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Autum 2018

A Sustainable and Viable Method to Recycle Fibreglass

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Preface

The report is the final project, completed as part of the requirements of the Master of Science in Sustainable Product Design and Innovation at the University of Southern Denmark Engineering Department.

Abstract

The project is an attempt to apply a piece of research (Wang, Cui et al. 2015) to recycle a 'real world' sample of polyester resin reinforced glass fibre composite and to analyse if the process can be made viable.

Introduction

It is a commonly held opinion that the release of gases like carbon dioxide from the combustion of carbon fuel such as oil gas and coal have since the beginning of the industrial revolution resulted in the warming of the planet. There is at the same time depletion of these finite resources.

Today there is therefore an economic incentive to use the most efficient building methods, using materials with the best strength/weight, ratio to minimize the use of raw materials.

In Europe there is general agreement that the circular economy is a requirement to obtain sustainability.

The use of correctly designed composite materials is a way of achieving a better strength to weight ratio, in comparison with steel. There is however a reluctance to use these materials due to the lack of a viable system to recycle these products.

The present methods of treatment of waste reinforced glass fibre is to grind the waste reinforced glass fibre and blend it with virgin material, or to incinerate along with other waste, or of coprocessing to cement which is carried out for instance by Neowa GmbH in Bremen.

Initially investigating this problem, I discovered there were three basic ways of trying to recycle fibreglass: mechanical, thermal or chemical.

The only example I came across of a company using mechanically recycled fibreglass was Hambleside Danelaw in the UK. The develop manger Ian Middleton was kind enough to let me know the following:

- We have the capability to use an impact flail type granulator to grind up our fibre glass waste for inclusion in a minority of our products
- Our own waste exceeds our internal needs / capacity for recycled fiberglass
- Where we do use it, it is used as an opaque bulk filler to "dilute" the resin rather than replace the strands of glass reinforcement.
- Many of our products are translucent and so recycled material is not usable in this (too opaque)
- In addition to our translucent products (think of daylight through factory or warehouse roofs), we have a range of lead flashing replacement products for use on pitched roofs where recycled filler is applicable

•

This response convinced me that at present there is a limited application of mechanical separation.

Apart from the co-processing previously mentioned the use of pyrolysis has been considered. Pyrolysis is the heating of a substance in an environment without oxygen. The process is used commercially for carbon fibre recovery by ELG Carbon Fibre Ltd in the UK. This seemed to be an energy intensive process which could be justified for carbon fibres but not for glass fibres. It also has another disadvantage that the matrix chemicals are only used as combustion fuels.

A chemical process I became aware of was high temperature solvolysis which involved using high temperature steam to hydrolyse the O-H bonds in the polyester chain molecules to break them into smaller elements. This method seemed unsatisfactory because of the high energy use and the reduction of fibre strength which was reported.(Sokoli, Simonsen et al. 2016)

Retaining the idea of separating the O-H bonds I discovered an enzyme which does this. It was discussed in 'Functional characterization and structural modelling of synthetic polyester-degrading hydrolases from Thermomonospora curvata'. The enzyme had been found to break the bonds in PET Polyethylene terephthalate. Professor Zimmermann from Leipzig University who conducted the research kindly offered to test my samples of fibreglass with the enzyme. The results were not that favourable compared with PET.

On examining a paper 'A bacterium that degrades and assimilates poly (ethylene terephthalate), another enzyme which degraded PET was described. It, however, could degrade a sheet of PET, a form of polyethylene, by 6 micrometres in a week, thereby making it unsuitable to deploy in the field.

The final method selected, and that which the report is based on is described in the paper "Chemical recycling of unsaturated polyester resin and its composites via selective cleavage of the ester bond." (Wang, Cui et al. 2015).

This procedure was found to be relatively simple and kept the temperature low to avoid damage to the fibres. The other main advantage was that it allowed the recovery of fibres and potentially useful chemicals thereby making the process more viable.

The project consists of a scientific investigation of the process and an analysis of the financial viability of the solution.

Literary review

In the paper Current Status of Recycling of Fibre Reinforced Polymers (Oliveux, Dandy et al. 2015) there is a discussion of what is described as Solvolysis, the use of a chemical solvent to degrade the resin.

The first attempt to do this was in 1976 by Yoon who used propylene glycol. The conclusion of the article is that 'polyester resins are generally easier to solvolysis than epoxy resins and so require lower temperatures to be degraded'.

The article notes that in the previous decade the method has been used to recycle composites, particularly carbon reinforced plastic.

The article also deals with another problem which is that the potential applications of recovered fibres are limited because of their 'discontinuous and fluffy nature'.

The author states the following 'Incorporation of glass fibres reclaimed from sheet moulded compound into dough moulded compound for compression moulding did not affect tensile, flexural or impact properties at concentrations up to 50%, but beyond this percentage all properties significantly deteriorated'.

Oliveux argues that because of the extra expense of the chemicals for solvolysis and the need to treat the fibres to restore the strength it only makes economic sense to use mechanical separation for glass reinforced plastic. In the case of the method of solvolysis used in this project the temperature is kept to 190°C to keep the aluminium chloride catalyst dissolved. This should avoid the strength reductions in fibres.

An interesting approach which appears in the paper A Novel Sonochemical Approach for Enhanced Recovery of Carbon Fibre from CFRP Waste Using Mild Acid–Peroxide Mixture, (Das and Varughese 2016) used ultrasound to breakdown the epoxy resin in a sample of carbon fibre reinforced polymer with a solution of nitric acid and hydrogen peroxide.

The text further explains that the use of ultrasound in aqueous solutions leads to the phenomenon of cavitation. 'The implosion of microbubbles created in the liquid due to the ultrasonic frequency leads to localized release of high energy and pressure'. This the author states helps in the formation of radicals in an aqueous solution.

The paper concludes that the use of ultrasound produces a threefold increase in the quantity of clean fibre produced and was more effective at high frequency.

This is logical as there is more energy being added to the reaction forcing the equilibrium to produce more radicals. The higher the frequency the more energy input.

The relevance of this information is that when heating the fibreglass acid mixture, by the microwave digestor the same increase can be achieved, because microwaves will produce cavitation.

It was not possible to find any detailed models of the cost of recycling glass reinforced plastic over normal disposal methods, but there is a paper Environmental and Financial Performance of Mechanical Recycling of Carbon Fibre Reinforced Polymers and Comparison with Conventional Disposal Routes.(Li, Bai et al. 2016)

The method used in the paper to access the cost of incineration, was to consider the combined cost of the pre-treatment of the composite, the transportation, the gate fee for incineration, and the charges for any resulting materials sent to landfill.

These prices were relatively easy to obtain for the test material used in the paper.

The cost of mechanical grinding of the composite included the capital investment and the running cost as well as any initial cost for dismantling the material. The author uses two previous research papers (Hedlund-Åström 2005) and (Bailey 2014) and adjusted the two models to correspond with the amount of composite treated. The electricity cost was calculated at the local industrial tariff.

One of the main conclusions reached by the author is that it may prove difficult to overcome the relative price differences between the various waste routes.



Figure 1 Cost comparison on landfilling with tax, landfilling without tax, incineration. (Li, Bai et al. 2016)

The first point to note is that the recycling process considered in the report is pyrolysis which is a heat intensive and therefore an expensive process

The landfill option is relatively cheap at present but is not really something that needs to be considered long term as it will progressively be restricted towards 2030 but incineration and co-processing remain a threat to the viability of the project. The price for incinerating 1000kg of glass fibre composite in Denmark by Alpha+ was quoted at a gate price of 750DKK.

The superior process of co processing the composite to make cement uses the matrix as fuel. The gate price is $165 \notin$ per 1000kg at the German Company Neowa who has a facility in Bremen. To these prices should be added the cost of transportation and the preparation work required.

This project is based on the paper Chemical Recycling of Unsaturated Polyester Resin and Its Composites Via Selective Cleavage of the Ester Bond(Wang, Cui et al. 2015).

Though it has been discussed in my previous project it is necessary to cover some of the main points to facilitate the understanding of the reader.

The aim of the process is selective cleavage; that is to break up the polyester molecules into suitable blocks which can be used again. This is done by a reaction with Acetic acid and a Lewis acid catalyst.

The process revolves around the selective cleavage of the C-O bond. A Lewis acid catalyst is used because of the double bond.



Figure 2 Selective Cleavage(Wang, Cui et al. 2015)

The suggested mechanism is shown below. The Al 3^+ acts as a Lewis acid and donates a pair of eletrons to the oxygen distrupting one of its covalent bonds and leading to the formation of a carbenium ion. The acyl exchange reaction takes place between acetate ions and ester bonds resulting in the cleavage of C–O bonds . The molecules then resonate between the forms shown eventually breaking up to the separate molecules and returning the catalyst.

The mechanism was deduced by examining an infra red spectrum of the degraded products which showed various resinonat peaks which correspond to particular bonds.



Figure 3 Suggested Reaction (Wang, Cui et al. 2015)

There were two experiments, one with the resin of Poly-maleic anhydride-phthalic anhydride-1,2propylene glycol cross-linked with styrene (PMPPS) and one with the corresponding glass fibre reinforced polymer composites (GFRP). The only difference being that glass fibres resulted from the experiments with (GFRP).

One of the apparent difficulties for industrialisation is the use of tetrahydrofuran (THF) and an ultrasonic cleaner to extract the aluminium catalyst from the reaction mix. THF is a very dangerous chemical particularly if it has not been stabilised, and in the details of the experiment there is no indication of the amount used.

The other extraction of the second product required the addition of water and further filtering. The glass reinforced plastic which was used in the project has fire retardant. There will therefore be other chemicals present.

It would be useful if all the products can be recuperated by fractional distillation.

Automatic Glass Fibre Length Measurement for Discontinuous Fibre Reinforced Composites ((Giusti, Zanini et al. 2018) describes a method of examining the residual glass fibre length in an injection moulded part. The process started by taking a sample from the moulded part. The matrix from the sample was then burnt off by using pyrolysis. The recovered fibres were then dispersed using ultra sound before they were placed on a scanner and scanned. The image was treated by a program CT-FIRE, which is supported by Matlab in order to obtain the individual fibre lengths automatically.



Figure 4 Main steps of the fiber length measurement technique (Giusti, Zanini et al. 2018)

The techniques used here are of interest to this project, particularly the method of dispersion the fibres and the measurement of the fibre lengths because both techniques can be applied to the recycled fibres in the experiments.

Scientific Investigation

Chemical separation

Procedure

The aim of these initial experiments was to confirm that the method of selective cleavage of the polyester molecules worked. There were two procedures used to try to achieve the selective cleavage.

In the original research an autoclave was used to heat the reaction mixture. This was also used in this project, but an attempt was also made to use a microwave digestor to achieve the same result more efficiently. The microwave digestor proved to be an unreliable piece of equipment, therefore the autoclave was used to test the effect of changing the reaction times and temperatures and the effect of removing the catalyst.

The procedure used for both options were similar, but the method of heating was different in so far as the digestor used microwave, and the autoclave was heated by an electrical heating element.

A catalyst of aluminium chloride (AlCl₃) of 2g mass was added, inside a fume cupboard, to the respective vessels, then the acetic acid (CH₃OOH) was gradually added to achieve the required 10% ratio of catalyst to acid. On one occasion however, this concentration was effectively increased to 25%. The messured fibreglass samples were added to the reaction vessels which were then closed.

Some of the samples were then heated in the microwave digestor at 180 $^{\circ}$ C for several periods of 180 minutes, the maximum possible, time.

The samples placed in the autoclave were heated at different temperatures up to 220°C for times ranging from 12 hours and above.



Figure 5 Microwave digestor



Figure 6 Autoclave

After the heating process in the autoclave the liquid produced was removed and kept for further analysis. The remains of the samples were washed in hydrochloric acid (HCl) and water, 3 times, as indicated in the original research, dried. examined under a microscope and photographs taken.

The liquid produced in the reaction vessels of the microwave digestor was collected, then centrifuged.

Discussion of results.

The results of the microwave digestor system were somewhat disappointing. It was assumed that there would be a gradual reduction in weight of the fibreglass samples but what in fact occurred was an increase.

This can best be illustrated by considering the experiment conducted on 01-10-18.

A total of 6 samples were used. Samples 1- 4 were heated in the microwave digestor , and 5-6 in the autoclave The samples in the autoclave consisted of one ground sample and one block sample. A sample 7 was left to soak in acetic acid overnight to have a comparison.



Figure 7 Fibreglass samples

For each sample the catalyst AlCl₃ was individually mixed with the acid to get a precise concentration. The concentration used was 2g of AlCl₃ to 8g og CH₃OOH.



Figure 8 Mixing of chemical

The samples in the microwave digestor were heated for 90minutes at 180°C. It was not possible to heat more than that time because the machine developed a fault which could not be overcome. The samples from the digestor were weighed after being allowed to dry for 24 hours

The samples in the autoclave were heated at 180°C for 21 hours.. These samples were found to have completely degraded. The resultant fibres were washed in dillute hydrochloric acid and water to clean them.

The following changes in sample mass where obtained.

Table 1 Samples

Sample	Form	T=0	T= 90mins	Drying time	Equipment
1	Block	0,87g	1.35g	21 hours	Digestor
2	Block	0,91g	1,43g	21 hours	Digestor
3	Block	1,2g	1,70g	21 hours	Digestor
4	Block	0,52g	0,69g	21 hours	Digestor
5	Block	1,45g			Autoclave
6	Powder	1,03g			Autoclave
7	Block	0,75g	0,81g after		Soaked 21
			soaking		hours



Figure 9 Sample 2 after drying

The samples of the cleaned fibres are shown below



Figure 4 Fibres from Sample 5



Figure 4a Fibres from Sample 6

The concentration of catalyst was 25% not 10%, and the decomposition time was almost double that used in the original research. This may be significant in the formation of the large amount of precipitate which formed over the samples as shown in Fig 3.

To check that weight gain was not simply due to absorption of acetic acid one sample was soaked for 21 hours. It can be seen from the results in Sample 7 this produces less weight increase in comparison to Samples 1-4 that were heated.

The reaction in the autoclave proved successful and fibres were recovered. It can be seen from the photographs that the effect of passing the fibreglass into a shredder before processing does not improve the result.

The samples were examined under a microscope and compared with a sample of virgin fibre.



Figure 10 Recycled fibre

The above photo shows that there remains some residue of matrix and the fibres are inter-messed which is to be expected as the sample was originally manufactured by pulsion. This can be compared with the virgin fibres donated by Fiberline.



Figure 11 Virgin Fibres

The fluid obtained from both processes was collected and centrifuged.



Figure 12 Solution after centrifuging

In order to find which chemical components were in the liquid residue an attempt was made to examine the fluid after it had been filtered via a $1\mu m$ filter using a Bruker Ramen spectrometer but unfortunately there was too much fluorescents in the liquid to obtain a result. Some of the fluid was added to Sodium Bicarbonate with which it reacted vigorously, showing the presence of acid in the solution.

The use of the microwave digestor was abandoned and an attempt to find the optimal time for the reaction in the autoclave was undertaken.

The first comparative experiment involved heating 2 samples of fibreglass of similar weight, sample1, 0,75g and Sample 2, 0,86g in a mixture of 2g AlCl3 and 20g CH3 OOH. The samples were measured inside a fume cupboard and placed simultaneously in the autoclave, at 12:33pm on 31-10-18, and heated at a temperature of 180°C. Sample 1 and 2 were removed from the oven at 10:44 the next morning and Sample 2 was then replaced in the oven to continue heating, and sample 1 left cool.

When Sample1 was opened the fibre, content was extracted by tweezers and washed in hydrochloric acid and then in water. The result can be seen below:



Figure 13 Sample1 after 22hours

It was observed that there were significant amounts of the block which had not decomposed. The sample was then replaced in the reaction vessel with the remaining Acetic acid and replaced in the autoclave while Sample 2 was extracted at 15:37

The second sample was cleaned and examined in a similar manner.



Figure 14 Sample 2 after 27 hours

The examination under microscope showed the following



Figure 15 Sample 1



Figure 16 Sample 2

These photographs would indicate that it is preferable to heat the mixture for a minimum of 26 hours at a temperature of 190°C.

The next samples were tested to see what would happen when the temperature was increased to 220° C.

The two new samples 1, and 2 had the respective weights of 1.01g and 1.02g were placed in a mixture of 2g of AlCl₃ and 18g of CH₃OOH. This concentration of catalyst was 11% by weight and it helped reduce problems with effervesce when filling the reaction vessels. The reaction vessels were placed in the autoclave at 5:21 pm on the 31-10-18. The sample 2 was removed at 10:43 am the next morning and sample 1 was removed at approximately 1pm the same day.

The resulting cleaned samples are shown below



Figure 17 Sample 1 and 2

The samples were also examined under the microscope



Figure 19 Sample 2

As can be seen from the above photos the extra 2 hours made no real difference.

A test was carried out to determine if the catalyst influenced the reaction.

Two further samples were prepared.

Sample 1 mass 0,61g was prepared without any catalyst but with 20g of CH₃OOH. Sample 2, mass 0,63g was mixed with 2g of AlCl₃ and 18g of CH₃OOH. The two reaction vessels were placed in the autoclave at 4:01 pm on the 1-10-18. The vessels were removed on the 2-10-18 at 11:51am. The temperature of the oven was 200°C.

The samples are shown below. Sample 1 is on the left and it has not fully decomposed unlike Sample 2 on the right.



Figure 20 Sample 1 and 2

The microscope examination confirms the effect of the catalyst on the Sample 2, and the result of no catalyst on Sample1.



Figure 21 Sample 2 with catalyst



Figure 22 Sample1 without catalyst

A final test was performed to check the effect of time.

Two more samples were prepared. Sample 1 had a mass 0,62g and Sample 2 with a mass of 0,63g. They were placed in their respective reaction vessels with 2g of AlCl₃ and 18g of CH₃OOH. The temperature used was 200°C.

Both vessels were placed in the autoclave at 6pm on the 2-11-18. Sample 2 was removed from the autoclave at 12:54am on 3-11-18. The sample removed and cleaned. The result is shown below.



Figure 23 Sample 2

Sample 1 was left until 3:01pm. It was observed that there was no remaining fluid in the reaction vessel and that the sample had only partially disintegrated. See below



Figure 24 Sample 1

The result was not expected. The lack of fluid indicates that leakage had occurred during the experiment. Therefore, the result cannot be considered reliable.

The initial research used THF (Tetrahydrofuran) to dissolve the resultant fluid from the reaction in an ultrasonic cleaner. The catalyst AlCl₃ is insoluble in the THF.

The THF available was not stabilised, it was therefore decided to try the effect of a small amount of THF, 5ml, with the equivalent amount of fluid from the reaction. The resultant fluid was then filtered. The precipitate obtained on the filter paper was photographed under the microscope. The result is shown below.



Figure 25 Filtered Precipitate

The precipitate was tested by dripping water onto it, since AlCl₃ reacts with water. There was no reaction. The indicates the precipitate is not AlCl₃.

Another interesting effect that was observed was the effect of mixing a sample of the reaction fluid, with ethanol. All the precipitate separated out immediately. This perhaps represents a better possibility of achieving separation than the use of the volatile THF.



Figure 26 Reaction fluid in ethanol

It can be deduced from the results that there is a balance between the reaction time and the cleaning effect on the fibres. It is clear from the results that 12 hours as in the original research is not adequate, but 24 hours results in a loss of the acid.

The increase in temperature from 180°C to 200°C produced a marginally improved result ensuring that all the catalyst was dissolved in the acetic acid.

A problem observed was the formation of a hard precipitate. This is a problem that would have to be resolved before industrialisation can be achieved. The solid precipitate could not be dissolved by hydrochloric acid or sodium hydroxide suggesting it is an organic compound.

Analysis of the fibres

Measurement of the fibres.

When chopped glass fibre is used in industry it is prepared from long rovings by cutting machines)(Masst ND). To have consistent mechanical properties it is desirable to have a consistent length of fibre throughout an injection moulded part.

It is therefore relevant to try and measure the lengths of the samples of recycled fibreglass and to find what is the variation in length. Adapting a method outlined in the article Automatic glass fibre length measurement for discontinuous fibre-reinforced composites (Giusti, Zanini et al. 2018)it is possible to make a comparison with the virgin fibre.

The scanned images were analysed using the program CT-FIRE supported by MATLAB and based on curvelet transform and FIRE algorithm. It can detect the individual fibres, even when they are bent or are crossing each other. The program was developed to measure collagen fibres. It traces on top of the photographs to show the fibres.

To examine the recycled fibres 4 samples were each placed on a scanner Epson XP-442 and individually scanned at 300 dpi.

The fibres were manually separated by tweezers, placed in a square 50mm x 50mm cut in 2 sheets of graph paper and then they were scanned.

A first attempt of scanning with higher number of dpi was tried but it had to be abandoned because of the excessive computer time required by the CT-FIRE program.

The traces of the recycled fibres are shown in the photographs below.



Figure 28 Recycled 1



Figure 29 Recycled 3



Figure 27 Recycled 2



Figure 30 Recycled 4

To check the calibration of the scanner a length of virgin fibres, were accurately cut to 25mm and scanned twice. The traces of those fibres are shown below:





Figure 32 Scan1

The lengths obtained are shown in the table

Table 2 Calibration Scan

	Scan1	Scan2
Median	41,647	41,814
Mode	30,181	30,438
Mean	86,33576	94,70081
Variance	7697,714	7618,305
Standard Deviation	87,73662	87,2829
Min	30,181	30,438
Max	315,19	291,79
Number of Fibres	21	16
Alignment		

The results for the recycled fibres were:

Table 3 Fibre length

	recycled4	recycled3	recycled2	recycled1
Median	52,412	53,465	47,22	59,295
Mode	30,537	30,332	30,195	30,156
Mean	57,05668	66,77708	55,08507	62,53917
Variance	523,6524	1375,608	672,8371	626,8723
Standard				
Deviation	22,88345	37,08919	25,9391	25,03742
Min	30,537	30,332	30,195	30,156
Max	138,94	196,65	132,12	132,02
Number of				
Fibres	53	60	27	29

Table 4 Fibre width

	recycled4	recycled3	recycled2	recycled1
Median	4,837	4,6257	4,518	5,3764
Mode	2,7807	2,3394	2,8075	2,4139
Mean	5,272975	5,163428	4,452119	4,963914
Variance	2,533315	3,071999	0,979223	2,718727
Standard				
Deviation	1,591639	1,752712	0,989557	1,648856
Min	2,7807	2,3394	2,8075	2,4139
Max	11,126	9,624	6,5342	7,7409
Number of				
Fibres	53	60	27	29

Table 5 Fibre angles

	recycled4	recycled3	recycled2	recycled1
Median	30,466	155,45	39,56	25,388
Mode	0	178,85	0	1,9415
Mean	59,46079	122,0448	64,94033	68,46902
Variance	3826,779	4329,655	3928,234	4591,183
Standard				
Deviation	61,86097	65,80012	62,67563	67,75827
Min	0	0	0	1,9415
Max	178,7	179,22	178,15	178,85
Number of				
Fibres	53	60	27	29
Alignment	0,545527	0,625767	0,370375	0,556488

Discussion of Results

The results obtained by the program cannot be considered accurate enough to be relied upon because the variation in the results is too great.

The attempts at calibration produced two different results for the same fibres, just repeating the scanning without moving anything.

The results obtained with the recycled fibres have a spread of data (standard deviation) which is enormous. However, using the calibration results obtained it gives a length of recycled fibre which is 15mm. That corresponds to the manually measured value. Manually measuring the recycled fibres gave lengths varying between 5 and 15mm.

The width of fibres would seem to be wildly inaccurate when compared to the lengths calculated. The width of fibres from the results gives a value of 1mm and typically fibres are between 3 and 20μ m diameter. (Wallenberger, Watson et al. 2001)

The testing of the fibres in thermo plastic

The fibres obtained by the recuperation process were of about 15 mm length.

All available methods for testing the tensile strength require enough length of fibre to be held in a grip which can produce enough friction to overcome the rupture strength of the fibre, hence this was not a viable solution.

To overcome the problem, it was decided to mix the recycled fibres into a thermoplastic test piece in the ratio of 15% by mass. As a comparison a second sample using hand cut virgin fibre was used.

Method

The method used for producing was vacuum forming. The mould was constructed on a glass plate as shown below.



Figure 33 Moulding Arrangement

An initial method tried was to calculate the volume of plastic that would fill the mould when it had become solid. The proportion of fibre to plastic in the first attempt was 10% by mass



Figure 34 Combined weight first test fibre and plastic

The mixture of plastic and fibre was added to the mould but was found to overflow the available area. Cloth was placed in strategic locations to avoid the production of air pockets; the surface was sealed with vacuum plastic and a valve installed to allow the air to be pumped out.



Figure 35 Moulding arrangement fully assembled

The air was then removed using the vacuum pump shown below, and the mould checked for leaks.



Figure 36 Vacuum pump

Once a partial vacuum of 500mb was achieved the tray was placed in the oven and heated while maintaining the vacuum.



Figure 37 Oven
The mould was then heated for a period of 30 mins at 205°C



Figure 38 Oven temperature

To improve the results in subsequent experiments the gap between the glass was adjusted to avoid overflow.

The proportion of fibre to plastic were increased to 15% The scrap HPDE was cut into as small pieces as possible to aid mixing

The proportions used for the recycled fibres are shown below





Figure 39 recycled fibres and plastic

The virgin fibres and the plastic were mixed manually as was the recycled fibres. **mathiasmoe**



Figure 41 Virgin fibres and plastic mixed

An extra glass plate was placed on the mixture and a separation cloth on top of that.



Figure 42 Assembly used in processing

The same heating procedure was followed.

Discussion of results

The resultant plates are shown below. The virgin fibres are shown on the right and the recycled on the left.

What can be immediately observed is that there were problems with the infusion of plastic into the fibres. The data sheet for the plastic stated the moulding temperature of the plastic had to be between 200°C and 280°C.



Figure 43 Virgin and recycled fibre blocks

To rectify the problem plastic was melted on to the recycled fibre test piece, using a blow torch. This did not give a satisfactory result as the sample became more brittle.



Figure 44 Blocks after repair attempt

There was pointless to load test the samples because apparently no bonding had occurred between the fibres and the plastic in either sample.

Analysis of the liquid residue

The determination of the liquid residue was carried out using gas chronometry. The work was carried out at Højvang Laboratorier in Dianalund.

The process chosen to examine the liquid produced was Gas Chromatography GC/MS with a quad pole unit mass detector.

The sample was dissolved in Dimethylacetamide then injected into the inlet pot.

GC/MS begins with the gas chromatograph, where the sample is volatized. This effectively vaporized the sample and separates its various components using a capillary column packed with a stationary phase. The compounds were propelled by an inert carrier gas. As the components became separated, they diffused from the column at different times, which is referred to as their retention times.

Once the components left the GC column, they were ionized by the mass spectrometer using electrons. Ionized molecules were then accelerated through the instrument's mass analyser, which was a quadrupole ion trap. It was here that ions were separated based on their different mass-to-charge ratios.

The final steps of the process involved ion detection and analysis, with compound peaks appearing as a function of their m/z ratios. Peak heights, meanwhile, are proportional to the quantity of the corresponding compound. Using computer libraries from the mass hunter program the compounds present where detected.

The precipitate was tested and found to contain 3,7% by weight aluminium. This was done using inductively coupled plasma mass spectrometry. The sample was injected into a plasma stream (Inductively Coupled Plasma (ICP)) which fully decomposed it into its constituent elements and those elements into ions. The analysis of the products was carried out in a similar way to the CG/MS process.

Discussion of Results

In the first run the complete spectrum was recorded and the following was observed.

The spectrum showed that the highest presence was acetic acid. In the case of the sample where THF was used THF showed the highest concentration.

The presence of two of the three components that were discussed in the original paper. 1,2-Benzenedicarboxylic acid and 1,2-Propanediol, diacetate, was identified using mass hunter.

However, the chain molecule poly-maleic anhydride-phthalic anhydride-1,2-propylene glycol crosslinked with styrene, was not found. This could be because it does not vaporize and is trapped in the inlet of the GC, or it is fractured in the analysis during EI and have fragments like those of the two identified components a further reason could be that the polymer component itself is out of range for the analysis. The machine used can only scan from 40 to 550. A further run was completed to obtain a clean spectrum. The results confirmed the presence of the two previously mentioned chemicals.

Spectrums



Figure 45 Propanediol diacetate spectrum



Figure 46 Benzenedicarboxylic acid Spectrum

Industrialisation

Design Constraints

The recycling process involves the heating of solid fibreglass in acetic acid. Therefore, it is necessary to consider what kind of reactor that would be required, as there is nothing available on the market.

The design constraints can be divided into fixed and variables.

Fixed Constraints

The reactor must withstand a pressure of 10 bar and a temperature of 200°C.

The material used to construct the vessel must be resistant to the chemicals

A safety valve which will release the pressure safely is required.

The electrical immersion heater along with all other electrical installations must conform to ATEX requirements.

A system to flush acid fumes from the reactor once the process is finished.

A basket is required to contain the fibres once the process is completed.

Variable Constraints

The time to heat up the reaction fluid.

A degree of thermal insulation on the parts which will be handled by the operator.

Thermal insulation to hold heat in the reactor.

Construction details

A possible solution for the design of a reactor is shown below.

The structure is made by using a standard pipe of bore diameter $30^{\prime\prime}$ and a $30^{\prime\prime}$ to $24^{\prime\prime}$ reducer in Aisi grade 316 stainless steel, which can resist acid.

The immersion heater is a standard immersion heater of 20KW made of AISI grade 316 stainless steel, from the Wattco company (see Appendix).



Figure 47 Reactor



Figure 48 Basket and Reactor

Calculation of heat required in the recycling process

Time to heat up the reaction mixture:

The time to heat the reaction mixture to 200° C is dependent on the specific heat capacity of the acetic acid and the metal of the reactor and the heat lost by convection on the surface of the reactor assuming a room temperature of 20° C.

Data

Specific heat capacity of acetic acid is approx. 121 J/mol*K I mole acetic acid = 60.05gTherefore Cp_{Acetic}= 2014 J/kgVolume = $0,68m^3$ Density = $1050Kg/m^3$ Mass (M_{Acetic})= 714 KgMass of stainless steel (M_{stainless})= 1307KgSpecific heat capacity (Cp_{stainless}) = 500 J/kgThermal Conductivity (K) =13.4 W/m-KCylinder height(L)=1,6mOuter diameter(D)= 0,76mUsing surface area As

$$A_s = \pi DL = \pi \times 0.76 \times 1.6 = 3.83m^2$$

The heat loss through conduction is given by

$$Q_{conduc} = kA \frac{(T_{\infty} - T_{Internal})}{t} = 13,4 \times 3,83 \times \frac{(20 - 200)}{0,00635} = 1454796W$$

t is the wall thickness= 0,00635m

Room temperature $(T_{\infty}) = 20^{\circ}$ C

Reaction temperature $T_{Internal} = 200^{\circ}C$

With no insulation

There is a need for installation jacket, referring to the Norwegian standard R-004(STANDARD 1999)

The insulating material is either cellular glass which conform to ASTM C552 and is suitable for temperatures from -260 °C to 430 °C.

Thermal conductivity, not greater than 0,0039 W/m-K as per ASTM C177 Average compressive strength per ASTM C165: 490 kPa.

It is recommended in the standard for diameters of 600mm and above thickness of insulation should be 80mm.

To calculate the heat flow with an insulating jacket applied it is assumed that the outside metal surface of the reactor is at 200 °C and the temperature of the room is at 20°C. The material used is cellular glass from the above standard in the jacket.

$$Q_{conduc} = kA \frac{(T_s - T_{Internal})}{L} = 0,0038 \times 3,83 \times \frac{(20 - 200)}{0,08} = 32W$$

Neglecting natural convection losses which will be minimal

The energy required to raise the temperature of the reaction and the reactor from $T_{room}=20^{\circ}C$ to $T_{reaction}=200^{\circ}C$ is given by the following:

$$Q_T = ((M_{Acetic} \times Cp_{Acetic}) + (M_s \times Cp_{Stainless})) \times (T_{Reaction} - T_{room})$$
$$Q_T = ((714 \times 2014) + (1307 \times 500)) \times (200 - 20) = 376469280J$$

This show that it will take 5,24 hours to reach the reaction temperature of 200°C with the 20KW immersion heater.

If one considers the reactor must run for 12 hours after reaching temperature of 200°C, then the energy used per batch treated will be

$$= (12 \times 60 \times 60 \times 32W) + 104.607 = 376584480J = 1487Kw$$
 hours

Structural Analysis

The structural integrity was studied using the non-linear package Finite element in Autodesk Fusion 360. The results show that the construction is feasible based on the 10bar pressure of Acetic acid at 200°C.



Figure 49 FEA Analysis

The separation of the fluid products.

The principle constituents of commercial interest are the three molecules mentioned in the original research ((Wang, Cui et al. 2015)which are 1,2-Benzenedicarboxylic acid and 1,2-Propanediol, diacetate. The poly-maleic anhydride-phthalic anhydride-1,2-propylene glycol cross-linked with styrene appears to have broken into smaller molecules. 1,2-Benzenedicarboxylic acid has a boiling point of 289°C and 1,2-Propanediol, diacetate boils at 56.9 °C. The boiling point of acetic acid is 118°C.

The simplest way to separate these chemicals from each other would be to use a still and successively boil off each chemical. However, if vacuum distillation is used the boiling points are lowered and the chemicals risk less degradation.

A partial vacuum is produced over the surface of the fluid. The vapour is passed through a series of condensers which remove each chemical in reverse order to the boiling point.



Figure 50 Solvent Recovery System Using Dry Pumping System (Group 2013)

This system would just require the purchase of a vacuum pump and some simple heat exchange condensers.

Commercial Potential

Introduction

To obtain finance for the development of the recycling process it is necessary to develop a business model that will convince potential investors that they will not lose their money.

The nature of scrap is that it is mostly not produced continuously.

Any business which wishes to address the customers' needs must have a collection service.

There are 4 design drivers and constraints that should be considered (Pigneur 2010)

- market forces
- industry forces
- key trends
- macroeconomic forces

Market Forces:

Market issues

The main issues effecting the market must be the price at which the alternative solutions can operate their services. This is a major threat to the viability of this recycling process.

Market segments

The market segments can be obtained from data on the use of fibreglass in Europe



Figure 51 Breakdown of glass fiber reinforced plastics (GRP) production in Europe (EU) (CCeV 2017)

The actual amount produced each year is shown in the diagram below



Figure 52 Production volume of glass fiber reinforced plastics (GRP) in Europe (EU)(Kunststoffe 2017))

There are no actual statistics showing the amount of fibre reinforced plastic being produced each year but by looking at the actual production and assuming a life of 10-15 years it is possible to estimate the potential amount of scrap produced.

The use of GRP by the transport sector and by the construction industry are the most significant followed by sports & leisure and electronics.

The automotive industry is governed by the End of Life Vehicle directive (Commisson 2018)which requires 95% by weight to be recycled. That represents a considerable customer potential on the surface, but the industry uses only chopped fibreglass in injected moulded parts as only these are suitable in the rapid production required and the plastics used are not necessarily made with polyester resin.

The building industry uses fibreglass for the manufacture of water tanks, shower trays, baths, thermal insulation and the manufacture of structural profiles. The profiles are made by an extrusion process known as pulsation. The tanks, shower trays, and baths are made by hand, with the use of a plug.

The obligation to recycle 70% of building materials by weight from the year 2020 may give an incentive to the demolition companies to consider recycling of fibreglass, but by its nature fibreglass is low weight, therefore it will possibly not be the first material selected for recycling.

In the leisure industry there is an interesting prospect particularly in the case of glass reinforced plastic boats. In its document: European Strategy for Plastics in a Circular Economy(Commission 2012)it is stated that 'in the case of recreational boats of which there are 80,000 boats per year that are at the end of their lives, apparently only 2000 are correctly dismantled. This leaves a significant litter problem in the ocean'.

The definition of a disruptive innovation is one which will provide a service to a section of the public who does not have access to that service.

Recreational boat owners represent probably the best customer potential. The owners usually have money and will probably only have to deal with the problem of decommissioning a boat a few times in their lives. At present they have very few options for disposal of their vessels.

The Eu financed research into the end of boat life in the Boat cycle project (Commission 2012).

The report concluded that it would be impractical to consider recycling glass reinforced composite hulls, but it would be best to concentrate on designing 100% recyclable designs. They did not mention how they planned to achieve this, but unless they propose to return to wooden or steel hulls there appears to be no immediate alternative.

In conclusion, to target the leisure boat industry to start a business would be the most logical course. A later step would be to upscale to include the building industry.

Needs and demands

There are no statistic relating to the amount of glass fibre waste produced in Europe, but it can be assumed from the statistics about production to be about 1 million tons per year that will return as scrap over 10 to 15 years.

The present methods of dealing with scrap is to burn it or co process it in cement manufacture.

The cost of incineration is low. City Containers A/S, a chemical disposal company, was kind enough to give the total price for the disposal of 1000kg of fibreglass as 640DKK and 1100DKK for use of a container. The process used is to crush the waste then use it in the district heating furnace.

The company Neowa charge 165€. per 1000kg to co-process scrap GRP.

A third company Roth International who crush the waste then use the crushed product to dilute virgin material charge 145€. per 1000kg.

At present there is no extra requirement for more capacity, but the decommissioning of more wind turbines will change this, and the recycling targets set by the European Union previously mentioned.



Figure 53 (Topham and McMillan 2017)





Switch costs

The process proposed uses more energy than simple incineration or co-processing, therefore it will be more expensive. However, the process is recycling not energy recovery. Therefore, it is preferable when considering the requirements of the circular economy. There is no extra investment required by the clients because they will need a collection and removal service regardless.

Revenue attractiveness

The willingness to pay more than the current disposal price will probably be very small and will require pressure from the legislation.

Industry Forces

Competitors

The competition to the new process can be considered as coming from incineration and coprocessing.

The cost of incineration of fibreglass can be analysed by adapting the study of a waste to energy plant in Croatia (Schneider, Kirac et al. 2012). The results are relevant because glass reinforced plastic has low calorific value and when burnt the residue must be disposed of.

The conclusion reached was that 'taking into account given parameters that determine revenues and costs, it could be seen that the waste to energy plant based on the technology of the combustion on the grate becomes marginally viable (with the annual capacity of 100.000 tonnes of waste) for the values of gate fee above $105 \notin/t$, if the costs of loan repayment (6% interest) are included'.



Figure 55 Price sensitivity (Schneider, Kirac et al. 2012)

It should also be noted the profit obtained from the installation (initial cost 52.100.000) is highly sensitive to the price.

The method of co-processing uses the substitution of fibre glass in the place of silicon dioxide, in the manufacture of cement. It was found that the only problem issue was the presence of boron in the E glass fibre used for reinforcement in the composite. Too much boron in cement can increase the time for the cement to set, although the ultimate strength is not affected. It was concluded from the study that if the use of composites in cement manufacture did not result in more than 0.2% boron oxide in the cement then there would not be a significant effect on the performance of the cement. This would mean that no more than about 10% of the fuel input to a cement kiln could be substituted with polymer composite material (Pickering ND).

Other drawbacks mentioned with co-incineration in cement kilns are that they rely on the GFRP waste being smaller than a designated size (20 mm_20 mm) and contain low concentrations of toxic materials or heavy metals; and no foreign materials (such as metal inserts or fasteners). It must have a specific calorific value (higher than 5000 kcal/kg), and must not generate dust such as pulverized glass fibres (Nomaguchi 2001)

New Entrants

The process studied is not protected by any patent, so it is relatively simple for a new entrant to enter the market and then begin to scale up the business.

Substitute Products and Services

There is a possibility that bio-degradable composites will eventually replace glass reinforced composites, or carbon fibre will become cheaper to use but probably not in the immediate future.

Suppliers and other value chain actors

The principle suppliers are the chemical companies which supply the acetic acid and aluminium chloride. The other main supplier is the electrical energy supplier. On the customer side there will be two principle groups, those who uses the fibres and the other being those who use the chemicals.

Stakeholders

The stakeholders will consist of the customers requiring scrap removed, the government environmental agencies who will require detailed applications and the clients for the recycled fibre and chemicals.

Key trends

Technology trends

There is one main technology which could superseded the recycling process technology and that is the use of enzymes to break down the polyester matrix. However, in my previous research I had the opportunity to test my fibreglass sample with an enzyme at the University of Leipzig. It was not successful, and a recent report from Japan shows that their enzyme could only remove 6 micrometres of PET in one week.

Another possibility which will probably render this process redundant is if biodegradable composites become readily available.

The large-scale production of cellulosic fibre composites is still limited by two important issues: compatibility with the polymer matrix and water absorption.(Melo, Carvalho et al. 2012) The technical challenge with these composites is to produce something which can survive in the environments without breaking down and can be degraded later.

Regulatory trends

The legislation which would govern recycling activity is driven by the directives from the European union.

The regulations covering the treatment of waste are outlined in the Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste, which was amended in 2008 and is still in force according to the document website of the European Union(Commission 2016)

Article 3 Paragraph 17 of the directive defines recycling as any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes, and specifically excludes conversion of the waste into energy.

Article 4 paragraph 1 defines the waste hierarchy in the following well known manner

- prevention;
- preparing for re-use;
- recycling;
- other recovery, e.g. energy recovery; and
- disposal.

It should be noted that in Article 4 paragraph 2, it states that when applying the hierarchy member states 'shall take measures to encourage the options that deliver the best overall environmental outcome'. This allows life cycle analysis to justify the deviation from the hierarchy.

In the directive preambles in paragraph 29 the following obligation is applied requiring Member States to support the use of recyclates, in line with the waste hierarchy and ´should not support the landfilling or incineration of such recyclates´.

The document is of interest for this project because it gives the framework of waste treatment and provides an argument which can be deployed to counter the present practice of incinerating waste glass reinforced plastic and or co-processing it.

The other document has recently been produced by the European Union is A European Strategy for Plastics in a Circular Economy(Commission 2018). The document outlines new objectives. These new initiative on plastics aims to address three interrelated issues:

- High dependence on virgin fossil feedstock,
- Low rate of recycling and reuse of plastics, and
- Significant leakage of plastics into the environment

Rozalina Petrova, the Policy Officer of the Waste Management & Secondary Materials DG Environment of the European Commission, was kind enough to advise me of the following: To implement the waste hierarchy the EU legislation defines targets for some waste streams; in the waste directive.

Relevant to fibreglass is the 70% material recovery target for construction and demolition waste by 2020 established in the Waste Framework Directive(Commission 2016) in Article 11.2.

There are also targets for end-of-life vehicles (Commisson 2018) which in Article 7 requires up to 95% recycling by weight. The electrical waste (Commission 2018) is probably less relevant because printed circuit boards are made of glass reinforced plastic, but they also contain copper which is outside the scope of this project.

Social and Cultural Trends

It is very difficult to find anybody who will declare themselves not in favour of environmental protection, particularly people with children. It would seem reasonable that any company which uses glass reinforced plastic would for its brand image be interested in having it associated with lowest environmental impact.

Due to the concern about the environment a new marketing trend of green marketing has developed., This has opened an opportunity for companies to follow this trend (Finisterra do Paço and Raposo 2010)

- The reasons which companies decide to get involved with green products:
- compliance with environmental pressures;
- obtaining competitive advantage; improving corporate images;
- seeking new markets or opportunities; and enhancing product value. (Chen 2010)

Therefore, the green market has become an important new market business to those companies as there is a demand for more environmentally friendly products, which are also known as green products.

In an article The Review of Green Products in Market, Advantages and Disadvantages (Mun and Yazdanifard)quote research that shows

People have become more willing to pay for green products (Chen and Chang 2013). Their willingness to buy green products will be greater than to buy traditional products as the consumers in the contemporary world marketplace generally exhibit a heightened awareness of environmental issues and consequently experience significant levels of environmental concern(Lin and Chang 2012).

It is also mentioned in the article that, 'consumers are more willing to purchase green products because green products have the least impacts and harmful effects toward the environment and human health (Chen and Chang 2013).

This article goes on to mention the gap between consumers intentions and their actual purchasing behaviour. One reason that influences consumers to not to buy green products is that consumers may consider green products to be less effective than conventional products (Lin and Chang 2012). A further apparent influence on the customer's choice is the perception of false claims and advertising, therefore, consumers try to punish marketers who deceive them with false ecological claims by not purchasing green products (Tucker, Rifon et al. 2012).

This leads to the situation 'where, one study suggests that though 40% of consumers report that they are willing to buy "green products," but only 4% actually do so'. (Luchs, Naylor et al. 2010)

Using this information, it should be possible to develop an honest marketing strategy which cannot be demolished.

Macro-Economic Forces

The global market conditions for recycling of plastics

The OECD produced a report Improving Markets for Recycled Plastics (OECD 2018)in which it outlined various recommendations to improve the recycling of plastic. It is not possible to obtain the same analysis for just glass reinforced plastic, but the barriers to recycling are interesting to consider.

The first barrier is that there is no differential demand for recycled plastics. This is partly a consequence of the cost structure of recycled production, but also reflects virgin plastics prices that are highly volatile and perhaps too low to reflect all external costs. The solutions recommended are

• Taxes on the use of virgin plastics or differentiated value added taxes for recycled plastics or plastic products;

- Reform of support for fossil fuel production and consumption;
- Introduction of recycled content standards, targeted public procurement requirements, or recycled content labelling;
- Creation of consumer education and awareness campaigns (concerning the environmental benefits of recycled plastics) to stimulate demand for products containing recycled plastics.

The second obstacle is the uncertainty about the availability and quality of the recycled product to remedy this problem

- Creation of certification standards for recycled plastics;
- Facilitation of better coordination and communication across the plastics value chain, including through the promotion of chemical information systems;
- Restrictions on the use of hazardous additives in plastics manufacturing.

The third problem identified is that the cost of recycled plastics production is relatively high. The main contributor to the relatively higher cost is identified as the fact that the waste must be collected over a large geographical area. The relevant policy changes are

- Introduction of more ambitious recycling rate targets and harmonization of the methods used to calculate these rates;
- Increased stringency of landfill and incineration fees to better reflect the full social cost of these activities.

The fourth barrier is that 2 billion people in the world have no access even to a basic rubbish collection system.

This is not relevant to the present case because fibreglass is used in the developed world.

Capital Market

In Denmark there are two possibilities to obtain government assistance funding, one through then innovation fund, the other is the Green innovation fund.

The innovation fund is the only real possibility for start-up firms as it will back people for one year with a grant of 1500DKK per month and free office space. The Green Fund will assist an established company to expand their production.

Another alternative is the use of crowd funding which is relatively cheap to obtain but it depends on the sales promotion used.

Commodities and Other Resources

The process depends on three elements, two chemical and one of energy. The main chemical used in the process is acetic acid which is widely used in the food and plastic industries. The price of the aluminium chloride is 265DKK per Kg (VWR International) and that of the acetic acid is 1800DKK for 20L. The price of electricity is $0.086 \in (0.61DKK)$ per Kw hours (Eurostat)

Economic Infrastructure

The infrastructure in the western part of the European Union is not a significant challenge. There are well-functioning roads and electrical power supply networks.

The method used to analyse the business model of the project is shown in the canvas below which was developed by Alexander Osterwalder and Yves Pigneur.



Figure 56 Business Canvass (Pigneur 2010)

Key Parterners

The key partnership that would be necessary to consider are the energy suppliers and the chemical suppliers of the acetic acid and aluminium chloride which are used in the process. It may also be necessary to deal with a chemical waste from the precipitate produced; therefore, a reliable chemical disposal company should be considered.

Key Activity

The key activity of any company using this technology would be the processing of scrap polyester resin glass reinforced plastic into marketable by-products.

Key Resources

To work with the process the company will need a collection service for the scrap, a building and the required process machinery reactor and a vacuum distillation system, and finally a distribution service

Value Proposition

The value proposition for this process is that all the glass reinforced composite is reused so none of it is burnt or used as fuel in recuperation.

The value proposition is aligned with the potential customers' needs, they all have fibreglass they need to scrap, and they need to be seen to respect the environment.

The main weakness of the value proposition is price compared with the competition from coprocessing and incineration.

The opportunity for the process will increase due to the increasing restrictions on landfill in Europe. There will be further opportunity if the possibilities of co-processing become saturated due to the largescale decommissioning of wind turbines, but what would really start a network expansion of the process would be that incineration becomes prohibitively expensive, or preferably illegal.

A further problem with the proposition is that process has no intellectual property rights protection, therefore, it can be copied by others.

Customer Segment

There are two basic sources of scrap reinforced glass fibre; that produced during manufacture in firms such as Tuco Marine in Svendborg, who told me they have a full skip collected once a month.

The other source of punctual demand will occur when glass reinforced composite products reach the end of life. An example of this are owners of boats which have come to the end of life and are faced with the same disposal problem,

The building industry can also have a need to dispose of solid glass reinforced composite waste. Fibreglass is used in the manufacture of bathtubs, tanks, swimming pools amongst other things, and with the new requirements of recycling imposed on the industry it would be a growing sector.

The customers for the recycled products are divided into two groups, the glass fibres and the recovered chemicals.

The fibres recovered were found to be in clumps and no method was found to separate. It would therefore seem logical to sell the fibres as scrap glass for which there is a market.

The other, possibly more, interesting market is for the chemicals.

Phthalic acid is used mainly in the form of the anhydride to produce other chemicals such as dyes, perfumes, saccharin, phthalates 1,2-Propanediol, diacetate is used as a solvent for glues, paints and nail polish remover.

Customer Relationships

The customer relationships in this kind of business would primarily be business to business. There may be the odd member of the public that wish to scrap their boat, but by having contact with the firms which sell new boats it would be possible to pick up scrap contracts when owners change their boat. The purchasers of the chemicals produced would have to be a chemical retail company.

Channels:

Appropriate trade fairs can enable the right contacts but of course this option costs.

A much cheaper option to communicate the advantage of this process would be to write articles on LinkedIn and have a good homepage with a well-chosen set of landing words. It is a relatively cheap solution in comparison and can allow the information to filter through to the decision makers in potential customers.

There are various awards competitions that can be entered. You may not win but it gives exposure.

Facebook is another good medium on which to write articles and inform the general-public.

Joining a business network like Anglelist.com or other networks could help make the right contacts.

Cost structure

The fixed cost of the business would be the plant and the machinery, and personnel cost for the people working there. The variable costs will be those that vary according to the amount of fibreglass processed. These will be for solvents used and electricity and transport

Revenue flows:

The revenue from the glass fibres would be a minimal 34 €s per 1000kg as it is scrap glass.

It would be possible to charge the customer a price comparable to that of the Stena company who were kind enough to quote me a price of 1900DKK per 1000 kg plus transport

The main running costs would be for the energy used in the process and the purchase of the chemicals.

The energy used per production run is 1487 Kw hours at a price (0,61DKK) per Kw hour which means the price per batch would be 907 DKK.

The price for the acetic acid based on the reactor volume of 0,68m3 acetic acid will be 6120 DKK. The aluminium chloride is10% of the weight of the acetic acid, 71,4Kg therefore the cost would be 18921DKK. This amount could be reduced by recovery of the catalyst from the precipitate.

The volume of the basket for the glass reinforced fibre scrap is 0,47 m3. If the volume of scrap is $0,3 \text{ m}^3$ the weight would be 537 kg.

If it is assumed that the 70% of scrap is glass the resale price would be around 20€ (149DKK)



1,2-Benzenedicarboxylic acid is sold by the chemical company Merk for 1320 DKK per kg and 1,2-Propanediol, diacetate for 248 DKK per litre.

Conclusion of the Project

The project set out to test the practicality of the recycling process described by the original research (Wang, Cui et al. 2015) with the use of commercial glass reinforced composites.

The process was found to work but there are other factors which must be considered:

- The quality of the recovered glass fibres was unsatisfactory for reuse for any other use than recycling as glass scrap. Further research is needed to find an effective separation method.
- An effective method of recovering the catalyst from the precipitate needs to be developed to make the process more economically viable
- At present the competition is significant because it is still possible to incinerate fibreglass. However, this will change in the future.
- The chemicals recovered show the best potential for making the process financially viable.

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Appendix



Tel: 514-488-9124 clients@wattco.com 1-800-492-8826

QUOTATION Quote Number: Q1882645 Date: 11/22/2018 Page: 1 of 2 Project Name: 1 Sales Rep: RD

University of Southern Denmark Sorøvej 29 Ruds Vedby DENMARK

	QUOTED LEADTI	ME		
	4-5 WEELS			
				EXTENDED
PART ID	DESCRIPTION	QUANTITY	PRICE	PRICE
FLI	VATTCO DIN250 (10") FLANGE HEATER (15 HAIRPIN ELEMENTS) 20 KW, 380 V, 3 PH (30.4 AMPS) (DENSITY 14.95 WATTS/SQ. IN.) (ACETIC ACIDAPPLICATION) (1 CIRCUIT) ANSI 150 LBS (STAINLESS STEEL 304 MATERIAL) FLANGE 5" STANDOFF 0.430" O.D. TUBE DIA. STAINLESS STEEL 316 SHEATH MATERIAL 39" IMMERSED LENGTH, 6" COLD SECTION THERMOCOUPLE TYPE K FOR TEMPERATURE CONTROL OR HIGH LIMIT CONTROL NEMA 7 (EXPLOSION PROOF – C1 D2 Gr B,C,D - HAZLOC CLASSIFICATION) ENCLOSURE WITH GASKET	1.00	6,495.00	\$6,495.0U
	MODEL # FLI1520X1439-TX			
	OPERATING PRESSURE: 145 PSI (10 BAR) OPERATING TEMPERATURE: 392 F (200 C) ASME STAMP NOT INCLUDED			

QUOTE IS VALID FOR 2 WEEKS.

Subject to WATTCO Terms and Conditions - latest version found at www.wattco.com/terms-and-conditions FOB: OUR PLANT DELIVERY: TBD Freight at your expense - Please notify us of your preferred transport and account number. Please sign a copy of this quote and return with your P.O. when you are ready to place your order.



QUOTATION Quote Number: Q1882645 Date: 11/22/2018 Page: 2 of 2 Project Name: 1 Sales Rep: RD

University of Southern Denmark Sorøvej 29 Ruds Vedby DENMARK

	QUOTED LEADTI	ME		
	4-5 WEELS			
PART ID	DESCRIPTION	QUANTITY	UNIT PRICE	EXTENDED PRICE
CTL1	CONTROL PANEL WATTCO CONTROL PANEL NEMA 4 BOX TYPE (MOISTURE RESISTANT) OTHER COMPONENTS: - MAIN DISCONNECT - CTRL TRANSFORMER - (1) CONTACTORS AND FUSES FOR - (1) LOADS OF 20 KW, 380 V, 3 PH - (1) TEMPERATURE CONTROLLER - (1) HILIMIT CONTROLLER - (1) 2 POSITION SELECTOR SWITCH "OFF-ON" - (1) GREEN LIGHT FOR "HEATER ON" - (1) RED LIGHT FOR "HEATER ON" - (1) RED LIGHT FOR "HIGH LIMIT" - JUNCTION TERMINALS FOR THERMOCOUPLES TYPE K - WIRING DIAGRAM	1.00	1,895.00	\$1,895.00
	CSA OR UL CERTIFIED	GRAND T	OTAL:	\$8.390.00 USD

QUOTE IS VALID FOR 2 WEEKS.

Subject to WATTCO Terms and Conditions - latest version found at www.wattco.com/terms-and-conditions FOB: OUR PLANT DELIVERY: TBD Freight at your expense - Please notify us of your preferred transport and account number. Please sign a copy of this quote and return with your P.O. when you are ready to place your order. ALL TAXES EXTRA

Experimental Report 21-9-2018

Introduction

The experiment involved the use of a microwave digestor to degrade samples of glass reinforced plastic submerged in acetic acid (CH₃COOH) with aluminium chloride (AlCl₃) acting as a Lewis acid catalyst. The experiment was based on that carried out by (Wang, Cui et al. 2015).

Chemicals Used

Acetic acid solution acid 1M

Aluminium Chloride

Method

A total of 6 samples were heated in the microwave digestor , three were in powder form and three were solid blocks.

First the aluminium chloride was mixed into the acetic acid. To ensure a consitant concentration for each sample a 120 ml of acid was measured out and poured into a glass beaker in the fume cupboard.

Next the aluminium chloride was opened in the fume cupboard to allow the fumes in the container to be vented, then 12g was weighed out and added to the acetic acid. This produced an exothermic reaction which resulted in some spillage of the powdered aluminium chloride.

A magnet was to mix the liquid for 3 minutes

While this was being done the weights of each sample of fibreglass were mesured.

Six containers were labeled and 20ml of the fluid of the mixture was added to each container used in the digestor machine.



Figure 58 Sample containers

The samples were heated at 100°C for 90 minutes; then the sample 3 and 4 were removed and the program run for a futher 90 minutes at a higher temperature of 180°C. The samples were left to dry in the fume cupbord over night and the weights taken the next morning.

To recover the powdered samples it required the use of filter paper. This meant the recovered weights were not accurate.

Results

The following changes in sample mass were obtained.

Sample	Form	T=0	T= 90mins	T=180 mins
1	Block	2.71g		2,75g
2	Block	2.36g		2,45g
3	Block	1.34g	1,35g	
4	Powder	0.84g	-	-
5	Powder	1.3g	-	1,04g
6	Powder	1.29g	-	-

All containers were opend after 90 minutes and all the solutions were clear. However, in the samples that were heated for a further 90 minutes the solutions had become brown in colour. A sample of this solution was centrifuged after being neutralized by sodium hydroxide. A powder deposit and a clear solution were obtained.

The effect of the process on the powdered samples are shown below



Figure 59 Sample 4-5-6

It can be clearly seen that sample 4 which was only heated up to 100°C. has hadly been affected but the other 2 samples 5 and 6 seem to have undergone chemical transformations.

Conclusion of Experiment

The experimental method suffered from many deficiencies which must be taken account of in the next experiment.

The exothermic reaction when the aluminium chloride was added to the acetic acid solution may be due to the reaction with water in the solution. Aluminium chloride is hygroscopic, chlorine molecules are displaced forming the hexahydrate $[Al(H_2O)_6]Cl_3$

When this hexahydrate is heated it breaks down to form aluminium hydroxide

 $Al(H_2O)_6Cl_3 \rightarrow Al(OH)_3 + 3 HCl + 3 H_2O$

All the samples showed an acid result when tested with litmus paper.

The other interesting result was the increase in mass of sample 1 and 2 even after 24 hours drying. (Wang, Cui et al. 2015)records that the weight of PMPPS increased when soaked in acetic acid. This could be a sign that the organic solvent has penetrated the matrix.
Experimental Report 24-9-2018

Introduction

The experiment involved the use of a microwave digestor and muffle oven to degrade samples of glass reinforced plastic submerged in acetic acid CH₃COOH with AlCl₃ acting as a Lewis acid catalyst. The experiment was based on that carried out by (Wang, Cui et al. 2015).

Chemicals Used

Concentrated acetic acid



Aluminium chloride



Method

1

A total of 6 samples were heated. Four were heated in the microwave digestor; one was in powder form. Two were heated in the autoclave; one was in powder form.

First the aluminium chloride was mixed into the acetic acid. To ensure a consitant concentration for each sample a 100 ml of acid was measured out and poured into a glass messuring cylinder in the fume cupboard.

Next the aluminium chloride was opened in the fume cupboard and 10g was weighed out.



Figure 1 acetic acid measure



Figure 60 Aluminium chloride

The 100 ml of acid was mixed with the chloride and a white suspention occurred which corresponded with the theory.



Figure 62 Powder in suspension

It was found that when the mixture was stirred at a temperature of 190°C the white suspention disappeared. This also corresponds with the theory.

The fluid was distributed equally among the six samples. Four samples were heated in the microwave digestor and 2 in the autoclave for 180 minutes at 190°C.

Results

The following changes in sample mass were obtained.

Sample	Form	T=0	T= 180mins	Equipment
1	Block	1.15g	1.94g	Digestor
2	Block	1.20g	1,82g	Digestor
3	Block	1.34g	1,35g	Digestor
4	Powder	2,78g	2,69g	Digestor
5	Block	1.96g	-	Autoclave
6	Powder	1.13g	-	Autoclave

The fluid inside the reaction vessels had become deep brown in colour after 180 minutes.

It was also found that there were solid deposits left in the samples after the liquid was filtered.



Figure 64 Sample 1 after 180 minutes



Figure 63 Filtered deposits

The totality of the liquid residue was centrifuged for 10 minutes. The result is shown below



Figure 65 Centrifuged fluid

A solid sand-like deposit at the bottom of the tube was observed.

The samples 1-3 are shown after processing in the microwave digestor



Figure 66 Samples 1-3

It can be seen that there has been significant degradation in all three samples.

The results of the autoclave treatment are shown below



Figure 67 Samples 5-6 (autoclave)

The solid block, sample 5, remained solid despite leaching.

Conclusion of Experiment.

Both processes degrade the glass reinforced composite, but the microwave process appears more effective for the given time span.

The precipitate needs to be tested to determine if the reaction is reconstituting the aluminium chloride catalyst.

The liquid produced needs to be analysed to see which chemicals are within.