Optimisation of the Production of Commingled Recycled Plastic Materials

A thesis submitted for the degree of Master of Engineering Science

by

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Abstract

The recycling of post-consumer plastic waste is a challenging task due to the commingled nature of the waste composition. Commingled plastic recycling is one of the most economically viable ways to manufacture plastics waste into commercial products. Similar to virgin polymers, fillers can be added to recycled plastics to improve engineering properties of the final products. The common operations of commingled plastic recycling however lack in depth knowledge in relation to the selection of the appropriate fillers, additives, and optimum processing variables. This project aimed to investigate three types of mineral fillers, talc, wollastonite and gypsum, for their abilities to modify the mechanical properties of commingled recycled plastic composites. The effectiveness of the fillers to improve the mechanical properties was considered to be influenced by interface bonding (between the filler and matrix) and extrusion variables. These factors were also investigated in this research. Mechanical test results showed that the talc reinforced composites were significantly better in mechanical properties compared to the gypsum and wollastonite composites (tensile strength and modulus improved by 170% and 20%, respectively at 0.26 v/v loading). Scanning electron microscopy (SEM) showed that gypsum formed large agglomerates in the matrix leading to inferior mechanical properties. The interface adhesion between filler and matrix was evaluated using several established models. The tensile or flexural strength of the composites was satisfactorily predicted using Turcsanyi and Nicolais-Narkis equations. For the tensile and flexural modulus of the composites the Einstein equation was found to give a good correlation.

In attempt to enhance the adhesion, the mineral fillers were pre-treated with silane coupling agents, 3-methacryloxypropyltrimethoxy silane (γ-MPS) and 3-aminopropyltriethoxy silane (γ-APS) before being blended with the plastics. This did not result in any significant improvement to the material properties. The γ-APS treatment, however, increased the tensile properties of the composites by approximately 5% compared to the γ-MPS treatment. The SEM investigations showed that the γ-APS treatment provided better adhesion of filler particles and hence voids were less likely to form in the matrix compared to the γ-MPS composites. Extruder parameters like screw rotation and barrel temperature did not have a significant influence on the mechanical properties of filler-recycled plastic composites.
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Journal paper

Conference papers
Ngothai, Y., Putra H., Ozbakkaloglu, T., Seracino, R., (2009), Effect of CaCO₃ Size on the Mechanical Properties of Recycled HDPE, 8th World Congress Chemical Engineering, Montreal, Canada, 23-27 August (accepted).

1 Introduction

The vast growth of civilisation in the past few decades has driven large consumption of plastic. Plastic plays an integral part in many aspects of human life and is almost irreplaceable in day to day activities. Due to its unique properties, it is almost impossible to substitute plastics in many applications, especially in packaging sectors. In its widely extensive applications, plastic can be found to be manufactured together with different types of material or product and hence exists in virtually any urban waste stream. Concerns however have been raised over the fact that the growing consumption has led to plastic waste filling up landfills and contaminating the environment and ecosystems.

Pressures have been put to governments, industry bodies and communities to divert plastic as much as possible from the waste streams. The South Australian Government has followed the lead of other countries by banning check-out style plastic bags in May 2009 and has actively encouraged communities to switch from petroleum based plastics to the plant based ones. Even if this could be achieved successfully, it will still leave issues such as plastic waste resulting from other domestic or general applications; or the high volume of plastics already contained in landfills. Plastics made from any source could potentially release methane, a greenhouse gas, when left to decompose anaerobically in landfills.

There are four methods of plastics recycling: mechanical or material, feedstock (hydro-cracking and pyrolysis), chemical (de-polymerisation) and energy (incineration) recycling. Mechanical recycling, which reprocesses the waste into a new material, appears to be the most environmentally sustainable solution.

Mechanical recycling of post-consumer plastic waste proves to be a challenging task due to the presence of multiple and random types of plastics in the waste. Even so products made of this material have been commercially developed and widely used in applications such as vineyard poles, park benches, and tables and decking boards.

Products made of the post-consumer (commingled) plastic waste alone are known to have inferior mechanical properties (Breslin et al., 1998). To enhance the properties, the plastic waste is normally blended with additives, often called fillers. Common fillers used in plastic
recycle include mineral particulates (e.g. talc, gypsum, calcium carbonate, gypsum and wollastonite) and fibrous fillers (e.g. glass fibre and saw dust).

This research aimed to investigate various factors that could optimise the production of commingled plastics composites using mineral fillers as mechanical reinforcement. These factors include physical properties of fillers, interface adhesion of filler and plastic resins and the operating parameters of extrusion process. Chapter 2 of this thesis previews the relevant literature, including the previous work undertaken by researchers as well as fundamental knowledge behind this research. Chapter 3 describes the experimental procedure involved. This covers sample preparation, testing methods, microscopy observations and sample calculation. Chapter 4 presents the results from the experimental works and discusses the interpretation of the data. Conclusions of the research and recommendations for further work are presented in Chapters 5 and 6, respectively.
2 Literature Review

First, this chapter reviews the basics of plastics recycling. It then looks into a number of previous works investigating the roles of fillers in modifying the mechanical properties of plastic composites. Following this, the interfacial adhesion of filler and polymer and how it can be improved by silane coupling agents will be discussed. The final section summarises the objectives of the research.

2.1 Plastics Recycling

There has been a steady increase in plastic consumption in Australia over the past few decades. In 2006, Australia consumed more than 1.5 million tonnes of plastic, of which only 16 % was recycled (PACIA, 2007). Polyolefin (low density polyethylene, high density polyethylene and polypropylene) resins were the largest polymer group recycled in the post-consumer waste stream (PACIA, 2007).

Sources from commercial, industrial and municipal sectors accounted for 96% of the total plastics recycled in Australia in 2006 (PACIA, 2007). Plastic wastes derived from these sectors consist of various polymer resins and is sometimes heavily contaminated with foreign materials, such as paper, soil and metal. There are various ways to recycle plastics waste. These are described in the following sub sections.

2.1.1 Methods of Plastics Recycling

Plastic recycling is not an uncommon practice and has been performed for a number of decades. Common methods of plastic waste recycling include (Fortelný et al., 2004; Perugini et al., 2005):

- Mechanical recycling: direct recovery (reprocessing) of plastic waste in the manufacture of new products (i.e. finished products or feedstock for another manufacture). This process obviously is only possible for thermoplastic polymers due to their ability to be reprocessed;
- Feedstock recycling: cracking process of plastic waste to break its bonds down into a range of different basic chemical components, which later can be used as feedstock in petrochemical and plastics manufacture (e.g. pyrolysis and hydrocracking);
• Chemical recycling: depolymerisation of plastic waste to produce monomers for feedstock for production of virgin polymers; and
• Energy recycling: recovery of plastics waste into fuels.

Of the above methods, mechanical recycling appears to be the most environmentally friendly and the most economical (Perugini et al., 2005).

2.1.2 Commingled Plastics Recycling

The recycling of post-consumer plastic waste is a great challenge due to random presence of different types of plastics and severe contamination from foreign materials such as paper, soil and metals. Waste segregation is considered to be a costly and time consuming procedure, therefore the direct recycling of commingled plastics is still a more cost-effective practice (Camacho and Karlsson, 2001; Pawlak et al., 2002).

For this reason, it has been widely suggested to directly process the waste. Typically the raw material used in this process contains at least 50% polyolefin resins (High density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP)) as a carrier matrix which encapsulates high-melt plastics, thermosets and additives (Breslin et al., 1998; Mustafa, 1993). Figure 2-1 shows an example of a flowchart of commingled plastics recycling.

Figure 2-1: Flowchart of commingled plastics recycling (reproduced from Walter Kaminski, 2000) a) Conveyor; b) Shredder; c) Washer; d) Air Classifier; e) Mill; f) Magnetic separation; g) Rotary scrubber; h) Belt screen; i) Dryer; j) Extruder; k) Silo
Plastic waste is firstly shredded into small fragments or flakes using shredders. Subsequent treatments of material sorting taking place after the shredding include washing, air separation (removes glass from raw material), metal/magnetic separation (removes metals) and scrubbing, in which the material is washed with a special detergent and stripped of any dirt, food residue and label-adhesive materials (Caboolture Council, 2007; Hurd, 2001). Following the removal of the contaminants, the mixed plastic flakes are fed into an extruder, which runs at a melting temperature range of the main fraction of resin. There are two common ways of manufacturing products from the extruded plastics (Mustafa, 1993). The first method originated from a German technology known as Recyclopast in which plastic strands extrusion are conveyed to a cutting mill, where the strands are reduced to small fragments/pellets. Finally, the pellets are conveyed to storage silos or containers as shown in Figure 2-1. The pellets can be moulded into desired products using an injection or compression moulder.

The other method, which was pioneered by Advanced Recycling Technology and Superwood, is to force out the melted plastics through an extruder orifice into a mould of the final product. Following this, pressure is applied to continuously inject the melted plastics. A number of moulds with the same length are normally mounted on a carousel that rotates in a large water bath, where cooling occurs. The mouldings are then ejected pneumatically from the moulds for further cooling.

The most common products from the methods mentioned above are widely known as “plastic lumbers”. To date products made of commingled plastics waste are used in various applications such as: (Mustafa, 1993; Breslin et al., 1998)

- agriculture: vineyard posts, horse stalls and tree guards;
- marine engineering: pier and dock surfaces, boat docks, sea walls and beach erosion control;
- recreational: park benches, picnic tables and playground equipment;
- industrial: planks, signposts, traffic barriers and flooring pallets; and
- gardening: garden walkways, fences, garden furniture and compost bins.

In those applications, recycled plastics are often used to substitute timber. This would benefit the environment in reducing greenhouse gas emissions as a result of deforestation and
minimising the use of treated timber, namely CCA (Copper Chromium Arsenate) timber. To prolong the service life of timber, it is often preserved with CCA. Preserved timber has already been banned from domestic uses in Australia due to its toxic arsenic content which is a potential carcinogen. The reason timber is impregnated with CCA is that wood is susceptible to biological degradation from fungi or insects. Plastic is resistant to such problems and could be used as an alternative to timber.

A similar operation to Advanced Recycling Technology has also been adopted by Advanced Plastics Recycling (APR) of South Australia. Advanced Plastics Recycling operates a special technique that converts thermoplastic waste in landfill into numerous extruded products. Given no classification of plastic waste is performed by APR, an efficient and economic plastic recycling can be performed. Of the plastic waste acquired by APR, the low and high density polyethylene resins make up the major fraction.

Consistent sourcing of feedstock is a major challenge to this operation due to the “commingled” nature of the plastics waste, which often varies in composition and quality. This can result in mediocre mechanical properties. To improve the product quality, the raw material is often blended with fillers. The fillers used are often the same as those frequently used in virgin plastic processing, such as calcium carbonate and glass fibre. Reinforcement of recycled plastic by fillers will be explained in the following section.

2.2 Effect of Fillers as Reinforcement of Recycled Plastic Materials

The term fillers in plastics engineering originally referred to any material blended together with plastic, dispersed in plastic matrix and hence constitutes a certain volume percentage of the final product. In plastic manufacturing, the primary purpose of filler insertion is primarily to reduce production cost. However in many cases fillers are also added to reinforce the plastic. Fillers are classified into two categories, active and inactive fillers, based on their effect on the mechanical properties of the plastic product (Lipatov, 1995). Active fillers mainly result in reinforcement or improvement of mechanical properties while the inactive ones are intended for other purposes, such as colouring and cost reduction (Lipatov, 1995). Further explanation about the filler categories are explained in sub-section 2.2.3.
Fillers can be found in several forms, such as particulates (e.g. CaCO₃, carbon black and gypsum) and fibres (e.g. glass fibre and saw dust). Particle size of fillers can range from as small as a few nanometres (mostly particulates) to several millimetres (fibres). Figure 2-2 shows microscopy images of a number of particulate fillers.

![Figure 2-2: Particulate fillers, from left to right: wollastonite and talc](image)

Common fillers frequently used in mechanical recycling of plastics are glass fibre, saw dust, calcium carbonate and gypsum. Glass fibre is considered to be a highly active filler material due to its excellent reinforcement in plastic composites. Despite this fact, recyclers often avoid or minimise the use of glass fibre due to its high cost. Instead, they turn to lower cost alternatives, such as mineral fillers. It has been reported that mineral fillers can enhance the strength and stiffness of polymers (Leong et al., 2004; Turcsanyi et al., 1988; Wypych, 1999).

Filler particles can function as stress concentrators in the composite under loading, which may reduce shear yielding and hence increase the stiffness of the composite (Zuderduin et al., 2003). The inclusion of fillers however also introduces a phenomenon called *debonding* when the composite is deformed under load.

Debonding can be explained as the formation of micro pores or crevices occurring at polymer-filler interface, transverse to the load direction, during loading of the composite. In particulate filled polymers, debonding is a dominant factor in deformation mechanism, along with the shear yielding of the polymer (Dubnikova et al., 1997a, Renner et al., 2005). Debonding occurs intensively at the beginning of loading up to yielding and hence can influence the yield or tensile strength of filled polymers (Renner et al., 2005).
The concentration and joining of pores lead to crack propagation and thus control the fracture behaviour of filled polymers. Often efforts in polymer reinforcement are aimed at minimising the debonding mechanism. The magnitude of debonding and how it governs the deformation mechanism of filled polymers are affected by filler loading, particle size and interaction between the filler and matrix. These factors will be further explained in the following sub sections.

2.2.1 Effects of Filler Content

It is well understood that the addition of filler would improve mechanical properties of polymers up to a critical concentration, generally at 0.2 v/v filler content (Dubnikova et al., 2004; Wypych, 1999), beyond which further increase would have adverse effects on the properties. Different deformation mechanisms take place in low and high filler contents.

Deformation in low filler content (< 0.2 v/v) is mainly governed by micro homogeneous mechanism where crack propagation of the polymer matrix is initiated by individual debonding of filler particles (Dubnikova et al., 1997b; Zuiderduin et al., 2003). This is shown in Figure 2-3. This indicates that the magnitude of matrix deformation in the vicinity of different particles is dependent of the adhesion of the individual particles.

![Figure 2-3: Debonding of particles in low filler content (reproduced from Dubnikova et al., 1997b)](image)

In high filler content (> 0.2 v/v), where inter-particle spacing is small, debonding is characterised by craze-like zones with micropores, initiated by debonded particles (Dubnikova et al., 1997b; Zuiderduin et al., 2003). This is shown in Figure 2-4. In this case, debonding of one of the particles basically affects the stress-strain state of the neighbouring
particles (Dubnikova et al., 1997b). There are two factors characterising the debonding of high filler content (Dubnikova et al., 1997b). The first is the presence of regions beyond the craze-like zones where particles stay bonded to the matrix (indicated by arrows in Figure 2-4) and secondly further deformation takes place more intensively in the craze-like zones than in the normal zones due to the extreme differences in detachment.

![Figure 2-4: Craze-like debonding in high filler content (reproduced from Dubnikova et al., 1997b)](image)

According to Dubnikova et al. (1997b), the transition between the two debonding mechanisms occurs at a critical concentration of the filler, which is normally determined through experiments.

### 2.2.2 Effects of Particle Size of Fillers

The performance of fillers as reinforcement of polymers is often attributed to their particle size. Particle size of fillers is also important as a cost parameter for plastic recyclers. In general, material costs increases with finer particle size.

The effects of particle size on mechanical properties of polymers have been largely studied, mostly however on virgin polymers. There have been largely diverse outcomes from various researches with regard to this matter. In general, smaller particle size results in greater improvement of tensile modulus (Ismail et al., 1997; Khalil et al., 2006; Turcsanyi et al., 1988; Wypych, 1999). In contrary, case studies where larger particle size gives higher modulus are shown by Bose et al. (2005) and Texeira et al. (2006). Additionally, several
other researchers reported the mechanical properties are independent of particle size (Hiljanen-Vainio et al., 1998; Wong et al., 1999).

Filler size contributes in different ways in debonding progression. In low filler content (< 0.2), particle size has been found not to be a significant factor in debonding (Dubnikova et al., 1997b).

Figure 2-5: Craze-like zones in high filler content of (a) small and (b) large particle sizes (reproduced from Dubnikova et al., 1997b)

Meanwhile, the growth of debonding in high filler content is controlled by particle size. For small particles (Figure 2-5(a)), the concentration or extent of the craze-like zones is smaller compared to that of large particles (Figure 2-5(b)) (Dubnikova et al., 1997). In other words, the crazes are more localised in the case of small particles, whereas the crazes are uniformly distributed for the large particles. The increase of the concentration of craze-like zones (or micropores) causes a reduction in the effective cross-section for loading and subsequently results in a reduced load (i.e. lower yield or tensile strength).

2.2.3 Adhesion between Polymer and Fillers

The formation of chemical bonding is considered to be responsible for the adhesion between filler particles and polymer matrix.

2.2.3.1 Interface Adhesion between Filler and Polymer

In a filler-polymer system, there exists an imaginary interface separating the filler and polymer host. Adhesion or interaction between the two phases is established by the formation
of attractive bonding at the interface. The interaction of the filler and polymer matrix can be classified into three categories (Lipatov, 1995):

- active fillers capable of engaging autonomously with the polymer host;
- inactive fillers requiring chemical additives (e.g. surfactants) to be able to bind with the polymer matrix via formation of chemical bonds at the interface; and
- inactive fillers not capable of forming adhesion at the interface even with the help of additives

One type of filler may be active in some polymer resins and be inactive in the others, depending on the natural bonding at the interface. Where there is a weak or no activity between filler and polymer surfaces, interface bonding might be initiated using additives called coupling agents.

Basically, coupling agents are chemicals that form or strengthen the interface bonding between polymers and fillers. The action can be achieved because coupling agents possess two bonding groups, one of which attaches to a repeating unit of the polymer and the other to the surface of the fillers. The chemicals are usually added in a small amount (i.e. approximately at levels of 0.1-4 %w/w of the total weight of the filler) when mixed with fillers (Wolf, 2000), silane-based coupling agents are regularly used in practice thanks to good compatibility with a great range of fillers. Other coupling agents include titanates, aluminates, phosphate (Liu et al., 1996), stearic acid, stearates and chlorinated paraffins (Wolf, 2000).

2.2.3.2 Silane coupling agents

The general structure of silane groups is \((X)_{3}Si(CH_{2})_{3}Y\), where \(X\) is the hydrolysable bonding group attached to the surface of the filler and normally consists of a short-chain alkoxy group (OCH₃, OCH₅), an acyloxy group (CH₃OO), hydroxyl (OH) or chloride (Cl), while \(Y\) reacts with the polymer and is called the functional group, which is a long hydrocarbon chain, such as vinyl, methacrylate, amino or mercapto. Figure 2-6 shows chemical structure of silane groups reacting to a filler surface.
The selection of the appropriate silanes should consider a functional group compatible with the targeted polymer. Although there is no fundamental rule regarding this relationship, researchers have pointed out notable improvement in stiffness and yield strength of polyolefin composites with the use of methacrylate and amino silanes (Arencon et al., 2003; Bikiaris et al., 2000; Demir and Tişcer, 2001; Akin-Öktem and Tişcer, 1994; Tselios et al., 1999). Two commercial types of silanes, 3-methacryloxypropyltrimethoxy silane (γ-MPS) and 3-aminopropyltriethoxy silane (γ-APS) have specifically gained large attention by the researchers. The chemical structures of Amino-propyl and Methacrylate silanes can be observed from Figure 2-7 below.

\[
\sigma_c = \sigma_p \left( 1 + a\phi_f^b \right)
\] (2-1)
where $\sigma_p$ is the (tensile or flexural) strength of the host (polymer) matrix, $\phi_f$ is the volume fraction of the filler, $a$ is a constant dependent on adhesion between matrix and filler and $b$ is another constant accounting for particle shape and is equal to unity for spherical particles. However, his equation only applies at low concentrations of filler (Wypych, 1999).

With an assumption that filler addition results in a decrease in material strength (i.e. load applied is only sustained by the matrix), Nicolais and Narkis (1971) developed the no-adhesion theory based on the Einstein model:

$$
\sigma_c = \sigma_p \left(1 - a\phi_f^{2/3}\right)
$$

(2-2)

The symbol $a$ is a packing factor of the filler particles but often made constant (Bliznakov et al., 2000; Carmen et al., 2007; Maiti and Sharma, 1992). The value $a$ for spherical filler particles is 1.21 (Nicolais and Narkis, 1971).

Another model used to describe the adverse effect of filler in polymer strength is the porosity theory. The theory considers the presence of filler to be analogous to voids in the polymer matrix, detrimental to the material strength (Bliznakov et al., 2000; Maiti and Lopez, 1992; Maiti and Sharma, 1992). According to this theory, the specific change in (tensile or flexural) strength $\frac{d\sigma}{\sigma}$ is directly proportional to the porosity ($P$) as shown in the Equation 2-3 below:

$$
-\frac{d\sigma}{\sigma} = kP
$$

(2-3)

Constant $k$ is related to stress concentration, which also describes the degree of adhesion between polymer and filler. The negative sign indicates decrease in strength as a result of an increase of filler content. Substituting porosity with filler volume and integrating the expression leads to the following:

$$
\sigma_c = \sigma_p \exp(-k\phi)
$$

(2-4)

According to the equation above, adhesion is in contrary with constant $k$, where large $k$ values mean little adhesion exists between the polymer and filler.
A modification to Equation 2-2 was proposed by Turcsanyi et al. (1988) and is called the Turcsanyi model. This model is given as below:

\[
\sigma_e = \sigma_p \left[ \frac{(1-\phi_f)}{(1+A\phi_f)} \right] \exp(B\phi_f) \tag{2-5}
\]

The constant \(A\) accounts for filler packing factors (≈ 2.5 for particulate fillers) and the constant \(B\) is an adhesion parameter, where better adhesion is given by an increase of \(B\) values. The term \((1-\phi_f)/(1+A\phi_f)\) refers to the reduction of the effective load-bearing cross-section of the matrix due to filler content. Rearrangement of Equation 2-5 gives:

\[
\ln \left[ \frac{\sigma_e}{\sigma_p} \left( \frac{1+2.5\phi_f}{1-\phi_f} \right) \right] = B\phi_f \tag{2-6}
\]

Excellent correlations of a range of filler-polymers mixtures were established by Equation 2-6 in a study by Turcsanyi et al. (1988). Other studies by Szazdi et al., 2007 and Zou et al., 2004 also found good correlations using this model. Several combinations of polymer-filler blends studied by Turcsanyi et al (1988) are listed in Table 2-1. From Table 2-1, the following observations can be made:

- the same filler can be active in one polymer but not in other polymers;
- different types of fillers result in different level of adhesion in a polymer, where talc and wollastonite are generally more active than CaCO3;
- treatment of fillers may or may not improve filler adhesion; and
- particle size, in most cases significantly influences the adhesion quite significantly.
Table 2-1 Levels of adhesion (B values) of filler-polymer pairs (reproduced from Turcsanyi et al., 1988)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Type</th>
<th>Shape</th>
<th>Size (µm)</th>
<th>Specific surface area (m²/g)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Glass</td>
<td>sphere</td>
<td>12.7-38.1</td>
<td></td>
<td></td>
<td>0.246</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>58.4</td>
<td>0.5</td>
<td></td>
<td>0.791</td>
</tr>
<tr>
<td>ABS</td>
<td>Glass, treated</td>
<td>sphere</td>
<td>12.7-38.1</td>
<td></td>
<td></td>
<td>1.059</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>3.6</td>
<td>2.20</td>
<td></td>
<td>1.189</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>8.6</td>
<td>2.4</td>
<td></td>
<td>1.610</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>1.1</td>
<td>8.1</td>
<td></td>
<td>1.859</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>0.08</td>
<td>16.5</td>
<td></td>
<td>1.859</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>1.6</td>
<td>5.0</td>
<td></td>
<td>1.932</td>
</tr>
<tr>
<td>PP</td>
<td>Silica</td>
<td>sphere</td>
<td>0.6</td>
<td>18.4</td>
<td></td>
<td>2.073</td>
</tr>
<tr>
<td>PP</td>
<td>Wollastonite</td>
<td>fibre</td>
<td>length &lt; 10</td>
<td></td>
<td></td>
<td>2.537</td>
</tr>
<tr>
<td>PP</td>
<td>Talc</td>
<td>slate</td>
<td>13.6</td>
<td>3</td>
<td></td>
<td>2.566</td>
</tr>
<tr>
<td>PP</td>
<td>Talc</td>
<td>plate</td>
<td>5.7</td>
<td>5.9</td>
<td></td>
<td>2.692</td>
</tr>
<tr>
<td>PP</td>
<td>Talc</td>
<td>plate</td>
<td>2.8</td>
<td>8.4</td>
<td></td>
<td>2.753</td>
</tr>
<tr>
<td>HDPE</td>
<td>CaCO₃</td>
<td>sphere</td>
<td>3.5</td>
<td>1.2</td>
<td></td>
<td>3.348</td>
</tr>
<tr>
<td>HDPE</td>
<td>Talc</td>
<td>plate</td>
<td>13.6</td>
<td>3.0</td>
<td></td>
<td>3.926</td>
</tr>
<tr>
<td>PP</td>
<td>SiO₂</td>
<td>sphere</td>
<td>0.04</td>
<td></td>
<td></td>
<td>5.702</td>
</tr>
<tr>
<td>PP</td>
<td>SiO₂</td>
<td>sphere</td>
<td>0.007</td>
<td></td>
<td></td>
<td>6.474</td>
</tr>
</tbody>
</table>

*larger B values indicate improved filler-polymer adhesion

2.3.2 Tensile and Flexural Modulus

Several mathematical equations have been developed to describe tensile and/or flexural modulus of plastic composites filled with particulate fillers. The Einstein equation has also been used to predict modulus properties (Bliznakov et al., 2000; Kalaprasad et al., 1997). This is shown by Equation 2-7:
Parameters, $E_c$ and $E_p$ are the tensile moduli of the composite and polymer, respectively. The values of constant $b$ can vary according to the degree of interaction between the filler particles and polymer. It has been found that $b$ equals unity for poor adhesion of filler and 2.5 for perfect adhesion at low filler contents (Bliznakov et al., 2000).

A modification to the Einstein model was proposed by Guth and Smallwood (1992) and has been used by several authors (Bliznakov et al., 2000; Maiti and Sharma, 1992; Kalaprasad et al., 1997) and is given by the following equation:

$$E_c = E_p \left(1 + b \phi_f \right)$$  \hspace{1cm} (2-7)

Another frequently used equation to predict the tensile moduli of plastic composites is Kerner’s equation (Equation 2-9) (Bliznakov et al., 2000; Maiti and Sharma, 1992; Kalaprasad et al., 1997). In this model $\tau_p$, is the Poisson’s ratio of the polymer matrix.

$$E_c = E_p \left[1 + \frac{15\phi_f \left(1 - \tau_p\right)}{\left(1 - \phi_f \right) \left(8 - 10 \tau_p\right)}\right]$$  \hspace{1cm} (2-9)
2.4 Effects of Extrusion Condition on Mechanical Properties

The mechanical properties of polymer composites are influenced by the manufacturing process. Compounding, in particular, is considered the most critical step in the manufacturing. Extruders are generally used for compounding to achieve good distribution of filler particles in the polymer phase. Good distribution of filler particles ensures homogeneity for load-bearing capacity.

The quality of mixing in an extruder is influenced by its screw rotation and barrel temperature. The change in screw rotation determines the degree of shear rate applied to polymer melt and residence time of the melt (Modesti et al., 2005). The barrel temperature contributes to the shear force exerted to the polymer melt (Modesti et al., 2005). Some research has shown the importance of these variables on mechanical properties of polymer composites. However, diverse results have been reported from a number of studies.

Studies by de Moura Giraldi et al. (2005) and Modesti et al. (2005) show that increases of tensile properties of several filler-polyolefin blends are achieved with increase of screw speed. Meanwhile, Adewole et al. (1994) investigated combined effects of screw rotation, compatibiliser (Kraton rubber) and polymer fraction on flexural, tensile and impact properties of HDPE-PP blends. It was found screw rotation is less influential on modifying the mechanical properties than the other variables.
2.5 Objectives

In the manufacturing of recycled plastic products, numerous attempts have been intensively directed towards the improvement of mechanical properties of the products. It is not uncommon that the selection and addition of fillers tend to lack rigorous scientific experimentation depth. Material costs often come as the most significant factor to select the filler to use.

The main scope of this project is to investigate the behaviour of mineral fillers as reinforcement to *commingled* recycled plastics. In doing so, the research is also to:

- investigate the effectiveness of silane coupling agents to promote the activity or bonding of mineral fillers in recycled plastics composites; and
- study the effect of a number of extrusion parameters on the mechanical properties of recycled plastic composites.
3 Experimental Procedures

This chapter will discuss the experimental aspects of the research. Firstly, the characteristics of materials and preparation of the mechanical test samples will be outlined. Following this, the experimental setup of the mechanical tests and morphology analysis will be detailed.

Section 3.1 will present the practical aspects of the study. This includes material preparation, sample manufacturing and sample testing. Section 3.5 gives an interpretation of the results of the mechanical test on the filler-commingled recycled plastic composites (RPCs) using a number of predictive models already established. The sample preparation and statistical analysis of the study of the effect of extrusion factors will be given in Section 3.6.

3.1 Effect of Mineral Fillers on Mechanical Properties of RPCs

This scope of study examined the effect of three kinds of mineral fillers (i.e., gypsum, wollastonite and talc) on the mechanical properties of commingled recycled plastics. In addition, an investigation into the effect of pre-treatment of some fillers with two commercial silanes, γ-MPS and γ-APS on the properties of the resulting composites was undertaken. The material specifications and material preparation in each scope are explained in detail in the following subsections.

3.1.1 Materials

A batch of commingled plastics used as raw material for test samples was supplied by Advanced Plastic Recycling (APR) Pty Ltd of South Australia. The sample batch had been cleaned to remove soil and dirt, and then sorted from foreign materials, such as paper and metals. The plastics were sourced from packaging materials (plastic bags, shrink wrap containers, drink bottles and beverage crates), factory off-cuts and expanded polystyrene foam.

The major composition of the mixture, determined by flotation was 70-80 wt% polyolefin resins (LDPE, HDPE and polypropylene) and polystyrene foam, while the remaining fraction was made up of other resins, such as polycarbonate, nylon, expanded polystyrene foam and polyethylene terephthalate (PET). The waste as received was already shredded into tiny and soft “flakes”, with sizes ranging from 5 to 10 mm, as shown in Figure 3-1. The density of the plastic feedstock was 950 kg/m$^3$ and melt flow index was 0.811 g/10 minutes.
To minimise contamination, the non-polyolefin resins were removed in the laboratory prior to further processing by means of flotation. However the floating fraction (polyolefin components) was still contaminated with polystyrene foam and traces of other resins (e.g. nylon and PET).

![Mixed plastic "flakes" supplied by APR](image)

Mineral fillers, talc, wollastonite and anhydride gypsum were blended with the commingled plastics waste supplied by APR in different propotions. Table 3-1 presents the specifications of the mineral fillers. Glass fibre (E-type glass) was used for comparison to the mineral fillers. The glass fibre had an average diameter and length of 10 μm and 3.2 mm, respectively. The fillers were dried in an oven for 24 hours prior to blending-compounding with the plastic waste.

**Table 3-1: Physical properties of the mineral fillers**

<table>
<thead>
<tr>
<th>Filler</th>
<th>Particle shape</th>
<th>Specific gravity</th>
<th>d&lt;sub&gt;10&lt;/sub&gt; (μm)</th>
<th>d&lt;sub&gt;50&lt;/sub&gt; (μm)</th>
<th>d&lt;sub&gt;90&lt;/sub&gt; (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc (Mg₃Si₄O₁₀(OH)₂)</td>
<td>plate</td>
<td>2.76</td>
<td>3.3</td>
<td>14.5</td>
<td>42.4</td>
</tr>
<tr>
<td>Wollastonite (CaSiO₃)</td>
<td>acicular</td>
<td>2.96</td>
<td>3.5</td>
<td>20.8</td>
<td>59.5</td>
</tr>
<tr>
<td>Anhydride gypsum (CaSO₄)</td>
<td>sphere</td>
<td>2.9</td>
<td>1.0</td>
<td>4.8</td>
<td>45.9</td>
</tr>
</tbody>
</table>
3.1.2 **Samples Preparation**

The preparation of mechanical test samples involved three major stages, compaction of plastic flakes, compounding and injection moulding, as illustrated in Figure 3-2. Due to the non-existence of in-house facilities to do this at the School of Chemical Engineering, the University of Adelaide, these processes were carried out externally at multiple facilities as shown below.

![Schematic diagram of sample production and testing](image)

**Figure 3-2: Schematic diagram of sample production and testing**

3.1.2.1 **Compaction of Plastic Flakes**

Due to the light and fluffy nature of the plastic flakes, it had to be compacted to ensure consistent feeding to the barrel of and distribution in the extruder. The compaction of the waste was the first-stage of extrusion, where the plastic flakes were run through an extruder and the extruded strands were chopped into small “pellets” with 2-3 mm diameter.

This stage was performed at Plastic Granulating Services (PGS) of South Australia using a John’s single screw extruder (Figure 3-3) having a screw length and diameter (L/D) ratio of 15. The pellets were produced at the rate of 5 kg/h with the optimum screw rotation being 110 RPM while the temperatures of the rear/feeding, centre/mixing and front/die zones in the barrel were respectively set at 210°C, 210°C, and 220°C. The extruded strands were chopped into small pellets having diameters of 2–3 mm. To obtain continuous output of the extruded strands was a challenging process due to the inconsistent flow of the product strands out of the extruder dies, where the strands often snapped off or expanded into a larger diameter. This condition was particularly encountered when a batch of the raw material fed through the
extruder barrel contained considerable “contamination” of polystyrene foam, non-polyolefin polymers or nylon.

Figure 3-3: John’s single-screw extruder at Plastic Granulating Services

3.1.2.2 Compounding

Compounding or blending of fillers and the plastics “pellets” was performed by using a laboratory-scale extruder, a Brabender co-rotating intermeshing twin screw extruder having screw diameters of an L/D ratio of 20. The feeding, mixing and die temperatures of the extruder barrel were set at 170°C, 195°C and 195°C. The screw rotation was set at 70 RPM for this operation. The mixture strands were chopped into small pellets (2-4 mm diameter) using a mechanical granulator.

3.1.2.3 Injection Moulding

Injection moulding was carried out to manufacture tensile and flexural specimens with specifications based upon ASTM D 256 and D 790, respectively. This process was undertaken at the PGS laboratory and carried out using a Battenfeld injection moulder (Figure 3-4).

The injection pressure was adjusted at 137 bar (2000 psi) for all samples. The front/die, mixing and feeding temperatures across the barrel were set at 240°C, 235°C and 180°C, respectively.
3.1.3 Mechanical Testing

Tensile and flexural tests were performed using in-house facilities at the University of Adelaide. Both series of tests were performed in accordance with the respective ASTM standards.

3.1.3.1 Tensile Test

Several dog-bone specimens similar to type II specimens from ASTM D 256 (Figure 3-5) were tensile-tested using an INSTRON 5543 mechanical tester with a constant strain rate of 0.1 mm/mm/min and maximum load of 1 kN. Axial displacement was recorded using a clip-on extensometer with a 50 mm gauge length. The setup of the tensile test apparatus is depicted in Figure 3-6.
All tensile samples were tested on the INSTRON machine at the polymer laboratory at the School of Chemical Engineering, except for those for the study of effect of filler particle size and effect of extrusion conditions (Sections 3.3 and 3.6).

The tensile test results obtained from the INSTRON 5543 were automatically calculated by the Bluehill® data acquisition package (INSTRON) based on the engineering stress-strain data. The results for the samples tested using the Mohr and Federhaff machine were determined from the engineering stress-strain data recorded by a data acquisition package. The procedure to calculate tensile properties from the engineering stress-strain data is explained in Appendix A.

<table>
<thead>
<tr>
<th>Dimensions in millimetres (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₃     Overall length</td>
</tr>
<tr>
<td>L₁     Length of narrow parallel-sided portion</td>
</tr>
<tr>
<td>R      Radius</td>
</tr>
<tr>
<td>b₂     Width at ends</td>
</tr>
<tr>
<td>b₁     Width of narrow portion</td>
</tr>
<tr>
<td>H      Thickness</td>
</tr>
</tbody>
</table>

Figure 3-5: Dog-bone shaped tensile specimens
3.1.3.2 Flexural Testing

Flexural testing was carried out in line with ASTM D 790. In each test run, a rectangular specimen of 127 mm by 12.7 mm by 3 mm was horizontally rested on a 50.8 mm support span and tested with the three-point bending method. All flexural samples in this research were tested using the INSTRON 5543 machine. The setup of the test is shown in Figure 3-7. A cross-head rate of 1.23 mm/min was applied to each specimen. The test was terminated after an engineering strain of the specimen reached 5%. Flexural strength and modulus of the samples were determined by the Bluehill® data acquisition package from INSTRON.
3.1.4 **Morphology observation**

A Philips XL-20 scanning electron microscope was then used to observe the inner surface of the tensile-tested specimens. Small sections adjacent to the fracture point of the samples were cut by using a razorblade and coated with carbon prior to the microscopy observation.

3.2 **Flexural Testing of Large-scale samples**

Flexural testing was undertaken on several large scale specimens manufactured by APR. The testing was performed to compare the flexural properties of the commingled plastics composites with those from other studies and with timber materials commonly used in load bearing applications. The production and flexural testing of the samples are explained as follows.

3.2.1 **Samples preparation**

Advanced Plastic Recycling supplied a number samples of cylindrical posts made of different material compositions. The first type of the samples had similar composition to that of the raw material used in section 3.1 (i.e. 70-80 wt% polyolefin resins (LDPE, HDPE and polypropylene) and polystyrene foam, 20-30 wt% polycarbonate, nylon, expanded polystyrene foam and PET). This is later known as the base mix. The second type consisted of the base mix (70 wt%) blended with 30 wt% wood flour. The third type consisted of the
base mix (50 wt %) and gypsum (50 wt %). The composite beams were manufactured by the APR extrusion process as described in Section 2.1.2.

3.2.2 **Flexural testing of large-scale specimens**

The cylindrical posts had a nominal length of 1200 mm and diameter of 100 mm. Three-point bend testing was performed on the posts based upon ASTM D 790. The equipment set up is shown in Figure 3-. The test was carried out using a SIEDNER flexural test machine which was located in the School of Civil, Environmental and Mining Engineering at the University of Adelaide.

The flexural properties were determined using the engineering stress-strain data as recorded by a data acquisition package for the testing machine. The calculation method for this is explained in Appendix A.

![Figure 3-8: Three-point bending test of a large-scale specimen](image)

**3.3 Effect of Filler Particle Size**

The study was performed to investigate the effect of particle size of fillers on mechanical properties of polymer composites. To justify the true effect, it was decided to employ a single polymer resin as a matrix. This attempted to eliminate any possible interaction of the filler and multiple polymer resins. The materials used, sample preparation and mechanical testing are detailed further in the following sub-chapters.
3.3.1 **Materials**

Calcium carbonate was selected as filler for the purpose of this part of the study as opposed to the talc, wollastonite or gypsum used in the previous section. To investigate the true impact of particle size, it was expected that the filler should be available in diverse ranges of particle distribution. None of the fillers used previously satisfied this criterion and after some research, calcium carbonate was found to be an alternative.

Five different grades of calcium carbonate (CaCO₃) were to be blended with a recycled grade HDPE resin at 10, 20, 30 and 40 wt% of the total composite weight (i.e. 0.04, 0.08, 0.13 and 0.19 v/v). Because it readily had more different commercial grades than the other minerals. Table 3-2 gives the specifications of the different calcium carbonate grades. The recycled HDPE pellets were supplied by PGS of South Australia. The HDPE resin had a melt flow index of 0.21 g/10 minutes and bulk density of 0.97 g/cm³.

Table 3-2: Material specifications of different grades of CaCO₃

<table>
<thead>
<tr>
<th></th>
<th>Specific gravity</th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omya 1</td>
<td>2.7</td>
<td>0.6</td>
<td>2.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Omya 10</td>
<td>2.7</td>
<td>1.5</td>
<td>11.5</td>
<td>31.8</td>
</tr>
<tr>
<td>Omya 20</td>
<td>2.7</td>
<td>2</td>
<td>18.1</td>
<td>52.4</td>
</tr>
<tr>
<td>Omya 50</td>
<td>2.7</td>
<td>2.2</td>
<td>25.0</td>
<td>102.4</td>
</tr>
<tr>
<td>Circal 1000 MV</td>
<td>2.7</td>
<td>29.6</td>
<td>174.4</td>
<td>474.9</td>
</tr>
</tbody>
</table>

Note:

Particle size distribution (i.e. $D_{10,50,90}$) was determined by a light scattering method using a Malvernizer 2000.

3.3.2 **Sample preparations**

The tensile and flexural test samples used in this part of the study were manufactured through the same process details as in the study of the commingled recycled plastic composites, except that the HDPE pellets did not need a compaction stage. In the injection moulding stage, a higher temperature range (i.e. 245°C, 270°C and 200°C for die, mixing and feeding zones, respectively) was applied to the HDPE-CaCO₃ blends.
3.3.3 Mechanical Testing

The tensile test specimens of the recycled HDPE-CaCO₃ blends were tested on a Mohr and Federhaff (Figure 3-9) testing machine in the School of Civil, Environmental and Mining Engineering of the University of Adelaide. This was done because rupture of the HDPE composites could not be achieved by the ultimate load capacity of the INSTRON 5543 machine. The Mohr and Federhaff machine was set at 10 kN capacity and equipped with the same extensometer as used in testing with the INSTRON 5543 machine for axial strain measurement.

![Mohr & Federhaff tensile tester](image)

Figure 3-9: Mohr & Federhaff tensile tester

The flexural test of the recycled HDPE-CaCO₃ blends was conducted by using the 5543 INSTRON machine. The testing procedure was consistent with that described in Section 3.1.

3.3.4 Morphology observation

The morphology observation of the HDPE-CaCO₃ blends was carried out with the same procedure as that for the commingled plastic samples.
3.4 Effect of Silane Coupling Agents

In this part of study, two commercial silane coupling agents were investigated for their influence on the mechanical properties of the commingled plastics composites. The experimental procedures involved are detailed in the following sections.

3.4.1 Materials

Two commercial silane coupling agents, 3-methacryloxypropyltrimethoxy silane (γ-MPS) and 3-aminopropyltriethoxy silane (γ-APS) were used to treat talc and wollastonite, which were then compounded together with the recycled plastic pellets from the compaction stage in Section 3.1.. The specifications of the two silanes are given in Table 3-3.

Table 3-3: Material specifications of the silane coupling agents

<table>
<thead>
<tr>
<th>Silane</th>
<th>Molecular weight</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-MPS</td>
<td>248.35</td>
<td>1.05</td>
</tr>
<tr>
<td>γ-APS</td>
<td>221.37</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The procedure of the silane treatment of the fillers was carried out in the following steps:

1. Pre-treatment of fillers

Prior to the silane treatment, talc and wollastonite were dried in an oven for 24 hours at 80°C to evaporate moisture to avoid any effect on the bonding between filler surface and the hydroxyl group of the silanes.

2. Silane treatment of fillers

Hydrolysis of silanes (wet blending) was chosen as the method to treat the fillers as suggested by some researchers (Akin-Őktem and Tınçer, 1994; Khalil et al., 2006).

The two commercial silanes, γ-MPS and γ-APS were applied to the fillers at 0.5%, 1% and 2% with respect to the total weight of the filler. These are equivalent to 0.01, 0.03 and 0.05 of the volume of the filler. The silanes were added to deionised water and the aqueous
solutions were stirred for 15 minutes. Deionised water was prepared in the following proportions:

- 500 millilitres of water to 322 gram of talc and
- 450 millilitres of water to 322 gram of wollastonite.

While still being stirred, the filler was gradually added into the aqueous solutions of the silanes and the stirring continued for another 30 minutes. After the mixing was completed, the wet filler was dried in an oven at 80 °C for 24 hours. The dried filler was then ground in a mortar to break up the large clumps of filler particles that flocked together during the treatment process.

3.4.2 **Mechanical testing**

The tensile and flexural testings of the silane treated specimens were conducted through the same experimental process explained in Section 3.1.

3.4.3 **Morphology observation**

The procedure of morphology observation of the silane treated specimens was in line with that detailed in Section 3.1.
3.5 Interface Adhesion of Filler and Recycled Plastics

The degree of adhesion between the mineral fillers and commingled plastics waste in Section 3.1 was analysed using established mathematical models. The mathematical models investigated relate the mechanical properties to filler concentration. As all the models predict the mechanical properties in regards to volume content, the weight percentages of the fillers needed to be converted to a volume ratio. To convert weight percentages \( W_f \) into volume ratios \( \phi_f \), the following equation was used:

\[
\phi_f = \frac{W_f / \rho_f}{W_f / \rho_f + W_p / \rho_p}
\]

(3-1)

The weight content of the polymeric matrix is given by \( W_p \) and densities of the filler and matrix are \( \rho_f \) and \( \rho_p \), respectively.

3.5.1 Tensile and Flexural Strength

The tensile and flexural strength data of the plastic composites were plotted following the predictive models (i.e. Nicolais-Narkis, porosity and Turcsanyi models) mentioned earlier. Before data plotting, adhesion coefficients involved in the models need to be determined. A calculation procedure using the Nicolais-Narkis model is detailed below.

- The Nicolais-Narkis model is given as:

\[
\sigma_c = \sigma_p \left(1 - a \phi_f^{\frac{2}{3}}\right)
\]

(3-2)

- This equation can be rearranged into:

\[
\frac{\sigma_c - \sigma_p}{\sigma_p} = -a \phi_f^{\frac{2}{3}}
\]

(3-3)

- A linear regression method was then used to obtain the slope of the equation or a value with the intercept set to zero (i.e. \( \sigma_c = \sigma_p \) when \( \phi = 0 \))

- A total error of each set of data of the fillers was determined from the average of the individual data error (in percentage), which was determined from variations between the calculated and experimental \( \sigma_c \) values; and

- The theoretical and experimental \( \sigma_c/\sigma_p \) values were plotted against volume percentages of the fillers.
A more detailed sample calculation is given in Appendix C. The same data-fitting procedure applies to porosity and Turcsanyi models.

3.5.2 **Tensile and Flexural Modulus**

The tensile and flexural moduli of the plastic composites were plotted according to Einstein, Guth-Smallwood and Kerner models. A similar calculation procedure to the one explained above was followed to determine the constants in the predictive models. A calculation procedure of Einstein model is given below as an example.

- The simple Einstein model is given as:
  \[ E_c = E_p \left( 1 + a\phi_f \right) \]  
  \[ (3-4) \]

- This equation can be rearranged into
  \[ \frac{E_c - E_p}{E_p} = a\phi_f \]  
  \[ (3-5) \]

The linear regression method was used to obtain the slope of the equation (i.e. \( a \)) value with the intercept set to zero.

- Once constant \( a \) had been established a theoretical \( E_c \) was calculated for every filler volume fraction. A percentage variation between the theoretical \( E_c \) and experimental \( E_c \) was then calculated for each volume fraction. A total error was determined from averaging out the individual variations.

- The theoretical and experimental \( E_c/E_p \) data were plotted against volume percentages of the fillers.

Data plotting to Guth and Smallwood and Kerner equations was carried out following Equations 2-8 and 2-9, respectively. A more detailed sample calculation is given in Appendix C.
3.6 Effect of Extrusion Condition

The analysis of the effects of various extrusion parameters on the mechanical properties of recycled plastic composites consisted of three steps: dependent variable (factor) selection, experimental design and statistical analysis.

3.6.1 Independent Variables Selection

The literature review showed that the process variables in the extrusion process were considered to have significant influence on the mechanical properties of polymer composites. These were filler content, screw rotation and melt temperature. The levels of the independent variables are presented in Table 3-4. The low, medium and high levels of each variable are denoted as -1, 0 and +1, respectively.

The polymer resin chosen for this study was the same HDPE grade used in the study of filler particle size. A grade of calcium carbonate from the study of filler particle size (i.e. OMYA 1) was also utilised in this work.

Table 3-4: Independent Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Low (-1)</th>
<th>Medium (0)</th>
<th>High (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ mass fraction</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Screw rotation (RPM)</td>
<td>70</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Barrel temperature (°C)</td>
<td>160,185,185</td>
<td>170,195,195</td>
<td>185,205,205</td>
</tr>
</tbody>
</table>

The procedures of sample preparation, mechanical testing and morphology observation were consistent with those mentioned in the study of filler particle size.

3.6.2 Experimental Design

The experimental runs were modelled after the Box-Behnken method (Montgomery, 2005), which is a method of response surface design and specifically used to effectively analyse experiments involving three levels of variations. The main advantage of this design is that a lower number of experimental runs are required than those for normal factorial methods (Montgomery, 2005).
The experimental runs of the Box-Behnken design are summarised in Table 3-5. The codified factor levels are indicated in parentheses. The experimental set involving the middle levels of the factors were replicated for three runs. The replicated runs mainly serve as a magnitude of the experimental error (Adewole et al., 1994).

Table 3-5: Experimental runs based on Box-Behnken design

<table>
<thead>
<tr>
<th>Run</th>
<th>CaCO$_3$ (X$_1$, wt %)</th>
<th>Mixing rate (X$_2$, RPM)</th>
<th>Zone 3 Temperature (X$_3$, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40 (+1)</td>
<td>90 (+1)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>2</td>
<td>40 (+1)</td>
<td>70 (-1)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>3</td>
<td>20 (-1)</td>
<td>90 (+1)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>4</td>
<td>20 (-1)</td>
<td>70 (-1)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>5</td>
<td>40 (+1)</td>
<td>80 (0)</td>
<td>205 (+1)</td>
</tr>
<tr>
<td>6</td>
<td>40 (+1)</td>
<td>80 (0)</td>
<td>185 (-1)</td>
</tr>
<tr>
<td>7</td>
<td>20 (-1)</td>
<td>80 (0)</td>
<td>205 (+1)</td>
</tr>
<tr>
<td>8</td>
<td>20 (-1)</td>
<td>80 (0)</td>
<td>185 (-1)</td>
</tr>
<tr>
<td>9</td>
<td>30 (0)</td>
<td>90 (+1)</td>
<td>205 (+1)</td>
</tr>
<tr>
<td>10</td>
<td>30 (0)</td>
<td>90 (+1)</td>
<td>185 (-1)</td>
</tr>
<tr>
<td>11</td>
<td>30 (0)</td>
<td>70 (-1)</td>
<td>205 (+1)</td>
</tr>
<tr>
<td>12</td>
<td>30 (0)</td>
<td>70(-1)</td>
<td>185 (-1)</td>
</tr>
<tr>
<td>13</td>
<td>30 (0)</td>
<td>80 (0)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>14</td>
<td>30 (0)</td>
<td>80 (0)</td>
<td>195 (0)</td>
</tr>
<tr>
<td>15</td>
<td>30 (0)</td>
<td>80 (0)</td>
<td>195 (0)</td>
</tr>
</tbody>
</table>

The recycled HDPE pellets were compounded with CaCO$_3$ (OMYA 1) in the Brabender twin-screw extruder according to the compositions set in Table 3-5.

3.6.3 Statistical Analysis

The Box-Behnken design is capable of analysing full polynomial models up to order 2, which include linear, interaction and curvature effects for the factors (Adewole et al., 1994):

\[ Y = d_0 + d_1X_1 + d_2X_2 + d_3X_3 + d_{11}X_1^2 + d_{22}X_2^2 + d_{33}X_3^2 + d_{12}X_1X_2 + d_{13}X_1X_3 + d_{23}X_2X_3 \]  (3-6)
The independent variables or factors are denoted by $X_{1,2,3}$, while $Y$ is a dependent variable which might or might not be influenced by the factors. The response effects, $d_{0..23}$, are determined by multiple linear regression.

To quantify the statistical relevancy of all functions (linear, quadratic and interaction) in the polynomial interaction of the variables, the $F$-test (square of effects/square of residual) and significance probability or $p$-value were calculated by analysis of variance often known as ANOVA. (Montgomery, 2005)

A factor is statistically relevant if the corresponding $p$-value is less than the nominated significance level, $\alpha$. In this experiment the $\alpha$ was set to 0.05. For an experimental design with $n$ factors and $k$ levels of the factors, the $p$-value is said to be less than the $\alpha$ if the $F$ distribution with $k-1$ variables and $k(n-1)$ degree of freedom (DF) is less than the calculated $F_o$ value. The $F_o$-value is given by Equation 3-7 (Montgomery, 2005).

$$F_o = \frac{MS_i}{MS_{error}}$$

where $MS_i$ is the mean square of a factor and $MS_{error}$ is the error mean square. The ANOVA tables are given in Appendix D. The ANOVA calculation of the data results was performed by a statistical package, STATISTICA 6.0.
3.7 Error Analysis

Data obtained from the mechanical tests of five test specimens were averaged. The average of a set of test results, $x$ is calculated by adding the individual results and dividing this sum by the number ($n$) of individual results, as shown in Equation 3-7 below:

$$
\bar{x} = \frac{x_1 + x_2 + x_3 + x_4 + \ldots}{n}
$$

A standard deviation (SD) value is determined for each data set and calculated using Equation 3-8 below:

$$
SD = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2 + \ldots}{n - 1}}
$$

A relative standard deviation (RSD) of 10% was used to determine statistical significance of the data. Samples which contributed to an RSD of more than 10% were not accounted for in the calculation. The relative standard deviation is obtained by dividing the standard deviation by the average value and multiplied by 100% and shown in the Equation below.

$$
RSD = \left( \frac{RS}{\bar{x}} \right) 100\%
$$
4 Results and Discussion

4.1 Effect of Mineral Fillers on Mechanical Properties of RPCs

This part of the study investigated the effects of various mineral fillers on the mechanical properties of recycled plastic composites. Results of the tensile and flexural tests performed and morphology observation of the tensile test specimens are discussed here.

4.1.1 Mechanical Properties

The tensile properties of the recycled plastic composites containing different fillers are plotted against volume fractions of filler in Figure 4-1. The tensile strength was determined at the break points of the specimens, while the modulus was calculated as the slope of stress-strain curve at 1% strain (i.e. secant modulus). The data for the tensile properties is summarised in Table B1 (Appendix B) together with its standard deviation.

Figure 4-1 clearly shows the addition of glass fibre results in the largest improvement in the tensile properties, especially in tensile modulus. Increases of 300% in tensile modulus and 30% in tensile strength over unfilled samples were achieved with 0.26 v/v glass fibre content. Within the mineral filler group, talc was found to be the most effective where the composites having 0.26 v/v talc showed increases of almost 170% in the modulus and 20% in strength. It is reported that the tensile strength of filled polymers may increase or decrease with increased filler content (Bose and Mahanwar, 2005; Hiljanen Vainio et al., 1997; Ismail et al., 1997; Khalil et al., 2006; Ulutan and Gilbert, 2000).
Figure 4-1: Tensile strength (a) and tensile modulus (b) of filler-recycled plastic composites

Figure 4-1 shows that the tensile strength provided by talc increases with increasing filler content, whereas that provided by wollastonite and gypsum decreases once the filler content reaches a certain level. In the gypsum case, the reduction in strength may be caused by agglomeration of gypsum particles, which increases at high filler content. This will be further discussed in the morphology section (4.1.2). As for wollastonite, the large wollastonite particles possibly disrupt matrix continuity, thereby decreasing the effective load-bearing cross-sectional area. Figure 4-1 (b) shows that the tensile modulus increases with increasing
content of fillers, which is a common finding by other researchers (Bose and Mahanwar, 2005; Ismail et al., 1997; Khalil et al., 2006; Ulutan and Gilbert, 2000).

Figure 4-2 shows the flexural strength and flexural modulus of the plastic composites. The flexural strength was determined at the maximum stress of the stress-strain curve, while the modulus was calculated using the slope of stress-strain curve at 1% strain (i.e. secant modulus). The data for the flexural properties is presented in Table B.1 (Appendix B).
The addition of glass fibre at 0.26 v/v resulted in increases of nearly 200% in the flexural modulus and 30% in the flexural strength over the plastic without filler. For the mineral fillers, talc still dominates both the flexural strength and modulus, although the relative performance differences between the mineral fillers are not as significant as those observed for tensile properties. At 0.26 v/v content, talc increases the flexural modulus by as much as 65% over that of the unfilled polymer and increases the strength by as much as 40%. Overall, the flexural strength of the composites increases with increasing filler content.

Generally flexural moduli of thermoplastic composites are lower than their tensile moduli. This has also been reported by other researchers and might be because in flexural testing the maximum stress occurs at the surface, where the filler concentration is relatively low compared to that in the core section (Leong et al., 2004; Wypych 1999). In injection-moulded composites, filler particles tend to accumulate in the core rather than on the surface, because as the blend passes the moulding gate, particles move from the gate (i.e., the front surface) to the interior (Wypych, 1999). Furthermore, during cooling of moulded specimens, filler particles tend to migrate from cold regions (outer skin) to the melt or core (inner section) (Wypych, 1999).

Gypsum was not found to improve tensile and flexural properties as much as talc and wollastonite. This could be because the particle size of gypsum is smaller than those of the other two minerals, and when no surface coating by a coupling agent is present, small particles tend to agglomerate (Wypych, 1999). This will be discussed in the morphology section (4.1.2).

Particle shape can also influence the filler performance. The plate-like structure of talc and fibre-like (acicular) structure of wollastonite particles creates high aspect ratios, which improve wetting with the polymer matrix and hence reduce micro voids between the filler and matrix (Leong et al., 2004). In addition, talc is known to have a high degree of lubricity or dispersion due to much lower Van der Waals forces holding together its crystal structure (Wypych, 1999).

4.1.2 Morphology Observation

Figure 4-3 shows the SEM images of the base plastic using secondary electron (SE) diffraction (a) and backscatter electron (BSE) diffraction (b). It is observed from the figure
that there is no indication of separation of polymers in the control sample, which may indicate satisfactory mixing was achieved. White specks in the body of the matrix observed in Figure 4-3(b) possibly indicate the non polyethylene polymers present in the mixed plastic.

Figure 4-3: SEM images of the base plastic: (a) SE (b) BSE diffraction

The inferior tensile and flexural properties of the anhydride gypsum filled samples could be caused by severe agglomeration, which is shown in Figure 4-4. Gypsum agglomerates formed in all the samples of different weight percentages of gypsum filler and their extent increased with increasing filler additions. The voids formed in the vicinity of the gypsum particles could be caused by the particles agglomerating, which could have been increased by subsequent debonding and therefore could have initiated crack propagations.

Figure 4-4: SEM images of 0.12 (a) and 0.25 (b) v/v gypsum blends
The SEM micrographs of the composites filled with 0.12 and 0.24 v/v wollastonite are shown in Figure 4-5. Micro-voids are observed in the vicinity of wollastonite particles. These are larger in size and more common in the blend with 0.24 v/v wollastonite. In comparison to gypsum and wollastonite, talc tends to disperse better in the matrix and to create less voids in the matrix as depicted in Figure 4-6. This might be the reason for the talc blends having the highest strength and modulus.

Figure 4-5: SEM images of 0.12 (a) and 0.24 (b) v/v wollastonite blends

Figure 4-6: SEM images of 0.13 (a) and 0.26 (b) v/v talc blends

Extensive agglomeration in gypsum may be formed because the gypsum particles are inclined to agglomerate more than talc and wollastonite. The micrographs of filler particles show that the primary particles of gypsum naturally clump together (Figure 4-7 (a)), while particles of talc (Figure 4-7 (b)) and wollastonite (Figure 4-7 (c)) barely come into contact with each other. Agglomeration leads to non-uniform filler dispersion and inhomogeneous mechanical properties; moreover, it inhibits the activity of filler particles on the polymer matrix (Lipatov, 1995).
Agglomeration of filler particles is complex and is influenced by many variables, including particle size, chemical groups on the particle surface, filler production method, moisture level and surface treatment (Wypych, 1999). Some fillers possess a natural tendency to agglomerate, especially when strong van der Waals bonds form among particles (Wypych, 1999). In addition, small particles have a stronger tendency to agglomerate (Leong et al., 2004; Wypych, 1999; Wong et al., 1999). As a result the small particles of gypsum might have intensified the formation of agglomerates.

![SEM micrographs](image1)

Figure 4-7: SEM micrographs of: (a) anhydrite gypsum, (b) talc and (c) wollastonite

In the case of glass fibre, Figure 4-8 shows the orientation of glass fibre in a cross-section of the matrix. At 0.13 v/v filler content, the fibres seem to be aligned in parallel along the longitudinal axis. At 0.26 v/v glass fibre, the spacing between the fibres becomes smaller; in fact, the fibres come into contact and become less oriented.
4.2 Effect of Filler on Mechanical Properties of Large Scale Samples

The engineering properties of recycled plastic composite profiles vary depending on the composition of the profiles. A number of flexural tests were undertaken on full scale samples of different composites. The samples were obtained from products manufactured by the Advanced Plastic Recycling (APR) process. The tests aimed to compare the performance of the composites with the studies undertaken by other researchers.

Table 4-1 shows the flexural properties measured for different compositions of recycled plastic profiles and different types of timber compiled from previous research. The base composition obtained from APR is represented by mix A. It can be seen that the properties vary depending on the material composition. The APR base mix has very low flexural properties compared to the other composites which were blended with fillers.

The mixed plastic waste (APR plastic) gave an inferior stiffness compared to other recycled plastic products found in the literature. This is due to the high presence of LDPE, which is naturally more ductile than other polymers commonly recycled (e.g. HDPE, PS, PP and PET), in APR material. The blend containing more HDPE as studied by Zarillo and Lockert (1993) has a stiffness of nearly three times the value obtained by the unfilled APR plastic. For blends filled with 20% fibre glass, the one having HDPE as the matrix is nearly five times stiffer than the APR plastic blend.
The stiffness of the mixed plastic waste has a value of up to 10-15 % of the timber values. Compared to white cedar timber, which is normally used in low-load bearing applications (e.g. outdoor furniture and garden walkway), the engineering properties of reinforced recycled plastic blends are still very inferior. However, recycled plastic profiles may be suitable for these applications, considering plastic is resistant to moisture and biological attacks. As for engineering applications requiring high-load bearing, such as railway sleepers (represented by red gum timber in Table 4-1), recycled plastic products may not be a suitable alternative for timber.

Table 4-1: Flexural properties of different recycled plastic composites

<table>
<thead>
<tr>
<th>Material composition (weight composition)</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A: mixed waste plastic (70-80% polyolefin, LDPE, HDPE and PP; and 20-30% polystyrene foam, polycarbonate, PET and nylon)</td>
<td>430</td>
<td>&gt; 8.06</td>
<td>Test result</td>
</tr>
<tr>
<td>70 % Mix A + 30 % wood flour</td>
<td>911</td>
<td>22.5</td>
<td>Test result</td>
</tr>
<tr>
<td>50 % Mix A + 50 % gypsum</td>
<td>1225</td>
<td>19.5</td>
<td>Test result</td>
</tr>
<tr>
<td>60 % Mix B (80-90 % polyethylene and 10-20 % polyvinyl chloride (PVC), polyethylene terephthalate (PETE) and polyamides); 30 % fibre glass; 10 % CaCO₃, and 5 % compatibiliser</td>
<td>1003</td>
<td>18.8</td>
<td>Banerjie (1991)</td>
</tr>
<tr>
<td>50 % Mix B; 30 % glass fibre; 15 % compatibiliser; and 5 % impact modifier</td>
<td>3378</td>
<td>38.7</td>
<td>Banerjie (1991)</td>
</tr>
<tr>
<td>Post consumer HDPE with 20 % fibre glass</td>
<td>3100</td>
<td>-</td>
<td>Breslin et al (1998)</td>
</tr>
</tbody>
</table>
4.3 Effect of Filler Particle Size

In the previous study, particle size effect was investigated for different types of fillers and it is important now to compare the findings with the size effect from a single type of filler. Different grades of calcium carbonate having different particle size distribution were blended with recycled high density polyethylene.

4.3.1 Mechanical Properties

Several dog-bone shaped specimens moulded from the HDPE resins and different types of CaCO₃ were tensile-tested using the Mohr and Federhaff testing machine. The procedure of the test is detailed in section 3.3.3. The tensile test results were calculated from the stress-strain charts produced by a data acquisition package for the testing machine. The tensile strength was determined at the break point of the stress-strain curves and the tensile modulus was calculated from the slope of the curves at 1 % strain. Difficulties were experienced when compounding CaCO₃ (Circal-1000 MV) filler with HDPE pellets. This is due to severe blockage of bridging of CaCO₃ particles in the feeding throat of the extruder. Therefore, the blends with Circal-1000 MV were only prepared up to 30 wt% or 0.13 v/v.

The tensile strengths and moduli of the composites are presented in Figure 4-9. The tensile strength of the composites tends to increase with higher filler content, except for those blended with OMYA 50 and Circal-1000 MV. The same tendency can also be observed in the case of tensile modulus of all grades of CaCO₃, except the Circal-1000 MV blends. According to Wypych (1999), large particles are found to cause defects in the polymer matrix since no interaction is present among the two phases, which may result in the decline of tensile properties for the composites with Circal-1000 MV.

For the composites filled with particle sizes smaller than OMYA 50, it appears that particle size has little impact on the tensile strength and tensile modulus. The differences in tensile strength and tensile modulus are within 5 % for the different particle sizes.
Flexural properties of the CaCO\textsubscript{3}-HDPE composites are given in Figure 4-10. In general the flexural strength and flexural modulus of the blends increase with higher filler content, with the exception of the CMV blends. Similar to the tensile properties, particle size of CaCO\textsubscript{3} is not a significant factor in modifying the flexural properties of the composites with OMYA 1, OMYA 10 and OMYA 20.
4.3.2 Morphology Observation

Morphology observation using the SEM was performed on the CaCO₃-HDPE specimens from the tensile test. Particle size can be an important factor in filler-polymer interaction. It contributes to the extent of particle dispersion as well as the mechanism of particle debonding.
As can be seen in Figure 4-11 and Figure 4-12 (i.e. at 0.04 and 0.08 v/v CaCO₃ content), there does not seem to be significant difference in particle dispersion for all particle size. Particle agglomeration is apparently not an issue at these percentages of CaCO₃. At higher CaCO₃ filler levels (0.13 and 0.19 v/v), however, the degree of agglomeration becomes more significant (Figure 4-13 and Figure 4-14).

Detachment of CaCO₃ particles from the HDPE matrix can be clearly observed from SEM micrographs of OMYA 50 and CMV fillers in Figure 4-11 to Figure 4-14. The larger particle size of the two CaCO₃ grades is responsible for these findings. Due to its broad range of particle size distribution, OMYA 10 and OMYA 20 consist of a fraction of large particles, which can be observed detaching from the matrix, especially in Figure 4-13 and Figure 4-14. The detachment of the particles becomes more severe with the increasing CaCO₃ content.

As shown in Figures 4-12 to 4-14, there is noticeable debonding of individual particles. The extent of any opening of the micro pores nucleated by the debonding is subject to the size of the individual particles. The larger the size of the particles, the greater the opening of the pores (Dubnikova et al., 1997a). This tends to reduce the effective cross-section of the polymer matrix to sustain load, which means a lower strength results. The reduction of the sustainable load is analogous to the reduction of the engineering stress, or in this case the tensile strength. This might explain the slight increase of tensile strength of OMYA 1 compared to OMYA 10 and OMYA 50 filled HDPE, as found in the mechanical property section.

At 0.19 v/v filler content (Figure 4-14), a combination of individual and craze-like debonding can be observed in the cases of the composites filled with OMYA 1 and OMYA 10 particles. This has resulted in polidispersity of the CaCO₃ particles. As for the composites with 0.19 v/v OMYA 20 and OMYA 50, individual debonding of the particles is significant.
Figure 4-11: SEM images of HDPE tensile samples at 0.04 v/v CaCO₃ content: (a) Omya 1 ($D_{50}=2.1$ μm), (b) Omya 10 ($D_{50}=11.5$ μm), (c) Omya 20 ($D_{50}=18$ μm), (d) Omya 50 ($D_{50}=25$ μm) and (e) Circal 1000 MV ($D_{50}=174.4$ μm)
Figure 4-12: SEM images of HDPE tensile samples at 0.08 v/v CaCO$_3$ content: (a) Omya 1 ($D_{50}=2.1$ $\mu$m), (b) Omya 10 ($D_{50}=11.5$ $\mu$m), (c) Omya 20 ($D_{50}=18$ $\mu$m), (d) Omya 50 ($D_{50}=25$ $\mu$m) and (e) Circal 1000 MV ($D_{50}=174.4$ $\mu$m)
Figure 4-13: SEM images of HDPE tensile samples at 0.13 v/v CaCO₃ content: (a) Omya 1 (D₅₀ = 2.1 μm), (b) Omya 10 (D₅₀ = 11.5 μm), (c) Omya 20 (D₅₀ = 18 μm), (d) Omya 50 (D₅₀ = 25 μm) and (e) Circal 1000 MV (D₅₀ = 174.4 μm)
Figure 4-14: SEM images of HDPE tensile samples at 0.19 v/v CaCO$_3$ content: (a) Omya 1 ($D_{50}$= 2.1 μm), (b) Omya 10 ($D_{50}$= 11.5 μm), (c) Omya 20 ($D_{50}$= 18 μm), (d) Omya 50 ($D_{50}$= 25 μm)
4.4 Interface Adhesion of Filler-Recycled Plastics

4.4.1 Tensile and Flexural Strength

The predictive models used to study the interface adhesion between the fillers and polymer were Turcsanyi, Nicolais-Narkis and porosity. Another model proposed by Turcsanyi et al. (1988) takes into account both active and inactive effects of fillers on tensile strength and is given as:

\[
\sigma_c = \sigma_p \left[ \frac{(1 - \phi_f)}{(1 + A\phi_f)} \right] \exp(B\phi_f) \tag{3-5}
\]

Here the constant \( B \) is an adhesion parameter for the filler where large values of \( B \) indicate better adhesion or activity of the filler. The term \((1 - \phi_f)/(1 + A\phi_f)\) measures the extent to which filler reduces the effective load-bearing cross-section of the matrix. The quantity \( A \) is a packing factor of the filler; for particulate fillers, \( A \approx 2.5 \) (Turcsanyi et al., 1988).

Table 4-2 and Table 4-3 summarise the constants for each filler from the three equations derived from tensile and flexural strength, respectively. Negative values of the Nicolais-Narkis and porosity constants resulted from the increase of strength due to filler addition. This indicates that the fillers developed good interface adhesion in the composites. This is obviously not in agreement with the concept behind both Nicolais-Narkis and porosity theories, where there is no load transfer to the filler and hence load is always carried by the matrix.

It can be seen that values of \( B \) derived for tensile strength are similar to those obtained for flexural strength. The \( B \) value for tensile strength of talc filled composites is similar to that estimated by Turcsanyi et al. (1988) for talc-HDPE composites (i.e. 3.93) and Zhou et al. (2004) for talc filled polyester amide. The \( B \) values demonstrate that talc exhibits the strongest interaction or adhesion with the polymers in the matrix; gypsum exhibits the weakest interaction, and wollastonite falls in between. These findings are consistent with the behaviour described above for the mechanical properties.
### Table 4-2: Constant values of the predictive models (Tensile Strength)

<table>
<thead>
<tr>
<th>Filler</th>
<th>$B$ (Turcsanyi)</th>
<th>$\Delta R^*$ (%)</th>
<th>$a$ (Nicolais-Narkis)</th>
<th>$\Delta R^*$ (%)</th>
<th>$k$ (Porosity)</th>
<th>$\Delta R^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>3.01</td>
<td>5.96</td>
<td>-0.07</td>
<td>4.88</td>
<td>-0.13</td>
<td>4.97</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>3.38</td>
<td>6.78</td>
<td>-0.20</td>
<td>5.04</td>
<td>-0.28</td>
<td>5.55</td>
</tr>
<tr>
<td>Talc</td>
<td>4.01</td>
<td>5.50</td>
<td>-0.62</td>
<td>2.20</td>
<td>-0.96</td>
<td>4.37</td>
</tr>
</tbody>
</table>

*Mean value of relative differences between experimental and computed tensile/flexural strength of composites

### Table 4-3: Constant values of the predictive models (Flexural Strength)

<table>
<thead>
<tr>
<th>Filler</th>
<th>$B$ (Turcsanyi)</th>
<th>$\Delta R^*$ (%)</th>
<th>$a$ (Nicolais-Narkis)</th>
<th>$\Delta R^*$ (%)</th>
<th>$k$ (Porosity)</th>
<th>$\Delta R^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>3.58</td>
<td>1.19</td>
<td>-0.29</td>
<td>3.26</td>
<td>-0.47</td>
<td>2.25</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>3.66</td>
<td>1.89</td>
<td>-0.37</td>
<td>1.53</td>
<td>-0.56</td>
<td>1.52</td>
</tr>
<tr>
<td>Talc</td>
<td>4.37</td>
<td>3.18</td>
<td>-0.82</td>
<td>3.57</td>
<td>-1.23</td>
<td>2.52</td>
</tr>
</tbody>
</table>

*Mean value of relative differences between experimental and computed tensile/flexural strength of composites

The relative tensile strength and flexural strength are plotted against volume concentration of the fillers in Figure 4-15 and Figure 4-16, respectively. Overall, good correlations from the models can be drawn for both properties.

It can be observed from Figure 4-15 that the tensile strength data of the composites with talc and wollastonite deviate slightly from the linear correlations, especially at low filler concentrations. This might have been caused by the filler particles exhibiting different interaction pattern with different types of polymers. The flexural strength, however, relates very well to filler concentration (Figure 4-16), which is reflected in the smaller errors shown in Table 4-3.
Figure 4-15: Relative tensile strength of the composites blended with (a) talc, (b) wollastonite and (c) gypsum as a function of filler volume fraction. (Lines are drawn using corresponding equations)
Figure 4-16: Relative flexural strength of the composites blended with (a) talc, (b) wollastonite and (c) wollastonite as a function of filler volume fraction. (Lines are drawn using corresponding equations)
4.4.2 Tensile and Flexural Moduli

Figure 4-17 shows the relative tensile modulus (i.e. the ratio between the tensile modulus and the polymer tensile modulus) from the experimental results and that predicted by the Einstein, Guth and Smallwood and Kerner models. Figure 4-18 shows the same comparison for the relative flexural modulus.

The experimental data deviate markedly from the Guth-Smallwood and Kerner equations, while the Einstein equation gives the best fit for all fillers. Although the Einstein equation is considered to apply to composites having low concentrations of particulate fillers, the model gave good correlations over the entire range of volume fractions considered in this study.
Figure 4-17: Relative tensile modulus of composites with: (a) talc; (b) wollastonite; (c) gypsum fillers as a function of filler volume percentage, compared to the Einstein, Kerner and Guth-Smallwood models.
Figure 4-18: Relative flexural modulus of composites with: (a) talc; (b) wollastonite; (c) gypsum fillers as a function of filler volume percentage, compared to the Einstein, Kerner and Guth-Smallwood models
Table 4-4 shows values for the adhesion constant $a$ in the Einstein model applied to composites with mineral fillers. Again, talc exhibits the strongest interface adhesion compared to the other mineral fillers studied here. In addition, the values of $a$ are higher for the tensile modulus than for the flexural modulus. In flexure testing, the stress is sustained by the underside surface of the moulded specimens and surfaces normally contain less filler than the interior. This may have caused the flexural modulus to be lower than the tensile modulus, and hence, values for adhesion constants are lower.

Table 4-4: Constant a values of the Einstein model for the mineral fillers

<table>
<thead>
<tr>
<th>Filler</th>
<th>$a$ (Tensile modulus)</th>
<th>ΔR* (%)</th>
<th>$a$ (Flexural modulus)</th>
<th>ΔR* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>2.61</td>
<td>1.03</td>
<td>0.84</td>
<td>2.79</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>4.12</td>
<td>3.68</td>
<td>1.07</td>
<td>3.93</td>
</tr>
<tr>
<td>Talc</td>
<td>6.43</td>
<td>0.96</td>
<td>1.97</td>
<td>5.34</td>
</tr>
</tbody>
</table>

*Mean value of relative differences between experimental and computed tensile/flexural strength of composites
4.5 Effect of Silane Coupling Agents

The preceding results show that the inclusion of talc or wollastonite filler led to considerable improvements in tensile and flexural properties. Therefore, the study of coupling agents then focused on talc and wollastonite recycled-plastic composites. Small quantities of the silanes (0.01, 0.03 and 0.03 of filler volume) were added to 0.13 v/v talc and 0.12 v/v wollastonite composites.

4.5.1 Effect of silane treatment on mechanical properties

The effect of silane coupling agents on tensile and flexure properties of the blends of 0.13 v/v talc is given in Table 4-5. Different types and contents of silane coupling agents slightly improved (less than 10 %) the tensile properties over the untreated blend. Furthermore, both silane coupling agents appear to have no effect on the flexural properties of the talc blends (Table 4-5). Therefore, the optimum additions considering the largest increase in tensile properties for \( \gamma \)-MPS and \( \gamma \)-APS were found to be at 0.01 and 0.03 v/v, respectively.

Tensile and flexural properties of silane-treated wollastonite samples are given in Table 4-6. The tensile behaviour of the wollastonite blends improves with the addition of both silanes. The additions of \( \gamma \)-MPS and \( \gamma \)-APS at 0.03 v/v show optimum tensile properties. In general, \( \gamma \)-APS gives slightly better tensile strength and modulus than \( \gamma \)-MPS, although the differences are only around 5%. As found in the case of the silane treated talc composite, the flexural properties of the wollastonite blends were not affected by the silane coupling agents.
Table 4-5: Effect of silane coupling agent on tensile and flexure properties of 0.13 v/v talc blends

<table>
<thead>
<tr>
<th>Silane type and content*</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Flexure strength (MPa)</th>
<th>Flexure modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no silane</td>
<td>15.9</td>
<td>925.9</td>
<td>18.9</td>
<td>533.4</td>
</tr>
<tr>
<td>0.01-M</td>
<td>17.4</td>
<td>964.4</td>
<td>19.9</td>
<td>562.9</td>
</tr>
<tr>
<td>0.03-M</td>
<td>16.4</td>
<td>959.3</td>
<td>18.7</td>
<td>552.3</td>
</tr>
<tr>
<td>0.05-M</td>
<td>16.8</td>
<td>1009.3</td>
<td>19.3</td>
<td>561.7</td>
</tr>
<tr>
<td>0.01-A</td>
<td>16.8</td>
<td>890.1</td>
<td>18.3</td>
<td>541.4</td>
</tr>
<tr>
<td>0.03-A</td>
<td>17.8</td>
<td>1030.4</td>
<td>18.2</td>
<td>542.0</td>
</tr>
<tr>
<td>0.05-A</td>
<td>17.9</td>
<td>1049.1</td>
<td>17.6</td>
<td>530.3</td>
</tr>
</tbody>
</table>

* The figures 0.01, 0.03 and 0.05 indicate the additions of 0.01, 0.03 and 0.05 v/v of silane, respectively; while the alphabet character M and A denote γ-MPS and γ-APS, respectively.

Table 4-6: Effect of silane coupling agent on tensile and flexure properties of 0.12 v/v wollastonite blends

<table>
<thead>
<tr>
<th>Silane type and content*</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Flexure strength (MPa)</th>
<th>Flexure modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no silane</td>
<td>14.8</td>
<td>794.9</td>
<td>17.2</td>
<td>514.6</td>
</tr>
<tr>
<td>0.01-M</td>
<td>16.4</td>
<td>884.0</td>
<td>14.5</td>
<td>487.6</td>
</tr>
<tr>
<td>0.03-M</td>
<td>16.7</td>
<td>935.5</td>
<td>15.5</td>
<td>520.5</td>
</tr>
<tr>
<td>0.05-M</td>
<td>15.8</td>
<td>837.1</td>
<td>17.5</td>
<td>550.6</td>
</tr>
<tr>
<td>0.01-A</td>
<td>17.0</td>
<td>917.4</td>
<td>17.0</td>
<td>524.4</td>
</tr>
<tr>
<td>0.03-A</td>
<td>17.4</td>
<td>972.4</td>
<td>16.3</td>
<td>496.0</td>
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<tr>
<td>0.05-A</td>
<td>17.5</td>
<td>949.8</td>
<td>17.2</td>
<td>518.9</td>
</tr>
</tbody>
</table>

* The figures 0.01, 0.03 and 0.05 indicate the additions of 0.01, 0.03 and 0.05 v/v of silane, respectively; while the alphabet character M and A denote γ-MPS and γ-APS, respectively.
4.5.2 **Morphology Observation**

To improve the mechanical properties of a polymer, the filler needs to be “active” or to be able to engage autonomously with the polymer host (Lipatov, 1995). Where the filler is not readily active in a matrix of polymer or weak interface adhesion is present, chemical bonding needs to be established between those two phases (Bliznakov et al., 2000). This can be achieved through the addition of coupling agents (Plueddemann, 1991).

Some degree of improvement in the tensile properties found in the $\gamma$-APS treated talc composites might be explained by SEM observations on the sections near the fracture surface of the tensile-tested specimens (Figure 4-19 (a)). The SEM image shows that the talc particles seem to be covered by the matrix, indicating that interface bonding between the two phases is sufficient. This could be the contributing factor in the large improvement of the 0.03 v/v $\gamma$-APS talc blend.

The blends prepared with $\gamma$-MPS did not result in as high an increase in tensile behaviour as those treated with $\gamma$-APS. This might be explained by a SEM analysis of the talc blend prepared with 0.03 v/v $\gamma$-MPS as shown in Figure 4-19 (b). It is apparent that the voids in the vicinity of the talc particles are generally larger in scale and more widespread in the matrix than that found in the $\gamma$-APS blends.

In the case of the blends containing silane treated wollastonite, which can be seen in Figure 4-20, the wollastonite particles seem to bond better with the matrix, compared to the unmodified wollastonite mix. As found in the modified talc blends, the $\gamma$-APS blends (Figure 4-20 (a)) appear to have less micro-voids in comparison to the blends containing $\gamma$-MPS (Figure 4-20 (b)). This may have caused the $\gamma$-APS blends to have slightly higher tensile properties than the $\gamma$-MPS blends.
Figure 4-19: SEM images of talc composites blended with: 0.03 v/v γ-APS (a) and 0.03 v/v γ-MPS (b)

Figure 4-20: SEM images of wollastonite composites blended with: 0.03 v/v γ-APS (a) and 0.03 v/v γ-MPS (b)
4.6 Effect of Extrusion Conditions

As discussed in Section 2.4, the mechanical properties of extruded polymer composites can be affected by fluctuation of temperature, pressure or flow rate of the extrusion. The shear effects created by variations in melt temperature and screw rotation contribute to the extent of filler dispersion in the polymer matrix. The influences of these variables are now discussed.

4.6.1 Mechanical Properties

The tensile and flexural properties of the HDPE composites are presented in Table 4-7 and Table 4-8, respectively. The effect of the extrusion conditions as well as CaCO₃ content on the mechanical properties was modelled using ANOVA method and is discussed in the following section.
Table 4-7  Tensile properties of HDPE composites at various processing conditions and filler contents

<table>
<thead>
<tr>
<th>Mix</th>
<th>CaCO$_3$ content (% weight)</th>
<th>Screw rotation (RPM)</th>
<th>Barrel temperature ($^\circ$C)</th>
<th>Tensile strength (MPa)</th>
<th>Standard deviation (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Standard deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>20</td>
<td>70</td>
<td>185</td>
<td>31.52</td>
<td>1.76</td>
<td>1236.80</td>
<td>76.95</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>70</td>
<td>195</td>
<td>33.43</td>
<td>1.67</td>
<td>1273.40</td>
<td>82.99</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>80</td>
<td>185</td>
<td>31.68</td>
<td>2.03</td>
<td>1319.80</td>
<td>36.35</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>80</td>
<td>205</td>
<td>31.43</td>
<td>1.02</td>
<td>1206.80</td>
<td>82.95</td>
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<tr>
<td>3</td>
<td>20</td>
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<td>195</td>
<td>33.37</td>
<td>0.51</td>
<td>1260.00</td>
<td>59.54</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>70</td>
<td>195</td>
<td>32.58</td>
<td>1.53</td>
<td>1469.50</td>
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<td>11</td>
<td>30</td>
<td>70</td>
<td>205</td>
<td>35.26</td>
<td>2.38</td>
<td>1466.60</td>
<td>78.25</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>80</td>
<td>195</td>
<td>33.23</td>
<td>1.20</td>
<td>1493.60</td>
<td>72.37</td>
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<td>14</td>
<td>30</td>
<td>80</td>
<td>195</td>
<td>32.00</td>
<td>1.15</td>
<td>1423.40</td>
<td>76.04</td>
</tr>
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<td>15</td>
<td>30</td>
<td>80</td>
<td>195</td>
<td>34.62</td>
<td>0.79</td>
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<td>63.93</td>
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<td>10</td>
<td>30</td>
<td>90</td>
<td>185</td>
<td>33.03</td>
<td>0.38</td>
<td>1483.20</td>
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<td>9</td>
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<td>90</td>
<td>205</td>
<td>35.84</td>
<td>0.96</td>
<td>1516.50</td>
<td>83.84</td>
</tr>
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</tr>
<tr>
<td>18</td>
<td>40</td>
<td>70</td>
<td>185</td>
<td>33.00</td>
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<td>0.47</td>
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Table 4-8 Flexural properties of HDPE composites at various processing conditions and filler contents

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<td>1.29</td>
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<td>38.51</td>
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</table>
4.6.2 **Statistical Analysis**

To analyse the effects of extruder parameters on mechanical properties of the HDPE composites, a statistical approach called the *Box Behnken* method was used (Montgomery, 2005). The method is basically an orthogonal, rotatable response surface design, as shown below.

\[
Y = d_0 + d_1X_1 + d_2X_2 + d_3X_3 + d_{11}X_1^2 + d_{22}X_2^2 + d_{33}X_3^2 + d_{12}X_1X_2 + d_{13}X_1X_3 + d_{23}X_2X_3
\] (3-6)

An *F*-test and significance of probability (*p*-value) were calculated to evaluate the significance of the independent variables/factors (\(X_1, 2, ..., n\) the extrusion variables) on the dependent variables (\(Y\) or a mechanical property). The significance level (\(\alpha\)) was taken as 0.05, meaning for a factor to be considered to have significant influence, its *p*-value should be less than 0.05.

Table 4-9 shows the significance probability, *p*-value for each dependent variable. An independent variable/factor has a significant impact whenever its *p*-value is less than 0.05. The only property not relevant to the processing variables is tensile strength (\(Y_1\)) as none of the corresponding *p*-values of the equation terms is less than 0.05. The other properties (tensile modulus, flexural strength and modulus) were found to be linearly dependent of CaCO\(_3\) content. Screw rotation and barrel temperature did not have a significant effect on the mechanical properties of HDPE-CaCO\(_3\) composites over the ranges of the variable levels (i.e. none of the *p* values higher than 0.05 were found in the linear, quadratic and interaction terms of the equation – Montgomery, 2005).
Table 4-9: Significance probability (p-values) for dependent variables: Y1: Tensile strength; Y2: Tensile modulus; Y3: Flexural strength; Y4: Flexural modulus

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<tr>
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<th>p-value</th>
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<td>Y1</td>
<td>Y2</td>
<td>Y3</td>
<td>Y4</td>
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<tr>
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<tr>
<td>X₁ X₃</td>
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<td>X₂ X₃</td>
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4.6.3 Morphology Observation

Figure 4-21 shows the SEM micrographs of the HDPE-CaCO₃ composites at 30 wt% of CaCO₃ compounded at different screw rotations and barrel temperatures. It is shown in Figure 4-21 (a), (b), (c) and (d) that the dispersion of the CaCO₃ particles is uniform in the polymer matrix albeit Figure 4-21(b) shows signs of detachment of CaCO₃ particles off the matrix. The similarity of the extent of filler dispersion in each process scenario is in agreement with the statistical analysis above.
Figure 4-21: SEM micrographs of HDPE-CaCO₃ composites extruded at: (a) 90 RPM and 205 °C; (b) 90 RPM and 185 °C; (c) 70 RPM and 205 °C; (d) 80 RPM and 195 °C
5 Conclusions

This research aimed to address three main areas in relation to the improvement of the mechanical properties of commingled recycled plastic composites. The first phase of the research focused on the effectiveness of a range of mineral fillers to improve the mechanical properties of the composites. It was confirmed that the addition of talc as filler resulted in the largest improvement in mechanical properties (tensile and flexural) compared to wollastonite and gypsum. Filler dispersion and adhesion was the main factor contributing to the observed trends. It was from the blend morphology, that the agglomeration of gypsum particles interrupted the adhesion of the plastic matrix and hence reduced the tensile strength. Furthermore, the interface adhesion for talc particles was better than wollastonite, as indicated by the lower formation of voids. Therefore it is recommended that talc is used as filler reinforcement for recycled plastic composites.

Particle size had little impact on the mechanical properties of recycled plastic. In CaCO₃ filled composites, this applied to the mean size (d₅₀) less than 25μm. Large particles (d₅₀ equal to or larger than 25 μm) tend to detach from the polymer matrix and resulted in a reduction in the tensile and flexural properties.

Established mathematical models, the Turcsanyi and Nicolais-Narkis equations satisfactorily predicted tensile or flexural strength of commingled plastic composites while the Einstein equation was shown correlating well with the tensile or flexural modulus.

To improve the attractive bonding of filler and polymers, a second phase of the research investigated the use of silane coupling agents to improve the bonding. Silane coupling agents have little effect on improving the mechanical properties of commingled recycled plastic composites. The addition of γ-APS coupling agent results in more improvement in mechanical properties than that occurring from γ-MPS. SEM observation showed that fillers treated with γ-APS are better bonded and do not develop as many voids compared to γ-MPS, which led to the improvement in mechanical properties.

The last phase of the research was performed to investigate whether processing variables have an impact on the mechanical properties of recycled plastic composites. The mechanical properties of the recycled plastic composites were statistically analysed using the Box-
Behnken method as a function of filler content and extrusion parameters. It was found that screw rotation and melt (barrel) temperature did not have a significant effect on the tensile and flexural properties of filler-recycled plastic composites.
6 Recommendation

This study has produced some significant findings that will help further development of recycling practices of post-consumer plastic materials. Some recommendations that can be considered in the commercial manufacture and/or for future research are as follows:

- Raw material “contamination” was the major issue when manufacturing the commingled recycled plastic samples. Fractions of foamed polystyrene and non-polyolefin resins with higher melting temperature, could contribute to imperfections in the matrix body. It is recommended to limit the commingled composition to polyolefin resins. A means of resin separation (e.g. floatation or hydrocyclones) may be required although sorting at the material collection stage may be preferable.

- Compatibility of polymer resins was not considered in this study. This study was the first stage of a program of research looking at various variables and the use of a compatibiliser in commingled resins would be considered in the following stages of this research. Although there appeared to be homogenous mixing of the polymer components, it would be worthwhile to investigate improving inter-polymer bonding in the matrix by means of compatibilising agents.

- The combination of glass fibre and mineral fillers as reinforcement could be a likely way forward in the commercial development of recycled plastic composites. This type of reinforcement could achieve further improvement in the engineering properties of the composite plastic hence creating more opportunities in load-bearing applications. Future research should be carried out to determine the optimum process variables for the blend.
Nomenclatures

Alphabets

\( a \)  Constant representing interfacial adhesion for Einstein and Nicolais Narkis models

\( A \)  Constant accounted for packing factor (in Turcsanyi model)

\( b \)  Particle shape constant for Einstein model

\( B \)  Constant representing interfacial adhesion (in Turcsanyi model)

\( E_p \)  tensile or flexural modulus of polymer matrix

\( E_c \)  tensile or flexural modulus of polymer composite

\( k \)  Constant related to degree of adhesion of filler and polymer (in porosity model)

\( P \)  Degree of porosity in polymer matrix (in porosity model)

\( W_f \)  Weight percentage of filler

Greek symbols

\( \sigma_p \)  tensile or flexural strength of polymer matrix

\( \sigma_c \)  tensile or flexural) strength of polymer composite

\( \phi_f \)  Volume fraction of filler

\( \tau_p \)  Poisson’s ratio of polymer matrix (in Kerner’s equation)
References


Chemexper available on http://www.chemexper.com/chemicals/supplier/cas/2530-85-0.html accessed on 26th May 2009


Appendix A: Data Calculation from Engineering Stress-Strain Charts

This appendix provides some details to calculate tensile/flexural strength or modulus. From each run of tensile or flexural test, an engineering stress-strain chart was obtained, as shown in Figure A-1. Tensile or flexural strength ($\sigma_c$) was derived at the maximum stress endured by the specimen during the test (point b). Tensile or flexural modulus was determined from the slope of $\alpha$ which is drawn at 1 % strain. The modulus or the slope $\alpha$ is calculated as follows:

$$E = \frac{(a - 0)}{(1\% - 0)} = \frac{a}{1\%}$$  \hspace{1cm} (A-1)

![Engineering Stress-strain chart](image)

Figure A.1: Engineering Stress-strain chart

The engineering stress-strain chart was constructed from load-displacement data recorded from each tensile or flexural test. Load and displacement data can be converted to engineering stress and strain using the following calculations.

A.1 Tensile properties

When an axial load $F$ is applied to a specimen, the original gauge length $L_0$ will elongate into a new length $L$. The engineering strain is calculated by dividing the change in the specimen’s gauge length or displacement, $\delta$, by the specimen’s original gauge length $L_0$, as shown in
Equation A.1. Here the strain is assumed to be constant throughout the region between the gauge points.

$$\varepsilon = \frac{\delta}{L_0} = \frac{(L - L_0)}{L_0}$$ \hspace{1cm} (A-2)

The engineering stress, $\sigma$, is calculated by dividing the applied load $F$ by the specimen’s original cross-sectional area $A_o$. This calculation (Equation A-2) assumes that the stress is constant over the cross section and throughout the area between the gauge points.

$$\sigma = \frac{F}{A_o}$$ \hspace{1cm} (A-3)

A.2 Flexural properties

In a three-point bending test, load $F$ is introduced in the centre of support span’s length $S$ of a specimen having a rectangular cross section, with depth $d$ and width $b$. A setup of the test is illustrated in Figure A.2.

![Figure A.2: Three-point bending test](image)

The resultant engineering stress $\sigma$ is calculated as follows:

$$\sigma = \frac{3 F S}{2 b d^2}$$ \hspace{1cm} (A-4)

The engineering strain is calculated using the following equation:

$$\varepsilon = \frac{6 \delta d}{S^2}$$ \hspace{1cm} (A-5)
For cylindrical specimens with a span length $S$ and diameter $D$, the engineering stress is calculated as

$$\sigma = \frac{8 F S}{\pi d^3} \quad (A-6)$$

The engineering strain is calculated using the following equations:

$$\varepsilon = \frac{6 \delta D}{S^2} \quad (A-7)$$
## Appendix B: Mechanical Properties Data of Recycled Plastic Composites Blends

Table B.1: Tensile and Flexural Properties of Recycled Plastic Blends with Different Filler Additions

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<tr>
<th>Composite</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
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<td>13.77 (0.54)</td>
<td>480.67 (13.63)</td>
<td>15.30 (0.55)</td>
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<td>BP + 0.08 v/v Gc</td>
<td>13.56 (0.34)</td>
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<td>BP + 0.12 v/v G</td>
<td>14.27 (0.29)</td>
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<td>16.14 (0.30)</td>
<td>489.56 (13.01)</td>
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<td>17.93 (0.37)</td>
<td>570.23 (14.01)</td>
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<td>BP + 0.07 v/v Wd</td>
<td>15.55 (0.54)</td>
<td>722.11 (50.18)</td>
<td>15.89 (0.72)</td>
<td>515.39 (18.31)</td>
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<td>519.74 (21.67)</td>
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<td>1805.07 (37.39)</td>
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<table>
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<tr>
<th>Composite</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
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<td>455.89 (12.83)</td>
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<td>672.82 (25.85)</td>
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<td>BP + 0.07 v/v Wd</td>
<td>15.55 (0.54)</td>
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<td>14.76 (0.51)</td>
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<td>17.15 (0.57)</td>
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<td>BP + 0.18 v/v W</td>
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<td>912.45 (34.67)</td>
<td>18.04 (0.78)</td>
<td>587.40 (14.67)</td>
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<td>BP + 0.08 v/v Te</td>
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<td>15.94 (0.11)</td>
<td>925.89 (16.44)</td>
<td>18.86 (0.20)</td>
<td>533.39 (12.41)</td>
</tr>
<tr>
<td>BP + 0.19 v/v T</td>
<td>16.35 (0.47)</td>
<td>1055.52 (23.18)</td>
<td>18.53 (0.48)</td>
<td>558.62 (6.97)</td>
</tr>
<tr>
<td>BP + 0.26 v/v T</td>
<td>16.44 (0.76)</td>
<td>1240.29 (28.06)</td>
<td>21.23 (0.31)</td>
<td>754.22 (23.84)</td>
</tr>
<tr>
<td>BP + 0.08 v/v GFf</td>
<td>16.08 (0.27)</td>
<td>1430.84 (33.62)</td>
<td>15.94 (0.57)</td>
<td>583.66 (22.25)</td>
</tr>
<tr>
<td>BP + 0.13 v/v GFf</td>
<td>16.94 (1.23)</td>
<td>1685.63 (59.97)</td>
<td>17.58 (0.33)</td>
<td>768.58 (34.51)</td>
</tr>
<tr>
<td>BP + 0.19 v/v GFf</td>
<td>17.85 (0.36)</td>
<td>1784.95 (36.34)</td>
<td>19.22 (0.21)</td>
<td>1064.36 (23.00)</td>
</tr>
<tr>
<td>BP + 0.26 v/v GFf</td>
<td>18.08 (0.61)</td>
<td>1805.07 (37.39)</td>
<td>20.26 (0.24)</td>
<td>1308.43 (47.07)</td>
</tr>
</tbody>
</table>

---

- **a** The standard deviation of each data set is shown in parentheses.
- **b** BP indicates the base plastic obtained from APR; **c** G indicates the anhydride gypsum; **d** W indicates wollastonite; **e** T indicates talc; **f** GF indicates glass fibre.
Appendix C: Data Fitting of Tensile and Flexural Test Data

This appendix presents the sample calculation of the section 4.4 of this thesis. As an example, the following calculation steps the tensile strength data of talc filled samples are shown:

- Density of water at 25°C = 998.23 kg/m³
- Density of talc = 2.76 * 998.23 kg/m³ = 2755.11 kg/m³
- Density of the base plastic (determined by ASTM D792) = 950 kg/m³
- For 20 wt% talc, the volume fraction is:

\[
\phi_f = \frac{20}{\frac{2755.11}{20} + \frac{80}{950}} = 0.08
\]

- Rearrangement of Nicolais-Narkis equation gives:

\[
\frac{\sigma_c - \sigma_p}{\sigma_p} = -a \phi_f^{2/3}
\]

- calculate and \( \phi_f^{2/3} \) from variables of each \( \phi_f \) data
- determine the slope of the equation, \( a \) value, from pairs of \( \frac{\sigma_p - \sigma_c}{\sigma_p} \) and \( \phi_f^{2/3} \)
- the following table is obtained for talc filled samples:

<table>
<thead>
<tr>
<th>( \phi_w )</th>
<th>( \phi_f )</th>
<th>( \sigma_c )</th>
<th>( \phi_f^{2/3} )</th>
<th>( \frac{\sigma_p - \sigma_c}{\sigma_p} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.08</td>
<td>15.65</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>0.30</td>
<td>0.13</td>
<td>15.94</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>0.40</td>
<td>0.19</td>
<td>16.35</td>
<td>0.33</td>
<td>0.21</td>
</tr>
<tr>
<td>0.50</td>
<td>0.26</td>
<td>16.44</td>
<td>0.40</td>
<td>0.22</td>
</tr>
</tbody>
</table>
From linear regression, the slope of equation or \( a \) value of Equation B-1 is found to be -0.62. By using \( a \), the theoretical or calculated \( \sigma_c \) values can be computed for each volume percentage.

The error arising from data fitting (\%R) can be calculated as:

\[
\% R = \left| \frac{\text{Theoretical } \sigma_c - \text{Experimental } \sigma_c}{\text{Experimental } \sigma_c} \right| \times 100 \%
\]  

(C-2)

The total error for each set of the property data is obtained from the average of the individual \%R. The summary of the experimental, theoretical and \%R figures is given in Table C.2.

Table C.2: Experimental and Theoretical Tensile Strength

<table>
<thead>
<tr>
<th>( \phi_w )</th>
<th>( \phi_f )</th>
<th>( \sigma_c ) Experimental</th>
<th>( \sigma_c ) Theoretical</th>
<th>% R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.08</td>
<td>15.65</td>
<td>15.08</td>
<td>3.78</td>
</tr>
<tr>
<td>0.30</td>
<td>0.13</td>
<td>15.94</td>
<td>15.67</td>
<td>1.71</td>
</tr>
<tr>
<td>0.40</td>
<td>0.19</td>
<td>16.35</td>
<td>16.28</td>
<td>0.43</td>
</tr>
<tr>
<td>0.50</td>
<td>0.26</td>
<td>16.44</td>
<td>16.93</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average %R</td>
<td>2.20</td>
</tr>
</tbody>
</table>
Appendix D: Results of ANOVA Calculation

Table D.1: ANOVA Table for Tensile Strength (X₁)

<table>
<thead>
<tr>
<th>Factor</th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>F₀</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ content (X₁)</td>
<td>5.74605</td>
<td>1</td>
<td>5.746050</td>
<td>1.868301</td>
<td>0.229921</td>
</tr>
<tr>
<td>Screw rotation (X₂)</td>
<td>0.60688</td>
<td>1</td>
<td>0.606878</td>
<td>0.197323</td>
<td>0.675457</td>
</tr>
<tr>
<td>Barrel temperature (X₃)</td>
<td>0.38281</td>
<td>1</td>
<td>0.382813</td>
<td>0.124470</td>
<td>0.738622</td>
</tr>
<tr>
<td>X₁²</td>
<td>2.37540</td>
<td>1</td>
<td>2.375401</td>
<td>0.772350</td>
<td>0.419714</td>
</tr>
<tr>
<td>X₂²</td>
<td>0.67861</td>
<td>1</td>
<td>0.678612</td>
<td>0.220648</td>
<td>0.658320</td>
</tr>
<tr>
<td>X₃²</td>
<td>0.03131</td>
<td>1</td>
<td>0.031308</td>
<td>0.010180</td>
<td>0.923555</td>
</tr>
<tr>
<td>X₁ X₂</td>
<td>0.17640</td>
<td>1</td>
<td>0.176400</td>
<td>0.057356</td>
<td>0.820233</td>
</tr>
<tr>
<td>X₁ X₃</td>
<td>1.76890</td>
<td>1</td>
<td>1.768900</td>
<td>0.575149</td>
<td>0.482416</td>
</tr>
<tr>
<td>X₂ X₃</td>
<td>0.00423</td>
<td>1</td>
<td>0.004225</td>
<td>0.001374</td>
<td>0.971868</td>
</tr>
<tr>
<td>Error</td>
<td>15.37774</td>
<td>5</td>
<td>3.075548</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SS</td>
<td>27.33576</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* SS is the sum of squares of the factor; DF is the degree of freedom of the factor; \( MS = \frac{SS}{DF} \) is the mean square of the factor; the \( F₀ \) of a factor is given by \( \frac{MS}{MS_{error}} \); \( p \) is the significance probability.

b \( SS_{error} = Total \ SS - \sum SS_{factor} \)
Table D.2: ANOVA Table for Tensile Modulus ($X_2$)

<table>
<thead>
<tr>
<th>Factor</th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>$F_o$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ content ($X_1$)</td>
<td>401726.1</td>
<td>1</td>
<td>401726.1</td>
<td>363.4909</td>
<td>0.000007</td>
</tr>
<tr>
<td>Screw rotation ($X_2$)</td>
<td>2410.9</td>
<td>1</td>
<td>2410.9</td>
<td>2.1814</td>
<td>0.199722</td>
</tr>
<tr>
<td>Barrel temperature ($X_3$)</td>
<td>54.5</td>
<td>1</td>
<td>54.5</td>
<td>0.0494</td>
<td>0.832975</td>
</tr>
<tr>
<td>$X_1^2$</td>
<td>115.7</td>
<td>1</td>
<td>115.7</td>
<td>0.1047</td>
<td>0.759399</td>
</tr>
<tr>
<td>$X_2^2$</td>
<td>1885.0</td>
<td>1</td>
<td>1885.0</td>
<td>1.7056</td>
<td>0.248413</td>
</tr>
<tr>
<td>$X_3^2$</td>
<td>1687.8</td>
<td>1</td>
<td>1687.8</td>
<td>1.5272</td>
<td>0.271425</td>
</tr>
<tr>
<td>$X_1 X_2$</td>
<td>14.1</td>
<td>1</td>
<td>14.1</td>
<td>0.0128</td>
<td>0.914464</td>
</tr>
<tr>
<td>$X_1 X_3$</td>
<td>3770.0</td>
<td>1</td>
<td>3770.0</td>
<td>3.4111</td>
<td>0.124038</td>
</tr>
<tr>
<td>$X_2 X_3$</td>
<td>47.6</td>
<td>1</td>
<td>47.6</td>
<td>0.0431</td>
<td>0.843766</td>
</tr>
<tr>
<td>Error</td>
<td>5525.9</td>
<td>5</td>
<td>1105.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SS</td>
<td>417133.2</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.3: ANOVA Table for Flexural Strength ($X_3$)

<table>
<thead>
<tr>
<th>Factor</th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>$F_o$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ content ($X_1$)</td>
<td>57.65283</td>
<td>1</td>
<td>57.65283</td>
<td>78.32673</td>
<td>0.000306</td>
</tr>
<tr>
<td>Screw rotation ($X_2$)</td>
<td>1.57464</td>
<td>1</td>
<td>1.57464</td>
<td>2.13929</td>
<td>0.203428</td>
</tr>
<tr>
<td>Barrel temperature ($X_3$)</td>
<td>0.75331</td>
<td>1</td>
<td>0.75331</td>
<td>1.02345</td>
<td>0.358127</td>
</tr>
<tr>
<td>$X_1^2$</td>
<td>1.13282</td>
<td>1</td>
<td>1.13282</td>
<td>1.53904</td>
<td>0.269797</td>
</tr>
<tr>
<td>$X_2^2$</td>
<td>4.41874</td>
<td>1</td>
<td>4.41874</td>
<td>6.00327</td>
<td>0.057925</td>
</tr>
<tr>
<td>$X_3^2$</td>
<td>1.10846</td>
<td>1</td>
<td>1.10846</td>
<td>1.50594</td>
<td>0.274383</td>
</tr>
<tr>
<td>$X_1 X_2$</td>
<td>1.72243</td>
<td>1</td>
<td>1.72243</td>
<td>2.34007</td>
<td>0.186635</td>
</tr>
<tr>
<td>$X_1 X_3$</td>
<td>3.88441</td>
<td>1</td>
<td>3.88441</td>
<td>5.27733</td>
<td>0.070013</td>
</tr>
<tr>
<td>$X_2 X_3$</td>
<td>0.09286</td>
<td>1</td>
<td>0.09286</td>
<td>0.12616</td>
<td>0.736942</td>
</tr>
<tr>
<td>Error</td>
<td>3.68028</td>
<td>5</td>
<td>0.73606</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SS</td>
<td>75.46950</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table D.4: ANOVA Table for Flexural Modulus ($X_4$)

<table>
<thead>
<tr>
<th>Factor</th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>$F_o$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ content ($X_1$)</td>
<td>154896.2</td>
<td>1</td>
<td>154896.2</td>
<td>57.89592</td>
<td>0.000623</td>
</tr>
<tr>
<td>Screw rotation ($X_2$)</td>
<td>41.8</td>
<td>1</td>
<td>41.8</td>
<td>0.01562</td>
<td>0.905411</td>
</tr>
<tr>
<td>Barrel temperature ($X_3$)</td>
<td>0.0</td>
<td>1</td>
<td>0.0</td>
<td>0.00000</td>
<td>0.999832</td>
</tr>
<tr>
<td>$X_1^2$</td>
<td>1657.5</td>
<td>1</td>
<td>1657.5</td>
<td>0.61953</td>
<td>0.466873</td>
</tr>
<tr>
<td>$X_2^2$</td>
<td>3734.0</td>
<td>1</td>
<td>3734.0</td>
<td>1.39567</td>
<td>0.290575</td>
</tr>
<tr>
<td>$X_3^2$</td>
<td>1235.5</td>
<td>1</td>
<td>1235.5</td>
<td>0.46181</td>
<td>0.526961</td>
</tr>
<tr>
<td>$X_1 X_2$</td>
<td>1534.8</td>
<td>1</td>
<td>1534.8</td>
<td>0.57368</td>
<td>0.482947</td>
</tr>
<tr>
<td>$X_1 X_3$</td>
<td>3876.7</td>
<td>1</td>
<td>3876.7</td>
<td>1.44900</td>
<td>0.282564</td>
</tr>
<tr>
<td>$X_2 X_3$</td>
<td>662.1</td>
<td>1</td>
<td>662.1</td>
<td>0.24746</td>
<td>0.639967</td>
</tr>
<tr>
<td>Error</td>
<td>13377.1</td>
<td>5</td>
<td>2675.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total SS</td>
<td>182554.6</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix E: Publications

The publications from this research are attached in the following order at the end of the thesis.

**Journal paper:**

**Conference papers:**
Ngothai, Y., Putra H., Ozbakkaloglu, T., Seracino, R., (2009), Effect of CaCO$_3$ Size on the Mechanical Properties of Recycled HDPE, 8th World Congress Chemical Engineering, Montreal, Canada, 23-27 August (accepted).

*Journal of Applied Polymer Science, v. 112 (6), pp. 3470-3481, June 2009*

**NOTE:** This publication is included in the print copy of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:

http://dx.doi.org/10.1002/app.29861
8th World Congress Chemical Engineering, Montreal, Canada, 23-27 August 2009

NOTE: This publication is included in the print copy of the thesis held in the University of Adelaide Library.

NOTE: This publication is included in the print copy of the thesis held in the University of Adelaide Library.