Chapter 7

Auxiliary Properties of the Developed Porous Products

7.1 Introduction

This chapter looks into the formulation of the binder in terms of the properties of the products made and discusses what needs to change in the process to improve the material performance. A comparison will be carried out with some of the best commercially available acoustic absorbers. Other properties such as thermal are also investigated.

7.2 Material formulations for the optimum products developed

The most important raw materials for the production of the polyurethane binder are classified into five groups:

i. Polyols: Mainly used for making the binder soft

ii. Isocyanate: Methylene diphenyl diisocyanate (MDI) is mainly used for several applications, including rigid products. Isophoron diisocyanate (IPDI), used for several light UV stable polyurethane products other aliphatic isocyantes may also be used.

iii. Additives: Catalysts based on amines and organometal derivatives and stabilisers based on silicones or non silicones.

iv. Optional additives: Physical blowing agents, fire retardants, anti-oxidants, colorants, cross-linkers, etc.

A typical formulation is built on the entire system being 100% including polyol and isocyanate (Table 7.1). In this manner the select ingredients such as surfactants, catalysts, low boiling point foaming agents and fire retardants can be kept constant in the formulation. Water is the chemical blowing agent in the cold extrusion process; it reacts with isocyanate to form carbon dioxide gas.

Table 7.1: Typical binder formulations for different material densities

Typical binder composition	**Formulation by % weight**		
	Low density materials	Intermediate density materials	High density materials
Polyol	20	58	80
Fire retardant	3	3	3
Catalyst belend	4	4	4
Surfactant	1	1	1
Low b.p foaming agent	10	4	2
Isocyanate	62	30	10
Total weight (%)	100	100	100

To make low density materials using polyurethane binder high levels of forming agent is required as shown in table 7.1. The foaming agent used in the binder must have a low boiling point that is because the reaction of isocyanate with water is an exothermic reaction, during the reaction the low boiling point foaming agent changes to a gas creating foam. Also foaming agents with lower molecular weight are more effective at blowing the same density material, which is an economic advantage, thus the foaming agent used should have the right balance of boiling point and molecular weight.

Polyols (polyesters, polyethers, polyhydric alcohols) are the ingredients used commercially to mix with isocyanates in the manufacture of polyurethane binders. The reaction of polyurethane binders with water releases heat and carbon dioxide gas. The reaction temperature may reach above 100^{o}C. Amines or metallic salts, catalysts, auxiliary blowing agents (acetone, methyl chloride) and silicone surfactants are also added in the manufacture of polyurethane binders.

A typical formulation consists of the following, 50% polyol, 40% polyisocyanates, and 10% other chemicals. Polyisocyanates and polyols are liquid polymers that when combined with water, produce an exothermic reaction. The two polyisocyanates most commonly used are diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI). Both are derived from readily available petrochemicals. Though MDI is chemically more complex than TDI, this complexity allows its composition to be tailored for each specific application. Polyols are active hydrogen monomers based on polyesters, polyethers, or hydrocarbon materials that contain at least two active hydrogen atoms. The type and quantity of polyol used in the binders will determine whether the product produced is flexible or rigid. During the polymerisation process, the polyol and polyisocyanate molecule link and interconnect together to form a three dimensional product. Since both of the reactants are polyfunctional, there is then a high degree of cross-linking in the polyurethane as it cools. As a result it becomes very rigid. Table 7.2 shows the diverse polyurethane binders used in the experiments from Rosehill polymers and their properties.

Table 7.2: Binder properties

Binder Name	Isocyanate (%)	Viscosity (cps@25°C)	Appearance	Curing time (min)	Comments
FX1199	10 - 30	500 - 900	Brown	5 to 10	Material produced were resilient, rubber like with good recovery, show good results for impact damping.
FX1190	30 - 60	500 - 900	Straw	5 to 10	Materials produced were rigid due to high level of CNO. Good for acoustic absorption.
FX1239	10 - 30	225 - 425	Straw	30 to 40	Very easily injected into extruder barrel due to low viscosity. Low viscosity also facilitates with recycled granulates and fibres. Resultant products are good for absorption.
FX 457	10 - 30	1200 - 1700	Brawn	10 - 15	Binder foams hence products produced have high porosity, show good all-round performance.
TRIXENE	7.5 - 8.2	3500 - 6000	Straw	30	Because of the presence of 2,4' MDI isomer, trixenes reactivity with water is less profound hence samples produced show poor performance all-round.
FX1109	8.5 – 9.5	2500 - 3300	Light brown	30	Commercial binder, materials produced show good results for sound absorption and thermal insulation.
Pyrrolidone MDI	10 -30	5000	Green	30	Materials produced are low in density, show good absorption.

In order to determine the best binder for the production of acoustic products, the experiments were split into two parts:

- the batch process experiments
- and the extrusion experiments

The batch mixing procedure was used to determine the performance of the binders shown in table 7.2, as follows:

i. Weigh polymeric waste into mix bucket
ii. Add water and mix with food mixer for 2 minutes
iii. Add catalyst (Rosecat109) and mix for 30 seconds
iv. Add n-pentane and hand mix for 30 seconds.
v. Add FX457 and hand mix for 30 seconds
vi. Immediately take out of mix bucket and put in plastic mould tube
vii. Within 30 – 60 seconds the foaming starts and takes up to 30 - 60 seconds to stop (Note: Using less Rosecat 109 will delay the start of 'foaming')
viii. Leave for 15 to 30 minutes to cure and remove from mould tube
ix. Allow to dry out
x. Cut samples to the dimension and thickness
xi. Weigh for density and check acoustic / other physical properties

Using the extrusion process the procedure was as follows:

i. Weigh right amount of water
ii. Add in quantity by weight of Rosecat 109 and pentane to the water and mix
iii. Set the main screw speed, the hopper speed, the water pump speed and the binder flow rate.
iv. Let the extrusion process run for a couple of minutes, collect sample at end of die,
v. Allow to dry out, cut and check acoustic / other characteristic properties

The formulations in the following Figures 7.1 to 7.5 produced some of the best materials for sound absorption, impact sound insulation and thermal insulation.

Figure 7.1: Picture of sample Rayon_02 made using the formulation in Table 7.3

Table 7.3: Formulation for a product with good absorption and thermal and impact properties

Sample	Formulation	Content by weight (g)	Content (%)
Rayon_02	Tyre shred residue	300	60
	Binder FX1109	100	20
	Water	100	20
	Total	**500**	**100**

Figure 7.2: Picture of sample YL_01 made using the formulation in Table 7.4

Table 7.4: Formulation for a product with good absorption properties

Sample	Formulation	Content by weight (g)	Content (%)
YL_01	PVC Grains	150	30
	Nylon66 Fibres	100	20
	Binder Chemique xp106	100	20
	Water	100	20
	n-Pentane	50	10
	Total	**500**	**100**

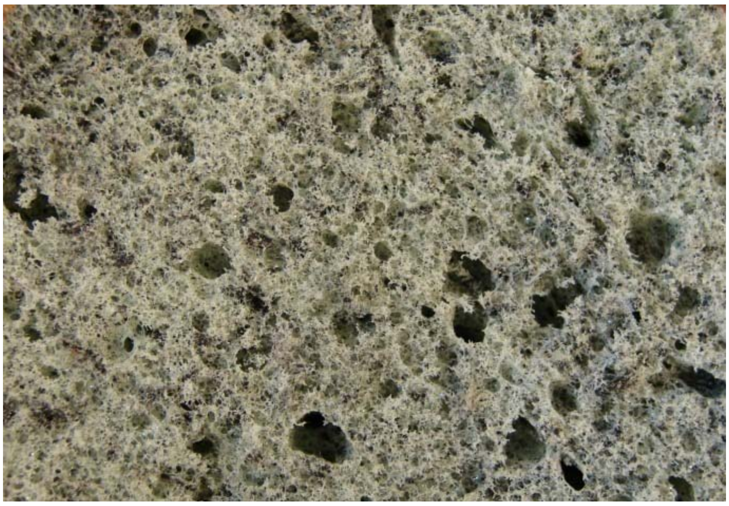

Figure 7.3: Picture of sample DB_02 made using the formulation in Table 7.5

Table 7.5: Formulation for a product with good absorption and thermal properties

Sample	Formulation	Content by weight (g)	Content (%)
DB_02	Dashboard crumb	135	30
	Binder FX457	140	31
	Water	100	23
	Rosecat109	35	8
	n-Pentane	35	8
	Total	**445**	**100**

The introduction of Rosecat 109 into the formulation and increasing the water level improved the acoustic and thermal performance of the materials, the catalyst in the formulation speeds up the curing process hence producing the desired pore size distribution for optimum performance.

Figure 7.4: Picture of sample TS_01 made using the formulation in Table 7.6

Table 7.6: Formulation for a product with good absorption and thermal properties

Sample	Formulation	Content by weight (g)	Content (%)
TS_01	Rayon Fibres only	85	19
	Binder FX457	140	31
	Water	150	34
	Rosecat109	35	8
	Pentane	35	8
	Total	**445**	**100**

Some waste streams require more water for full saturation i.e. fibrous waste; in this case the formulation needs to be changed accordingly. First step is to calculate water level needed to fully saturate the waste then binder is added to the water saturated waste (i.e. waste + water = 70%, then 30% binder should be added).

Figure 7.5: Picture of sample IM_07 made using the formulation in Table 7.7

Table 7.7: Formulation for a product with good impact properties

Sample	Formulation	Content by weight (g)	%Content
IM_07	Dashboard Crumb	250	50
	Binder FX1199	100	20
	Water	100	20
	Rosecat109	25	5
	Pentane	25	5
	Total	**500**	**100**

The formulations given in Tables 7.3 to 7.7 produced materials with low densities because of the foaming process. The sample foaming process is dependent on the mix time, for the production of low density materials it was necessary to mix for only around 10 seconds and no longer after the addition of the binder and leave the mix to foam, if mixing was carried out for any longer length of time after the addition of the binder or the sample compressed this lead to the foam being destroyed resulting in a high density product.

In the formulation the type and amount of polyol in the binder was critical, the lower molecular weight polyols produced products with a lower density. Another important ingredient in the formulation was the catalyst which influenced the speed of reaction, pore size and thermal conductivity. It was found using the catalyst in the formulation produced a small pore size distribution in the products. To be able to produce good performance for end use applications at the lowest possible cost commercially the following points were considered:

i. Waste materials that did not require any further processing were used in the formulation (i.e. tyre shred residue, car dashboard/bumper crumb).
ii. The waste content was maximised (minimum 50%).
iii. The binder was minimised to reduce cost.
iv. Lower water content to reduce the curing rate.

It was found using rosecat109 catalyst in the formulation produced materials with a small pore size distribution the larger pores were not produced hence the absorption coefficient was high, one of the reasons for this could be the catalyst speeds up the reaction not giving time for the larger pores to foam. Therefore not only does the catalyst influence the curing time but also the pore size during the foaming process.

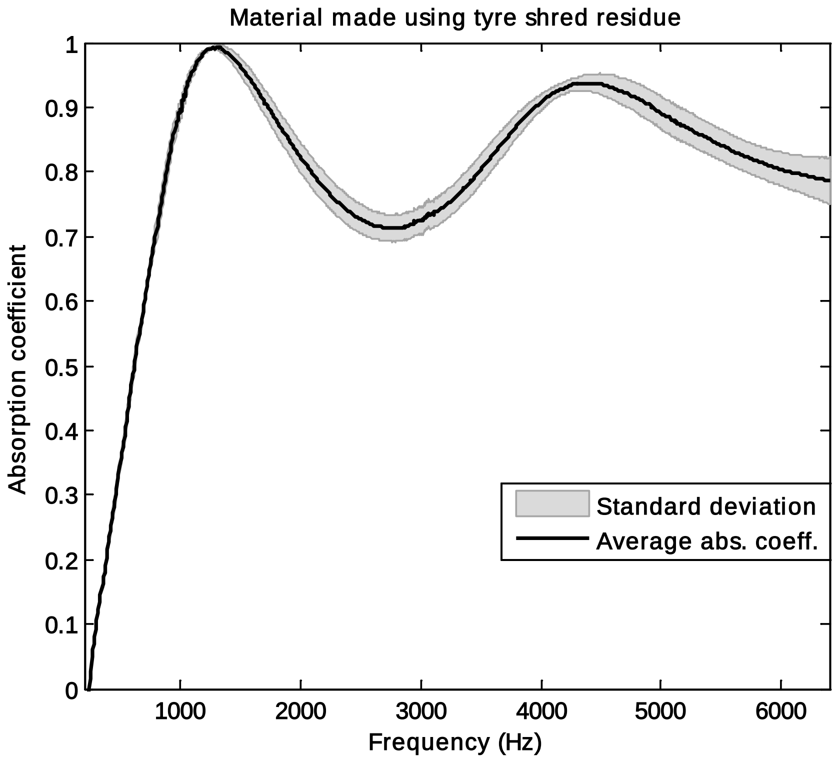

Figure 7.6: Material made using tyre shred residue TS-05 (thickness = 30mm)

Formulation for sample TS-05:

Table 7.8: Formulation for a product with good absorption

Sample	Formulation	Content by weight (g)	%Content
TS_05	Tyre shred residue	135	30
	Binder FX457	140	31
	Water	100	23
	Rosecat109	35	8
	n-Pentane	35	8
	Total	**445**	**100**

Single number rating for absorption coefficient for TS_05 = 4 (maximum). Varying percentage levels of catalyst in the formulation to optimise the pore size distribution can improve the acoustic and thermal properties of the material (Figure 7.7). The catalyst influences the curing time of the binder, trapping the escaping CO_2 gas. Another advantage of the addition of the catalyst is that it produces a homogeneous structure because the binder cures at the same time.

From the rate of reaction graphs (see chapter 3, section 3.9), the CO_2 gas is given off in the first 20 minutes, if the binder is made to cure in the first 10-20 minutes then the sample will foam trapping the CO_2 in the structure. Further work will need to be carried out to optimise the binder formulation i.e. influence of polyols molecular weight on the density and porosity of materials produced, which might further improve the absorption of the recycled products.

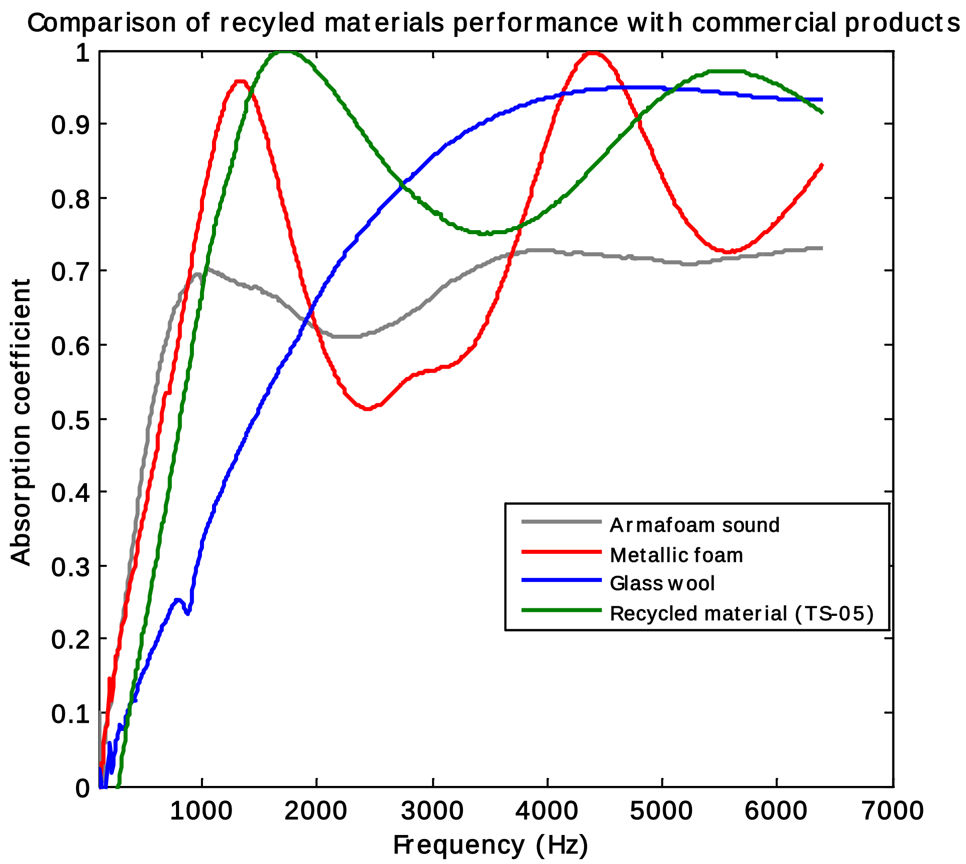

Figure 7.7: Comparison of recycled materials performance with commercial products (thickness = 25mm)

Table 7.9 shows the influence of different binders on the thermal conductivity results for materials made of car dashboard crumb, the best result for thermal conductivity was 0.04 W/(mK) obtained from the dashboard sample made using binder FX1109.

Table 7.9: Shows influence of binder on thermal conductivity of dashboard crumb

Name	Original Thickness (mm)	Compressed Thickness (mm)	Thermal Conductivity (W/(m*K))	Density (kg/m^3)
Dashboard_20% FX1190	20.25	19.78	0.101	344
Dashboard(2mm)_20% FX457	21.1	20.74	0.078	301
Dashboard_20% FX1109	21	20.4	0.04	270
Dashboard_20% FX1239	21.25	19.93	0.08	272

7.3 Trials at RAPRA using the rubber extruder

The purpose of the trials at RAPRA was to ascertain if a high pressure extruder was able to run our recipes and extrude a usable material. The starter recipe tried on the rubber extruder is shown in Table 7.10. This was enough for a 15 minutes run at 20 Kg/hr.

Table 7.10: Formulation for the initial trial

Sample	Formulation	Content by weight (g)	Content (%)
TS_1	Tyre shred residue	625	48
	Binder FX457	625	48
	Water	19	1.5
	Rosecat109	37.5	2.5
	Total	**1306**	**100**

The mixture was fed into the extruder, the material came out of the extruder very well (rod shaped) however after only a very short time the chemical reaction began and the mixture cured in the screw and the outlet using the formulation given in Table 7.10.

The Iddon rubber extruder (Figure 7.8) appeared to be on the small side, this made it difficult to make sufficient quantities to feed through the extruder before the catalyst began to cure the mix. The entrance hopper on the extruder was very small thus the mix had to be hand fed into the extruder.

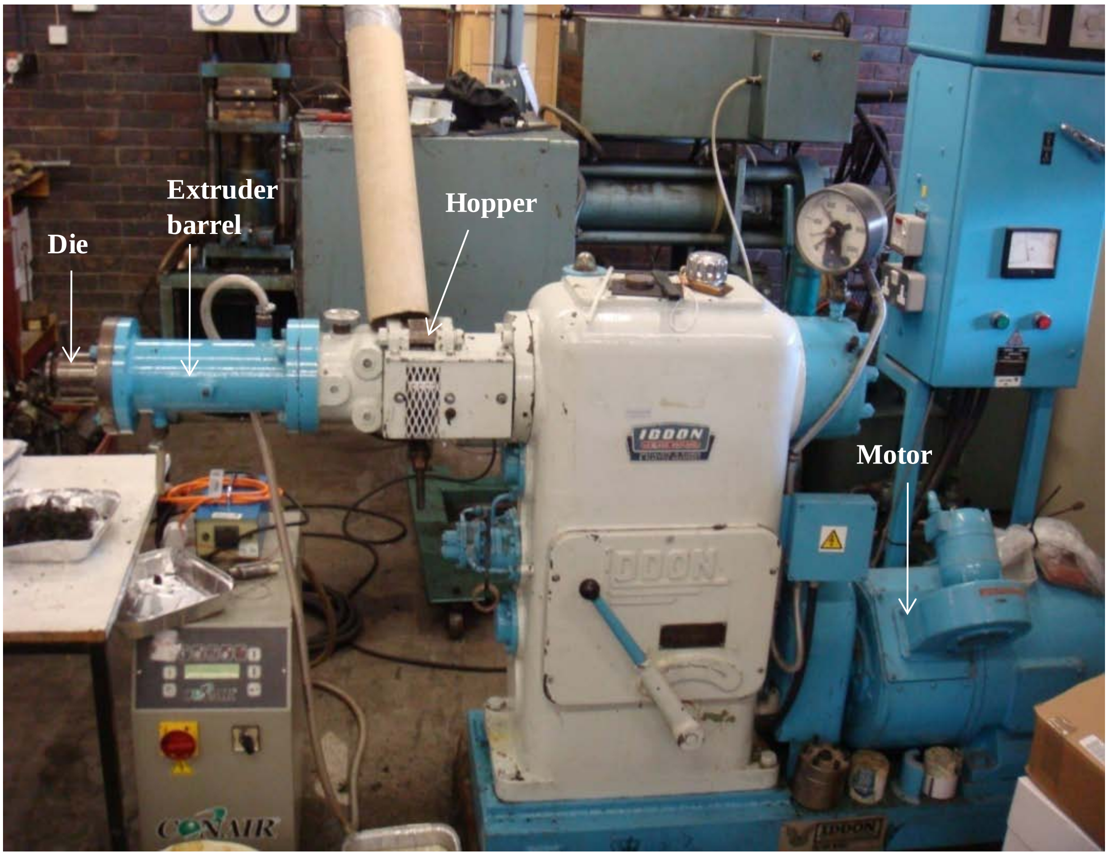

Figure 7.8: Rubber extruder at RAPRA

Please note that due to curing in the earlier trials no catalyst was used in the second trial (Table 7.11).

Table 7.11: Shows the formulation for the second trial

Sample	Formulation	Content by weight (g)	Content (%)
DB_1	Car dashboard crumb	625	48
	Binder FX457	625	48
	Water	19	1.5
	Total	1306	100

The waste fed in the extruder reasonably well. The material extruded very well and came out of the extruder rod shaped and did not stiffen until long after the extruding process (Figure 7.9). This formulation (Table 7.11) was tried with tyre shred residue waste; again the material extruded very well and came out of the extruder rod shaped.

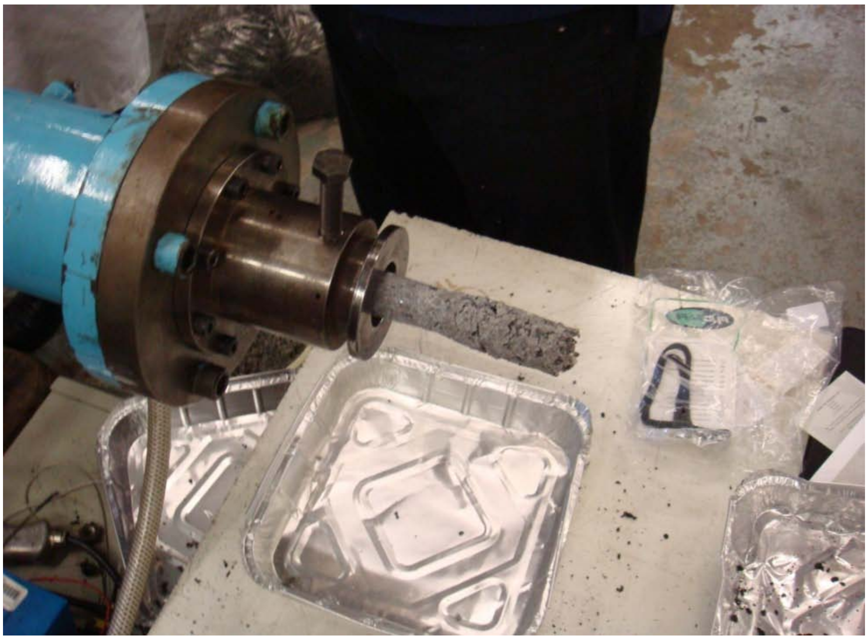

Figure 7.9: Picture of extrudate leaving the die

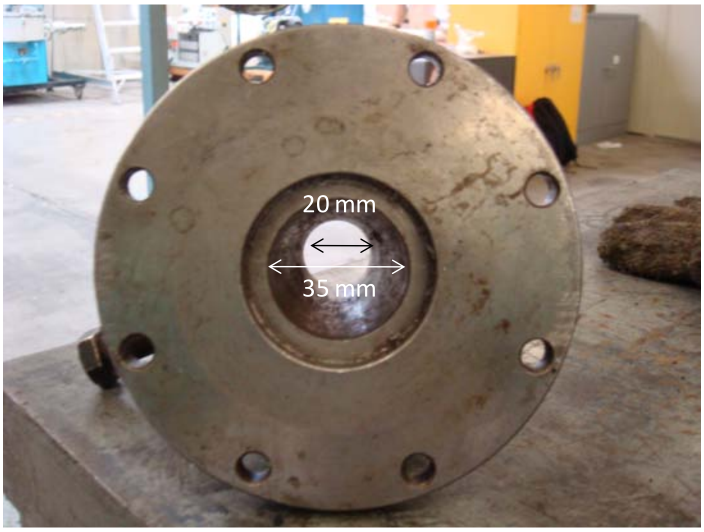

Figure 7.10: Die used at the end of the rubber extruder

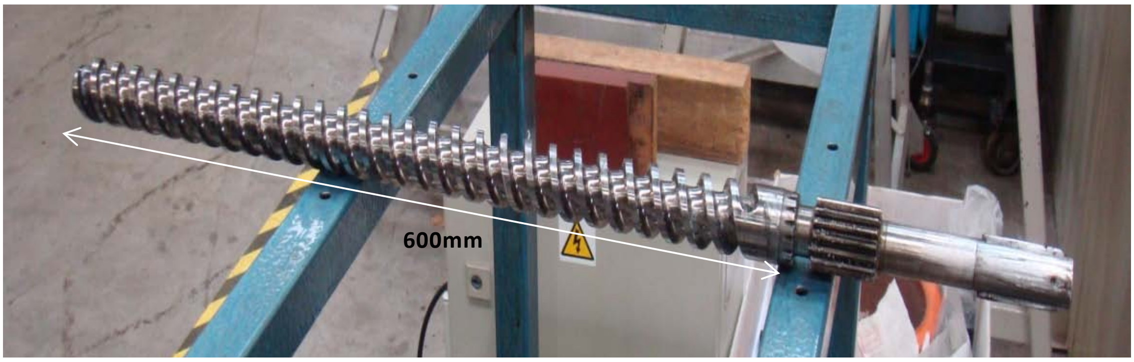

Figure 7.11: Screw used in the rubber extruder

Figure 7.12: Screw channel and pitch

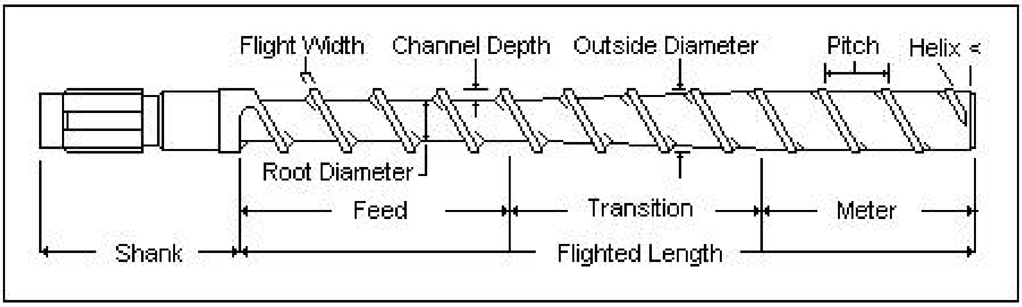

Figure 7.13: Schematic of standard screw used in hot extrusion

The rubber extruder screw (Figure 7.8) had a constant channel depth of 10 mm, whereas the screw used in the cold extrusion process has a channel depth of 35 mm. For the cold extrusion process the standard rubber extruder screw design is not an ideal screw design. According to extrusion theory (Crawford, (2001)) the channel depth in feed section needs to be large for better mixing (Figure 7.12), the rubber extruder screw compressed the material in the screw channel, for the cold extrusion process this compression has been eliminated by introducing a larger channel depth.

The maximum feed depth H_{max} can be calculated from:

$$H_{max} = 0.5\,.\,D - \left(\frac{2\,.\,M_T}{\pi\tau}\right)^{1/3} \tag{7.1}$$

where,

D = diameter of the screw

τ_s = allowable shear stress of the screw metal

M_T = torque at the circumference of the screw root

For the cold extrusion process the maximum screw feed depth can be calculated for the following conditions, D= 95mm, τ = 50 MPa, M_T = 10,000 Nm.

H_{max} is found from equation 7.1.

$$H_{max} = 0.5\,.\,\frac{95}{1000} - \left(\frac{2\,.\,10{,}000}{\pi\,.\,50.10^6}\right)^{1/3} = 47\ mm\ ,$$

Having run these trials on a commercial rubber extruder to ascertain if the process of extruding would lend itself to the production of our recycled materials commercially, we can now say that the commercial rubber extruder can process our materials using the formulation given in Table 7.10.

Other things to note is that the catalyst needs to be added towards the exit of the extruder as this would eliminate the prospect of the mixture curing in the screw. The catalyst could be injected just short of the end of the screw and the reaction would then take place in the extension nozzle.

By using extrusion theory screw deflection can be determined for optimum performance. Based on the design the lateral deflection of the screw as cantilever caused by its own weight can be estimated as follows:

$$\Delta = \frac{2\times 1000\times g\times \rho\times l^4}{E\times D^2} \qquad (7.2)$$

where

$g = 9.81\ m/s^2$, is acceleration due to gravity

$\rho = 7850\ kg/m^3$, is the density of the screw metal

$l = 1\ m$ is the length of the screw

$E = 210 \times 10^9 Pa$, is the elastic modulus of the screw metal

$D = 0.1\ m$, is the screw diameter

Inserting these values into equation 1 we obtain:

$$L = \frac{2 \times 1000 \times 9.81 \times 7850 \times 1^3}{(210 \times 10^9) \times (0.1)^2} = 0.073\ mm$$

This value does not exceed the flight clearance of 1 mm for the screw used in the cold extrusion process, so the mix flow between the screw and the barrel does not take on the role of supporting the screw to prevent contact between the screw and the barrel.

7.4 Sustainable acoustic material cost analysis model

A cost model was created to calculate the cost of materials produced using the cold extrusion process. In order to carry out a cost analysis of a sustainable product the following variables had to be taken in to account:

i. Volume of block produced
ii. Weight of block including scrap
iii. Density of block
iv. Cost of binder
v. Cost of mixing
vi. Cost of moulding
vii. Other labour costs (organisation etc.)
viii. Cost of packaging material
ix. Cost of energy and machine depreciation

An example of the cost analysis for tyre shred residue is presented in Table 7.12. Tyre shred residue material was considered to be without cost (material or transportation); rayon came already granulated to the right size. In the model the cost of binder was taken as £1.80, and density range of the material produced was taken as 200-400 kg/m^3. Trimming waste produced was taken as 10%. The cost analysis was performed by taking the cost of variables (i to ix) into account to calculate the final market price of the block produced using the cold extrusion process.

Table 7.12: A summary of the cost analysis model developed for sustainable materials

Description	Sustainable Acoustic Material Calculation								
		Total labour cost [£/hr]			£10.000				
		Binder concentration [% of Total mix]			20%				
Block-Volume in Production :				Production					
width		min	[mm]	1000.00					
		max	[mm]	1000.00					
		Average	[mm]	1000.00					
length		min	[mm]	10000.00					
		max	[mm]	10000.00					
		Average	[mm]	10000.00					
thickness		min	[mm]	200.00					
		max	[mm]	200.00					
		Average	[mm]	200.00			V [m^3]	2.00	
Weight Block without scrap (zero waste) :									
Density:			[kg/m^3]	100.00			[Kg]	200.0	
Weight Block incl. scrap (trim, etc) :									
Trim			[%]	10%					
Volatility			[%]	0%					
Scrap			[%]	10%		Total	[Kg]	240.0	
Cost formulation	GBP					Quantity			Content%
Scrap 1	0.000	100%	[£/Kg]	0.000	kg/block	192.00	[£/block]	0.00	0.0%
Scrap 2	0.000	0%	[£/Kg]	0.000	kg/block	0.00	[£/block]	0.00	0.0%
Binder (1239)	1.800	100%	[£/Kg]	1.800	kg/block	48.00	[£/block]	86.40	72.9%
Sum raw material					kg/block	240.00	[£/block]	£86.40	72.9%
Cost Grinding	GBP								
Output [kg/hr]	300								
Manpower [man/hr]	0.00			0.00	min/block	0.00			
Labour cost [£/hr]	10.00								
Labour cost/kg	0.000						cost/block	£0.00	0.0%
Cost sieving	GBP								
Output [kg/hr]	300								
Manpower [man/hr]	0.00		hrs/block	0.00	min/block	0.00			
Labour cost [£/hr]	10.00								%AT
Labour cost/kg	0.000						cost/block	£0.00	0.0%
Cost mixing	GBP								
Output [kg/hr]	400								
Manpower [man/hr]	1.00		hrs/block	0.60	min/block	36.00			%AT
Labour cost [£/hr]	10.00								
Labour cost/kg	0.025						cost/block	£6.00	5.1%
Cost Molding	GBP								
Output [kg/hr]	400								
Manpower [man/hr]	0.20		hrs/block	0.12	min/block	7.20			%AT
Labour cost [£/hr]	10.00								
Labour cost/kg	0.005						cost/block	£1.20	1.0%
Other labour cost (organisation, etc.)									
Output [kg/hr]	400								
Manpower [man/hr]	0.50		hrs/block	0.30	min/block	18.00			%AT
Labour cost [£/hr]	10.00								
Labour cost/kg	0.013						cost/block	£3.00	2.5%
Cost packaging material	GBP								
Carton/Pallet [£]	£3.500					Material	[£/Unit]	3.500	3.0%
blocks per carton/pallet	1								
wrapping and label cost [£]	£1.000					Material	[£/Unit]	1.00	0.8%
labels/carton	1								
						Total	[£/Unit]	£4.50	3.8%
Cost packaging labour	GBP								
Output [kg/hr]	280								
Manpower [man/hr]	0.50		hrs/block	0.43	min/block	25.71			%AT
Labour cost [£/hr]	10.00								
Labour cost/kg	0.018						cost/block	£4.29	3.6%
Cost Energy and Depreciation	GBP								
Energy overheads [£/kg]	£0.030					Energy	[£/block]	7.20	
Machine depreciation [£/kg]	£0.025					Machine Depreciation	[£/block]	6.00	
							cost/block	£13.20	11.1%
									100%
					min/block	86.91	Labour	£14.49	
							Material	£90.90	
							Energy and Machine Depreciation	£13.20	
							Sum	118.59	
SDC/block								£118.59	
SDC/m3								£59.29	

Based on the costing program in Table 7.12, which enabled us to look at the cost variables, the indications are that the extruded products can be competitive e.g. a material produced using the cold extrusion process with a density of 100 kg/m^3 at 20% binder, free waste and binder at £1.80/kg gives a total cost of £59.29/m^3. Wickes special thermal insulation sheet with a density of 140kg/m^3 is approximately £5/m^2 for 30mm thick, our materials made using recycled polymeric waste would cost £1.80/m^2 at 30mm. Costing of higher density products produced using the cold extrusion process show the cost per unit to be still competitive.