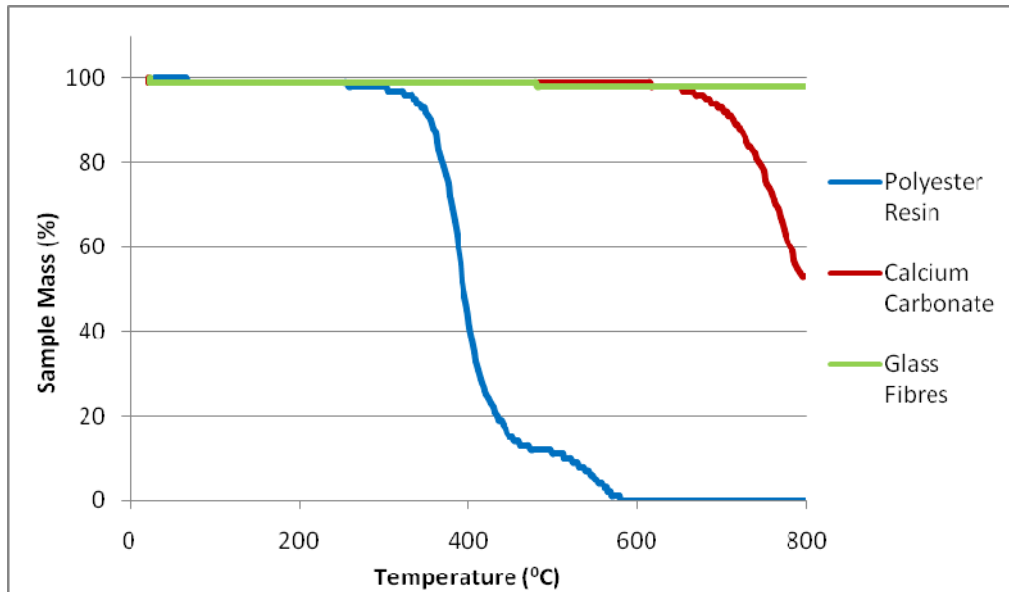
*Figure 4.10, TGA of Calcium Carbonate Filler, Polyester Resin and Glass Fibres.*

The cured polyester resin showed a two part total thermal degradation, firstly a mass loss of 70% between an onset of 375 $^{o}$C and final temperature of 460 $^{o}$C, followed by a degradation of the final 30% of the sample from an onset of 540 $^{o}$C until 620 $^{o}$C. The glass fibres did not show any appreciable degradation up to 800 $^{o}$C.

### 4.5.1.1.    Discussion

Comparing the results of the TGA tests for each of the individual constituents in the SMC showed that setting the furnace to a temperature of 650 $^{o}$C for the burn-off tests would allow the complete thermal degradation of all the resin without degradation of the filler or the fibre materials.

### 4.5.2. Results: Recyclate Material Content

Following the results of the TGA investigation the weight percentages of different ingredients in the classified recyclate grades were determined by burn-off and then acid digestion experiments, as discussed in Chapter 3. The results for all the different grades of recyclate tested are shown in Figure 4.11. The Coarse and the Fine fibre grades contain

nearly 30 and 40% more glass fibre respectively, by weight, than the original unclassified recyclate materials.
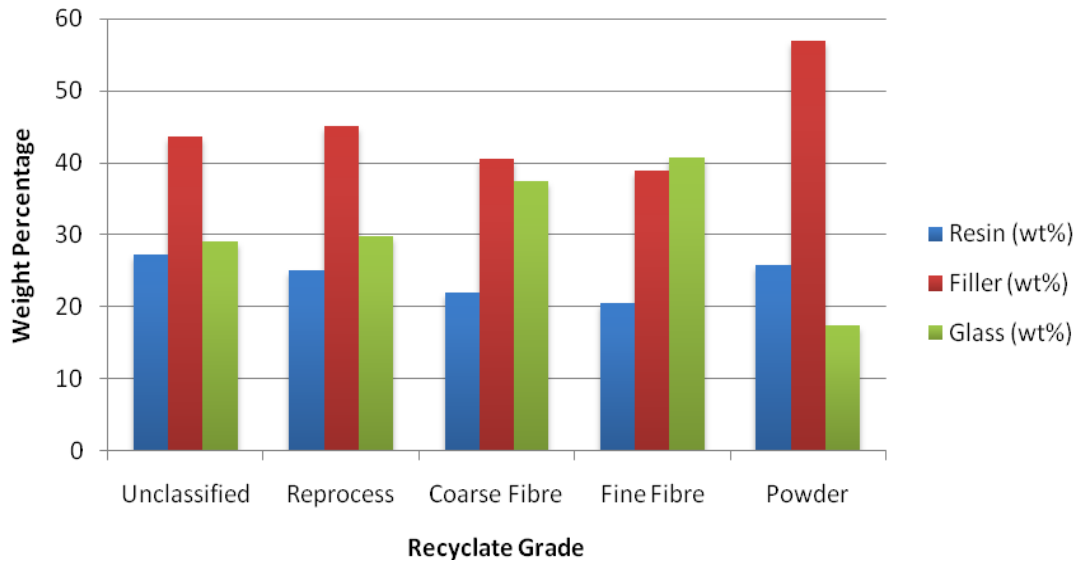


*Figure 4.11, Material Constituents in Different Recyclate Grades.*

### 4.5.3. Discussion

The results for the 'Unclassified' grade should represent the material percentages of the original SMC formulation. The similarity of the 'Reprocess' grade to the 'Unclassified' grade is further evidence that the large particles seen in the grade had not been broken down sufficiently into the different constituents and do require further processing. The large percentage of filler and resin materials in the 'Powder' grade support its potential use as a replacement for filler materials in new composite materials.

The combination of both the chosen granulation and classification methods appears to have achieved the desired fibrous recyclate grades from the waste SMC, in the Coarse and Fine fibre grades, both of which consist of a large percentage of reinforcing glass fibres. It is, however, also evident that there are still appreciable percentages of both filler and resin materials in both of these recyclate grades, which are being considered for use as direct replacement of the virgin glass fibre reinforcement in future composite formulations.

## 4.6. Particle Shape Analysis

### 4.6.1. Introduction

The purpose of this section is to investigate the physical differences between the two grades of recyclate which are going to be used for this research. As discussed in the literature review the characterisation of the size and shape of the recyclate particles has typically only been determined with various stages of sieve meshes. Only two previous authors [44], [42] have actually attempted more detailed analysis but both were unsuccessful due to the extreme variation in the recyclate particles observed.

### 4.6.2. Method

For this investigation image analysis methods were used as a means of comparing the two grades. A sample of the recyclate particles were distributed randomly onto a laboratory mat, with care taken to avoid recyclate particles touching one another to reduce the amount of image processing required later. As the images to be taken were only two-dimensional the mat was agitated slightly, and it was then assumed that the recyclate particles had then settled on their most stable plane, which will have the largest projected area, so that only the particle's finest dimension was not visible for measurement. Images of the recyclate particles in each of the grades were acquired using a digital camera mounted securely on a tripod. Over ten different images were taken, per grade, with newly distributed recyclate materials used for each image so that a large sample of particles was collected for the analysis. The laboratory mat used had a printed scale and a calibrated rule was also included in each of the images so that the correct scale could be accurately determined during the analysis.

The digital images were then processed, as demonstrated in Figure 4.12, using the open source image processing and analysis software package ImageJ [74]. Each image was calibrated by manually measuring along the pictured rule and mat's scale using the software. The images were then cropped to remove both the rule and any other unwanted objects leaving an image of only the recyclate particles on the mat. These images were

converted to greyscale using the '*8-bit*' ImageJ command so that they could be further converted to binary images by *thresholding*. The ImageJ command *'threshold'* was applied so that image intensity histogram dialog was opened, and by manually adjusting the upper and lower limits of the greyscale intensity the areas of interest, the recyclate particles, could be clearly distinguished from the background, leaving a simple binary image with the background one colour and the recyclate particles another.



**Scale Taken From Rule**          **Image Cropped to Region of Interest**          **Image Made Greyscale**

**All Particles Measured and Labelled**          **Recyclate Isolated by Thresholding**
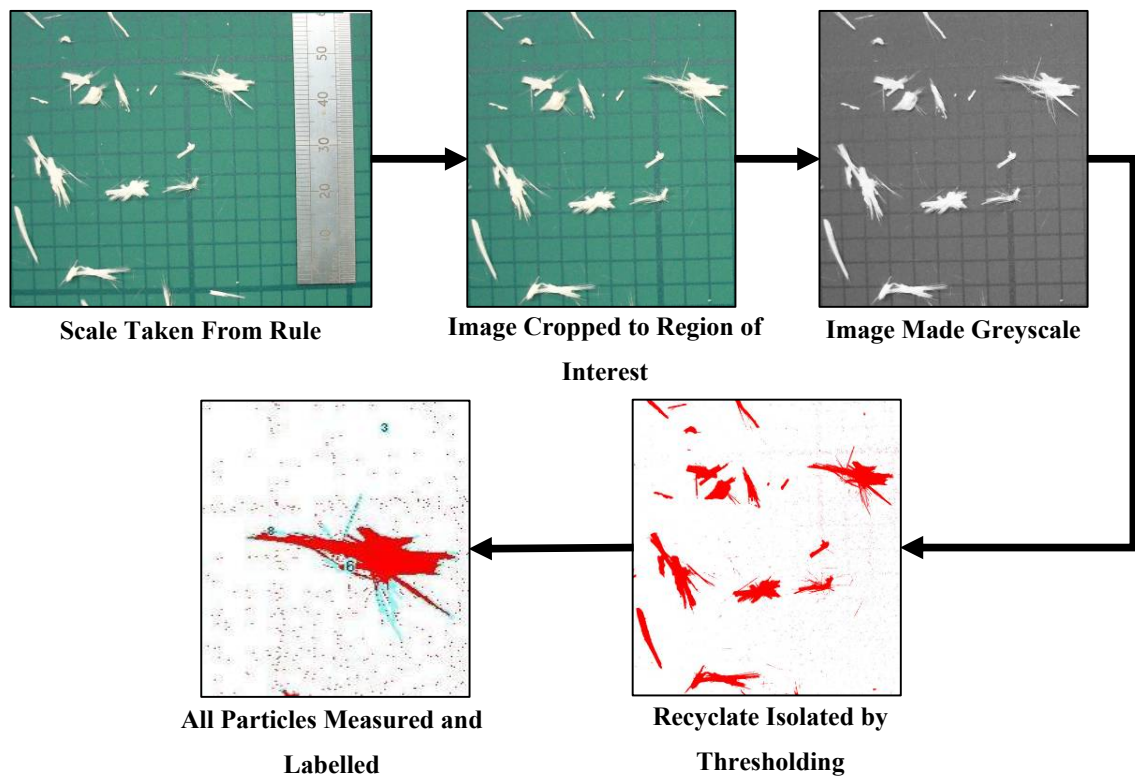
*Figure 4.12, Processing of Recyclate Images for Particle Analysis.*

The '*Particle Analysis'* and *'Measure Curve ROI'* ImageJ macros were applied to first identify each of the unique recyclate particles and then to automatically measure the desired dimensions. A threshold was applied to the particle measurement so that any remaining image noise was ignored, in the form of small particles ($<0.2$ mm$^2$) Any particles which touched the edge of the image were also discounted as their true dimensions could not be known. The macros were used to determine several measurements for each of the individual particles in the image:

- Perimeter: The length of the exact trace around the edge of the particle.
- Particle Area: Equal to the number of square pixels in bound by the perimeter of the particle.
- Circularity: Calculated using the formula in equation (4.2). A value of 1 equates to a perfectly spherical particle and as the value tends toward 0 the particle ever increasingly represents an elongated polygon.

$$Circularity = 4\pi \frac{Area}{Perimeter^2} \qquad (4.2)$$

- Curve Length: Firstly the two furthest two points on the particle's perimeter, defined by the perpendicular distance between two parallel lines (also known as the calliper length) are calculated, Figure 4.13. Then the distance between these two points is measured, whilst allowing for curves in the particle by following a centre line between the edges of the particle.
- Curve Width: Measures the greatest distance perpendicular to the curve length, inside the particle's perimeter.
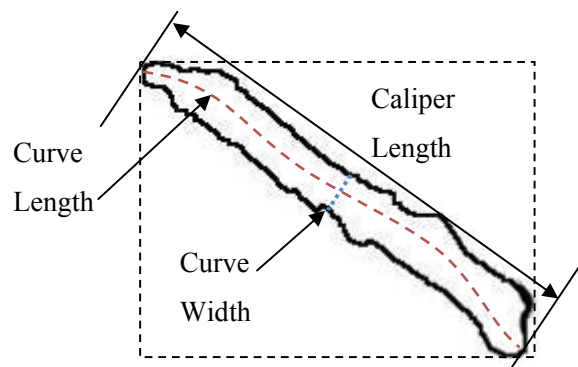


*Figure 4.13, Dimensions Measured of Recyclate Particles.*

After measurement a separate image was created with the particle perimeters and their individual labels overlaid on the original image of the recyclate, so that the particle analysis process to be validated. Any recyclate particles that were touching one another will have

92

been measured as one particle and any particles with internal cavities will produce inaccurate values for their dimensions and surface area, such as object 128 in Figure 4.14. All measure particles were visually inspected in this way, and the recorded dimension data from any erroneous objects removed, to ensure that the collected data was as accurate as possible before being analysed further.
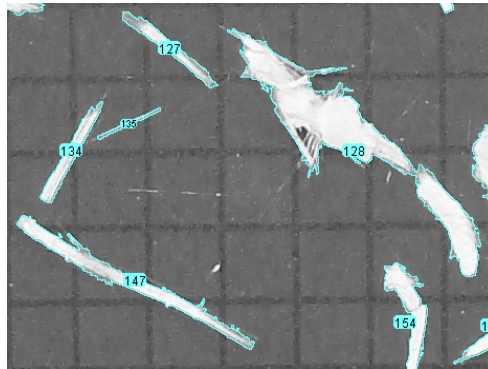


*Figure 4.14, Validation of Recyclate Particles Measured by the Software.*

Samples of over 500 validated particles were collected for each of the Fine and the Coarse fibre grades and the data exported to the software packages MS Excel and SPSS for further analysis.

## 4.6.3. Results: Particle Shape Analysis

Visual inspection of the two recyclate grades showed that they were both made up of a diverse mixture of very different particles of all shapes and sizes. The results from the image analysis are presented in the Figure 4.15 to Figure 4.18 and the statistical results are given in Table 4.1.

### 4.6.3.1.     Particle Area

The results for the measured area of the recyclate particles in Figure 4.15 and Table 4.1 clearly show a difference in the area of the recyclate particles in the Fine and the Coarse fibre grades. Whilst both grades are predominantly made up of small area particles the

Coarse grade has a greater distribution of larger particle areas, and the mean area for the Coarse grade is nearly twice that of the Fine.
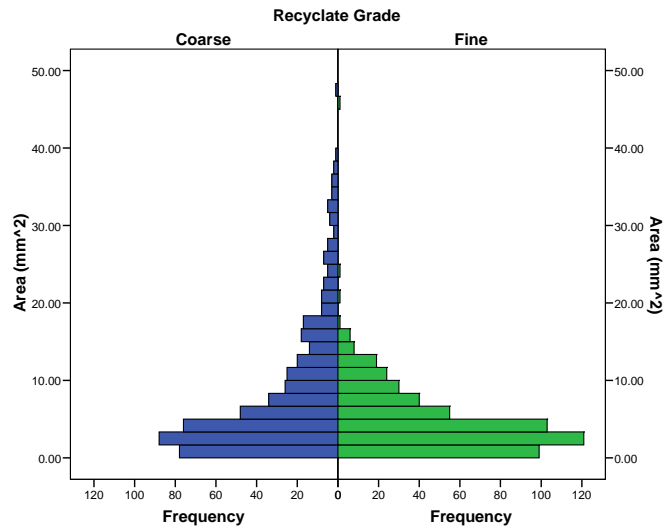


*Figure 4.15, Histogram of Area for the Fine and Coarse Recyclate Particles.*

### 4.6.3.2. Circularity

The Coarse particles are, on average, nearly twice as circular as the Fines and again spread over a wider distribution. These values indicate that on average the Fine recyclate particles are more elongated than the Coarse, Figure 4.16 and Table 4.1.
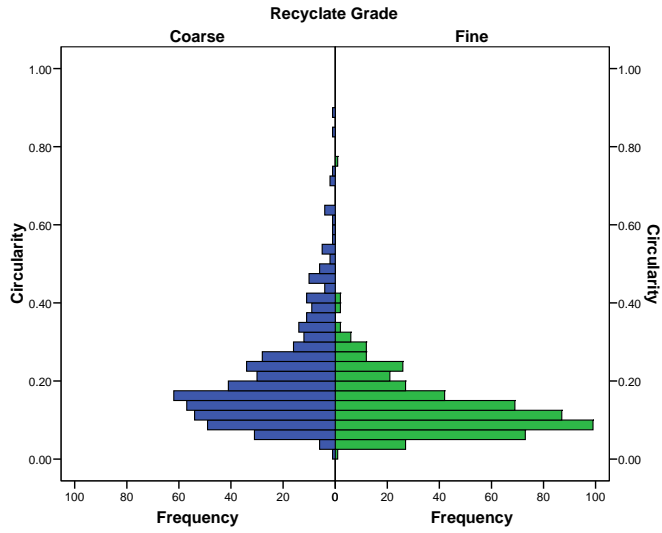
*Figure 4.16, Histogram of Circularity for the Fine and Coarse Recyclate Particles.*

### 4.6.3.3. Curve Length

The results for the curve lengths of the recyclate particles are very similar for both the Fine and the Coarse grades, Figure 4.17 and Table 4.1. The mean particle curve length for both grades is approximately 9 mm.
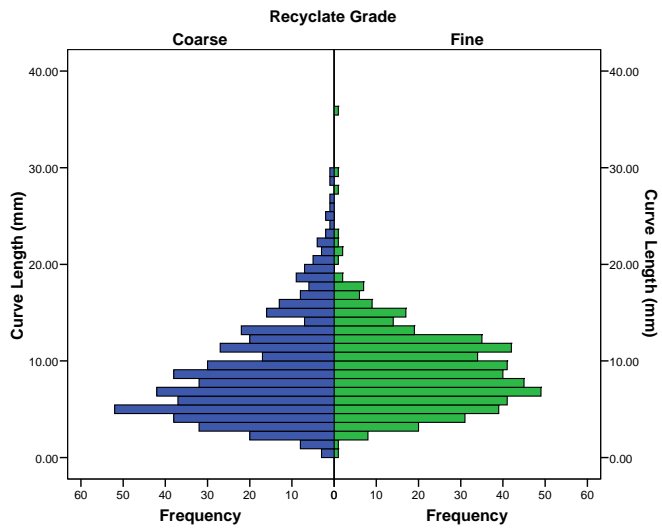


*Figure 4.17, Histogram of Curve Length for the Fine and Coarse Recyclate Particles.*

### 4.6.3.4. Curve Width

The measured curve widths of the Coarse recyclate particles are again spread over a much larger distribution and the average value higher than that of the Fine grade.
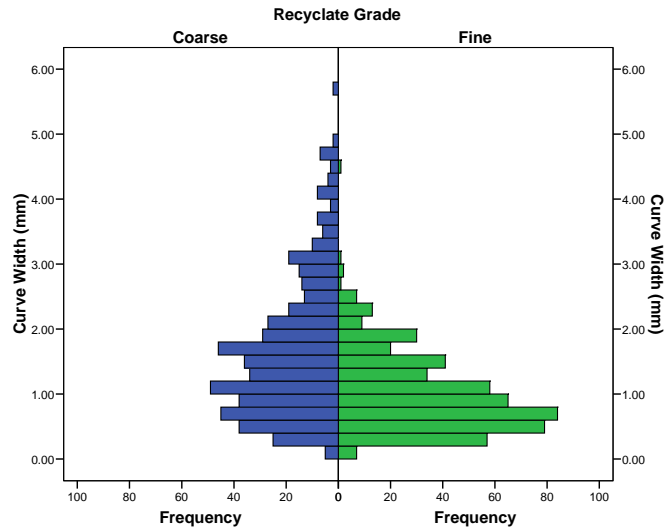


*Figure 4.18, Histogram of Curve Width for the Fine and Coarse Recyclate Particles.*

The results from the statistical analysis of the recyclate particle dimensions are given in the table below.

| | Fines | | | | Coarse | | | |
|---|---|---|---|---|---|---|---|---|
| | Min | Max | Mean | s.d. | Min | Max | Mean | s.d. |
| **Area (mm$^2$)** | 0.21 | 24.34 | 4.92 | 3.78 | 0.2 | 39.92 | 8.50 | 8.4 |
| **Circularity** | 0.02 | 0.42 | 0.13 | 0.07 | 0.02 | 0.73 | 0.21 | 0.13 |
| **Curve Length (mm)** | 1.51 | 29.13 | 9.07 | 4.04 | 0.73 | 20.78 | 9.00 | 5.29 |
| **Curve Width (mm)** | 0.13 | 3.17 | 1.01 | 0.58 | 0.15 | 5.76 | 1.71 | 1.1 |

*Table 4.1, Statistical Results from Recyclate Particle Measurements.*

### 4.6.4. Discussion

The results of the image analysis of the two classified grades of recyclate support the observations made by previous authors, that there is an extremely large level of variation in

the size and shape of recyclate particles produced by granulation. All of the above results in Figure 4.15 - Figure 4.18 and the results in Table 4.1 show that for both the Fine and the Coarse recyclate grades the variation in each of the measured particle dimensions were very large. The histograms and the standard deviations all suggest that the range of particle shapes and sizes of the Coarse recyclate are even more diverse than those of the Fine grade. Due to the large variations it is difficult to accurately differentiate between the two grades. Given that the average particle curve lengths are very similar, in general the average results for the particle area, circularity and curve width indicate that the Coarse particles are typically wider and rounder than those found in the Fine grade.

An average fibre curve length of 9 mm for both grades compares well with the 6-12 mm fibre lengths typical of the chopped virgin glass reinforcements used in DMC manufacture, so the particles may be useful as replacement of reinforcement in such composites.

# Chapter 5

## 5. Fibre Testing

### 5.1. Introduction

In fibre reinforced composite materials the ingredients retain their individual identities (chemical and physical) however their combination produces material characteristics not possible with the individual constituents on their own [75]. Reinforcing fibres typically have very high strength and modulus but are manufactured as very fine fibres, whereas matrix materials have good resistance to environmental degradation. By combining the two it is possible to produce a material of desired shape with stiffness close to that of the fibres and with the environmental resistance of the resin.

Many theories and mathematical expressions have been developed which express certain mechanical properties of composite materials in-terms of the properties, quantities and arrangement of its constituents. They are based on a number of simplifications which mean that they should be used with caution when attempting to predict the mechanical properties of an actual manufactured composite part. In this chapter the investigation and theoretical modelling of properties of the reinforcing fibres is introduced to highlight the importance of the reinforcing fibre and their properties, in relation to the overall mechanical performance of a composite. The virgin fibres and recyclate fibres were characterised for direct comparison rather than for predictive calculations of the properties of any actual manufactured SMC or DMC composites.

### 5.2. Literature Review

One set of models used for the calculation of the properties of a composite material are known as the 'Rule of Mixtures' which relate the mechanical properties of a composite to the sum of the equivalent properties of its constituent parts [76]. For example a simple fibre reinforced polymer composite such as that in Figure 5.1, where the reinforcing fibres are

continuous and distributed in a uniform geometric array, the load applied to the composite in the direction of the fibres, $L_c$, is expressed by the rules of mixtures as:

$$L_c = L_m + L_f \qquad (5.1)$$

Where the subscripts $c$, $m$, and $f$ correspond to the values for the composite, matrix and fibre respectively.
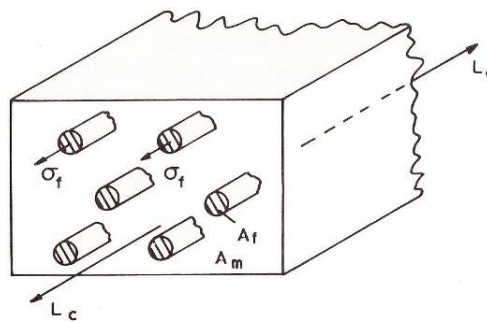


*Figure 5.1, Schematic Diagram of a Unidirectional Reinforced Composite [13].*

This model assumes that there is a perfect bond between the resin and the fibres and if it is further assumed that an applied load results in an equal strain in both fibre and matrix, though this is not strictly true of an actual polymer composite as different Poisson contractions in the different materials will result in other stresses. From equation (5.1) and these assumptions 'Rule of Mixtures' for composite longitudinal stress and for composite longitudinal modulus can be derived:

$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f) \qquad (5.2)$$

Where $\sigma_c$ stress on the composite and therefore its constituents and $V_f$ is the volume fraction of fibres in the composite.

$$E_c = E_f V_f + E_m (1 - V_f) \qquad (5.3)$$

Where $E_c$ is the Young's modulus of the composite and its constituents.

From equations (5.2) and (5.3) it can be seen that the performance of the composite depends on the relative performance of the fibre and the matrix, and it will also vary with fibre volume fraction.

However it is assumed throughout that the fibres are continuous until the ends of the composite and that they act independently, i.e. on reaching the fibre breaking strain the weaker fibres fracture and cease to have any effect, with the remaining fibres taking a disproportionate share of the load. Whilst the efficiency of the fibre in stiffening the composite is reduced as the fibre lengths decrease, the shortened lengths created by fibre fracture will in fact continue to play a part in the reinforcement and the effects at the fibre ends are important. This has been investigated analytically by Cox [77], using what is termed the 'shear-lag model', based on the assumptions that the resin and the fibre remain elastic and are both perfectly bonded together. In the regions of the fibre ends the strain in the fibre will be less than in the matrix, the variation of shear stress at the interface along the length of the fibre and the resulting tensile stress in the fibre are both represented in Figure 5.2.
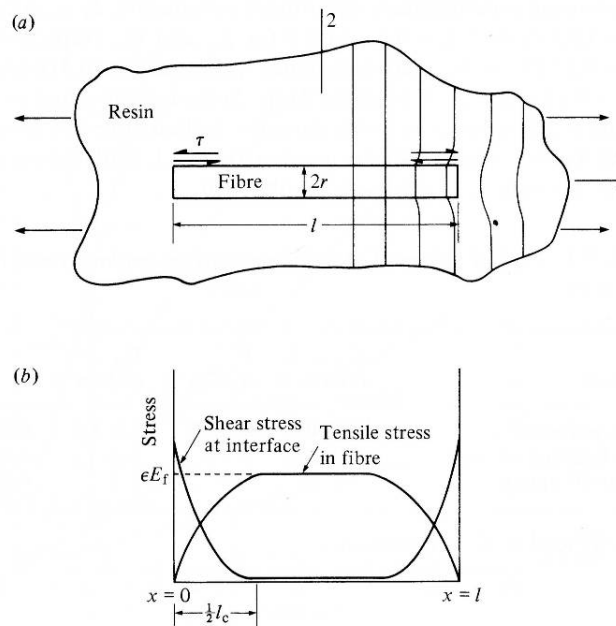
*Figure 5.2, Diagram of (a) Deformation Around a Short Fibre in a Matrix with Tensile Load Applied Parallel to Fibre (b) Variation of Tensile Stress in the Fibre and Shear Stress at Fibre-Matrix Interface [76].*

There have been many theories and associated models developed for this stress build up in reinforcing fibres, such as for Cox's case above. These models and Figure 5.2 demonstrate that there are regions in the fibre that do not carry the full load and therefore the average stress in a short fibre is less than that of a continuous fibre. The fibres reinforcing ability decreases towards the two ends and these regions are known together as the critical fibre length, $l_c$. For a fibre to be able to be able to achieve the maximum stress, i.e. the fibre's fracture stress, the total length of the fibre must be greater than the critical fibre length. The relationship between the critical fibre length and the ultimate fracture strength $\sigma_f^*$ of the fibre are expressed by:

$$l_c = \frac{\sigma_f^* r}{\tau_{IF}} \qquad\qquad (5.4)$$

Where $r$ is the radius of the fibre and $\tau_{IF}$ the interfacial shear stress between the fibre and the matrix.

If a fibre is of length $l < l_c$ then the shear stress transferred along the fibre cannot build up enough to cause fibre fracture and the work of failure of the composite is predominantly characterised by pull-out of the fibres from the matrix and matrix failure. When $l > l_c$ the work of failure in the composite failure is characterised by fibre breaking and/or pull-out, with the matrix strength having a smaller proportional contribution [56].

## 5.2.1. Discussion

The performance of a composite has been shown to depend upon the fibre and matrix strengths, the dependence of these strengths on the fibre volume fraction and the strength of the interface between the matrix and the reinforcement. These characteristics will be investigated further in this chapter for the direct comparison of the properties of individual recyclate glass fibres with those properties of virgin glass fibres.

Many of the assumptions used in the above modelling approaches are not true of real composite materials and application of such models for predicting the properties of composite materials such as SMC and DMC are further complicated by several factors such as; they are three phase materials, the reinforcement is discontinuous, the fibre length is spread over a distribution of sizes and the constituents are randomly orientated throughout the composite. Models have been developed to take into consideration these variable reinforcing fibre characteristics, such as with the use of correction factors to allow for the fibre orientations and fibre length distributions [77], [78] and the effective efficiency of the fibrous reinforcement in different testing directions. The results from the fibre comparisons performed in this chapter will not be used to determine predictive models for the strengths of the resulting composites, but could provide an insight into any potential mechanical differences between such composites reinforced with virgin fibres and those reinforced with recyclate fibres.

## 5.3. Single Fibre Experimental Methods

### 5.3.1. Fibre Diameter

To know the fibre area, required for later calculations, the fibre diameters needed to be measured, for both the virgin and the recyclate fibres. The diameters of individual fibres are dependent upon the production process and therefore a sample of fibres was measured and average results calculated. The diameters of the glass fibres were measured directly using SEM software during fibre imaging for both the virgin and recyclate fibres.

### 5.3.1.1.    Results: Fibre Diameter

High magnification SEM analysis of the recyclate fibres prior to pull-out testing was used to measure their diameters, over 50 individual fibres were measured for each fibre type. The images seen in Figure 5.3 show that the recovered recyclate fibres retained a significant amount of SMC paste as coating on the surface. Whilst virgin fibres had a relatively smooth surface and there is only occasional evidence of a thin sizing coating, as mentioned in previous investigations [45], [39], [40].
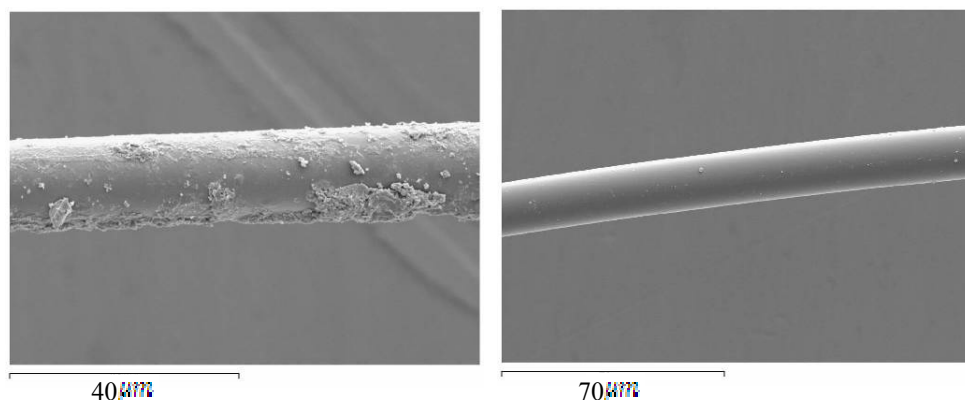


*Figure 5.3. SEM Image of (a) Recyclate and (b) Virgin Glass Fibres.*

The results of the measurements of the glass fibre diameters are given in Table 5.1. Despite the resin coating shown on recycled fibres the average diameters for both were found to be similar at an average of approximately 15.7 micrometers. This value was used for both the

virgin and the recyclate fibres as required in the calculations in the remainder of the investigation.

| | Virgin Fibre Diameter (µm) | Recyclate Fibre Diameter (µm) |
|---|---|---|
| **Average ± S.D.** | 15.66 ± 1.02 | 15.80 ± 0.80 |
| **Max** | 18.07 | 17.74 |
| **Min** | 13.98 | 14.03 |

*Table 5.1, Results of Fibre Diameter Measurements.*

## 5.3.2. Micro-Tensile Testing

For both the single fibre tensile and the single fibre pull-out tests a micro-tensile testing machine rig was used. Slight modifications were made to the grips for each of the different tests however the test method and remaining apparatus used were identical, and are described below.

### 5.3.2.1.     Apparatus

The micro-tensile testing rig consisted of several sections as shown in Figure 5.4. The testing machine used was a Biax-200 Micromaterials ultra low load tensile test machine. The load during tests was recorded by a 10 N load cell (Transducer World) and the displacement of the sample recorded by a linear variable displacement transducer (LDVT), both of which were interfaced with a computer so that the results were recorded and could be analysed further. The position of the LDVT and the cross-head speed could be adjusted and accurately controlled using the Biax-200 software for each test. A microscope was positioned directly above the test grips and connected to digital video camera, the real-time image of the test setup from the camera was output on a PC monitor. This image allowed accurate mounting of every individual test specimen and live monitoring of the test's progress. Adjustable light sources allowed the controlled projection of bright light onto the specimens so that a clear image was seen through the microscope and video camera.
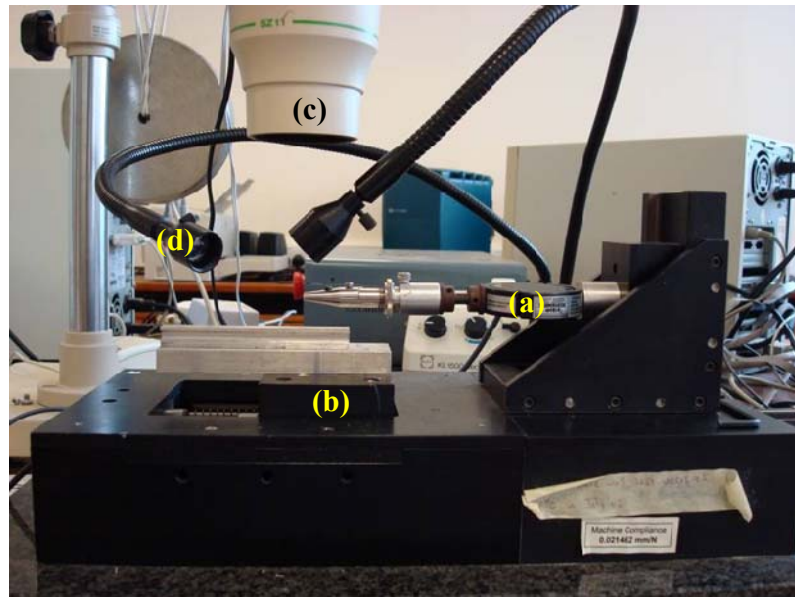
*Figure 5.4, Micro-Tensile Testing Rig: (a) Load Cell, (b) LDVT, (c) Microscope and (d) Adjustable Light Source.*

## 5.4. Single Fibre Tensile Testing

### 5.4.1. Introduction

Single fibre tensile testing has been used extensively to analyse the properties of virgin glass fibre materials and often to investigate the use of fibre size coatings and the effects of testing environments, with the aim of improving the fibre's strengths [79], [80]. However to date there have been no investigations into the strengths of recycled glass fibres obtained by mechanical recycling, or comparison with virgin fibres. Some work has been done on the glass fibres recovered by thermal recycling methods such as pyrolysis and fluidized bed [28]. As mentioned in the Chapter 2 thermal recycling methods typically result in thermal degradation of the fibres, as a result the recovered fibres that have been tested  have shown greatly reduced mechanical properties in comparison with virgin fibres, which in turn has been shown to affect their usefulness as reinforcement in new composite materials. Even at the lowest possible temperature required for successful pyrolysis, approximately 450 $^{o}$C,

the fibres saw 50% reductions in their strength, and at higher temperatures even greater degradation was observed [29].

## 5.4.2. Analysis Method

The 'weakest link model' is often used to describe the failure of brittle materials as being due to a catastrophic growth of independent pre-existing flaws. For brittle fibres used as reinforcing materials, such as glass fibres, each independent flaw then corresponds to an individual failure stress and failure at the weakest flaw (that with lowest failure stress) leads to immediate failure of the entire fibre. It is well known that the scatter in the strengths of glass fibres [81] caused by these randomly distributed flaws can be described by the Weibull distribution function [82]. The cumulative probability of failure, $P_f(\sigma_f)$, of a fibre at an applied stress, $\sigma$, can be described by the two parameter function:

$$P_f(\sigma_f) = 1 - \exp\left(-\frac{l}{l_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right)$$
(5.5)

Where $l$ is the tested fibre length, $l_0$ is the longest fibre length that contains only one flaw. The two unknown parameters $\sigma_0$ and $m$ are the Weibull scale parameter and the Weibull modulus or shape parameter respectively.

These unknown parameters may then be determined by linear regression [83]. By manipulating and re-arranging equation (5.5), which when testing samples of a fixed gauge length, can then be rearranged into the form of an equation for a straight line [84]:

$$\ln\left[\ln\left(\frac{1}{1-P(\sigma_f)}\right)\right] = m\ln(\sigma) - m\ln(\sigma_0)$$
(5.6)

If $\ln(\sigma)$ is plotted against $\ln\left[\ln\left(\dfrac{1}{1-P(\sigma_f)}\right)\right]$ then a straight line should appear, for which the slope will be the Weibull modulus, *m*, and from the intercept the characteristic strength may be obtained, $\sigma_0$.

The main problem of this method is how to best estimate the probability values so that the plotted values are unbiased estimators of the real values. The recorded values for the fibre tensile strengths are first sorted into ascending order and then each given a rank number, *i*, 1 for the smallest value to *n* for the *n*th value. These rank values are used to calculate the probability of failure values, $P_i$, so that the straight line plot may be drawn, this can be done using a mathematical function known as a probability index (or estimator), of which many examples exist in the literature [85], [86]. For this investigation the calculation of the *i*th strength was done with the following estimator as it has been shown to provide the least biased results [87], [88]:

$$P_i = \frac{i - 0.5}{n} \qquad (5.7)$$

From the distribution, equation (5.6), the average fracture stress, $\langle\sigma\rangle$, of the fibres at a fixed gauge length, *l*, can be calculated by [84]:

$$\langle\sigma\rangle = \sigma_o l^{-\frac{1}{m}}\Gamma\left(1 + \frac{1}{m}\right) \qquad (5.8)$$

Where $\Gamma$ is the gamma function.

Equation (5.8) shows that the average fracture stress of a glass fibre is not constant but dependent on fibre length. The mean failure strengths $\langle\sigma_1\rangle$, and $\langle\sigma_2\rangle$ of two specimens of the same material with respective gauge lengths $l_1$ and $l_2$ are therefore related by the equation:

$$\frac{\langle \sigma_2 \rangle}{\langle \sigma_1 \rangle} = \left(\frac{l_1}{l_2}\right)^{1/m}$$

(5.9)

This means that by investigating the value of the Weibull parameters at a set gauge length for a specific type fibre and calculating its mean strength, the strength of the same fibre at any other gauge length may be extrapolated. For example values at extremely short lengths typical of the critical fibre length for which experimental investigation is not possible [86], for similar reinforcing fibre – resin matrix systems critical fibre lengths have been calculated to 200-500 μm [89], [36].

### 5.4.3. Experimental Method

Testing and sample preparation has been done following the methods described by ASTM D3379-75 'Standard test method for tensile strength and Young's modulus for high-modulus single-filament materials'. Investigations by previous authors into the effects of sample size and the different probability estimators on the accuracy of the distribution model [90], [87] suggest a sample size of a minimum of 30 specimens be tested for the most accurate results. Over 50 specimens were prepared and successfully tested for each of the three different gauge lengths; 5 mm, 10 mm and 15 mm respectively, for both the virgin and the recyclate fibres. Experiments should ideally be performed over as many gauge lengths as possible, for this investigation the maximum testable gauge length (15 mm) was limited by the length of the fibres available in the recyclate after the granulation process.

Virgin E-glass fibre bundles were supplied by Menzolit UK, chopped from the continuous rovings used to produce automotive SMC, and the recycled fibre bundles were removed from the unclassified recyclate materials. The individual fibres to be tested were then extracted from these bundles, with care taken to avoid the creation of further defects, immediately prior to specimen preparation. Each fibre was fixed to a prepared cardboard mounting, using a fast drying cyanoacrylate adhesive, which had a gauge length cut-out made in the centre, as illustrated in Figure 5.5.
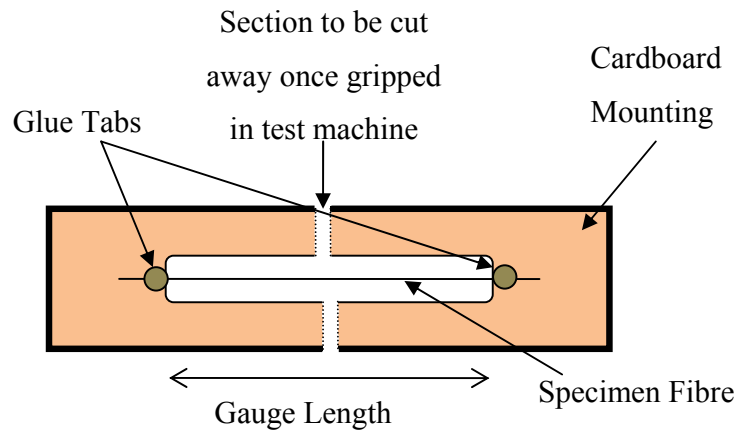
*Figure 5.5, Mounted Single Fibre Tensile Test Specimens.*

The cardboard mounted specimens were then placed so that the specimens was aligned axially between the jaws of the testing machine, and then gripped in place. Both sides of the cardboard mounting were then cut away to leave just the glass fibre suspended between the grips, so that only the fibre is loaded during the test. Tensile testing was performed using the micro-tensile testing set-up, Section 5.3.2, at a strain rate of 5% per minute, until the fibre failed. The load cell and LDVT were interfaced with a computer so that the load and displacement values were recorded during the tests. All test data recorded was then exported and analysed further using the statistical software package SPSS v.15.

Fibre stress and strain at failure were calculated from the load – displacement data recorded during the test using the following equations according to the standard. Tensile strength of fibre at failure:

$$\sigma_f^* = \frac{F_{max}}{A_f} = \frac{4F_{max}}{\pi d_f^{\,2}} \qquad\qquad (5.10)$$

Where $F_{max}$ is the maximum recorded load and the fibre surface area, $A_f$, calculated using the fibre diameter $d_f$.

Strain of fibre at Failure:

$$\varepsilon_f^* = \frac{X}{l}$$
(5.11)

Where $X$ is the recorded extension and $l$ the original fibre length.

For such small samples the calculation of the Young's modulus must also take into account the compliance of the testing system, $C_a$. This was done in accordance with the ASTM D3379-75, where the true compliance of the fibres, $C$, is equal to:

$$C = C_a - C_s$$
(5.12)

The Fibre's Young's Modulus, $E_f$, can then be calculated as:

$$E_f = \frac{l}{C.A_f}$$
(5.13)

### 5.4.4. Results: Single Fibre Tensile Testing

All spcimens exhibited a linear force-deflection response until a brittle failure resulting in a sharp drop in the load to zero, Figure 5.6:
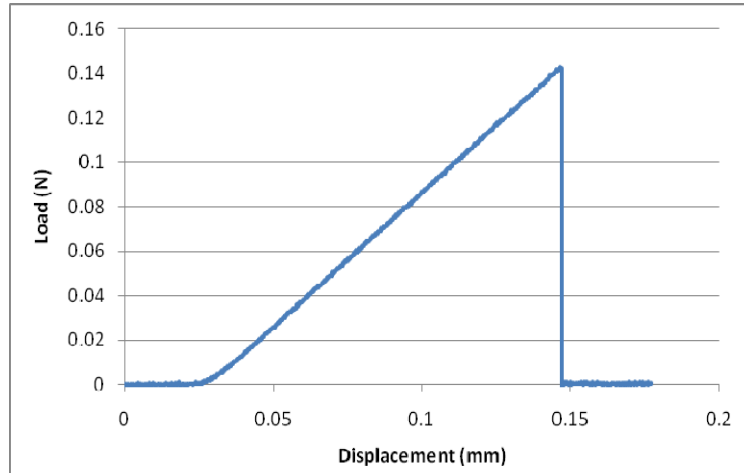
*Figure 5.6, Typical Single Fibre Tensile Test Load-Displacement Plot.*

The average strain, strength and Young's modulus of all tested samples at each gauge length were calculated from the recorded test data and are included in Table 5.2. The results for the properties of the virgin glass fibres are in good agreement with values in the literature [79], [91], [83], [76] who all report the strengths of virgin E-glass fibres in the region of 2-3.5 GPa.

| | Gauge length (mm) | | |
|---|---|---|---|
| *Virgin Fibre* | **5** | **10** | **15** |
| **Failure Strain (%)** | 3.6 ± 0.6 | 3.1 ± 0.7 | 3.1 ± 0.7 |
| **Tensile Strength (GPa)** | 2.08 ± 0.59 | 2.09 ± 0.56 | 2.1 ± 0.61 |
| **Young's Modulus (GPa)** | 69.2 ± 13.5 | 70.35 ± 9.89 | 71.1 ± 13.5 |
| *Recyclate Fibre* | **5** | **10** | **15** |
| **Failure Strain (%)** | 2.8 ± 0.9 | 2.6 ± 0.7 | 2.4 ± 0.7 |
| **Tensile Strength (GPa)** | 1.72 ± 0.59 | 1.64 ± 0.48 | 1.48 ± 0.46 |
| **Young's Modulus (GPa)** | 66.6 ± 14.1 | 64.9 ± 11.8 | 65.2 ± 10.3 |

*Table 5.2, Average Results from Tensile Testing of Virgin and Recyclate Fibres.*

The average results for the recyclate fibres appear to be lower than those of the virgin fibres at the equivalent tested gauge lengths, however the results need to be investigated further statistically before any conclusions can be made.

111

## 5.4.5. Results: Weibull Analysis

In Figure 5.7 - Figure 5.9 the results of the Weibull linear regression analysis are plotted for each of the tested gauge lengths. In each graph the results for all of the virgin and the recyclate fibres are plotted on the same axis along with lines of their respective Weibull strength distributions, the equations of which are calculated using the calculated Weibull parameters, as shown in Table 5.3. For each of the plots coefficient of correlation values, $R^2$, were calculated to give an indication of the linearity of the data – a goodness of fit. This gives an estimation of the proportion of the total variation in the data that is explained by the model, a maximum value of 1.0 indicates a perfect model which in this case that would mean all data points exactly fitting the straight line of the probability distribution.
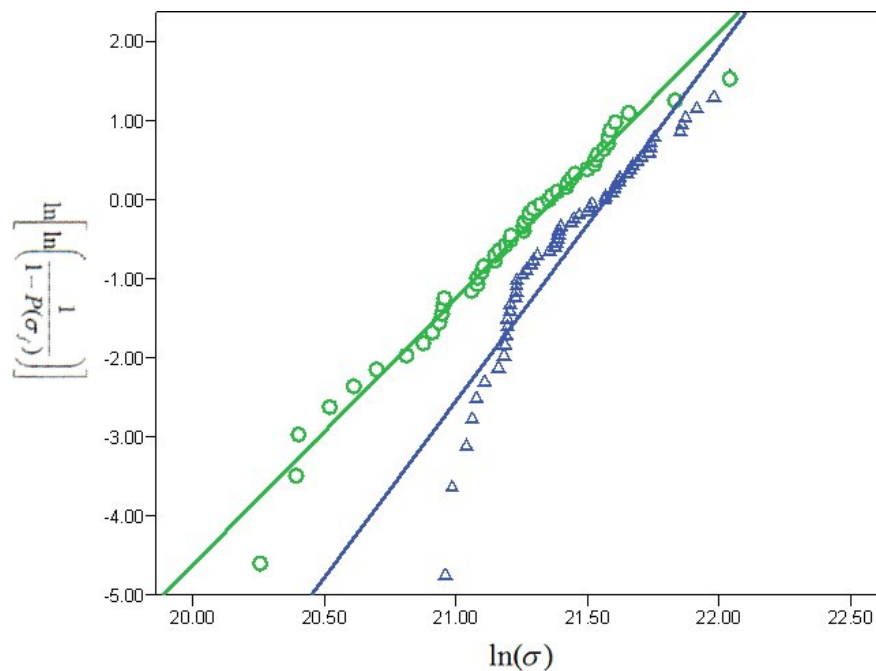


*Figure 5.7, Weibull Plot for Both Fibre Types, Recyclate (o) and Virgin (Δ) Glass, at Gauge Length 5 mm.*

112
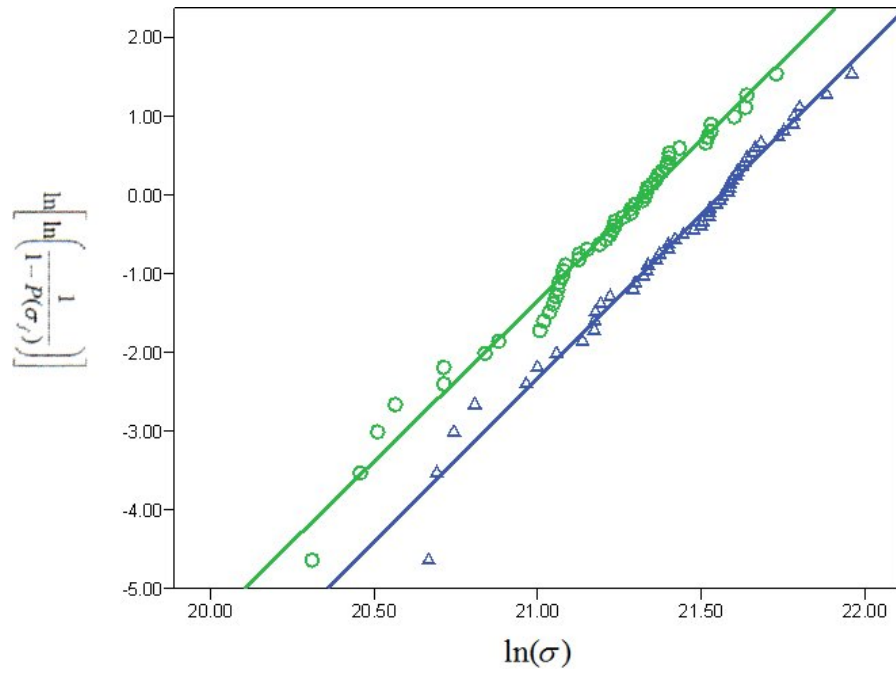
Figure 5.8, Weibull Plot for Both Fibre Types, Recyclate (o) and Virgin (Δ) Glass, at Gauge Length 10 mm.
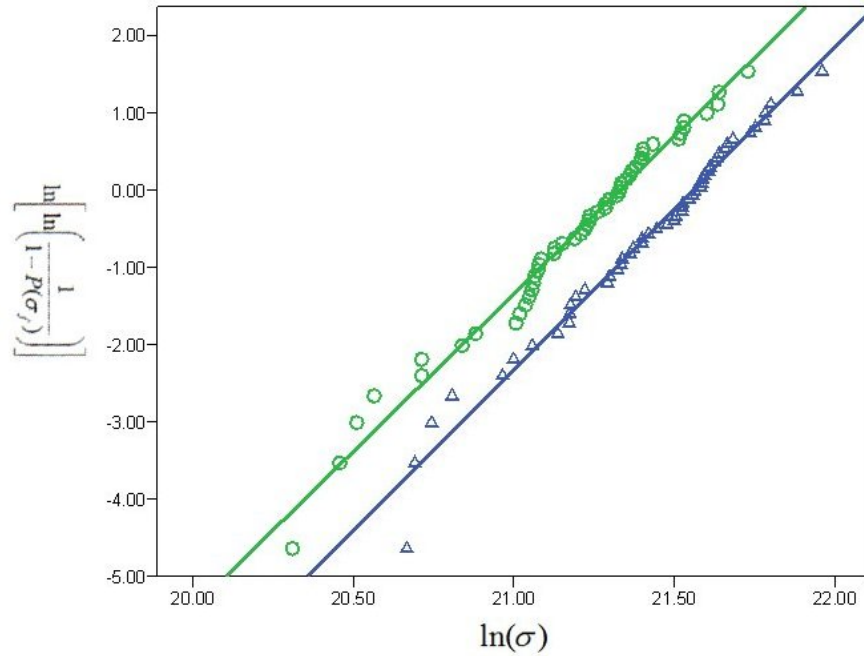


*Figure 5.9, Weibull Plot for Both Fibre Types, Recyclate (o) and Virgin (Δ) Glass, at Gauge Length 15 mm.*

113

| Gauge Length (mm) | Fibre | m | $\sigma_0$ | $\langle\sigma\rangle$ | $R^2$ |
|---|---|---|---|---|---|
| 5 | Virgin | *4.2* | *2.34* | *1.45* | *0.92* |
| | Recyclate | 3.37 | 1.91 | 1.06 | 0.98 |
| 10 | Virgin | 4.16 | 2.31 | 1.21 | 0.98 |
| | Recyclate | 4.07 | 1.84 | 0.98 | 0.98 |
| 15 | Virgin | 4.19 | 2.41 | 1.15 | 0.96 |
| | Recyclate | 3.65 | 1.65 | 0.71 | 0.99 |

*Table 5.3, Values of the Weibull Parameters from Single Fibre Tensile Tests at Each Gauge Length.*

## 5.4.6. Discussion

As discussed in the introduction the strength of a reinforced composite is heavily dependent on the strength of the individual constituents and their respective volume fractions. Expressing the strength of a composite in terms of the individual strengths of its components is again an over simplification as the tensile strength of brittle fibres, such as reinforcing glass fibres, exhibit a large degree of scatter. This variation is attributed to the presence of pre-existing flaws introduced during processing and handling [92], as a result $\sigma_f^*$ is not accurately characterized by a single average value and must be characterised statistically. The recyclate fibres tested in this investigation have been through several stages of processing including; compounding, moulding, grinding and separation, each of which is likely to have introduced new flaws to the surfaces of the fibres potentially reducing their individual strengths. The purpose of this testing was to compare the strengths of the fibres recovered from the recyclate with those of the virgin glass fibres used to make the original composite.

Results in Table 5.3 show that there is a significant decrease in the properties of the recyclate fibres compared with the virgin fibres. There is a drop in the average strength of the recyclate glass fibres, between 18 and 30%, in comparison with the virgin glass fibres.

Where the virgin glass fibres average strengths appears to be independent of fibre length, at these short gauge lengths tested, the recyclate glass fibres clearly show a gradual decrease in tensile strength with increasing fibre length (approximately 13% decrease in fibre strength between 5 and 15 mm gauge length).

The shift in the Weibull plots also clearly demonstrate the difference in average characteristic strengths of the virgin and the glass fibres, $\langle \sigma \rangle$, with the recyclate fibres being weaker than the virgin fibres at all tested gauge lengths. The mean characteristic strengths of the recyclate fibres are weaker at each gauge length and both types of fibres show the expected drop in strength with increased gauge length.

All of the plots and $R^2$ values for the recyclate fibres show a good fit to the linear Weibull probability model, which indicates the applicability of the Weibull statistics for analysis of the test data. The lowest $R^2$ is that of the virgin fibres at 5 mm gauge length for which, whilst still a good fit, it appears it may be possible to fit more than one straight line to the data points, which is in general an indication of a multimodal distribution. For virgin glass fibres at short gauge lengths such characteristics have been recorded by previous authors and are explained by the existence of another type of defect found inside the material existing alongside the external surface flaws [92]. The external surface flaws dominate the failure of the fibres at larger gauge lengths, but for shorter fibre lengths failure of these internal defects can also result in failure of the entire fibre.

The Weibull modulus, '$m$', determines the shape of the distribution, as the Weibull modulus increases the probability of failure is more concentrated around the mean stress. In the case of virgin glass fibres, the shape parameter '$m$' appears to be consistent and higher than that of the recyclate ranging from 4.2 - 4.16, whereas the recyclate fibre's values for '$m$' ranged between 4.07 – 3.37. The reduction in the Weibull modulus values for the recyclate fibres indicates greater scatter in the fibre strengths and that the the flaws are less evenly distributed along the length of the fibre.

These results are not unexpected given the large amount of handling and processing the recyclate fibres have been subject to. As explained in the introduction the strength of virgin glass fibres are affected by the existence of surface flaws introduced during manufacture and processing, the recycling and classification processes will have likely caused further flaws on the fibres resulting in their reduced average characteristic strength and the increased scatter in the results. Whilst there is a drop in the strength of the recovered fibres in this study, to around 60-80% of the virgin fibres, similar investigations into the recycling of SMC composites by thermal methods recorded much larger reductions in the fibres strengths, to between 30-50% [28] of the virgin fibres. During thermal recycling techniques, such as the fluidised-bed method, the glass fibres are not only subject to the granulation stage but also exposed to high temperatures, collision with the silica particles and further handling after processing. These additional processes will further contribute to an increased flaw population and weakening of the fibre strengths, potentially making a mechanical recycling process the more commercially viable of the two for production of a useful reinforcing material.

## 5.5. Fibre – Matrix Interface Strength

### 5.5.1. Introduction

The discussion of the strength of fibre reinforced composite materials in Section 5.2 indicated that the interface strength between the matrix and the fibre is also critical in determining the resultant composite's mechanical properties. A good interface is required so that the stresses acting on the matrix are transferred to the fibres, to utilise their high strength and stiffness. Composites with a weak interface tend to have relatively low strength and stiffness but a high resistance to fracture, whereas composites with a strong fibre-matrix interface tend to have high strength and stiffness but lower resistance to fracture. Therefore to understand the potential strength of a fibre reinforced composite and compare different reinforcing materials it would be advantageous to have some understanding of, and be able to record measurements for, this interface.

## 5.5.2. Analysis Method

A number of experimental techniques have been developed for the characterisation of the fibre-matrix interfacial properties or adhesion. The most common of these methods include the single fibre fragmentation, fibre pull-out, indentation and droplet micro-debonding tests, as illustrated in Figure 5.10, all of which are reviewed in detail by Herrera-Franco and Drzal [93] and Zhandrov and Mader [94].

The micro-debond droplet test method [95] involves the curing of a spherical droplet of resin around a fibre. The test involves moving the blades of a micro-vice parallel to the fibre to apply a steadily increasing load to the droplet until it is sheared off from the fibre surface. The interfacial properties can be determined from measurements of the maximum load required to cause the debonding and the droplet's size. The micro-debond droplet test was not used for this investigation as it was not possible to accurately produce symmetrical micro-droplets on the fibre surface with the chosen resin system, due to flow of the resin along the fibre at the high temperatures required for the resin curing reaction.

For the fragmentation test [96] a single fibre is embedded in a resin material and a test sample cured to form a tensile test specimen, as seen in Figure 5.10 (c). During the test the embedded fibre fractures under continued application of strain, and as the test continues the resulting fractured fibre lengths also fracture. The test is complete when the fibre lengths will no longer fracture i.e. they have reached their critical fibre length. Interfacial strength properties can be determined from measurement of the resulting critical fibre lengths and knowing the fibres tensile strength. The limited recyclate fibre lengths available for testing, from the recyclate materials, and again the change in resin viscosity during the curing reaction mean it was very difficult to prepare accurate usable samples. The fragmentation test requires also a transparent matrix for observation of the fibre fracture process and if tests were to be performed later using DMC or SMC pastes for comparison this would not be possible.

The indentation test [97] method requires a single fibre embedded in a matrix, perpendicular to a cut and polished surface to be compressively loaded to produce fibre debonding or slippage. There is a high risk that the indentation tests will result in fibre crushing rather than push-out [93] and this method was not chosen for this investigation.
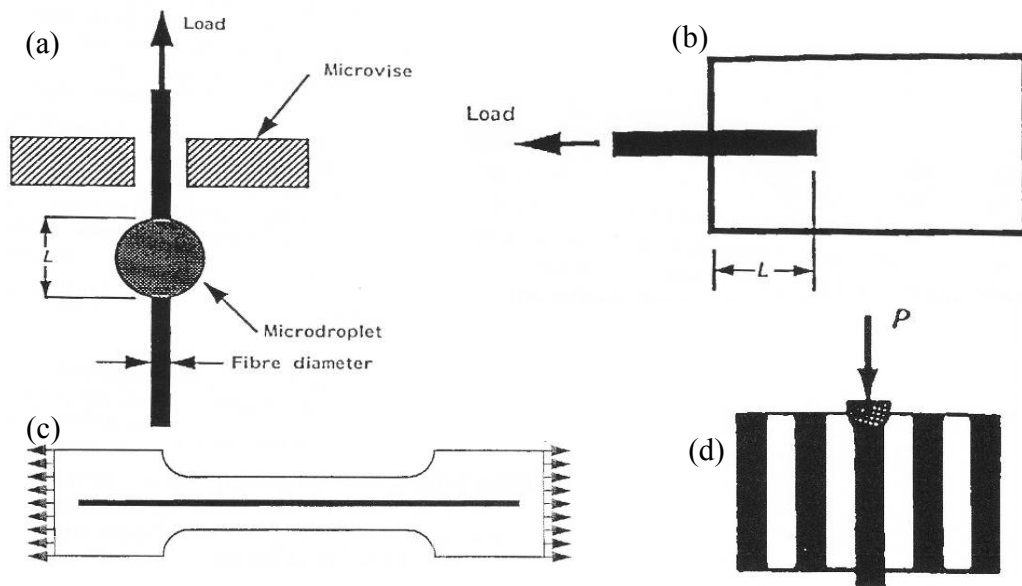


*Figure 5.10, Schematic Diagrams of Interfacial Test Methods; (a) Droplet Micro-debond, (b) Pull-out, (c) Fragmentation and (d) Indentation [93].*

Whilst there are a variety of experimental methods for investigating fibre-matrix interfacial properties, the pull-out test was chosen for this investigation because it provides direct measurement of debonding force vs. embedded length, it allows calculation of several interfacial parameters and most closely simulates one of the processes of failure in reinforced composites [98], [99].

### 5.5.2.1. Single Fibre Pull-Out

The pull-out test has been widely used to observe both differences in the interfacial strength and the different pull-out mechanisms for a range of fibres in various matrices, as discussed in depth by DiFrancia et al. [100]. As mentioned in Chapter 2 the reinforcing fibres used in SMC manufacture are coated with a size during the manufacturing process. The size is

believed to fulfil many functions, such as; protecting the fibres from environmental degradation, binding the individual filaments together to form rovings and to provide a strong chemical link between the glass fibres and the polymer matrix. Many types of silanes are commercially available and the exact selection is based on the chemical composition most compatible with the chemical structure of the resin. This chemical selection has often been the focus of the few previous interface investigations involving glass fibres embedded in a polyester matrix [101], [102], [103]. In an attempt to optimise the composites performance by establishing the conditions for the strongest interface between fibres and matrix. Although the interfacial parameters of many virgin fibres embedded in a range different polymer matrices have been investigated, no attempt has ever been made to investigate the strength of the interfacial properties of recycled glass fibres obtained through mechanical recycling. In this section the single fibre pull-out test was used to compare the interfacial shear strength between the different reinforcing fibres, recyclate and virgin, in a polyester matrix so that they may be directly compared.

### 5.5.2.2.     Pull-Out Data Analysis

The shape of the force displacement curve generated by the successfully pull-out of a fibre from a resin matrix depends on the intrinsic characteristics of the interface. In general there are three types of load-displacement curves commonly observed for brittle fibre/resin systems [104], [105], as illustrated in Figure 5.11 Where $\sigma_i$ is the initation of debonding stress, $\sigma_d$ is the maximum debonding stress and $\sigma_{fr}$ the frictional resistance stress.
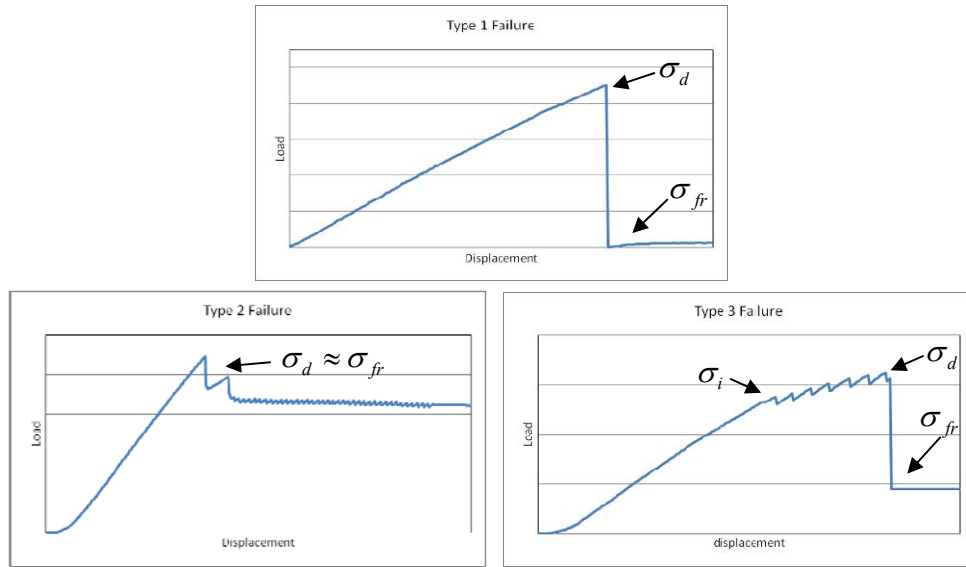
*Figure 5.11, Typical Load - Displacement Failure Mode Plots for Pull-Out Tests.*

For tests where the fibre-matrix interface is very strong, or very weak, and the embedded fibre length very short a load-displacement curve similar to the Type 1 failure is typically observed. The debonding process is totally unstable such that immediately on initation the total debonding process happens so rapidly that it cannot be fully observed. Immediately after initiation of interface failure the load immediately drops to near zero, therefore only the maximum debond stress may be recorded.

A type 2 failure process is more common of systems with weaker interface and for slightly longer embedded fibre lengths. It represents a stable debonding process where after initation the complete debonding process is also observed along with frictional resistance. After the failure of the interface the load falls to a slightly lower value and the fibre is then progressively extracted from the matrix with the frictional resistance between the fibre and matrix surfaces being recorded until pull-out is complete.

A more complex plot has also previously been observed for various fibre-matrix systems, that of Type 3 failure, typical of even longer embedded fibre length. After intiation of the debonding process the load continues to steadily increases, with some 'stick-slips' observed during an intial stable debonding process, then at maximum load there is unstable

120

debonding process and sharp load drop with potentially some frictional resistance against the remaining process. This 'stick-slip' process has been attributed to [106], [107] frictional forces whereby as the debonded area increases so does the interfacial frictional forces, between the fibre and the resin. The frictional forces resist further interface debonding until the fibre slips, either once the applied load exceeds the frictional resistance, or possibly due to poissons contraction of the fibre.

If the shear stress is assumed to be evenly distributed along the embedded fibre length then the strength of the interface can be determined by balancing the tensile stress on the fibre and the shear stress at the interface [102], $\tau_d$, which at failure it is given by:

$$\tau_d = \frac{L_d}{2\pi r l_e} \qquad\qquad (5.14)$$

Where the $L_d$ is the load recorded at initiation of debonding, $r$ the radius of the fibre and the length of the fibre embedded in the matrix is $l_e$.

However, as discussed in Section 5.2, the stress distribution in a short fibre in an elastic matrix is not uniform, and therefore several theoretical models have been developed to determine the interfacial shear stress under these conditions for a range of fibre and matrix materials. Thorough analysis of the different models and theory are discussed by Di Francia *et al.* [100], Kim *et al.* [105], Zink *et al.* [108] and Herrera-Franco and Drzal [93]. The models have generally been designed from two approaches:

1. A mechanical based approach, whereby the interface fails when the interfacial shear stress exceeds the shear strength required for debonding.
2. A fracture energy based approach, characterises the interface by its work of fracture.

Two examples of such models commonly applied to pull-out test data will be discussed below; Lawrence's model [109] analyses the results from a mechanical model neglecting

the frictional effects, and Goa *et al.'s* model [110] uses an energetic based approach which takes frictional effects into account.

**Model 1: Lawrence's Model**

Lawrence's model [109] developed previous work by Greszczuk [111] and expands equation (5.14) for the case of a fibre embedded in an elastic matrix where the shear stress varies along the embedded length of the fibre. The value for the maximum shear stress in this model is reached where the fibre enters the matrix and the interface fails when the maximum value exceeds the interfacial shear strength, $\tau_d$. The average shear strength, $\tau_a$, can be defined as:

$$\tau_a = \frac{L_d}{2\pi r_f l_e} = \tau_d \frac{\tanh(\alpha l_e)}{\alpha l_e} \qquad (5.15)$$

Where α, an elastic constant, is equal to:

$$\alpha = \sqrt{\frac{2\mu_m}{r_f^2 E_f \ln(R/r)}} \qquad (5.16)$$

Where $\mu_m$ matrix shear modulus, $R$ radius of matrix, $E_f$ Fibre Young's modulus, $r$ radius of fibre, $l_e$ embedded fibre length.

It is assumed in this model that the fibre is embedded in a semi-infinite matrix, whereby $R \gg r$, and that the load at the embedded fibre end is zero.

**Model 2: Goa et al.'s Model**

Energetic based models characterise the interface in terms of its fracture toughness, where on initiation of debonding crack propagation takes place when fibre strain energy at the crack front is higher than the fracture energy of the interface, $G_i$. Outwater and Murphy

[112] proposed that for continued crack propagation the fibre tensile stress at the crack front must be:

$$\sigma_d = \sqrt{\frac{4E_f G_i}{r}}$$

<div align="right">(5.17)</div>

However this model assumes that the matrix is not involved in the energy dissipation, there are no frictional energy effects and the debond load is not dependant on fibre length. Gao *et al.'s* [110] model takes these factors into consideration and a model the crack as a partially pre-debonded region, of length $(l_e - z)$, propagating stably along the embedded length with constant interfacial fracture toughness (or energy absorption) [105]. The partial debond, $\sigma_d^p$, stress is expressed as:

$$\sigma_d^p \approx \sigma_{Fo} + (\bar{\sigma} - \sigma_{Fo})\{1 - \exp[-\lambda(l_e - z)]\}$$

<div align="right">(5.18)</div>

Where:

$$\sigma_{Fo} = \sqrt{\frac{4E_f G_i}{r(1 - 2k v_f)}}$$

<div align="right">(5.19)</div>

$$\bar{\sigma} = -\frac{q_o}{k}\left(1 + \frac{\gamma \, v_m}{\varphi \, v_f}\right)$$

<div align="right">(5.20)</div>

$$\lambda = \frac{2\mu k}{r}$$

<div align="right">(5.21)</div>

$$\gamma = \frac{r_f^2}{R^2 - r^2}$$

<div align="right">(5.22)</div>

$$\varphi = \frac{E_m}{E_f}$$

<div align="right">(5.23)</div>

$$k = \frac{\varphi v_f + \gamma v_m}{\varphi(1 - v_f) + 1 + v_m + 2\gamma}$$

<div align="right">(5.24)</div>

Where $\sigma_{Fo}$ represents the frictionless debond stress, $\bar{\sigma}$ is a function of the residual clamping stress on the fibre and the material properties, and $\lambda$ is a function of the frictional coefficient $\mu$. The material properties are the Young's modulus', $E_m$ and $E_f$, the Possion's ratios, $\nu_m$ and $\nu_f$ of the matrix and the fibres respectively. $r$ and $R$ are the radii of the fibre and the matrix respectively.

Debonding is complete when $(z = l_e)$ then the total debond stress can be written as:

$$\sigma_d = \sigma_{Fo} + (\bar{\sigma} - \sigma_{Fo})\{1 - \exp[-\lambda l_e]\} \qquad (5.25)$$

Once the debonding is complete the only resistance to pull-out is the frictional resistance acting over the debonded length, the frictional force is found by replacing, $\sigma_{Fo} = 0$, into Equation (5.25):

$$\sigma_{fr} = \bar{\sigma}\{1 - \exp[-\lambda l_e]\} \qquad (5.26)$$

The crack is considered to start at the free end and any debonding initiating at the embedded end is ignored. A zero interphase thickness is assumed with any difference in the matrix at the interface and in the bulk homogeneous matrix ignored. For a catastrophic failure the maximum pull-out load may be reported as the maximum load seen in the load displacement graph, however for non-catastrophic failure such that in Type 2 failure care must be taken as the maximum load may be a combination of the load required to debond and frictional effects.

There is no obvious justification for the specific choice of models based on either of the approaches for the prediction of debonding for specific fibre-matrix combinations. Comparison of both the Lawrence's and the Gao et al.'s models using the same set of experimental data, from pull-out tests using glass fibres embedded in polyester resin, was performed by Delfolie et al. [102]. The study found that the accuracy of the chosen model

was dependent on the type of debonding process recorded. They showed that the mechanical model best fitted data for an unstable debonding process and the energetic model best fitted results for a stable Type 2 failure. Whilst Lawrence's model showed good agreement with the experimental data over the entire range of embedded fibre lengths, 50-750 µm, Gao et al.'s model over estimated for the shorter embedded fibre lengths.

### 5.5.3. Experimental Method

There is no standard method for the single fibre pull-out test and experimental methods have varied greatly, often dependent on the fibre and resin materials used, with the sample preparation methods designed accordingly. A typically test consists of a single fibre being partially embedded, $l_e$, in a block of resin as shown in Figure 5.12. The free end of the fibre is then gripped and a steady load is applied until the embedded length is debonded from the matrix and then pulled-out.
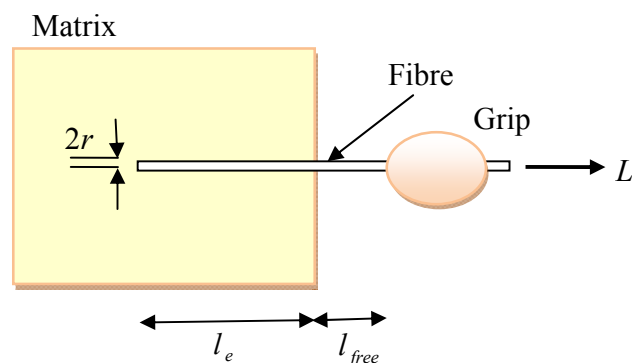


*Figure 5.12, Single Fibre Pull-Out Test Specimen Set-Up.*

During sample preparation and testing it is important to keep the free length, $l_{free}$, of the fibre as small as possible, as to reduce the chance of the fibre sample failing before debonding occurred and to minimise the energy stored in the free fibre which would otherwise contribute to the pull-out process [113]. The matrix block is to be of sufficient size and gripped in such a way that deformation of the matrix is taken to be negligible.

During the test the load and displacement of the system are recorded so that the debonding process may be investigated further.

Pull-out test specimen preparation for this investigation was performed in three stages using specifically designed apparatus:

### 5.5.3.1.    Stage 1

The virgin and recyclate glass fibres used were collected and handle in the same manner as described in Section 5.4.3 for the single fibre tensile testing. To allow more accurate handling of the individual fibres during sample preparation they were initially set in small epoxy (EPOTEK 375) 'pucks', with a free length of fibre protruding perpendicularly from the puck. This was done using a specially designed rig shown in Figure 5.13, a fibre was held above the resin compartment vertically using a needle held in the metallic frame. Epoxy resin was then poured into the mould cavities around the fibre and cured at 120°C for one hour. Once removed from the mould the free fibre end could be cut to a desired length, using a razor blade, and more easily handled for embedding in polyester resin for pull-out.



(a)                                                                 (b)
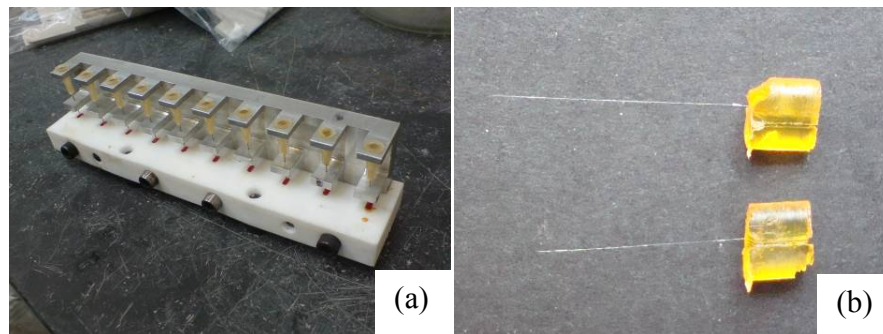
*Figure 5.13, Pull-Out Sample Preparation Stage 1: (a) Mould Tool and (b) Free Fibres in Epoxy Pucks.*

### 5.5.3.2.    Stage 2

A fibre embedded in an epoxy puck was then clamped into a new sample holder and lowered over mould cavities in another sample preparation rig, Figure 5.14, so that the free

end of the fibre could be embedded in polyester resin at controlled depth. The same polyester resin as described in Chapter 3 for the manufacture of SMC was used to fill the mould cavities, with addition of the correct ratio of initiator, and cured in two stages: firstly from 90°C to 120°C over three hours and then a post-curing for one hour at 150°C.
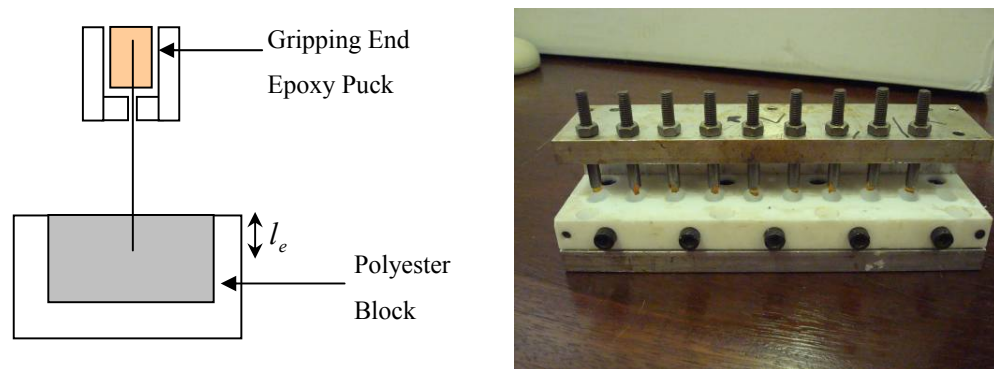


*Figure 5.14, Pull-Out Sample Preparation Stage 2: Schematic Diagram of Embedding Fibre in Polyester Resin and Image of Rig Used.*

### 5.5.3.3. Stage 3

Once cool the embedded fibre specimens are removed from the rig, the epoxy puck was cut off and the free fibre length left protruding from the polyester block was measured using a Mitutoyo PJ300 Shadow Graph [114]. Measuring the free length here allowed the calculation of the embedded length after pull-out. Finally a new small epoxy tab was glued to the free fibre length, as close as possible to the polyester block, to make it easier to grip in the test machine. The free fibre length between the grip and the matrix block was also measured using the shadow graph.

Testing was performed using the micro-tensile testing rig, described in Section 5.3.2, with the inclusion of a specially designed clamp to securely hold the pull-out specimens, Figure 5.15. The microscope and video output on PC screen were used to ensure that the fibre was carefully aligned axially between the grips and the sample gripped securely. Tests were run at a crosshead speed of 0.001 mm/s and were visually monitored throughout using the microscope, until pull-out was complete or the sample failed in the fibre. The load

displacement results were recorded throughout the test and exported to be analysed further in MS Excel.
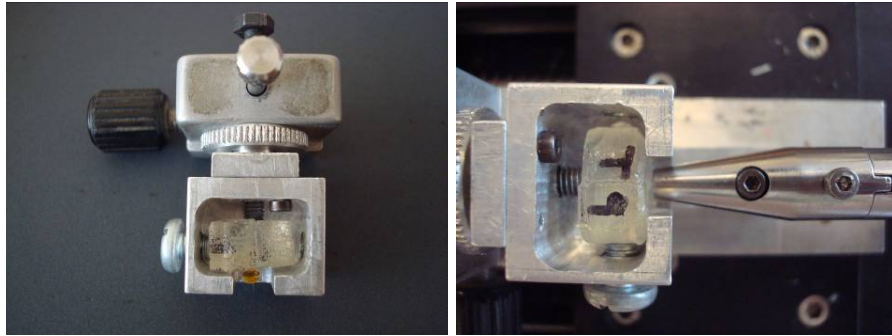


*Figure 5.15, Sample Holder for Pull-Out Specimens.*

Once the successful tests were complete the pulled-out fibres were carefully removed from the test grips and measured, again using the shadow graph, to establish the embedded length. Several pulled-out fibres were also later imaged using the SEM to inspect the resulting fibre surface.
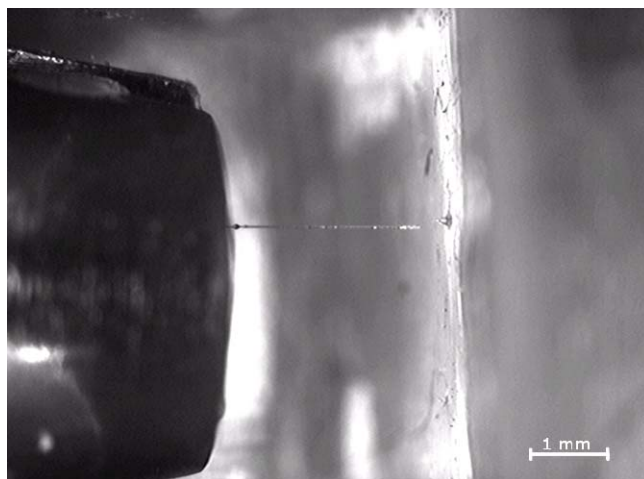


*Figure 5.16, Image of Successful Single Fibre Pull-out Test Seen Through Microscope.*

## 5.5.4. Results: Pull-Out Test

Many test specimens, both virgin and recyclate fibre, were produced for the pull-out testing. However due to the variable strength of the free fibre length (between grips and matrix) and the high likelihood of fibre failure before pull-out at long embedded lengths, a large number of the samples failed before debonding was initiated. Over 30 complete tests were recorded for each fibre type for analysis.

The relationship between the embedded fibre length and the maximum load required for debonding is shown for both the virgin and recyclate fibres in Figure 5.17. This plot shows a clear difference between the behaviour of the virgin and the recyclate fibres when extracted from the same matrix. The recyclate fibres show a trend towards increased debond load with increased embedded length, and it was possible to pull-out embedded fibre lengths of up to 5 mm. The virgin fibres show no such trend with very short fibre lengths also being pulled-out at high loads, the successful pull-out of embedded lengths appears to be restricted to very short lengths, with an apparent cut-off point at 1.5 mm.
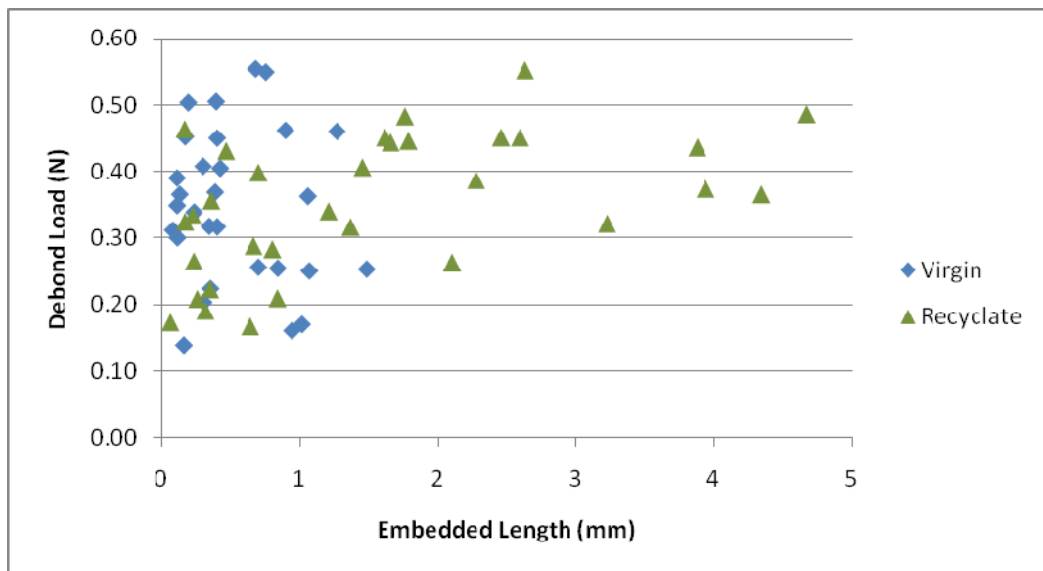


*Figure 5.17, Maximum Debonding Load Versus Embedded Length for Virgin and Recyclate Fibres.*

There was a clear difference in the types of failure mode plots, as discussed in Section5.5.2.2, observed for the virgin and for the recyclate glass fibres. The virgin fibre pull-out tests were predominantly characterised by a Type 1 failure plot, as shown in Figure 4.9 and Figure 5.20, typical of a strong matrix-fibre interface and an unstable debonding process. At debonding the virgin fibres typically showed a sharp drop in the load to nearly zero, with only 9 of the 30 tested samples showing any frictional force for the remainder of the pull-out process, split between both Type 2 and Type 3 failures. Examples of the three types of load-deflection plots recorded during the testing are shown below.
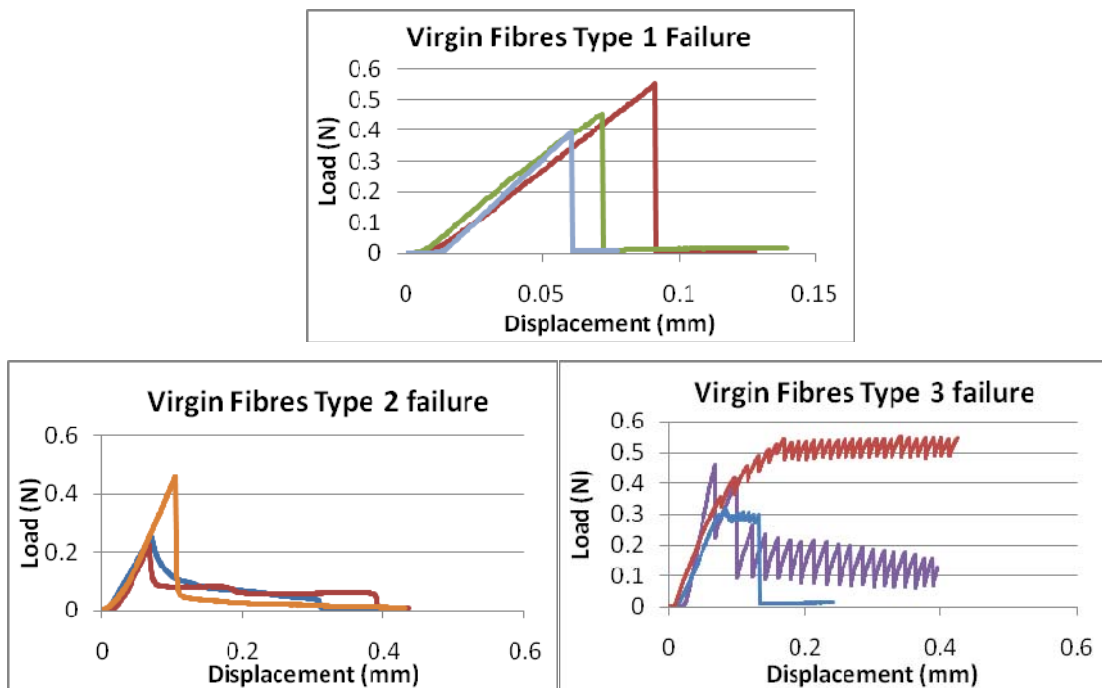


*Figure 5.18, Load Displacement Plots for the Virgin Fibre Pull-out Tests and Different Failure Modes.*

The recyclate fibres pull-out tests showed much greater variation, all three types of possible plot were recorded as shown in Figure 5.19 and Figure 5.20. For the majority of recyclate fibre tests frictional resistance after debonding plays a greater role in the pull-out process. A total of 24 of the 31 tested specimens showed significant frictional resistance after the initial debonding, again split near evenly between the Types 2 and Type 3 failure modes.
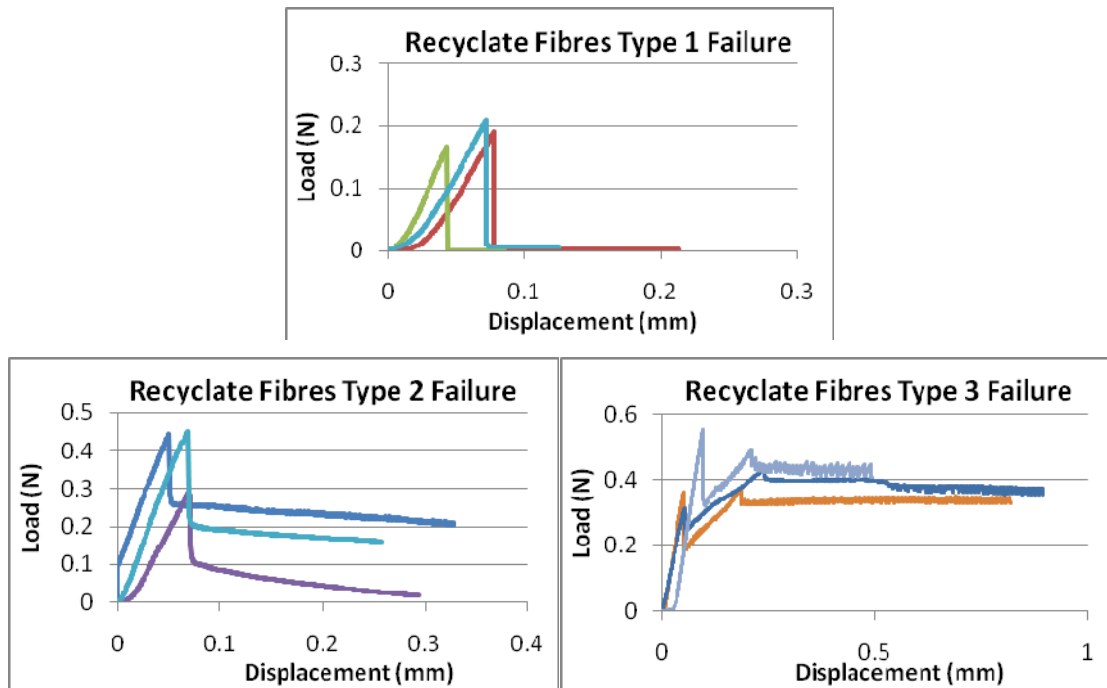
*Figure 5.19, Load Displacement Plots for the Recyclate Fibre Pull-out Tests and Different Failure Modes.*

The total count for each of the observed failures mode for both the virgin and the recyclate fibres are shown in the figure below.
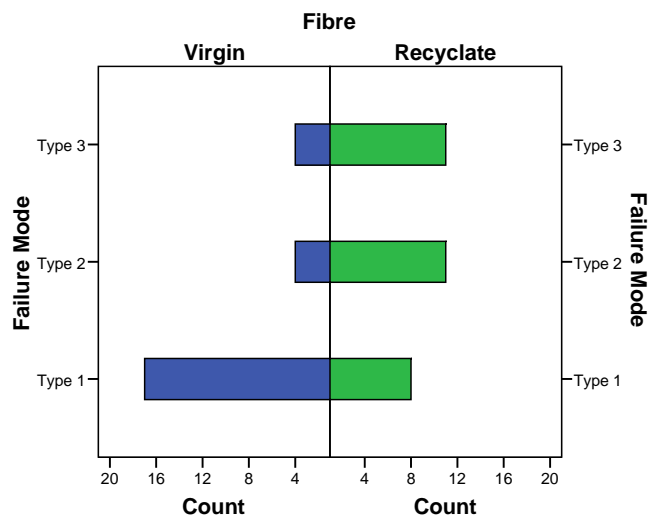


*Figure 5.20, Histogram of Failure Modes for Pulled-out Virgin and Recyclate Fibres.*

## 5.5.5. Results: Pull-Out Modelling

Due to the extremely short fibre lengths pulled-out for both fibre types and the lack of frictional resistance recorded from the virgin fibres samples the use of an energetic based model for the interface toughness was not appropriate. Therefore calculation of the interfacial shear strengths, $\tau_d$, were performed using the mechanical approach by fitting Equation (5.15), to the experimental data. The values for the debond force were taken as the maximum recorded load during the pull-out test for both the Type 1 and Type 2 failure modes, the Type 3 failures cannot be used due to the increase in load after debonding caused by the frictional forces.
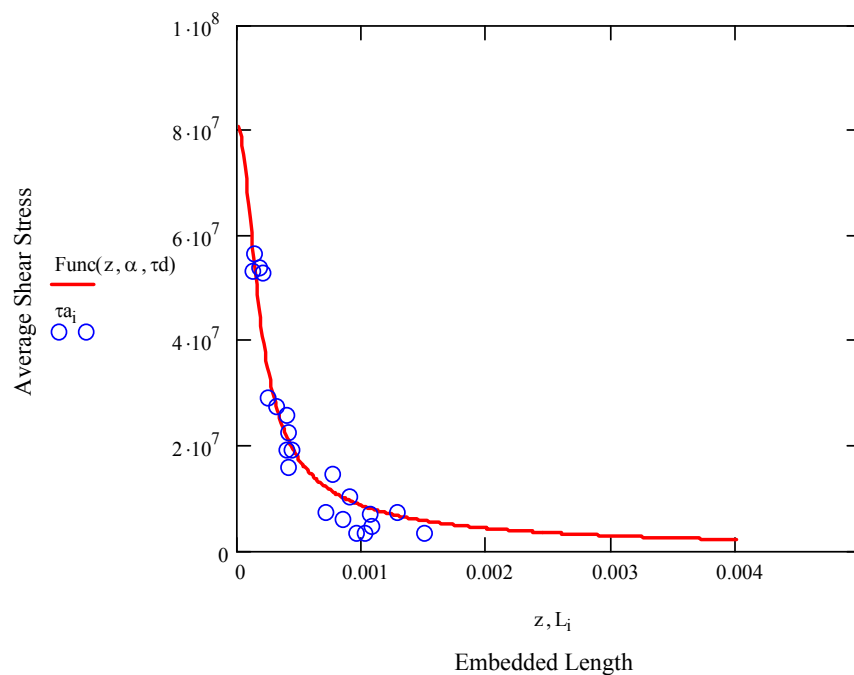


*Figure 5.21, Average Shear Stress vs. Embedded Length for Pulled-Out Virgin Glass Fibres (Experimental Results o and Lawrence's Model —).*

132
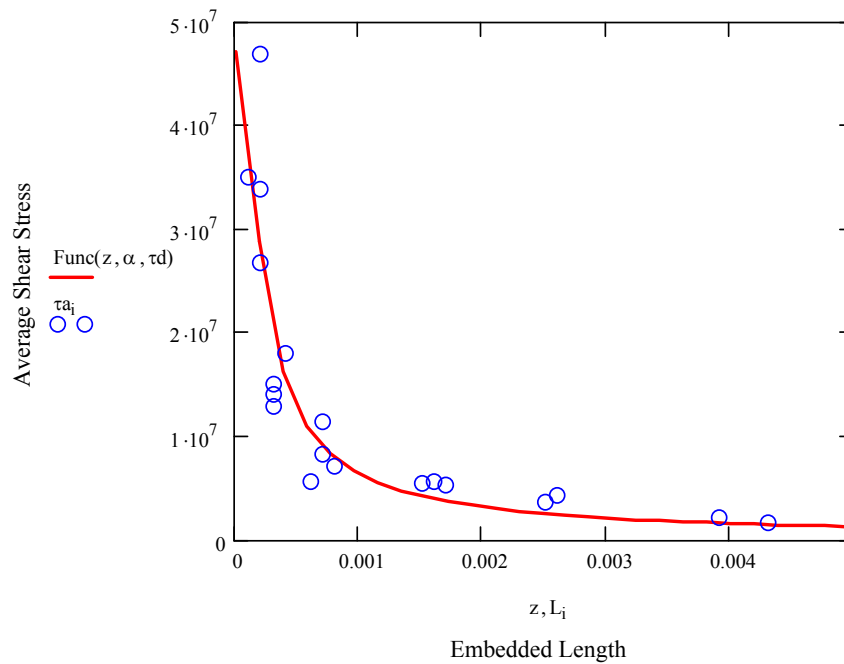
*Figure 5.22, Average Shear Stress vs. Embedded Length for Pulled-Out Recyclate Glass Fibres (Experimental Results o and Lawrence's Model —).*

Both Figure 5.21 and Figure 5.22 show a good fit of the theoretical model with the recorded experimental data, suggesting that the use of the mechanical modelling approach is suitable for these experiments. The results show that the interfacial shear strength of the recyclate fibre are significantly weaker, 47 MPa, compared with that of the virgin glass fibres at 82 MPa.

## 5.5.6. Results: Scanning Electron Microscopy

The first indication that the interfacial properties of recyclate fibres were likely to be significantly different than those of the virgin fibres was the dramatic differences in the fibre surfaces seen in Figure 5.3. However the SEM images of the pulled-out recyclate fibres, seen in Figure 5.23, each appear to show a relatively clean surface along the fibre length.
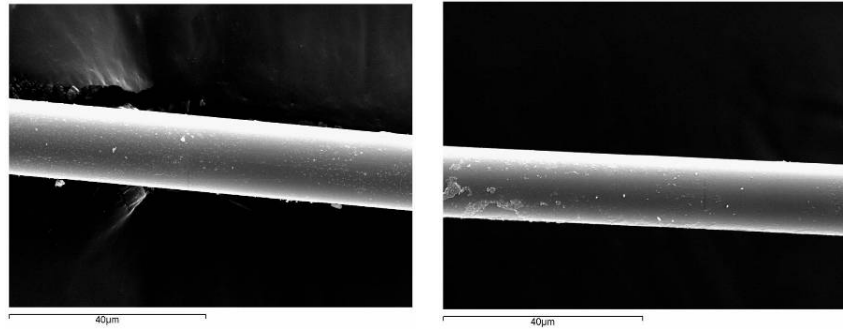
*Figure 5.23, Fibre Surface of Two Recyclate Fibres Embedded Length after Pull-Out Testing.*

The degree to which there is an SMC paste coating on the recyclate fibres is an entirely random process, no two fibres will be the same. Therefore images were taken along a pulled-out recyclate fibre, at the embedded length and the free length using the SEM, Figure 5.24. By following along the length of a recyclate fibre it can be seen that the specimen used had a rough surface with evidence of paste coating along it prior to testing, on the section of the fibre not embedded.  However after pull-out the embedded length of the fibre has come out apparently clean with no such similar paste coating.
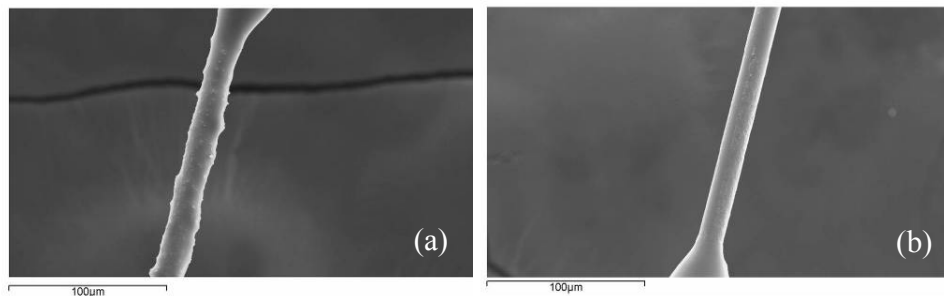


*Figure 5.24, Either Side of a Recyclate Fibre after Pull-Out, (a) Free Length of Fibre not Embedded and (b) Embedded Section of Fibre.*

## 5.5.7. Discussion

The pull-out testing established clear differences between the interfacial shear strengths of virgin and recyclate fibres embedded in a polyester matrix. There were also differences observed in the maximum length of fibre that could be pulled-out and in the processes after

134

the initiation of debonding. The different failure modes observed are likely to be a function of the embedded fibre length pulled-out, as illustrated in Figure 5.25. A Type 1 failure mode is common for short embedded lengths where the stored energy is enough to completely remove the fibre immediately after debonding, as seen for the virgin glass fibres. The likelihood of observing frictional resistance increases as the embedded fibre length increases, as the fibre area potentially in contact with the polyester matrix after debonding also effectively increases.
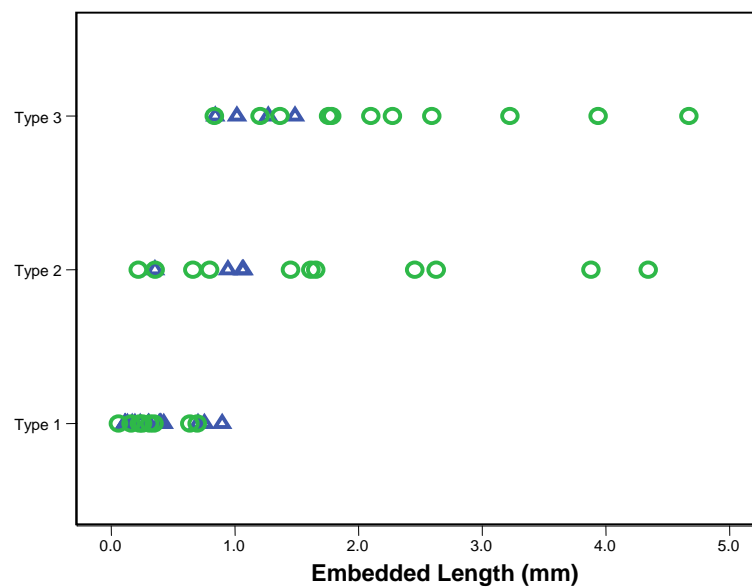


*Figure 5.25, Plot of Failure Mode against Embedded Length for Virgin (Δ) and Recyclate (o) Fibres.*

The strong interface between the polyester resin and the virgin glass fibres meant that it was only possible to pull-out virgin fibres up to a maximum of 1.5 mm. Fibres with longer embedded lengths resulted in failure at the free fibre length before the load required to initiate debonding could be reached. Even though the recyclate fibres have been shown to have lower strengths, in Section 5.4, their weaker interface with the polyester resin meant it was possible to pull-out fibres up to 5 mm in length.

135

The results of any pull-out tests are strongly dependant on the experimental procedure so the calculated interfacial parameters should not be taken as absolute [115], but can provide a direct comparison of different systems tested under the same conditions. The differences in the cut-off points observed for the maximum fibre length that could be successfully pulled out from the matrix also relate to the critical fibre length, as discussed in Section 5.2. For this investigation the critical fibre length for the virgin glass fibres in the polyester matrix appeared to be around 1.5 mm, whilst the weaker interfacial bond strength between the recyclate fibres and the polyester matrix meant that fibres up to 5 mm embedded length were successfully pulled out. A fibre length longer than the critical fibre length, $l_c$, is required for effective reinforcement of the matrix by the fibre, otherwise the tensile stress in the fibres shorter than $l_c$ will be less than that of a continuous fibre under the same loading conditions resulting in a reduction in the fibres reinforcing efficiency.

SEM images have shown the surface of the virgin fibres prior to testing to be relatively smooth and constant, as they are only a function of the manufacturing method used and surface coating applied. The recyclate fibres, however, have been shown to be very different, Figure 5.3, with paste materials randomly coating the fibre's surface. The degree and total area of SMC paste coating on each individual recyclate fibre will be unique, as it will be obtained in an uncontrollable manner during the fracture processes at the recycling stages. The varying degree and shape of this coating on the recyclate fibre surfaces will in part explain the variation in the recyclate failure modes and the frictional resistance after debonding observed. Whilst the regular, identical virgin fibres have predominantly experienced Type 1 failure processes, the results for the virgin glass fibres have been split between all three possible modes, as shown in Figure 5.20. A dominant or constant observed post debonding failure mode is not expected when the surface or interface between the fibres and the matrix is not identical for all test specimens.

The SEM images seen in Figure 5.24 appear to show that the recyclate fibres after pull-out are clean of the SMC paste coating, so it is possible that after debonding the SMC paste coating act as debris between the fibre surface and the resin. This will potentially increase

136

the roughness and friction between the two during the pull-out process after debonding [104], contributing to in the increased observation of stable and partially stable debonding processes with frictional resistance.

In general it is appreciated that a composite with a poorer interface between reinforcing fibres and the matrix that fibre pull-out and debonding failure mechanisms will dominate during fracture and therefore result in a tougher composite [102], [56]. Whilst a stronger interface results in reduction of the composite toughness, due to brittle failure of the reinforcing fibres, the compressive and flexural strengths will increase [113], [100]. The weaker interface and increased frictional resistance after fibre debonding observed for the recyclate fibres may potentially result in a composite with increased toughness and reduced flexural strength if recyclate fibres are used to directly replace virgin fibres.

# Chapter 6

# 6. Dough Moulding Compound Trials

## 6.1.  Introduction

Whilst the majority of automotive components are moulded from SMC, rather than DMC, the greater simplicity in the manufacturing technique for DMC allows easier experimentation for the inclusion of recyclate materials as a potential replacement for virgin reinforcement, and is therefore investigated first before SMC composites are considered. In this chapter the results of the investigations into incorporating the Fine and Coarse grades of recyclate into new DMC composite formulations, as a replacement for virgin glass fibre reinforcement, are presented and discussed.

Firstly the manufacturing conditions and processes used to manufacture DMC with the recyclate fibres are investigated to establish the best technique for incorporation of recyclate materials, with minimal effect on the resulting composite's mechanical properties, both flexural and impact. In the next section different reformulation techniques are considered, to allow for the difference in glass content of the recyclate materials and to incorporate the maximum possible level of recyclate, with minimal degradation of the composite's mechanical properties. Finally a chemical treatment is used in an attempt to further improve the properties of the most heavily recyclate loaded composite formulation.

## 6.2.  DMC Composite Mixing Time

### 6.2.1. Introduction

In this section the effects of the manufacturing conditions, primarily the mixing time of the reinforcing fibres, on the mechanical properties of the new DMC composites are investigated and discussed.

In the previous mechanical recycling investigations discussed in the literature review the mixing of the recyclate materials during DMC manufacture, and its effect on the composites mechanical properties, had not been considered or investigated. It is therefore assumed that recyclate materials have been added and mixed along with any virgin reinforcing fibre materials, in accordance to the standard production method. In this research it has been shown, however, that the recyclate materials are very different from the virgin glass fibres - in appearance, shape and strength, and it is the purpose of this section to analyse what effect the mixing times of these new reinforcing materials have on the final mechanical properties of the composite.

As discussed in Section 2.6.3 the production of DMC is done entirely in one high-shear mixer. This process involves a high energy input into the material to completely wet out and disperse the reinforcing and the filler materials. This high energy mixing process intrinsically results in fibre degradation and fracture, which in turn affects the mechanical properties of the resulting composite. A study by Burns and Pennington [59] has shown that the mixing conditions for DMCs dramatically affect the level of degradation of the virgin fibres, which results in differences in the composite's tensile, flexural and impact strengths. The study showed that a mixing time of around five minutes for the virgin glass fibres was required for optimal composite mechanical properties. A mixing time greater than five minutes resulted in a dramatic drop off in the composite's mechanical properties, which plateaued after 30 minutes mixing time, due to the complete degradation of the reinforcing fibres. Too short a mixing time, less than two minutes, whilst limiting the fibre degradation, still resulted in poor composite properties due to inadequate dispersion and wetting of the ingredients. The formulation of the composite was also shown to have an effect, whilst higher reinforcing fibre volume fractions theoretically produce stronger composites, in the case of DMC increased concentrations of glass fibres can also result in increased fibre degradation, as the mixture becomes harder to process and greater energy input is required from the mixer.

## 6.2.2. Experimental Manufacturing Method

For this investigation the standard formulation as provided by Menzolit UK was used as the control standard and then modified to include the recyclate materials. During the manufacture of this standard DMC formulation a mixing time of four minutes is used, at the third stage of the raw composite's manufacturing process, for the incorporation of the virgin fibres. Based on knowledge of the mixing process and the results from this investigation's previous chapters, three experimental mixing procedures were therefore proposed for the inclusion of recyclate materials as replacement of virgin glass fibres, as described below and illustrated in Figure 6.1:

1. The SEM images, Figure 5.3, appear to show that the recyclate materials have a larger surface area as compared to the virgin materials and it was therefore proposed that they would require an increased mixing time to ensure that all fibres are properly wetted. The recyclate materials were therefore to be mixed for four minutes prior to the addition of the remaining virgin fibres and as a result receiving a total of eight minutes mixing.

2. Addition of the recyclate materials at the same time as the virgin fibres, for a total mixing time of four minutes. An identical procedure to the standard manufacturing method, Section 2.6.3, and replication of the method used in previous investigations.

3. Given that the recyclate fibres have already been processed once and also subject to the high energy granulation process, it is suggested they are likely to be more susceptible to degradation during another mixing process. The results of the single fibre tensile test in Chapter 5 have already shown that they are weaker than the virgin fibres. Taking these factors into consideration a final mixing procedure was proposed with the recyclate materials to be introduced halfway through the mixing of the virgin fibres, therefore receiving a reduced two minutes mixing.
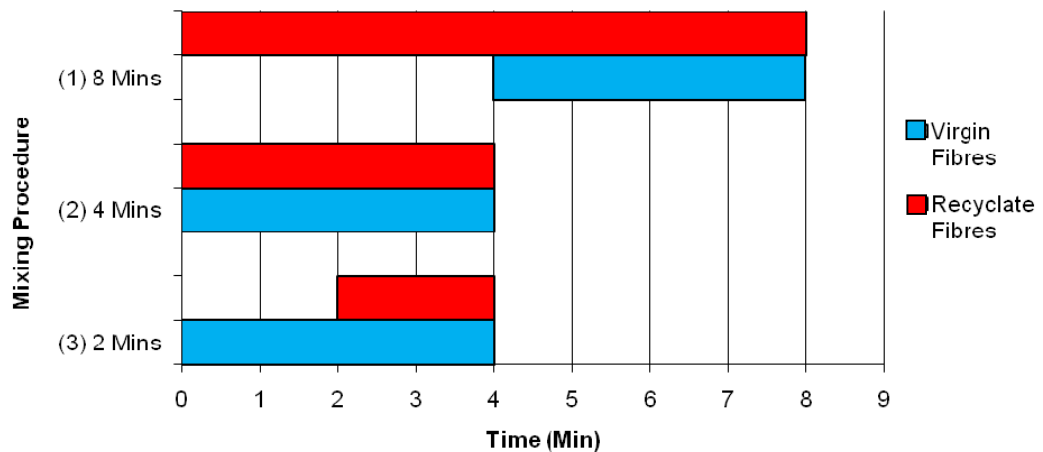
*Figure 6.1, Mixing Procedures for the Reinforcement in DMC Composites Containing the Recyclate Materials: (1) Increased Mixing, (2) Normal Mixing and (3) Reduced Mixing Process.*

For these investigations the Fine and Coarse grades of recyclate were both used to replace 10% of the virgin glass fibres, by weight, for each of the proposed mixing times. A total of six composite reformulations were therefore formulated and two batches of each of these were manufactured, so that a total of 24 different panels were made for mechanical testing and comparison. To act as a control, batches of DMC were also manufacture using the standard formulation without any modification, no recyclate materials, and using the standard mixing procedure.

All DMC batches were manufactured using the high shear mixer shown in Figure 2.7. The raw materials were then moulded according to the procedure described in Section 3.5.2 and then test specimens were prepared for analysis and comparison, by the methods as described in Chapter 3.

## 6.2.3. Results and Discussion: Mixing Time

### 6.2.3.1.    Flexural Testing

All flexural testing specimens failed at the surface under tension. A typical stress-strain plot recorded from the flexural testing is plotted in Figure 6.2, showing the typical curve

characteristics:

1. The initial part of the plot, labelled (a), is a straight line as the sample initially deforms elastically.
2. Elastic deformation continues until the matrix failure strain is reached and a knee-point is observed, labelled (b). Here matrix cracking and permanent damage of composite begin, resulting in a reduction of the composite's modulus.
3. Another straight line region is observed after the knee-point as the reinforcing fibres now bear majority of load, labelled (c).
4. Finally a rapid drop in stress is observed when the fibre breaking strain is reached and failure of the specimen occurs, labelled (d).
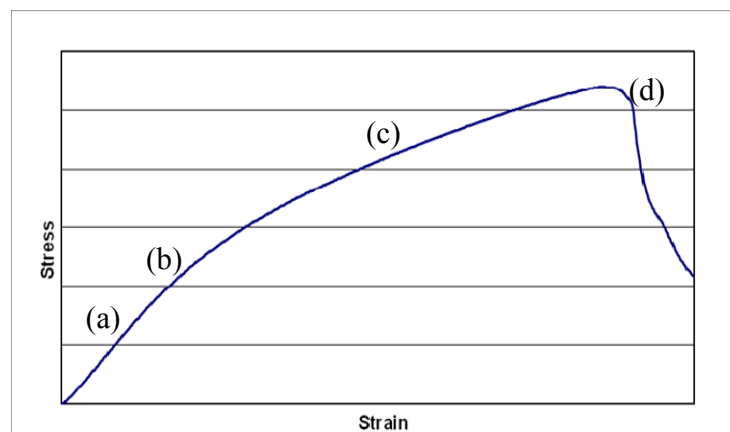


*Figure 6.2, Typical Stress-Strain Curve for a Tested DMC Sample.*

The following graphs show the calculated average results for the measured mechanical properties for each of the different formulations, representing the data from 32 test samples. The error bars represent the standard deviations of the data. Tables of the values used to create these graphs and the load-displacement plots of the tested samples for each formulation can be found in Appendix B.

The graph in Figure 6.3 and the statistical analysis in Table 6.1 show that the standard 4 minutes mixing time produced the composite with poorest flexural strengths. The strengths

of Fine and the Coarse recyclate based composites are significantly lower than the standard formulation, 25% and 20% lower respectively. Both the adjusted 2 and 8 minutes mixing procedures show good comparison with the standard formulation for both grades of recyclate, with the average results for the Fine recyclate composites producing the strongest materials.
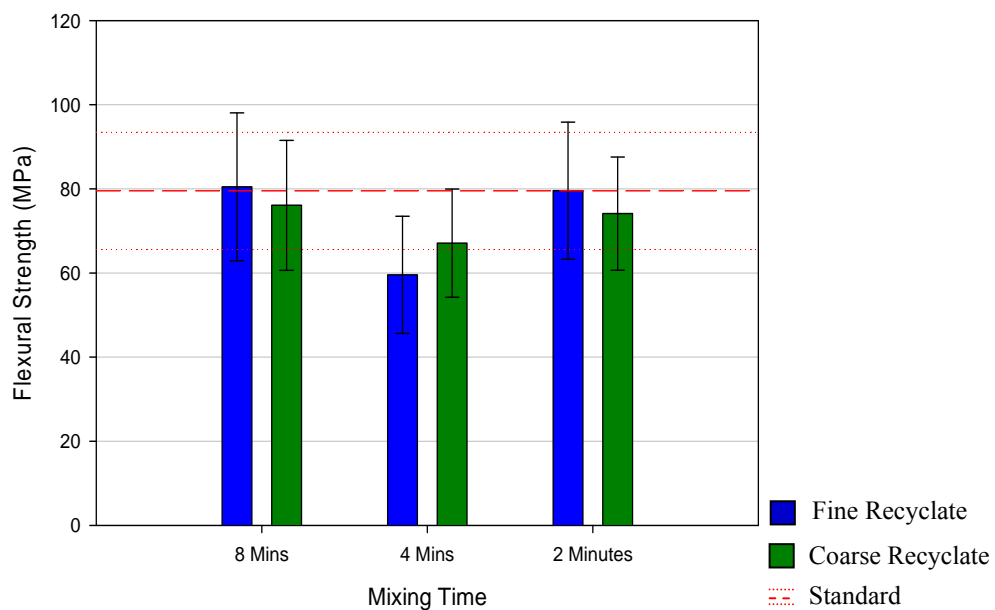


*Figure 6.3, The Effect of Mixing Time on the DMC Flexural Strength.*

The results for the flexural modulus show that both the mixing time and the recyclate grade affect the resulting composite's properties. There is a significant difference between the modulus values for the Fine and the Coarse grades of recyclate at each mixing time. Whilst the Fine recyclate reinforced materials are nearly identical to those of the standard formulation those with the Coarse recyclate reinforcement are all more compliant than the standard, with reductions between 7-14%. The effect of mixing procedure on the flexural modulus is less clear, with the 2 minutes providing the poorest results and 8 minutes producing the stiffer composites.
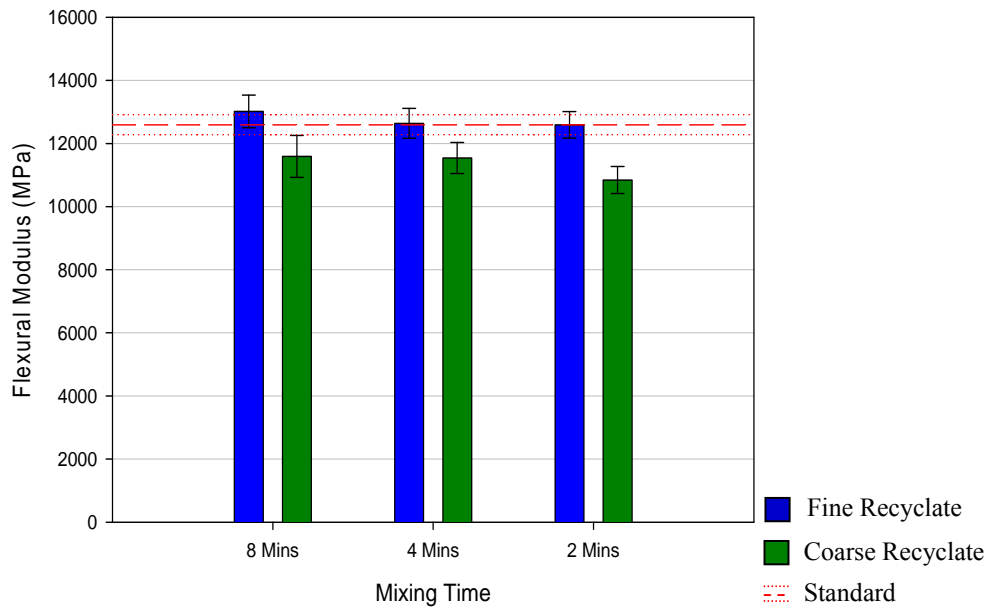
*Figure 6.4, The Effect of Mixing Time on the DMC Flexural Modulus.*

### 6.2.3.2. Impact Testing

The results from the Charpy impact testing of the DMC formulations are very similar to those seen of the flexural strength. Both the 2 and the 8 minutes mixing procedures have produced a stronger composite than the standard 4 minutes mixing procedure. Whilst the strengths of the 2 and the 8 minutes mixing procedures are very similar to those of the standard the formulation, for both the Fine and the Coarse recyclate the composites mixed for 4 minutes are both weaker.
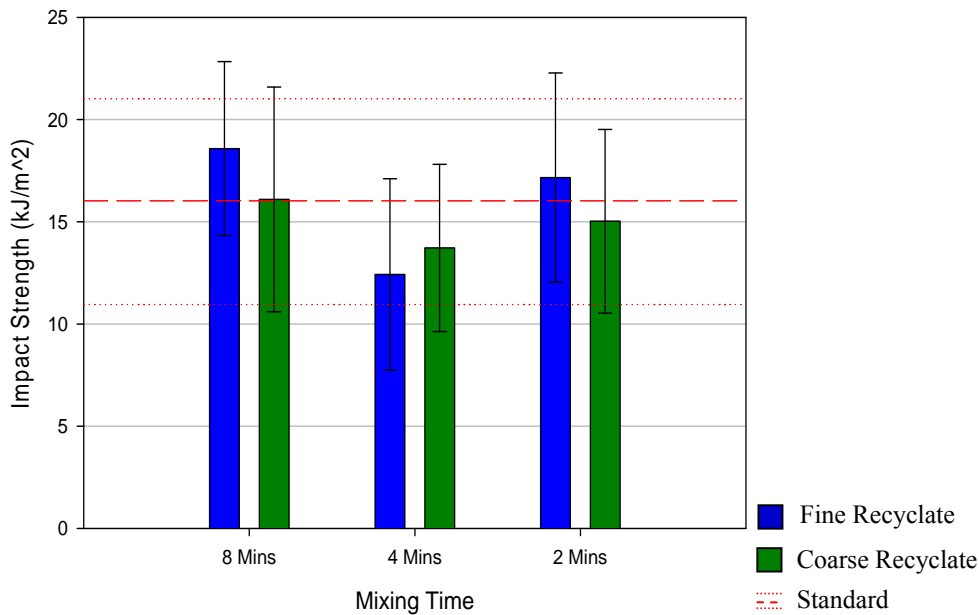
*Figure 6.5. The Effect of Mixing Time on the DMC Impact Strength.*

## 6.2.4. Results: Statistical Analysis of Mechanical Results

As discussed in Chapter 3 and as seen in the results in Figure 6.3 - Figure 6.5 the results from the mechanical testing of composites such as DMC are prone to a large amount of variation. Statistical analysis has been used to further investigate the effects of mixing time on the results of the mechanical testing. The mean values of the composite's mechanical properties at different recyclate mixing times are compared against the standard DMC and against one another, for both the Fine and Coarse recyclates. Table 6.1 show the results of these comparisons for all of the formulations and all mechanical tests. The numbers shown are the 'P-values' which give a measure of the significance of the difference between the means of the two formulations compared. P-values of less than 0.05 mean that there is a significant difference between the two means of the two formulations compared and are highlighted by a '*'.

| | Flexural Strength | | Flexural Modulus | | Impact Strength | |
|---|---|---|---|---|---|---|
| *Formulations Compared* | Fine | Coarse | Fine | Coarse | Fine | Coarse |
| Std - 2 Mins | 0.99 | 0.50 | 1.000 | 0.00* | 0.92 | 0.68 |
| Std - 4 Mins | 0.00* | 0.01* | 0.99 | 0.00* | 0.01* | 0.14 |
| Std - 8 Mins | 0.99 | 0.81 | 0.06 | 0.00* | 0.28 | 0.99 |
| 2 Mins - 4 Mins | 0.00* | 0.16 | 0.99 | 0.00* | 0.00* | 0.71 |
| 2 Mins - 8 Mins | 1.00 | 0.96 | 0.03* | 0.00* | 0.65 | 0.81 |
| 4 Mins - 8 Mins | 0.00* | 0.05* | 0.06 | 0.99 | 0.00* | 0.21 |

*Table 6.1, Statistical Comparison of the Results from Mixing Time Investigation, significant P-Values are highlighted by '*'.*

Table 6.2 compares the general effects of the different experimental factors, i.e. the grade of recyclate and the mixing time, on the results of the different mechanical tests using the data from all tests and formulations.

| | Flexural Strength | Flexural Modulus | Impact Strength |
|---|---|---|---|
| Recyclate Grade | 0.51 | 0.00* | 0.11 |
| Mixing Time | 0.00* | 0.00* | 0.00* |
| Grade - Mixing | 0.05* | 0.03* | 0.05* |

*Table 6.2, Between Group Comparison of Results from Mixing Time Investigations, significant P-Values are highlighted by '*'.*

It can be seen that the mixing time had a significant effect on all of the resulting composites mechanical properties, whilst the use of different recyclate grades only effected the flexural modulus.

## 6.2.5. Results: SEM Images

SEM images were taken of the fracture surfaces of specimens from each of the DMC formulations used to investigate the effect of mixing time, after the Charpy impact tests. All of the tested DMC specimens had fractured into two halves at the midpoint during testing, the specimens for imaging were prepared and investigated by the methods described in Chapter 3. The different fracture surfaces observed are analysed and discussed below.

### 6.2.5.1.    Standard DMC

Figure 6.6 displays two SEM images of the fracture surfaces of the standard DMC formulation, with no recyclate materials, after Charpy impact testing. These are the surface features of a typical impact fractured DMC material. The main mode of failure of the composite appears to be fibre pull-out with many long lengths of glass fibres protruding from the fracture surface and holes in the matrix left by the fibres resulting in a very large fracture surface. The images also show a good dispersion of the glass fibres with individual fibres clearly dispersed in all directions and separated from the original fibre tows.
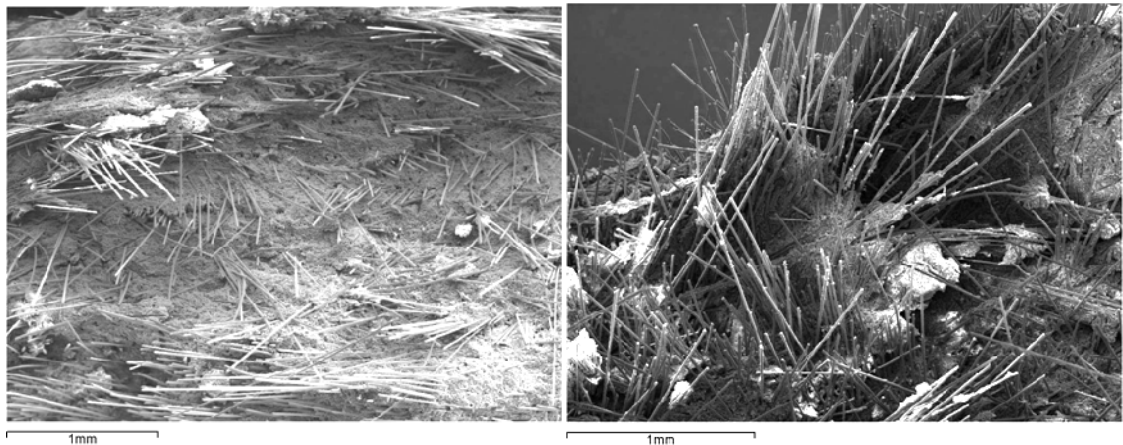


*Figure 6.6. Fracture Surfaces of Standard DMC after Charpy Impact Testing.*

### 6.2.5.2.    Eight Minutes Mixing

Figure 6.7 shows two fracture surfaces from composites with 10% of the reinforcement replaced by recyclate, image (a) shows a composite made with the Fine and image (b) shows a composite made with the Coarse fibre recyclate grade. Both of these fracture

surfaces appear to be very similar to those of the standard DMC seen in Figure 6.6. There appears to be good dispersion of the fibres in all directions and pull-out appears to be the dominant fracture mechanism with a large total fracture surface area.
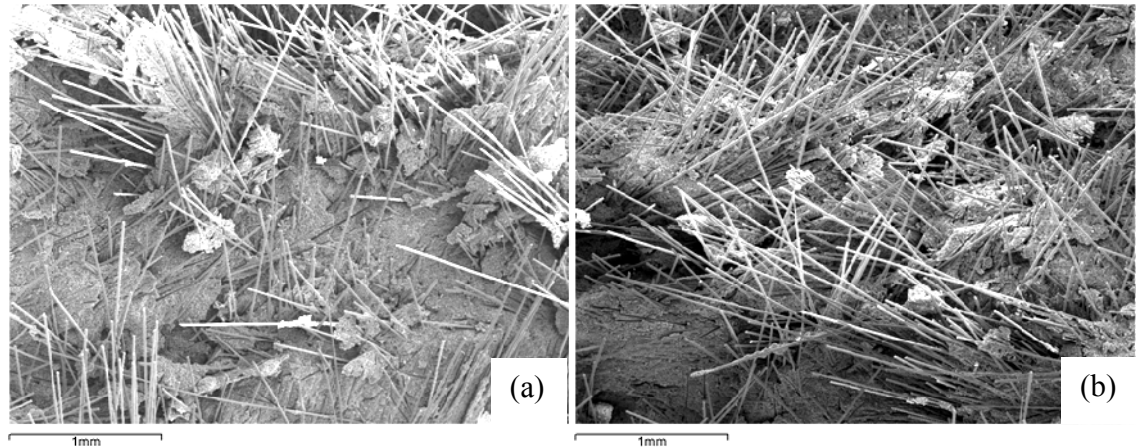


*Figure 6.7, Fracture Surfaces of 10%wt Recyclate DMC, Mixed for 8 Minutes, after Charpy Impact Testing: (a) Fine Recyclate and (b) Coarse Recyclate.*

### 6.2.5.3.    Four Minutes Mixing

The images below in Figure 6.8 are those of the fracture surface for the composites including recyclate materials mixed for 4 minutes. These surfaces appear very different to those seen of the standard DMC samples. The fibres do not appear to have been properly dispersed from their original rovings and as a result do not protrude from the fracture surface in all directions, but remain together in bundles. As well as pull-out there appears to be areas of matrix fracture, parallel to and between the fibre bundles.
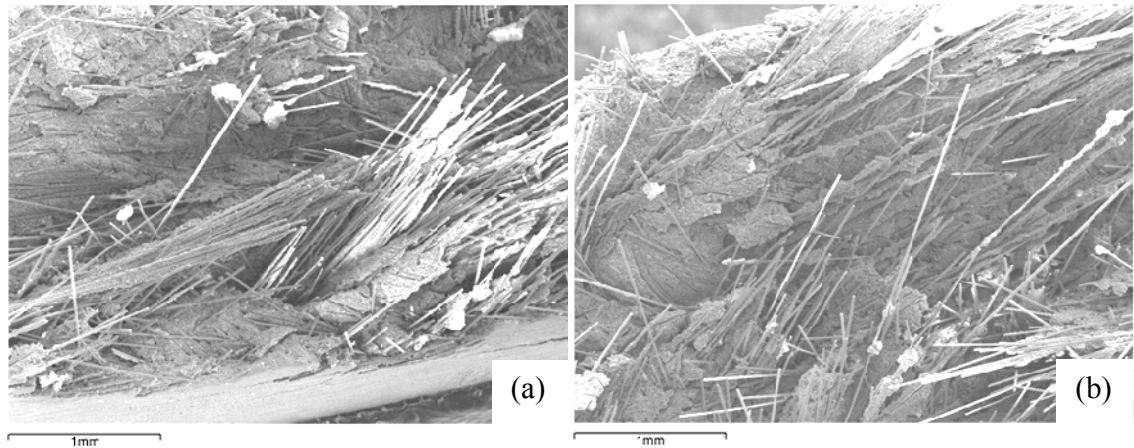
*Figure 6.8, Fracture Surfaces of 10%wt Recyclate DMC, Mixed for 4 Minutes, after Charpy Impact Testing: (a) Fine Recyclate and (b) Coarse Recyclate.*

### 6.2.5.4. Two Minutes Mixing

The SEM images of the fracture surfaces for the DMC formulations including recyclate and mixed for 2 minutes are shown below in Figure 6.9. These surfaces show well dispersed fibres that have been separated from their tows and many fibres protruding from the surface in all directions, as well as some areas of matrix fracture in image 6.9 (b).



*Figure 6.9, Fracture Surfaces of 10%wt Recyclate DMC, Mixed for 2 Minutes, after Charpy Impact Testing: (a) Fine Recyclate and (b) Coarse Recyclate.*

### 6.2.6. Discussion: Mixing Time

The results of this investigation all indicate that the mixing time does have a significant effect on the mechanical properties of new DMC formulations made with the incorporation of recyclate materials as a replacement for virgin reinforcing fibres.
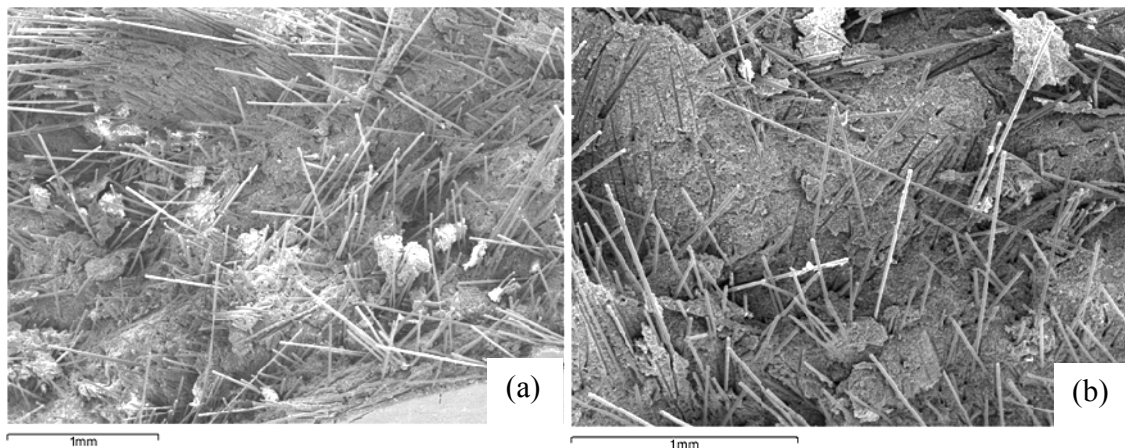
Replicating the standard mixing procedure, by incorporating the virgin and recyclate fibres together for a total mixing time of 4 minutes, has produced the composites with the poorest mechanical properties, overall. Nearly all mechanical results for the manufactured composites containing both grades of recyclate materials have been significantly weaker than those of the standard composite. SEM images of the fracture surfaces, created by impact testing, indicate that this mixing procedure results in poor dispersion of reinforcing materials throughout the composite and that the virgin fibres are not adequately separated from their rovings. These observed differences in the moulded composite will have contributed significantly to the observed mechanical weaknesses.

The investigations in Chapter 4 showed that both of the recyclate grades are only around 40% glass fibre, so the direct weight replacements effectively result in a drop in the content of formulations overall glass fibre reinforcement. Despite these differences the modified mixing procedures, at 2 and 8 minutes, have both produced composites whose mechanical properties have compared well with those of the standard formulation. The graphs and statistical analysis show that there is very little difference between the uses of either mixing procedure, the 8 minute mixing procedure produced the better results across all tested mechanical properties. SEM inspection of the fracture surfaces also show that both procedures share many of the characteristics observed of the standard DMC material. These improved results could mean that there are two factors to be considered when incorporating recyclate materials as replacement of virgin fibres, the fibre wetting and the fibre degradation. It is possible, as hypothesised in Section 6.2.2, that the two minutes mixing time does prevent the further degradation of the recyclate materials, whilst the eight minutes mixing time allows all of the recyclate materials to be properly wetted. Each of these is an important factor in determining the ability of a reinforcing material to provide

effective reinforcement, but only it appears that one can be optimised as determined by the mixing procedure used.

As well as showing that the mixing time procedure does affect the properties of the resulting composites, these results also suggest that it is possible to replace virgin reinforcing fibres with recyclate, at a 10%wt replacement, without the dramatic reductions in mechanical performance, as have been observed in all previous investigations [38], [42], [5] where similar virgin fibre replacements have been made.

Statistical analysis, taking into consideration the large amount of scatter in results, suggests that there is no significant difference between the use of either the Fine or the Coarse recyclate as a replacement for virgin fibre reinforcement for any of the tested formulations, with the exception of the flexural modulus for which the coarse fibre produced poorer results for all mixing times.

## 6.3. DMC Composite Reformulation

Initial results suggest that the recyclate materials can be used to replace virgin reinforcing fibres in DMC formulations, and the necessary changes to the mixing conditions have been established to maximise the resulting composite's mechanical properties.

In this section tests were performed to investigate the reformulation method and the recyclate loadings used. Attempts were made to replace larger quantities of virgin fibres whilst aiming to retaining the mechanical performance of the resulting composite.

### 6.3.1. Introduction

Whilst it was shown in section 6.2 that the recyclate materials could be used to replace 10% of the virgin glass fibres, by weight, without significantly degrading the mechanical properties of the composite, this was a relatively low loading of recyclate materials. The

more recyclate that can be incorporated into the new DMCs the more materials are being recycled and less of the expensive raw ingredients are required. The ideal situation is to use as much recyclate as possible in the new materials without degrading the materials mechanical properties, now that the ideal production method had been established the volume of materials used to replace virgin fibres was increased.

As established by the compositional analysis in Chapter 4 the different recyclate grades contain varying amounts of resin, filler and fibre. It is clear that if virgin fibres are being replaced with recyclate by a simple 1:1 weight replacement the effective glass content of the formulation is therefore reduced. As a result the volume of reinforcement in the composite is reduced and this will likely result in a drop in the mechanical strength of the composite. As discussed in the Chapter 2 the loss in glass content when using recyclate has been mentioned by several authors, though only Bledzki [38] and DeRosa [2] appear to have taken this into consideration. Despite making adjustments to keep the total glass content of their formulations consistent there has still always been a reduction in the mechanical performances of the composites at higher loadings.

## 6.3.2. Method

Both the Fine and the Coarse grades of recyclate were used to replace virgin glass fibre reinforcement in new DMC composites, using the 8 minute mixing procedure described in Section 6.2. The reformulations were performed by two methods:

1.  A 'by weight' replacement of virgin fibres, using the same weight of recyclate to replace the weight of virgin fibres removed.
2.  A formulation 'by glass content', using the required weight of recyclate so that the total weight of glass in the formulation was kept the same.

As the recyclate grades are only approximately 40% glass fibre, to maintain the composite overall glass content an increased weight of recyclate will have to be used. As a result there will be an increased quantity of the recycled filler and resin materials also being added to

the compound. To compensate for this an equivalent weight of the standard filler will be removed. The effects of these reformulations are demonstrated in Table 6.3.

| | Resin (g) $(1.4\ g/cm^3)$ | Filler (g) $(2.5\ g/cm^3)$ | Virgin Fibre (g) $(2.55\ g/cm^3)$ | Recyclate (g) $(\sim1.85\ g/cm^3)$ |
|---|---|---|---|---|
| **Standard DMC** | 335 | 960 | 240 | - |
| **By Weight 10%** | 335 | 960 | 216 | 24 |
| **By Weight 20%** | 335 | 960 | 192 | 48 |
| **By Content 10% (Fine Recyclate)** | 335 | 925 | 216 | 59 — Filler 35 / Glass 24 |
| **By Content 10% (Coarse Recyclate)** | 335 | 919 | 216 | 65 — Filler 41 / Glass 24 |
| **By Content 20% (Fine Recyclate)** | 335 | 891 | 192 | 117 — Filler 69 / Glass 48 |
| **By Content 20% (Coarse Recyclate)** | 335 | 878 | 192 | 130 — Filler 82 / Glass 48 |

*Table 6.3, The Weights of Major Material Constituents in DMC for Different Reformulations.*

The investigations were performed for both reformulation methods at 10% and then 20% replacements of virgin fibres, with both of the recyclate grades. The resulting raw compounds were moulded and specimens cut for mechanical testing as described in Chapter 3, for comparison against one another and a standard DMC composite.

### 6.3.3. Results 10% Replacements

### 6.3.3.1.        Flexural Testing

The flexural strength results for the reformulations by weight and by glass content are shown in Figure 6.10 and Table 6.4. The different reformulation method does not appear to significantly affect the strength of the composite, all results are comparable with the standard DMC formulation, within 5-10%, and only the Fine materials appear to be effected by the increased recyclate in the 'by content' reformulation.
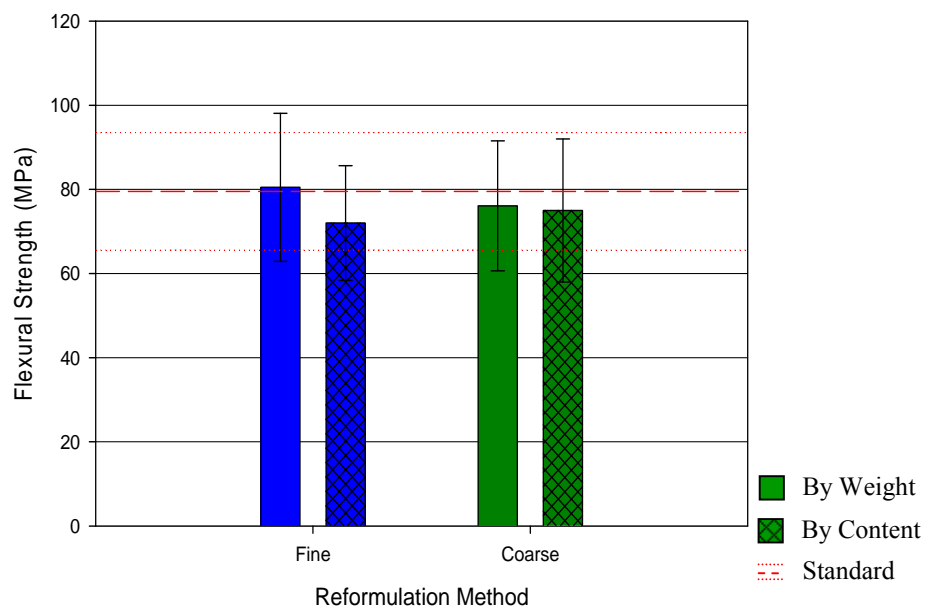


*Figure 6.10, The Effect of Reformulation Method on the DMC Flexural Strength at 10% Replacement.*

The averages of the flexural modulus results follow a similar pattern to those of the flexural strength, with the Coarse grade materials being less affected by the reformulation method. Other than the Fine materials reformulated by weight, all of modulus values were poorer than those of the standard formulation, though only by 6-9%.
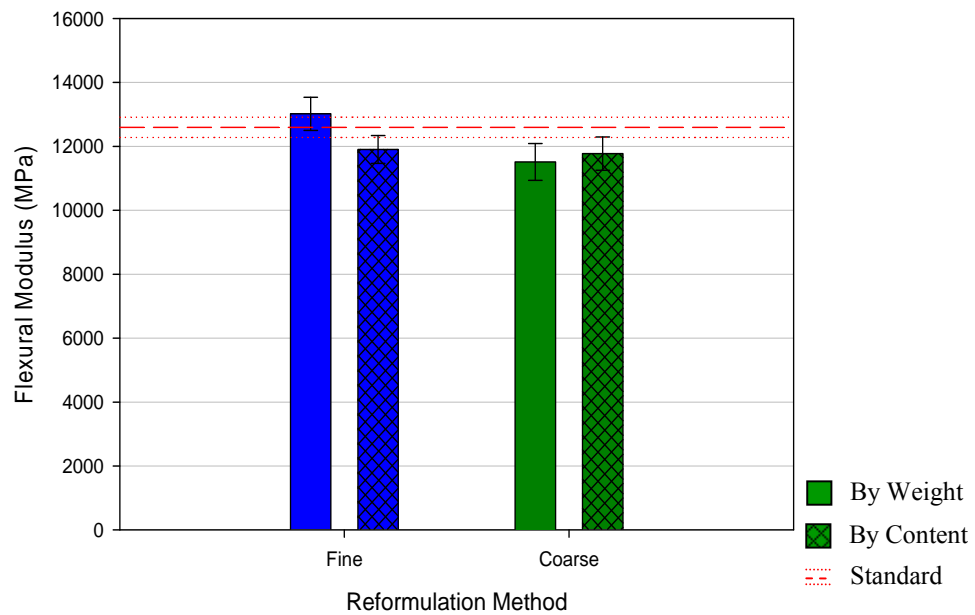
*Figure 6.11, The Effect of Reformulation Method on the DMC Flexural Modulus at 10% Replacement.*

### 6.3.3.2. Impact Strength

Figure 6.12 shows that the impact strengths of the new DMC materials were also not affected by the reformulation method. All the average results are equal, to if not slightly higher, than those recorded for the standard materials though analysis in Table 6.4 shows that none of the differences were significant.
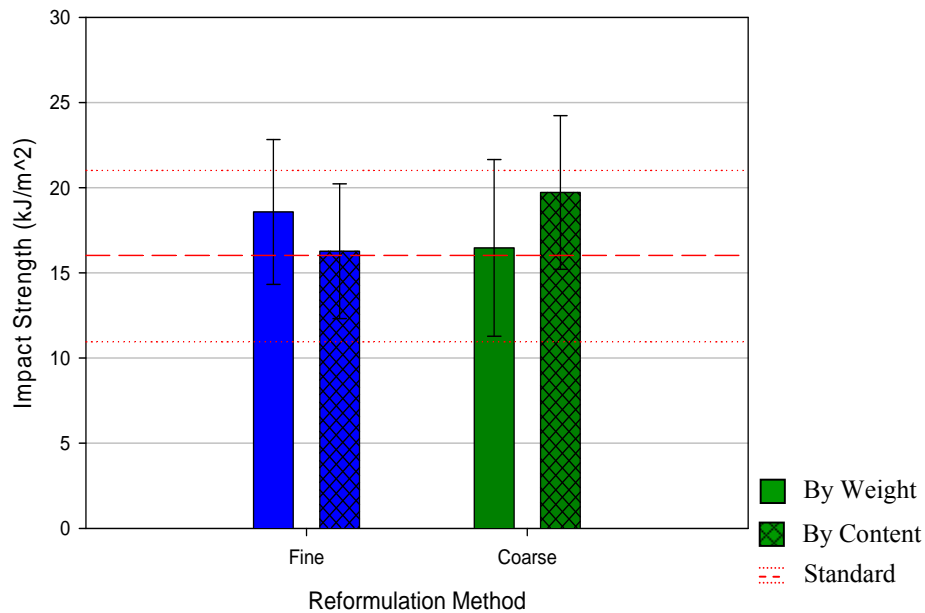
*Figure 6.12, The Effect of Reformulation Method on the DMC Impact Strength at 10%*
*Replacement.*

## 6.3.4. Results 20% Replacements

### 6.3.4.1.        Introduction

The 10% replacements of the virgin fibres used above still represent a relatively small
quantity of the total fibres in the composite so an increased percentage was investigated in
the following section. Using both of the reformulation methods 20% of the virgin fibres
were replaced to see if even higher loadings could be used without negatively affecting the
mechanical performance, and again whether there is a difference between the reformulation
methods used, or not.

### 6.3.4.2.        Flexural Testing

The flexural strength results for the increased recyclate replacement of virgin fibres at, 20%
by weight of virgin fibres, are shown in Figure 6.13. All flexural strength values have
decreased between 10-22% of that of the standard. The 'by weight' results for both grades
are similar to, and both the 'by content' replacements are significantly poorer than, the
results for the standard formulation. Once again there does not appear to be any significant

difference between the use of the Fine or the Coarse recyclate as the graphs show very similar values.
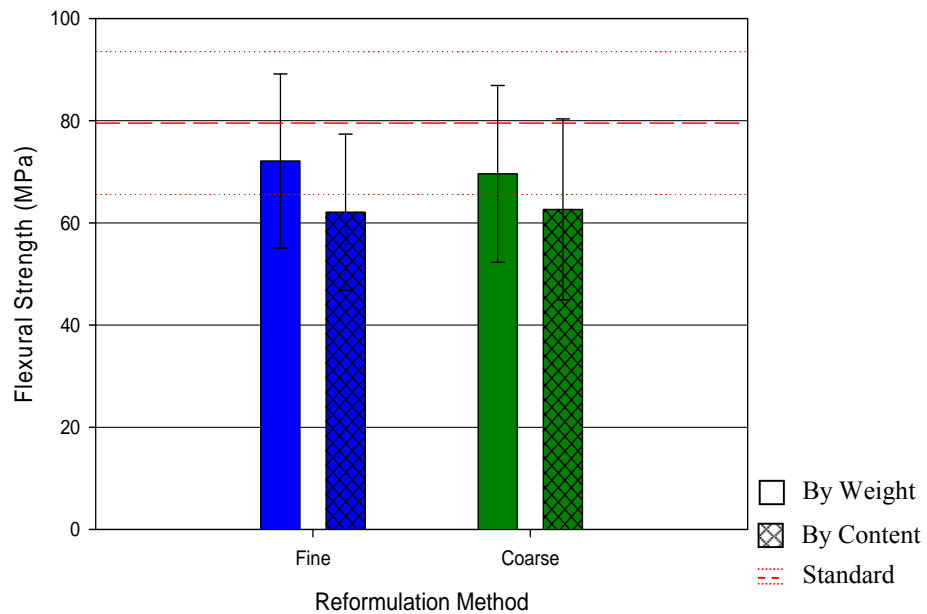


*Figure 6.13, The Effect of Reformulation Method on the DMC Flexural Strength at 20% Replacement.*

As with the 10% replacements the flexural modulus appears to be significantly affected by the inclusion of recyclate for all grades and reformulation methods, Figure 6.14. All results are poorer than the standard by between 8-12% and again there is little difference between the use of Fine and the Coarse recyclate grades.
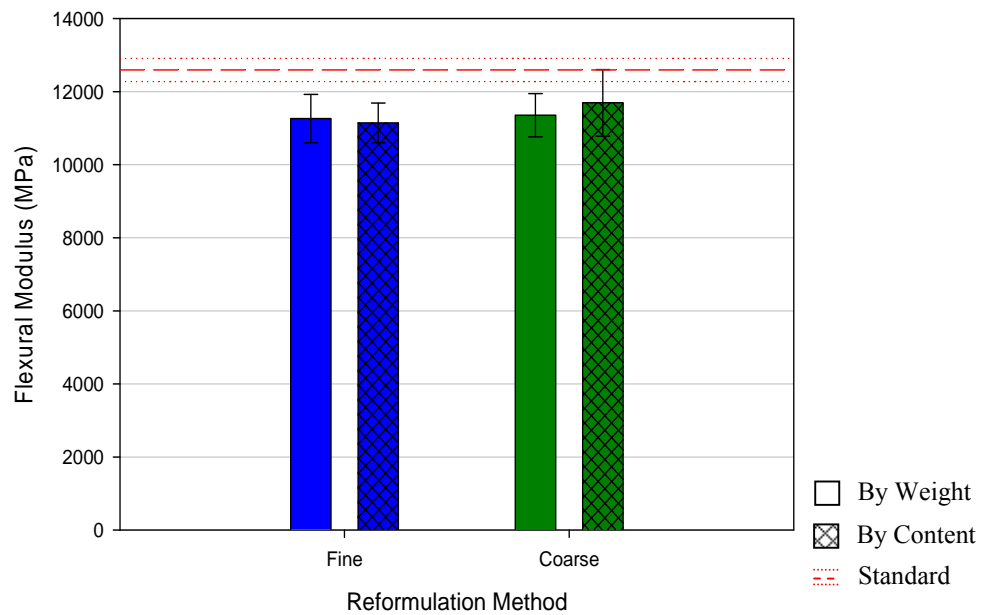
*Figure 6.14, The Effect of Reformulation Method on the DMC Flexural Modulus at 20% Replacement.*

### 6.3.4.3.　　　Impact Testing

The impact strength results appear to follow the pattern seen in the flexural strength results, with the 'by content' reformulations producing the weakest composites. The 'by weight' formulations are again very similar to, however the 'by content' reformulations are between 12-19% poorer than, the standard. The averages suggest that there is little difference between the use of the Fine or the Coarse recyclate, and Table 6.4 shows that, due to the large scatter in the impact testing results, none of the results are statistically significantly different to the standard.
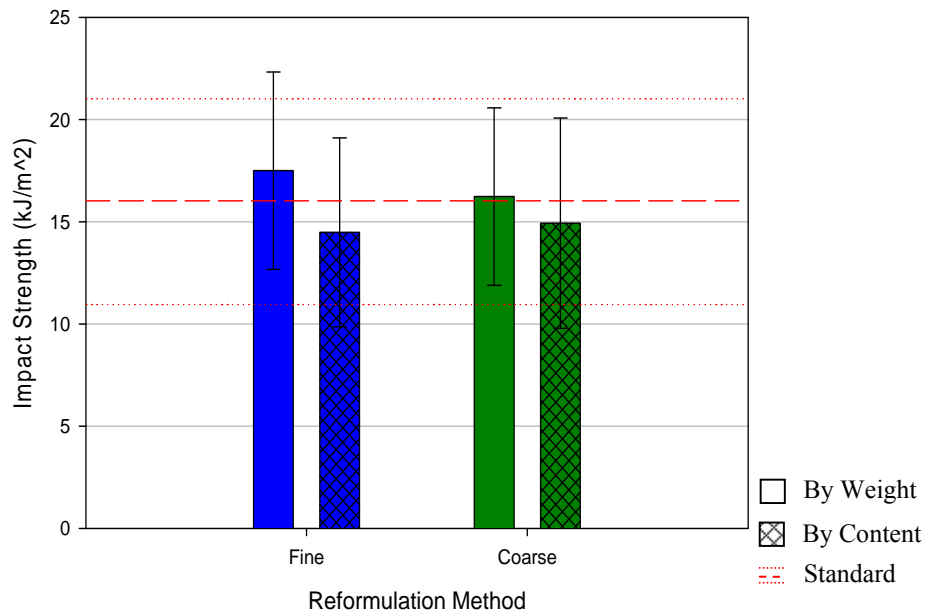
*Figure 6.15, The Effect of Reformulation Method on the DMC Impact Strength at 20%*
*Replacement.*

### 6.3.4.4. Statistical Analysis

Statistical analysis, as described in Section 3.7.4, was used to further investigate the differences between the tested reformulations, in comparison with the standard materials and one another. In Table 6.4 all of the statistical comparisons of the mechanical tests are presented, for both the 10% and the 20% replacements by weight (WT) and by glass content (GC). *P*-values less than 0.05 represent significant differences between the means of the two formulations compared, and are highlighted by a'*'.

|  |  | Flexural Strength | | Flexural Modulus | | Impact Strength | |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Fine | Coarse | Fine | Coarse | Fine | Coarse |
| 10% Replacement | STD - WT | 0.99 | 0.93 | 0.14 | 0.00* | 0.35 | 0.99 |
|  | STD - GC | 0.34 | 0.82 | 0.00* | 0.01* | 0.99 | 0.13 |
|  | WT - GC | 0.00 | 0.99 | 0.00* | 0.53 | 0.27 | 0.13 |
| 20% Replacement | STD - WT | 0.35 | 0.13 | 0.00* | 0.00* | 0.88 | 0.99 |
|  | STD - GC | 0.00* | 0.00* | 0.00* | 0.00* | 0.48 | 0.78 |
|  | WT - GC | 0.04* | 0.46 | 0.96 | 0.51 | 0.07 | 0.83 |

*Table 6.4, Statistical Comparison of the Results from Reformulation Investigation, significant P-Values are highlighted by '*'.*

In Table 6.5 all of the test data is used to compare the general effect of the different experimental factors, i.e. the recyclate grade and the reformulation method, on the results of the different mechanical tests.

|  | Flexural Strength | Flexural Modulus | Impact Strength |
| --- | --- | --- | --- |
| Recyclate Grade | 0.42 | 0.07 | 0.51 |
| Reformulation Method | 0.00* | 0.00* | 0.52 |
| Grade - Mixing | 0.60 | 0.17 | 0.60 |

*Table 6.5, Between Group Comparisons of Results from Reformulation Investigations.*

## 6.3.5. Discussion: Reformulation Method

These experiments have shown that with the use of considered reformulation methods higher loadings of recyclate materials can be incorporated into DMC formulations without compromising their mechanical strengths. There was near 2.5 times the weight of recyclate materials in the 10% 'by content' reformulations, used to maintain the glass content, than in the 10 % 'by weight' reformulation. Despite the increased recyclate loadings the

mechanical properties observed of the composites were not found to be significantly degraded.

However, despite the success of these adjustments at lower recyclate loadings both the flexural and impact strengths showed the general trend of decreasing strengths with increased loadings of recyclate materials, whilst the flexural modulus showed least variation, as shown in Figure 6.19 - Figure 6.21.

The flexural strength results show that for both grades of recyclate replacement of the virgin reinforcing fibres results in a composite with reduced flexural strength. As the quantity of recyclate in the DMC formulations increases the flexural strength also decreases.
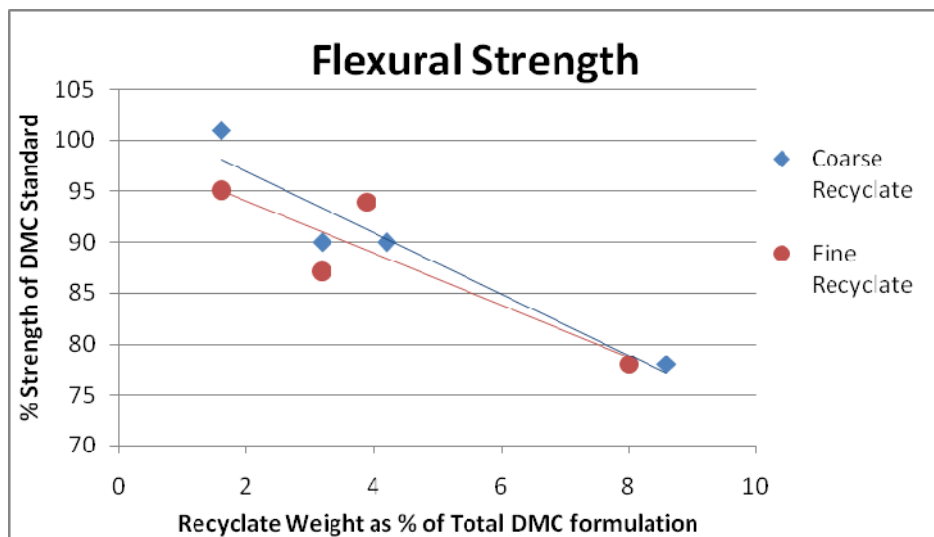


*Figure 6.16, Percentage Change and Trend Lines for DMC Composite's Flexural Strength with Increased Recyclate Content.*

The flexural modulus of all composites containing recyclate materials are lower than the value recorded for the standard DMC formulation, however these reductions do not appear to be further degraded dramatically with increased quantities of recyclate. The results in Section 5.4.4 showed that whilst the flexural strength was degraded the modulus of the recyclate fibres was still comparable with that of the virgin glass fibres. As a result there

161

has been a slight drop in the modulus of the DMC composites but this has not been greatly affected as the percentage of recyclate has been further increased.
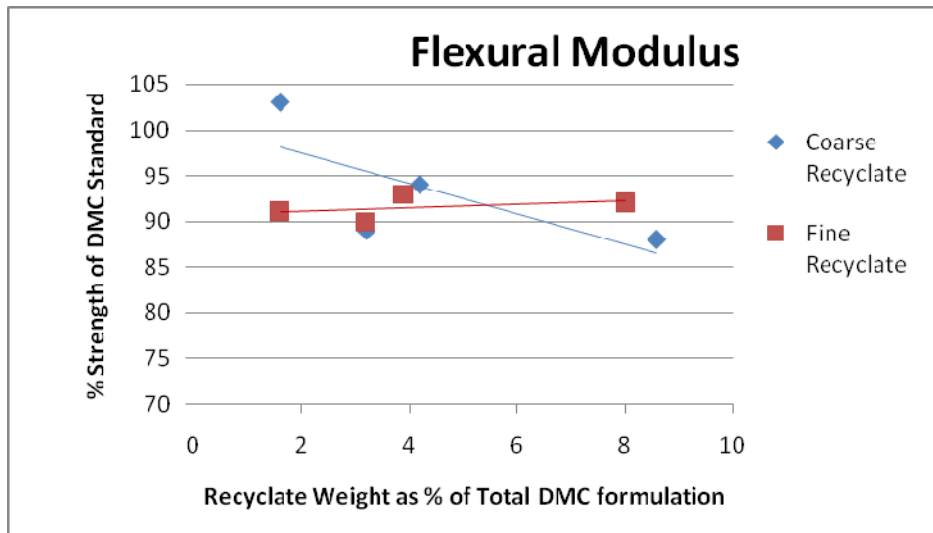


*Figure 6.17, Percentage Change and Trend Lines for DMC Composite's Flexural Modulus with Increased Recyclate Content.*

The impact strength results show a similar degradation of properties with increased recyclate loading as observed for the flexural strength results, however only at the very highest loadings were the results significantly poorer that those of the standard.

*Figure 6.18, Percentage Change and Trend Lines for DMC Composite's Impact Strength with Increased Recyclate Content.*
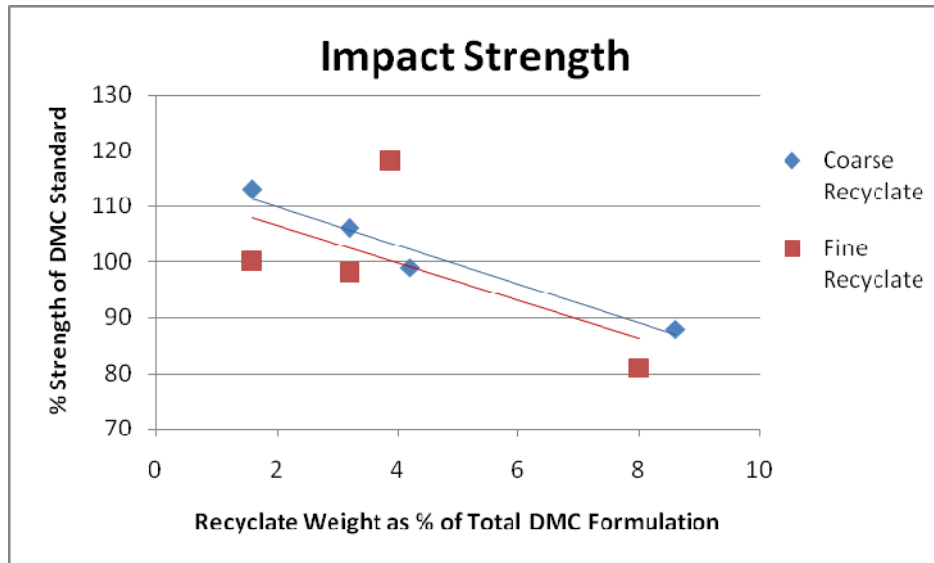
Generally an increase in a composite's mechanical properties would be expected when the percentage of reinforcing materials is increased. However this does not appear to be the case with the use of the reinforcing recyclate grades. Increasing the fibre content does not improve the mechanical properties and therefore other factors must also contribute to the weaknesses observed. There are several possible explanations for these observed effects:

In Chapter 5 it was established that the recyclate fibres are weaker than the virgin fibres, with increased flaw densities. They would therefore not be capable of providing the same level of reinforcement as virgin glass fibres. These weakened fibres may also be susceptible to more fibre degradation during the mixing process. As the quantity of recyclate is increased more potentially abrasive materials, such as the cured resin, are incorporated into the formulation which may contribute to increased amounts of fibre degradation.

Relating these results to the discussion in Section 5.5.7, the weaker interface between the recyclate fibres and the virgin resin in new composites will result in poorer stress transfer between the two, and therefore potentially produce a composite with poorer flexural strength and modulus than that reinforced with virgin glass fibres. The frictional effects and

163

increased pull-out fibre length observed during the pull-out testing may well have contributed to the observed increases in Charpy impact strengths seen in Sections 6.3.3 and 6.3.4.

Increased recyclate loadings to compensate for the glass content of the total formulation also meant an increase in the quantity of filler and resin materials from the recyclate. Whilst the reformulation 'by content' was designed to take these material differences into account, the effect on paste viscosity with increased recyclate materials was not considered. Previous investigations have seen greater increase in paste viscosity with the addition of recyclate materials over traditional fillers [5], [42], [46], due to an increased absorption of the resin by the recyclate materials as compared to calcium carbonate [5]. This increase in paste viscosity may also contribute to increased levels of degradation in the reinforcing fibres during mixing [59], and will have reduced the ability of paste to wet-out all of the reinforcing materials effectively.

## 6.4.  DMC Chemical Treatment

### 6.4.1. Introduction

The previous section showed that at greatly increased loadings the inclusion of recyclate materials causes deterioration in the mechanical properties of the composite. The purpose of this section was to investigate if a chemical treatment could be used to modify the performance of the recyclate reinforced composite. Whilst the addition of any new chemicals would increase the cost of the recyclate, they may also potentially allow the replacement of greater levels of the expensive virgin fibres.

Careful control of the manufacturing conditions of DMC is essential for ensuring that all of the ingredients are properly dispersed and wetted, to achieve maximum mechanical performance. As discussed in Section 6.3.5 a potential cause of the weaknesses observed in the tested composites may be the paste viscosity changes, as observed by previous authors [5], [42], [46], caused by the addition of recyclate during mixing. The increase in the paste

viscosity may result in increased degradation of the reinforcing fibres in the composite, as greater energy input is required to effectively mix the materials, and may also affect their wetting and dispersion during the mixing process. Wetting is extremely important as the contact between the resin and the filler/fibre materials is essential for bonding between them and determining the interfacial properties. Dispersion of all of the ingredients throughout the materials is also essential to produce a homogeneous composite and to ensure that there are no agglomerations, or flocculations, which could act as stress concentrators and reduce mechanical performance.

As discussed in the Chapter 2 chemicals known as wetting and/or dispersive agents are added to the SMC formulations to act as viscosity reducers, to aid the dispersion and wetting of the filler and reinforcing materials in composites. These substances are designed to reduce the interfacial tension between particles in the composite paste and act as a deflocculant, thereby also reducing paste viscosity and allowing higher filler loadings. The exact chemical structure of the additive is designed dependant on the exact resin and filler materials used in the composites.

## 6.4.2. Experimental Method

The replacement of 20% of the virgin fibres when reformulated 'by content' produced the poorest performing composite in all of the previous sections, and included the greatest quantity of recyclate, so was chosen for this investigation. A wetting agent designed specifically for use with the unsaturated polyester resins and calcium carbonate filler used in the SMC formulation was chosen, BYK® W-996 [25]. The wetting agent was added at 8 % of the weight of filler materials and added to the paste mixture along with polyester resin and other wet ingredients, prior to the addition of filler and reinforcing fibres. Again an unmodified standard DMC formulation was manufacture to act as a control, for comparison of the composite's mechanical properties.

### 6.4.3. Results Chemical Treatment

### 6.4.3.1.    Flexural Testing

The results in Figure 6.19 appear to show improvements in the average flexural strengths of both of the composites made with the wetting agent, using the Fine and the Coarse recyclate grades, with 15% and 10% increases respectively. However, Table 6.4 shows that the only significant improvement is that of the Fine recyclate, which is a significant improvement over the untreated material and not significantly weaker than the standard DMC.
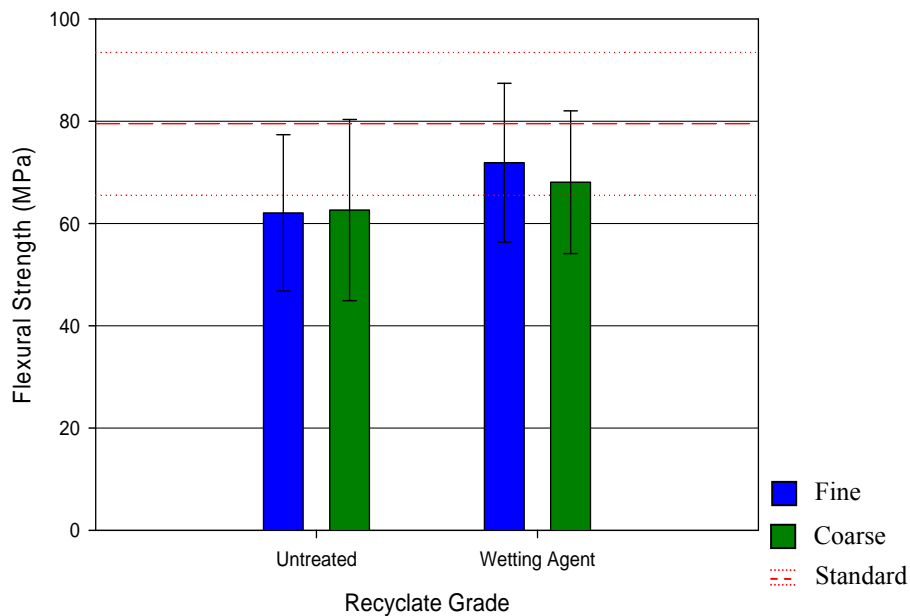


*Figure 6.19, The Effect of Wetting Agent on the DMC Flexural Strength.*

No improvements in any of the composite's flexural modulus are observed over the untreated materials and they are all still significantly poorer than the standard DMC.
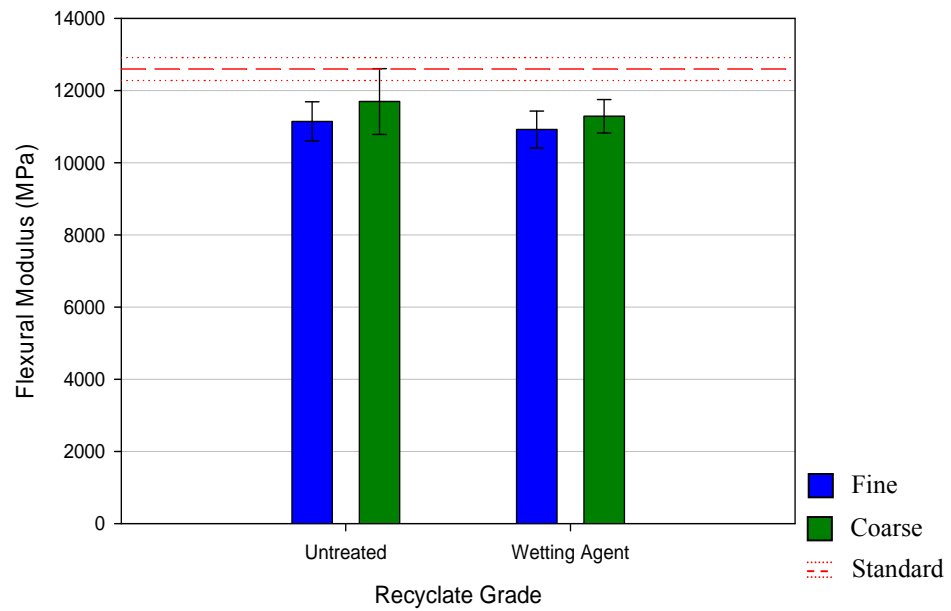
*Figure 6.20, The Effect of Wetting Agent on the DMC Flexural Modulus.*

### 6.4.3.2.    Impact Testing

The impact strength results show similar increases with the use of the wetting agent, as seen in the flexural strength results. However the statistical analysis shows that it is only the improvement for the Fine recyclate materials that is significantly improved over the untreated composites.
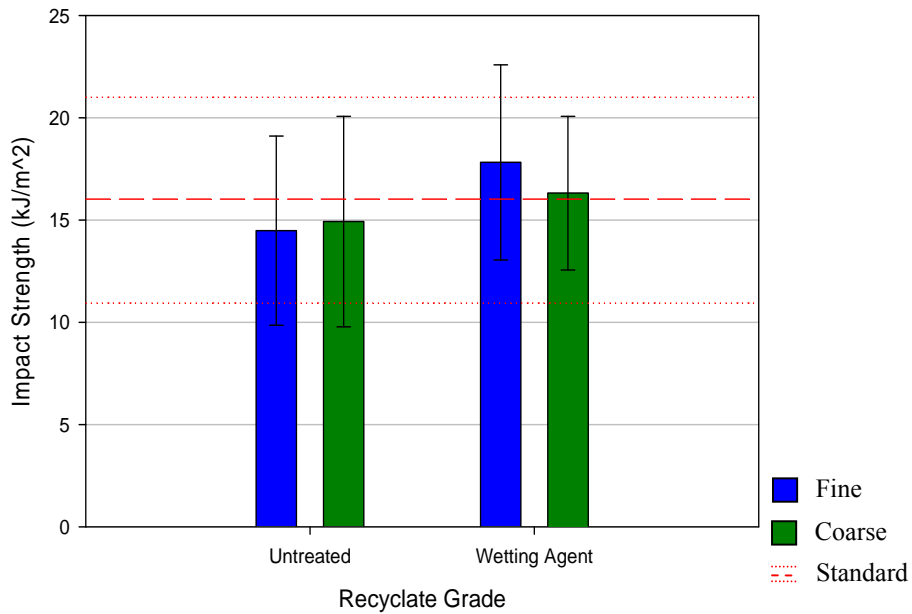
*Figure 6.21, The Effect of Wetting Agent on the DMC Impact Strength.*

## 6.4.4. Statistical Analysis

Table 6.6 shows the statistical comparisons of the mechanical results of the DMC composites from the chemical treatment of recyclate materials investigation.

|  | Flexural Strength | | Flexural Modulus | | Impact Strength | |
|---|---|---|---|---|---|---|
|  | **Fine** | **Coarse** | **Fine** | **Coarse** | **Fine** | **Coarse** |
| **Standard - Untreated** | 0.00* | 0.00* | 0.00* | 0.00* | 0.27 | 0.44 |
| **Standard - Wetting** | 0.12 | 0.01* | 0.00* | 0.00* | 0.48 | 0.99 |
| **Untreated - Wetting** | 0.03* | 0.37 | 0.39 | 0.17 | 0.02* | 0.47 |

*Table 6.6 Statistical Comparisons of the Results from Chemical Treatment Investigation, significant P-Values are highlighted by '*'.*

Table 6.7 compares the effect of the different experimental factors, recyclate grade and addition of wetting agent on the resulting composite's mechanical properties.

|  | Flexural Strength | Flexural Modulus | Impact Strength |
|---|---|---|---|
| **Recyclate Grade** | 0.56 | 0.03* | 0.53 |
| **Treatment** | 0.01* | 0.00* | 0.06 |
| **Grade - Treatment** | 0.44 | 0.54 | 0.25 |

*Table 6.7, Between Group Comparisons of Results from Chemical Treatment Investigations.*

### 6.4.5. Discussion: Chemical Treatment

The use of a wetting agent resulted in an improvement in the flexural and impact strength of the DMC composite materials. The investigation has shown than 20% of the virgin glass fibres may be replaced with the Fine grade of recyclate with a reformulation 'by content' without significantly affecting the composites flexural or impact strengths. Whilst the results for the Coarse recyclate appear to be improved, statistical investigation did not find these results to be significant. This investigation suggests that a change in the DMC pastes viscosity, caused by the addition of large quantities of recyclate materials, may be responsible for some of the deterioration observed in the mechanical properties of the resulting composites and that chemical modification of the DMC formulation may potentially be used to improve them.

## 6.5. Overall Discussion

The investigations in this chapter have highlighted the different manufacturing techniques required for the successful inclusion of recyclate materials as a replacement for virgin glass fibres. It has been shown that the recyclate materials should be treated differently from the existing reinforcing virgin glass fibres and therefore be incorporated into new DMC formulations as a new material and not simply in parallel with them. The mixing procedure should be adjusted to include the addition of the recyclate materials, this investigation found that an increased mixing time of eight minutes resulted in a composite with the best mechanical properties. Using the standard mixing procedure, with a four minute mixing

time, resulted in the poorest mechanical properties and will have been a factor in the degradation of the composite's mechanical properties observed by previous authors discussed in Section 2.7.5.

The exact formulation of the DMC composite can also be adjusted to allow for differences in the resulting composite's glass content, when incorporating the recyclate, so that higher loadings may be used without having a detrimental effect on the mechanical properties and similar levels of virgin fibres replaced.

As the quantity of virgin fibres replaced by recyclate is greatly increased, degradation of both the impact and flexural strengths has been observed. The mechanical properties of DMC composites containing highest loadings of recyclate may be improved by the addition of a wetting agent to formulation indicating that the wetting of the reinforcing materials in a composite including recyclate may be an issue and contribute to the observed degradations.

All of the experiments have shown that there is little difference between the use of either the grades of recyclate, Fine or Coarse, producing similar results for all mechanical properties tested. It may therefore be possible to combine the two grades and use them as one reinforcing grade, as a result fewer classification stages would be required. Reducing the cost of the classification stage would contribute to an increase in the financial viability of such a recycling method.

# Chapter 7

## 7. Sheet Moulding Compound Trials

### 7.1. Introduction

In this chapter the Fine and Coarse grades of recyclate are used to replace reinforcing virgin glass fibres in SMC formulations. The development and implementation of a novel and unique production technique are introduced and then the resulting composite materials are then characterised by mechanical testing and the results presented.

DMC composites have been investigated initially due to their ease of manufacture, however SMC materials represent the market share of the two composites and are typically used to mould much larger components, therefore potentially allowing the consumption of greater quantities of recyclate.

As discussed in Chapter 2 the previous investigations that have incorporated recyclate into new SMC formulations have all used a fine powder grade of recyclate as a replacement for standard fillers in the paste. The coarser more fibrous recyclate cannot be successfully incorporated in to the new SMC formulation in this way because, during the composite manufacturing process the SMC paste on the carrier sheet has to pass through a fine gap at the doctor boxes, Figure 7.1. This gap is used to control the thickness of the layer of paste on the carrier film and is typically only 1.5 mm high, the coarser recyclate materials have been shown to be predominantly have dimensions larger than this, in Chapter 4, and would therefore cause blockages resulting in uneven paste distribution and may even cause catastrophic tears in the carrier film.

*Figure 7.1, SMC Doctor Box Spreading Paste Layer on Carrier Film.*

## 7.2. SMC Recyclate Distribution Unit

### 7.2.1. Introduction

The virgin glass fibres used as reinforcement in SMC are supplied in rovings, which are made up of many continuous fibre filaments brought together to form a strand and then wound into a cylindrical bale. Many of these continuous glass fibre strands are fed from storage units, Figure 7.2, to the SMC manufacturing line along pipes, drawn through by rollers inside the fibre chopping unit. A fibre chopping unit sits directly above the SMC production line and uses a system of rollers and razor blades to continually draw the strands and then cut them to length (typically 25 mm) at controlled rate. After being cut the strands fall randomly under gravity from the chopping unit onto the paste and carrier film below.
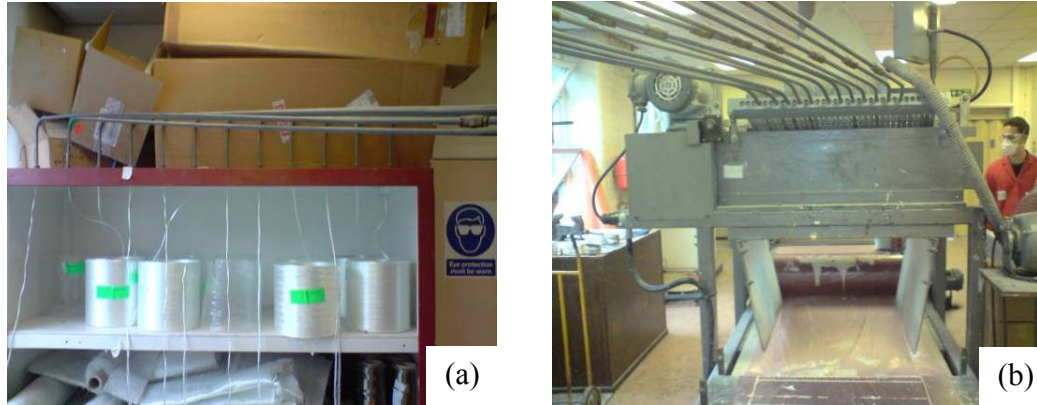
*Figure 7.2, SMC Manufacturing Line Glass Fibre Feed System: (a) Fibre Rovings in Storage and (b) the Strands Fed through Pipes to the Chopping Unit above Production Line.*

## 7.2.2. Machine Design

It is obviously not possible to simply process the recyclate materials in the same way as the virgin fibres because of their discontinuous nature, meaning they cannot be directly incorporated at the same stage of manufacture as the virgin fibres, as was possible with the DMCs. Therefore a system had to be specifically designed so that the recyclate materials could be incorporated into the new SMC compounds as reinforcement, in an accurate and controlled manner.

A machine was designed, built and trialled in-house and after several trials and modifications a final working version was used for the SMC investigations. The novelty of the design has meant that a patent has been successfully applied for. Figure 7.3 shows two perspectives of the final recyclate distribution machine from the design drawings. Each working section of the design is shaded in different colours and described in depth below. More detailed images and descriptions of the design can be found in Appendix C.
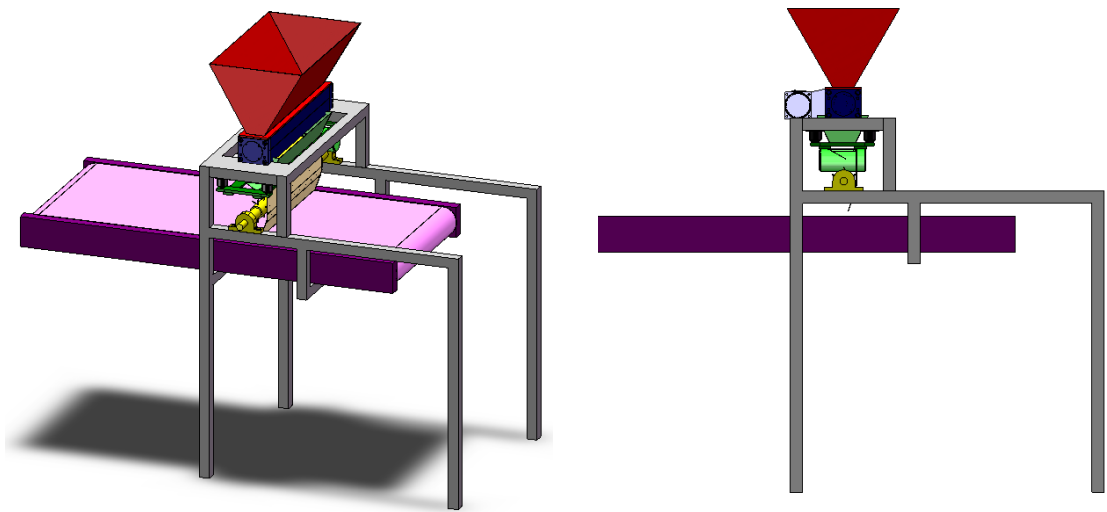
*Figure 7.3, Design Images of the Recyclate Distribution Machine.*

**Stage 1 (Red): Storage Hopper**

At the top of the machine is a large, steep-sided hopper into which the recyclate materials are stored prior to the machine's operation.

**Stage 2 (Blue): Controlled Recyclate Feed**

The hopper guides the recyclate materials towards the recyclate feed unit, which is used to control the rate at which the recyclate is fed in to the rest of the machine. It consists of four chambers, on a central axis, each divided plastic fins. The recyclate falls under gravity into one of the chambers as they pass below the base of the hopper and is moved, in the chamber, to the bottom of the unit where it falls under gravity in to the next stages.

**Stage 3 (Green): Vibrating Sieve Section.**

The recyclate materials fall from the feed unit on to a vibrating sieve mesh. The purpose of this section is not to screen the materials but to steady their flow onto the final stages. Because the feed unit is made of four separate chambers there is not a truly steady, continuous supply of recyclate (there is a slight pause between chambers) and the sieve section steadies the rate of material supply.

**Stage 4 (Yellow): Flail Unit**

To give an even coating of the recyclate materials on the conveyor and to break any bundles of fibres that may have developed during handling or the above processing stages there is a final 'flail' section. The recyclate materials are forced to collide with a cylindrical shaft with many steel pins protruding from its centre, which is rotating at high speed, by a backing plate as they fall between the sieve section and the conveyor.

**Stage 5 (Purple) Belt Conveyor**

A variable speed conveyor moves the recyclate from the recyclate distribution unit to the SMC line, allowing the recyclate to be fed over the doctor box and onto the paste at the same stage as the standard filler at the desired rate.

## 7.3. Apparatus

For the SMC manufacture in this research the SMC pilot plant at the research facilities of Menzolit UK was used. The pilot plant is an exact replica of the larger scale SMC line used in their factory, but the pilot plant allows shorter runs of SMC to be manufactured for testing, without having to disrupt factory production.



*Figure 7.4, The SMC Pilot Production Line at Menzolit UK.*

The recyclate distribution line was designed and built specifically for this pilot plant but could easily be adapted for the main production line in the factory. The entire unit was

fixed to a frame and mounted on wheels, so that it could be used without having to make any modifications to the SMC pilot line, being moved into place once the doctor boxes have been filled with paste.



*Figure 7.5, The SMC Distribution Machine In Place Over the SMC Pilot Plant.*

## 7.4. SMC Manufacturing Method

The total percentage of the glass fibre reinforcement in any SMC composite formulation is controlled during the manufacturing process by the complex interactions of:

1. The total amount of SMC to be made in the production run.
2. The speed at which the carrier film is pulled through the production line, which allows more or less reinforcement to build-up on top of the paste layer.
3. The thickness and density of the paste layers on each of the carrier films, determined by the height of the doctor box blades.
4. The rate at which the reinforcing fibres are cut from their continuous tows, controlled by the chopping unit's speed.

To accurately incorporate the recyclate as reinforcement the rate at which the distribution unit feeds the recyclate materials becomes another factor in this production control. Variable rate controls were fitted to the recyclate feed and conveyor motors on the

distribution unit so that the flow and feed of recyclate materials could be precisely controlled. A spreadsheet was created so that the relationship between all of the manufacturing factors could be correlated. By choosing the desired percentage of the virgin glass fibres to be replaced by recyclate, for this investigation 20%, the other production factors could then be optimised. Using the 'Goal Seek' feature in EXCEL, the composite's overall reinforcement level was retained at 30% of the composite, by weight, with 20% of that made up of the recyclate, by weight.

| Doctor Box Height (mm) | Paste (Kg\min) | Glass (Kg\min) | Recyclate (Kg\min) | Total SMC (Kg\min) | Reinforcement (Wt %) | Recyclate (Wt %) | % Glass Replaced |
|---|---|---|---|---|---|---|---|
| 1.30 | 4.62 | 1.80 | 0.45 | 6.87 | 32.75 | 6.55 | 20.00 |
| 1.35 | 4.80 | 1.80 | 0.45 | 7.05 | 31.92 | 6.38 | 20.00 |
| 1.40 | 4.98 | 1.80 | 0.45 | 7.23 | 31.13 | 6.23 | 20.00 |
| 1.45 | 5.15 | 1.80 | 0.45 | 7.40 | 30.39 | 6.08 | 20.00 |
| 1.50 | 5.33 | 1.80 | 0.45 | 7.58 | 29.67 | 5.93 | 20.00 |
| 1.55 | 5.51 | 1.80 | 0.45 | 7.76 | 28.99 | 5.80 | 20.00 |
| 1.60 | 5.69 | 1.80 | 0.45 | 7.94 | 28.35 | 5.67 | 20.00 |

*Table 7.1, Calculation of the Production Settings for a 20% of Virgin Glass Fibres in a SMC Material.*

Two 7.5 Kg production runs were manufactured with each of the recyclate grades for moulding and mechanical testing. A further 15 Kg batch was made with the Fine recyclate for moulding trials and surface finish analysis. To act as a control, a batch of SMC was also manufactured using the standard formulation without the inclusion of recyclate materials.

The raw materials were stored in a maturation chamber after manufacture, for 24 hours, to allow the paste thickening process to complete before handling and moulding.
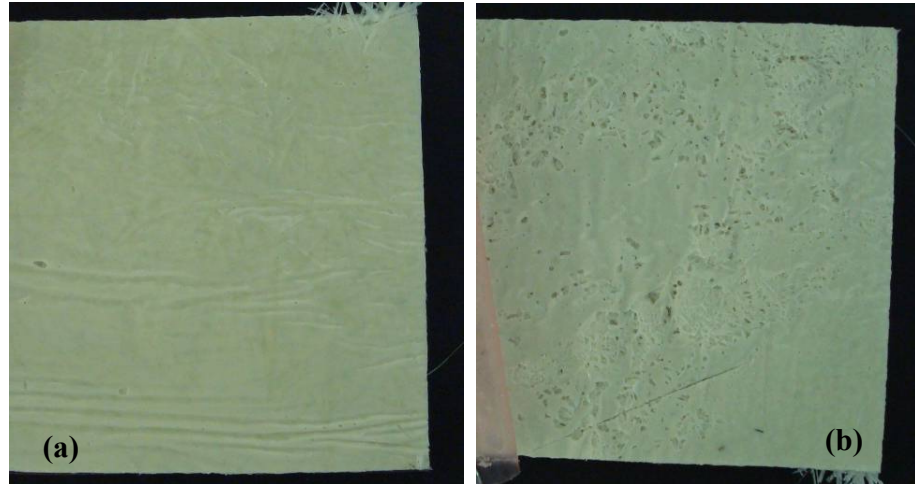
## 7.5. SMC Raw Material

As a direct consequence of the way in which the recyclate distribution unit introduces the recyclate materials into the SMC production process, the raw SMC sheets are produced with a sandwich structure like appearance, as illustrated in Figure 7.6. The recyclate materials fall onto the bottom paste layer, before the virgin fibres fall on top of them and then the top paste layer is introduced. The two types of reinforcing fibre are not blended together and although the compression rollers and maturation process ensures all fibres are wetted by the resin paste, the recyclate and virgin fibres remain on as two distinct layers.
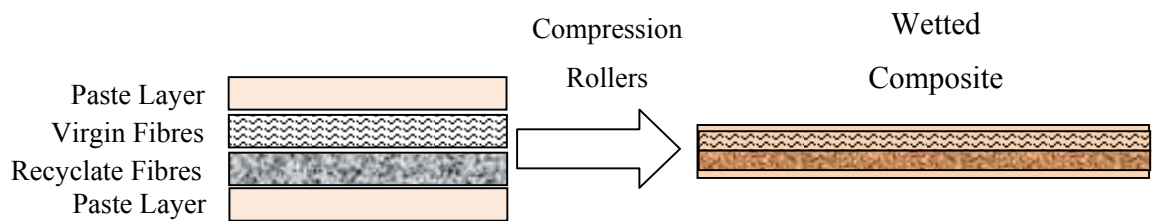


*Figure 7.6, Reinforcing Fibre Layer Effect in New SMC Raw Materials.*

As shown in Figure 7.7 this layering of reinforcement materials affects the appearance of the raw SMC material. On the side of the raw material where the recyclate materials are present the sheet appears to be covered in lots of small holes where the resin has flown through and around the rough recyclate particles. Several bumps or mounds on the surface of the raw sheets containing recyclate, as compared to the perfectly smooth standard raw materials are also observed.

*Figure 7.7, Raw SMC Sheet (a) Standard Material and (b) Containing Recyclate Materials.*

## 7.5.1. Moulding Charge Trials

As the raw SMC sheet is only a few millimetres thick several layers of the raw material have to be built up to form the mould charge, so that the there is enough materials to fill the entire moulding. A critical property of standard automotive SMC mouldings is their high quality surface finish, raw SMC materials are homogenous and the mouldings show a consistent glossy finish through. However, the raw recyclate reinforced materials had been observed to have different surface appearances on either side, and it is likely that the way in which the charge is built up before moulding will affect the appearance of the final cured panel [116]. Trials were performed by moulding several panels with the recyclate based SMC, either building the charge with the recyclate side of the SMC sheets on the outside of the charge recyclate or keeping the recyclate sides of the sheets to the centre of the charge, as depicted in Figure 7.8, using the same charge weight and shape throughout.
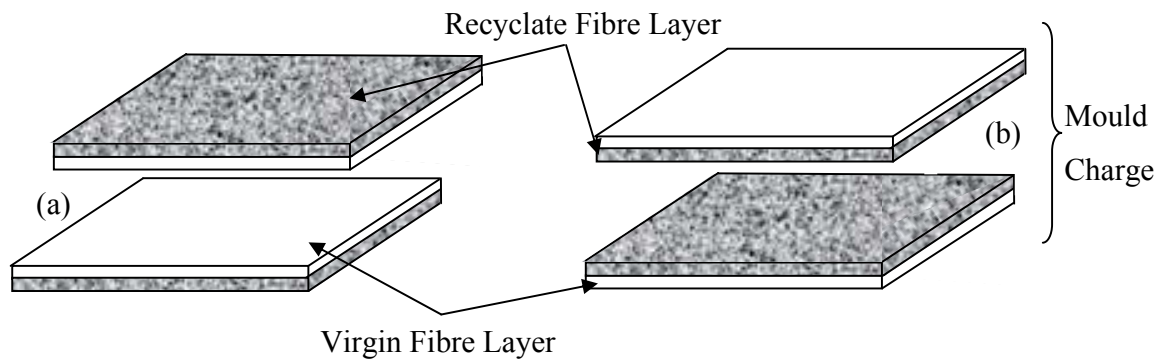
*Figure 7.8, Layering of Mould Charge to Position Recyclate Fibre Layer on (a) Outside or (b) Inside of Panel.*

Visual inspection of the moulded panels was used to compare the surface finish of the recyclate reinforced panels with that of a standard formulation panel. Having the recyclate near the outside of the charge resulted in a panel with a very mottled and matt surface finish, whereas with the recyclate near the centre of the charge a moulded panel with a near perfect, shiny Class A finish was produced as desired. Previous investigation into the layering of multiple SMC plies with different reinforcing materials by Caberera-Rios and Castro [116] showed that the mechanical properties, tensile strength and modulus, were unaffected by the different possible mould charge designs. As a result all panels produced for mechanical testing were moulded from charges with the recyclate materials towards their centre to optimise the surface appearance.

## 7.6.  Results: Mechanical Characterisation

Below the results from the mechanical testing of the SMC formulations containing the Fine and the Coarse recyclate materials, at a 20%wt replacement of virgin glass fibres, are presented. The data used to produce these graphs and load-displacement plots of the tested specimens for each reformulation and the standard materials are presented in Appendix B.

### 7.6.1. Flexural Testing

Figure 7.9 and Table 7.2 show that the use of both of the recyclate grades results in a drop in the flexural strength of the resulting composite, in comparison with the standard materials. There is not a significant difference between the use of either of the recyclate grades, the Fines showed a 15% drop and the Coarse a 20% drop.
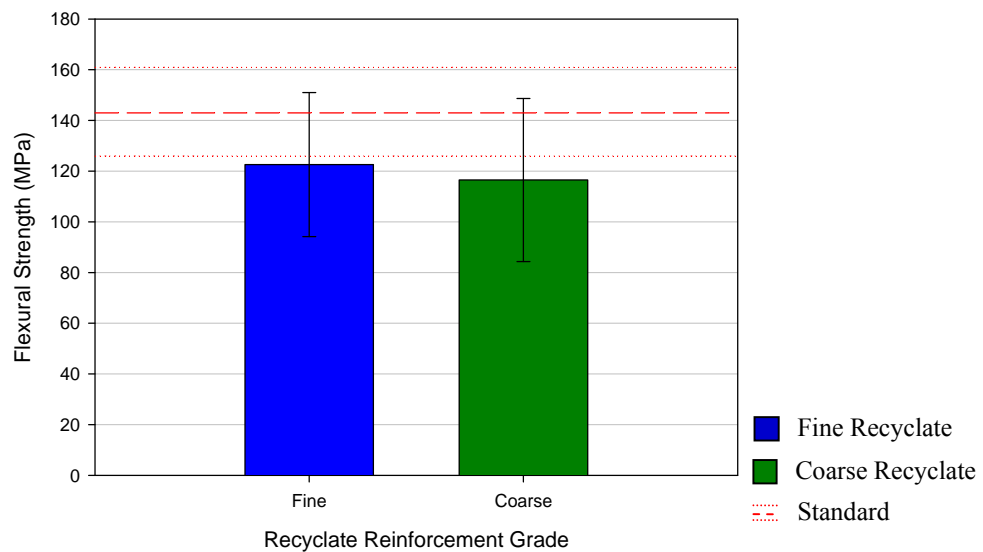


*Figure 7.9, The Effect of Recyclate Reinforcement on the SMC Flexural Strength.*

### 7.6.2. Flexural Modulus

The measured flexural modulus of the materials are almost identical for the SMC with either grade of recyclate, and whilst they appear to both be approximately 4% higher than the average values for the standard SMC, the statistical analysis show that the differences are not significant.
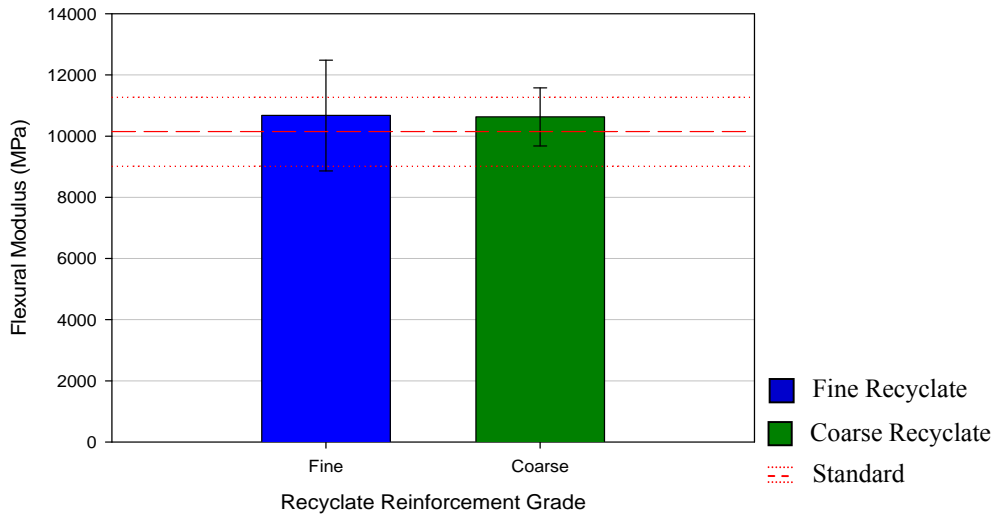
*Figure 7.10, The Effect of Recyclate Reinforcement on the SMC Flexural Modulus.*

### 7.6.3. Impact Strength

Similar to the flexural strength, the impact strengths of the composites contacting both the Fine and the Coarse grade of recyclate are poorer than those of the standard materials, with drops of 17% and 25% drops in comparison with the standard respectively.
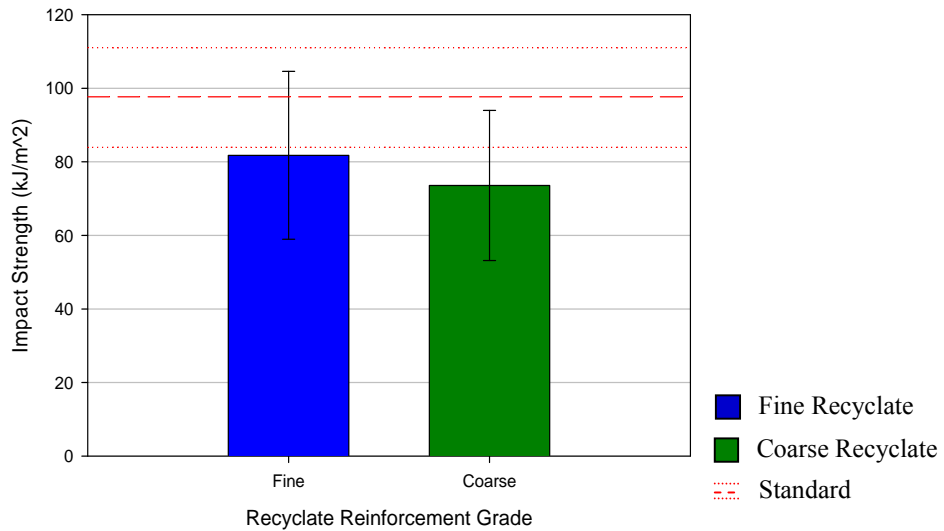


*Figure 7.11, The Effect of Recyclate Reinforcement on the SMC Impact Strength.*

## 7.6.4. Statistical Analysis

Statistical analysis was again used to compare the effect of the different formulations on the composite's mechanical properties; the results are shown in Table 7.2. It can be seen that both of the recyclate grades produced composites with significantly different impact and flexural strengths but comparable flexural moduli, as compared to the standard material.

|  | Flexural Strength | Flexural Modulus | Impact Strength |
|---|---|---|---|
| **Standard - Fine** | 0.02* | 0.46 | 0.01* |
| **Standard - Coarse** | 0.00* | 0.51 | 0.00* |
| **Fine - Coarse** | 0.67 | 0.99 | 0.25 |

*Table 7.2, Statistical Comparison of the Results from SMC Investigations, Significant P-Values are highlighted by '*'.*

## 7.6.5. Discussion

It has been shown that it is possible to use recyclate materials from mechanically recycled waste SMC as reinforcement in new SMC composites, as a replacement for virgin glass fibres. A novel system has been successfully designed and built that allows the controlled inclusion of recyclate during the manufacturing process for us as a reinforcement rather than a filler, without disrupting the existing manufacturing line.

For all mechanical tests performed there was no statistical difference between the use of either the Fine or the Coarse recyclate. Both the flexural and the impact strengths of the resulting SMCs were reduced. The fine recyclate SMC saw a 15% drop in both the flexural and impact strengths and the coarse recyclate SMC 20% and 25% drops respectively. However the flexural modulus remained comparable with that of the standard SMC formulation for both. The reformulations were done 'by weight' so there will have been a reduction in the total glass content of the SMC, as discussed of the DMC in Section 6.3, effectively resulting in 12% less total reinforcement in the composite. This difference will have contributed to the reduction in strengths observed.

Inspection of the produced raw SMC sheet showed that there were wetting-out and fibre distribution issues caused by the way recyclate materials are introduced into the manufacturing process. This layering effect of the recyclate slightly affects the quality of the surface finish if the mould charge is not built properly and is likely to also have affected the composite's strengths.

## 7.7. Automotive Component Moulding Trials

### 7.7.1. Introduction

SMC is used to produce exterior automotive component components because of its ability to produce a Class-A surface finish (equivalent to polished steel), meaning one of the composite's most critical properties is the appearance and quality of the visible moulded surfaces. Previous investigations have shown that the type of reinforcement used in SMCs affects the resulting part surface finish [15]. Even different types of virgin glass fibres can cause surface issues and a loss of the Class-A finish. Whilst the panels produced for mechanical testing had flowed throughout the mould well and appeared to have a good surface finish, the performance of the recyclate components formed in a real mould tool were also investigated.

### 7.7.2. Method

A 15 Kg batch of SMC with 20% of the virgin reinforcement replaced by the Fine recyclate, by weight, was manufactured on the Menzolit pilot plant and taken to an industrial composite moulding company Mitras Automotive. Mitras Automotive mould, assemble and paint a range of composite components for the automotive and other markets from both SMC and DMC. A commonly used automotive rear spoiler moulding was chosen for the investigation, as several components could be moulded from the 15 Kg of

SMC and it combined large flat sections for inspection of the surface finish with other sections with complex moulding and flow geometries.

## 7.7.3. Results

All parts were moulded successfully, Figure 7.12, there were no moulding problems and the materials flowed throughout the moulding and the complex geometries effectively. In the factory the validation of a moulded part's surface finish is performed by visual inspection. Whilst testing equipment does exist for the quantification of the surface profile it is expensive and time consuming. Visual inspection of the recyclate reinforced SMC moulded parts found several visually obvious bumps on the part's surface, distributed randomly across the moulding. The defects occurred randomly across the external surface of the moulding and were approximately 10-20 mm in diameter. A standard SMC component must be completely free of surface defects with a smooth Class-A finish across all surfaces.



(a)                                    (b
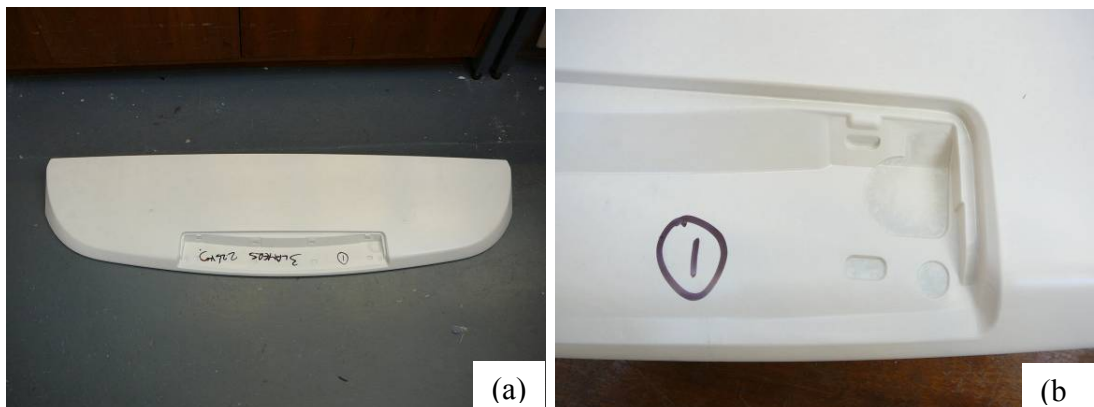
*Figure 7.12, Automotive Rear Spoiler Sections Moulded from Fine Recyclate Reinforced SMC.*

## 7.7.4. Surface Defects

The observed bumps were most likely caused by the addition of the recyclate materials rather than the virgin fibres or any mould flow conditions. Further investigation was performed to establish their exact causes. A section was cut from the part with visually

obvious bumps, by bandsaw, so that one complete bump was preserved by and another bisected by the cut. The sample was then place in an oven at 650 $^{\circ}$C for one hour to burn off the resin and leave reinforcing fibres and filler materials, as shown in Figure 7.13
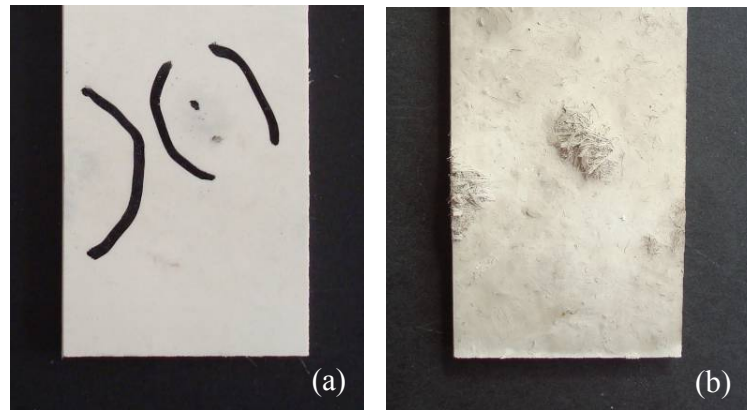


*Figure 7.13, Surface Defects on SMC Moulding Viewed from Above (a) Before and (b) After Resin Burn Off.*
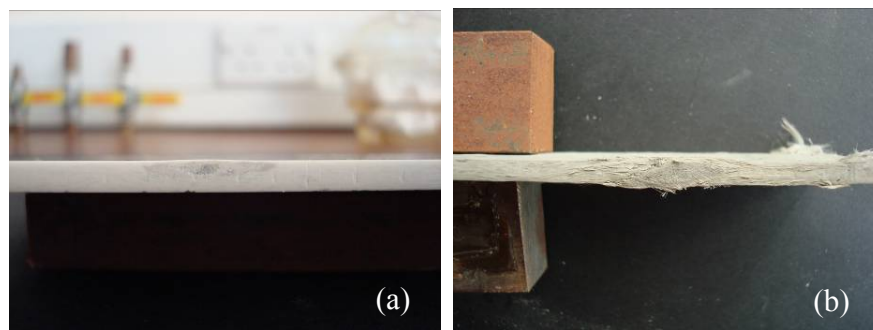


*Figure 7.14, Surface Defects on SMC Moulding Viewed from the Side (a) Before and (b) After Resin Burn Off.*

The images above clearly show that the bumps that appear on the surface of the SMC mouldings are caused by balls or clumps of fibrous materials within the composite. Such defects are not seen in standard SMC materials and the fibres in the image are not in the tight bundle form of virgin fibres, so it is highly likely that they are caused by the recyclate materials. Whilst there is the 'Flail' section in the SMC distribution line, designed to break these bundles, clearly some still get into the SMC materials and slight redesign of the machine would be required to resolve these material issues.

## 7.7.5. Part Painting

The majority of exterior automotive components are also painted, along with the rest of the vehicle, to improve their appearance and give a desired colour. The automotive painting process involves several different coatings applied at curing temperatures in excess of 80 $^{o}$C. Common defects that can occur during the painting process, such as paint pops and pin holes and are commonly believed to be caused by internal moisture and air filled cavities in composite [117]. SEM inspection of the recyclate reinforced SMC mouldings, Figure 7.15, indicates that the bundles in composite may potentially cause such painting defects.
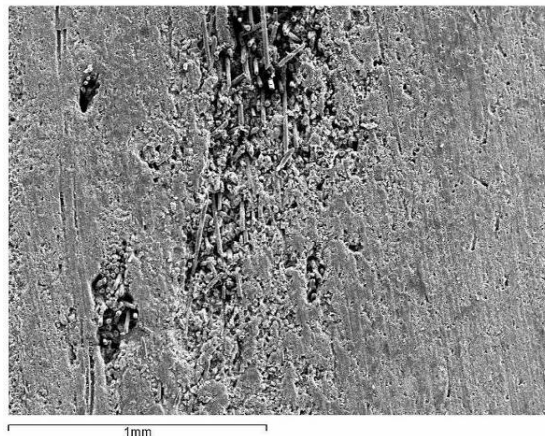


*Figure 7.15, SEM Image of Defect in SMC Caused by Clump of Recyclate Materials.*

To investigate the any surface defects caused by the recyclate reinforced SMC, several of the moulded rear spoiler sections were then processed on the painting line at Mitras Automotive. Further visual inspection of the final painted parts, Figure 7.16 below, showed that the parts painted successfully alongside normal SMC formulation parts and no further defects occurred, though the bumps were more visually apparent on the painted surface.

*Figure 7.16, Painted SMC Mouldings and Bumps on the Surface.*

## 7.7.6. Discussion

Perhaps the most important property of an SMC used to make automotive exterior body panels is the surface finish, and moulding trials have shown that a surface defects occur on the moulded parts surface when recyclate materials are used as reinforcement. Further investigation showed that the surface bumps were only caused by bundles of fibres formed during handling and processing of the recyclate materials. A change to the SMC distribution line could be made to eliminate this problem allowing, therefore allowing production parts with a Class-A finish across the moulding.

# Chapter 8

## 8. Overall Conclusions

This chapter brings together all the important results obtained from each of the experimental chapters. The principle aim of this investigation was to investigate the potential of using mechanically recycled automotive composites as a replacement for virgin reinforcing materials in new composites.

Investigation into the production of the recyclate materials have shown that by the use of a considered granulation process it is possible to preserve some of the original glass fibres for consideration as a reinforcing material in new composites. From the extremely diverse mix of particle size and shapes in the recyclate the desired grades can then be recovered with the use of controlled air classification.

Direct comparisons of the individual recyclate fibres and the virgin glass fibres have shown degradation in both the tensile strength and the strength of the interface between the fibres and a polyester resin, both values reduced to around 60% of those recorded for the virgin fibres. These are important mechanical properties in relation to the ability of the fibres to reinforce a composite material and indicate that composites that replacing virgin fibres with recyclate materials will result in a weaker composite material.

In DMC composite manufacture it has been shown that the collected recyclate materials should not be treated in the same way as the virgin materials. New production techniques have been established so that they can be successfully used to replace virgin glass fibres whilst having minimal effect on the composite's mechanical properties. As the loadings of recyclate greatly increase the properties of the composite are further degraded, though the addition of a wetting agent has been shown to help reduce this effect.

A unique and novel production technique for the manufacture of recyclate reinforced SMCs has been designed. Fibrous recyclate grades have therefore been used successfully to

replace virgin glass fibres during the manufacturing process, used as a reinforcement rather than a filler.

In nearly all of the composites manufactured in this investigation there have been no significant difference between the uses of either the Fine or Coarse grades of recyclate materials as a replacement for virgin fibres, in either new DMC or SMC formulations. As a result it may be possible to reduce the number of stages required for classification of the recyclate materials, keeping the Fine and Coarse together as one fibrous grade which would reduce the overall cost of the production process.

# 9. Future Work

The large scope of this investigation meant that several subject areas were investigated that could potential be the focus of a thesis on their own. Promising areas of results and research that could be explored further for the advancement of the use of recyclate and development of manufacturing techniques are suggested below.

The addition of a wetting agent to the raw composite manufacture improved some of the DMC composite's properties and could therefore be investigated further. To investigate the effect of the wetting-out process on the mechanical properties of composites incorporating large quantities of recyclate experiments using other available chemical wetting or dispersive additives, increased quantities of the additives or even additional resin or styrene could be performed.

It has been shown in this investigation that the strength of the interface between the recyclate fibres and the polyester resin is not strong as that between the virgin fibre and the resin. This could potentially be improved with the silane treatment of the recyclate materials to promote better adhesion and improve the strength of the interface. This could be explored both through the use of the single fibre pull-out test and manufacture of new DMC or SMC composites.

The successful development of a novel machine that allows the successful inclusions of recycled fibrous materials into new SMC formulations as reinforcement could be used for further investigations. Further experimentation using different reformulations with the glass fibre SMC recyclate from this investigation, such as 'by content' to adjust for the reduction in glass content or by blending virgin and reinforcing fibres in the machines hopper to eliminate the layering effect. Other recycled or fibrous materials could be processed using the equipment to produce and investigate new SMC formulations, such as for the incorporation of virgin or recycled carbon fibres or natural fibres.

# 10. Appendix A – Mould Flow Analysis

In this appendix the tests used to confirm the isotropic properties, as discussed in section 3.6.2, of the moulded DMC and SMC panels manufactured for mechanical characterisation throughout this thesis are presented.

### *Test Method*

During the moulding of the composite panels for mechanical testing the mould charge was always placed in the centre of the mould before the press was closed and the part moulded. The testing was performed to determine if the flow of the mould charge materials, from the centre to fill the remainder of the mould during manufacture, had any effects on the mechanical properties of the resulting composite test specimens. Four sets of four samples were cut for mechanical testing and characterisation as shown in the figure below:

- A. Samples were cut perpendicular parallel to the direction of material flow and parallel with the edge of the moulding.
- B. Samples were cut parallel to the direction of material flow, at $45^{o}$ to the edges of the moulding.
- C. Samples were cut parallel to the direction of material flow and parallel with the edge of the moulding.
- D. Samples were cut perpendicular to the direction of material flow, at $45^{o}$ to the edges of the moulding.
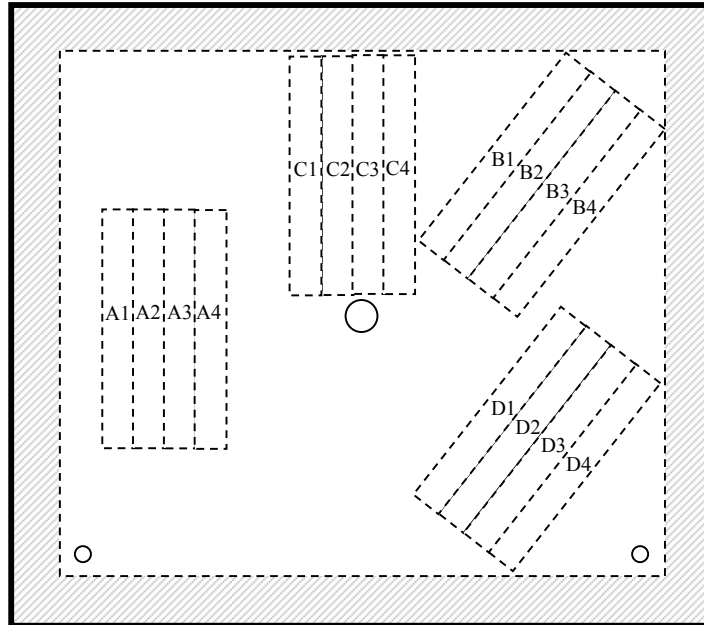
Raw DMC and SMC materials for moulding were provided by Menzolit UK, based upon the DMC and SMC formulations provided for the manufacture in this investigation. Four test panels were moulded, for both the SMC and DMC, so that both three-point flexural and Charpy impact tests could be performed. A total of 16 test specimens for each orientation for each mechanical test, both parallel and perpendicular to the direction of flow.
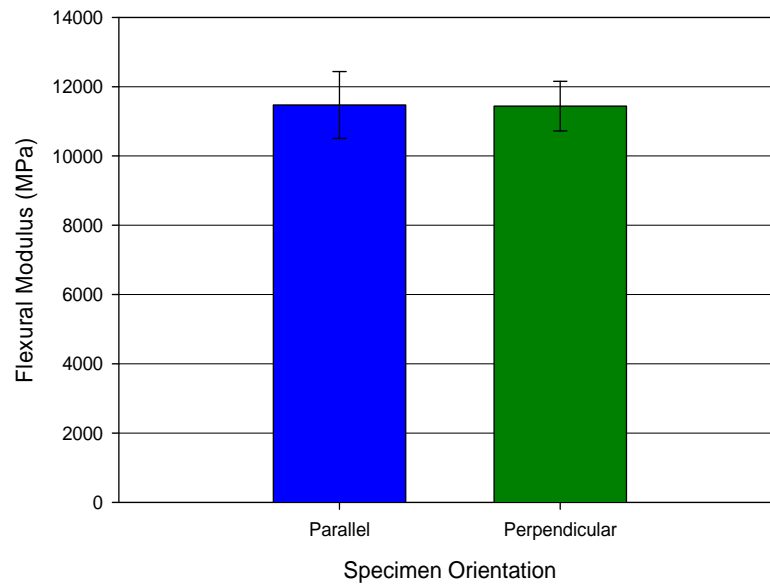
### Testing Results DMC

Below the graphs of the test results on the DMC specimen's orientation from both the flexural and impact tests are presented:
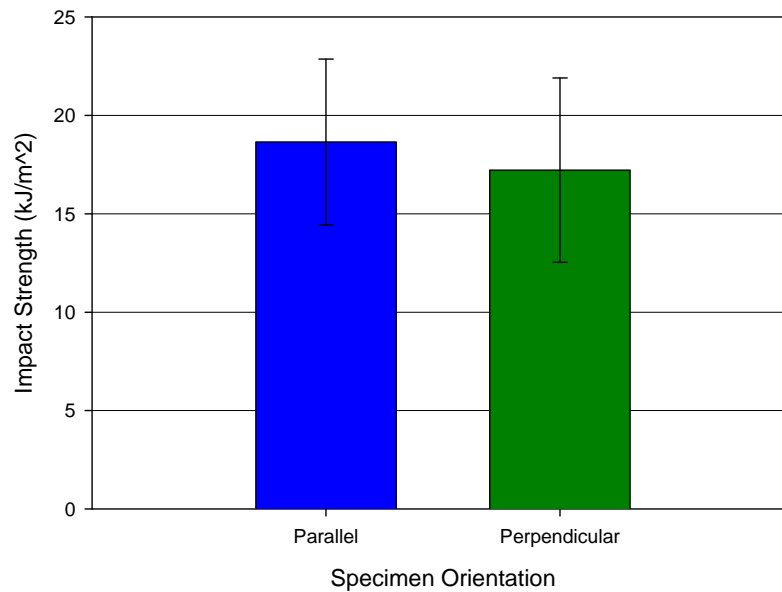
The average flexural strengths of the specimens cut in either orientation:
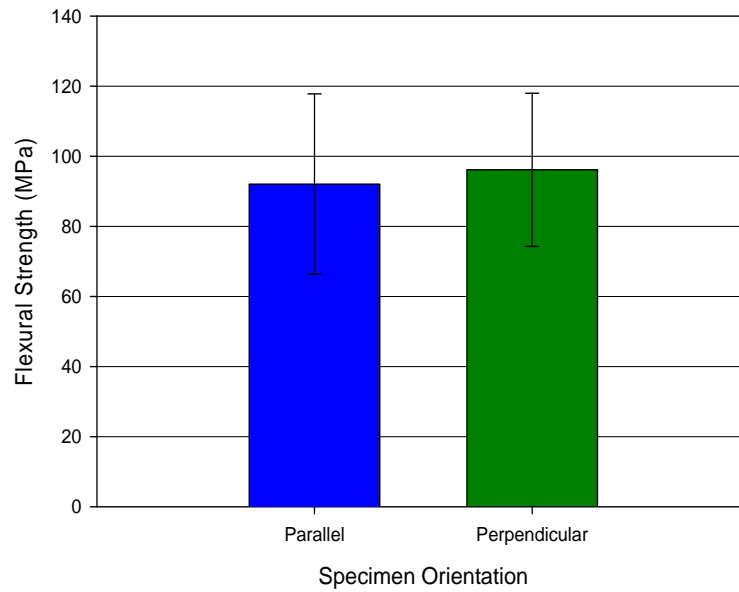
The average flexural modulus of the specimens cut in either orientation:

The average impact strengths of the specimens cut in either orientation:

All of the test results show that there is little difference between the specimens cut either parallel or perpendicular to the direction of flow of materials in the mould. Further analysis of the results was performed to identify if these differences between the mean values were significant or not, similar to the method described in Section 3.7.4. If the differences were significant the P-values given in the tables would be less than 0.05.
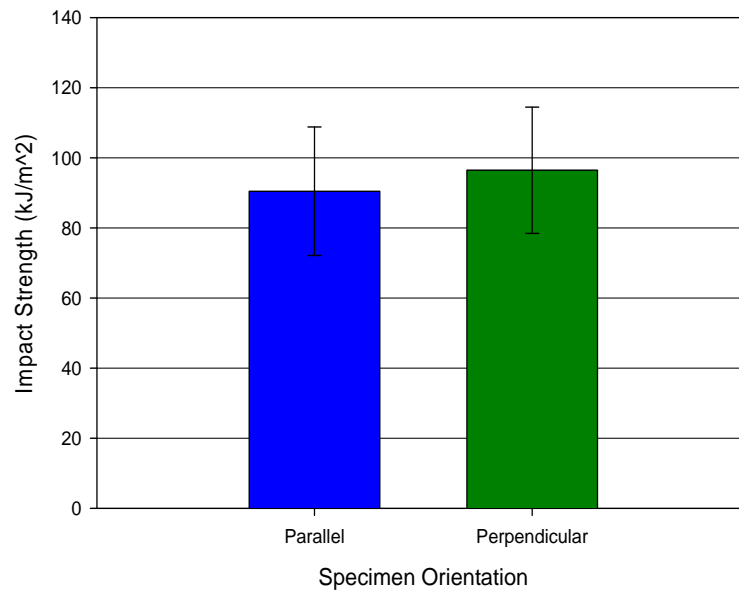
|  | **Flexural Strength** | **Flexural Modulus** | **Impact Strength** |
|---|---|---|---|
| **Sig**. | 0.687 | 0.953 | 0.89 |

The statistical analysis confirms that these are no significant differences between the mechanical properties of the tested DMC specimens, indicating that test specimen orientation does not affect the properties.
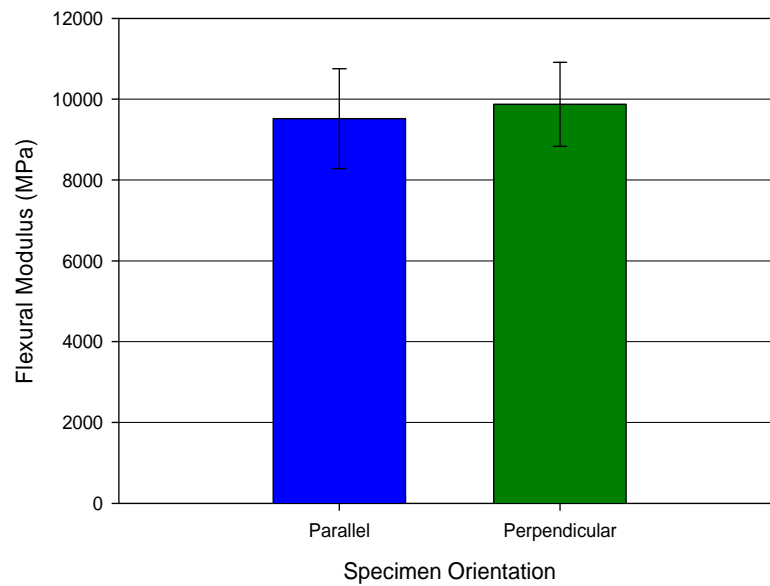
### *Testing Results SMC*

Below the graphs of the test results on the SMC specimen's orientation from both the flexural and impact tests are presented.
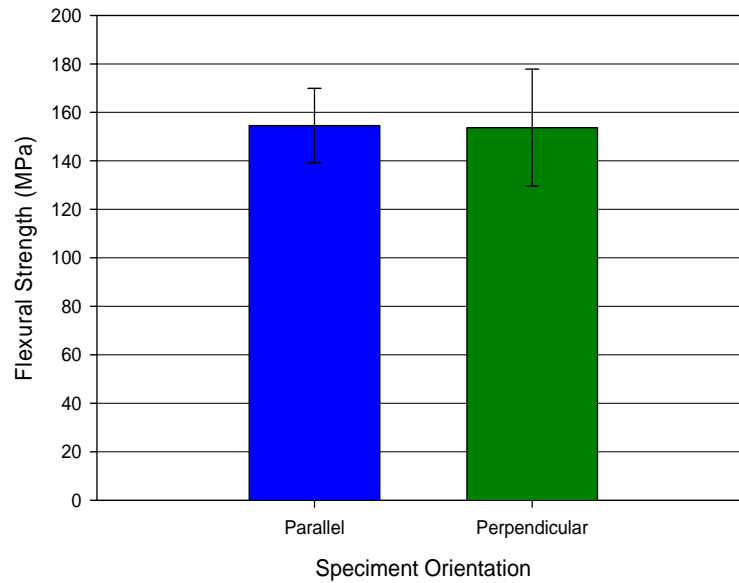
The average flexural strengths of the specimens cut in either orientation:



The average flexural modulus of the specimens cut in either orientation:

The average flexural strengths of the specimens cut in either orientation:



Statistical analysis of the test results shows that there are no significant differences between the test specimens cut in either direction:

| | Flexural Strength | Flexural Modulus | Impact Strength |
|---|---|---|---|
| Sig. | 0.93 | 0.659 | 0.497 |

# 11. Appendix B – Composite Test Data

In this appendix all of the average results and standard deviations, from the mechanical testing, used to produce the bar graphs presented in the results chapter of the thesis are given along with load-displacement graphs from the relevant tests.

### DMC Standard Materials

For this thesis DMC control batches were manufactured using an unmodified standard DMC formulation, 100% virgin glass fibre reinforcement used, on which the future recyclate based formulations were all based. The average mechanical properties of these standard materials were investigated, to act as a control and therefore a comparator for all recyclate based DMC formulation. The graphs below show the load – deflection results recorded for each of the tested three-point flexural standard specimens, from the standard DMC formulation, used to calculate the averages.
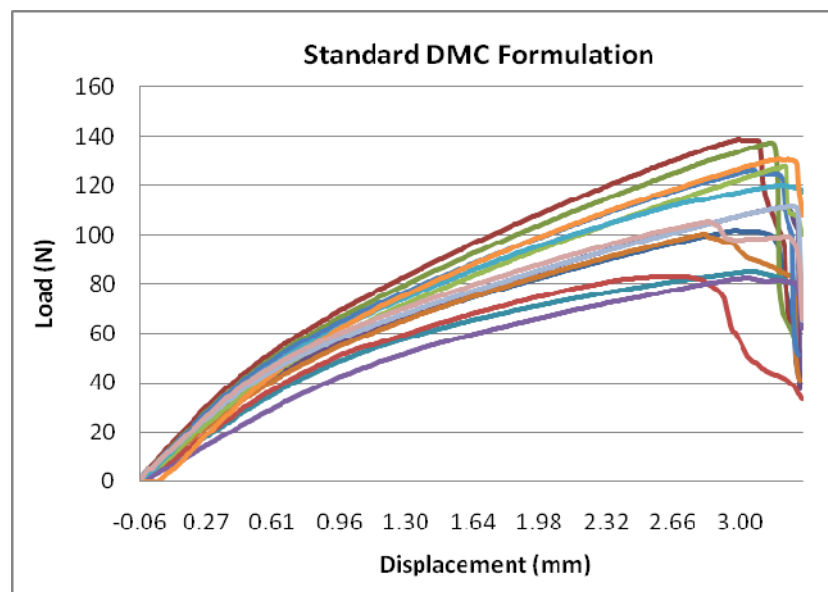
### DMC Mixing Times Results Data

The following tables give the average results and standard deviations used to produce the graphs in Section 6.2.3.

The values for the composite formulations flexural strength:

| | Flexural Strength (MPa) | | | |
| --- | --- | --- | --- | --- |
| | Fine | | Coarse | |
| Material | Mean | s.d. | Mean | s.d. |
| Standard | 79.52 | 13.96 | 79.52 | 13.96 |
| 2 Minutes | 80.59 | 16.30 | 74.13 | 18.39 |
| 4 Minutes | 59.59 | 13.92 | 65.89 | 11.28 |
| 8 Minutes | 80.49 | 17.58 | 76.08 | 15.46 |

The values for the composite formulations flexural modulus:

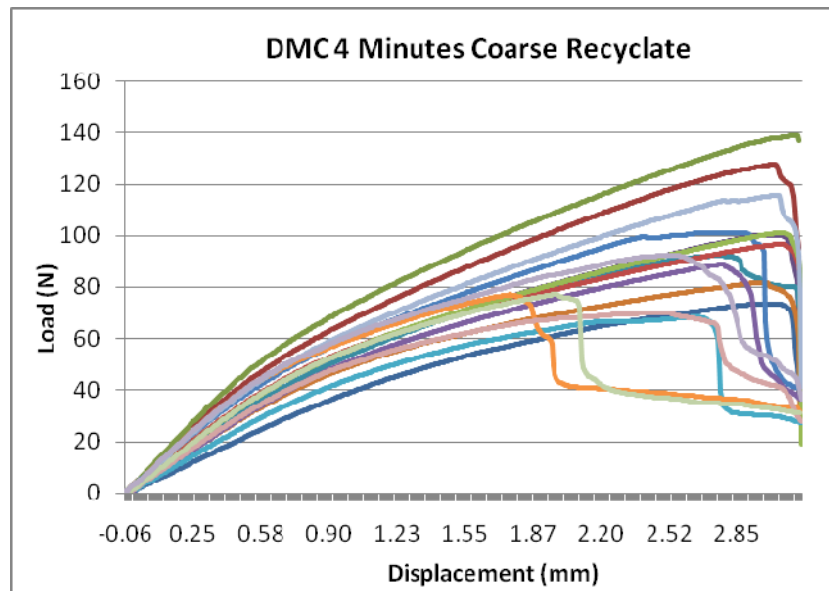| | Flexural Modulus (MPa) | | | |
| --- | --- | --- | --- | --- |
| | Fine | | Coarse | |
| Material | Mean | s.d. | Mean | s.d. |
| Standard | 12594.91 | 317.08 | 12594.91 | 317.08 |
| 2 Minutes | 12593.16 | 421.59 | 10843.73 | 440.65 |
| 4 Minutes | 12638.04 | 489.56 | 11833.59 | 478.93 |
| 8 Minutes | 13018.41 | 527.85 | 11789.88 | 664.83 |

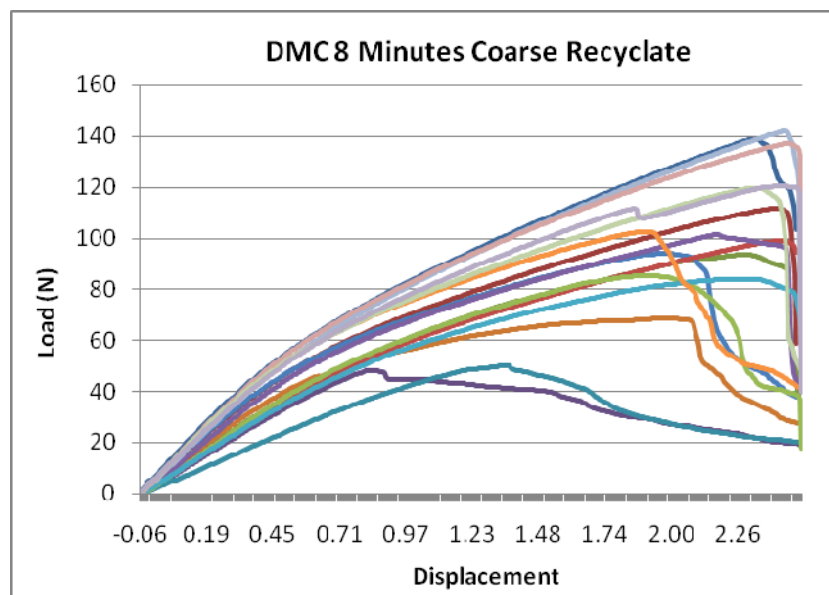The values for the composite formulations impact strength:

| | Impact Strength (kJ/m^2) | | | |
|---|---|---|---|---|
| | Fine | | Coarse | |
| Material | Mean | s.d. | Mean | s.d. |
| Standard | 16.40 | 4.74 | 16.40 | 4.74 |
| 2 Minutes | 17.17 | 5.12 | 15.02 | 4.50 |
| 4 Minutes | 12.42 | 4.36 | 13.72 | 4.09 |
| 8 Minutes | 18.58 | 4.25 | 16.09 | 5.50 |

The graphs below show the load – deflection results recorded, for each of the three-point flexural tested specimens, from each of the different type of DMC formulation tested when investigating the effect of mixing time for both the Fine and the Coarse recyclate.

DMC 2 Mins Fine Recyclate



DMC 4 Minutes Coarse Recyclate

DMC 4 Minutes Fine Recyclate



DMC 8 Minutes Coarse Recyclate
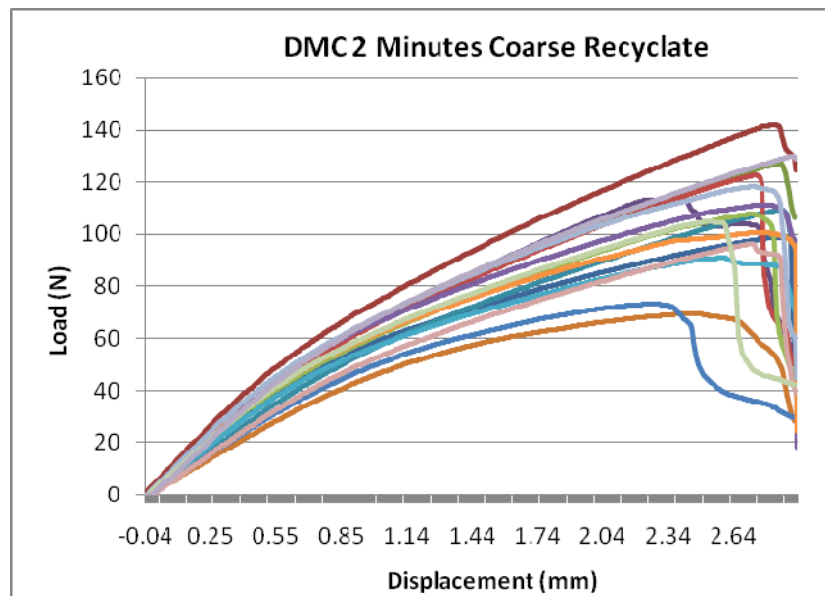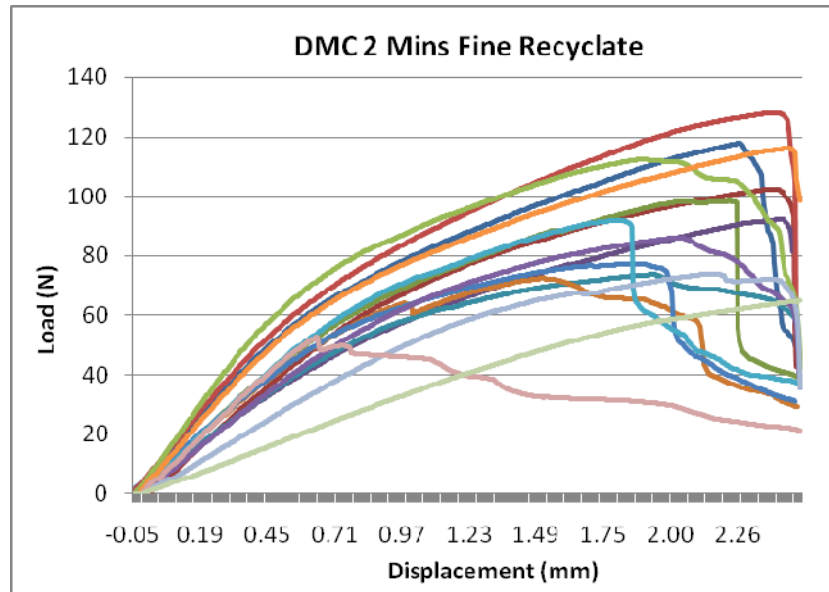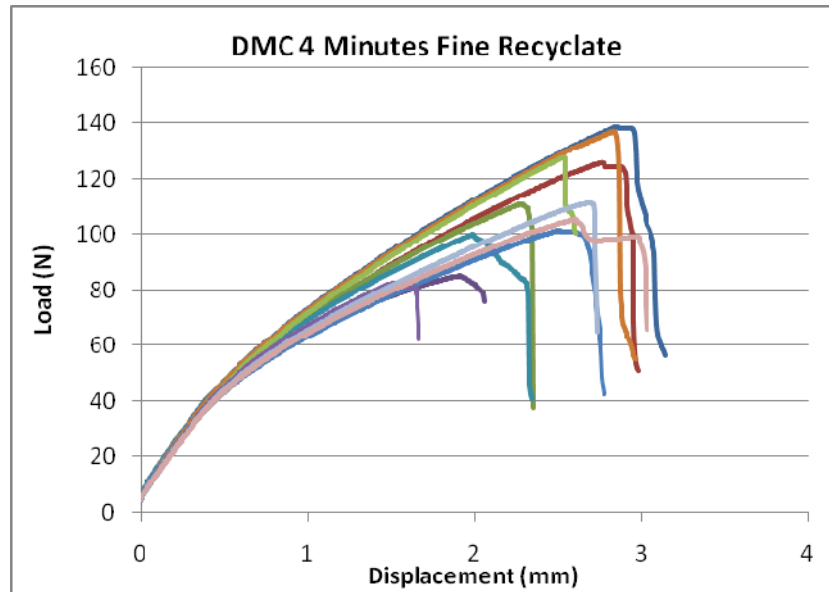
### DMC Reformulation Results Data

The following tables give the average and standard deviation results used to produce the graphs in Sections 6.3.3 and 6.3.4 investigating the effect of reformulation on the composite's properties.

The values for the composite formulations flexural strength:

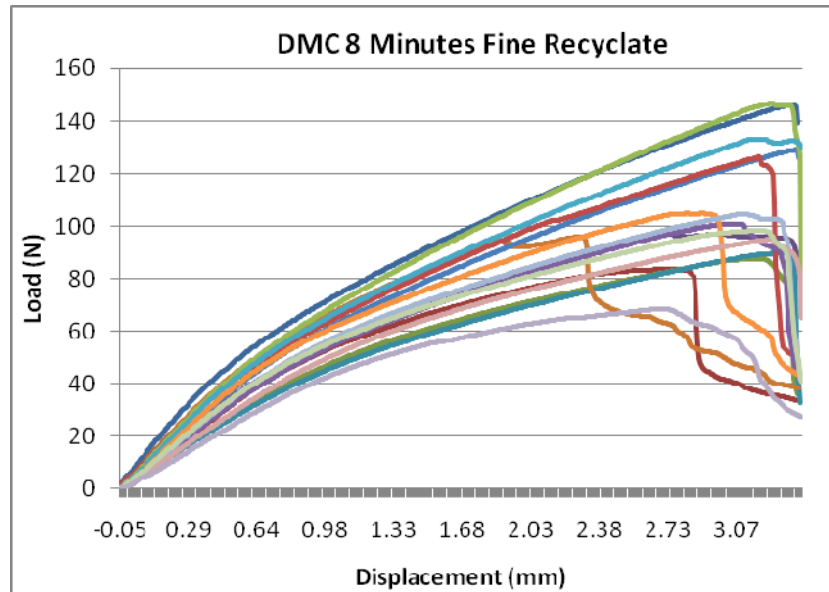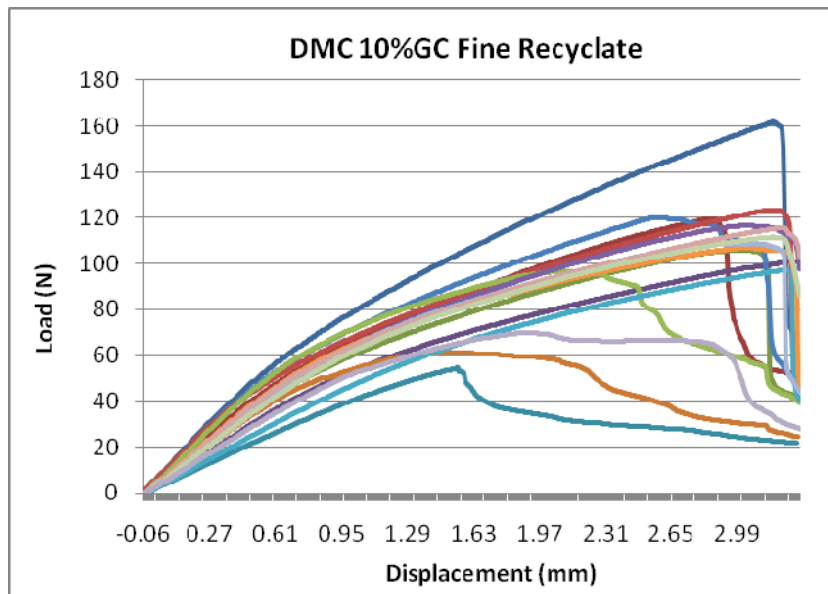| | Flexural Strength (MPa) | | | |
| --- | --- | --- | --- | --- |
| | Fine | | Coarse | |
| Material | Mean | s.d. | Mean | s.d. |
| Standard | 79.52 | 13.96 | 79.52 | 13.96 |
| 10%WT | 80.49 | 17.58 | 76.08 | 15.46 |
| 10%GC | 72.01 | 13.63 | 75.00 | 17.00 |
| 20%WT | 72.11 | 17.03 | 69.57 | 17.31 |
| 20%GC | 62.07 | 15.27 | 62.62 | 17.72 |

The values for the composite formulations flexural modulus:

| Material | Flexural Modulus (MPa) | | | |
|---|---|---|---|---|
| | Fine | | Fine | |
| | Mean | Mean | Mean | Mean |
| Standard | 12594.91 | 317.08 | 12594.91 | 317.08 |
| 10%WT | 13018.41 | 527.85 | 11513.70 | 576.11 |
| 10%GC | 11903.97 | 434.99 | 11773.52 | 519.65 |
| 20%WT | 11262.14 | 658.72 | 11353.85 | 591.04 |
| 20%GC | 11143.06 | 542.87 | 11692.90 | 909.77 |

The values for the composite formulations impact strength:

| Material | Impact Strength (kJ/m^2) | | | |
|---|---|---|---|---|
| | Fine | | Fine | |
| | Mean | Mean | Mean | Mean |
| Standard | 16.40 | 4.74 | 16.40 | 4.74 |
| 10%WT | 18.58 | 4.25 | 16.46 | 5.19 |
| 10%GC | 16.27 | 3.95 | 19.41 | 4.73 |
| 20%WT | 17.50 | 4.83 | 16.23 | 4.34 |
| 20%GC | 14.48 | 4.62 | 14.92 | 5.14 |

The graphs below show the load – deflection results recorded, for each of the three-point flexural tested specimens, from each of the different type of DMC formulation tested when investigating the effect of reformulation, for both the Fine and the Coarse recyclate.

**DMC 10%GC Coarse Recyclate**



**DMC 10%GC Fine Recyclate**

DMC 20%WT Coarse Recyclate



DMC 20% WT Fine Recyclate

DMC 20%GC Coarse Recyclate



DMC 20%GC Fine Recyclate
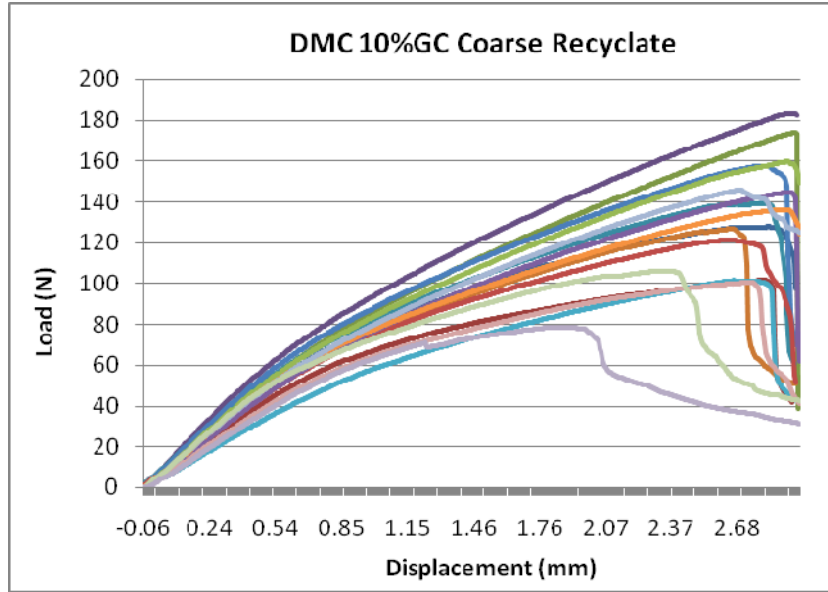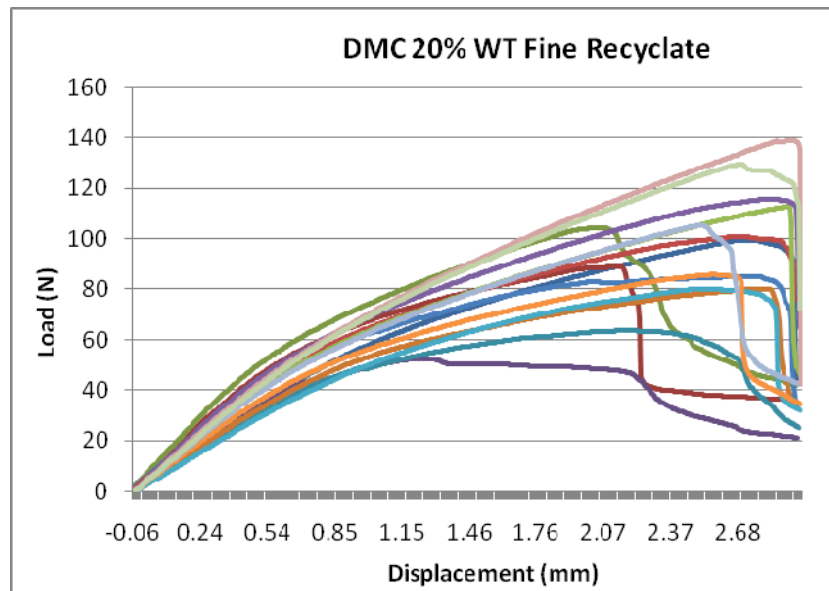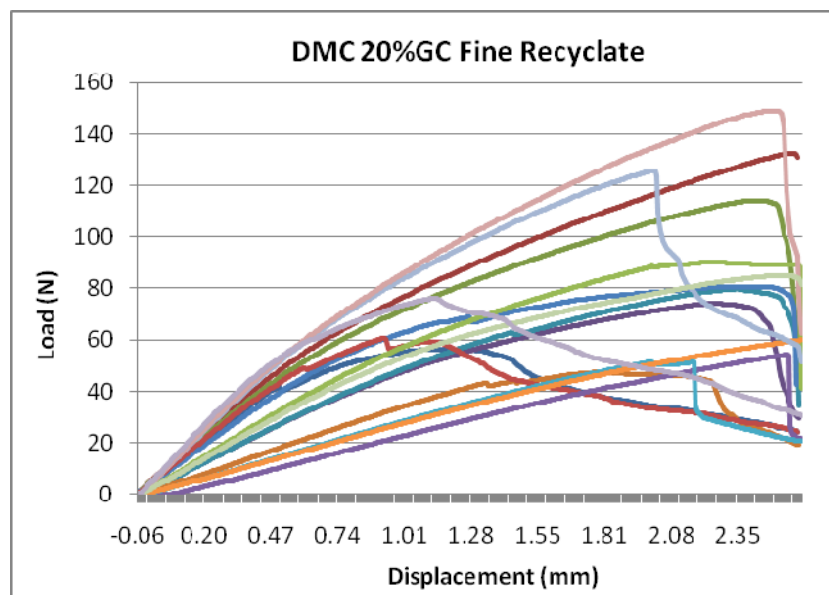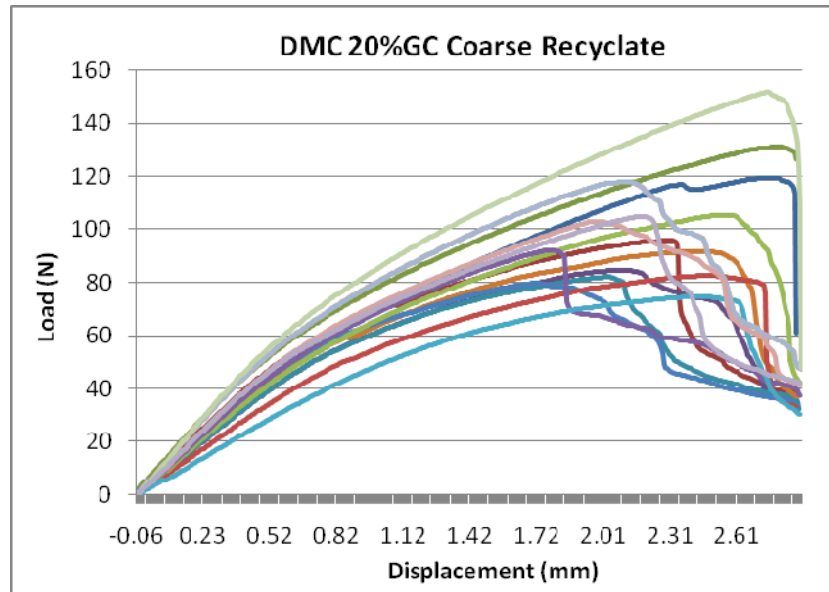
### DMC Chemical Treatment Results Data

The following tables are the average and standard deviation results used to produce the graphs in Section 6.4.3 for the investigation in to the use of chemical treatments.

The values for the composite formulations flexural strength:

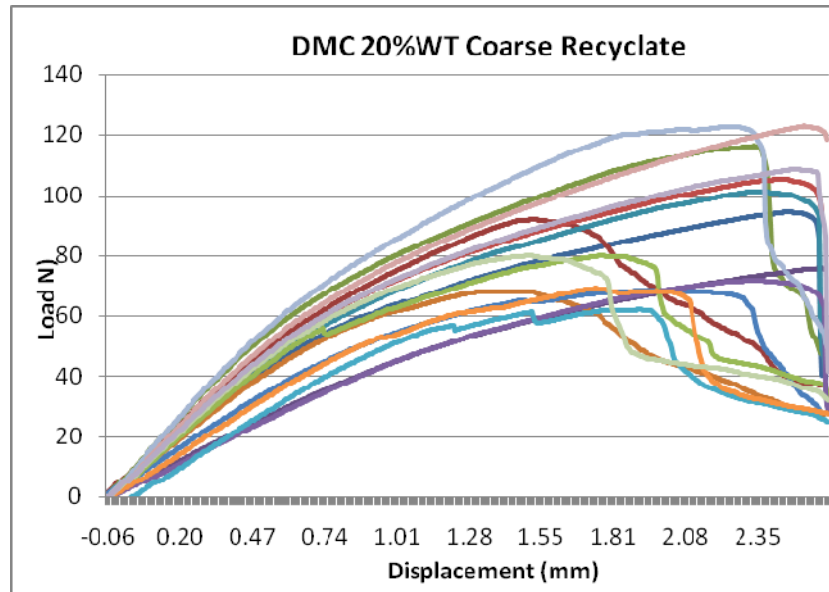| | Flexural Strength (MPa) | | | |
|---|---|---|---|---|
| | Fine | | Coarse | |
| Material | Mean | s.d. | Mean | s.d. |
| Standard | 79.52 | 13.96 | 78.62 | 13.27 |
| 20% Weight | 72.11 | 17.03 | 69.57 | 17.31 |
| 20% Content | 62.07 | 15.27 | 62.62 | 17.72 |
| 20% GC Wetting Agent | 71.89 | 15.53 | 68.07 | 13.98 |

The values for the composite formulations flexural modulus:

| | Flexural Modulus (MPa) | | | |
|---|---|---|---|---|
| | Fine | | Fine | |
| Material | Mean | Mean | Mean | Mean |
| Standard | 12594.91 | 317.08 | 12594.91 | 317.08 |
| 20% Weight | 11262.14 | 658.72 | 11353.85 | 591.04 |
| 20% Content | 11143.06 | 542.87 | 11692.90 | 909.77 |
| 20% GC Wetting Agent | 10919.41 | 511.83 | 11285.80 | 465.23 |

The values for the composite formulations impact strength:

| | Impact Strength (kJ/m^2) | | | |
|---|---|---|---|---|
| | Fine | | Fine | |
| Material | Mean | Mean | Mean | Mean |
| Standard | 16.40 | 4.74 | 16.40 | 4.74 |
| 20% Weight | 17.50 | 4.83 | 16.23 | 4.34 |
| 20% Content | 14.48 | 4.62 | 14.92 | 5.14 |
| 20% GC Wetting Agent | 17.82 | 4.77 | 16.32 | 3.75 |

The graphs below show the load – deflection results recorded, for each of the three-point flexural tested specimens, from each of the different type of DMC formulation tested when investigating the effect of chemical treatment for both the Fine and the Coarse recyclate.

DMC Wetting Agent Coarse Recyclate



DMC Wetting Agent Fine Recyclate
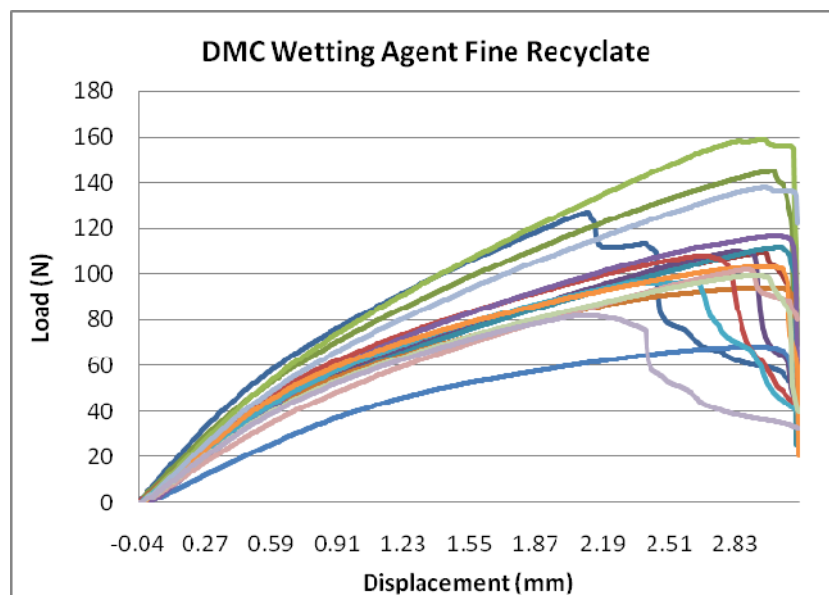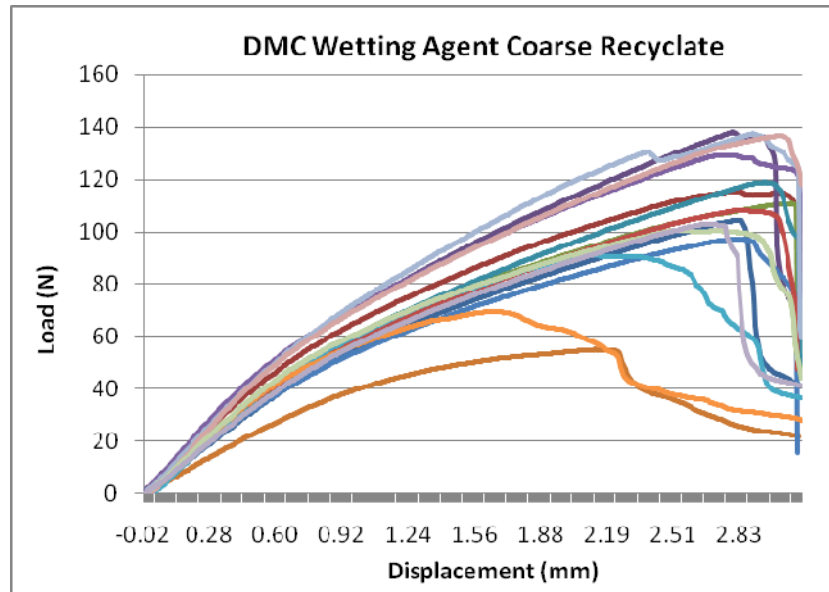
### SMC Results Data

The following tables are the average results used to produce the graphs in Section 7.6 for the manufacturing of SMC with recyclate materials.

The values for the composite formulations flexural strength:

|  | Flexural Strength (MPa) | |
| --- | --- | --- |
| Material | Mean | s.d. |
| Standard | 143.73 | 17.24 |
| Fine Recyclate | 122.58 | 28.39 |
| Coarse Recyclate | 116.49 | 32.16 |

The values for the composite formulations flexural modulus:

|  | Flexural Modulus (MPa) | |
| --- | --- | --- |
| Material | Mean | Mean |
| Standard | 10145.40 | 1125.89 |
| Fine Recyclate | 10578.00 | 1810.53 |
| Coarse Recyclate | 10545.00 | 949.75 |

The values for the composite formulations impact strength:

|  | Impact Strength (kJ/m^2) | |
| --- | --- | --- |
| Material | Mean | s.d. |
| Standard | 97.70 | 13.32 |
| Fine Recyclate | 81.77 | 22.81 |
| Coarse Recyclate | 73.57 | 20.40 |

The graphs below show the load – deflection results recorded, for each of the three-point flexural tested specimens, from each of the different type of SMC with both the Fine and the Coarse recyclate.

SMC Standard Test Data



SMC Coarse Recyclate

SMC Fine Recyclate
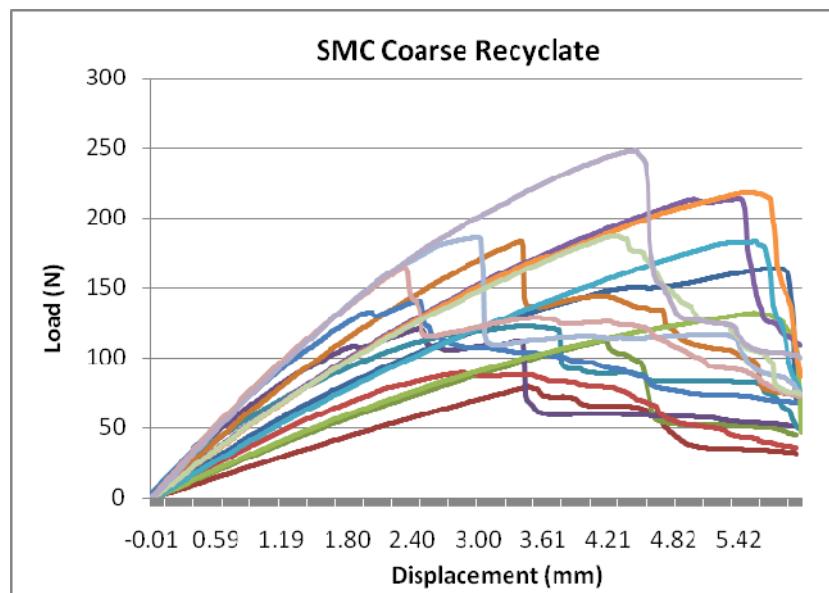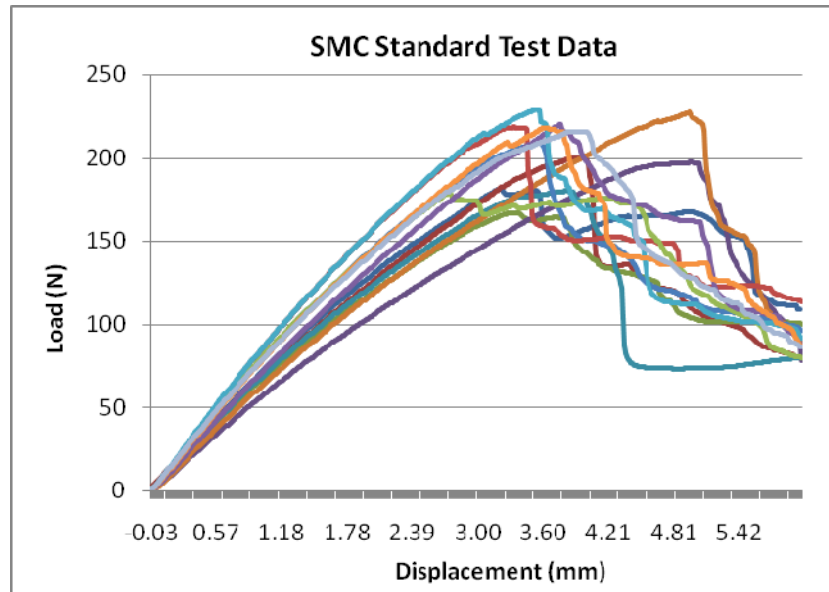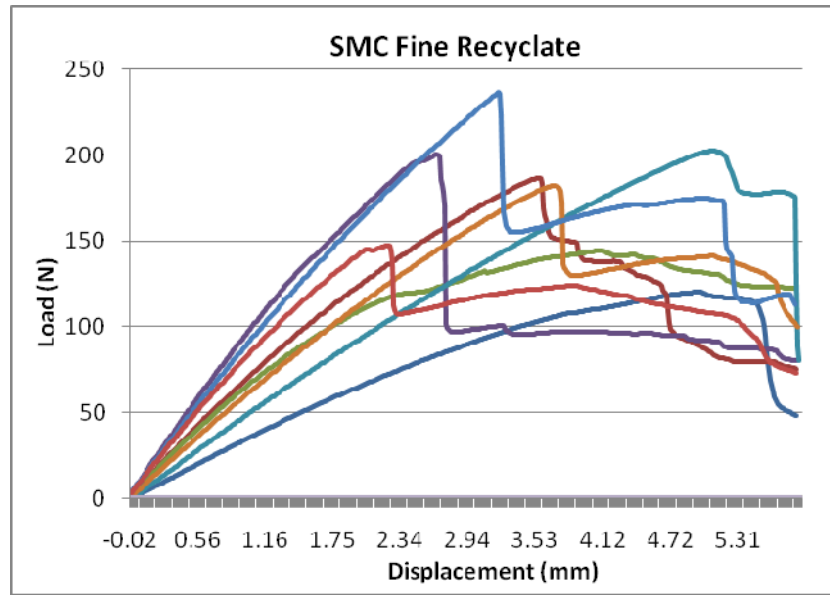
# 12. Appendix C – Recyclate Distribution Line

In this appendix further technical drawings, 3D images and operation diagrams are given for the recyclate distribution line to make its operation clearer.

### Whole Machine

The images below show further 3D images of the SMC recyclate distribution line from front and isometric perspectives.
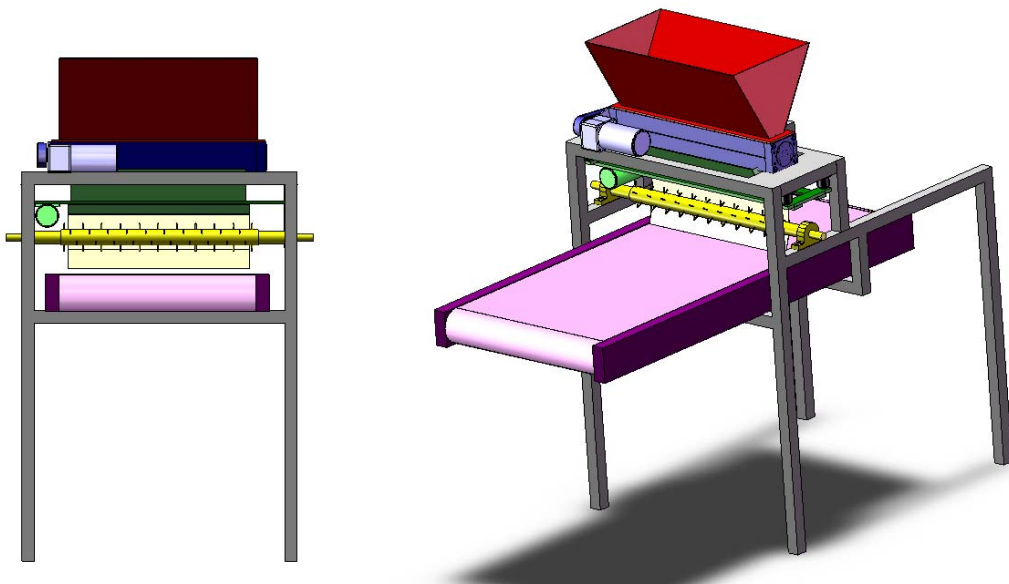
## *Operational Stages*

Further images of each operational stage of the SMC recyclate distribution line are shown in the following sections. They sit together as shown in the labelled side view below:
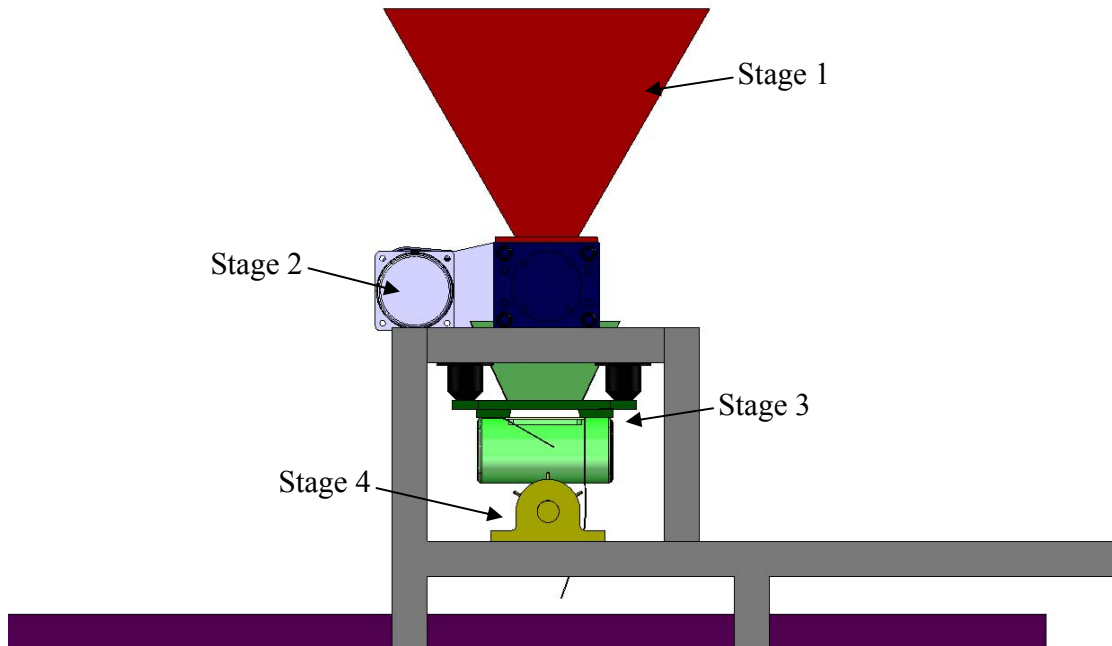


## Stage 1: Storage Hopper

The feed hopper is the first stage of the machine which is used to hold the recyclate materials and direct them towards the recyclate feed section.
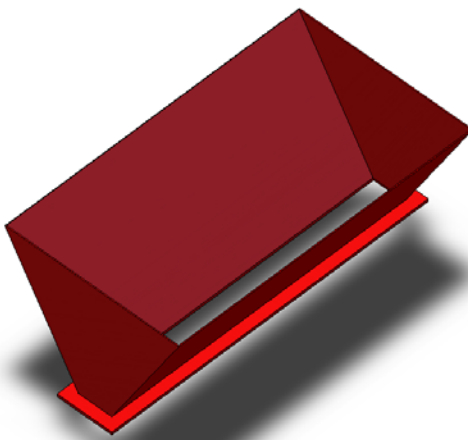
**Stage 2: Controlled Recyclate Feed**

Several design images of the recyclate feed section are shown below, the feed unit is used to move the recyclate materials from the hopper to the remainder of the system in a controlled rate.
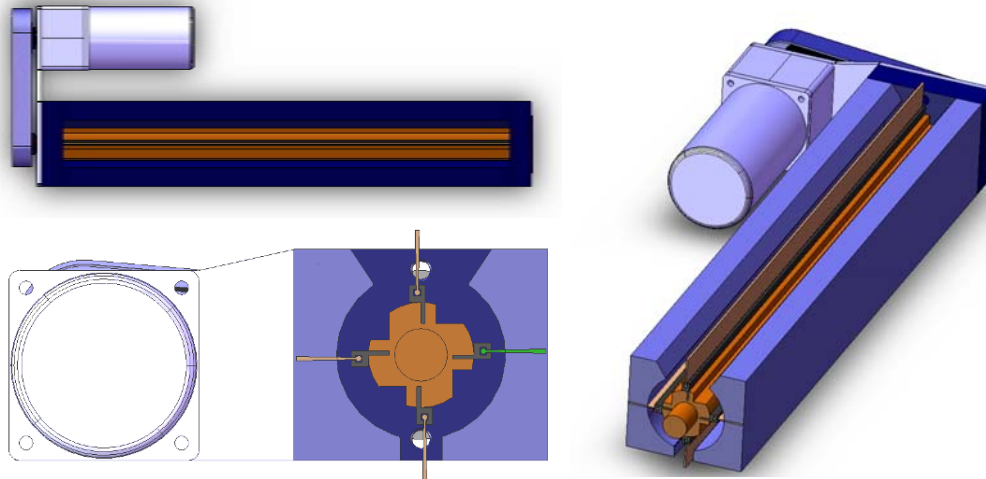


This image shows a cross section of the feed unit operates and how the materials move through it.
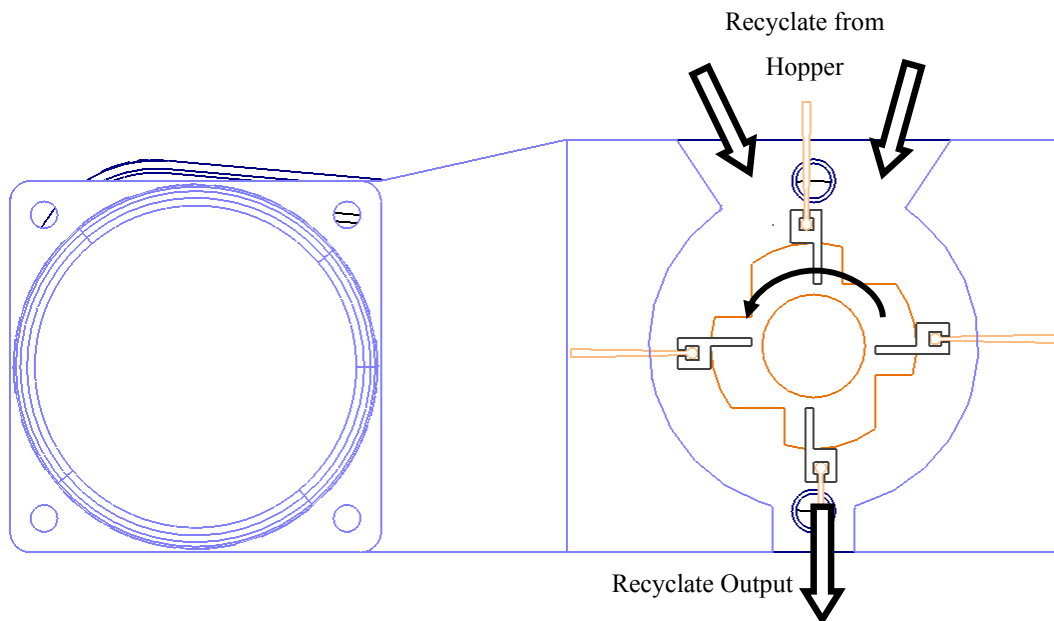
**Stage 3: Vibrating Sieve Section**

The whole of the vibrating sieve section, green, sits on rubber mounts, black, and collects the recyclate materials from the feed section and is used to steady the flow and spread the recyclate materials across the width of the machine.
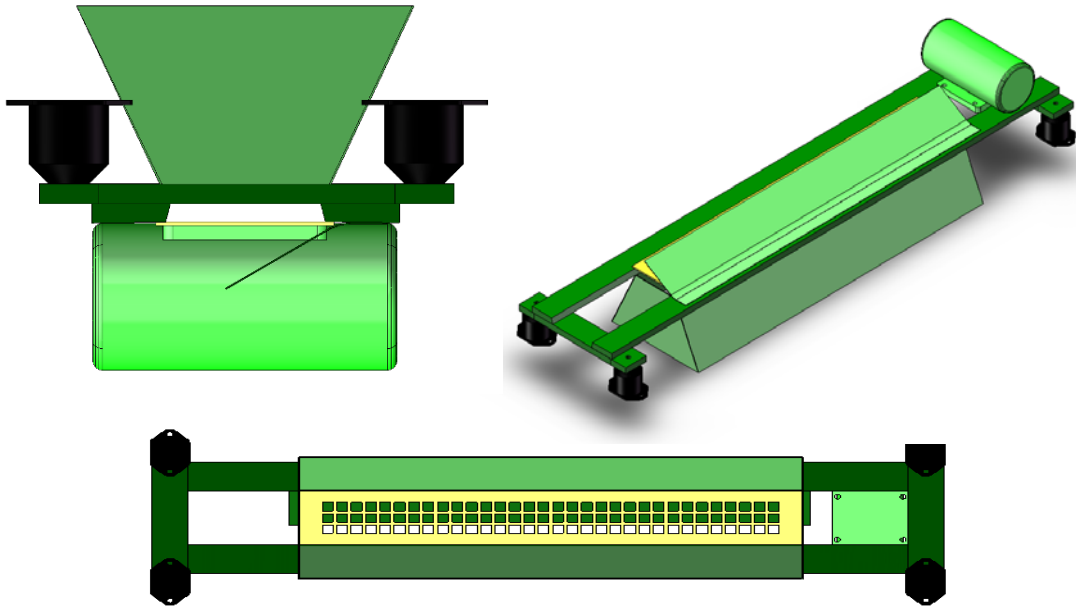
**Stage 4: Flail Unit**

The recyclate materials from the vibrating sieve section fall onto the flail unit. The unit consists of a large steel shaft rotating at high speed, from the centre of which a large number of steel pins protrude. The recyclate is guide on to and the behind the rotating shaft by steel backing plates, as the materials pass over the using they collide with the steel pins facilitating the disruption of any bundles of materials and their even distribution across the width of the conveyor below.

Recyclate materials
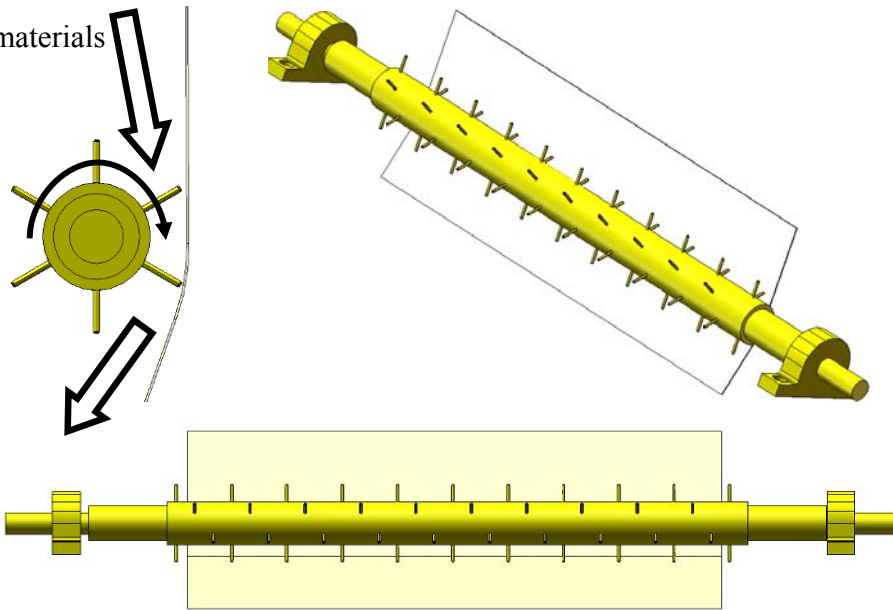
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