3.1 Introduction

The aim for this research was to develop a continuous process for recycling granular and fibrous particles into quality materials for sound and vibration damping having different physical characteristics. A novel extruder prototype was designed and used to carry out experiments with many different formulations of binders like latex, styrene butadiene rubber and polyurethanes to produce vibro-acoustic products. After several initial trials with different types of binders the methyl diphenyl isocyanate (MDI) binder was found to be the best. Section 3.6 explains the chemistry of the binder in more detail; also in this chapter the cold extrusion process used to produce vibro-acoustic materials is explained.

3.2 The batch process

The batch process involves introducing the granules, fibres, adhesive into a big cylinder like a concrete mixer (Swift, 2000). After the granules are introduced the cylinder is closed and the binder added; the cylinder is rotated in order to better distribute the binder. Once this operation is finished, all the granules are dispersed into the mould. The granular mixture is then manually distributed in order to get a more homogeneous surface, avoiding difference in the final density of the block. The troubles with the
traditional batch process is that the process is not continuous, involves considerable amount of manual work and it is a stop-start process which can be messy at times.

3.3 The cold extrusion process

One of the methods used to recycle wastes such as plastics, vulcanised rubber, fibres and other polymeric mixes from different sources is to reduce it into granules followed by rebounding by adhesives. A novel system for mixing and dispensing the binder on the granular waste continuously was carried out by the cold extrusion process. The single screw extruders were first applied in the food industry and are used for pumping lubricating oils. The earliest applications of extruders date back to around 1890s. For the extrusion process, the material is usually supplied in the form of granules or powder. It is fed from a hopper on to the screw; it is then conveyed along the barrel. At the end of the extruder the material passes through a die to produce an extrudate of the desired shape. The use of different dies means that the extruder screw/barrel can be used as the basic unit of several processing techniques.

The research carried out on extrusion systems to date requires heat (Benkreira, 2007). The aim of this research is to develop a process for recycling a range of polymeric waste materials such as fibrous waste, rubber crumb waste and a mixture of fibrous and granular waste. It is not feasible to use hot extrusion for these types of materials because of the thermo-plastic nature of the polymeric and elastomeric waste, friction and back pressures caused by the screw of a standard extruder and also because of the polymeric waste having different melting points. The new cold extrusion process is flexible enough to be able to handle different waste streams, and is able to produce
good quality materials for sound absorption and vibration damping; the process is continuous and has a low carbon footprint.

### 3.4 The novel cold extrusion technology

The new and innovative idea is to make porous materials for acoustic applications using a continuous cold extrusion process. An important advantage of the cold extrusion process is that different kinds of wastes can be processed simultaneously, like rubber and plastic etc. For this purpose the trial prototype of a laboratory extruder was designed and built (see Figure 3.1). Unlike in the case of the batch process, here the granules can be feed continuously and mixed in the barrel of the extruder. Water and binder can be injected from the top of the barrel (Figure 3.1) and various dies can be added to the end of the barrel to shape the extrudate which can then be cured naturally or under the influence of a chemical catalyst or heat.

![Figure 3.1: Schematic view of the cold extrusion process](image)

The initial cold extrusion equipment setup was very basic and consisted of two small hoppers, barrel (52mm diameter pipe), square pitch mixing screw, and a peristaltic
pump for addition of binder from the top of the barrel (see Figures 3.2-3.4). The cold extrusion equipment was designed to run with a range of screw speeds, which allowed a range of flow rates to be achieved, but if the output rate was increased, then the residence time was reduced which might result in poor mixing. Thus a compromise was needed between the different objectives. The screw used in the initial setup was an Archemedian type screw (Figure 3.5 and 3.6), total length was 450mm, flight pitch was 50mm, channel depth was 50mm, channel to depth ratio was 1:1, and length to diameter ratio was 9:1. The screw was chosen to provide the optimal power efficiency at an acceptable output rate and acceptable mixing and pumping within the operating range of the extruder. The initial screw was a square pitch mixing screw.

The first series of experiments were to study the general ability of the extruder to wet, mix and bind small randomly shaped polymeric particles. For this purpose the binder and the water were kept at constant ratios in order to have the right and desired chemical reaction. A special control unit was constructed to maintain the desired working parameters such as the flow rate out of the hoppers, speed of the main screw in the barrel, speed of the binder pressure vessel, speed of the water pump. When the speed of the screw in the barrel is increased all the other working parameters can be increased proportionally. The best performance of the extruder with the barrel diameter of 52mm was achieved by using a combination of granules diameter ~ 2-10mm, using the smaller granules to form the frame of the product structure. The pressure in the barrel/die was a factor in determining the final weight and the mechanical characteristics of the end product. With the same granulometry and quantity of binder, the higher the pressure, the larger was the contacting surface and consequently higher is the adhesion.
The percentage of binder used in the process varies according to the kind of granules/fibres, their granulometry, pressure, and amount of water used in the process.

**Figure 3.2:** The prototype extruder

**Figure 3.3:** The barrel with the injection ports
**Figure 3.4:** The inside of the hopper

**Figure 3.5:** Picture of a square pitch mixing screw

**Figure 3.6:** Schematic of the square pitch mixing screw used in the prototype extruder
The binder was injected from a nozzle attached to the top of the barrel (see Figure 3.3). The water was added first so that the granules are coated. The water can be added with a catalyst, an innovative idea highly reducing the curing time and speeding up the production. The isocyanate reacts with water giving a porous material which cures at room temperature so that no extra heat is required to cure the material. The stoechiometry of this reaction is explained in chapter 4.

The cold extrusion process was shown to be able to produce acoustic porous materials in a fast and continuous way using a pre-granulated polymeric waste. Figure 3.7 presents photographs of the types of waste used in the preliminary trials. These included recycled tyre shred residue and car dashboard crumb. One particular type of material used in this work was carpet waste in the form of PVC-backed carpet tiles with nylon/polypropylene pile. It was fed into a tripe blade, vertical rotation granulator. The granulated output passed through a screen of 2mm aperture, before being conveyed into a cyclone system that separated the material into granular (PVC tile backing) and fibrous (nylon pile) components. The distinct granular and fibrous components were then bagged off. Carpet fibre was placed in one of the extruder hoppers and the rubber grain into the other hopper of the extruder. The material was then allowed to feed into the barrel of the extruder. A target output of 8 kg/hr was maintained. The screw speed was kept to 20 rpm (17mm/sec) to give the material more residence time in the barrel, along with a corresponding reduction in the hopper feed rate to maintain an equivalent channel fill fraction. Variable pump speeds were used to feed the binder and water from the top of the barrel. Variable DC motor speeds drove both screws in the hoppers. Both hoppers were calibrated by measuring the output versus motor speed.
Figure 3.7: Raw waste and the end products (left - tyre shred residue, right - car dashboard crumb)

A summary table showing which material streams were selected for further study is shown in Table 3.1. PVC carpet tile waste, tyre shred residue and auto dashboard residue were considered to have the greatest potential from the list shown in chapter 2 Table 2.1.

Table 3.1: Material shortlist summary table

<table>
<thead>
<tr>
<th>Material</th>
<th>Acoustic Function</th>
<th>Possible main markets</th>
<th>Main concerns</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC Carpet tile waste</td>
<td>Absorption (excellent), Impact (excellent)</td>
<td>Building industry (floors/walls)</td>
<td>Availability, granulation</td>
</tr>
<tr>
<td>Rayon (tyre shred residue)</td>
<td>Absorption (excellent), Impact (excellent)</td>
<td>Building industry (floors/walls)</td>
<td>None</td>
</tr>
<tr>
<td>Auto dashboard / semi rigid polyurethane</td>
<td>Absorption (good), Barrier (good)</td>
<td>Automotive industry, Building industry</td>
<td>Location</td>
</tr>
</tbody>
</table>
Based on the information and the potential performance of the waste stream, list below provides summary details of the technical performance and commercial information of the three materials selected for further study.

i. Tyre shred residue – 100 tonnes per week ends up in the landfill, ground ready to use, rayon fibres with some rubber crumb content, good potential acoustic properties.

ii. Car dashboard crumb – Semi rigid polyurethane, vehicle end of life waste. European Union requires to recover 85% of materials from vehicles that have been scraped, 50 tonnes per year of semi rigid polyurethane currently being recovered and raising to 200 tonnes over next few years.

iii. PVC backed carpet tiles - Bitumen backed carpet is biggest (280,000 tonnes per year to landfill) but potentially harmful due to volatile organic compounds and more difficult to grind than PVC backed. PVC backed has been used by work carried out by WRAP (Waste and Resources Action Plan) and give good acoustic properties.

The main problem experienced during the preliminary trials was that the extruder was not able to produce acoustic products. This happened because the extrudate was balling up and the polyurethane binder would not bond the granules together. Instead the binder balled up and the granules were left unbounded. Other problems included the peristaltic pump not delivering enough binder, the hoppers were too small and wrong binder formulation was used, which did not allow any porosity within the material to be developed.
In general, the performance of the extruder is related to several aspects including the quality of the product it produces, energy consumption, rate of production and pressure profiles within the extruder. The quality of the extrudate was defined in terms of the ability of the extruder to homogenise the mixture before it reached the die and to achieve a uniform delivery rate. The compositional inhomogeneity of the extrudate affects the appearance, the porosity, mechanical properties and acoustic properties of the extrudate. It was important to balance the addition of binder, water, PVC granulates and fibres. Instabilities occurred if the water and binder were unable to coat the grains and fibres due to a high output rate from the hoppers. Material break up occurred when the flow rate was higher than the rate at which binder was added. The output rate was found to be a function of the screw speed, diameter of the barrel and the screw geometry. The cold extrusion equipment was designed to run with a range of screw speeds (5 rpm to 40 rpm), which allowed a range of flow rates to be achieved, but if the output rate was increased, then the residence time was reduced which might result in poor mixing. Thus a compromise was needed to balance the following aspects related to the extrusion process: (i) uniform feeding conditions from individual hoppers; (ii) injection position of binder along the barrel; (iii) product handling i.e. manual compaction, automatic compaction i.e. calendaring; (iv) heating drying of extrudate. These were addressed during the scale-up phase detailed in the following section.

3.5 Extruder scale up – The initial design

The maximum flow rate out of the prototype extruder was approximately 8 kg/h. There were several problems with this machine which were highlighted in the previous section. Because of these the prototype extruder had to be scaled up and redesigned. An
important part of the design process was to develop a screw which can convey and mix elastic particles and fibres of various sizes and lengths. The design of the screw was based on past experience and knowledge of the flow behaviour of granulated carpet and rubber waste. The screw has been designed to give maximum flow volume, i.e. with as large a channel depth as possible and to give good mixing of the material. The internal diameter of the extruder barrel was 100 mm and the diameter of the screw diameter was 98 mm. The screw flight pitch was 100 mm with a flight thickness of 3.18 mm. Figure 3.8 presents a drawing of the scaled-up extruder design.

![Figure 3.8: Injection ports in extruder barrel](image)

The screw flights were supported by a 15 mm central shaft. The barrel length was kept to 1 meter and the overall length including the hopper was 1.3 meters. The complete assembly was made out of stainless steel (Figure 3.9).
14 liquid injection ports 120 mm apart have been placed along the length of the barrel and on both sides i.e. 180° apart (see Figure 3.9). The binder and water were injected from the top of the barrel (Figure 3.8) using the ports offset from the end of the extruder barrel by 850mm and 130mm, respectively. Provisions have also been made to incorporate a pressure transducer near the exit of the barrel. The screw was driven by an inverter controlled 1.5kW geared motor. The feed to the extruder hopper was via two hoppers placed above the throat. Variable speed geared motors were used to drive primary screws inside these hoppers. These primary screws have long flights welded at various positions to prevent bridging of the coarse raw material (Figure 3.10).
The new extruder had larger hoppers. A special pressure vessel was used to deliver the binder. A peristaltic pump was used to deliver the water and variable speed geared motors were used to control the screw speed in the hoppers with flights to agitate particles.

**Figure 3.10**: Image of the material inside the stainless steel hopper

**Figure 3.11**: Image of the feed section
These primary screws were used to feed the granulated waste at precise rates into the main hopper. Variable speed pumps were used to feed the binder and water at various points along the extruder. The material coming out of the extruder was collected in suitable size trays pushed along on a conveyor. The material was left to cure and the samples analysed thereafter. Laboratory trails carried out with the new extruder have shown that even at the lower screw speeds, it was possible to achieve material flow rates in excess of 40kg/hr or greater. Experimentally this was not desirable so modifications were required to accommodate low throughputs.

Figure 3.12: Picture of the extruder with die
The original geared drive motor had a speed range of 20 to 100 rpm. This motor had to be replaced with a new one with a lower speed range (0 to 70 rpm) which was better at regulating the flow at low speeds.

In preparation for continuous sheet production, we designed and made in house two "fish-tail" dies to fit onto the end of the extruder. The die slot sizes were 150 x 50 mm and 200 x 40 mm. One important aspect of the extruder operation was the measurement of pressures particularly when the dies are fitted. For further scale-up there was a need to measure also the power requirement, the new extruder design had allowed for insertion of torque transducers on the drive shaft. The initial laboratory trials with the die (Figure 3.14) were not successful because of the back pressure which built up in the
extruder and resulted in the blockage of the screw. As a result, the prototype die design had to be modified in order to stop the blockage from reoccurring.

The purpose of the die was to produce material in sheet form, increase the back pressure and help with mixing and adhesion of the granules. Another option considered was to increase the pressure down the barrel by varying the screw pitch, so that the mixture would be pressurised as it was pushed down the barrel. Mixing was further improved by inserting “pins” in the extruder barrel, trials using tyre shred residue and car dashboard crumb were better mixed with water and binder with the pins inserted in to the barrel.

Figure 3.14: Picture of the prototype die
3.6 Modifications made to the initial design

For the injection of the binder, the air pressure vessel and the peristaltic pump were found to have insufficient pressure. A new inverter driven gear pump by TEE electrical motors was installed which was capable of delivering high viscosity liquids at suitable flow rates and high pressures. The whole set-up was calibrated. The water was sprayed into the first injection point along the barrel using the gear pump whilst binder was pumped using a pressure vessel further along the barrel (e.g. at the 6th injection point along the barrel see Figure 3.8). In order to improve the injection of binder in the extruder throat it was decided to reduce viscosity of the binder by increasing the binder temperature to 50°C.

The extruder barrel was merely acting as a mixer and conveyor and when a die plate was introduced, blockage problems started to occur so modifications were required. In modifying the extruder attention was given to the following processing problems:

i. A more rigid barrel section with mixing pins and injection ports to enable staged injection of binder/reagents and improve mixing. The pins could be adjusted for length or removed completely if required.

ii. Introduce a tapered end section with curved corners and smooth internal surface eliminating material stagnation and providing uninterrupted flow into the die.

iii. Create a support spider at the delivery end of the screw to locate the screw end and eliminate contact between the screw and the barrel.

iv. Create a tapered nose section to the screw which would continue the screw flight into the die preventing any material holdup.
The modifications made to the design and fabrication of a scale up version of the extruder allowed processing waste materials in excess of 100kg/hr. Certain other aspects of the new design, pre-wetting in the hopper, improved mixing in the barrel were modified.

Depending on the amount of catalyst added to the water the curing rate of the products could be controlled, for the formulation in which catalyst was included binder was added at a later stage i.e. further along the barrel because of curing occurring at a much shorter time.

Die for sheet production was also modified. Majority of the solutions to problems occurring in the cold extrusion process involved trial and error. Other improvements made to the extruder are shown schematically in Figures 3.15 to 3.29.

![Figure 3.15: The dimensions of the main screw inside the barrel](image-url)
Figure 3.16: Cut in the screw to allow insertion of pin

End of flight to be level with end of barrel

Figure 3.17: End of screw flight
Figure 3.18: Wiping flight at end of die

Figure 3.19: Schematic of the flange connected at the end of the barrel
Figure 3.20: Picture of the flange attached to barrel

Figure 3.21: Schematic casing for the die
The initial die exit was made to 40mm diameter but during the calibration it blocked at the exit at higher speeds and the screw had stalled. The same phenomenon occurred with wet and dry waste. The outlet was then bored out to 50mm (Figure 3.22) which performed better. However, blockages would reappear at higher throughput speeds, so it was subsequently bored out to 73mm. In this way the backpressure has reduced considerably and the extruder did not block even at the maximum speeds on the screw. A further extension tube was attached to the existing outlet to enable rod shape extrudate to be produced and increase slightly the backpressure for better compaction.

**Figure 3.22:** Casing for the die (back view)
Figure 3.23: Casing for the die (front view)

Figure 3.24: Schematic of extruder die in casing
Figure 3.25: Extruder die in casing (back view)

Figure 3.26: Extruder die in casing (front view)
Figures 3.25-3.27 show the modified die casing and the insert screw to avoid a blockage occurring at the die exit. Figure 3.28 shows the nozzle attached to the end of the die to enable rod shapes to be extruded.
Figures 3.29 and 3.30 show the mechanism for the addition of water into the hopper area of the extruder.
Designing an extruder, with minimum weight and energy consumption was crucial. It is important when scaling up an extruder to produce consistent products which have the same characteristics as those developed in a smaller extruder. Most of the successful applications involving extrusion design and scaling are based on dimensional analysis coupled with trial and error, and a keen sense of observation.

Trials were carried out using new product formulations from a range of waste materials including post manufacturing PVC backed carpet waste, car dashboard crumb, car bumper crumb, tyre shred residue waste. The results of these trials are presented in chapter 5.

The extrusion process was ran under a wide range of operating conditions using design of experiments so that helpful feedback was obtained from testing the materials for their acoustic and non-acoustic properties. The results from the testing instruments were then used to identify the general behaviour of the extruder, thus this general behaviour of the extrusion process was used to describe the local behaviour and to choose the optimum variable settings.

**Figure 3.30**: Schematic of extruder with die attached
The cold extrusion process was run in a wide range of set conditions (e.g. binder vessel pressure, water pump, and screw speed). The effects of set operating variables have been examined experimentally by Maddock (1957). Maddock measured output rate fluctuations obtained by cutting and weighing the extrudate at defined instances of time. It is difficult to model the extrusion process for materials which have properties that are highly variable and largely unknown. Therefore, in a majority of cases the parameters of this process were determined from a series of experiments. In this work statistical tools were used in order to determine semi-empirical relations between the parameters of the extrusion process and the acoustical and related non-acoustical characteristics of the resultant porous materials. By using design of experiments the capability of the cold extrusion process to produce a good quality product was found. Also design of experiments helped in evaluating how the product quality and performance of the process changed with different settings of the variables. It is important to obtain good quality products at an acceptable rate and cost, the extruder once designed, constructed, was a system that produced good quality products and through design of experiments a better understanding of the process was achieved.

3.7 The chemical process for making the porous materials

A porous material consists of a large number of interconnected pores, forming a cellular network. A pore is the basic unit of the material. The pore is not circular as shown in Figure 3.31, and is interconnected to other pores in a tortuous way.
The acoustic properties of the materials depend on the properties of each individual pore, in particular:

i. The nature of the polyurethane elastomer itself, which constitutes the pore frame

ii. The thickness of the pore frame (t)

iii. The overall size of the pore (d)

iv. The internal diameter of the pore (w), which is the size of the opening

v. The presence of residual membranes in the pore and their thickness

vi. The anisotropy of the structure and the morphology (shape) of the pore

The material remains a complex assembly of an elastomer with recycled matter integrated in a matrix and air in the pores in which all these parameters (i-vi) are interdependent. The frame of these materials is typically made of an elastomer. The nature of the elastomer influences directly the properties of the thickness of the pore frame, such as the hardness, the elasticity, the fatigue. For example, the hardness and
elasticity are influenced by the cross-linking level of the polymer, depending on the formulation type and the concentration of reactive sites in the basic raw materials. Pore frame thickness, overall pore size, size of the pore opening and the material density are all related. An increase of the material density leads to an increase of the thickness of the pore frame, and hence a decrease of the pore opening and the air content in the material.

The formation of the porous structure itself starts from nucleation points which become the future individual pores. At each nucleation point, gas molecules are formed. These nucleation points become micropores, which increase in volume under the pressure of the gas released during the chemical reaction. Spherical at the beginning, the pores reach an irregular structure at the end of the foaming process.

During this process, the pores remain closed, otherwise the gas would escape and the material would not grow anymore. However, at the end of foaming process, the membranes of the pores blow open, at least partially. This is an essential step in the production of flexible materials. If the pore remains closed, the material would shrink during the cooling since the material formation is an exothermic process and the temperature inside the material can easily reach 100°C. During the cooling, the gas which would remain encapsulated in a closed pore would exert a depression force, leading to the contraction of the pore, and the shrinkage of the material. Therefore, a
newly prepared material always contains open pores. The ratio between closed and open pores affects the physical properties of the material, such as the acoustic performance, thermal insulation, and its hardness at compression.

The pore size can be expressed in number of pores per unit area. This definition is confusing because the pore is a volume (tri-dimensional unit), which is reduced by pore count to a one-dimensional value. In the pore size distribution calculations the whole pore volume is taken into account to characterise properly a material's two parameters which should be taken into account, the average volume of the pores which is per m$^3$, and the pore count.

### 3.8 The chemical reactions occurring in the cold extrusion process

From a chemical point of view a urethane is the ester from a carbamic acid (Bruins, 1969),

$$\begin{align*}
\text{R}_2\text{N} & \quad \text{C} \quad \text{OR} \\
\text{O} & \\
\text{H} & \\
\end{align*}$$

A polyurethane is the repetition of this group in a macro-molecular chain and may be obtained by the polymerisation reaction of a polyalcohol (polyol) with a polyisocyanate,

$$\begin{align*}
n\text{HO} \quad \text{R} \quad \text{OH} & + \quad \text{OCN} \quad \text{R}_1 \quad \text{NCO} \quad \rightarrow \quad \left[ \begin{array}{c}
\text{R} \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{R}_1 \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{O} & \\
\text{H} & \\
\text{H} & \\
\end{array} \right]_n
\end{align*}$$
In order to obtain a porous material, this polymerisation reaction is combined with an expansion reaction, done either by a chemical process, where water is added to the blend, reacting with the isocyanate and generating carbon dioxide gas, this reaction will be explained in more detail in the next section. It can also be obtained by a physical process, using a low boiling point foaming agent which is transformed into its gaseous state under the influence of the temperature rise, developed during the exothermic polymerisation reactions. The 4,4’ MDI isomers reaction with water is more pronounced than the isomer 2,4’ diphenylmethane diisocyanate. Figure 3.32 shows the MDI binder isomer.

Figure 3.32: 4,4 diphenylmethane diisocyanate isomer (green – carbon atoms, gray – hydrogen atoms, red – oxygen atoms, blue – nitrogen atoms)

Atomic charges of the molecules 4,4’ diphenylmethane diisocyanate are shown in Figure 3.33.
Figure 3.33: Atomic charges of 4,4’ dipheylmethane diisocyanate isomer (software used HyperChem)

Figure 3.34: 2,4’ dipheylmethane diisocyanate isomer
Atomic charges of the molecules 2, 4' diphenylmethane diisocyanate are shown in Figure 3.35.

**Figure 3.35:** Atomic charges of 2,4' diphenylmethane diisocyanate isomer

**Figure 3.36:** MDI molecule with polyol geometry optimised for the reaction
Figure 3.37: The atomic charges of MDI molecule with polyol
The high reactivity of the isocyanate is described in more details below:

**Figure 3.38:** The initial reaction occurring between water and MDI
One pair of electrons is shared with the nitrogen, in a double bond, these electrons leave and rest on the nitrogen, giving it a negative charge (Figure 3.38). The nitrogen atom is unstable having a negative charge, so it solves its charge problem by attracting hydrogen from the water (Figure 3.39).

**Figure 3.39**: The intermediate molecular structure formed during the reaction of water with MDI
The nitrogen then attracts hydrogen from the same place, when this happens, we end up with an amine and carbon dioxide gas is expelled (Figure 3.40).

Figure 3.40: The end product with CO$_2$ gas expelled
What is important in this reaction is the carbon dioxide gas that is expelled and the rate at which it is expelled. The carbon dioxide creates the unique pore size distribution which can be effectively controlled by varying the parameters of this process. When the reaction begins, the mixture is a viscous liquid, and any carbon dioxide that is produced bubbles away. But as the reaction progresses, and molecular weight increases, the mixture becomes more and more viscous, until it becomes a solid. When this happens, the carbon dioxide bubbles are trapped in the viscous liquid, they stay there trapped and it is these bubbles that give the material its porosity.

By controlling the stoichiometry between MDI binder and water different kinds of porous structures can be produced depending on the amount of chemical bonds formed between MDI and hydroxyl groups. Water to MDI ratio needs to be kept under control in order to have the right and desired chemical reaction. Water coats the polyamide and PVC grains allowing the reaction to occur. In a fast reaction (couple of seconds), MDI reacts with the hydroxyl groups of polyamide and PVC and carbamic acid is created as an intermediate product forming the bonds between recycled grains and fibres. The reaction of MDI with water is initiated by the NCO-groups; if a catalyst is added to the water a further reduction in the curing time is observed. During the curing of the material, liquid evaporates. Initially, the binder and water evaporate from the external surface of the material. As curing continues pores open in the structure under the internal gas (CO₂) pressure and the evaporation continues largely from the compact surface while liquid flows in the inter particle capillaries. The small pores at the surface region provide a capillary attraction on the internal liquid in larger pores, leading to liquid flow and evaporation. The whole process of curing takes around half an hour at room temperature depending on the amount of water added to the process. This process
was used to develop porous samples with a controlled pore size distribution, 30mm thick material samples were prepared for acoustic absorption experiments and 10mm resilient samples were prepared for impact sound insulation experiments. The main feature of the chemistry of materials made using MDI binder is that it can be combined with an infinitely large variety of polyols leading to materials of a different hardness, i.e. flexible, supersoft, rigid, semi-rigid etc. It can be combined with whatever quantity of blowing agent leading to a density from 7 to 1000 kg/m³. High production speed is achieved because the material cures at room temperature within half an hour and no extra heat is required. The material can be extruded into sheets, can be laminated, and moulded. Depending on the nature of the polyol, flexible materials can be divided generally in two families, the polyether and polyester. Polyether polyol: are mainly derived from a blend of propylene oxide and ethylene oxide,

\[
R\left[O \left(\text{CH}_3\right)\left(\text{CH}_2\text{O}\right)_x\left(\text{CH}_2\text{CH}_2\text{O}\right)_y\text{H}\right]_n
\]

Polyester polyol: as for example condensation polymer derived from di-ethylene glycol and adipic acid,

\[
R\left[O \left(\text{C}_4\text{H}_8\right)\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O}\right]_n
\]
3.9 Rate of reaction of 4,4 diphenylmethane diisocyanate with water

The MDI binder to water ratio is one of the key process parameters. Therefore, the effect of water on 4,4 diphenylmethane diisocyanate rate of reaction will be investigated in this section. The mixture of water with MDI was stirred and left in the reaction vessel, reaction rates were measured for different water to MDI ratios. After the experiment the cured sample was cut and porosity was measured. Low porosity was observed for MDI to water ratio of 1:20 and the highest for 1:1. The porosity closely follows the ratio of MDI to water ratio (Figure 3.41). Overall, the 1:5 ratio of water to MDI gives a sample with good acoustic properties compared to other ratios as it is shown in chapter 5. Therefore, it was set as the default value in the experiments.

![Figure 3.41: Rate of reaction of MDI binder with water](image-url)
For binder to water ratio of 1:1 the rate of reaction is fast, more CO$_2$ is produced because of more interactions between CNO and H$_2$O, more CO$_2$ gas is trapped inside the sample hence the sample is more porous. Least amount of CO$_2$ is given off for reaction 1:20, because not enough binder molecules are present to produce CO$_2$ gas to create the porosity. The rate of reaction can be worked out from the gradient of the curves shown in Figure 3.41. The initial gradient of the graph in cm$^3$/min gives an accurate measure of how fast CO$_2$ was being produced, i.e. $k_r$

$$\frac{d[CO_2]}{dt} = k_r[CNO][H_2O]$$  (3.1)

where $k_r$ is the first order constant describing the rate of reaction in cm$^3$/min. The values of $k_r$ obtained for a range of binder to water ratios are presented in Table 3.2. Figure 3.42 presents the dependence of the material porosity on the rate of reaction. It shows that the porosity increases linearly with the increase in the rate of reaction. As a result high binder to water ratios correspond to materials with lower porosity values.

<table>
<thead>
<tr>
<th>MDI:H$_2$O</th>
<th>Porosity</th>
<th>Rate of reaction ($k_r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>81.5</td>
<td>19.8</td>
</tr>
<tr>
<td>1 : 5</td>
<td>73</td>
<td>10.9</td>
</tr>
<tr>
<td>1 : 10</td>
<td>68.5</td>
<td>7.0</td>
</tr>
<tr>
<td>1 : 15</td>
<td>68</td>
<td>4.6</td>
</tr>
<tr>
<td>1 : 20</td>
<td>66</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Additional experiments were carried out to determine the influence of small water to binder ratios on the resultant material porosity, i.e. the effect of the increasing binder level. The results of these experiments shown in Figure 3.43 suggest that the CO₂ level progressively increases with fixed water level to increasing binder levels.

**Figure 3.42**: Influence of rate of reaction on the porosity of tyre shred residue
Figure 3.43: Rate of reaction of water with MDI

Table 3.3: Reaction rates of water with MDI binder

<table>
<thead>
<tr>
<th>H2O:MDI</th>
<th>Porosity</th>
<th>Rate of reaction (k_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>1:5</td>
<td></td>
<td>84</td>
</tr>
<tr>
<td>1:10</td>
<td></td>
<td>90.7</td>
</tr>
<tr>
<td>1:15</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>1:20</td>
<td></td>
<td>92.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H2O:MDI</th>
<th>Rate of reaction (k_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>20</td>
</tr>
<tr>
<td>1:5</td>
<td>25.6</td>
</tr>
<tr>
<td>1:10</td>
<td>47</td>
</tr>
<tr>
<td>1:15</td>
<td>62.2</td>
</tr>
<tr>
<td>1:20</td>
<td>48</td>
</tr>
</tbody>
</table>
There seems to be a saturation point in the obtained set of experimental data whereby the fastest rate of reaction is achieved for water to binder ratio of 1:15. For this ratio the right amount of water molecules are present to react fully with the binder molecules to produce the high porosity products. Beyond this point any increase in the binder level results in a progressive reduction in the reaction rate. With water to binder ratio of 1:20 respectively the sample foams up, reaching a peak in porosity followed by pore collapse as the material frame is unable to support itself resulting in the reduced porosity of the cured product.

Therefore, it is possible to conclude that the use of MDI binder for the production of acoustic materials is dictated by the production of CO₂ gas. The influence of increasing

**Figure 3.44:** Influence of rate of reaction on porosity for increasing binder levels
binder level is more pronounced in comparison with the effect of increasing the water levels. It can be shown that almost 3 times more CO$_2$ gas is produced when water to binder ratios are changed from 1:1 to 1:20 respectively compared with changing the MDI:H$_2$O ratios, for 1:1 ratios the results are similar for both set of experiments (see figures 3.41 and 3.43). In all of the experiments the initial rate of reaction was fast; the reaction reaches a peak after around 10 minutes then slows down and eventually comes to a stop. For scale up production from experimental level, a numerical model can be developed for use with new binder formulations. This model will allow the prediction of the CO$_2$ profiles under a variety of binder to water ratios.

### 3.10 Pore size distribution of the extruded samples

One of the key characteristics of porous materials is the pore size distribution which controls the acoustic absorption mechanisms. The pore size distribution is unique function of the parameters of the cold extrusion process and it needs to be measured and analysed. In this work the pore size distribution of the developed samples was measured optically by using the optimas software. The software was calibrated using an image of a 1mm graticule taken at 2.5x magnification under an optical microscope. This enabled accurate measurement of the pore size and pore location. The optimas software was configured so that the region of interest was the entire image, from which the pore area was extracted. Within the software an image threshold was set, which enabled the software to focus on the pores that were present in the foreground and to exclude the fainter background frame (see Figure 3.45).
This threshold is very much dependant on the lighting conditions used when the image is taken. Therefore, the lighting conditions were kept constant when the images were taken under the microscope for the analysis. From this data the pore size distribution based on the equivalent sphere diameter was determined. The equivalent sphere diameter was defined as the diameter of a sphere with the same area as that of the irregular pore.

Figure 3.46 shows examples of pore structures created using the cold extrusion process.
Pore size distribution histograms are constructed by placing the pores of the same size into individual bins. The number of samples in each of the bins is counted and the data is normalised by dividing by the total number of pores, such that the total area in the histogram is equal to one.

\[
\text{Area of one pore of this diameter} = \frac{\pi (\Psi)^2}{4} \quad (3.2)
\]

\[
\text{Equivalent area of pores} = \text{pore count} \times A \quad (3.3)
\]

\[
\log_2(\text{pore size, mm}) = \log_2\left(\frac{A}{n}\right) \quad (3.4)
\]

\[
\text{The probability function} = \frac{\text{pore count}}{\text{Total pore count}} \quad (3.5)
\]
where, $\Psi$ is the pore diameter, and $A$ is the area of one pore of this diameter. Appendix G shows typical probability density function data for a sample made from polymeric waste and Figures 3.47 to 3.50 shows the pore size distribution graphs for different water to binder ratios.

**Figure 3.47**: Graph of pore size distribution for water to MDI ratio 1:5

**Figure 3.48**: Probability density function graph for water to MDI ratio 1:5
Figure 3.49: Graph of pore size distribution for binder to water ratio 1:20

Figure 3.50: Probability density function graph for binder to water ratio 1:20
In sample with 1:5 water to binder ratio (Figure. 3.47) the larger pores lie between 3mm to around 8mm, whereas in sample with a binder to water ratio 1:20 (see Figure. 3.49) very few large pores are present, the micro-pores lie between 0-2 mm.

3.11 Fume analysis test of the extruded samples

A fume analysis test was carried out on the extruded samples to check for their chemical composition and any harmful compounds given off during burning. The procedure involved setting a sub-sample of the extruded material alight with a Bunsen burner. The samples produced copious black smoke. A portion of the smoke was collected on a glass fibre filter paper (Whatman GF/A) using air drawn through a portable dust sampler at an initial rate of 4 L/min. In addition to these samples, a blank filter paper was also prepared using air drawn through the filter for approximately the same time as for the samples.

Each filter paper was extracted with one aliquot of ~3 ml DCM:MeOH (dichloromethane:methanol 2:1, v/v). The solvent extract was then transferred to a clean glass vial. Excess BSTFA (N, O- bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane) was added to derivatise the sample. An additional drop of DCM was added to ensure thorough mixing of sample and reagent, and the sample was left overnight. The samples were diluted in DCM for analysis by gas chromatography coupled to a mass spectrometer (GC-MS).

Analysis was carried out by combined GC-MS using a Hewlett Packard 5890 series II GC connected to a 5972 series mass selective detector. The splitless injector and interface were maintained at 300°C and 340°C. Helium was the carrier gas at constant inlet pressure. The temperature of the oven was programmed from 50°C (2 min.) to
340°C (10 min.) at 10°C/min. The GC was fitted with a 15m x 0.25mm, OV1 phase fused silica column (MEGA). The column was directly inserted into the ion source where electron impact (EI) spectra were obtained at 70 eV with full scan from m/z 50 to 700.

The results are presented as total ion chromatograms of the BSTFA derivatized solvent extract (Figure 3.51). These show each separated component of the solvent extract as discrete peaks, the area under each peak being representative of the abundance. Where identified, components have been labelled: P = Phthalate plasticiser

![GC-MS spectrum for fume of extruded sample](image)

**Figure 3.51:** GC-MS spectrum for fume of extruded sample

C = Fatty acid, with selected carbon numbers and degree of unsaturation.
The control (filter only no sample see Figure 3.52) yielded a number of components similar to the extruded sample. This is not surprising as identical sample preparation treatment and analysis was carried out, the sample therefore represents contamination from the filter and any contamination introduced during sampling, sample preparation and analysis. Although not quantified, these components are relatively low in abundance in comparison to the other samples. Only the C_{18:0} fatty acid was also extracted in significant abundance from the other samples, and this can therefore be excluded from interpretation.

The solvent extract from the soot was dominated by a number of phthalate plasticisers (the most abundant being bis(2-ethylhexyl)phthalate). There are also a series of peaks after 22 minutes retention time, which have mass fragments at m/z 73, 117 and 131 (Figure 3.51).
Figure 3.53: The mass fragments

Those at earlier retention times appear to be constituted of a series of co-eluting components, which are not well resolved at higher retention times.

\( M/Z \, 73, \, 117 \) are characteristic of a silyl derivative of a carboxylic acid functional group (Figure 3.53). It is likely that the 113 mass represents the addition of a \( \text{CH}_2 \) unit.

3.12 Two level factorial design used for the exploration of the cold extrusion process

There were a number of parameters which related to the cold extrusion process. In order to understand their effect on the acoustical and related non-acoustical properties of the extrudate it was necessary to conduct experiments whereby one parameter was varied and the others were kept unchanged. In order to obtain a representative set of process relationships without resorting to a very large number of experiments a two factorial design was used in this work. The two factorial design is represented \( 2^x \) were \( x \) is the number of input variables at two levels each and a total of \( 2^x \) experiments, with the number of experiments increasing exponentially as \( x \) increases. A full factorial design
includes all the interaction effects. For example in the cold extrusion process there was interaction between five variables (PVC grain hopper speed, fibre hopper speed, water pump speed, binder flow speed and main screw speed). Therefore $2^5$ designs were chosen for each set of experiments, eight experiments were carried out for each set. These were sufficient to evaluate a chosen portion of the main effects and the interaction effects. In the design of experiments the set extruder operating conditions (e.g. fibre flow, PVC grain flow, binder flow etc.) are called factors and were varied together instead of one at a time to estimate the effect of the interaction as well as the factors.

The two level factorial designs involved simultaneous adjustment of experimental factors at two levels, high and low, by restricting the tests to only two levels, the number of experiments are minimised. Montgomery provides a detailed discussion in his book design and analysis of experiments (2000). In the cold extrusion process a chosen portion of the input variables was explored, within this region minimum and maximum levels were set, for example for the water pump the range is 1-120 rpm for a set of 8 experiments the minimum chosen was 20 rpm and maximum 60 rpm. The performance of the product was affected by the extruder settings, i.e. the flow rate of material from the hoppers, water to binder ratio and the screw speed.

The input variables used for the prototype extruder are given in Tables 3.4. Applying design of experiments to the cold extrusion process the following factors or set operating conditions were chosen:

i. The set fibre hopper speed (kg/hr)

ii. The set PVC grain hopper speed (kg/hr)
iii. The set peristaltic water pump speed (kg/hr)

iv. The set binder pressure vessel flow (kg/hr)

v. The set screw speed (rpm)

For each set of experiments different variable settings were chosen so that the cold extrusion process could be optimised. For some set of experiments two replications were carried out for better estimation of the error rate in the experiments. At the start of each experiment the process was given a minute to settle and around 5 minutes to collect the sample. The design of experiments is presented in Tables 3.4-3.5.

**Table 3.4:** A typical table of design of experiments (1= maximum setting, -1= minimum setting

<table>
<thead>
<tr>
<th>Runs</th>
<th>Binder (psi)</th>
<th>Grain (Kg/h)</th>
<th>Fibre (Kg/h)</th>
<th>Water (rpm)</th>
<th>Screw speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
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<tr>
<td>8</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

**Table 3.5:** Table of extruder variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Minimum setting for variables</th>
<th>Maximum setting for variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>Grain</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Fibre</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>Screw speed</td>
<td>6</td>
<td>12</td>
</tr>
</tbody>
</table>
If the output flow rate is increased the porosity of the extrudate decreases, both objectives cannot be optimised at the same time, one of the objectives has to be constrained while optimising the other. For example, if the objective was to maximise the output while keeping porosity more than 80%, then the operating conditions for the process would be, screw speed at 12 rpm and binder flow at 45 psi.

Simultaneously adjusting the factors together in the design of experiments as shown in Table 3.3 instead of one at a time to find the effects on the products made was found to be less effective than experiments carried out by varying one factor at a time in terms of acoustic property monitoring trends. Hence the designs of experiments were only used to get an idea of the extruder operating conditions and not for exploiting material optimisation.

### 3.13 Summary

This chapter focused on the material manufacturing process. The cold extrusion technology was discussed starting from the prototype extruder to the larger modified version. In the second half of the chapter the chemical process for making the porous materials was discussed. In addition, the influence of water on the MDI adhesive has been determined.