Strengthening Rotationally Moulded Products: Development of a Rotomouldable Thermoplastic Composite

A thesis submitted in partial fulfilment of the requirements for the degree of

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by

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To Andrea,

who helped me keep most of my sanity as I wrote this thesis

Abstract

Rotational moulding is a process with a range of unique benefits, currently experiencing significant growth within industry. A primary limitation of the process, however, is the restricted range of suitable materials and the subsequent limitations placed upon the mechanical performance of rotationally moulded products.

The aim of this research project was to develop a rotational moulding material which possessed substantially improved mechanical properties over conventional, rotationally moulded polyethylene grades. This was attempted through the development of a fibre-reinforced thermoplastic composite which was amenable to the rotational moulding process. Although the development of rotationally moulded composites has been previously reported in literature, these materials have largely proven to be unsatisfactory in terms of mechanical performance.

The composite material developed here is distinct from those previously reported in that it utilises melt-compounded composite granules of a significantly larger size than are normally considered suitable for rotational moulding. These granules are intended to be moulded as an inner layer within a rotationally moulded product, with the outer moulded layer formed from conventional, unfilled polymer powder. In this way, the average length of the fibres within the moulded article is maximised while retaining the benefits of the melt-compounding process and giving an excellent external moulded finish. In order to achieve a sufficient degree of composite granule flow and coalescence during rotational moulding, it was found necessary to base the composite granules on high melt-flow, injection moulding grades of polypropylene and polyethylene. The most successful of the resultant composite materials was shown to be superior to the previously utilised rotational moulding grade of unfilled, high-density polyethylene by approximately 65% in offset yield strength (0.5% offset) and over 95% in tensile modulus.

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(in no particular order)

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Chapter 1:

Introduction

1.1 Rotational Moulding

Rotational moulding (often abbreviated to rotomoulding) is a processing method that has found application with polymer materials since the late 1930's [1], and the basic principles of the technique can be traced even further back into history. Despite its age, however, rotational moulding is a growth industry that has benefited greatly from recent technological and processing advancements; it was identified in 2003 as having the fastest growth rate of any plastic manufacturing method [2]. The development and tailoring of advanced materials to suit the rotational moulding process is an important factor in maintaining this trend, and necessary to allow the fullest potential of the method to be realised.

1.1.1 The Rotomoulding Process

As applied to thermoplastic polymers, rotational moulding is a low pressure, relatively high temperature method of producing primarily hollow objects in a wide range of sizes and geometries, which then find use in a variety of applications. Although the rotational moulding process has also been successfully applied to the processing of thermoset polymer resins and other material groups, these variations make up only a minor share of commercial operations [2], and largely fall outside the scope of this research.

The basic, conventional procedure of the thermoplastic rotomoulding process (as illustrated in Figure 1.1) is to firstly charge a metal mould with a pre-determined amount of polymer powder, following which the mould is sealed (although typically vented in some manner to prevent pressurisation [3] and rotated bi-axially as heat is applied to the mould exterior. This heating stage is continued until the polymer charge has melted and consolidated into a defined article, whereupon it may be cooled and de-moulded.

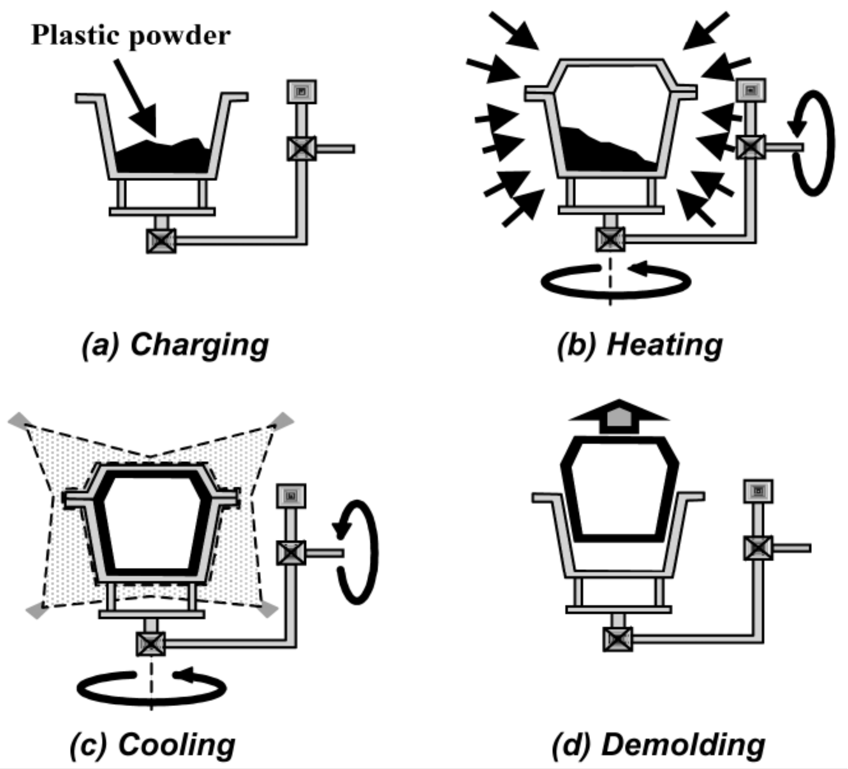

Figure 1.1: The basic processes of rotational moulding [1]

Superficially, this process bears a resemblance to centrifugal casting, which also uses mould rotation as an aid to producing hollow articles from both metals and plastics [2]. The primary difference between the techniques lies in the speed of mould rotation, which is typically less than 12rpm in the case of rotational moulding [2] and as high as 3000rpm for centrifugal casting [4]. The low rotational velocity of the rotomoulding process ensures that heat conduction through the mould walls, rather than centrifugal force, is the primary factor in determining polymer distribution throughout the mould cavity. As the heated mould surfaces are rotated through the powder ‘pool’ sitting in the bottom of the mould, the polymer adheres to and is progressively built up on the mould walls. Continued heating then acts to melt and consolidate the distributed powder layer, completing the conversion of the initial powder charge into a defined moulding.

1.1.2 Process Characteristics and Attributes

The rotational moulding process holds several advantages over comparable polymer forming techniques, making it an attractive proposition for producing a wide range of products. It may be used to make one-piece parts of complex geometry that would be difficult or impossible to mould using other methods, is amenable to product sizes ranging from ping-pong balls to multi-thousand litre tanks, and is capable of producing stress-free and seamless articles using moulds that, due primarily to the low pressure requirements, are relatively cheap to construct [1, 5]. By manipulation of the various processing parameters, the material distribution within the mould and the wall thickness of the resultant product may be controlled [6], while the low rotational velocities of the process free any requirements for mould symmetry. The importance of draft angles within the mould is also minimised, unlike with moulds designed for injection or blow moulding [7]. Some example products that illustrate the potential of rotational moulding are shown in Figure 1.2 and Figure 1.3.

Figure 1.2: Example of a rotationally moulded product - The outer hull of this Galloway International Ltd Mac boat is a one-piece polyethylene moulding [8].

Figure 1.3: Example of a rotationally moulded product - This bio-filter illustrates the complex product geometry achievable with rotational moulding [9].

However, like any process, rotational moulding also has inherent disadvantages and peculiarities which must be understood if optimal results are to be obtained. A limited selection of suitable materials is a primary drawback of the process - this is discussed in more detail elsewhere within this report. Additional disadvantages include a tendency for relatively long cycle times [2], difficulties associated with the moulding of bosses, solid ribs and certain other features, and a general restriction to the moulding of hollow articles. However, this latter drawback may be overcome in certain instances via post-moulding operations and suitable mould design, allowing the production of essentially solid products [6]. Perhaps the greatest limiting factor for rotational moulding is the perception currently held by many designers that it is an unsophisticated process - suitable only for the manufacture of basic products. While this mistaken belief persists, the capabilities of the process will remain under-utilised.

1.1.3 Material Requirements

In order to be suitable for use in conventional rotational moulding, thermoplastic polymers must meet a set of particular requirements. Firstly, the chosen material must be able to be produced as a powder with suitable particle morphology, and this powder must sinter or coalesce to an acceptable degree under the low-shear and pressure conditions of rotational moulding. Secondly, the relatively long processing times at elevated temperature necessitates excellent thermal stability of the polymer melt. The third primary requirement is that the chosen polymer must possess suitable physical and mechanical properties for the envisioned product, at a cost that is not prohibitive. Any additional material requirements, such as a particular colour, flame retardant properties or resistance to sunlight-induced degradation can often be met by the inclusion of various additives within the chosen base polymer. This is common practice within the rotomoulding industry.

These material demands have resulted in various polyethylene (PE) grades being predominant within the rotational moulding industry, making up an estimated 90% of all rotomoulding polymer consumption [2]. PVC plastisols are also utilised in significant amounts, with other materials such as polycarbonate, nylon, polypropylene, unsaturated polyesters, ABS, acetal, acrylics, cellulosics, epoxies, fluorocarbons, phenolics, polybutylenes, polystyrenes, polyurethanes and silicones being used only sparingly [1]. However, despite the popularity of polyethylene, its recognised shortcomings in terms of strength, stiffness and allowable upper service temperature restrict it from use in many potential applications [10].

1.2 Polymer-matrix Composite Materials

Polymer-matrix composites are materials that have been developed over many years, and are both widely accepted and highly utilised. Consisting of either a thermoplastic or thermoset polymer that encapsulates a distinct particulate or fibrous phase, they may be tailored to meet a wide range of mechanical, economic and other material requirements.

Perhaps the most common reason for introducing a dispersed phase into a polymer matrix is for the purposes of mechanical reinforcement, where the net result is an increase in such properties as strength, stiffness or impact resistance relative to the original unreinforced material. This is best achieved with a fibrous reinforcement rather than a particulate addition, as the aspect ratio (length to diameter ratio) of the individual reinforcing particles or fibres, along with the bond strength between the reinforcement and the matrix, is paramount in determining the degree of strengthening that can be obtained.

As a group, fibre-reinforced composite materials can be subdivided on the basis of matrix type, the length of the fibrous reinforcement, and any coherent alignment that these fibres possess within the composite material. In the case of classification based upon fibre length, composites may be separated into discontinuous (short-fibre) and continuous (long-fibre) types, although the precise distinction between the two is not universally agreed upon. The definition given by Callister [11] assigns those composites which contain fibres of less than fifteen times the critical fibre length (l_c) *(a calculated value, based on the fibre diameter and fibre-matrix bond strength, below which the reinforcing effect of the fibres is deemed to be relatively ineffective)* to be short-fibre reinforced, while composites with an average fibre length above this threshold are considered to effectively behave as though reinforced with continuous fibres. Of the two groups, continuous fibre reinforced composites exhibit the greatest reinforcing efficiency and subsequent strengthening effect, but many composite processing methods make the preservation of such long fibres impractical. In these cases, short-fibre reinforcement, sometimes with fibre lengths dropping well below the $15l_c$ division, may be the only processable composite option.

As with fibre length, the orientation of the fibres within the matrix is both an important parameter in determining material performance, and often constrained by the composite processing method. In general terms, maximum composite strength and stiffness is realised in an aligned fibre composite, in the direction of fibre alignment. However, the reinforcing efficiency of such aligned fibres is virtually nonexistent when the composite is tested perpendicular to the alignment direction [11]. Randomly aligned and partially aligned fibre composites fall between these two extremes.

1.3 Research Objectives

This research was undertaken in conjunction with Industrial Technical Solutions (ITS) Ltd of Tauranga, New Zealand, and Gallagher Group Ltd of Hamilton, New Zealand. The primary objective was to develop materials and processing solutions that could be used to improve on the mechanical properties of products moulded from the available rotomoulding polyethylene grades. To meet this aim, the primary research focus was on the development of a rotationally mouldable, fibre-reinforced composite material, but the use of various unreinforced polymers and polyethylene foams was also examined.

1.4 References

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Chapter 2:

Literature Review

Rotationally Moulded Composites

The application of the term ‘composite’ to rotational moulding may be extended to cover a number of different material types, but this review deals primarily with those polymeric materials which incorporate a dispersed particulate or fibrous phase for the purposes of mechanical reinforcement. Those products which incorporate structural additions such as moulded-in inserts and load-bearing skeletons are not here deemed composite materials; neither are foam-filled mouldings. Multi-layer polymer products, such as may be created by moulding a second charge of a dissimilar polymer over a previously moulded polymer layer, have been described as composite materials in literature [7], but are also not examined in this section.

Dispersed phase, rotomoulded composite materials have been developed with both thermoplastic and thermoset matrices, though the use of thermoplastics appears to be predominant. Although the experimental work conducted during this research deals solely with thermoplastic-matrix composites, the few reports of rotationally moulded thermoset-matrix composites available are also briefly covered, in the interests of completeness. These material groups are examined separately in the following review.

Thermoplastic-matrix Composites

Generally, attempts to develop rotomouldable thermoplastic composites may be divided into two broad categories – those where the reinforcing phase is brought into contact with molten polymer during the rotational moulding process itself (termed here “dry-mix” processing), and those where the reinforcing phase is melt-compounded with the polymer matrix in an additional step, prior to rotational moulding. These approaches are considered separately as follows.

“Dry-mix” composite processing

The dry-mix method of producing rotomoulded composites is perhaps the simplest approach, whereby the additive particulate or short fibre is dispersed throughout the polymer powder charge and moulded directly. The primary difficulty with this method, however, is ensuring that the tumbling action of the rotomoulding process does not then separate the matrix and reinforcement phases due to particle size or density differences. This can result in inadequate dispersion of the reinforcing material throughout the final moulding, preventing effective reinforcement of the polymer matrix. The tendency for phase segregation is noted by Martin et al. [10] and Yan et al. [5] as applying particularly to composites containing fibrous materials. Such an effect was observed by Torres and Aguirre [12] during their work with natural-fibre reinforced polyethylene, with the fibre fractions of their composites found to be relegated to the inner surfaces of the moulded specimens by the rotomoulding process. In order to address the subsequent problems of poor interior surface finish and ineffective reinforcement of the matrix, Torres and Aguirre applied an additional layer of unreinforced polymer over the interior of the composite mouldings. This encapsulated any exposed fibre, and by this method, rotomoulded composite cylinders were produced which exhibited increases in compressive strength of up to 54% relative to unreinforced mouldings. Interestingly, a similar study by Torres and Díaz [13], published one year after that of Torres and Aguirre [12], reports “adequate dispersion” [13] of a range of natural fibres throughout rotationally moulded polyethylene, without mentioning the use of an additional, encapsulating polymer layer. It is possible that the high rotational velocities (up to 60rpm) used during the moulding of these specimens contributed to this result. The fibre length used and the mechanical properties of the composites produced by Torres and Aguirre are not stated.

Though dry-mix processing has proven largely unsuitable for use with high aspect ratio fibrous reinforcements, some success has been reported in incorporating particulate phases via this method. The published work of Yan et al. [5] describes the rotational moulding of a range of particulate additives with polyethylene powder, the addition of which increased the tensile modulus of the material by up to ~60% relative to unfilled polyethylene. However, in all cases where the tensile modulus was improved by the addition of the dry-mixed particulates, a corresponding decrease in the tensile strength of the composite was noted. Whether this decreased strength could be considered acceptable in exchange for improved stiffness would depend upon the envisaged usage of the material.

In addition to the difficulty in achieving a suitable distribution of reinforcement when utilising the dry-mix composite preparation method, the lack of significant pressure and shear during processing may result in poor wetting of the particles or fibres by the polymer melt. This can significantly impact upon the effectiveness of the reinforcing additive, as well as affect the moulding performance of the composite material [5].

These characteristics of the dry-mix process pose significant challenges for the preparation of effective composite materials.

Composite processing via melt compounding

In order to overcome the problems of phase segregation and inadequate wetting of the reinforcement which can occur with use of the ‘dry-mix’ processing method, the component materials of the composite may be combined prior to rotational moulding via the use of a melt compounding technique. This approach allows shear and/or pressure, which are lacking from the rotational moulding process, to be used to improve bonding between the composite phases. Following the compounding process, the material must be re-ground or pelletised into a form suitable for rotational moulding, but as the reinforcement is now encapsulated within the polymer granule, problematic phase segregation can no longer occur.

Some success in the production of melt-compounded and rotationally moulded composites has been reported, such as the work of Yan et al. [5] in which glass beads of 6.5μm diameter were used to reinforce rotationally moulded linear medium-density polyethylene (LMDPE). A 2vol% addition of glass beads to the matrix material was found to give an improvement of over 20% in tensile modulus, without an associated decrease in tensile strength as occurred with dry-mixed reinforcement. Further increases in tensile modulus (>40% relative to the unfilled polymer) could be achieved if a slight strength loss (~10%) could be tolerated. The use of melt compounding for the production of rotomoulded composites has also been reported by Martin et al. [10], with their work on polyethylene-layered silicate nanocomposites, by both Siaotong et al. [14] and Wang et al. [15] for the processing of flax-fibre reinforced polyethylene, and by Yuan et al. [16] for the reinforcement of polyethylene with wollastonite microfibres. The addition of flax fibres to polyethylene by Siaotong et al. was found to cause a decrease in tensile strength, which was attributed to thermal degradation of the flax fibres. However, Wang et al. reported a “very slight” [15] increase in tensile yield strength for composites containing 10wt% of chemically treated flax fibre, relative to unreinforced matrix material. The wollastonite microfibres used as a reinforcing addition to LMDPE by Yuan et al. were also shown to result in a small (~2MPa) improvement in tensile strength, when utilised at a loading of 5% of the system volume. It is not clear in these latter three studies what other mechanical properties were affected by the addition of these reinforcing materials.

Though melt-compounding addresses the major problems of the aforementioned ‘dry-mix’ technique, it also introduces a new obstacle to the production of effective rotationally moulded composites. This arises when the compounded composite is reduced into small particles suitable for rotomoulding, with powder having a narrow size distribution of under 500µm generally considered to be suitable for the process [2]. All of the aforementioned literature investigations in which melt-compounded, rotationally moulded composites are prepared, incorporate such a powder-grinding step. Where the reinforcing addition to the polymer consists of fibres substantially larger than the dimensions of these final powder particles, the reduction in fibre length caused by the grinding process can severely restrict reinforcing efficiency [17]. As an added complication, the use of hard or abrasive filler materials may cause unacceptable wear upon the grinding equipment itself.

In recognition of these problems, an approach is described by Wilson [17] in his patent application “Improvements in or relating to rotational moulding”, whereby the fibre/polymer composite material is introduced into the mould in the form of "elongate particles". It is proposed that these particles, consisting of a fibrous reinforcement coated with thermoplastic material, have a diameter of less than 1mm and an average aspect ratio of at least 3:1; markedly different from the morphology of "conventional" rotomoulding powders. Such particle dimensions allow a greatly increased average fibre length to be retained in the moulded article, relative to that achievable with standard grinding techniques, and therefore increase the potential reinforcing efficiency of the fibre addition. It is claimed that these elongate particles may be either moulded directly or combined with a polymer or composite powder of more conventional morphology, the function of which is to fill the spaces between the oversize particles and prevent any problems with poor polymer coalescence or inadequate reproduction of mould detail. Wilson states that this invention yields "substantial improvements" in tensile strength and flexural modulus compared to "more conventional methods" [17].

Thermoset-matrix Composites

Rotationally mouldable composites based on thermoset matrices appear to receive scant attention in literature, even though such materials are not subject to several of the processing issues which make the rotomoulding of thermoplastic-matrix composites problematic. The use of a liquid thermosetting resin in place of thermoplastic powder avoids any problems related to incomplete material sintering and coalescence, wetting of the reinforcement phase may be enhanced due to the relatively low resin viscosity, and segregation of the reinforcing phase from the polymer matrix is controllable [18].

One of the few commercial examples of rotomoulding with thermoset-matrix composites is the "Specific Position Rotational Molding (SPRM)" [19] technique, developed by RevCo International Ltd., of Auckland, New Zealand [20]. The work conducted by La Franchie [20] with this process included moulding trials with a range of polyester-matrix composites, utilising combinations of hollow glass spheres, milled glass fibre, fumed silica, *Pinus radiata* wood fibres and *Pinus radiata* wood flour as reinforcing materials. Despite the composites showing encouraging processing behaviour, the addition of the reinforcing phases to the polyester resin was found in all cases to have a detrimental effect upon the ultimate tensile and flexural strength of the moulded specimens.

Other examples of thermoset-matrix composite moulding processes, which exhibit varying degrees of commonality with “conventional” rotational moulding, are described by Stayner [18], Ogasawara [21] and Usui [22]. The technique reported upon by Stayner was developed by the Patentech Corporation of Illinois, U.S.A., as a method of producing small, hollow products from both particulate and short-fibre reinforced thermoset resins. This process utilises biaxial rotation of a hollow mould, in accordance with what has been described elsewhere within this thesis as conventional rotomoulding practice. However, centrifugal force is identified by Stayner as a material distribution mechanism within the Patentech moulding process, thus indicating that this technique may share more commonality with centrifugal casting than with conventional rotomoulding. Despite this observation, the Patentech method has been termed “rotational moulding” by the author of the paper.

The moulding processes outlined by Ogasawara et al. [21] and Usui [22] are likewise somewhat removed from the definitions of conventional rotomoulding. The technique described by Ogasawara et al. in the paper “A New Continuous Rotation Molding Process for RP Composites – CRM process” [21] was developed for the production of glass-fibre reinforced thermoset pipes of large diameter, and is similar to rotational moulding only in that a slowly rotating mould is central to the process. This method utilises mechanical application of the composite mixture to the interior wall of an open-ended, uni-axially rotating mould. The process is claimed by Ogasawara et al. to possess economic advantages over the competing “centrifugal rotation molding” method of producing similar pipes, due to decreased complexity of the moulding equipment required. The moulding technique detailed by Usui was also developed for the production of reinforced, thermoset-matrix pipes; specifically tapered profile pipe sections which can be bent during manufacture. This process utilises a mandrel around which fibrous reinforcement may be wound, following which the fibre form can be placed within a flexible mould and impregnated with liquid resin. Rotation of the mould is then used to control the distribution of this resin to some extent, and rotation is maintained until the resin has partially hardened. The mould and semi-hardened product may then be bent into the desired shape before the curing reaction is completed.

Overall, commercial utilisation of thermoset-matrix composite rotomoulding appears very limited. This may change, however, as process development continues to advance the applications and capabilities of the technique.

Polymer Oxidation and Stabilisation

The stabilisation of polymers against oxygen, heat, and/or radiation (including UV exposure) induced degradation is not a concern limited to those products created using rotational moulding, but is of particular importance given the process characteristics of a long cycle time at high temperature, coupled with the availability of oxygen to the polymer melt. These conditions encourage accelerated thermo-oxidative degradation, and must be accounted for if optimal material properties are to be achieved both immediately post-moulding, and also retained throughout the service lifetime of the product.

The mechanisms and effects of polymer oxidation, the methods of countering such degradation, and the techniques for predicting both short- and long-term oxidative stability are discussed below.

Thermo-oxidative Degradation

Polymers are characterised by a relatively limited thermal stability, and when the bounds of this stability are exceeded, degradation of the polymer results. This degradation can negatively impact the mechanical, physical and processing characteristics of the material, and must be avoided or minimised if optimal performance of the end-use products is to be achieved. Unfortunately, the long cycle duration at high temperatures and free exposure to oxygen inherent in the basic rotational moulding process represent a severe test for the thermal stability of the common roto-moulding polymers, and pose a significant concern when selecting suitable materials.

As mentioned above, polymer stabilisation and degradation remains an issue throughout the service life-time of the moulded product. However, it is the occurrence of thermo-oxidative degradation during the processing stages which is the initial hurdle to be overcome. Oxidative degradation of the common rotational moulding polyolefins - polyethylene and polypropylene - occurs when the demands of the heating cycle exceed the capacity of the polymer stabilisation system to prevent or retard the oxidation reaction in the presence of air. Thermo-oxidative degradation then occurs via the following processes:

$RH + O_2 \rightarrow R^\bullet + products$ (Reaction 1)

$R^\bullet + O_2 \rightarrow RO_2^\bullet$ (Reaction 2)

$RO_2{}^\bullet + RH \rightarrow ROOH + R^\bullet$ (Reaction 3)

$ROOH \rightarrow RO^\bullet + {}^\bullet OH \rightarrow R^\bullet + RO^\bullet + H_2O$ (Reaction 4)

[23-25]

Reaction 1 is the initiation stage of the oxidation process, where the polymer molecules (RH) combine with oxygen to form carbon-centred polymeric radicals $(R^\bullet)$ and other products [24, 25]. These radicals can then react with oxygen to form peroxyradicals $(RO_2^\bullet)$ as shown in Reaction 2. The peroxyradicals react in turn with other polymer molecules, yielding hydroperoxides $(ROOH)$ and also re-forming more carbon-centred polymeric radicals (Reaction 3). Reaction 4 shows decomposition of the low thermal stability hydroperoxides into the very reactive $RO^\bullet$ and ${}^\bullet OH$ radicals [24], which subsequently produce new carbon-centred polymeric radicals. In this way, the oxidation process generates its own initiator in a closed loop process, explaining its auto-accelerated character [23, 26]. In the absence of stabilisers to inhibit the above reactions, bi-molecular termination of the radical species also occurs - Reactions 5, 6 and 7.

$R^\bullet + R^\bullet \rightarrow inactive - products$ (Reaction 5)

$$R^{\bullet} + RO_2^{\bullet} \rightarrow inactive - products \qquad \text{(Reaction 6)}$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow inactive - products \qquad \text{(Reaction 7)}$$

[25]

The primary outcome of these oxidative reactions is either chain scission (decrease in molecular weight) or molecular enlargement/crosslinking due to recombination reactions [24, 27]. Both types of reactions take place simultaneously, but one reaction will predominate over the other depending upon processing conditions, the polymer molecular structure and the presence of molecular imperfections [24]. It was reported by Cramez et al. [27] that crosslinking dominated over chain scission during the rotational moulding of polyethylene, while the reverse was true for rotationally moulded polypropylene. Tcharkhtchi and Verdu [23] state that "…in an excess of oxygen, chain scission generally predominates", and also that "…chain scission and crosslinking can co-exist in the same sample, but in different thickness layers." This is attributed to the dependence of the oxidation process upon the diffusion of oxygen into the polymer melt [23, 27], which leads to the existence of oxidation thickness profiles. In the case of most rotomoulding-caused oxidation, this dependence upon the diffusion of oxygen limits the occurrence of degradation to a finite depth from the inner (air exposed) surface of the polymer moulding.

The implication with polymer thermo-oxidative degradation being confined towards the inner surface of a rotationally moulded article is that the negative effects upon mechanical, material and processing properties will also not necessarily extend throughout the polymer layer. In fact, the research of Oliveira et al. [28] showed the degradation reactions within a polyethylene rotomoulding to be only significant within a layer of about 30μm thickness located at the inner moulded surface. Even this highly localised degradation, however, affects the crystalline structure of the polymer beyond the depth that the oxidation reactions took place. It is this difference in polymer morphology which can significantly affect the mechanical properties of the moulded article [27, 29].

Where thermo-oxidative degradation has occurred upon a polyethylene or polypropylene moulding, perhaps the most significant effect is embrittlement, or loss of impact strength, by the polymer. Other mechanical properties may also be adversely affected, the product appearance may be changed, and the processing behaviour of the polymer can be altered [27, 30].

Antioxidants and Processing Stabilisers

With the thermo-oxidative degradation of polymers established as an undesirable phenomenon, there arises the need to prevent the oxidation reaction from occurring during the rotational moulding cycle. It may be possible to limit the exposure of the polymer melt to oxygen and excessive heat in some instances but, as previously explained, extensive heating is a necessary attribute of the thermoplastic rotational moulding process. The use of an inert nitrogen atmosphere in the mould interior has been suggested by Tcharkhtchi and Verdu [23] as a method of avoiding the occurrence of oxidative degradation. However, the research of Cramez [31] shows that although oxidation may be delayed using this technique, it is not prevented entirely. Also, the diffusion of bubbles from within the polymer melt, which is an important factor in the polymer sintering process, has been shown to be significantly slowed in the presence of a nitrogen atmosphere [27]. This leads to a requirement for increased heating, which offsets the delayed oxidation effects of the inert atmosphere and results in costs additional to those already associated with the expense of providing the inert atmosphere itself.

The addition of chemical antioxidants and stabilisers to the susceptible polymer has been found to be the most effective method of preventing oxidative degradation from occurring [24]. Suitable antioxidant types can include certain phosphites, phosphonites, sulphides, sterically hindered phenols, hindered amines, lactones, and a multitude of other species, all of which act to disrupt the thermo-oxidative degradation reactions in some way [23, 24, 32].

The specific antioxidant additives used in this research, Ciba Specialty Chemicals Inc. IRGANOX 1010 and IRGAFOS 168, are a sterically hindered phenolic primary antioxidant and a hydrolytically stable phosphite processing stabiliser/secondary antioxidant, respectively. The chemical structures of these compounds are shown in Figure 2.1.

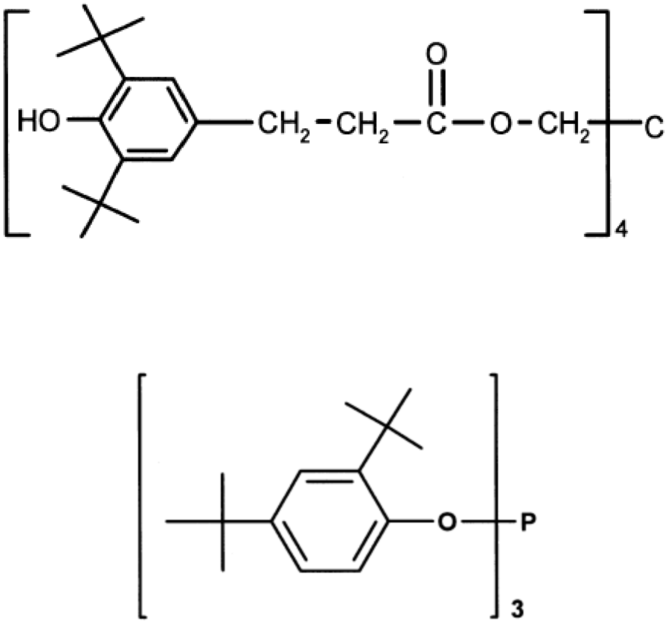

Figure 2.1: The molecular structures of Ciba IRGANOX 1010 *(top)* and Ciba IRGAFOS 168 *(bottom)*, the two antioxidant additives used in this research [24].

The binary combination of this phenolic antioxidant and phosphite processing stabiliser comprises a relatively "traditional" stabilisation system [24], which is well proven for use with polyolefins and was recommended for use in this research by Ciba Specialty Chemicals Inc. technical personnel. It is the function of the sterically hindered phenol to act as a hydrogen atom donor and free radical scavenger, providing melt processing stability while also conferring a degree of short- or long-term thermal stability to the product [24]. The added phosphite processing stabiliser works synergistically with the primary antioxidant, decomposing hydroperoxides into inert products and providing processing stability and colour maintenance [24]. As the antioxidant species are consumed during these reactions, the polymer is protected against thermo-oxidative degradation for only a finite period [27].

The effectiveness with which antioxidant additives confer protection against thermo-oxidative degradation is highly dependent upon the polymer type, as well as the concentration of added antioxidants and the processing conditions to which the polymer is subjected. Polyethylene combines a medium thermal stability in the presence of oxygen with the possibility of using very powerful antioxidants [23], making it particularly suitable for use in rotational moulding. Polypropylene, however, exhibits a lower thermal stability than polyethylene due to differences between the molecular structures of the two polymers. The oxidation rate of polypropylene at 130ºC is said to be of the same order of magnitude as the oxidation rate of polyethylene at 160ºC [23], a processing disadvantage for polypropylene which is exacerbated by the higher melting and processing temperatures of the material.

Short-term Thermal Stability Prediction

Whether oxidative degradation has occurred during a rotational moulding cycle may be revealed by any of a number of tests that can be performed upon the moulded product, such as microscopic examination to look for changes in polymer morphology, impact testing to determine whether embrittlement has occurred, or just looking for the visual characteristics of an “overcooked” moulding. However, such checks reveal little about the remaining stabilisation capacity of a non-degraded moulding, or the point at which oxidation began in a degraded one. In order to obtain this information without extensive moulding trials, it is necessary to utilise alternative test methods.

A number of factors may be used as the basis for monitoring the thermo-oxidative degradation of a polymer sample, including variation of sample density, weight, carbonyl content, oxygen content, heat flow, viscosity [29], or via the direct detection of active antioxidant species [33]. The most useful of the test methods based upon these characteristics allow real-time monitoring of the occurrence of oxidation under controlled heating conditions. Two of the most widely utilised techniques, which fulfil this criterion, are Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA), which continuously monitor the heat flow into a polymer sample and the mass of a polymer sample, respectively. The occurrence of polyolefin oxidation is indicated in DSC analysis by an exothermic reaction [34], while rapid sample weight decrease is indicative of thermo-oxidative degradation when using the TGA technique. A more detailed discussion of these two techniques is provided in the methodology section of this thesis.

With either DSC or TGA, the common measure of the thermal stability of a polymer sample is the Oxidation Induction Time (OIT). This is the length of time the sample resists thermo-oxidative degradation at a set, constant temperature while under a controlled atmosphere. When conducted at relatively high temperatures (above the melting point of the polymer), OIT determinations via the TGA or DSC analysis methods are relatively rapid, easy to perform and require very little material. The data obtained may be used for the purposes of material comparison or to determine the remaining stabilisation capacity of a moulded article, but care must be taken when using OIT data to predict the processing stability of any particular polymer. This arises because neither thermal analysis technique takes into account such factors as the application of shear to the polymer melt, or accurately simulates the degree to which antioxidants are lost through volatilisation. These effects can have a significant influence on the stability of a polymer system [35, 36], leading to the view held in some quarters that OIT results cannot be used to assess the processing stability of polyolefinic compounds [37]. Rotational moulding, however, due to the lack of shear, low pressure, and the free exposure of the polymer melt to air, is more closely simulated by these thermal analysis methods than most other processing techniques.

Overall, it has been stated that the short-term prediction of polyolefin thermal stability, via either processing or simulation experiments, poses “no real problem” [35]. As long as the limitations and characteristics of the test procedures are recognised, useful and relatively accurate predictions may be made.

Long-term Prediction

Accurately predicting the stabilised lifetime of a polymer article under service conditions can be problematic, compared to making the short-term predictions discussed previously, but is crucial in ensuring that the product will perform satisfactorily throughout its service lifetime. As this service life may extend for many years, there arises the need for an accelerated testing technique - to determine in a reasonable time whether oxidative degradation might be a concern at some distance into the future. The common methods for this assessment are similar to those utilised for short-term stability prediction - involving the use of DSC and TGA for the determination of OIT values.

The base premise of long-term stability prediction using thermal analysis methods is to relate the oxidative stability of the polymer at elevated temperatures with subsequently shortened test times, to the length of time that stability is maintained under service conditions. Multiple attempts to generate accurate lifetime predictions from accelerated testing have been published in the literature, with varying levels of success being attained. The linear extrapolation of *ln*(OIT) vs. reciprocal temperature plots, based upon data obtained from elevated temperature testing, has been advocated as a method of estimating the ambient temperature oxidative lifetime of polymers [38, 39]. However, this technique is not without its complicating factors. The extrapolation of OIT data gathered from tests performed above the melting temperature of the polymers has been found to be an unreliable method of determining service durability [35, 36, 40-44], with extrapolation across other key transition temperatures, such as glass transitions, also advised against [36]. The use of pressurised oxygen as a substitute for an air atmosphere during testing, as has been used to accelerate the onset of oxidative degradation [36], was shown by Woo et al. [45] to result in changed oxidation activation energy in some instances, complicating service lifetime predictions. Also, it has been stated that in many situations, the antioxidant loading exceeds the equilibrium solubility level within the polymer at end-use temperatures. Therefore, the diffusion, exudation and eventual loss of the antioxidant become the limiting factors for durability [46].

All of these factors may prevent the accurate prediction of polymer service lifetimes. Therefore, all such predictions based upon accelerated thermal analysis techniques must be treated with caution.

Materials Review

Polyethylene

Polyethylene, the predominant polymer within the rotational moulding industry [2], is a material that is available in a multitude of grades and variations. These variations may be classified on the basis of density, molecular weight, degree of molecular branching, and/or the polymerisation processes used in their production. This system is somewhat inexact, due to the overlap and conflicts which can occur between classifications, but is nevertheless in common use.

Primary classification of polyethylene grades is often on the basis of density, with the abbreviations ULDPE (ultra-low density polyethylene), VLDPE (very-low density polyethylene), LDPE (low density polyethylene), MDPE (medium density polyethylene), and HDPE (high density polyethylene) widely recognised [47]. The exact range of density values encompassed by each of these terms is not widely agreed upon, but as an example, Crawford [2] has classified LDPE, MDPE and HDPE as respectively corresponding to the density ranges 915-929 kg/m^3, 930-939 kg/m^3 and 940-965 kg/m^3. This system of classification does not specifically address any other aspects of the polymer grade, although some correlations do exist between the density of the polyethylene and its molecular weight, molecular structure, mechanical performance, and the method by which it was polymerised. Two polyethylene types not commonly classified in terms of density are High Molecular Weight Polyethylene (HMWPE) and Ultra-high Molecular Weight Polyethylene (UHMWPE), which are defined by Biron [47] as possessing molecular weights approximately in the 200,000 – 500,000 and 3,000,000+ ranges, respectively. In contrast, “conventional” LDPE and HDPE grades have molecular weights ranging from a few thousands to 300,000, depending on end use [47].

A further distinction between polyethylene grades may be made on the basis of the polymerisation process by which they were produced. The oldest of the three main techniques is free radical vinyl polymerisation, which produces LDPE with a branched structure [47]. Ziegler-Natta polymerisation, in contrast, is used to produce HDPE, MDPE, and linear low-density polyethylene (LLDPE) grades [47]. The most recently developed method – metallocene catalysis polymerisation - allows polyethylenes of all densities to be produced while also giving improved control of branching, molecular weight distribution and structural uniformity during the polymerisation process. As such, this polymerisation technique allows the processing characteristics and mechanical properties of the polyethylene grade to be precisely tailored [47]. Metallocene-catalysed polyethylenes have only become commercially available within the last 15 years [48].

Those polyethylene grades which are suitable for rotational moulding usually fall within the LDPE, LLDPE, MDPE or HDPE classifications [2]. The general characteristics of these material types are discussed below. It is also important to note that the classification of any particular polyethylene grade into one of these groups does not necessarily indicate that the grade is suitable for rotational moulding.

- ***Low Density Polyethylene:*** LDPE grades generally exhibit good flow behaviour, very good environmental stress cracking resistance (ESCR), high flexibility and high toughness at low temperatures. In strength and stiffness, however, LDPE is typically inferior to LLDPE, MDPE and HDPE [2, 47].

- ***Linear Low Density Polyethylene:*** LLDPE grades are characterised by having shorter molecular side branches off the primary molecular chain than LDPE, although the branches are still more numerous and longer than those exhibited by HDPE. LLDPE exhibits improved strength, stiffness, creep behaviour and ESCR over LDPE, while retaining the low-temperature toughness characteristic of the grade [2, 47].

- ***Medium Density Polyethylene:*** MDPE exhibits characteristics between those of LDPE and HDPE [2].

- ***High Density Polyethylene:*** HDPE is used for the majority of all polyethylene goods that have structural applications [47], due to higher strength, higher stiffness and improved creep behaviour relative to polyethylenes of lower density. However, HDPE also exhibits decreased low-temperature impact strength and can be prone to warping [2].

In general, an increased polyethylene density corresponds to increases in tensile strength, stiffness, hardness, creep resistance, chemical resistance, barrier properties and shrinkage, while ductility, ESCR, and impact strength are decreased[2]. Weatherability shows no definitive trend in relation to density [2]; neither does the ease with which the polymer flows when molten. This latter property is of particular significance when selecting any thermoplastic for rotational moulding, as it provides a useful indication of the materials processing behaviour. Ease of melt-flow is commonly quantified as a Melt Flow Index (MFI) value, which is calculated as the weight of molten material which can flow through an orifice of standard dimensions under specified conditions of temperature, applied pressure and test time. A high MFI value therefore corresponds to low viscosity and easy flow. In the case of polyethylene, increases in MFI have also been associated with decreases in chemical resistance, ductility, ESCR, impact strength, molecular weight, tensile strength and weatherability [2]. Rotational moulding grades of polyethylene usually have a MFI in the range of 2-8 g/10min (ASTM D1238 - 190C, 2.16kg) [2].

Polypropylene

Polypropylene currently accounts for only a small percentage of the overall polymer usage by the rotationally moulding industry. However, as it is a stiffer, lower density alternative to polyethylene which also has a higher allowable service temperature, there is increasing interest in more fully utilising this material [49]. As has already been mentioned, polypropylene is inherently more susceptible to processing induced thermo-oxidative degradation than polyethylene, which is a significant limitation on its use. Polypropylene also suffers from a generally poor impact strength when rotationally moulded [2, 49], and difficulties associated with producing polypropylene powder of acceptable quality [50]. Nevertheless, these deficiencies may be overcome to some extent, and in recent years rotationally mouldable grades of polypropylene have become commercially available [2].

The form of polypropylene applicable to rotational moulding is the isotactic or crystallisable type, as opposed to atactic (noncrystallizable) polypropylene which is a soft, tacky material used in adhesives, sealants and caulk products [51]. Isotactic polypropylene (from this point on simply referred to as "polypropylene") may be divided into the subfamilies of homo-polymers and co-polymers, which are examined separately below:

- ***Homopolymer Polypropylene:*** Homopolymer polypropylene (HPP) is the most widely used polypropylene variant [51], and is formed from the polymerisation of propylene monomers alone [47]. HPP is rigid but can be rather brittle [47].

- ***Copolymer Polypropylene:*** Polypropylene copolymers are created by the polymerisation of propylene with another olefin monomer, most commonly ethylene [47, 51]. The comonomer can either be randomly inserted into the polypropylene molecular backbone, which forms a random copolymer polypropylene, or a block structure polypropylene can be formed by inserting several comonomer sequences into the polypropylene sequences. The former structure induces an amorphous morphology and therefore a better transparency, while the latter structure favours crystallinity. Both copolymer types are characterised by improved impact resistance and decreased rigidity relative to HPP [47].

- ***Impact Copolymer Polypropylene:*** Polypropylene impact copolymers are physical mixtures of homopolymer polypropylene and high-ethylene random-copolymer polypropylene. Impact resistance at low temperatures is enhanced at the expense of material stiffness [51].

As with polyethylene, the MFI value of a polypropylene grade provides a useful indication of the ease of melt-flow during the rotational moulding process. MFI values cannot be directly compared across the two polymer types, however, due to differing test conditions under which the MFI values are commonly determined [52].

Coupling Agents

A coupling agent may be defined as any chemical substance designed to react with both the reinforcement and matrix of a composite material in order to promote a stronger bond between the two phases. As the strength of this interface is crucial in determining the mechanical performance of the composite material as a whole, there is correspondingly a significant interest in the use of coupling agents during composite production. The type of coupling agent utilised in any particular application is largely determined by the nature of the composite’s constituent materials.

A common obstacle to the formation of strong bonds between the reinforcement and matrix phases of a composite is the difference in polarity which may exist between the two materials. While many types of filler and reinforcement are polar in nature [51], polyethylene and polypropylene – the matrix polymers utilised in this research – are both non-polar. This incompatibility results in poor adhesion between the two phases, a correspondingly weak interface, and a sub-optimal transfer of stress from the matrix to the reinforcement when the composite is loaded [53]. The addition of a coupling agent to such a composite provides a chemical “bridge” between the phases, allowing the otherwise incompatible materials to be closely bonded. The coupling agent achieves this by having a molecular structure with two functional domains: one domain which is capable of forming entanglements or segmental crystallisation with the polymer matrix, and the other which will interact with the reinforcement phase via such mechanisms as covalent bonds, ionic interactions and hydrogen bonds [53].

The coupling agents used in this research are based on maleic anhydride and organosilanes, selected for their easy availability, commercial acceptance and proven effectiveness with a range of composite materials. Both maleic anhydride and organosilanes may be either applied to the reinforcing phase prior to melt compounding [14, 16, 54] or, alternatively, grafted on polymer molecules before addition to the composite system [10, 53, 55]. When applied directly to the reinforcement, coupling agents fall under the more general term “sizing”. In the composite industry, sizing refers to any surface coating applied to a reinforcement in order to protect it from damage, aid in processing, or improve the mechanical properties of the composite [56].

Process Adaptations

A wide range of improvements and adaptations have been made to the basic rotational moulding process, thus tailoring the technique to the demands of particular materials and applications. These variations are too numerous to all be detailed here, but several of these developments which are relevant to this research are briefly examined below.

Real-time temperature monitoring

In commercial production environments, the traditional method for establishing the correct amount of heating for any particular polymer product was by trial-and-error [1]. Subsequent mouldings were then controlled on the basis of elapsed time for each of the moulding stages. This approach was both wasteful and imprecise, as many external variables can influence the amount of heating applied to a polymer charge within a fixed time period. A far better method of controlling the rotational moulding cycle is to monitor the temperatures of the moulding process, particularly the internal mould temperature. The air temperature within the mould has been shown to provide a direct indication of many key stages within the moulding process: the point at which the powder begins to stick to the mould, the time at which all of the powder has melted, the peak temperature attained at the inner surface of the polymer layer, and the point at which the moulded article has solidified [6]. The peak internal air temperature (PIAT) reached inside the mould is of particular importance, as the internal temperature at which the optimum properties of the polymer are achieved has been shown to be largely unaffected by mould design, mould construction or other process variables [57]. Internal-mould temperature monitoring can be used to eliminate the trial-and-error approach to moulding and provide close, reliable control over the entire rotomoulding cycle [2].

Multi-layer moulding

"Basic" rotational moulding, as previously described, utilises a single, homogenous polymer charge to mould the desired article. However, it is sometimes advantageous to produce products made from multiple layers of different polymers, thus combining the positive attributes of two or more materials into a single moulding. This is achievable with the rotational moulding process, and is used commercially to create such items as "high-barrier" fuel tanks comprised of an outer layer of polyethylene and an inner layer of nylon [2]. To ensure that the different polymers are segregated into distinct layers within the final moulding, such techniques as multiple-stage mould charging and variation of particle size may be used. These processes are examined in more detail within the literature review section "Rotational Moulding of Thermoplastic Foams" included in this thesis.

Mould pressurisation

Rotational moulding is classified as a low-pressure process, traditionally conducted at atmospheric pressure throughout the moulding cycle [1, 2]. It is this lack of pressure which contributes to the low-cost moulds and relatively stress-free product characteristics of the rotational moulding process. However, mild pressurisation of the atmosphere inside the mould at specific points within the moulding cycle has been found by many researchers to be beneficial [2, 3, 58, 59], without negating the advantages of low-pressure moulding. The two primary benefits of mould pressurisation are shortened heating times due to accelerated bubble removal from the polymer melt, and a decreased tendency for the moulded product to warp during the cooling process. In both cases, the applied internal pressure need not be particularly high, with a pressure of approximately 10kPa judged to be adequate [3]. When pressurisation is used for the purposes of bubble removal it is typically only applied after the polymer charge has melted within the mould [2, 59], and acts to physically remove the bubbles from the molten polymer. The application of internal air pressure during the cooling stages of the rotomoulding process holds the solidifying product against the mould walls, promoting even cooling and symmetrical product shrinkage [2, 3]. Thus, warping of the product is minimised [48]. It is not desirable to excessively restrict the overall shrinkage of the polymer, as residual stresses can then be generated which lead to warping of the product at a later date [60].

Polymer Foams

Polymer foam consists of a dispersion of gas bubbles distributed throughout a solid polymer matrix [61], giving a low-density cellular material which exhibits a number of useful properties. In rotational moulding, polymer foams find application either as a mouldable material in their own right, or alternatively as partial or complete fillers for otherwise hollow rotomoulded articles. In this latter role, the addition of a suitable polymer foam can significantly improve the strength, stiffness, energy absorbing properties (shock, vibration and sound) and insulating capabilities of a rotomoulded product [62].

The polymer foams which find application in rotational moulding may be divided into two groups: those where the foaming process takes place during the rotational moulding cycle - utilising the heat and mould rotation of the process - and those foams which are injected into the product interior only after the rotomoulding cycle is complete. Foamed polyurethane is the common example from the latter processing category, and can impart useful properties to the rotationally moulded article when used as a cavity-filling material [2]. However, the incompatibility between polyurethane and rotomoulded thermoplastics - and subsequent weak interface between the two materials – severely limits the reinforcing effects of this foam type [2, 63]. In contrast, rotationally moulded thermoplastic foams, created during the rotational moulding process itself, can be closely bonded or integral with the solid polymer skin of the product. This gives much greater potential for mechanical reinforcement of the article by the foamed material.

Physical Foaming and Chemical Foaming

In order to produce a foamed thermoplastic polymer, a means of creating the dispersed gas phase within the matrix is required. Numerous methods exist which may be used to accomplish this [64], but the most widely used techniques may be divided into two groups – physical foaming methods and chemical foaming methods [61, 65]. Selection of the most suitable foaming method is highly dependent on the chosen polymer processing technique (ie. rotational moulding, compression moulding, extrusion etc).

Physical foaming of a molten thermoplastic is accomplished without the occurrence of any chemical reactions – the gas phase may be either injected into the polymer melt [61], or the required gas can be evolved in the molten polymer through the use of a physical blowing agent (PBA). These agents are dispersed throughout the matrix polymer and initiate the foaming process by undergoing a change in physical state [65]. In contrast, chemical foaming techniques utilise a dispersed chemical blowing agent (CBA) which generates the required gaseous phase via chemical decomposition [61, 65]. Each foaming method possesses useful attributes.

Although physical foaming has been applied to the rotational moulding process in some instances [66, 67], many physical foaming techniques require elevated mould pressures to be employed successfully [63, 68]. As this requirement does not align itself well with the low-pressure characteristics of the rotomoulding process, chemical foaming techniques are generally considered to be better suited than physical foaming techniques for foam processing via rotational moulding [61, 68].

The adoption of a chemical foaming method for a particular polymer system requires careful selection of a suitable blowing agent, as the final foam structure is strongly dependent on this choice [61, 63]. Chemical blowing agents are characterised on the basis of decomposition temperature (if, as is common, the decomposition reaction is thermally activated [65]), the decomposition rate, whether the decomposition reaction is endothermic or exothermic, and by the amount of gas generated [63]. A common choice for the foaming of rotationally moulded polyolefins, and widely recognised as the leading chemical blowing agent around the world [69], is azodicarbonamide [2, 69, 70]. This is an exothermic-decomposing powder which yields approximately 230ml of gas (measured at standard temperature and pressure) per gram of solid material [2], corresponding to approximately 32% of the original powder mass. The gas evolved is a mixture of about 65% nitrogen, 32% carbon monoxide and 3% other gases – including ammonia and carbon dioxide [69]. Unmodified azodicarbonamide decomposes rapidly and completely within the 195-215ºC temperature range [2], but this activation temperature may be lowered through changes to the particle morphology or by the addition of catalysts [69]. Combining the azodicarbonamide powder with the matrix thermoplastic prior to rotational moulding may be accomplished either by dry-blending or extrusion-based melt compounding techniques [71].

Despite the continuing popularity of azodicarbonamide as a chemical blowing agent, it is currently being challenged by endothermic CBA's in a variety of applications [70]. Endothermic chemical blowing agents are not subject to the toxicity concerns that restrict the use of azodicarbonamide in food-contact materials [70], react in a more controlled manner due to their heat-absorbing nature, and produce a finer-celled foam structure than is achievable with exothermic CBA's [70]. A fine-celled structure with a narrow cell-size distribution improves the tensile strength of the foam as well as giving a smooth surface appearance [63, 70]. It is expected that due to both technical and regulatory concerns, the usage of endothermic CBA's will continue to grow more rapidly than the usage of exothermic CBA's [70].

Rotational Moulding of Thermoplastic Foams

As mentioned previously, thermoplastic foam mouldings may be created which do not incorporate any layers of solid, unfoamed polymer. This review, however, focuses on thermoplastic foam encapsulated within a rotomoulded solid-polymer shell for the purposes of enhancing the properties of the original moulding.

Rotationally moulded thermoplastic foams have been successfully produced from a number of different polymers, including polypropylene [68, 72, 73], polystyrene

[66] and various grades of polyethylene [61, 62, 74, 75]. It is foamed polyethylene which appears to be predominant within literature, as might be expected given the global popularity of unfoamed polyethylene in the rotomoulding industry and the desire to achieve a strong bond between the foamed and unfoamed polymer layers. Regardless of the type of foamed polymer, however, the processing principles are near identical when using such foams for reinforcing hollow mouldings.

As both the solid and foamed-polymer layers of a multiple-layer moulding are created during a single rotomoulding cycle, a strategy is needed to ensure that the two material types form discrete layers and not a partially-foamed mix. One method of achieving this is to delay the introduction of the foamable material into the mould until part-way through the heating stage of the rotomoulding cycle. This gives time for the original, non-foaming polymer charge to be distributed onto the mould walls and form the outer skin of the product. The thermoplastic/blowing agent mix can then be deposited into the mould, where it will adhere to the existing polymer layer due to the continuing mould rotation and heating. Early in the development of skin/foam rotational moulding, deposition of this second “shot” of material into the mould was achieved manually [61], involving removal of the mould from the oven and introduction of the foamable polymer through a trap-door [61] or vent tubes [2] in the mould. An improvement on this manual method was patented in 1990 [61], whereby the foamable polymer charge is contained within an insulated “drop box” attached to the primary mould. Remote control can then be used to transfer the shot from the drop box to the mould interior at the desired point within the rotomoulding cycle, without interruption of either heating or mould rotation. Another method of sequentially charging the mould without delaying the process has also been developed, whereby the foamable charge is contained within a flexible plastic bag and placed within the mould at the start of the process. The plastic bag is constructed so that it will rupture under certain thermal conditions during moulding, thus releasing the charge at the correct stage within the process [2, 73].

As an alternative to sequentially charging the mould, it is also possible to achieve segregation of the skin and foam layers via a single-shot process – where the two material types are mixed together in the mould before heating begins. The polymer charge intended to form the outer skin of the product must then separate itself from the foamable polymer during the moulding process, so that the layered structure is retained in the final product. A common method of achieving this is to use foamable polymer pellets, while the non-foaming charge is retained as a conventional powder [2, 72]. In principle, this difference in particle size ensures that the finely ground non-foaming polymer is preferentially laid down on the mould wall, while the larger pellets of foamable polymer form the inner layer.

Regardless of which method is used to distribute the foamable polymer within the moulding, it is important that, firstly, the adhesion of the non-foaming polymer layer to the mould interior precedes the adhesion of the foamable polymer charge, and secondly, that the polymer to be foamed undergoes lay-up, sintering and coalescence before decomposition of the chemical blowing agent. If the blowing agent activates before the foamable polymer matrix has formed a homogenous melt, a portion of the generated gases may be lost and expansion of the foam may be incomplete [68]. When the foamable polymer has been correctly distributed on the mould walls before the blowing process begins, the foaming reaction will proceed from the mould wall towards the centre of the moulding [68]. The amount of foamable polymer and the ratio of expansion will determine whether the foam layer completely or only partially fills the product cavity.

Once the foaming process has been initiated, it is desirable to utilise only the minimum of heating necessary to achieve full expansion of the foam [63]. This is both for economic reasons and because extending the heating stage beyond this point is detrimental to the foam structure itself [63]. It has been previously mentioned that a small cell size and narrow size distribution are desirable attributes for polymer foam, and excessive heating is known to result in cell coalescence and cell coarsening within the foamed structure [63]. However, the heating requirements of the foam fraction must be balanced against those of the outer polymer skin, where extended heating is often necessary to ensure a satisfactory degree of bubble removal. Further allowances should be made for the decreased cooling rate that results from the inclusion of foam within a rotomoulded product [2, 74], and the subsequent increase in overall cycle time.

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Chapter 3: Methodology

The development and optimisation of the processing and testing methods detailed in this chapter was, in itself, a significant part of the overall research effort. In many cases, these methods were continually modified and improved over the course of the project. Although these progressive developments are detailed in order for each technique, it must be noted that there is no implied chronological order between the individual groups of related methods.

Materials

Below is a list of the primary materials used in the course of this research. The data listed under each product tradename is reproduced from the commercial data sheets for each material.

Polymers

Basell Polyolefins Moplen HP640S – Polypropylene Homopolymer (HPP)

Injection moulding grade *Obtained form:* Granules
Melt flow index: 45g/10 min (ISO 1133 – 2.16kg / 230°C)
Density: 0.905 g/cm^3 (ISO 1183)

Basell Polyolefins Moplen HP741T – Polypropylene Homopolymer (HPP)

Injection moulding grade *Obtained form:* Granules
Melt flow index: 60g/10 min (ISO 1133 – 2.16kg / 230°C)
Density: 0.905 g/cm^3 (ISO 1183)

Borocene Compact™ RM8346 – Linear Medium Density Polyethylene (LMDPE)*

Rotational moulding grade – Metallocene-catalysed polyethylene
Obtained form: Powder
Melt flow index: 6.0g/10 min (ISO 1133 – 2.16kg / 190°C)
Density: 0.934 g/cm^3 (ISO 1183)

* General characteristics of LMDPE are as described for MDPE (section 2.3)

Cotene 3923 – High Density Polyethylene (HDPE)

Rotational moulding grade – Octene-copolymer polyethylene .

Obtained form: Powder

Melt flow index: 2.0g/10 min (ASTM D1238 – 2.16kg / 190°C)

Annealed density: 0.942 g/cm^3 (ASTM D1505)

Cotene 3924 – Linear Medium Density Polyethylene (LMDPE)*

Rotational moulding grade – Octene-copolymer polyethylene .

Obtained form: Powder

Melt flow index: 4.6g/10 min (ASTM D1238 – 2.16kg / 190°C)

Annealed density: 0.938 g/cm^3 (ASTM D1505)

Cotene 3979 – High Density Polyethylene (HDPE)

Rotational moulding grade *Obtained form:* Powder

Melt flow index: 4.5g/10 min (ASTM D1238 – 2.16kg / 190°C)

Annealed density: 0.947 g/cm^3 (ASTM D1505)

Cotene 9042 - Linear Medium Density Polyethylene (LMDPE)*

Rotational moulding grade *Obtained form:* Powder

Melt flow index: 4.0g/10 min (ASTM D1238 – 2.16kg / 190°C)

Annealed density: 0.939 g/cm^3 (ASTM D1505)

Cotene 9800 – Polypropylene Copolymer (CPP)

Rotational moulding grade *Obtained form:* Powder

Melt flow index: 13.0g/10 min (ASTM D1238 – 2.16kg / 230°C)

Annealed density: 0.900 g/cm^3 (ASTM D1505)

Dow Plastics DOWLEX 2517 – Linear Low Density Polyethylene (LLDPE)

Injection moulding grade *Obtained form:* Granules

Melt flow index: 25g/10 min (ASTM D1238 – 2.16kg / 190°C)

Density: 0.917 g/cm^3 (ASTM D792)

ExxonMobil HMA 018 – High Density Polyethylene (HDPE)

Injection moulding grade *Obtained form:* Granules

Melt flow index: 30g/10 min (ASTM D1238 – 2.16kg / 190°C)

Density: 0.954 g/cm^3 (ASTM D4703 / D1505)

Vanglobe Rotathene® Octene 8539 – Linear Low Density Polyethylene (LLDPE)

Rotational moulding grade – Octene-copolymer polyethylene

Obtained form: Powder

Melt flow index: 5.2g/10 min (ASTM D1238 – 2.16kg / 190°C)

Density: 0.939 g/cm^3 (ASTM D1505)

Foamable polymers

Cotene 9031BA4 – Polyethylene / Blowing agent Blend

Obtained form: Powder *Blowing agent:* Exothermic-decomposing chemical type

Activation temperature: ~150ºC *Foam density:* 0.24 g/cm^3

Cotene 9031BA8 – Polyethylene / Blowing agent Blend

Obtained form: Powder *Blowing agent:* Exothermic-decomposing chemical type

Activation temperature: ~150ºC *Foam density:* 0.12 g/cm^3

Coupling agents

Clariant Licocene® PE MA 4221 – Maleic anhydride grafted Polyethylene Wax

Metallocene catalysed *Obtained form:* Fine granules

Degree of grafting/modification: Low *Drop point:* 125ºC

Clariant Licocene® PE MA 4351 – Maleic anhydride grafted Polyethylene Wax

Metallocene catalysed *Obtained form:* Powder

Degree of grafting/modification: High *Drop point:* 125ºC

Clariant Licocene® PE SI 3361 – Trimethoxy vinyl silane grafted Polyethylene Wax

Metallocene catalysed *Obtained form:* Fine granules

Degree of grafting/modification: High *Drop point:* 115ºC

Clariant Licocene® PP MA 6252 – Maleic Anhydride Grafted Polypropylene Wax

Metallocene catalysed *Obtained form:* Granules

Degree of grafting/modification: High *Drop point:* 140ºC

Clariant Lab sample H11339 – Maleic Anhydride Grafted Polypropylene Wax

Metallocene catalysed *Obtained form:* Powder

Degree of grafting/modification: High *Drop point:* 156ºC

Honeywell A-C 950P – Maleic Anhydride Grafted Polypropylene

Obtained form: Powder

Degree of grafting/modification: Unknown

Fibres

“Lab Glass” glass fibre – 700 tex glass-fibre roving. Unknown composition and sizing.

Nylon-6 fibre – Obtained as rope from Nautilus Braid Ltd, Christchurch, New Zealand

Polyethylene terephthalate (PET) fibre - Obtained as rope from Nautilus Braid Ltd, Christchurch, New Zealand

Vectran (polyester-polyarylate liquid crystal polymer) fibre

Obtained as yarn from Braidmakers Ltd, Auckland, New Zealand

Specific gravity: 1.41 *Melting point:* 330°C

Tenacity: 23 grams per denier

Owens Corning 415A CRATEC Glass Fibre – Chopped Strands CS04-415A-14C

Reinforcement for polyethylene *Chop length:* 4mm

Fibre diameter: 14µm *Specific gravity:* 2.52-2.68 (ASTM D1505)

Miscellaneous

Clariant Licowax OP P – Partly saponified ester of montanic acids

Lubricant additive – for flow promotion, release effect and/or improved surface finish of elastomers, thermosets and engineering resins. *Obtained form:* Powder

Density: 1.01-1.03g/cm^3 (20ºC) – DIN 53479

Drop forming point: ~101ºC – DGF-M-III 3

Flash point: ~220ºC – DIN 51758 (closed cup)

Kraton Polymers MD-6932 – Styrenic Block Copolymer

Hydrogenated styrene-ethylene/butylene-styrene (SEBS) midblock

Polyolefin modifying additive *Obtained form:* Pellets

Melt flow index: 16-18g/10 min (230ºC, 2.16kg)

Paraffin Liquid – APS Finechem, a division of Asia Pacific Specialty Chemicals Limited

Density: 0.87-0.89g/mL *Obtained form:* Liquid

MAC-787/2 water-based semi-permanent release film (organic resin water emulsion)

McLube Division, McGee Industries Inc. *Obtained form:* Liquid

Water based emulsion of a film forming resin which cures to form a colourless, non-oily, chemically inert and thermally stable film coating designed to release rotationally moulded parts and materials.

Antioxidants/processing stabilisers

Ciba Specialty Chemicals IRGANOX® 1010 – Phenolic Primary Antioxidant

Sterically hindered phenolic antioxidant *Obtained form:* Powder

Melting range: 110-125°C *Flashpoint:* 297ºC

Specific gravity (20ºC): 1.15g/cm^3

Ciba Specialty Chemicals IRGAFOS® 168 – Phosphite Processing Stabiliser

Hydrolytically stable phosphite processing stabiliser / secondary antioxidant *Obtained form:* Powder *Melting range:* 183-186°C

Specific gravity (25ºC): 1.03g/cm^3

Materials Handling

Polymer and Fibre Storage

Throughout the course of this research, the polypropylene, polyethylene and fibrous reinforcement materials were stored without temperature or humidity control within the laboratory environment. Exposure to sunlight was restricted. This was judged to be representative of a commercial production environment and did not conflict with the storage recommendations of the various material manufacturers. Tests showed that the moisture uptake of these materials was negligible during storage, and as such, both the fibres and polymers were processed in most cases without further drying.

Mixing of Materials

Prior to compounding and/or moulding, all material combinations were thoroughly mixed by hand and by shaking within a sealed container. Latex gloves were worn when necessary to prevent contamination of the materials.

Extrusion Compounding

A ThermoPrism TSE-16-TC co-rotating twin-screw extruder (16mm bore, 15.6mm screw diameter, L/D ratio 25:1) was used for melt compounding of a range of composite materials. This extruder is pictured in Figure 3.1.

Figure 3.1: The ThermoPrism TSE-16-TC extruder used over the course of this research.

Temperature control of this extruder is separated into five zones down the length of the barrel and die, each of which is controlled independently. A pressure transducer is fitted at the die to ensure that pressures remain at safe levels during operation. Screw speed is variable in the range of 0-500rpm, and the barrel is ported in three locations for the installation of barrel vents or other accessories. Material input may be accomplished via vibratory feeder, and a range of dies can be fitted. Those dies used for melt-compounding during this investigation were all of the single, circular aperture type, with aperture diameters of 10mm, 6mm, 3mm and 1.5mm utilised. The specific extrusion parameters used for each material are recorded in the Results and Discussion chapter of this thesis.

Granulation and Micronising

A Castin granulator was used to convert extruded material into a form suitable for rotational moulding, injection moulding, thermal analysis, flow analysis, or micronising. This granulator was fitted with either a 6mm or 8mm aperture screen which provided an upper limit to the produced granule size, with the overall granule size distribution found to be largely dependent on the form of the material input. When used to granulate material extruded using the 6mm or 8mm dies, angular granules of irregular size were found to result. Material extruded through the 3mm and 1.5mm extrusion dies prior to granulation, however, was found to yield granules which were more regular in both size and shape. After granulation, the material was sieved to eliminate unwanted size fractions, and in some cases passed through the microniser to give the granules a more rounded, equiaxial morphology (see below). The characteristics of the granules used in each of the subsequent moulding and test processes are given in the Results and Discussion chapter of this thesis.

Where necessary, a Powder King PK-18 Pulveriser/Microniser was used to grind both polymers and composites to fine powders. As the powders produced were never directly rotomoulded, the constraints on particle morphology which are necessary to ensure successful powder flow during rotational moulding [2] did not apply. Therefore, no attempt to examine or control the particle morphology was made. The microniser was also used in some instances to round the angular composite granules produced by the granulator, giving a more regular granule size and improved packing density. The spacing between the grinding plates was set at 0.5mm for grinding powder and 3mm when rounding granules.

Rotational Moulding

Micro-oven

During the course of this research, rotational moulding was conducted using two different sets of moulding equipment. The simpler of these two sets, termed the “micro-oven”, was used only for certain trials early within the project before being superseded by more sophisticated equipment. Fabricated by ITS Ltd for the purposes of small scale development work, the micro-oven rotomoulding setup was based on a small, electrically heated oven - as might be found in a domestic kitchen. This was modified to allow closed-loop computer control of the oven temperature, and variable-speed, uni-axial rotation of a small mould within the oven confines. During moulding, the mould internal air temperature was monitored with a hand-held digital thermometer and thermocouple probe. The micro-oven setup is shown in Figure 3.2.

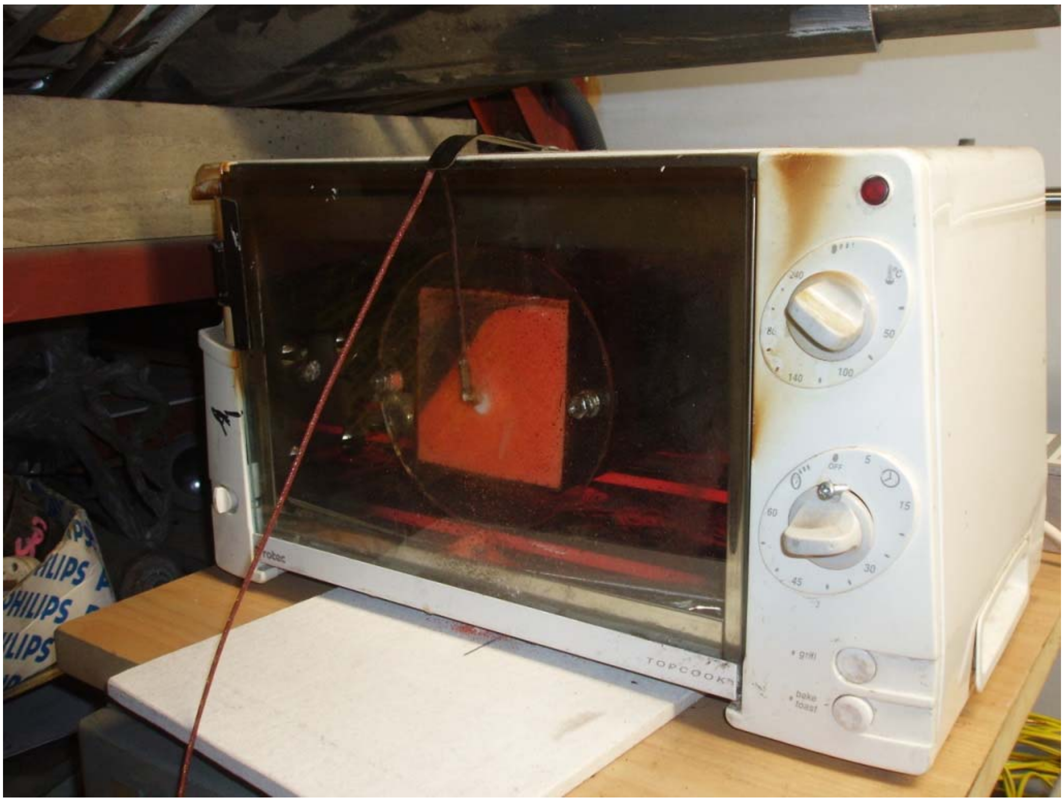

Figure 3.2: The "micro-oven" rotational moulding apparatus.

The mould used in the micro-oven was of square cross-section with internal dimensions of 90mm x 90mm x 152mm *(152mm length along mould rotation axis)*. Mould construction was of 3mm thick mild steel, with removal end-plates to allow charging of the mould and removal of the moulded article. The tempered-glass end-plate which can be seen in Figure 3.2 was temporarily installed to allow visual observation of the moulding process (the unmelted polymer charge contained within the rotating mould may be clearly seen in this picture), but was not used during the moulding of tested specimens. A hole drilled in the centre of the outermost end-plate (as can be seen facing forward in Figure 3.2) allowed passage of the temperature probe and also acted as a vent, so that the mould interior remained at atmospheric pressure during the moulding process. This hole could be manually cleared in the event that it became blocked with molten polymer.

The moulding procedure utilised with the micro-oven equipment was as follows: *(Please see the Results and Discussion chapter of this thesis for the specific process settings used for each batch of specimens)*

- Firstly, the mould was removed from the micro-oven, disassembled, and all interior surfaces coated with MAC-787/2 mould release agent in accordance with the manufacturers application instructions. Re-treating of the mould with the release agent was performed as necessary (typically a light application every five moulding cycles).

- The mould was then reassembled, charged with the desired amount of polymer powder and threaded onto the drive-spindle inside the micro-oven. All equipment components were at room temperature at this stage.

- With the temperature probe in place and the oven door closed, computer control was used to raise the temperature inside the oven and maintain it at the desired level. Mould rotation was started as soon as heating began.

- Heating was continued until the mould internal air temperature had reached the desired value, at which time the oven door was opened, heating ceased, and a fan used to cool the mould exterior. The temperature of the air inside the mould would continue to rise for a short period after the cessation of heating, reaching peak internal air temperature (PIAT) several minutes after the cooling process had begun. Estimation of the magnitude of this temperature overrun was based on previous experience, allowing the target PIAT to be attained with a reasonable degree of accuracy (±3ºC).

- Once the desired de-moulding temperature had been reached, mould rotation and fan cooling were ceased. The mould was removed from the oven, disassembled, and the moulded specimen removed. All equipment was allowed to cool to room temperature before beginning another moulding cycle.

Although the micro-oven rotomoulding setup was not a perfect simulation of a commercial rotational moulding process, it proved sufficient for the purposes of basic material evaluation while incurring minimal running costs.

Research & Development System

The purpose of the rotational moulding setup referred to as the "Research & Development System" (R&D System) at ITS Ltd was to replicate the production rotational moulding process, so that development work could be accurately conducted without occupying the equipment devoted to actual production. To this end, the R&D system is significantly more sophisticated than the aforementioned micro-oven and is suitable for use with much larger moulds. The R&D system is shown in Figure 3.3.

Figure 3.3: The "R&D System" rotational moulding setup

This equipment consists of a LPG-fired oven (the oven chamber is behind the black door marked “R+D system” in Figure 3.3) and movable turret system, which allows the mould (which is clamped onto the grille plate seen in Figure 3.3) to be placed into and removed from the oven as necessary without interrupting mould rotation. The turret allows for full biaxial rotation of the mould with independent speed control for each axis. Oven temperature is computer controlled, with the computer also providing data logging of the mould internal air temperature, external mould temperature, and oven temperature throughout the entire rotomoulding cycle. Air-cooling of the mould is accomplished using a bank of fans placed outside the oven chamber.

A multitude of different moulds may be successfully used with the R&D system, but the mould utilised for the majority of this research was the previously described cuboid mould of internal dimensions 90mm x 90mm x 152mm, which was constructed from 3mm thick mild steel and with removable end-plates. This mould was chosen as it produces a moulding of sufficient size for subsequent mechanical testing with minimal consumption of material – an important factor given the time-consuming preparation needed for some material samples. Several modifications to the mould were necessitated by the transition from micro-oven to R&D system, including fitting an improved temperature probe for monitoring of mould internal air temperature, addition of a vent tube/air inlet for both mould venting and mould pressurisation when desired, and fabrication of a port in one of the end-plates to allow multi-shot mould charging without removal of the end-plate in its entirety. This mould is shown fitted to the turret of the R&D system in Figure 3.4, with the compressed-air line for mould pressurisation visible running down from the top centre of the frame, and the temperature probe entering the right-hand end of the mould.

Figure 3.4: The small sample-mould fitted to the turret of the R&D system rotational moulding equipment.

The only other mould used during the course of this research was a cuboid mould with internal dimensions of 50mm x 140mm x 640mm, also constructed of 3mm thick mild steel. This mould was used for the production of several foamed polyethylene samples, where a larger moulding was desired for testing purposes and direct comparisons between samples from the two different moulds were not required.

The operating procedure of the R&D system was as follows: *(Please see the Results and Discussion chapter of this thesis for the specific process settings used for each batch of specimens)*

- As described in the operating procedure for the micro-oven, the mould was first coated with release agent if necessary.

- The reassembled mould was charged with material, bolted onto the turret and connected to the temperature probe and pressurisation lines (if pressurisation was to be applied during the mould cycle). The oven was preheated at this stage to approximately 280ºC.

- With the oven at the desired temperature, the oven was opened and the mould wheeled in. Mould rotation commenced immediately, and the oven set temperature was then raised to 300°C.

- As with the micro-oven, the duration of the heating stage was judged on the basis of the temperature of the air inside the mould. If the moulding was single shot (i.e. no additional material added to the mould after heating began), then this stage was continued until the desired PIAT (minus allowance for temperature overrun due to delayed heat conduction) was reached. With two-shot mouldings, the mould was removed from the oven as soon as the first material charge had finished melting, as indicated by a rapid rise in mould internal air temperature. Mould rotation was then stopped long enough for the port in the mould to be opened and the second shot of material funnelled in. The mould could then be returned to the oven and heating continued until the desired peak temperature had been reached.

- At the cessation of the heating stage, the mould was removed from the oven and allowed to cool either with or without fan assistance. The use of fans hastened the cooling process, but was found to result in unacceptable levels of product warpage with some materials. In these cases, the mould was allowed to partially cool before the fans were switched on. The parameters of the cooling process used for each material are listed in the Results & Discussion chapter of this thesis alongside the relevant results.

- In the instances that mould pressurisation was used to minimise the occurrence of product warpage, compressed air at a pressure of approximately 10psi (~70kPa) (gauge pressure, not absolute pressure) was supplied to the mould interior immediately after the mould was removed from the oven. This pressure was then maintained for the duration of the cooling cycle. 70kPa is a significantly higher pressure than the ~10kPa recommended by Crawford et al. [3], but this value has been found to be effective by ITS Ltd during previous work. Pressurisation of the mould during the heating stage of the rotomoulding process, in order to aid in bubble removal from the polymer melt, was also attempted but found to be inadvisable. The high MFI polymers in use at that time were found to leak from the mould joins when an internal pressure of 70kPa was applied, creating a dangerous situation as molten polymer was dispersed within the confines of the oven. Whether this problem would arise with more viscous polymers or lower pressures was not investigated.

- Once the desired de-moulding temperature had been reached, mould rotation, fan cooling and mould pressurisation were ceased. The mould was disconnected from the turret, disassembled, and the moulded specimen removed. All equipment was allowed to cool to room temperature before beginning another moulding cycle.

Figure 3.5 shows the temperature traces logged during a typical single-shot moulding conducted with the R&D system. This particular moulding was of Cotene 9800 polypropylene copolymer with a targeted PIAT of 250ºC, but the characteristic features of the plot are common to the moulding of many materials.

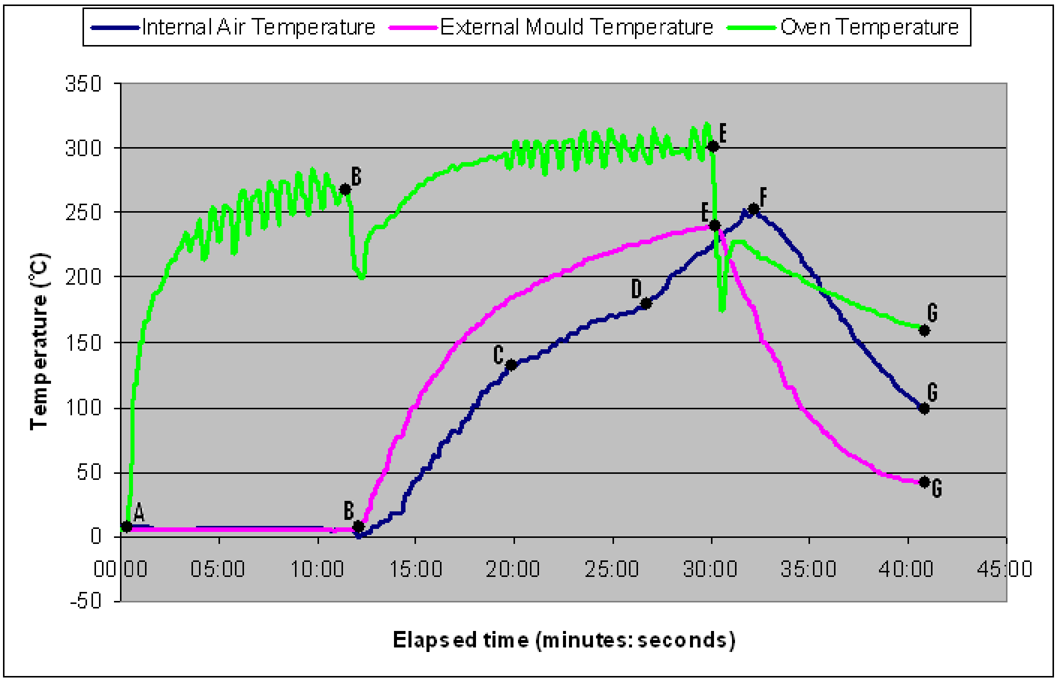

Figure 3.5: Plot of temperature data logged during a typical single-shot rotomoulding cycle.

On this plot, point A indicates the time at which pre-heating of the oven was started, with the mould and turret removed. Point B corresponds to when the charged mould was introduced into the pre-heated oven, as evidenced by a rise in both external-surface and internal-air mould temperatures and a brief dip in oven temperature as the oven door was opened. Mould internal air temperature then rises at a relatively steady rate until point C is reached, where melting of the polymer charge and its adherence to the walls of the mould begins. The rate at which the internal temperature is seen to rise decreases during this process, due to the energy requirements of the solid-liquid transformation. Once the melting stage is complete - point D - the internal air temperature of the mould rises sharply again. The melt plateau of this example plot is not as well defined as was seen for some other mouldings, but can nevertheless be distinguished with a reasonable degree of accuracy. Point E marks the time at which heating was ceased and the mould removed from the oven. This point was calculated as the value of internal mould air temperature which would allow the correct PIAT to be reached – in this case 250ºC. PIAT temperature is marked by point F, and as can be seen, is attained significantly after the cessation of direct heating. This is due the delayed conduction of heat through the mould walls and the molten polymer layer to the mould interior where the temperature probe is located. Once PIAT has been reached, the mould and product are cooled until the product may be demoulded. This marks the end of the rotomoulding cycle and is indicated by point G.

It may be observed from Figure 3.5 that the external mould temperature is more rapidly influenced by the application of heating and cooling than the temperature inside the mould, as might be expected. The plot of external mould temperature does not appear to indicate the occurrence of polymer melting or record rises in the temperature of the polymer layer after heating has ceased. With the rotomoulding and data logging equipment used during the research, monitoring of the external mould temperature proved to be of limited practical value. The oscillation in oven temperature which may also be noted from Figure 3.5 is a characteristic of the oven control system.

As multi-shot moulding was also utilised during this research, a plot of internal mould temperature during a two-shot rotomoulding process is shown in Figure 3.6. Several points of difference exist between the single-shot and two-shot temperature plots, although the major process stages may be still be recognised. For clarity, the plot of external mould temperature has been omitted.

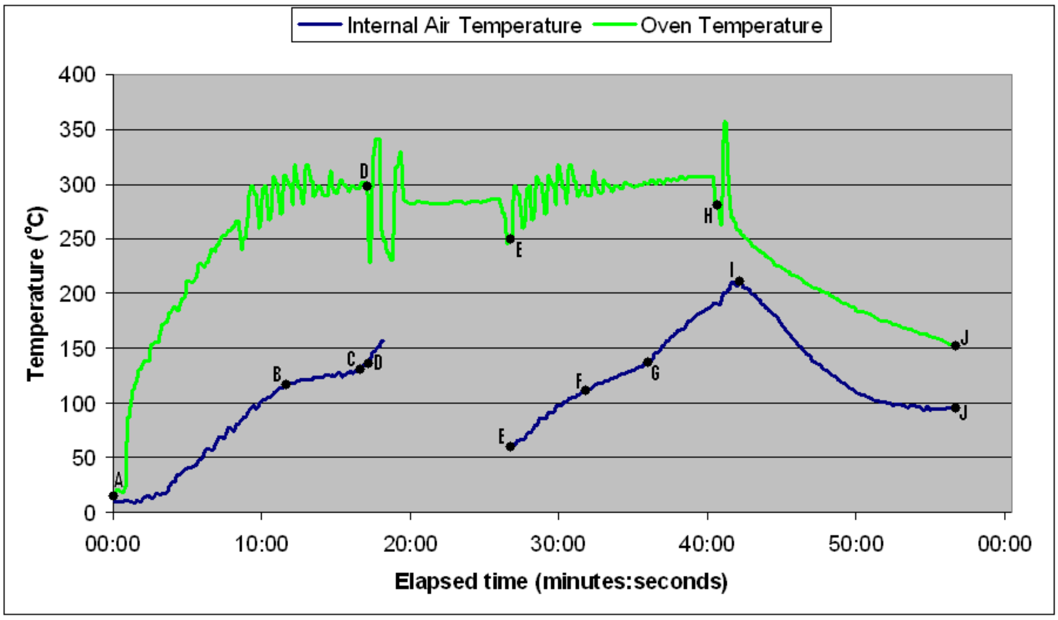

Figure 3.6: Plot of temperature data logged during a typical two-shot rotomoulding cycle.

As with the previous example, the introduction of the mould into the rotomoulding oven (point A) causes a rapid rise in mould internal temperature until melting of the initial polymer charge begins (point B). Heating is continued until the melting process is complete (point C), but the mould is then removed from the oven as soon as the end of the melt plateau is confirmed (point D). With the mould removed from the oven, the second charge of material (a non-foaming polyethylene in this case) may be placed within the mould. The mould is then returned to the oven (point E) and heating is continued. The gap in internal air temperature data between points D and E that may be seen in Figure 3.6 is due to disconnection of the internal air temperature probe during the charging process. Once the second charge of material has been deposited within the mould, the temperature plot then follows the characteristics of the previously described single-shot process: melting of the second polymer charge between points F and G, removal of the mould from the oven at point H, PIAT reached at point I, and de-moulding of the product at point J.

Melt-flow Simulation

Determination of the rotational moulding processability of any particular material is probably best achieved, naturally enough, by actual rotational moulding trials. However, such trials require a considerable amount of both material and time while not allowing for easy visual observation of the granule sintering and coalescence processes. For these reasons, an alternative technique was needed for investigation of the rotomoulding characteristics of the materials under development.

The method developed in response to this need was based on the use of a controlled-temperature laboratory hotplate, upon which samples of material could be heated under low pressure and shear conditions representative of those encountered in the rotational moulding process. It was deemed important that the heat flow through the sample mimicked that of the rotational moulding process as closely as possible, where the heat is applied to the outer layer of the polymer moulding and is progressively conducted through to the mould interior. It was also desired that the rotational moulding simulation would allow some estimation of the corresponding mould internal air temperature in the rotomoulding process, thus aiding the correlation of results between the two methods. The setup illustrated in Figure 3.7 was fabricated in order to achieve this.

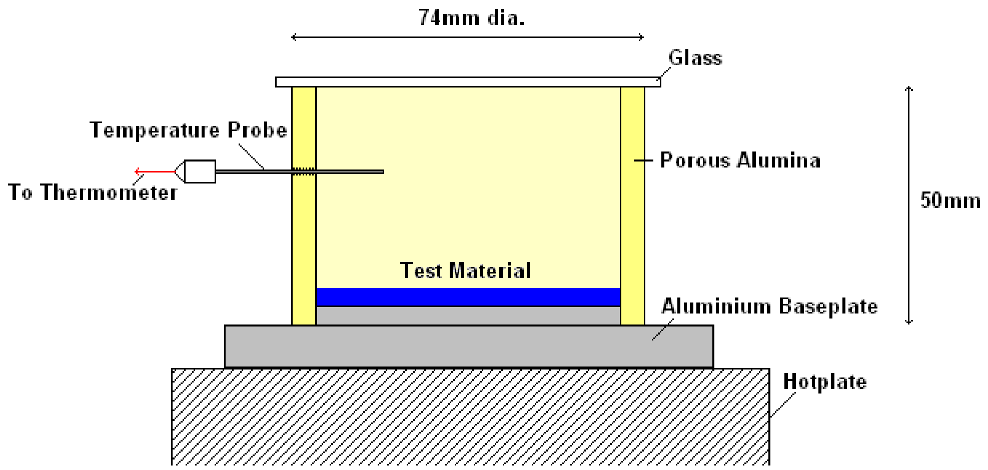

Figure 3.7: A cross-sectional view of the equipment developed for rotomoulding melt-flow simulation.

The construction of this chamber consisted of a circular aluminium baseplate upon which was placed a short length of porous alumina tube (5mm wall thickness) and a heat-resistant glass lid. Due to the insulating nature of the porous alumina, this construction ensured that the polymer or composite charge was heated predominantly through the aluminium baseplate, analogous to the process by which the polymer layer is heated during rotational moulding. Insulation of the sides and top of the chamber was also intended to allow the air temperature within the sample chamber to closely reflect the temperature at the surface of the polymer, rather than be influenced by the conduction of heat through the chamber walls. The air temperature within the sealed chamber was monitored using a digital thermometer and a temperature probe inserted through a hole drilled into the alumina wall of the chamber. The method used to establish the melt-flow behaviour of polymer and composite samples was as follows:

- The hotplate was first preheated to a temperature of 300ºC, corresponding to the oven set temperature used in the rotational moulding process.

- Once the hotplate was at temperature, 15g of the chosen powder or granules were measured into the chamber and distributed evenly across the chamber baseplate. This charge weight was calculated to correspond to a final layer thickness of approximately 5mm. The chamber was then capped and placed on the hotplate.

- The chamber remained on the hotplate until a satisfactory degree of particle coalescence was observed through the glass lid of the chamber, at which point the elapsed test time, internal air temperature and polymer surface temperature were noted. This latter measurement was taken using an infrared thermometer. In the case that successful coalescence was not observed, heating was allowed to continue until the temperature of the polymer rose above that considered reasonable for the rotomoulding process. This was often accompanied by visual indications of significant thermal degradation of the polymer. The test was terminated at this point.

- Once the test was complete, the material sample could be cooled and removed from the chamber for later examination.

This method was successfully used to assess the melt-flow behaviour of a range of polymer and composite materials under simulated rotational moulding conditions. The technique was found to give a reliable indication of whether the chosen material would flow and coalesce satisfactorily at any point throughout the rotational moulding cycle, or whether coalescence would remain incomplete before the onset of major thermal degradation. Relating the temperature data from the test method to the rotational moulding process was found to be unreliable, however, and this problem was not successfully resolved during the time that the test was utilised. Despite this, the simulation technique was found to be a valuable tool during the material development process.

Extrusion of Test Specimens

As is outlined in this chapter, the processes by which a melt-compounded composite material may be rotationally moulded, machined and mechanically tested are both time consuming and labour intensive, making this method impractical for testing a large number of material combinations within a limited time. For these reasons, alternative processing and testing methods were developed for use during the initial “material screening” trials (Section 4.3) conducted in the early stages of this project.

The criteria for the selection of an alternative production method to rotomoulding were twofold: that a significant decrease in sample production time could be achieved, and that the results obtained - showing the mechanical performance of the different material combinations relative to one another - would remain applicable to the rotomoulding process. Compression moulding of material sheets was considered as a likely processing method, but was disregarded due to equipment complications and the requirement that individual test specimens must still be prepared using time consuming machining processes. Injection moulding of melt-compounded composite granules, while allowing rapid production of test specimens without machining, subjected the material to additional high pressure and high-shear conditions which would otherwise not be present during the production of rotationally moulded composites. It was felt that the application of such forces may invalidate the test results, by introducing a bias against those fibres prone to breakage under high shear conditions. For these reasons, it was decided that the most suitable sample production method would be to adapt the extrusion compounding process for the direct production of test specimens. Although this technique differs markedly from rotational moulding, extrusion compounding comprises a step in the rotomoulded composite production process and so determining the material performance at this processing stage was felt to be relevant.

The extruder used for this process was the same ThermoPrism TSE-16-TC as used for all other melt compounding during the course of this research, the details of which are given in section 3.3. It was found, however, that the existing circular-aperture dies for this extruder were unsuitable for the production of test specimens. This was due to the extruded material warping extensively as it cooled, even when the extrudate was supported as it exited the extruder die. The solution to this problem was to extrude the molten composite directly into a tube, such that the material was constrained upon cooling and could not warp to any significant extent. The new extrusion die and associated equipment which were machined to achieve this are shown fitted to the extruder in Figures 3.8 and 3.9.

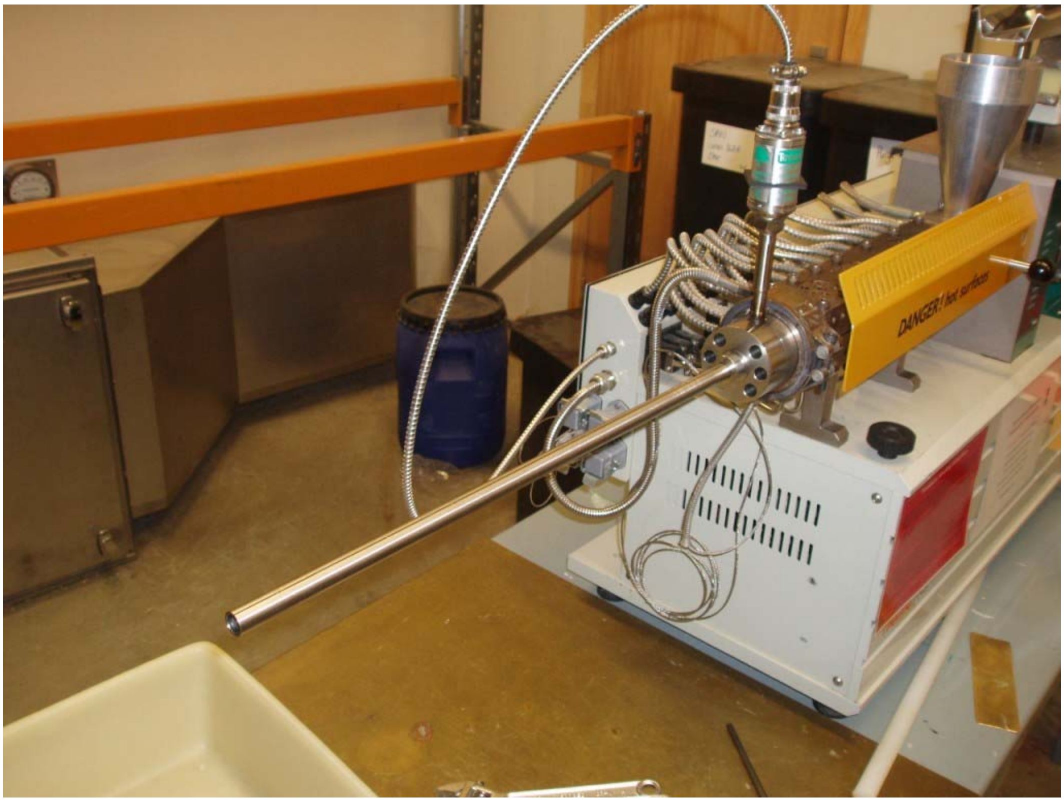

Figure 3.8: The rod-extrusion apparatus fitted to the extruder

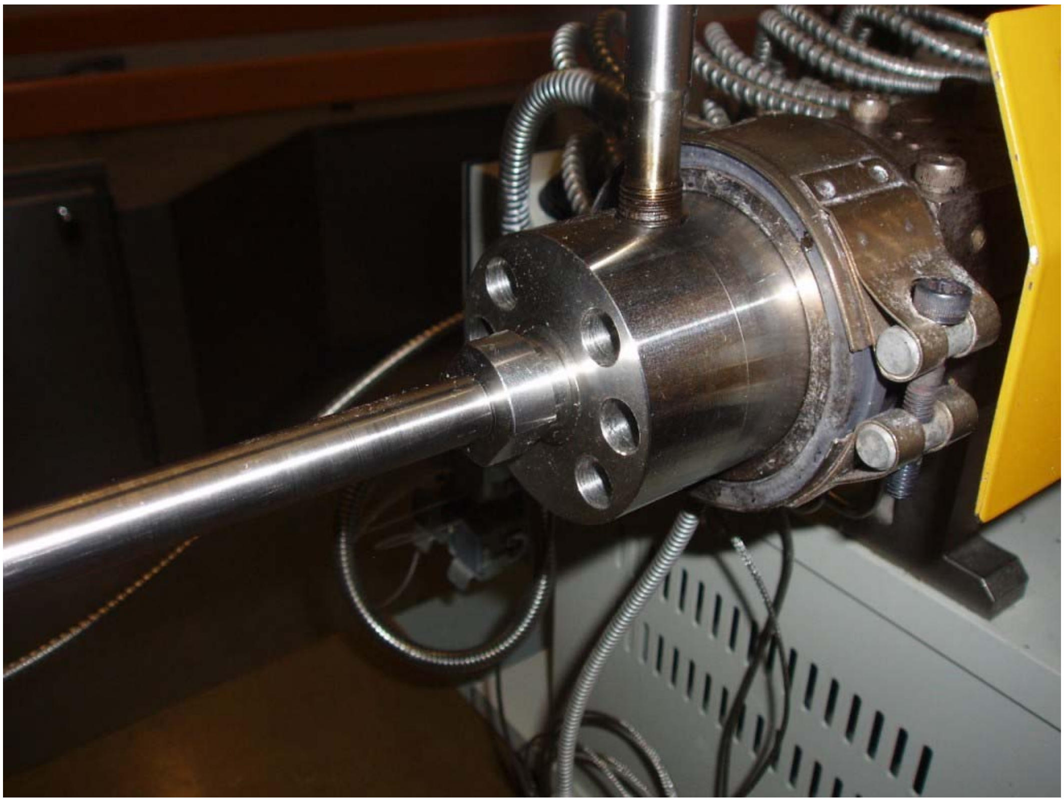

Figure 3.9: Close-up view of the rod-extrusion apparatus

This apparatus consisted of three primary elements; the die itself, the extrudate tube, and the adaptor used to connect the two. The method by which test specimens were produced using this equipment was as follows: *(Please see the Results and Discussion chapter of this thesis for the specific process settings used for each batch of specimens)*

- Prior to extrusion, the material sample was thoroughly mixed to ensure even dispersion of all material components. The extrudate tube was coated internally with MAC-787/2 mould release agent, which was re-applied when necessary between sample production runs. The extruder and associated attachments were then preheated to processing temperature, with insulation placed around both the extrudate tube and the die in order to minimise heat loss from these components. Despite this, the extrudate tube remained relatively cool during the extrusion process.

- With the equipment at operating temperature, material was manually fed into the extruder where it was melt compounded and extruded into the attached tube. The rate by which material could be passed through the extruder was limited by the torque limits of the extruder motor. Material feeding was conducted as fast as possible in order to maximise the length of the extruded specimen produced before solidification of the material occurred within the extrudate tube. As solidification occurred, the operating pressure at the extruder die would exceed safe limits and force the process to be halted.

- Once allowable pressure had been exceeded or the extruded material had completely filled the extrudate tube, the tube could be unscrewed from the die and cooled. The solidified sample rod could then be gently tapped out and machined into test specimens as described in section 3.9.3.

Using this method, a wide range of polymer and polymer composite samples were successfully produced and tested. The property values obtained could not be directly compared with samples produced by rotational moulding, but this method fulfilled the requirements for which it was created.

Injection Moulding

Injection moulding of samples was used primarily during the course of this research to provide a reference against which rotationally moulded materials could be compared. The injection moulding machine utilised was an Engel Boy-15S, fitted with a die for the production of ASTM D638-03 “Standard Test Method for Tensile Properties of Plastics” Type I tensile test specimens. The operating parameters used for each batch or specimens are listed in the Results and Discussion chapter of this thesis.

Machining of Test Specimens

Sheet Milling

As has been previously described, the form in which the majority of the rotationally moulded samples were produced was that of a hollow cuboid, 90mm x 90mm x 152mm in dimensions. In order to convert these mouldings into specimens suitable for tensile testing and Charpy impact testing, it was necessary to section the mouldings into individual sheets which could be machined to a controlled and consistent thickness. This was achieved by the following process:

- Firstly, the moulded sample was clamped into a milling machine and the four largest exterior faces of the moulding (the ends of the moulding were sacrificed during the machining process) milled flat. This was necessary to remove any warping of the specimen that may have occurred during moulding, and to provide a flat and smooth surface for the vacuum table used later in the machining process. The best surface finish was found to be achieved by using a multi-insert face mill of 80mm cutting diameter, running at a speed of 500rpm.

- Following this first milling process, the moulding was sectioned into four individual sheets using a bandsaw.

- The individual sheets could now be fixed to the bed of the milling machine using a vacuum chuck, and milled to the thickness specified by each testing method. This process is shown in Figure 3.10. Milling parameters were the same as previously described.

Figure 3.10: Milling a polymer sample sheet to a controlled thickness. The sample is retained in place by vacuum.

CNC Profile Milling

Cutting the polymer sheets into test specimens was accomplished using a MAXNC 15 CNC mill and MACH3 computer control software. The specimen dimensions as specified by the relevant test standard were entered into the control program, and a 1/8” HSS milling cutter was used to cut the required specimen geometry. Any burrs created on the edges of the specimens by the machining process were carefully removed with fine abrasive paper, in accordance with ASTM D638-03 “Standard Test Method for Tensile Properties of Plastics”.

Turning Rod Specimens

Those material samples produced using the extrusion technique detailed in section 3.7 were converted into test samples using a metalworking lathe. Impact test and tensile test specimen dimensions and geometry are detailed in sections 3.10.3 and 3.11.3 respectively. In either case, machining was conducted using high rotational speeds, minimal feed rates, small cutting depths and a custom-ground High Speed Steel (HSS) lathe tool to minimise deformation of the relatively flexible specimens.

Tensile Testing

General

All tensile testing was conducted using an Instron 4204 tensile testing machine, fitted with a 5kN load cell and controlled via Instron Series IX version 8.2.00 software. An Instron 50mm extensometer was fitted for measurement of specimen strain.

Prior to testing, all specimens were conditioned at 23 ± 2ºC and 50 ± 5% relative humidity for not less than 40 hours, in accordance with ASTM D638-03 “Standard Test Method for Tensile Properties of Plastics”. Testing was also conducted at 23 ± 2ºC, but the humidity of the testing environment could not be reliably controlled within the range of 50 ± 5%. However, no evidence was seen during the course of this research that variations in atmospheric humidity affected the results of the tensile testing in any way.

Type I (flat) Specimens

All tensile test specimens cut from flat material were of the Type I geometry and dimensions, as described in ASTM D638-03 “Standard Test Method for Tensile Properties of Plastics”. All material specimens except foamed polymers were 3.2 ± 0.1mm in thickness, foam specimens were 5.0 ± 0.1mm in thickness. Testing procedure was in accordance with ASTM D638-03, with testing speeds of 5mm/min, 20mm/min or 50mm/min used dependent on the material tested. This was in accordance with the ASTM guideline “select the lowest speed that produces rupture in 0.5-5 minutes for the specimen geometry being used.” The testing speed used for each batch of specimens is noted in the Results and Discussion chapter of this thesis, and care must be taken when comparing values obtained from use of the two different speeds.

Rod-type Specimens

The specimen dimensions and testing procedures for those samples produced via the extrusion method were based on the guidelines given for rigid rod specimens by ASTM D638-03 “Standard Test Method for Tensile Properties of Plastics”. The sample dimensions utilised are illustrated in Figure 3.11.

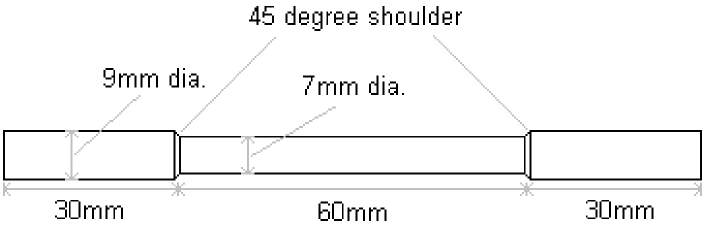

Figure 3.11: Dimensions of the rod-type tensile test specimens.

These dimensions differ from those specified in ASTM D638-03 in the following ways:

- Overall length reduced from the recommended 370mm to 120mm - necessitated by the limited length of the material available for testing. The length of the reduced diameter section was retained as 60mm however, in accordance with the ASTM recommendation of 57mm and to allow sufficient room for an extensometer to be fitted. The decrease in overall length was therefore achieved primarily by shortening the area available to be gripped in the tensile testing machine. Despite this, no slipping of specimens from the grips during testing was noted.

- Shoulders of specimen modified from radius profile to 45º angles. This change was necessitated by the machining methods used to create the specimens, as consistent radii could not be cut using the equipment available. It is recognised that the presence of such abrupt transitions in diameter are potentially undesirable due to stress raising effects, but to successfully cut a more gradual slope than the selected 45º would require continual, time consuming changes to the setup of the lathe used. Several specimens with more gradually tapering shoulders of 10º were in fact machined in this way, and found to exhibit no significant differences in tensile test properties compared to their counterparts with 45° shoulder angles.

- Diameter of centre section increased from recommended 60% of original nominal diameter to approximately 80%. This was found to be necessary as sample diameters of less than 7mm showed unacceptable deformation during the machining process. Increasing the original nominal diameter of the specimens to maintain the 60% value was impractical without redesigning the extrusion processing equipment.

Tensile testing was conducted using grips fabricated specifically for effective holding of these cylindrical specimens. Testing speed was 5mm/min and initial grip separation was set at 70mm. All other test parameters and procedures were in accordance with ASTM D638-03.

Charpy Impact Testing

General

All impact testing was conducted with a Ray-Ran Universal Pendulum Impact System utilising a notched Charpy-type test. Prior to testing, all specimens were conditioned at 23 ± 2ºC and 50 ± 5% relative humidity for not less than 16 hours, in accordance with International Standard ISO179 – 2nd edition "Plastics – Determination of Charpy Impact Strength". Testing was also conducted at 23 ± 2ºC, but the humidity of the testing environment could not be reliably controlled within the range of 50 ± 5%. However, no evidence was seen during the course of this research that variations in atmospheric humidity affected the results of the impact testing in any way.

Type 1 (flat) Specimens

The majority of test specimens were of the Type 1 geometry and dimensions, as described in ISO179 – 2nd edition "Plastics – Determination of Charpy Impact Strength." Those samples which deviate from the standard dimensions, such as those produced by injection moulding, are so noted next to the relevant impact data. Samples were notched prior to conditioning with a single, type A notch placed for edgewise impact testing, using a GBE Scientific New Zealand Notch Cutter.

Impact testing was conducted using impact energies ranging from 2.0-7.5J, dependent on the material tested. This was in accordance with ISO179 – 2nd edition, which states that the hammer mass and impact velocity shall be selected such that the energy absorbed by the test specimen corresponds to between 10% and 80% of the total hammer energy. The hammer mass and impact velocity used for each specimen are recorded in the Results and Discussion chapter of this thesis. All other test parameters and procedures were in accordance with ISO179.

Rod-type Specimens

Specimen dimensions and testing procedures for those samples produced via the extrusion method were based on the test standard ISO179 – 2nd edition "Plastics – Determination of Charpy impact Strength", suitably adapted for use with cylindrical sample geometry. Specimen dimensions are given in Figure 3.12.

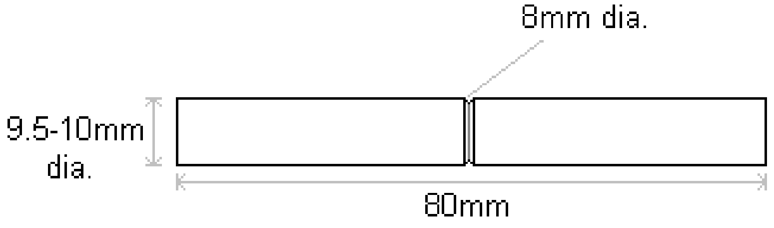

Figure 3.12: Dimensions of the rod-type Charpy impact test specimens

Due to difficulties in precisely aligning a linear notch opposite the point of hammer contact, all rod-type specimens were notched around their full circumference. The notch profile consisted of a 45° angle with minimal base radius, and was cut during the specimen machining process (section 3.9.3). All other test parameters and procedures were in accordance with ISO179 – 2nd edition for Type 1 samples.

Scanning Electron Microscopy

Microscopic analysis of the samples was conducted using a Hitachi S-4700 Field Emission Gun Scanning Electron Microscope (FEG-SEM). Prior to observation, the samples were sputter-coated with platinum using a Hitachi E-1030 Ion Sputter.

Thermal Analysis

During the course of this research, Differential Scanning Calorimetry (DSC) and combined Differential Thermal Analysis / Thermo-Gravimetric Analysis (DTA-TGA) techniques were used to determine the thermo-oxidative stability of a range of polymers, additives and polymer composites. These two thermal analysis techniques are considered separately in the following sections.

DSC

The technique of Differential Scanning Calorimetry is based upon measurement of the heat flow to and from a material sample as a function of temperature, thus revealing the presence of exothermic and endothermic reactions. The onset of oxidation in a polyolefin sample is revealed by this method as an exothermic peak, corresponding to the time at which any antioxidants within the polymer sample can no longer inhibit the oxidative reaction. Differential Scanning Calorimetry was used in this investigation both to quantify the stability of polymer samples as Oxidation Induction Time (OIT) values, and to simulate the heating cycle of the rotomoulding process and thus provide a qualitative determination of oxidative stability. These two methods are detailed below:

Determination of Oxidation Induction Time

This testing method was based on ASTM D 3895-03 “Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry”. The differential scanning calorimeter used was a TA Instruments DSC 2920, and the test method was as follows:

- Approximately 5mg of the sample material was placed within an open aluminium sample pan, which was then placed upon the detection cell along with an empty reference pan.

- A gas flow of 50mL/min of argon was supplied to the test chamber.

- Heating was then commenced at a rate of 20°C/min until the desired isothermal test temperature was reached. This temperature is shown alongside the test results in the Results and Discussion chapter of this thesis, and was selected to best assess the rotomoulding performance of the tested material. The flow of argon was maintained throughout this heating cycle.

- Five minutes after the start of isothermal operation, the gas flow to the sample chamber was changed from 50mL/min argon to 50mL/min air at atmospheric pressure. This point was recorded as the zero time of the experiment.

- Constant sample temperature was maintained until the exothermic peak characteristic of sample oxidation was displayed. The test was continued for a minimum of two minutes after the steepest point of the exotherm was noted. The test was then considered complete.

- The resultant heat-flow vs. time graph was analysed using Universal Analysis Version 2.3C, Copyright 1998 TA Instruments, Inc. The plot gradients prior to the occurrence of oxidation and at the steepest point of the exothermic peak were extrapolated and intersected. The oxidation induction time was then measured from the zero time of the experiment to this intersection point.

Thermal Simulation of Rotational Moulding

This method was not based on an existing test standard, but utilises the same theory and equipment as the OIT determination method detailed above. Although isothermal OIT values are useful for comparing the oxidative stability of different polymers, they do not provide a direct indication of whether a polymer will undergo oxidation during rotational moulding. This shortcoming was addressed by modifying the above method to more closely simulate the rotational moulding process. This involved the following process modifications:

- An air atmosphere was applied throughout the analysis cycle, at a flow rate of 50mL/min.

- The heating programme consisted of raising the sample from room temperature to the desired peak temperature at a rate of 10°C/min, followed by a 1 min isothermal dwell time and then cooling of the sample back to room temperature at a rate of 20°C/min. These heating and cooling rates represent typical values taken from actual rotational moulding cycles. The peak analysis temperature corresponds to the peak mould internal air temperature (PIAT) during the rotomoulding process.

As with the OIT determination method, the occurrence of sample oxidation was indicated by the presence of the characteristic exothermic peak. Due to the difficulty of assigning a precise oxidation onset point under non-isothermal test conditions, this test method was used only for qualitative analysis purposes.

DTA-TGA

The analysis techniques of Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) were conducted simultaneously upon material samples using a TA Instruments SDT 2960 thermal analyser. These methods were used as an alternative to DSC analysis for the purposes of both measuring the OIT of samples and for conducting thermal simulations of the rotomoulding cycle. The reason for utilising both DSC and DTA-TGA methods was due to delays in equipment availability, and the results from each method were found to be interchangeable to a limited extent.

The information gathered by DTA is similar to that obtained from DSC analysis, with both methods capable of detecting exothermic and endothermic changes within the test sample. The DTA method achieves this by measuring the temperature difference between the sample and a reference under identical heating conditions, rather than by detecting the heat flow directly as measured by DSC. Thermo-gravimetric analysis accurately measures the weight of the sample as a function of temperature, recording the occurrence of volatilisation or gas uptake by the sample. The onset of polyolefin oxidation is theoretically indicated by both an exothermic reaction and a decrease in sample weight, but the DTA-TGA method proved only capable of detecting the oxidation of polypropylene samples and not the more thermally stable polyethylene. This is attributed to insufficient equipment sensitivity. As a result, all polyethylene samples were analysed using DSC.

The test methods used with the DTA-TGA for OIT determination and thermal simulation of rotational moulding were the same as described above for DSC analysis, with the exception that the flow rate of both argon and air was increased from 50mL/min to 150mL/min.

Comparison of OIT values obtained using both DTA-TGA and DSC analysis showed a sufficient agreement for these methods to be considered interchangeable for the purposes of this research. This may be not be advisable, however, if highly accurate determinations are required.

References

1. *Crawford, R.J. and M.P. Kearns, Practical Guide to Rotational Moulding. 2003: Rapra Technology Ltd.*

2. *Crawford, R.J., et al., Mould pressure control in rotational moulding. Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture, 2004.* ***218****(12): p. 1683-1693.*

Chapter 4: Results and Discussion

Commercial Rotomoulding Polymers

In order to establish reference values against which the formulated composite materials could be compared, a range of commercially available, rotomoulding-grade polymers were tested early in the course of this research project. The chosen materials were Borocene Compact™ RM8346 LMDPE, Cotene 3923 HDPE, Cotene 3924 LMDPE, Cotene 3979 HDPE, Cotene 9042 LMDPE, Cotene 9800 CPP and Vanglobe Rotathene® Octene 8539 LLDPE *(see section 3.1 of this thesis for material specifications).* The tensile properties, impact strength and oxidative stability of these polymers were established, and these results are shown in the following sections.

Samples of these polymers were rotationally moulded using the micro-oven rotomoulding method (methodology section 3.5.1), following which they were machined into sheets (methodology section 3.9.1), CNC milled into tensile and impact test specimens (methodology section 3.9.2), and tested in accordance with ASTM standard D638 – 03 “Tensile Properties of Plastics” (methodology section 3.10.2) and ISO standard 179 2nd edition “Plastics – Determination of Charpy Impact Strength” (methodology section 3.11.2) respectively. The moulding and testing variables specific to this batch of specimens are listed below, and graphical representations of the results obtained are shown in Figure 4.1 and Figure 4.2.

Rotational Moulding (micro-oven):

Material form: Powder *Charge weight:* 400g

Oven set temperature: 260ºC *Mould rotation speed:* 5rpm

Target PIAT:* 200ºC (All PE grades except Cotene 3979 HDPE)
210ºC (Cotene 3979 HDPE)
250 ºC (Cotene 9800 CPP)

Demoulding Temperature: 90 ºC

*(*All target PIAT values were based on previous moulding experience by ITS Ltd)*

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Two specimens per material
(4 samples/grade for Cotene 3923 and Cotene 3924)

Testing speed: 50mm/min

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact

Repetition: Three specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

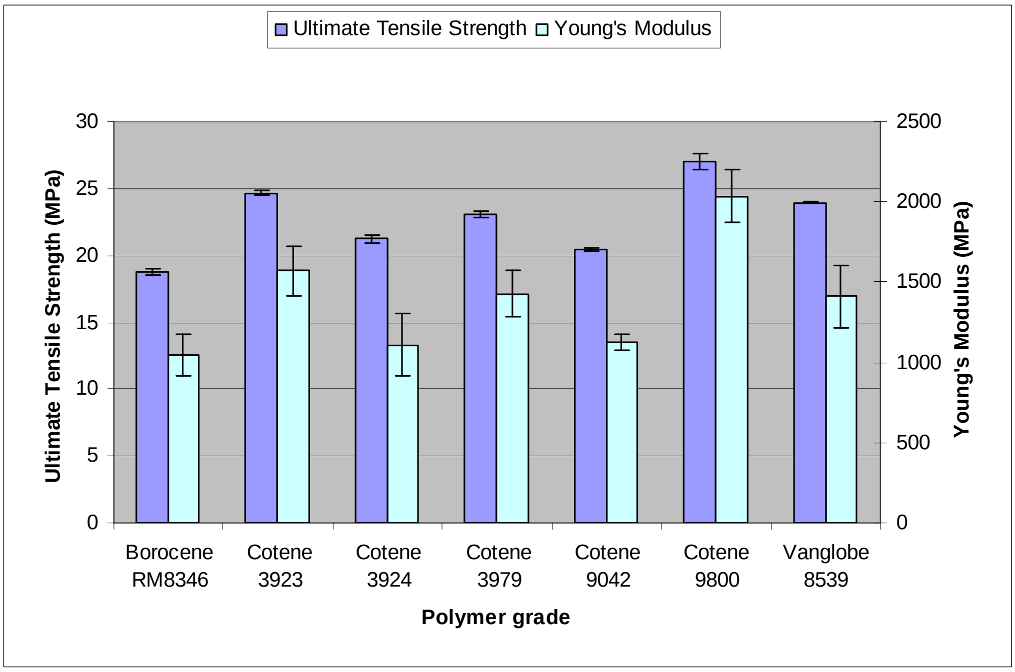

Figure 4.1: Tensile properties of commercial rotomoulding polymer grades. Error bars ±1 standard deviation.

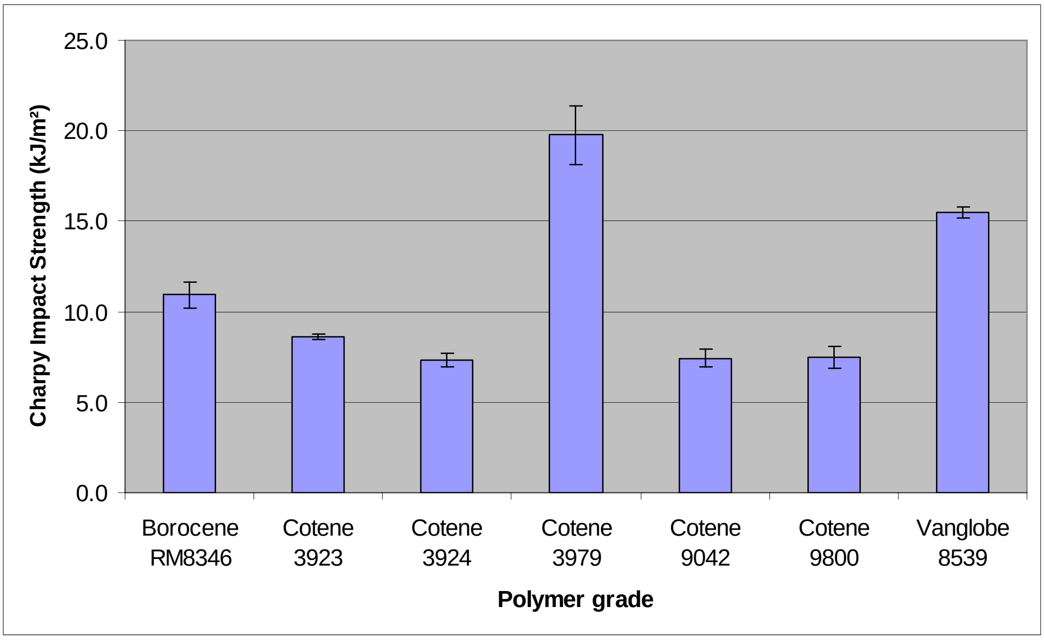

Figure 4.2: Notched Charpy Impact strength of commercial rotomoulding polymer grades. Error bars ±1 standard deviation.

It may be seen from these results that there existed considerable variation of mechanical properties between the different polymer grades. As was expected, the sole polypropylene grade tested exhibited the highest values of both ultimate tensile strength and Young’s modulus, although impact resistance was low in comparison with some grades of polyethylene. Based on these results and commercial considerations, the polymer grades Cotene 3979 HDPE, Cotene 9800 CPP and Vanglobe 8539 LLDPE were chosen as the basis for the development of fibre-reinforced composites. Although it is recognised that testing such a small number of samples from each polymer grade is not ideal, limited material availability and time constraints prevented a more rigorous testing program from being conducted. Nevertheless, the results obtained were deemed sufficient for the purposes of base-material selection.

Rotational Moulding of Granules

It is widely accepted that the only forms of polymer or composite material suitable for thermoplastic rotomoulding are either fine powders or micropellets, typically with particle sizes of 500µm or less [2]. Use of larger granules than this is claimed to incur penalties such as increased heating cycle times [2], irregular, matte outer product surfaces containing many pinholes [2], lumpy interior product surfaces [76], and poor reproduction of mould detail. As previously discussed, it is this particle size constraint which severely limits the reinforcing efficiency of fibres introduced via the melt-compounding method of composite preparation. However, the melt-compounding method also exhibits several advantages over the "dry-mix" method of producing rotationally moulded composites, which is a process not subject to the same restrictions on fibre length. Therefore, it would be advantageous to be able to rotationally mould melt-compounded composite granules or pellets which were significantly larger than those normally deemed suitable for the process, in order to increase the average length of the fibres contained within the final moulding.

A brief series of trials were conducted to ascertain the rotational moulding performance of coarsely granulated polyethylene of a conventional rotomoulding grade. The material used was previously-rotomoulded Cotene 3979 HDPE scrap, which was cut into strips and granulated to give particle sizes ranging from approximately 2-5mm. The trials were conducted using the micro-oven rotational moulding method to the process parameters listed below:

Rotational Moulding (micro-oven):

Oven set temperature: 260ºC	*Mould rotation speed:* 5rpm
Target PIAT: 210ºC	*Demoulding Temperature:* 90 ºC

The first trial moulding consisted of a 300g charge of granulated polyethylene, moulded using a single-shot process. This was judged to be successful as the resultant article showed even wall thickness, excellent interior surface finish and reasonable reproduction of detail from the admittedly simple mould. A large number of pinholes and small voids were noted, however, on the external surface of the moulding. These may be seen in Figure 4.3.

Figure 4.3: Single-shot rotational moulding from granulated Cotene 3979 HDPE.

In an attempt to improve the external finish of the moulded product, a multi-layer moulding was then produced with an outer skin of conventional, powdered Cotene 3979 HDPE and an inner layer of the same polymer in granulated form. This was produced using a two-shot process, where the charge of granulated polymer was manually placed inside the mould only once the polymer outer skin had adhered to and melted upon the mould interior surface. The two polymer charges were of different colours so that they could be easily differentiated on examination of the product. The resultant moulding showed an excellent exterior surface finish, with good reproduction of mould detail and an absence of voids or pinholes – of comparable quality to a moulding produced solely from polyethylene powder. Sectioning the moulding showed that the granules had also successfully distributed and coalesced into an even polymer layer, and that although the line segregating the two polymer layers was somewhat irregular, the outer product surface had not been breached by the granular material. Bonding between the two polymer layers was proven to be excellent with no possibility of delamination occurring.

Following this success, a moulding strategy was trialled where the aforementioned Cotene 3979 HDPE powder and granules were mixed at the start of the rotomoulding cycle and moulded using a single-shot process. The difference in particle size between the granules and powder was relied on to separate the two materials into distinct layers during rotational moulding, as has been used for the single-shot moulding of thermoplastic foam skinned with solid polymer. In this instance, however, separation of the powder and granules proved to be incomplete, with a dispersion of both materials present throughout the thickness of the moulded article. This failure was suspected to be due at least in part to the particular granule morphology in use at that time. As the single-shot processing method for producing multi-layer products was not further utilised during the course of this research, further investigations into this phenomenon were not conducted.

The results of these trials indicated the potential for the development of a rotomouldable composite based on melt-compounded granules, which could then be moulded in conjunction with an outer layer of conventional, powdered polymer. In this manner, products both effectively reinforced and possessing an excellent exterior surface finish could be produced. Further trials with two-shot moulding of Cotene 3979 HDPE powder and granules showed the capability of this dual material system to give acceptable moulding performance even when used with moulds of relatively complex geometry. Although slight lumpiness at the interior surface of these mouldings was sometimes evident, this was cosmetic only and would not compromise the reinforcing effect of a composite material layer.

Screening of Potential Composites

Based on the encouraging results obtained from the moulding trials with granulated polyethylene and the disappointing tensile strength exhibited by the Cotene 9042 LMDPE / glass fibre “dry-mixed” rotomoulded composite (section 4.5), the decision was made to focus on the development of a melt-compounded, granular composite material as a method of improving the mechanical properties of rotationally moulded products. Cotene 3979 HDPE and

Cotene 9800 CPP were selected as potentially suitable matrix polymers based on the results reported in section 4.1, and a range of fibres and coupling agents were obtained. The component materials of each composite formulation were melt-compounded and extruded using the rod-production method (section 3.7), which was selected to hasten the process of trialling the large number of different material combinations. Following extrusion, the samples were machined into test specimens and the impact and tensile properties of these specimens determined. The material, processing and testing parameters specific to these samples are shown below.

Material Combinations

Reference	**Polymer matrix**	**Fibre** (chop length)	**Coupling agent**
PE	Cotene 3979	None	None
PE/MA	Cotene 3979	None	Clariant PE MA 4351
PE/SI	Cotene 3979	None	Clariant PE SI 3361
PE/Nylon	Cotene 3979	Nylon 6 (10mm)	None
PE/Nylon/MA	Cotene 3979	Nylon 6 (10mm)	Clariant PE MA 4351
PE/Nylon/SI	Cotene 3979	Nylon 6 (10mm)	Clariant PE SI 3361
PE/PET	Cotene 3979	PET (10mm)	None
PE/PET/MA	Cotene 3979	PET (10mm)	Clariant PE MA 4351
PE/PET/SI	Cotene 3979	PET (10mm)	Clariant PE SI 3361
PE/Glass	Cotene 3979	Lab Glass (12mm)	None
PE/Glass/MA	Cotene 3979	Lab Glass (12mm)	Clariant PE MA 4351
PE/Glass/SI	Cotene 3979	Lab Glass (12mm)	Clariant PE SI 3361
PE/Vectran	Cotene 3979	Vectran (10mm)	None
PE/Vectran/MA	Cotene 3979	Vectran (10mm)	Clariant PE MA 4351
PE/Vectran/SI	Cotene 3979	Vectran (10mm)	Clariant PE SI 3361
PP	Cotene 9800	None	None
PP/MA	Cotene 9800	None	Honeywell MA PP
PP/PET	Cotene 9800	PET (10mm)	None
PP/PET/MA	Cotene 9800	PET (10mm)	Honeywell MA PP
PP/Glass	Cotene 9800	Lab Glass (12mm)	None
PP/Glass/MA	Cotene 9800	Lab Glass (12mm)	Honeywell MA PP
PP/Vectran	Cotene 9800	Vectran (10mm)	None
PP/Vectran/MA	Cotene 9800	Vectran (10mm)	Honeywell MA PP

- **All fibre additions 30% of entire system by volume**

- **All coupling agent additions 3% of entire system by volume**

Sample Extrusion:

Extruder zone temperatures (from feed point to die):

PE matrix composites: 100ºC 140ºC 180ºC 215ºC 215ºC
PP matrix composites: 100ºC 150ºC 200ºC 250ºC 250ºC

Screw speed: 150rpm

Sample cooling: Compressed air

Tensile Testing:

Specimens: Rod-type

Repetition: Three specimens per material

Testing speed: 5mm/min

Impact Testing:

Specimens: Rod-type

Repetition: Three samples per polymer grade

Hammer impact:

1.042kg @ 3.8m/s (7.5J) (All Vectran fibre samples)
1.188kg @ 2.9m/s (5.0J) (All PE samples with PET or nylon fibre)
0.475kg @ 2.9m/s (2.0J) (All other samples)

It should be noted that the Owens Corning glass-fibre and Clariant grafted-polypropylene waxes were not available at the time that these trials were conducted, hence their omission from the above list. Nylon-6 fibre was not used in conjunction with polypropylene as the melting point of this fibre was below the selected peak extrusion temperature. These relatively high extrusion temperatures were selected for two reasons: to aid in the production of suitable long specimens, and to more closely imitate the characteristics of the rotomoulding process. The peak extrusion temperatures of 205ºC and 250°C correspond to the rotomoulding target PIAT values for Cotene 3979 and Cotene 9800, respectively.

The results from the tensile and impact tests conducted on these samples are shown in Figure 4.4 and Figure 4.5.

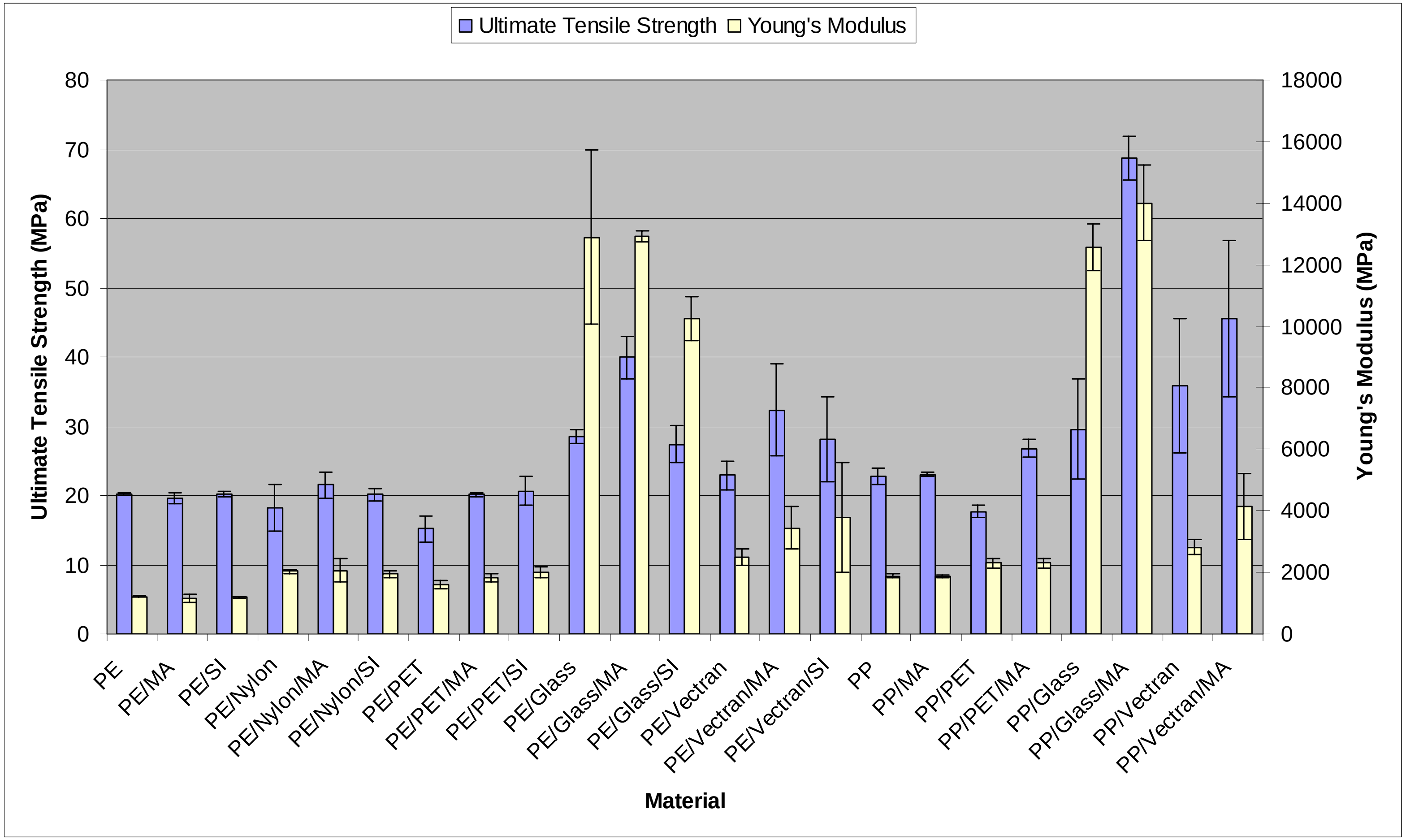

Figure 4.4: Tensile properties of extruded rod samples. Error bars ±1 standard deviation.

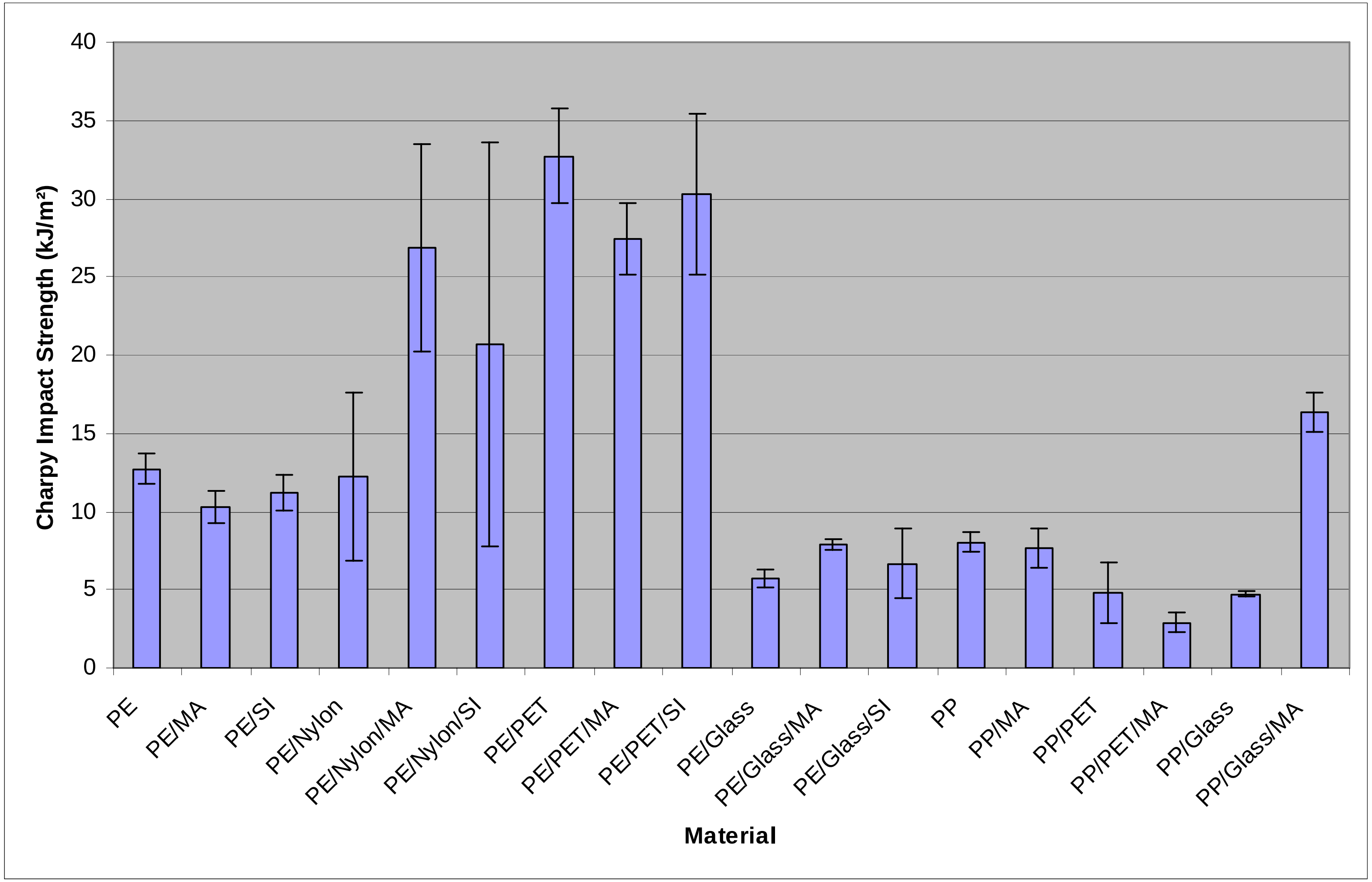

Figure 4.5: Notched Charpy impact strength of extruded rod samples. Error bars ±1 standard deviation.

A number of observations can be made from these results. It may be noted that while the addition of coupling agent additives did not significantly affect the tensile or impact properties of the unfilled polymers, the majority of composite samples based on both matrix materials showed improvements in ultimate tensile strength, Young's modulus and Charpy impact strength following the addition of a coupling agent. Of the tested fibres, glass and vectran were shown to be the most effective at improving the tensile properties of both polyethylene and polypropylene, with the addition of the maleic anhydride coupling agent seen to be beneficial in all cases. The addition of glass fibre, in particular, was shown to result in significantly enhanced material strength and stiffness, with an improvement of over 200% in ultimate tensile strength and over 600% in Young's modulus seen for the polypropylene/glass fibre/maleic anhydride composite relative to unfilled polypropylene. The strengthening effect of the glass fibre is even more notable when these materials are compared on the basis of yield strength rather than ultimate tensile strength, as the glass-fibre composites undergo much less deformation than the corresponding unfilled polymers before the peak strength value is reached. This is an important property when the material is to be applied in a product which has strict limits upon allowable deformation.

In terms of improving impact strength, vectran fibre was found to be the most effective reinforcement material. Those composite samples containing vectran fibre are not shown in Figure 4.5 only because breaking the test specimens proved to be beyond the limits of the test equipment, with the maximum impact energy of 7.5J insufficient to cause specimen fracture. Complete dissipation of 7.5J of impact energy by the test specimen corresponds to an impact strength of approximately 150kJ/m^2, although in practice the rebounding of the pendulum after impact reduces this theoretical value. The true impact strength of these vectran composite samples was not determined during the course of this research. Of the other fibre types, the addition of PET fibre was found to be effective at improving the impact strength of polyethylene but detrimental to polypropylene. This was attributed to melting of the PET fibre at the high temperatures used to process the polypropylene matrix, as the fracture surfaces of the polypropylene/PET samples showed no evidence of a distinct fibrous phase. In contrast, those polyethylene specimens containing PET fibre, as well as all those composites containing vectran fibre, showed extensive fibre pull-out from the matrix at the fracture surface of the impact specimens. Composites containing nylon-6 fibre did not exhibit fibre pull-out to the same extent. Nevertheless, those polyethylene/nylon-6 composites which incorporated a coupling agent can be seen to be comparable in impact strength to the polyethylene/PET fibre composites. Glass fibre, while excellent at improving the tensile properties of both polyethylene and polypropylene, proved to be detrimental to impact strength in the majority of cases. The sole exception to this was the polypropylene/glass fibre composite with the addition of maleic anhydride coupling agent. This composite exhibited an impact strength over 100% higher than that of unfilled polypropylene and almost 30% higher than the unfilled Cotene 3979 HDPE - a rotomoulding polyethylene grade touted for its high impact resistance.

Based on these results, glass fibre was selected as the most suitable reinforcement material for the development of a rotomouldable composite, to be used in conjunction with either a polyethylene or polypropylene matrix. The glass fibre grade used in these trials, however, was to be replaced with a commercially available grade tailored specifically for the reinforcement of polyolefins. It was accepted that this change in material would require the addition of coupling agents to the composite to be re-examined. Although vectran fibre composites were also proven by these trials to be worthy of further development, the high price of vectran fibre made this material comparatively less attractive than glass fibre for the purposes of this research. Also, the addition of vectran fibre to either matrix material was noted to result in a greater increase in material viscosity and subsequent difficulty of extrusion than experienced when processing glass fibre reinforced composites. It was expected that this increased viscosity would prove to be a hindrance during rotational moulding.

Polypropylene Matrix Composites

Cotene 9800 Polypropylene

Based upon the results of the trials outlined in section 4.3, a composite mixture of 67vol% Cotene 9800 polypropylene, 30vol% “lab glass” glass fibre and 3vol% Honeywell maleic anhydride (which is equivalent to the “PP/Glass/MA” composite in section 4.3) was extrusion compounded (methodology section 3.3), granulated, and then rotationally moulded using the R&D system method. The tensile and impact properties of the moulded composite were then determined. The material, processing and testing parameters specific to these samples are shown below.

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

100ºC 135ºC 170ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 6mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* No

Sieved: Yes *Retained size fraction:* 2.0-6.3mm

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box*Charge weight:* 500g

Double/single shot process: Single shot

Oven set temperature: 300ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Target PIAT: 250ºC

Cooling: Immediate fan cooling upon mould removal from oven

Internal mould pressurisation: None

Demoulding Temperature: 70 ºC

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)
Repetition: Three specimens per material
Testing speed: 5mm/min

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact
Repetition: Three specimens per material
Hammer impact: 0.475kg @ 2.9m/s (2.0J)

Rotational moulding of these composite granules proved largely unsuccessful, for although the granules conformed to the mould contours, the degree of flow and coalescence by the granules was unsatisfactory. This may be seen in Figure 4.6.

Figure 4.6: The poor rotomoulding granule coalescence seen with the Cotene 9800 PP/glass fibre composite.

This incomplete coalescence resulted in an excessively weak moulding of which the mechanical properties could not be accurately determined, due to the presence of extensive voids and flaws throughout the moulded structure. In an attempt to more effectively bind these granules together, a second moulding trial was conducted in which 400g of composite granules were mixed with 100g of Cotene

9800 polypropylene powder. This powder addition effectively filled the voids that existed between the composite granules, and allowed the mechanical properties of the moulding to be determined by tensile and impact testing. These results are shown in Figure 4.7 and Figure 4.8, along with the properties of rotomoulded, unfilled Cotene 9800 polypropylene for comparison.

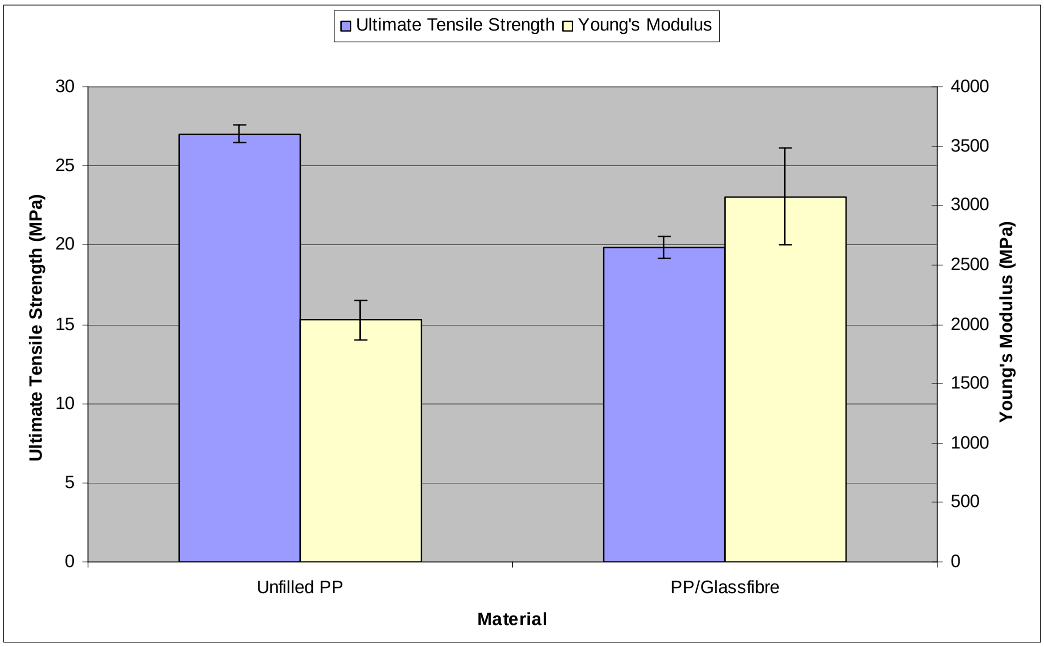

Figure 4.7: Tensile properties of rotationally moulded PP/Glass/MA composite compared to unfilled polypropylene. Error bars ±1 standard deviation

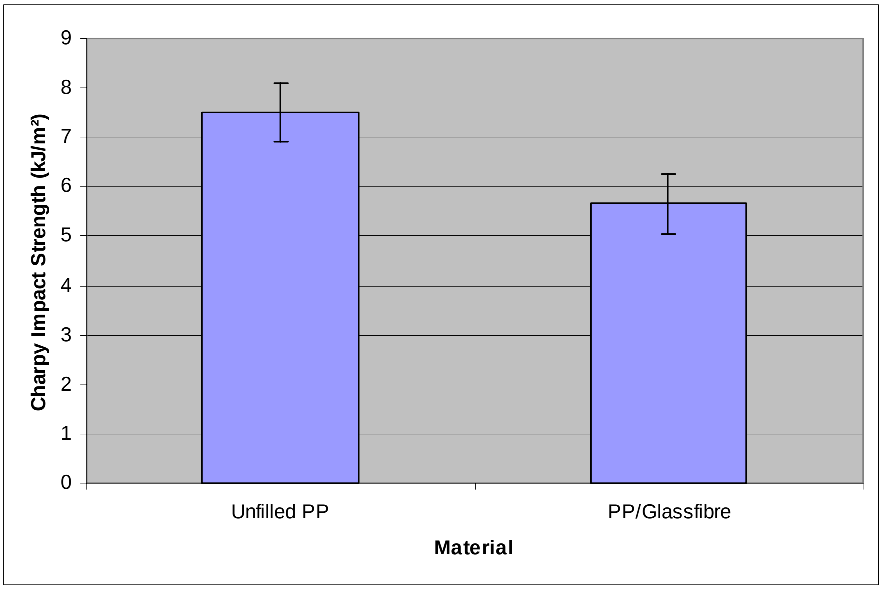

Figure 4.8: Notched Charpy impact strength of rotationally moulded PP/Glass/MA composite compared to unfilled polypropylene. Error bars ±1 standard deviation

It is evident from these results that although the addition of polypropylene powder to the composite granules improved the appearance of the moulded article, the mechanical properties were still dictated by the poor flow of the granular composite. Examination of the tensile and impact specimen fracture surfaces revealed that crack propagation had largely bypassed the composite granules, instead running along the granule boundaries. This prevented the reinforcing potential of the glass fibre addition being effectively utilised. The mechanical properties of this moulding may also have been compromised to some extent by thermal degradation of the maleic anhydride coupling agent, as was determined to be an issue in later work (section 4.6.1).

Following the processing failure of this composite material, the fraction of glass fibre within the composite was lowered to 20vol% and a new batch of granules produced and moulded as described previously. No significant difference in the degree of material flow was noted, with granule coalescence remaining insufficient. Although the poor external appearance of these mouldings could be easily addressed by coating the moulded composite layer with an outer skin of conventional, powdered rotomoulding polymer (as described in section 4.2), this approach would not solve the poor mechanical properties exhibited by the composite layer. At this stage, further flow testing of the composite granules proceeded using the melt-flow simulation method (methodology section 3.6) rather than rotational moulding itself, due to the smaller material samples needed. The maleic anhydride coupling agent added to the previously prepared composites was omitted here, as it was not seen to significantly impact the coalescence behaviour of the granules. This testing showed that unfilled Cotene 9800 polypropylene granules would coalesce successfully under simulated rotational moulding conditions, while the Cotene 9800 polypropylene/20vol% composite material would not coalesce regardless of granule morphology. Even when this composite was micronised into powder, particle coalescence remained incomplete. By further lowering the glass fibre fraction within the composite to 10vol% some improvement in granule coalescence was seen, but was judged to still be inadequate for rotational moulding purposes. However, a greatly improved degree of coalescence was noted when a sample of Cotene 9800 polypropylene/10vol% composite material was passed through the extrusion compounding process twice, prior to being granulated and tested for flow behaviour. This improvement was hypothesised to be primarily due to thermal degradation of the polypropylene matrix caused by the extra processing, which resulted in polymer chain scission and a decrease in composite melt viscosity. This result indicated that the melt flow index of the selected polymer matrix may strongly influence the rotomouldability of the composite material.

Basell Moplen HP741T and HP640S Polypropylene

Following the development of composites based upon Cotene 9800 polypropylene (MFI: 13g/10min), two high MFI polypropylene grades were obtained so that the effect of matrix viscosity upon the processing behaviour of the composite materials could be ascertained. These two grades were Basell Moplen HP640S polypropylene (MFI: 45g/10min) and Basell Moplen HP741T polypropylene (MFI: 60g/10min), both of which are grades formulated primarily for injection moulding. Samples of both polymers were injection moulded and then tensile tested to determine the performance of these grades relative to those previously used. The processing and testing parameters for this work are shown below.

Injection Moulding:

Die: ASTM D638 – 03 Type I tensile test specimen
Peak processing temperature: 200ºC

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)
Repetition: Five specimens per material
Testing speed: 20mm/min

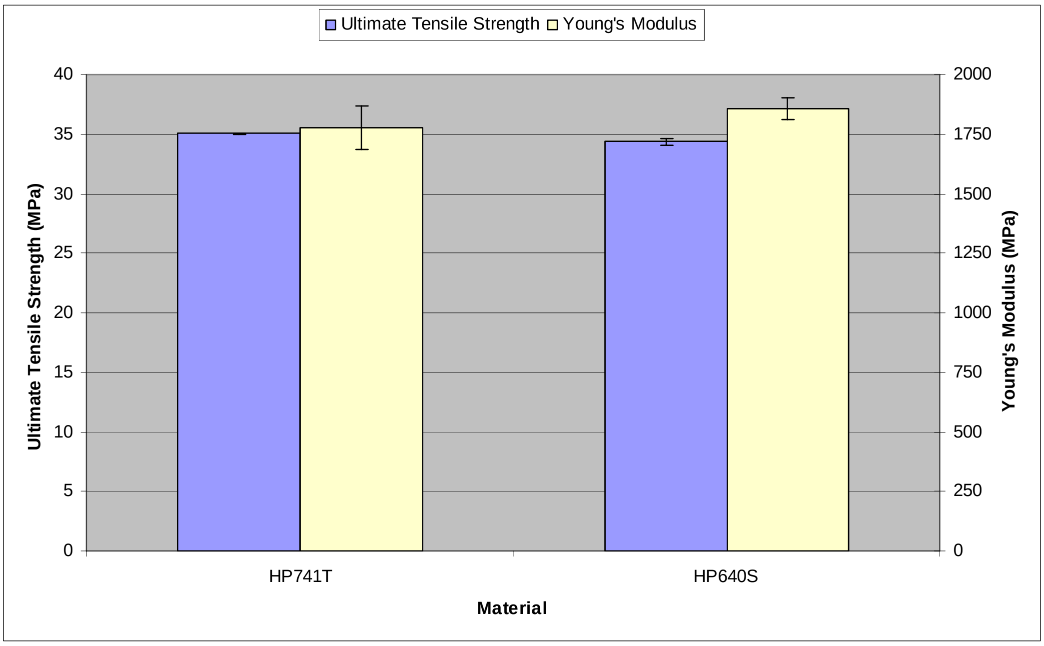

Figure 4.9: Tensile properties of injection moulded high-MFI polypropylene grades. Error bars ± standard deviation

As can be seen in Figure 4.9, both Basell HP640S and HP741T polypropylene grades appear superior in tensile strength to the previously tested Cotene 9800 polypropylene, although Young's modulus is slightly reduced. It must be noted, however, that any comparisons made between Cotene 9800 and the other two polypropylene grades based upon this data must account for the differences in processing methods and testing parameters which were used. Nonetheless, these results show that the tested high-MFI polypropylene grades are at least comparable to Cotene 9800 in tensile properties.

Composite Melt-flow Simulation

As had been previously conducted with the Cotene 9800 polypropylene grade, samples of both Basell HP640S and HP741T polypropylene were extrusion compounded with “lab glass” glass fibre, granulated, and then tested using the melt-flow simulation technique. The processing parameters specific to these samples are given below.

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):
100ºC 135ºC 170ºC 200ºC 200ºC
Screw speed: 150rpm
Die: Single aperture, 10mm diameter
Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* Yes
Sieved: Yes *Retained size fraction:* 2.8-3.5mm

The results of this testing indicated that by increasing the melt-flow index of the polypropylene matrix, significant improvements in the rotomoulding processability of the fibre-reinforced composite could be made. Both HP640S- and HP741T-based composites showed improved granule flow and coalescence over comparable materials based upon Cotene 9800 polypropylene, with HP741T proving to be the more effective of the two grades. Visual examination of the moulded plaques resulting from the flow-simulation tests showed that HP741T/20vol% glass fibre composite granules displayed similar melt-flow behaviour to the previously tested Cotene 9800/10vol% glass fibre granule sample. By reducing the percentage of glass fibre compounded with the HP741T polypropylene matrix to 10vol%, coalescence of the composite granules was improved to the extent where only slight residual lumpiness was visible on the surface of the moulded plaque, and no evidence of voids along the granule boundaries could be seen. This composite was therefore judged suitable for rotational moulding trials based upon these simulation results.

Thermo-oxidative Stability Analysis

As both Basell HP741T and HP640S polypropylene grades are intended for injection moulding use rather than rotational moulding, these materials lack the enhanced oxidative stability that typifies rotomoulding thermoplastic grades. The high temperature oxidative stability of these two polypropylenes was measured and contrasted against that of commercial rotomoulding polymers on the basis of Oxidation Induction Time (OIT) values. The results from this testing are shown in Figure 4.10.

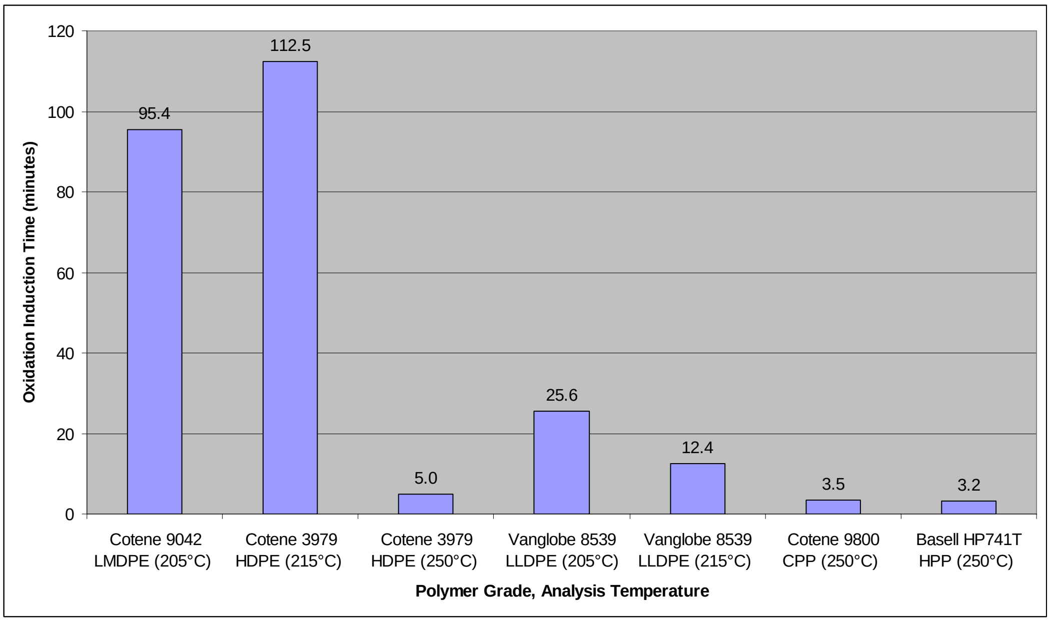

Figure 4.10: High-temperature oxidative stability of HP741T polypropylene compared to rotomoulding grade polymers. Estimated error ±10%

It may be seen that a range of analysis temperatures have been used in these determinations. These were selected to reflect the peak rotomoulding temperature normally utilised with each material: 205°C for Cotene 9042 LMDPE, 205°C for Vanglobe 8539 LLDPE, 215°C for Cotene 3979 HDPE, and 250°C for the polypropylene grades. In addition, Vanglobe 8539 LLDPE was also tested at 215°C so that a direct comparison of oxidative stability with Cotene 3979 HDPE could be made, and Cotene 3979 was tested at 250°C for direct comparison to the polypropylene grades.

The results of these analyses show that the Cotene polyethylene grades are well stabilised at their respective peak processing temperatures, with both resisting the onset of oxidative degradation for over 1½ hours. This is particularly impressive considering that these polymers would only be subjected to such temperatures for a few minutes during actual rotational moulding. The other rotomoulding polyethylene grade tested - Vanglobe 8539 LLDPE – survived approximately 25 minutes at 205ºC and 12 minutes at 215ºC under an air atmosphere. Although this is significantly less than the competing Cotene polyethylene grades, 25 minutes of resistance to oxidation at peak rotomoulding temperature represents more than sufficient stability for the polymer to be rotationally moulded without oxidative degradation occurring. The reduced OIT value of this grade also does not necessarily translate into decreased long-term stability at ambient temperature, for as has been previously explained in the literature review chapter of this thesis, predictions of stability based upon high-temperature thermal analysis have been shown to be unreliable.

The low OIT value obtained from the testing of Cotene 9800 polypropylene is significant, however. This value is so low as to suggest oxidative degradation of this polymer may occur during normal rotational moulding when the suggested peak mould internal air temperature of 250ºC is utilised. This observation is supported by the results of further thermal analysis, where a sample of Cotene 9800 polypropylene powder was subjected to a thermal simulation of the rotational moulding cycle using the DTA-TGA technique. The data plot resulting from this testing is given in Figure 4.11, where it can be seen that the exothermic peak and sharp decrease in sample weight indicative of oxidation occur before the peak temperature of the simulated rotational moulding cycle has been reached.

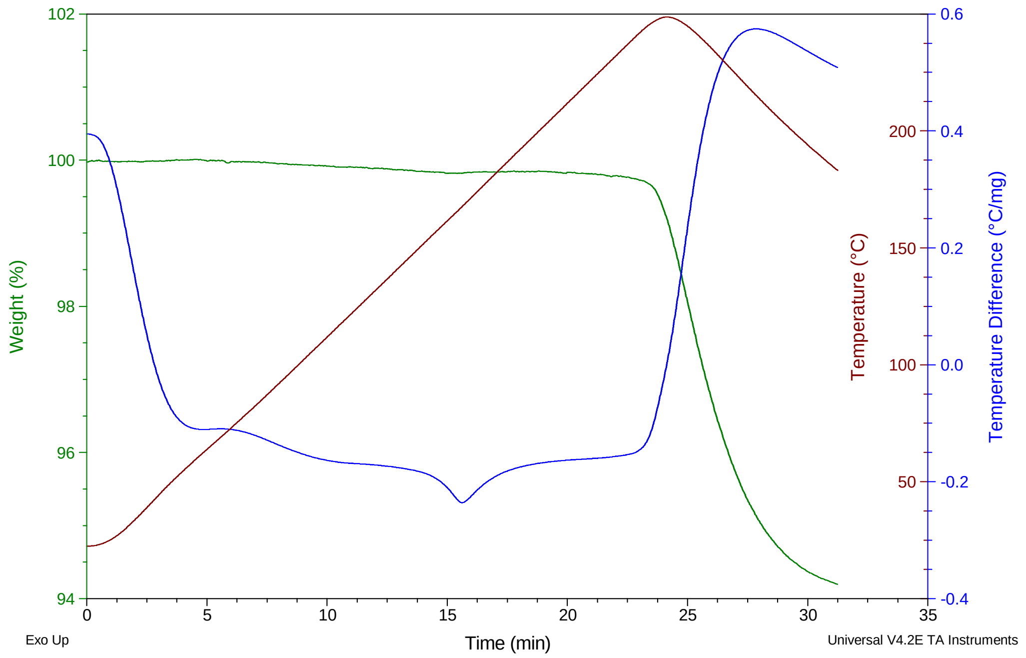

Figure 4.11: DTA-TGA analysis showing oxidative degradation of Cotene 9800 polypropylene during simulated rotational moulding.

To confirm the occurrence and extent of degradation that this polymer grade undergoes during rotational moulding would require further investigation, which did not fall inside the scope of this research. However, a comparison between the mechanical properties of Cotene 9800 PP samples when rotationally moulded (section 4.1) and when processed by rod extrusion (section 4.3) gives no evidence that the mechanical performance of this material was adversely affected by the rotational moulding cycle. Nonetheless, it appears from the results of this thermal analysis that the oxidative stability of Cotene 9800 may be marginal for rotomoulding to the parameters utilised in this research.

When analysed at 250°C, the polymer grades Cotene 3979 HDPE and Basell HP741T HPP exhibited similar levels of oxidative stability to Cotene 9800 polypropylene and were both deemed to be insufficiently stabilised for rotational moulding at this temperature.

Antioxidant Addition Trials

As the polypropylene grade Basell HP741T had been shown by thermal analysis to be insufficiently stabilised against thermo-oxidative degradation during rotational moulding, the addition of extra antioxidants to the polymer was deemed necessary before composite formulation work could continue. The chosen stabilising additives were Ciba Specialty Chemicals Inc. IRGANOX 1010 and IRGAFOS 168, described as a sterically hindered phenolic primary antioxidant and a hydrolytically stable phosphite processing stabiliser/secondary antioxidant, respectively. Samples of polypropylene with varying levels of antioxidant addition were prepared by extrusion compounding, followed by granulation and micronisation of the extruded material. OIT values for these materials were then determined by DSC and DTA-TGA thermal analysis. The processing parameters specific to these samples are given below.

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 10mm diameter

Material Cooling: Air cooled (non-forced)

The levels of antioxidant addition recommended by Ciba Specialty Chemicals Inc. for polymer stabilisation are 500 – 4000ppm of IRGANOX 1010 and 500 – 2000ppm of IRGAFOS 168. Based on the results of previously conducted thermal analysis, in this research a range of polypropylene samples stabilised with up to 8000ppm of each additive were prepared. The OIT values for these samples are shown in Figure 4.12.

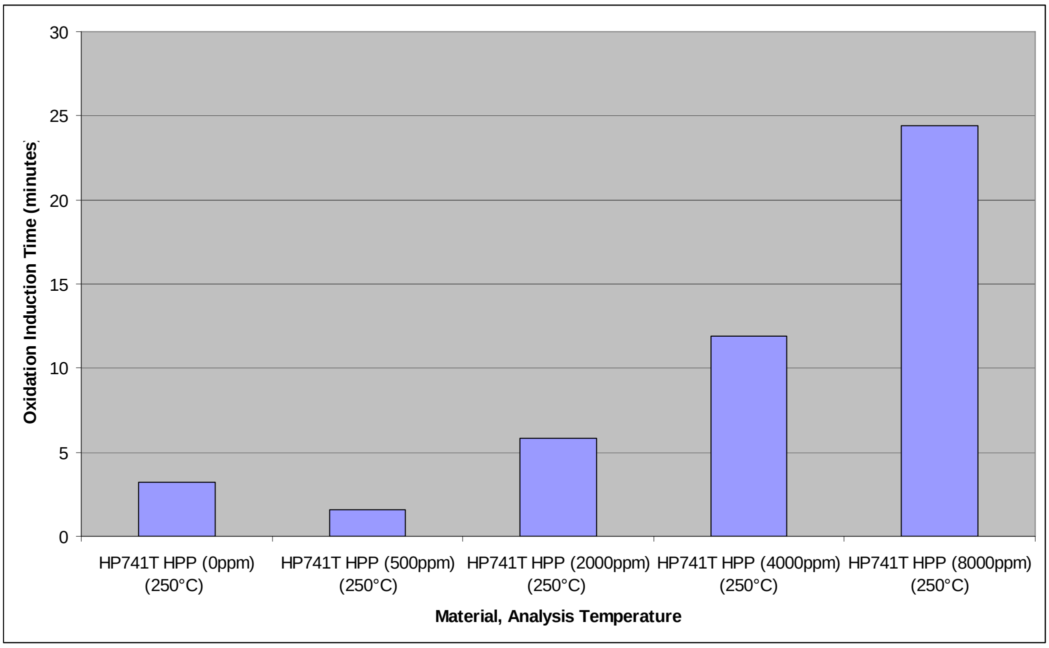

Figure 4.12: High-temperature oxidative stability of stabilised HP741T polypropylene samples. Estimated error ±10%

In each case, equal amounts of the IRGANOX and IRGAFOS stabilisers were added to the polymer. The level of each antioxidant is shown in brackets in Figure 4.12, along with the isothermal analysis temperature. It can be seen that the increase in polymer OIT is broadly proportional to the increase in additive level at antioxidant levels of 2000ppm and above. An addition of only 500ppm of each antioxidant was not seen to increase the oxidative stability of this polymer, and this phenomenon was also noted in later work with a stabilised polyethylene grade. It is hypothesised that this small amount of added antioxidant does not completely compensate for the antioxidant consumed during the extrusion compounding and micronising processes. The reference sample of polypropylene to which no extra stabilisation had been added was not subjected to extrusion compounding prior to thermal analysis.

Based upon these results, 8000ppm of each antioxidant additive was judged to give ample extra stabilisation to allow Basell HP741T polypropylene to be rotationally moulded without undergoing thermo-oxidative degradation. Later analysis of rotationally moulded Basell HP741T so stabilised confirmed this, with significant stabilisation capacity found to remain in the moulded polymer.

Oxidative stability was also found to be retained after the stabilised polypropylene had been compounded with both glass fibre and coupling agent prior to rotational moulding. It is possible that the addition of these materials to the polypropylene may have caused some decrease in the oxidative stability of the polymer, but the magnitude of this effect, if present, could not be reliably determined due to considerable scatter of the obtained OIT values. This variation was attributed to inhomogeneities within the moulded material, the effect of which was exacerbated by the small size of the thermal analysis samples. As both Gugumus [40] and Klyosov [53] make reference to the addition of fillers causing decreases in polymer oxidative stability, this effect should not be discounted.

Rotational Moulding Trials

Once a suitable level of stabilisation for the HP741T polypropylene had been established, composite granules based upon this material were produced and rotationally moulded. The following composite formulations were chosen:

- HP741T polypropylene (stabilised) / 10vol% “lab glass” glass fibre / 3vol% H11339 maleic anhydride coupling agent

- HP741T polypropylene (stabilised) / 20vol% “lab glass” glass fibre / 3vol% H11339 maleic anhydride coupling agent

The Clariant H11339 coupling agent used here was a direct replacement for the Honeywell A-C 950P coupling agent previously used, and had been shown in trials to be similarly effective. Efficient dispersion of the coupling agent and antioxidant additions throughout the composite material was encouraged by pre-mixing these components with micronised polypropylene powder, which comprised 25% of the total polypropylene fraction. The remaining polypropylene within the composite formulation was retained in granular form, as it was received. The composite mixtures were extrusion compounded, granulated, and then rotationally moulded to the parameters given below. A batch of extrusion compounded HP741T polypropylene granules, stabilised with 8000ppm of each antioxidant but without additions of either glass fibre or coupling agent, were also rotationally moulded as a reference material. All of the resultant mouldings were then tested for impact and tensile properties.

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 10mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* No

Sieved: No

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box*Charge weight:* 400g

Double/single shot process: Single shot

Oven set temperature: 300ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Target PIAT: As indicated in Figure 4.14

Cooling: Immediate fan cooling upon mould removal from oven

Internal mould pressurisation: None

Demoulding Temperature: 70 ºC

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Three specimens per material

Testing speed: 5mm/min

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact

Repetition: Three specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

Rotational moulding of these materials bore out the results of the earlier melt-flow simulation tests: the composite containing 10vol% glass fibre showed an excellent degree of granule flow and coalescence, while the composite containing 20vol% glass fibre exhibited poorer granule flow and significant lumpiness of the interior moulded surface. This can be seen in Figure 4.13. No significant voids were noted at the granule boundaries within either composite moulding. Rotational moulding of the unfilled HP741T polypropylene granules was successful with excellent material flow observed.

Figure 4.13: Rotomoulded samples produced from HP741T polypropylene-matrix composite granules, containing 10vol% glass fibre (left) and 20vol% glass fibre (right).

The results of the tensile and impact testing conducted on these materials are shown in Figure 4.14.

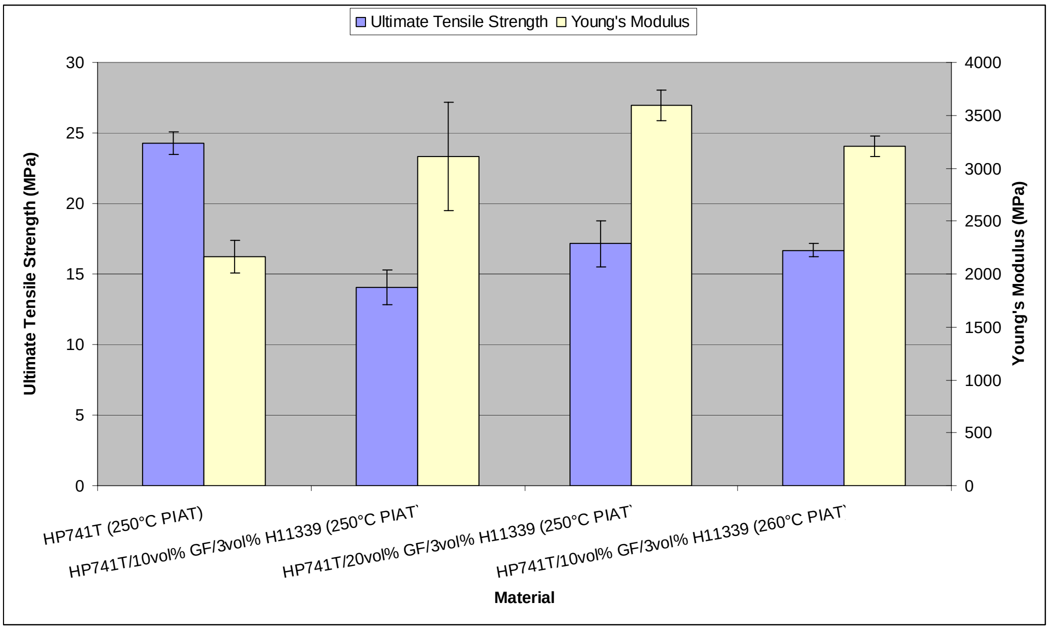

Figure 4.14: Tensile properties of rotationally moulded HP741T polypropylene/glass fibre composites. Error bars ±1 standard deviation.

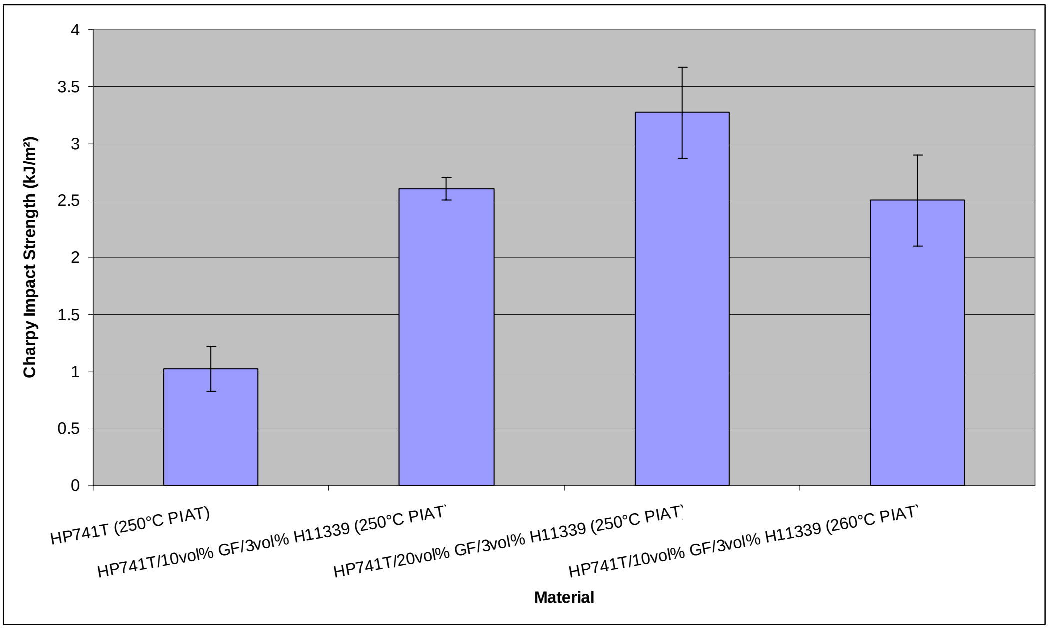

Figure 4.15: Notched Charpy impact strength of rotationally moulded HP741T polypropylene/glass fibre composites. Error bars ±1 standard deviation.

It may be seen from these results that the mechanical properties of these rotationally moulded composites were relatively poor, with both impact strength and ultimate tensile strength lower than that exhibited by the commercial rotomoulding grades of unfilled polyethylene and polypropylene. Some increases in Young's modulus were noted, however. By comparison with the rotomoulded sample of unfilled HP741T polypropylene, it is evident that the addition of glass fibre and coupling agent has resulted in a significant reduction in ultimate tensile strength. It also appears that the rotomoulding process itself has significantly weakened the unfilled HP741T polypropylene sample. This is apparent when the properties of this moulding are compared to those obtained from injection moulded HP741T polypropylene samples.

In order to ascertain the reasons for the poor performance of these materials, a number of tests were conducted. Firstly, the remaining stabilisation capacity of the rotomoulded samples was determined on the basis of oxidation induction time, using DTA-TGA analysis. As has been previously mentioned, these tests showed that the unfilled HP741T sample retained a significant level of antioxidants post-rotomoulding. Although a conclusive result could not be obtained for the composite samples, indications were that this material too was adequately stabilised. Secondly, extruded rod specimens were produced from the same mix of stabilised HP741T polypropylene, 20vol% glass fibre and 3vol% H11339 coupling agent as had been rotomoulded, following the same processing methods and parameters as described in section 4.3 "Screening of Potential Composites". These samples were then impact and tensile tested as is also described in that section. The results of this testing showed that the HP741T-matrix composite material when processed in this manner was comparable in mechanical properties to the best of the previously extruded and tested composite materials (Cotene 9800/30vol% glass fibre/3vol% MA coupling agent), and far superior in all tested mechanical properties to the rotationally moulded samples tested above. Therefore, it appears that the poor mechanical properties of the rotomoulded composites were a result of the processing methods and not inherent to the material.

There remain a number of possible factors which may have contributed to the failure of these rotomoulded composite samples, including oxidation of the matrix polymer which was not detectable by the thermal analysis, thermal degradation of the coupling agent additive (later shown to be a concern, see section 4.6.1), entrapment of air bubbles within the composite granules during the extrusion process (see results section 4.6.2), or poor mechanical coupling between the rotomoulded composite granules despite the appearance of adequate granule coalescence. However, composite development work with all polypropylene matrix materials was abandoned before these factors could be investigated.

Dry-mix Rotationally Moulded Composites

A strong case has been made in the literature review section of this thesis for rotomoulded composite materials to be processed using melt compounding rather than dry-mix techniques. However, during the course of this research a small number of composite mouldings were prepared by the dry-mix method for the purposes of comparison to those materials which were extrusion compounded. These mouldings were produced and tested as follows:

- **Cotene 9042 LMDPE / 20wt% (~8vol%) "lab-glass" glass fibre – 6mm fibre chop length.**

  This composite was prepared early in the course of this project, before the "Screening of Potential Composites" (section 4.3) was undertaken. The chopped glass fibre was thoroughly mixed with the polymer powder charge prior to rotational moulding, which was then conducted using the "micro-oven" rotomoulding method to the following parameters:

  Rotational Moulding (micro-oven):

Charge weight: 400g	*Oven set temperature:* 260ºC
Mould rotation speed: 5rpm	*Target PIAT:* 200ºC
Demoulding Temperature: 90 ºC	

- **Vanglobe 8539 LLDPE / 20vol% Owens Corning 415A glass fibre** *and* **Vanglobe 8539 LLDPE / 20vol% Owens Corning 415A glass fibre / 3vol% Clariant PE MA 4351 coupling agent.** These composites were prepared after the conclusion of the development work undertaken with Basell HP741T polypropylene, and prior to the work conducted with high-MFI polyethylene matrices. The production of rotomoulded composites using the dry-mix preparation method was re-examined here so that the effects of the newly acquired Owens Corning glass fibre, as a substitute for the previously utilised "lab-glass" glass fibre, could be ascertained. The component materials were thoroughly mixed before being rotationally moulded using the "Research & Development System" method. The processing parameters are listed below:

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box *Charge weight:* 400g

Double/single shot process: Single shot

Oven set temperature: 300ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Target PIAT: 250ºC

Cooling: Immediate fan cooling upon mould removal from oven

Internal mould pressurisation: None

Demoulding Temperature: 70 ºC

Test specimens were machined from each of the composite mouldings, and the impact and tensile properties of these specimens then determined. The parameters of this testing are given below, and the results are shown in Figure 4.18 and Figure 4.19. The tensile and impact properties of the corresponding, unfilled matrix polymers when rotationally moulded are shown for comparison.

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Three specimens per material

Testing speed: 50mm/min (Cotene 9042 LMDPE matrix)
5mm/min (Vanglobe 8539 LLDPE matrix)

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact

Repetition: Three specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

In all cases the chopped glass fibre appeared reasonably well distributed throughout the moulded polymer and the rotomoulding process was not disrupted to any significant extent by the fibre addition. The produced mouldings displayed even wall thickness and reasonable reproduction of mould detail, although both the interior and exterior surface finishes were marred by exposed fibre bundles and associated voids. The interior surfaces of the Vanglobe 8539 LLDPE / glass fibre mouldings in particular showed a significant proportion of the glass fibre only poorly bonded to the polymer matrix. This distribution effect is the same as noted by Torres and Aguirre [12], and also mentioned by several other authors.

Due to the lack of shear during rotational moulding, in the absence of a melt-compounding process the glass fibre remains as distinct bundles in the moulded article rather than being separated into individual fibre filaments. This may be seen in Figure 4.16, which shows as sheet machined from one of the Vanglobe 8539 LLDPE / glass fibre mouldings. These tightly packed fibres were shown by Scanning Electron Microscopy (SEM) to be only poorly impregnated by the matrix polymer, as can be seen in Figure 4.17. As a large proportion of the fibre filaments are not directly bonded to the matrix material, the strengthening effect of the fibre addition is limited.

Figure 4.16: Typical fibre distribution in a rotationally moulded “dry-mix” polyethylene/glass fibre composite.

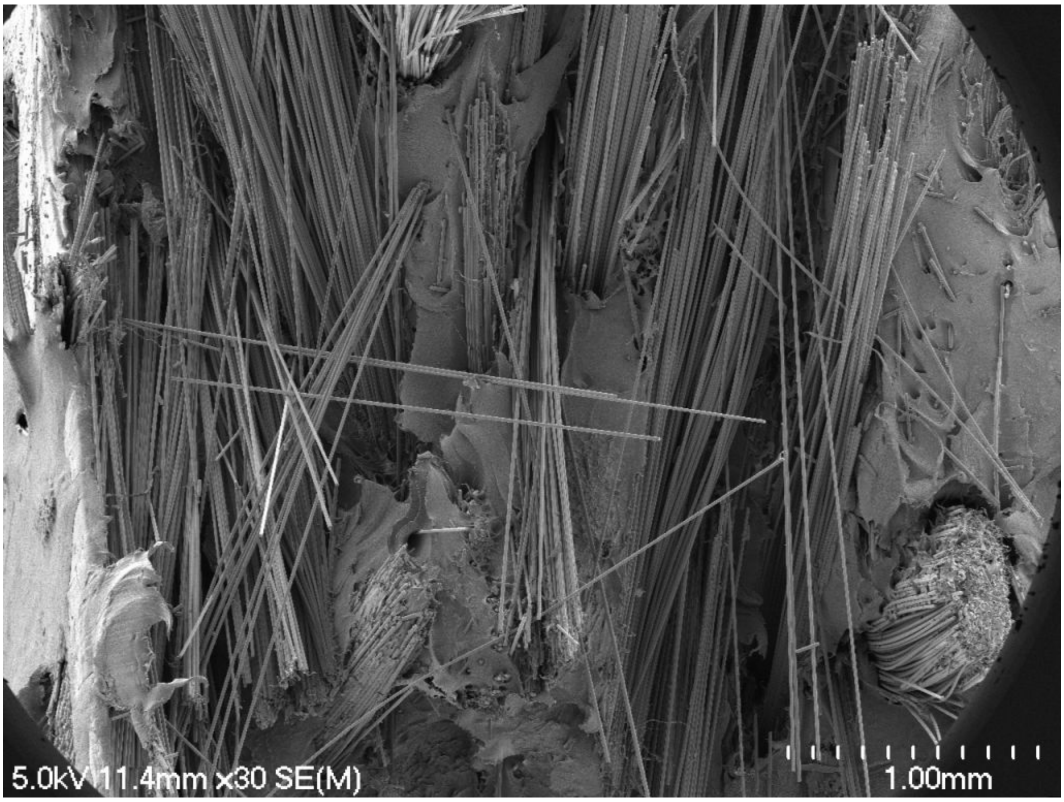

Figure 4.17a: SEM image of the fracture surface on a "dry-mix" Vanglobe 8539/glass fibre composite impact-test specimen.

Figure 4.17b: SEM image of the fracture surface on a "dry-mix" Vanglobe 8539/glass fibre composite impact-test specimen.

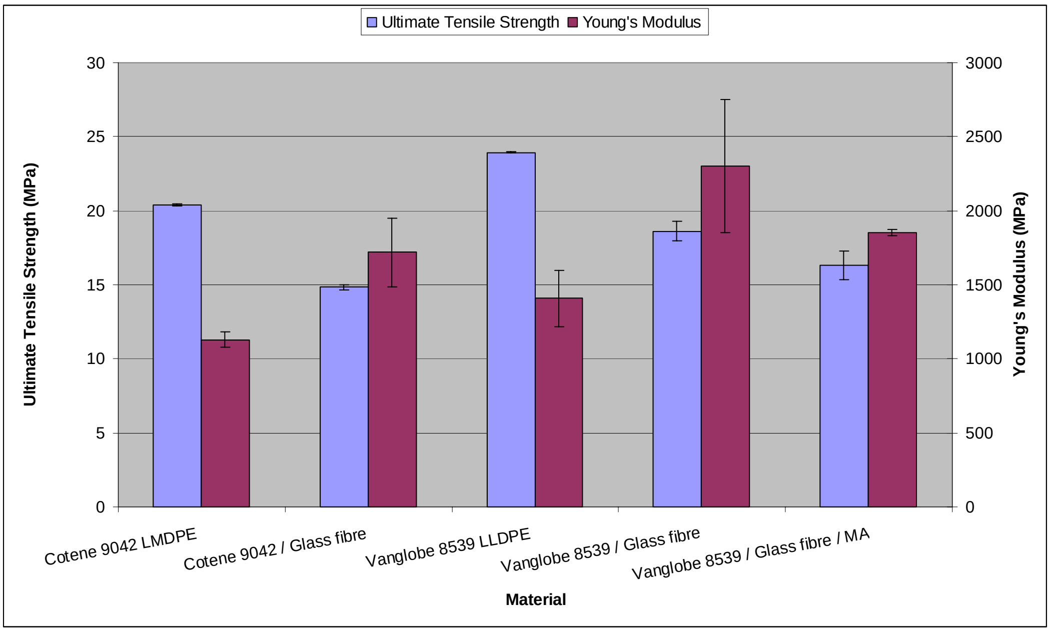

Figure 4.18: Tensile properties of "dry-mix" rotationally moulded composites. Error bars ±1 standard deviation

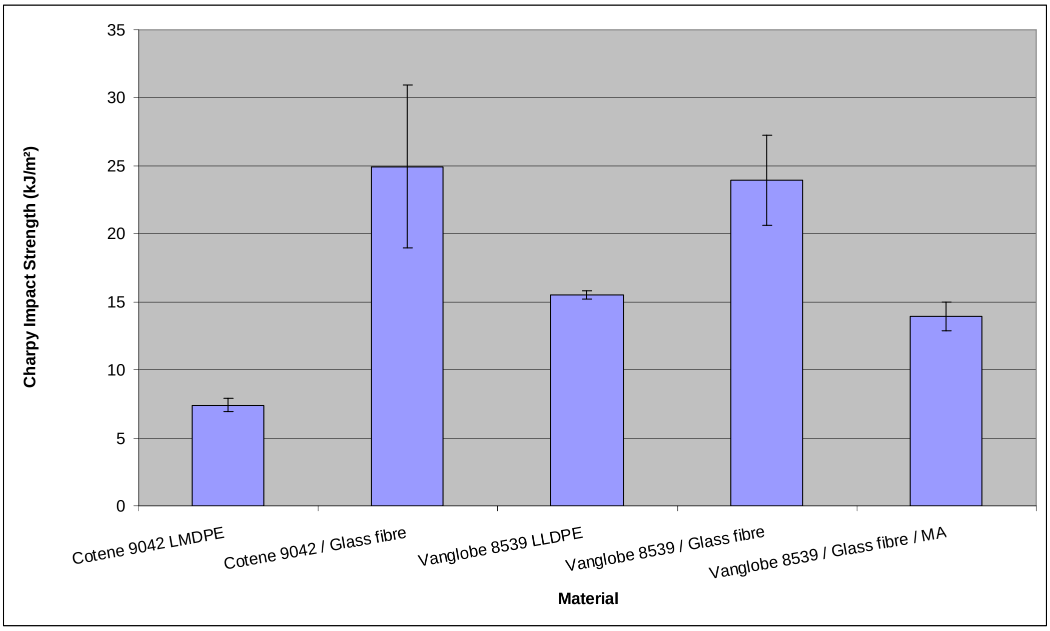

Figure 4.19: Notched Charpy impact strength of "dry-mix" rotationally moulded composites. Error bars ±1 standard deviation

The tensile test results reflect the relatively poor degree of fibre bonding, with the addition of glass fibre decreasing the ultimate tensile strength of the material in each case. The addition of glass fibre did result, however, in significant increases in Young's modulus and also in notched Charpy impact strength for two out of the three composite materials. The only composite to show decreased impact strength relative to the unfilled matrix material was the moulding containing the Clariant PE MA 4351 coupling agent. The addition of the coupling agent to the composite was in this case shown to be detrimental to all tested mechanical properties. As this coupling agent had been previously used with success during the production of extruded-rod composite specimens (section 4.3), this was an unexpected result. DSC thermal analysis of the coupling agent using the method "Thermal simulation of rotational moulding" (section 3.13.1), later revealed that this grafted polyethylene likely underwent thermo-oxidative degradation during the rotational moulding cycle. It is not known whether such degradation may have weakened the polymer matrix itself, or alternatively, reduced the interfacial strength between the matrix and fibre. Another possible contributing factor to this result was later shown to be that this coupling agent was less effective when used in conjunction with the Owens Corning 415A glass fibre than with the previously used "lab-glass" grade.

It should be noted that the above calculated mechanical properties of the “dry-mix” prepared composites may not accurately represent the average properties of the entire moulded composite layer. This is because the fibre-rich interior moulded surface is removed during the specimen machining process, thus preventing the high concentration of poorly bonded fibres from influencing the results. Nevertheless, these dry-mix composites showed that a useful combination of mechanical properties could be achieved by incorporating fibrous reinforcement using this preparation method, provided that a decreased quality of surface finish could be tolerated.

Polyethylene Matrix Composites

Polypropylene was initially chosen over polyethylene as the preferred matrix polymer for the development of rotomouldable composites, based on the test results which are summarised in section 4.3. However, it was nevertheless recognised that polyethylene did display several notable advantages. These include a higher inherent thermal stability than polypropylene, generally increased impact resistance, and a glass transition temperature that is below the foreseeable service temperatures for any of the products envisaged to result from this research. In addition, a commercial rotomoulding grade of polyethylene was the most likely material to be used as the outer skin of any dual-layer rotomoulded composite product. Utilising polyethylene rather than polypropylene for the matrix of the composite layer would enhance bonding to the polyethylene outer skin and also keep the processing temperatures required for the rotomoulding of each layer similar. For these reasons, polyethylene was eventually selected to supersede the use of high-MFI grades of polypropylene, following the poor performance of the polypropylene-based rotomoulded composite samples (section 4.4).

As had been conducted during the formulation of the polypropylene matrix composites, the melt-flow simulation technique was used to determine the feasibility of basing a glass-fibre reinforced composite material upon commercial grades of rotational moulding polymer. A small batch of Cotene 3979 HDPE (MFI: 4.5g/10min) granules reinforced with 10vol% of “lab-glass” glassfibre were extrusion compounded and prepared as has been previously described. These granules were then tested and shown to exhibit very similar melt-flow behaviour to those composite granules based on Cotene 9800 polypropylene and containing the same percentage of glass fibre. Therefore, as had been discovered during the research with polypropylene-matrix composites, a high-MFI polyethylene grade was seen to be needed if successful rotational moulding of these granules was to be achieved.

Dow Plastics DOWLEX 2517 LLDPE

The only potentially suitable high-MFI polyethylene grade available at the time that a replacement for the polypropylene matrices was first sought was Dow Plastic DOWLEX 2517 LLDPE (MFI: 25g/10min). This polyethylene grade exhibited a suitable increase in melt flow index over the rotomoulding polyethylene grades tested in section 4.1, but was shown to be deficient in both strength and stiffness as can be seen in Figure 4.21. This polyethylene grade is formulated primarily for processing via injection moulding, and as such also lacks the enhanced oxidative stability that rotational moulding necessitates.

Stability Analysis and Antioxidant Addition

As conducted with the injection-moulding grade polypropylene HP741T, the oxidative stability of the Dow 2517 LLDPE grade was established on the basis of oxidation induction time. Samples of this polymer were then extrusion compounded with varying levels of the antioxidants Ciba IRGANOX 1010 and IRGAFOS 168, granulated, micronised and reanalysed. The parameters of the extrusion process are given below, and the OIT values determined for each material are shown in Figure 4.20.

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):
110ºC 130ºC 150ºC 160ºC 160ºC
Screw speed: 150rpm
Die: Single aperture, 10mm diameter
Material Cooling: Air cooled (non-forced)

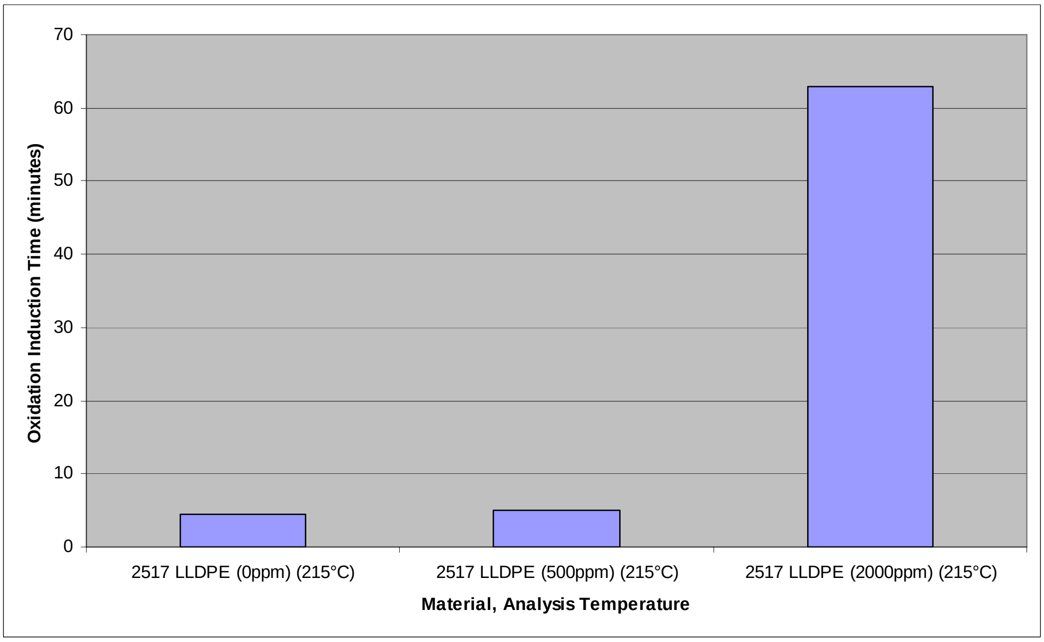

Figure 4.20: High-temperature oxidative stability of stabilised DOWLEX 2517 LLDPE samples. Estimated error ±10%

The isothermal analysis temperature for these samples was chosen to be 215°C, as this corresponds to the target PIAT for the rotational moulding of Cotene 3979 HDPE which was the polymer grade most likely to be chosen as the outer skin of any dual-layer composite moulding. It can be seen from Figure 4.20 that at this temperature and in the absence of any added antioxidants, the OIT of Dow 2517 LLDPE is significantly below that of the previously tested rotomoulding grades of polyethylene, as is to be expected. An addition of only 500ppm of each antioxidant did not significantly change the OIT value of the tested sample, due either to poor distribution of the added antioxidants through the polymer or antioxidant consumption during the extrusion and/or micronising processes. An addition of 2000ppm of each of IRGANOX 1010 and IRGAFOS 168 was required to raise the OIT value of the polymer to a level comparable to that of the commercial rotomoulding grades of polyethylene. The effectiveness of this level of stabilisation was then tested when the Dow 2517 LLDPE was compounded with 30vol% of glass fibre, and no decrease was seen in the resultant OIT value. Samples of Dow 2517 LLDPE, both unmodified and containing 2000ppm of each additional antioxidant, were also subjected to thermal simulations of the rotational moulding cycle prior to OIT determination. The results of these tests showed that only a relatively minor consumption of the added antioxidant was experienced during simulated rotational moulding, with even the polymer sample which did not contain additional stabilisation not seen to oxidise until after the simulated moulding cycle had been completed. This indicates that the majority of antioxidant consumption within this material occurs only at temperatures close to the peak test level of 215°C, and therefore a typical rotomoulding cycle which subjects the polymer to PIAT for only a short duration does not have as great a tendency to oxidise the material as might be expected based upon the isothermal analysis data. Despite possibly being excessive, a stabilisation level of 2000ppm of each antioxidant was adopted for the subsequent work with this polyethylene, to ensure that oxidation did not compromise the tested mechanical properties or processing behaviour of the material.

Composite Melt-flow Simulation

The melt-flow simulation technique was used to determine the percentage of glass fibre which could be compounded with this polymer while still retaining adequate levels of granule flow and consolidation. The component materials of each composite sample were thoroughly mixed, extruded and then granulated. The processing parameters specific to these samples are given below:

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):
100ºC 125ºC 150ºC 175ºC 175ºC
Screw speed: 150rpm
Die: Single aperture, 10mm diameter
Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* Yes
Sieved: Yes *Retained size fraction:* 2.8-3.5mm

By this method, it was determined that an addition of 20vol% of Owens Corning 415A glass fibre to the Dow 2517 LLDPE was near the maximum level if a sufficient degree of granule flow and coalescence for rotational moulding was to be retained. The addition of paraffin liquid (white mineral oil) to the composite system prior to extrusion compounding was also trialled, as this additive has been identified by Chaudhary et al. [77] as enhancing particle coalescence and bubble removal in rotationally moulded polyethylene. In these trials, however, the addition of 3vol% of paraffin liquid was not seen to significantly affect the melt-flow properties of the composite granules.

It may be observed from these tests and also from later work that MFI values cannot be directly compared between polypropylene and polyethylene grades as a measure of composite granule flow. In this particular instance, Dow 2517 LLDPE (MFI: 25g/10min (190°C/2.16kg)) was seen to accept an addition of twice as much glass fibre as the previously trialled Basell HP741T polypropylene (MFI: 60g/10min (230°/2.16kg)) while maintaining a similar degree of granule flow and coalescence. The system of assigning MFI values to different polymers makes use of a range of test conditions, thus often preventing direct comparisons from being made between different polymer types or grades. The melt flow index of any particular polymer is also not the sole factor in determining the flow of the composite materials based upon it.

Effects of Coupling Agents

Following the successful stabilisation and composite flow testing conducted with the Dow 2517 polyethylene grade, the effects of the different coupling agents had upon the mechanical properties of a Dow 2517 LLDPE / Owens Corning 415A glass fibre composite system were investigated. Although the addition of both maleic anhydride and silane based coupling agents to melt-compounded polyethylene/glass fibre composites had been previously been shown to be beneficial (section 4.3), the different grades of polymer and fibre used here necessitated that the performance of the coupling agents be re-examined.

As a result of the decreased mechanical properties seen to accompany the introduction of the Clariant PE MA 4351 coupling agent to the polyethylene/glass fibre “dry-mix” moulding described in section 4.5, all of the coupling agents listed in this materials section of this thesis (section 3.1) were checked to see if likely to be subject to thermo-oxidative degradation during rotational moulding. This was accomplished using DSC analysis to simulate the heating cycle of the rotomoulding process, as is described in methodology section 3.13.1. The peak temperatures of the simulation cycle were specified to be 205°C for the polyethylene-specific coupling agents and 250°C for the polypropylene-specific coupling agents – representative of the peak rotomoulding mould-internal air temperatures for typical polyethylene and polypropylene grades, respectively. This testing revealed that all of these coupling agents were prone to thermo-oxidative degradation under typical rotomoulding heating conditions for their respective polymer matrices. Those coupling agents formulated upon grafted polypropylene, however, showed sufficient thermal stability for inclusion in rotationally moulded polyethylene. Therefore, the coupling agents Honeywell A-C 950P and Clariant H11339 were selected for inclusion in the following trials.

Samples of the following materials were prepared by extrusion compounding, granulation and injection moulding. The previously outlined objections to the use of injection moulding for providing an indication of rotomoulded material performance were felt not be relevant in this case, as only the relative effects of the different coupling agents were being investigated. Tensile and impact tests were then conducted on the produced specimens. The processing and testing parameters specific to these samples are given below:

Composite Formulations:

- Dow 2517 LLDPE (stabilised)
- Dow 2517 LLDPE (stabilised) / 30vol% Owens Corning 415A glass fibre
- Dow 2517 LLDPE (stabilised) / 30vol% Owens Corning 415A glass fibre / 3vol% Clariant H11339
- Dow 2517 LLDPE (stabilised) / 30vol% Owens Corning 415A glass fibre / 3vol% Honeywell A-C 950P

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 10mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* No

Sieved: No

Injection Moulding:

Die: ASTM D638 – 03 Type I tensile test specimen

Peak processing temperature: 200ºC

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Five specimens per material

Testing speed: 5mm/min

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact

(Notched dimensions 10.0mm wide x 3.1mm thick)

Repetition: Five specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

It may be noted in the above parameters that the peak extrusion compounding temperature is higher than that previously used with polyethylene-matrix composites. This increase was adopted to encourage even distribution of the IRGAFOS 168 antioxidant additive, which has a melting temperature range of 183-186°C. These parameters were utilised for all compounding of polyethylene-based materials conducted after this time.

The tensile and impact properties of the injection moulded samples are shown in Figure 4.21 and Figure 4.22

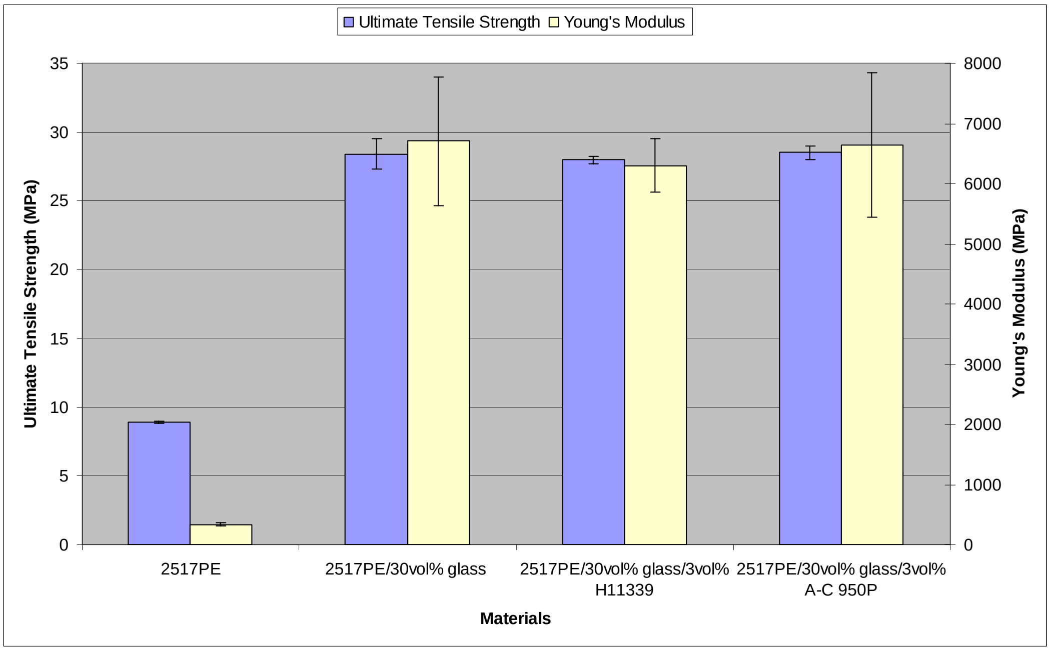

Figure 4.21: Tensile properties of injection moulded Dow 2517 LLDPE-matrix composites. Error bars ±1 standard deviation

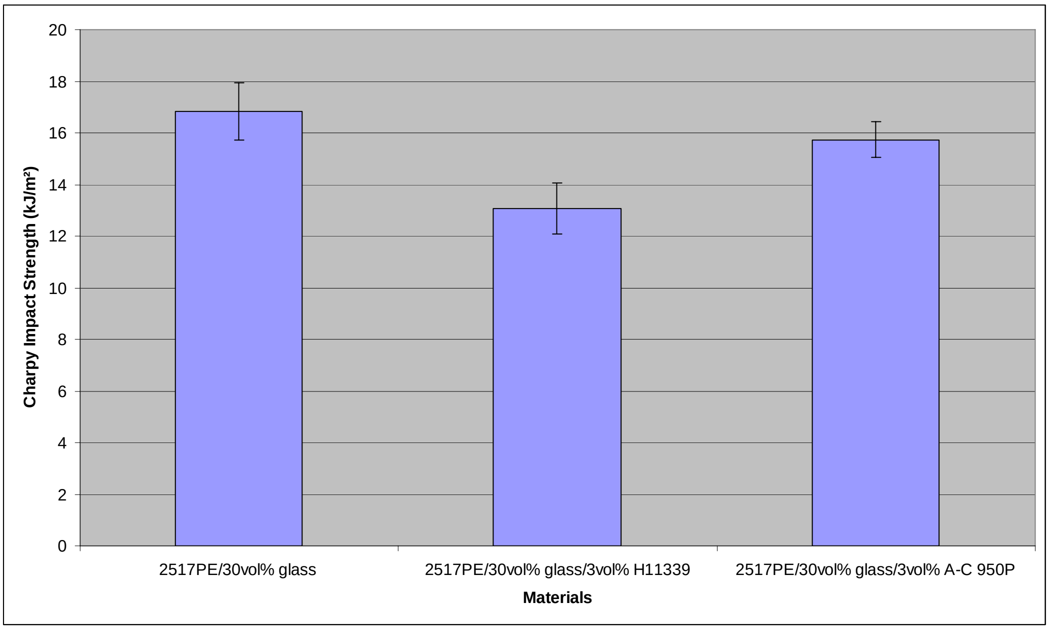

Figure 4.22: Notched Charpy impact strength of injection moulded Dow 2517 LLDPE-matrix composites. Error bars ±1 standard deviation

These results show that the tested coupling agents either have no significant effect or are detrimental to the mechanical properties of the moulded composites. It may also be noted that although the tensile properties shown for these samples represent a significant improvement over the properties of the unfilled polymer, they are relatively modest in comparison to some of the previously tested composite samples based upon stronger polymer grades. The impact performance of the composite samples relative to the unfilled polymer could not be determined, as unreinforced Dow 2517 LLDPE proved to be too flexible for impact testing to be conducted successfully. Although the previous caution about inferring the properties of rotomoulded composite materials based upon injection moulded samples does apply, this may be an indication that the relatively weak and flexible Dow 2517 polyethylene is a limiting factor upon the performance of this composites based upon it. This polyethylene grade was replaced with the stronger ExxonMobil HMA-018 HDPE grade before rotationally moulded composite samples could be prepared.

ExxonMobil HMA-018 HDPE

This high density polyethylene was acquired to replace the Dow 2517 LLDPE grade. It possesses a MFI higher than Dow 2517 along with substantially improved tensile strength and stiffness, although low-temperature flexibility is decreased. Thermal analysis revealed that, as an injection moulding polyethylene grade, ExxonMobil HMA-018 HDPE was deficient in terms of oxidative stability compared to the previously testing commercial rotomoulding polymers. Based upon the trials conducted with Dow 2517 LLDPE, an addition of 2000ppm of each of IRGANOX 1010 and IRGAFOS 168 antioxidants was selected as appropriate to improve the oxidative stability of this polymer to the necessary level for rotational moulding. This level of antioxidant addition was shown by thermal analysis to be sufficient for rotational moulding of both unfilled polymer and polymer-matrix composite samples.

Injection Moulding Trials

Injection moulding was used to assess both the mechanical properties of the unfilled ExxonMobil HMA-018 polyethylene and to further investigate the effect of coupling agents when used in conjunction with the polyolefin-compatible glass fibre Owens Corning 415A. It had been previously shown that oxidative degradation of the grafted-polymer coupling agents was a concern during rotational moulding, but this issue was disregarded for the purposes of these tests. By removing the influence of the rotational moulding process, the performance of these coupling agents with this composite system could be ascertained without having to account for the occurrence of thermo-oxidative degradation. These tests would then reveal whether pursuing the use of these coupling agents in a rotomouldable composite material was worthwhile.

The following material formulations were prepared by extrusion compounding and granulation prior to injection moulding. A fibre fraction of 20vol% was selected for these trials, based on the results of the melt-flow simulation testing conducted with Dow 2517 LLDPE-matrix composites. Tensile and impact tests were then conducted on the produced specimens and the results of this are given in Figure 4.23 and 4.24. The processing and testing parameters specific to these samples are given below:

Material Formulations:

- ExxonMobil HMA-018 HDPE (stabilised)
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 3vol% Clariant H11339
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 3vol% Clariant PE SI 3361
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 3vol% Clariant PE MA 4351

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 10mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* No

Sieved: No

Injection Moulding:

Die: ASTM D638 – 03 Type I tensile test specimen

Peak processing temperature: 200ºC

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Five specimens per material

Testing speed: 5mm/min (composite samples)
50mm/min (unfilled polymer samples)

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact
(Notched dimensions 10.0mm wide x 3.1mm thick)

Repetition: Five specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

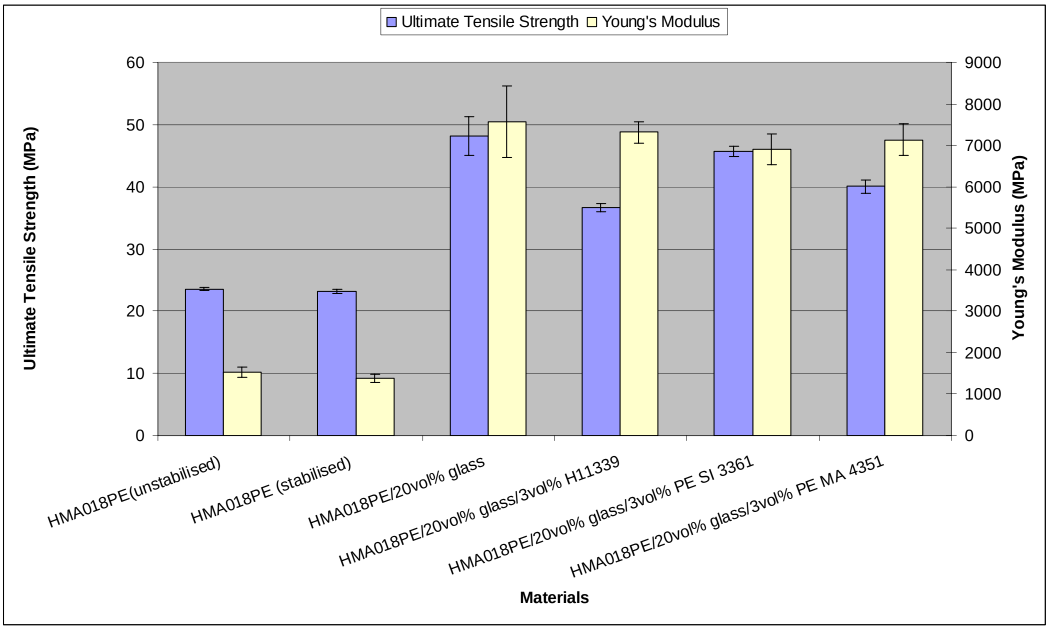

Figure 4.23: Tensile properties of injection moulded HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

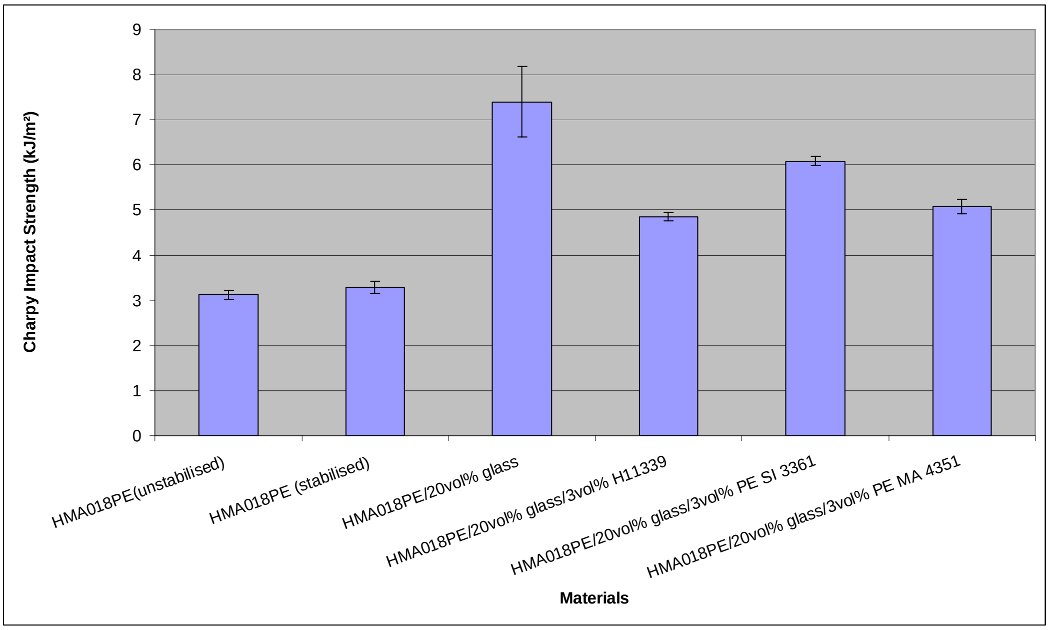

Figure 4.24: Notched Charpy impact strength of injection moulded HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

Two main conclusions may be drawn from these results: the melt compounding process and addition of antioxidants have not compromised the mechanical performance of the unfilled polymer, and the addition of any of the tested coupling agents to the composite material does not appear to be beneficial. As no evidence exists in this research that the coupling agents affect the properties of the polymer matrix itself, it is concluded that this polyolefin-specific grade of glass fibre does not require the addition of coupling agents in order to bond well with a polyethylene matrix. Therefore, no further attempts were made to include any of the listed coupling agents in the composite materials prepared after this time.

Composite Melt-flow Simulation

As conducted with the previously utilised polymer grades, the melt-flow simulation technique was used to identify suitable composite formulations prior to undertaking rotomoulding trials. Samples of the following materials were prepared by extrusion compounding and granulation, following which they were tested as described in methodology section 3.6.

Material Formulations:

- ExxonMobil HMA-018 HDPE (stabilised) / 15vol% Owens Corning 415A glass fibre
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 3vol% paraffin liquid
- ExxonMobil HMA-018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 3vol% Clariant OP-P

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):
150ºC 170ºC 190ºC 200ºC 200ºC
Screw speed: 150rpm
Die: Single aperture, 10mm diameter
Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm *Microniser granule rounding:* Yes
Sieved: Yes *Retained size fraction:* 2.8-3.5mm

These melt-flow simulations showed that granules comprised of ExxonMobil HMA-018 HDPE and 15vol% glass fibre could be expected to flow and coalesce to a satisfactory degree during rotational moulding, with only slight surface irregularities seen to remain on the melt-flow simulation sample. Raising the fraction of glass fibre to 20vol% resulted in what was considered to be only a marginal degree of granule coalescence, with significant surface roughness evident remaining on the melt-flow specimen. In an attempt to improve the flow of those granules containing 20vol% of glass fibre to a level more suitable for rotational moulding, samples containing two potentially flow-enhancing additives – paraffin liquid and Clariant Licowax OP-P – were prepared. Neither of these additives was seen to significantly alter the degree of granule flow and coalescence.

Rotational Moulding Trials - First Iteration

As an addition of 15vol% glass fibre to the HMA-018 HDPE grade had been shown to give a satisfactory degree of granule flow, it was this composite formulation which was adopted for rotational moulding trials. The composite granules were produced by extrusion compounding and granulation to the process parameters given below. Rotational moulding was conducted using both a single-shot process to produce a single layer moulding, and a two-shot process where the composite material formed the inner layer of the moulding and the exterior was formed from Vanglobe 8539 LLDPE powder. This latter moulding closely replicated the multi-layer construction likely to be utilised in the commercial products arising from this research. Rotationally moulding samples in this manner, however, complicated the machining of test specimens from the composite material layer. It was for this reason that multi-layer moulding was not more widely used during this research.

Material Formulation:

- ExxonMobil HMA 018 HDPE (stabilised) / 15vol% Owens Corning 415A glass fibre

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 200ºC

Screw speed: 150rpm

Die: Single aperture, 10mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 8mm	*Microniser granule rounding:* Yes
Sieved: Yes	*Retained Fraction:* 2.8-3.5mm

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box

Charge weight: Single-shot: 400g

Two-shot: 200g PE powder, 280g composite granules

Oven set temperature: 300ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Target PIAT: 205°C

Cooling: Fan cooling applied after internal air temperature <100°C

Internal mould pressurisation: 10psi upon cessation of heating

Demoulding Temperature: 50 ºC

Both of the produced mouldings showed relatively good granule flow, with an absence of significant voids or pinholes and only minor residual lumpiness evident at the interior moulded surface. The dual-layer moulding was seen to be slightly improved over the single-shot moulding in this respect. Segregation of the layers within the two-shot moulding was also seen to be good, with an even distribution of the composite and excellent bonding evident between the composite and unfilled polyethylene layers. The tensile and impact properties of the composite layers are shown in Figure 4.25 and Figure 4.26, and the parameters to which these tests were conducted are given below.

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Five specimens per material

Testing speed: 5mm/min (composite samples)

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact

Repetition: Five specimens per material

Hammer impact: 0.475kg @ 2.9m/s (2.0J)

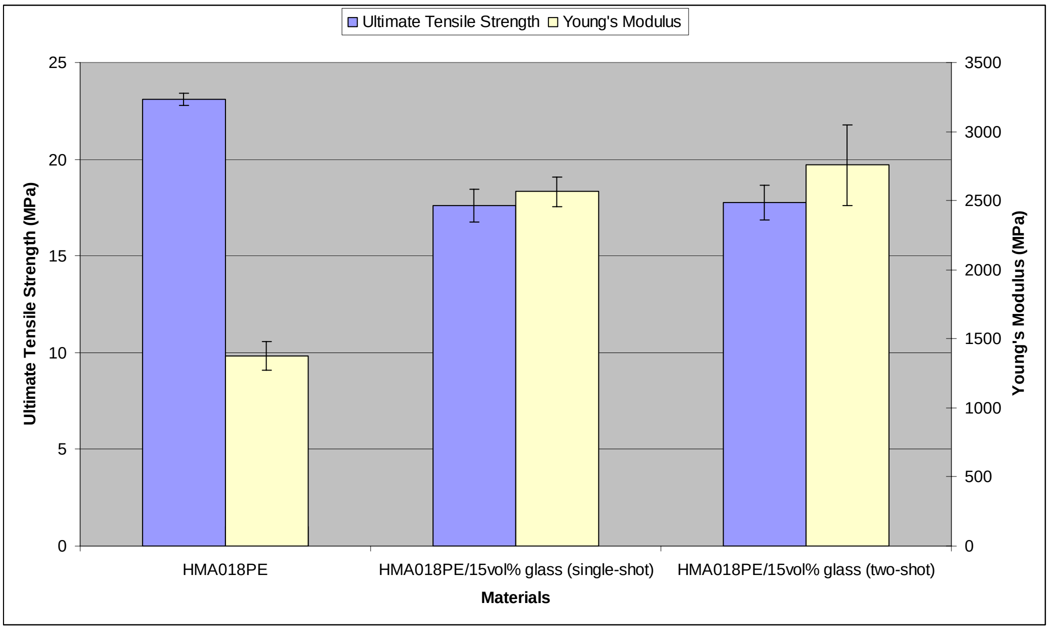

Figure 4.25: Tensile properties of rotomoulded HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

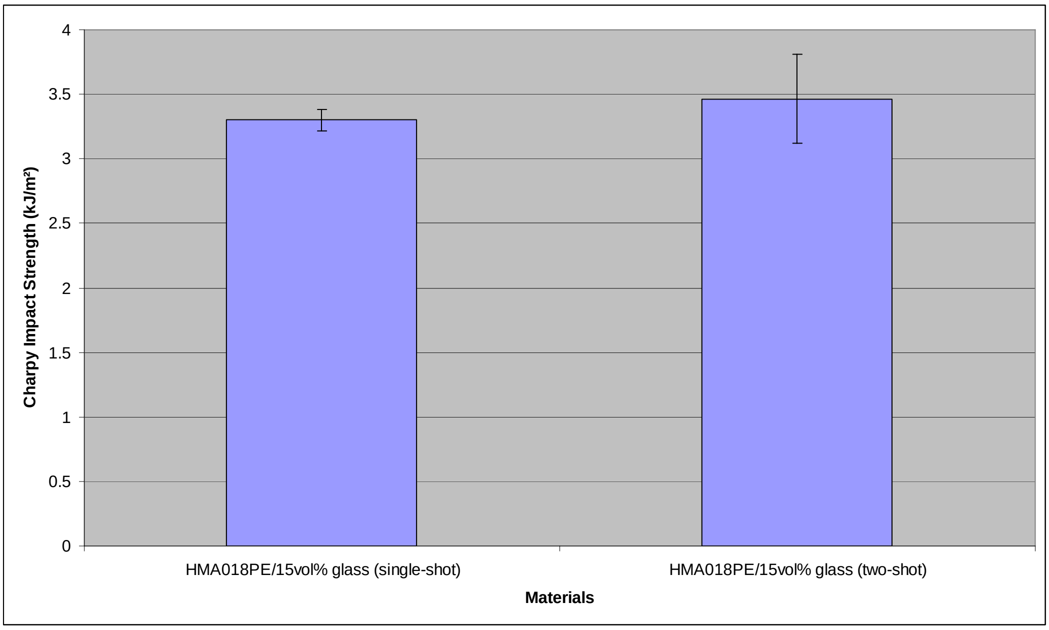

Figure 4.26: Notched Charpy impact strength of rotomoulded HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

It may be seen from Figure 4.25 and Figure 4.26 that there was no significant difference in the mechanical properties of the composite when moulded using a two-shot process as opposed to being rotomoulded as the sole material charge. In Figure 4.25 the tensile properties of the moulded composite are contrasted against the properties of injection moulded, unfilled HMA-018 HDPE, and this comparison shows that the ultimate tensile strength of the rotationally moulded composite is disappointingly poor. The rotomoulded HMA-018-matrix composites are also seen to be only slightly stronger than the previously prepared composites based on Basell HP741T polypropylene matrices. Although the Young’s modulus of the HMA-018-matrix composite samples represents a considerable improvement over that of both the unfilled HMA-018 HDPE and the commercial grades of unfilled rotomoulding polyethylene, the low tensile strength and low impact strength restrict this usefulness of this material. The impact strength of unfilled HMA-018 HDPE is not directly contrasted to the composite materials shown in Figure 4.26 as the different specimen dimensions utilised during testing prevent accurate comparisons from being made.

Following the moulding and testing of these samples, it was noted that a large number of small (approximately 0.25mm diameter) bubbles appeared to be entrapped within the composite material. Further investigations revealed that these bubbles were present within the composite granules prior to rotational moulding, and were then retained within the moulded structure. An example of these bubbles may be seen in Figure 4.27, which is a magnified image of a polished, rotomoulded composite sample. Although subsequently proven to be also present in the previously rotomoulded polypropylene-matrix composites, these bubbles had not been detected prior to the use of HMA-018 HDPE as they were obscured by the opacity of the polypropylene matrix. All composite samples prepared from melt-compounded granules by injection moulding were found to be bubble-free, however.

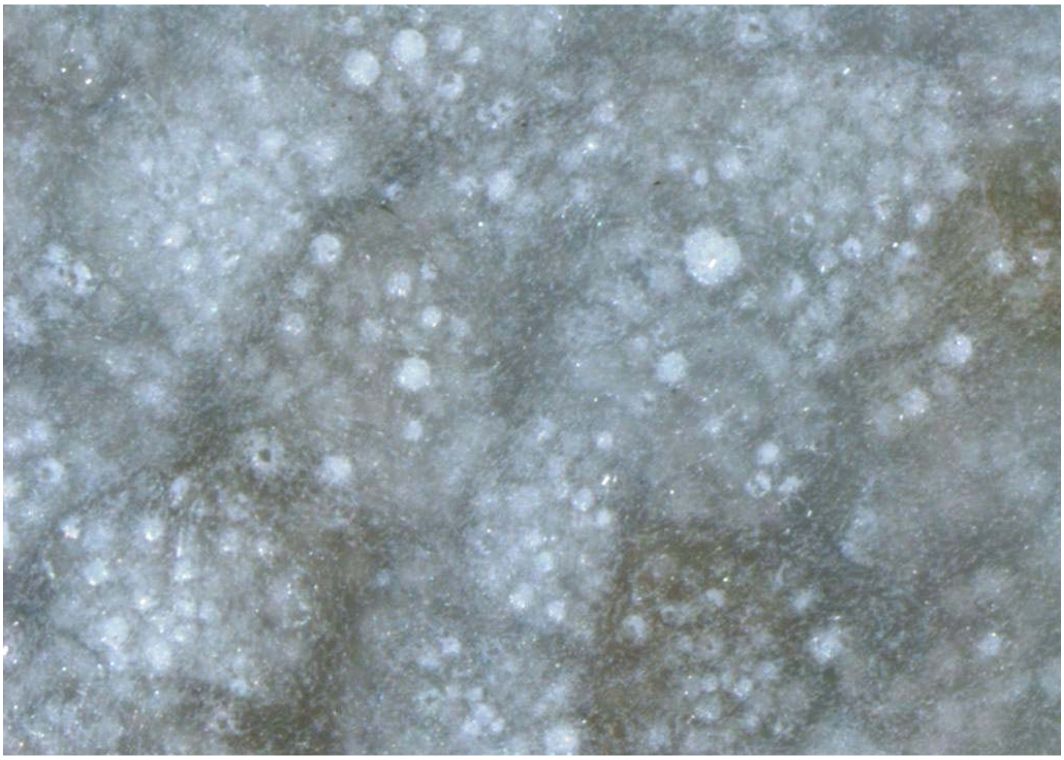

Figure 4.27: Microscope image of air bubbles entrapped within a rotomoulded composite sample.

The presence of these bubbles within the rotomoulded composites was identified as being potentially detrimental to mechanical properties, and therefore attempts were made to prevent their occurrence. Subsequent investigations showed that the bubbles were a result of air entrapment during the extrusion compounding process and were not attributable to moisture or the loss of volatiles from the component materials. Preventing the formation of these air bubbles during extrusion was eventually accomplished by applying a mild vacuum to the molten material as it passed through the extruder barrel, using the barrel access port closest to the extruder die. In the absence of an applied vacuum, variations in extrusion temperature, speed and die constriction were found to be ineffective at preventing bubble formation.

At the same time the problem of air entrapment was discovered and corrected, the previously utilised 6mm and 10mm aperture extruder dies were replaced with a die of 3mm aperture diameter. This smaller diameter die was found to improve the quality of the subsequent composite granules by reducing the percentage of fines and angular shards produced during the granulation process. As such, composite granules noted in this thesis as extruded using either the 3mm aperture die, or the later adopted 1.5mm diameter circular aperture die, may be regarded as being essentially bubble-free. The reduced extrusion screw speeds that can be seen to accompany the use of these tightly constricted dies were found to be necessary to keep the extrusion pressure at safe levels.

Rotational Moulding Trials - Second Iteration

Following the perfection of the process to obtain extrusion-compounded composite granules free of entrapped air, the previously tested composite formulation of HMA-018 HDPE / 15vol% glass fibre was re-examined. To this trial three new composite formulations were added, for the purposes of investigating different levels of fibre addition and the effects of a polyolefin modifying additive: Kraton MD-6932. This additive is a styrenic block copolymer purported to improve the ambient temperature impact resistance of polyolefins, and is similar to that successfully applied by Tinson et al. [78] for improving the sintering behaviour of polyethylene. The parameters of the extrusion, granulation and rotational moulding processes used with these composite materials are listed below.

Material Formulations:

- ExxonMobil HMA 018 HDPE (stabilised) / 15vol% Owens Corning 415A glass fibre
- ExxonMobil HMA 018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre
- ExxonMobil HMA 018 HDPE (stabilised) / 15vol% Owens Corning 415A glass fibre / 5vol% Kraton MD-6932
- ExxonMobil HMA 018 HDPE (stabilised) / 20vol% Owens Corning 415A glass fibre / 5vol% Kraton MD-6932

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):

150ºC 170ºC 190ºC 200ºC 165ºC

Screw speed: 75rpm

Die: Single aperture, 3mm diameter

Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 6mm

Micronise granule rounding: No

Sieved: No

Average granule size: ~3mm equiaxial

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box*Charge weight:* 450g

Double/single shot process: Single shot

Oven set temperature: 300ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Target PIAT: 205ºC

Cooling: Fan cooling applied after internal air temperature <100°C

Internal mould pressurisation: 10psi upon cessation of heating

Demoulding Temperature: 50 ºC

Examination of the resultant mouldings showed that the Kraton MD-6932 additive had not visually improved the sintering or flow behaviour of the composite granules to any significant extent. Despite this, excellent coalescence of those composite granules containing 15vol% glass fibre was achieved, with only minor pin-holes evident upon the exterior moulded surface and slight residual lumpiness on the moulded interior. The composite formulations containing 20vol% of glass fibre showed a greater tendency for lumpiness of the inner surface, but overall granule coalescence was still judged to be adequate. It appeared that the removal of the entrapped air bubbles from the composite granules aided in the rotomoulding of these materials.

The parameters of the tensile and impact testing conducted upon these mouldings are given below, and the test results are shown in Figure 4.28 and Figure 4.29. The mechanical properties of the previously rotomoulded sample of HMA-018 HDPE/15vol% glass fibre, which was subsequently found to contain entrapped air bubbles, are included for comparison.

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)
Repetition: Five specimens per material
Testing speed: 5mm/min (composite samples)

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact
Repetition: Five specimens per material
Hammer impact: 0.475kg @ 2.9m/s (2.0J)

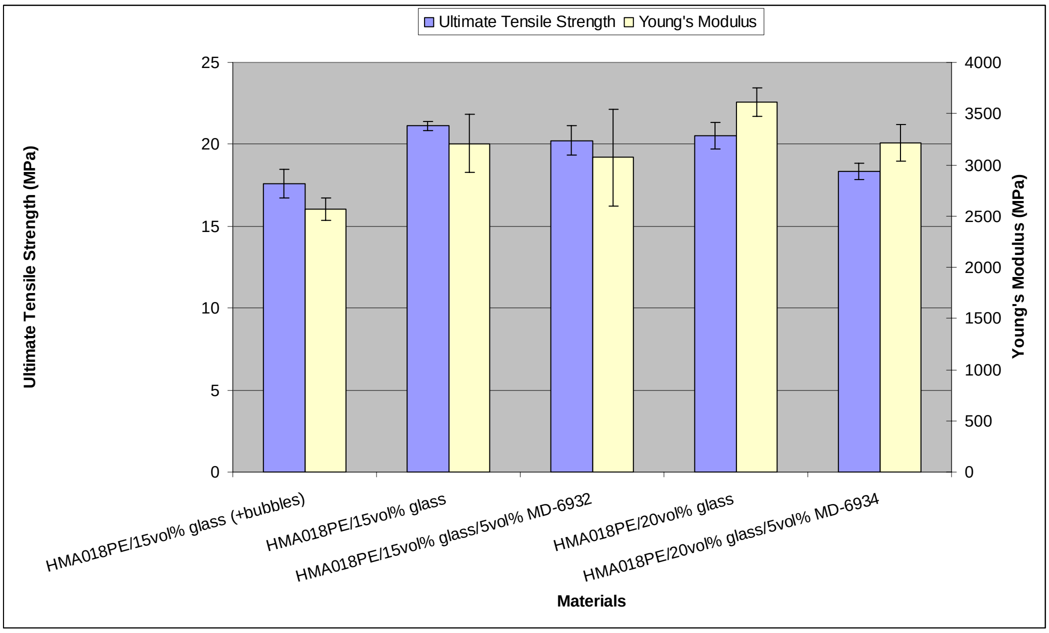

Figure 4.28 Tensile properties of rotomoulded, bubble-free HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

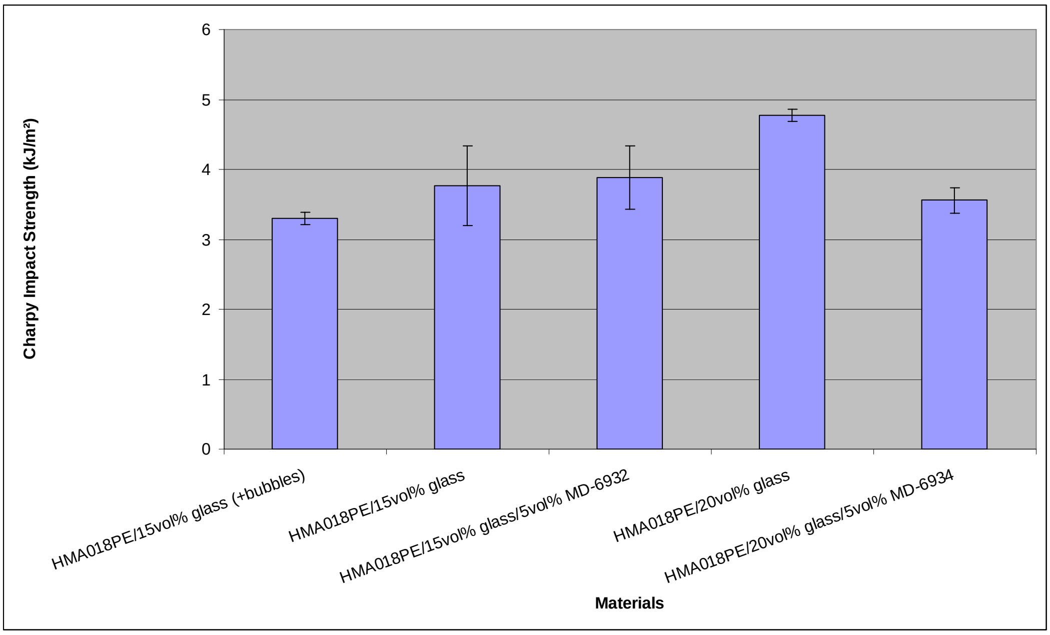

Figure 4.29: Notched Charpy impact strength of rotomoulded, bubble-free HMA-018 HDPE-matrix composites. Error bars ±1 standard deviation

These results show that by removing the entrapped air from the composite granules, the properties of the resultant moulding were improved by approximately 3.5MPa in ultimate tensile strength and approximately 650MPa in

Young’s modulus, as well as giving a slight increase in impact strength. The addition of Kraton MD-6932 was not shown to be beneficial to the tested tensile properties of the moulded composite in either case, while the effects of this additive upon impact strength were inconclusive. Putting aside those composites containing the Kraton additive, it may be seen that increasing the percentage of glass fibre from 15vol% to 20vol% gave improvements in both impact strength and Young’s modulus, although a minor decrease in ultimate tensile strength was recorded. Given the lesser degree of granule flow exhibited by the 20vol% glass fibre composite compared to the 15vol% glass fibre composite, neither composite was deemed to be clearly superior over the other.

Rotational Moulding Trials - Third Iteration

Despite the visually good granule coalescence exhibited by the bubble-free HMA-018 HDPE rotomoulded composites, close examination revealed that a granular structure was retained to some extent even after moulding. The path of crack propagation through the fractured test specimens was seen to follow these residual granule boundaries to a significant degree. Further strengthening of the composite material was therefore seen to depend primarily on improving the bonding and overlap between the composite granules, rather than improving the inherent material strength within the granules themselves.

One method of inhibiting crack propagation through the moulded composite layer was seen to be through modification of the granule morphology. Up until this point, near equiaxial granules of approximately 3mm diameter had been utilised in order to maximise granule packing density and retained fibre length. However, by using a comparatively longer and thinner granule, it was hypothesised that an improved degree of granule interlocking could be achieved and the strength of the moulded composite layer improved. The following trials were conducted to investigate this theory, with composite granules with dimensions of approximately 1.5mm x 4mm contrasted against those produced to the previous morphology. The effects of further lowering the fraction of glass fibre from 15vol% to 10vol% were also examined, in an attempt to enhance the degree to which the granules coalesced as much as possible. The material formulations and processing parameters utilised in this trial were as follows:

Material Formulations:

- ExxonMobil HMA 018 HDPE (stabilised) / 10vol% Owens Corning 415A glass fibre (to be produced both as 1.5mm x 4mm granules and 3mm equiaxial granules)
- ExxonMobil HMA 018 HDPE (stabilised) / 15vol% Owens Corning 415A glass fibre (to be produced as 1.5mm x 4mm granules)
- ExxonMobil HMA 018 HDPE (stabilised) (to be produced as 3mm granules)

Extrusion Compounding:

Extruder zone temperatures (from feed point to die):
150ºC 170ºC 190ºC 200ºC 165ºC
Screw speed: 75rpm
Die: Single aperture, 3mm or 1.5mm diameter as indicated
Material Cooling: Air cooled (non-forced)

Granulation:

Aperture Screen: 6mm *Microniser granule rounding:* No
Sieved: No

Rotational Moulding (R&D System):

Mould: 90 x 90 x 152mm box *Charge weight:* 450g
Double/single shot process: Single shot
Oven set temperature: 300ºC
Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm
Target PIAT: 205ºC
Cooling: Fan cooling applied after internal air temperature <100°C
Internal mould pressurisation: 10psi upon cessation of heating
Demoulding Temperature: 50 ºC

The degree of granule coalescence exhibited by all composite mouldings was excellent, with relatively good external and internal surface finishes obtained and only very minor lumpiness of the moulded interior surface seen. The moulding produced from unfilled HMA-018 HDPE, however, showed an uneven wall thickness and a high degree of shrinkage. The reasons for this poor moulding performance are not known. The tensile and impact properties of the moulded materials were determined to the test parameters listed below, and the results are shown in Figure 4.30 and Figure 4.31.

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)
Repetition: Five specimens per material
Testing speed: 5mm/min (composite samples)

Impact Testing:

Specimens: Rectangular cross-section, edgewise impact
Repetition: Five specimens per material
Hammer impact: 0.475kg @ 2.9m/s (2.0J)

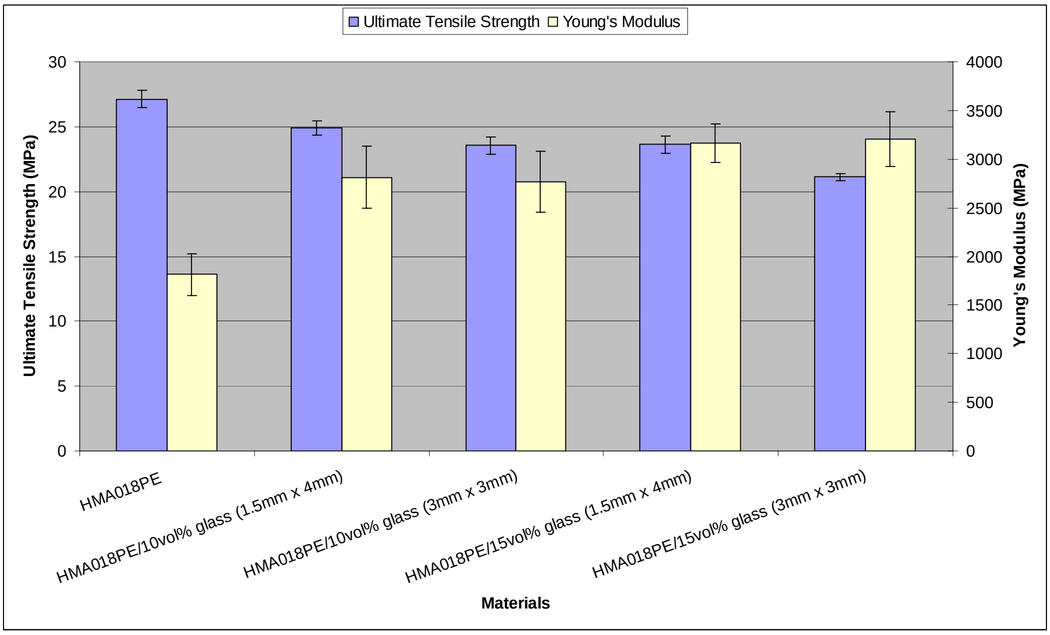

Figure 4.30 Effect of different granule morphology on the tensile properties of rotomoulded composites. Error bars ±1 standard deviation

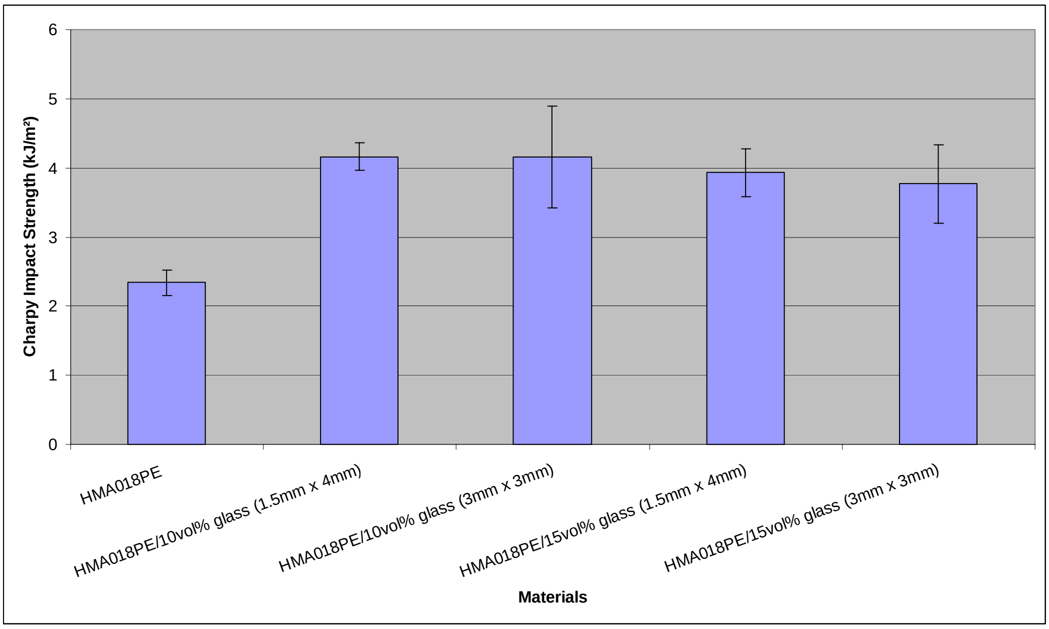

Figure 4.31 Effect of different granule morphology on the notched Charpy impact strength of rotomoulded composites. Error bars ±1 standard deviation

These results show that by changing the composite granule morphology from approximately 3mm x 3mm to 1.5mm x 4mm, a relatively small but significant increase in ultimate tensile strength can be obtained without detriment to either Young's modulus or impact strength. The effects of any decreases in average fibre length resulting from extrusion through the more tightly constricted die therefore appear to be masked by the improved degree of granule interlocking. Reducing the percentage of glass fibre from 15vol% to 10vol% can also be seen to have resulted in slightly improved ultimate tensile strength of the composite moulding, though with a corresponding decrease in Young's modulus. This trend is the same as that observed when the glass fibre fraction was reduced from 20vol% to 15vol%, and supports the theory that the tensile strength of these composite samples is dictated by the strength of the bond and degree of intermingling between the moulded composite granules, rather than the intra-granular strength. By reducing the fraction of glass fibre and improving the ease with which the individual composite granules could coalesce into a moulded layer, the overall tensile strength of the moulding was improved despite the individual granules being weaker. That the decrease in fibre fraction resulted in an inherently weaker composite material was shown by injection moulding samples of the above prepared composite granules, containing 10vol%, 15vol% and 20vol% of glass fibre. The high shear and pressure of the injection moulding process removed all evidence of a residual granular structure, giving homogenous test specimens with a high degree of fibre alignment. Tensile and impact testing conducted on these samples then showed that ultimate tensile strength, Young's modulus and notched Charpy impact strength were all reduced as the percentage of glass fibre was progressively lowered. Even when containing only 10vol% glass fibre, however, the injection moulded specimens were shown be approximately 80% stronger and 50% stiffer than the corresponding rotomoulded composite specimens.

Despite the improvements made to the granule coalescence and bonding, microscopic examination of the fracture surfaces of rotomoulded samples showed that crack propagation remained intergranular to a significant extent. This may be seen to some extent in Figure 4.32, which is a Scanning Electron Microscope (SEM) image taken of a fractured surface on a sample of HMA-018 HDPE/10vol% Owens Corning 415A glass fibre composite (1.5mm x 4mm granules). This image shows that the alignment of the glass fibre within each composite granule - a result of the extrusion compounding process – is maintained even after rotational moulding. The alignment of the individual granules within the moulded layer, however, appears to be random. This tendency for random granule distribution may be dependent upon the morphology of the granules, with elongated granules expected to show a tendency towards alignment parallel to the mould walls rather that a truly random orientation. This effect requires further investigation. In any case, it appears that in this image, those granules containing fibre aligned perpendicular to the direction of crack propagation have been pulled out in near entirety rather than sheared. This leads to the "holes" visible in the image.

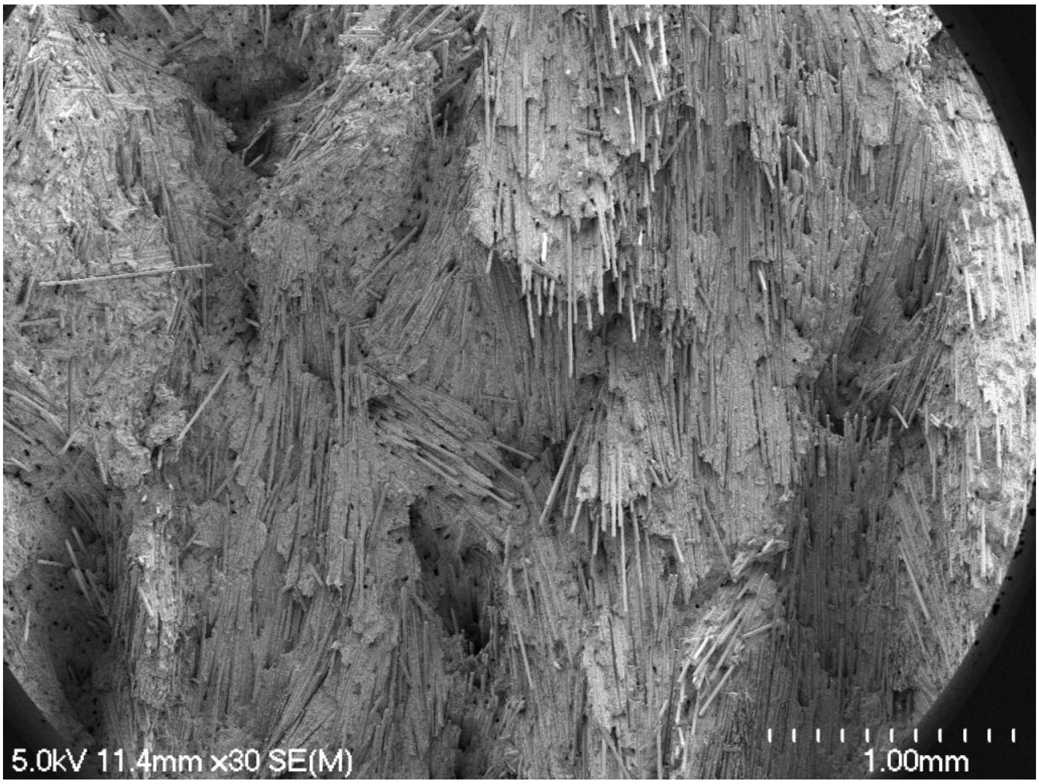

Figure 4.32: SEM image of the fracture surface of a rotomoulded HMA-018 HDPE / glass fibre sample, produced from granules with dimension of approximately 1.5mm x 4mm.

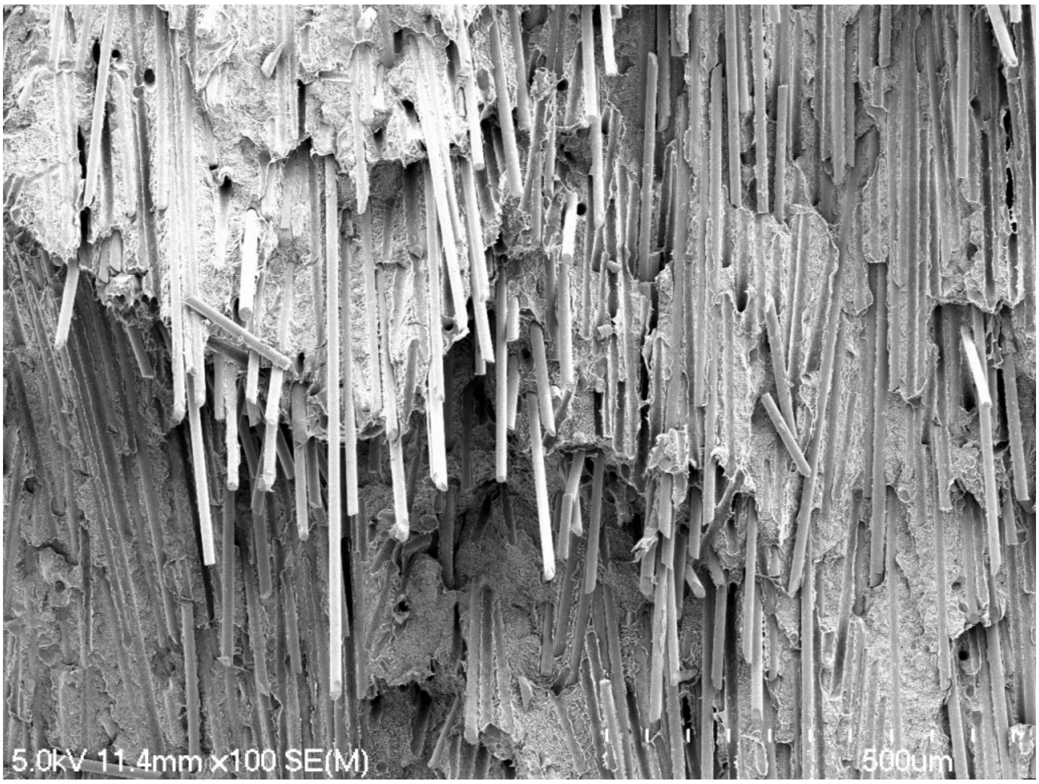

Figure 4.33: A further magnified view of the SEM image given in Figure 4.32

It may also be noted from examination of Figure 4.32, and in the further magnified view given in Figure 4.33, that excellent dispersion of the individual glass fibre filaments has been achieved with a high degree of fibre impregnation by the matrix polymer. This illustrates the advantages of the melt compounding process compared to the “dry-mix” preparation technique. Although average fibre length has been substantially reduced from the original 4mm by the extrusion compounding and granulation processes, average fibre length remains higher than would be achievable had the composite granules been micronised into powder of a conventional size for rotational moulding.

Advantages of Developed Composite

The HMA-018 HDPE / 10vol% Owens Corning 415A glass fibre composite, when prepared as extrusion compounded granules of 1.5mm x 4mm, represents the strongest fibre-reinforced material produced during the course of this research. Despite this, it may be seen that the ultimate tensile strength of this material remains below that of the unfilled HMA-018 HDPE grade, and only slightly improved over the rotomoulding grades of polyethylene shown at the start of this chapter. However, contrasting these materials on the basis of ultimate tensile strength does not reveal the true advantage of this composite material over the unfilled polymer grades. In many cases, the ultimate tensile strength of the unfilled polymers was seen to only be reached at high levels of sample strain and deformation. The ultimate tensile strength of these polymers is therefore often only of theoretical value, if the allowable deformation of the moulded product is less than that corresponding to the point at which ultimate tensile strength of the polymer is attained. Despite its shortcomings, ultimate tensile strength has been used as a measure of material performance throughout this thesis as it is a convenient and widely adopted basis for material comparison. But it is the strength of the polymer under limited strain which is the more valuable comparison in many instances. Figure 4.34 shows the tensile strength of the rotomoulded HMA-018 HDPE/10vol% Owens Corning 415A glass fibre composite plotted vs. sample strain, and compared against the “dry-mix” prepared Vanglobe 8539 LLDPE / 20vol% Owens Corning 415A glass fibre composite and rotationally moulded, unfilled Vanglobe 8539 LLDPE – which was one of the strongest and stiffest of the tested rotomoulding polyethylene grades.

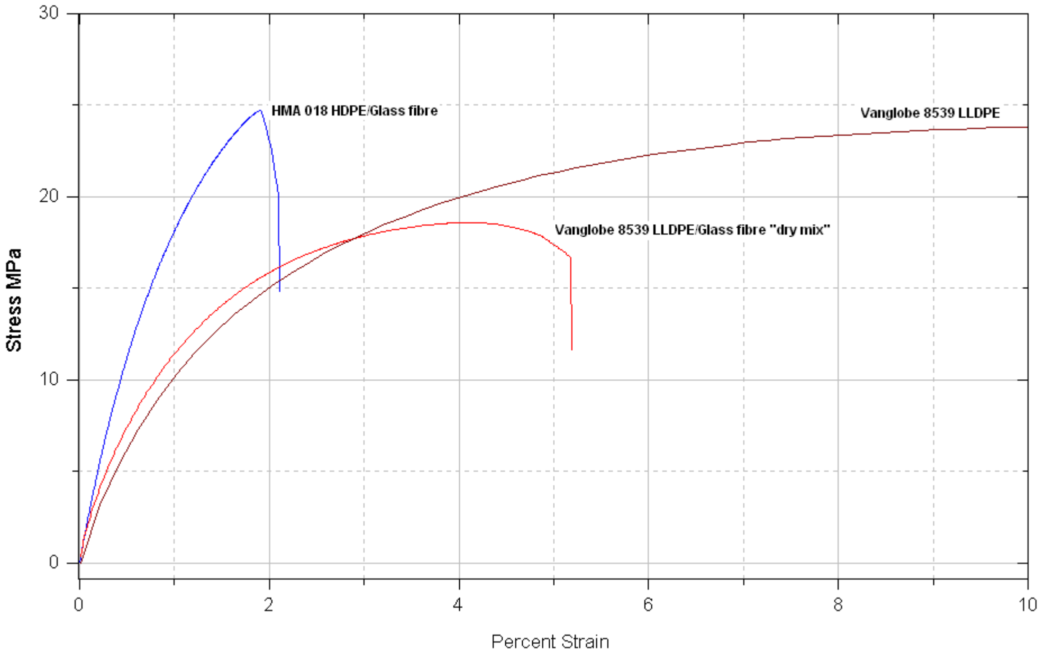

Figure 4.34: Tensile stress vs. strain plot for melt-compounded and rotomoulded HMA-018 HDPE/glass fibre composite compared to competing materials.

It may be seen from these plots that the melt-compounded composite material is markedly superior to both the “dry-mix” composite and the unfilled polyethylene in terms of tensile strength under limited strain conditions, although the ultimate tensile strength values of the three materials do not reflect this. At the arbitrarily selected offset value of 0.5%, the average offset yield strength of the melt-compounded composite, “dry-mix” composite and unfilled polyethylene were calculated as 20.8MPa, 11.6MPa and 12.5MPa respectively. By this measure, the melt-compounded composite material developed over the course of this research represents a significant improvement over both the unfilled polyethylene and the “dry-mix” composite, and when coupled with the high values of tensile stiffness that this composite has been shown to possess, represents a very useful material. The impact strength of the melt compounded composite material remains poor in relation to conventional, unfilled rotomoulding polyethylenes, but this is seen to be a result of the brittle matrix polymer which was utilised rather than attributable directly to the glass fibre addition. Therefore, scope exists to improve the impact performance of the composite material by utilising alternative matrix polymer grades.

Rotomoulded Polyethylene Foam

Although the main focus of this research was on developing rotomouldable composite materials, the use of foamed polyethylene as product reinforcement was also briefly investigated. These trials were conducted using two commercial foamable polyethylene grades: Cotene 9031-BA4 and Cotene 9031-BA8. Initial testing consisted of preparing rotomoulded foam samples using a two-shot moulding process, so that the resultant mouldings consisted of a layer of polyethylene foam encased within an unfoamed polyethylene shell. Test specimens could then be machined from the foamed polymer layer and the tensile properties of this material determined.

These two foamable polymer grades are of the exothermic-blowing type, both with an activation temperature of approximately 150°C. In accordance with the manufacturer's recommendations, the foamable polymer charge was placed into the mould as soon as melting of the initial, outer-skin polymer charge had been completed – as indicated by a rapid rise in internal mould temperature. Heating was then recommenced until the blowing agent activation temperature was attained, following which heating of the mould was ceased and the mould was removed from the oven. The exothermic decomposition of the blowing agent provides the necessary heat for the foaming reaction to progress from this point.

The material, processing and testing parameters of this work are listed below:

Moulded Specimens:

- Cotene 9042 LMDPE outer layer, Cotene 9031-BA8 foamed layer

- Cotene 9042 LMDPE outer layer, Cotene 9031-BA4 foamed layer

Rotational Moulding:

Mould: 50mm x 140mm x 640mm box

Charge weight: 1000g (outer skin), 500g (9031-BA8), 1000g (9031-BA4)

Double/single shot process: Double shot

Oven set temperature: 275ºC

Mould rotation speed: Major axis – 8rpm, minor axis – 2rpm

Observed PIAT: ~165°C

Cooling: Fan cooling once PIAT had been observed

Internal mould pressurisation: None

Demoulding Temperature: 100 ºC

The weight of the foamable polymer charges had been calculated to nearly fill the moulded cavity, thus giving the maximum thickness of material for testing while ensuring that the mould was not pressurised during the foaming process. These calculations were based upon the foam densities quoted by the manufacturer: 0.12g/cm^3 for Cotene 9031-BA8 and 0.24g/cm^3 for Cotene 9031-BA4. Examination of the produced mouldings, however, showed that the 9031-BA8 polymer charge had not foamed to the expected degree and that a large cavity remained. Subsequent testing of the density of these foam samples using a water-displacement method showed that while the density of the 9031-BA4 grade was very close to that stated by the manufacturer, the 9031-BA8 grade had foamed only enough to give a measured density of 0.17g/cm^3 – approximately 40% more dense than anticipated. The reason for this result is unknown.

The parameters of the tensile testing are given below, with the tensile test results shown in Figure 4.35.

Tensile Testing:

Specimens: Type 1 (ASTM D638-03)

Repetition: Three specimens per material

Testing speed: 20mm/min (composite samples)

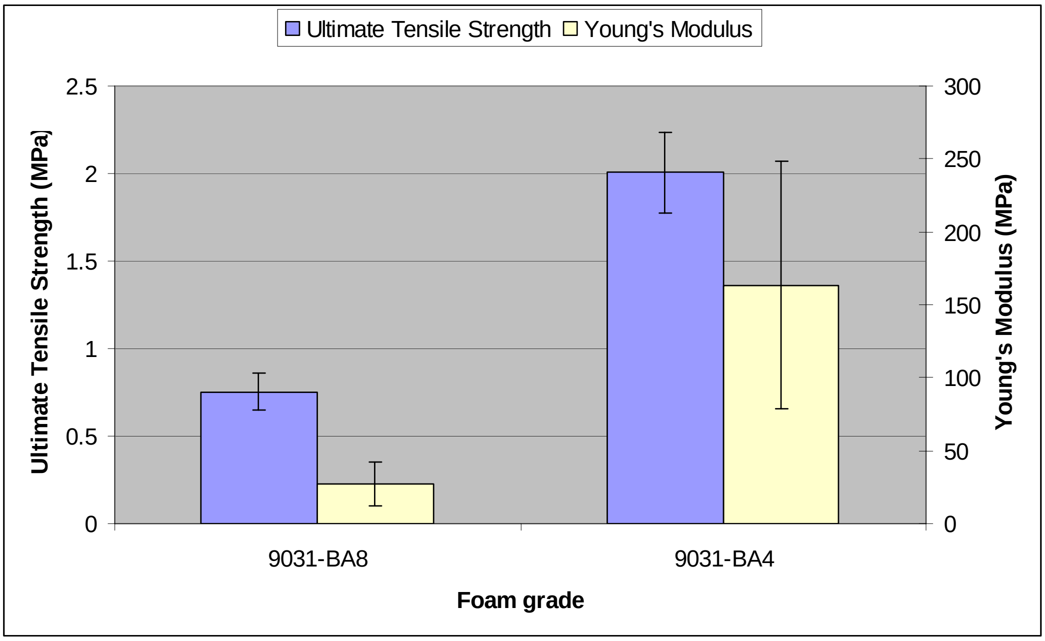

Figure 4.35: Tensile properties of rotomoulded polyethylene foam samples. Error bars ±1 standard deviation

As can be seen, the tensile properties of the foamed polymer samples were shown to be extremely poor. Given that these results are representative only of a single moulding of each foam grade and the number of test specimens was severely limited, this data is not put forth as conclusive. However, based upon these tensile test results, the use of foamed polyethylene for reinforcing rotationally moulded products was not deemed to be worth pursuing during the course of this research project.

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Chapter 5: Conclusions & Recommendations

The primary objective of this research project was to develop a rotationally mouldable material that represented a significant improvement over unfilled rotomoulding polyethylene grades. This was accomplished by developing a novel fibre-reinforced composite material which has been shown to possess a tensile yield strength and tensile stiffness substantially better than conventional rotomoulding polymers.

By utilising melt-compounded composite granules as feedstock for the rotational moulding process, the problems of poor fibre bonding, uneven fibre distribution and inadequate fibre length retention which have plagued other studies in this field have been largely overcome. The low quality of surface finish and poor reproduction of mould detail which typically accompanies the use of granules in rotational moulding was addressed by using a multi-shot rotomoulding process, where the fibre-reinforced composite layer is contained inside a shell of unfilled, conventional rotational moulding grade thermoplastic. The decreased material melt-flow and inadequate particle coalescence during rotational moulding that can result from the addition of a fibrous reinforcement was solved by using a matrix polyethylene with a high melt flow index, originally intended for injection moulding use. The strongest of the subsequently produced rotomoulded composites was shown to possess an offset yield strength (0.5% offset) over 65% higher than that of a structural grade of conventional rotationally moulded polyethylene, with an accompanying increase in Young’s modulus of over 95%. Further increases in stiffness could be achieved by increasing the fibre fraction of the composite, causing only a slight corresponding decrease in tensile strength. Although the impact strength of this composite remains relatively low compared to many rotomoulding polyethylene grades, potential to improve upon this performance is seen to exist through further material development.

The following are some of the major points arising from this research:

- Polymer or composite granules of a size considerably larger than normally considered usable were successfully processed using a dual-layer moulding technique, where the outer moulded layer is formed from a conventional, powdered thermoplastic polymer.
- The addition of glass fibre to conventional rotomoulding polypropylene and polyethylene grades using a melt compounding process was found to inhibit the melt-flow of the resultant granules or powder particles to a significant extent, preventing successful rotational moulding.
- The use of high melt-flow, injection moulding grades of polyethylene and polypropylene substantially improved the rotomoulding flow and coalescence of the melt-compounded composite granules, allowing glass fibre fractions of up to 20vol% to be successfully utilised. These polymer grades required the addition of extra antioxidants to be suitable for rotational moulding.
- The mechanical properties of rotomoulded products produced from melt-compounded granules are highly dependent upon the coalescence and bonding between the individual granules, with specimen fracture seen to be predominantly inter-granular in all cases.
- The effects of granule morphology upon the mechanical properties of the composite moulding were found to be significant. By utilising relatively long and thin composite granules, a degree of interlocking could be obtained and the mechanical properties of the moulding improved.

Although the results of this research are promising, many important factors have only been briefly touched upon during the course of this work. The composite materials developed here require further testing before they can be considered for commercial application, including assessment of long-term thermal stability, UV resistance, creep resistance and fatigue behaviour. The overall mechanical properties of a product comprised of the dual-layer composite/unfilled polymer structure detailed in this thesis remain to be tested, and expansion of the material processing methods used here from laboratory scale to industrial production would also introduce a number of new factors to be accounted for. However, the potential of this material and processing method has been proven.

Significant scope exists for further development and improvement upon the results obtained here. The following are a number of recommendations for expanding upon this work:

- The extrusion-compounding method used throughout this work severely restricts the average fibre length retained in the rotomoulded article when brittle materials such as glass fibre are used. Alternative melt-compounding methods of producing composite granules, such as thermoplastic pultrusion techniques, may resolve this problem.

- Mould pressurisation during the heating stage of the rotomoulding process has been shown elsewhere to be highly beneficial. The application of this technique to the moulding of melt-compounded composite granules may also prove to be advantageous.

- Expanding upon the concept of the dual-layer composite moulding, a three-shot process could be used to coat the inner moulded surface of the composite material layer as well as the exterior with an unfilled polymer. This would improve the overall surface finish of the product.

- Although the coupling agents utilised here were ultimately shown to not benefit the properties of the composite material, the future use of coupling agents should not be disregarded.

- Although glass fibre was selected as the most suitable fibre reinforcement for the purposes of this research, a wide range of other reinforcement types are also expected to be applicable to the process.