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with a major in Textile Engineering
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Separation for regeneration

STINA BJÖRQUIST

- Chemical recycling of cotton and polyester textiles



THE SWEDISH SCHOOL
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PREFACE

This Master thesis for the degree Master of Science with a major in textile engineering was made in collaboration with Chalmers University of Technology in Gothenburg. The thesis is a part of Mistra Future Fashion (MFF) program. MFF is a research program with a consortium of partners, from universities, companies and research institutes. MFF is financially supported by Mistra, The Swedish Foundation for Strategic Environmental Research.

My interest in the technical challenges that are related to achieving a more circular and sustainable textile industry has been a key motivation during the work on this master thesis. However, without the contribution from numerous people, it would not have been possible to carry on the ambitious work throughout this spring. First, a big thanks to Anna Palme for the supervision at Chalmers, for the hours shared in lab and for assisting in the refinement of this report. Thank you, Anna Petersson, for inspiring tips in general and valuable input regarding IR measurements in particular. I would further like to thank the staff of Forest Products and Chemical Engineering group at Chalmers and especially, the fellow master thesis workers, Axel, Ina, Jessica, Emma and Kajsa, for pep-talk and cups of coffee shared during this spring. I would also like to thank Hanna de la Motte, project coordinator of MFF task 4, for welcoming me with enthusiasm to this project. A warm thank you to co-supervisor Anders Persson, Swedish School of Textiles. The trust you have in your students and your sincere interest in the projects is highly valued.

I would like to send thanks to the people whom I worked with at Aalto University. Thank you for teaching me a lot about fibre spinning and for truly valorising my passion for materials and recycling.

Another warm thanks to the wonderful staff at Swedish School of Textiles, for introducing me to the fascinating world of textiles five years ago. The cross-disciplinary culture of the school is something unique that I will always carry with me. A special thanks to all the technicians that bring the theory to life in the laboratories – something extremely important for us students.

A warm thank you to Julia, for valuable feedback regarding this report but mostly for being a very good friend. I look forward to sharing many more ideas with you and to work on common projects in the future,

A handwritten signature in black ink, reading "Stina Björquist". The signature is written in a cursive, flowing style with a long horizontal stroke at the end.

Stina Björquist

ABSTRACT

In 2015, 96.7 million tonnes of textile fibres were produced world-wide. Our high consumption of textiles leads to an increased amount of textile waste. In Sweden, the majority of used clothing and textiles are incinerated due to the lack of recycling techniques. A large amount of post-consumer textile waste is made from blended materials. One of the most common blends, used in as near as all work-wear and service textiles, is cotton/polyester. To enable chemical recycling of such textiles, cotton and polyester must first be separated.

The aim of this thesis was to separate the materials by depolymerizing the polyester using alkaline hydrolysis. The focus of the work was on how such a process should be performed without a catalyst, in order to result in both a high yield and a high purity of the cotton residue. In order to recycle the residue as a raw material for manufacturing of man-made cellulosic fibres, the cellulose chains in the cotton must also be maintained as unaffected as possible.

The polyester in new sheets was completely depolymerized after 390 min at a temperature of 90°C using a 10% sodium hydroxide concentration and a 1% material-to-liquor concentration. The separation using these conditions gave high yields (above 96%) of the cotton residue regardless of the material fineness used in the process. Furthermore, the separation performed on old sheets show that a pure cotton residue could be produced using higher material concentrations. It was shown that the cotton residue from old sheets, laundered around 50 times, had an intrinsic viscosity comparable to dissolving pulps used for viscose fibre spinning.

This study concludes that alkaline hydrolysis without the use of a catalyst could be used to separate cotton and polyester in blended textiles. Furthermore, the findings show that cotton percentage in old sheets only decreased slightly after 50 launderings. Characterization of the materials using ATR FTIR spectroscopy indicate that an integrated textile recycling of hospital bed sheets could be performed since the sheets only contain cotton and polyester in all parts of the sheets.

Keywords: *cotton/polyester blends, chemical recycling, alkaline hydrolysis*

POPULAR ABSTRACT

Textile industry is facing great challenges in the future both in terms of producing new materials to cover the increased demand for textiles globally, but also to handle the waste generated by industry and consumers. Recycling techniques are well established for other materials such as paper and glass, but not for textiles. A large amount of waste textiles are however, blended material, a mix of several fibre types. Cotton/polyester is one of the most common blends. Most service textiles, used by hotels and hospitals, are made from cotton/polyester blends. Cotton and polyester are chemically different and a chemical process that separate the fibres could make it possible to recycle textiles from the service sector.

This thesis investigate a method for separating cotton and polyester by decomposing the polyester to its building blocks. The polyester building blocks could be used to produce new polyester. The cotton fibre is built up by cellulose macromolecules – present in all plant fibres. The method used to separate cotton and polyester is chosen in order to leave the cellulose as unaffected as possible. This is important in order to recycle the cotton by producing new man-made textile fibres, such as viscose.

The materials used in this study were new hospital bed sheets containing 50/50% cotton and polyester. Different process parameters, such as time and temperature, were investigated for the separation method. A pure cotton residue could be generated, also using old sheets and higher weight per cent of input material in the process. It was proven that the use of cut pieces of the sheets were as equally efficient as using a more fine material.

The cotton percentage in old sheets only decreased slightly after 50 launderings. Furthermore, chemical characterization of the different parts of the sheets such as seam and selvedge, show that the sheets contain only cotton and polyester. Therefore further work on the process could result in the development of a recycling technique of hospital bed sheets without removal of any parts of the sheets.

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LIST OF ABBREVIATIONS

ATR FTIR	attenuated total reflectance Fourier transform infrared (spectroscopy)
aq.	aqueous
CED	cupriethylenediamine
DP	degree of polymerization
EG	ethylene glycol
NMMO	N-methylmorpholine N-oxide
NMR	nuclear magnetic resonance
o.d.	oven dry
PET	poly(ethylene terephthalate), polyester
SEM	scanning electron microscopy
TPA	terephthalic acid
UV-Vis	ultra violet visible (spectroscopy)
wt%	weight per cent

1. INTRODUCTION

The high consumption of clothing and other textiles world-wide lead to a large amount of textile waste. Yet, there are only a few commercially viable recycling techniques for textiles. A major challenge for textile industry is to develop processes to convert used textiles to raw materials for manufacturing of new textile fibres. This Master thesis is focusing on such a process – to chemically separate cotton and polyester, using alkaline hydrolysis to depolymerize the polyester. The cotton residue could then be used to manufacture man-made cellulosic fibres and the monomers from the polyester could be used as raw chemicals or be re-polymerized into new polyester.

This introduction chapter aims to give the reader an overview of the project. Background, problem description, research questions and limitations are presented. This is followed by a series of chapters reviewing literature and advancements in relevant areas for the thesis. It includes chapters about recycling of textiles, polyester, and cotton as a cellulose source.

1.1 BACKGROUND

The textile industry is a large player on the global trade market of the 21st century. The share of clothing and other textile goods is around 7% of the world's total export (Allwood et al. 2006). In 2015, 96.7 million tonnes of textile fibres were produced world-wide according to the Fiber Year report (2016). A major part, 69 %, of these fibres are man-made, including both synthetic and cellulosic fibres. The share of polyester is growing rapidly. The share of produced natural fibres on the other hand is decreasing. The global demand for fibres and textiles will continue to rise in the future due to an increased population and a larger proportion of middle-class in highly populated countries.

Our consumption of textiles leads to a large amount of waste textiles. In many countries, landfilling is still the main option for *end-of-life textiles*, worn and unusable products. Morley et al. (2014) reported that, a total amount of 7.3 million tonnes of apparel waste was generated each year in Europe. From this waste, 4.3 million tonnes were sent to landfill or incineration. A study performed to map the Swedish consumption of textiles showed that the imports of textiles in Sweden equalled almost 15 kg per person and year (SEPA 2011). According to the same study, Swedish consumers throw 8 kg of textiles per person in the solid waste stream per year. Landfilling is not commonly used in Sweden. This means the textile waste in the solid waste stream will be incinerated together with the rest of the household's waste. Even though energy will be generated from the incineration, better processes to handle our textile waste need to be developed.

1.1.1 BLENDED TEXTILES

Blending is a commonly used technique in textile industry to obtain materials with an engineered profile suitable for a specific application. *Intimate blending* is to use specific weight ratio of two or more fibres in the manufacturing of spun or filament yarns. Other types of blending are *mixture yarns* made by plying yarns together or *fabric mixtures* where different yarns are used for the different yarn systems in the

manufacturing process e.g. warp and weft. Some of the reasons for blending are to increase performance, aesthetics and decrease production costs.

According to Ward et al. (2013), more than a third of post-consumer textile waste is blended materials. However, it is probably even more common if trimmings e.g. sewing thread and labels are considered. Polyester and cotton blended textiles, henceforth referred to as *polycotton* textiles, are with no doubt one of the most commonly used blend. These two fibres are the dominant ones amongst the man-made fibres and natural fibres respectively according to Textile Exchange's Preferred Fiber Report (2016). In terms of properties they also complement each other well and make an excellent material often used in workwear and other service textiles. In a LCA study of service textiles, Kalliala and Nousiainen (1999) showed that sheets in the hotel business of a 50/50 proportion of polyester and cotton have lower environmental impact compared to 100% cotton sheets. By adding polyester and make a polycotton blended fabric, the product life of workwear items will be longer. Additionally, less energy is needed to dry the clothes due to the low moisture regain of polyester. This makes polycotton blends suitable for all kinds of service textiles. (ETSA 2012).

1.2 PROBLEM DESCRIPTION

This Master thesis is addressing the problem of recycling blended textiles through an investigation of a process that separates cotton and polyester in blended fabrics. This process has been previously evaluated in another Master thesis (Peterson 2015) and was also included in the Doctoral thesis by Palme (2017). The work on the process resulted in an article, "Development of an efficient route for combined recycling of PET and cotton from mixed fabrics", describing the separation method (Palme et al. 2017). The separation method involve alkaline hydrolysis to degrade the polyester. In the previous work a phase transfer catalyst was also used to increase the process rate. The authors of the article found that the method has potential to separate polycotton sheets into pure waste streams of the polyester monomers and yet preserve the cotton residue. The focus of this thesis is to continue to investigate this process without the addition of a catalyst.

Pure cotton waste has been investigated as a source for producing a raw material for the manufacturing of man-made cellulosic fibres. These research initiatives have come so far that some of them even have commercialization on the horizon (Gullingsrud 2017). Therefore it is possible that also cotton from blended textiles, if separated into a pure cellulose fraction, could be used for production of man-made cellulosic fibres.

1.3 SCOPE AND RESEARCH QUESTIONS

The aim of this Master thesis is to investigate the separation process of cotton and polyester in polycotton woven hospital sheets using alkaline hydrolysis to depolymerize the polyester. The key parameters investigated are:

- Process conditions (including alkali concentration in the solution, process temperature and time)
- Mechanical pre-treatment of polycotton textiles (ground, shredded or cut)
- Effect of laundering (not laundered, laundered around 50 times)
- Concentration of polycotton material to alkali solution (1%, 3% or 5%)

The scope of this study is to verify the polycotton separation process without using a phase transfer catalyst that has been used in previous studies (Palme et al. 2017). The following two research questions have been used throughout the work:

- I. How should a separation process of cotton and polyester in blended woven textiles, using alkaline hydrolysis to depolymerize PET, be performed in order to give a pure and high cotton residue yield without the addition of a catalyst?*
- II. How does industrial laundering and tumble drying affect the cotton and polyester ratio in polycotton woven textiles?*

1.4 LIMITATIONS

The main focus of this work is on the process conditions in the separation of polyester from cotton and on the purity and yield of the cotton fibre residue. Basic analysis is carried out on the monomers of the depolymerized polyester to validate the process. However, no thorough investigation of these fractions is in the scope of this thesis.

2. RECYCLING OF TEXTILES

The *waste hierarchy* model (see Figure 1), is used to express the different levels of material recovery from waste. It was first adopted in 1975 by European Union (Williams 2015) and has been updated and analysed since then (Gharfalkar et al. 2015). The model proposes an order of actions that should be followed in order to minimize and manage waste.

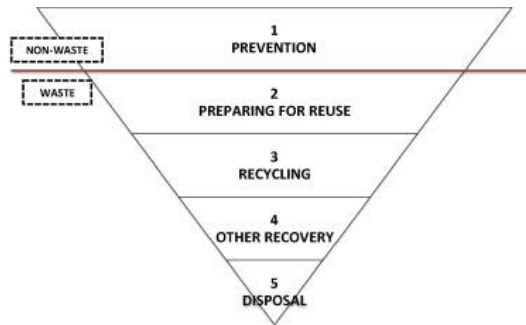


FIGURE 1 THE WASTE HIERARCHY MODEL¹

Preventing waste to be generated is of most significance, followed by reuse, then recycling and energy recovery (incineration). To dispose generated waste in landfills is the last step of the hierarchy. By landfilling waste, a great amount of resources will be lost. This is however not the only reason why landfilling is the worst option. Degradation of organic materials, such as textiles, in anaerobic environment in landfills, leads to greenhouse gas emissions. The waste in landfills does not only give off carbon dioxide but also other gases like methane that has a larger influence on global warming (USCC 2011). Therefore it is absolutely necessary that we establish methods for handling the constantly increasing levels of textile waste.

The most preferable waste alternative, according to the waste hierarchy is reuse. However, since some goods cannot be reused as they are, due to being e.g. damaged or worn-out, these should instead be recycled. Recycling require new resources such as energy and chemicals. However, it may still be a more beneficial waste management option compared to incineration (Zamani et al. 2015).

Textile waste may either be generated during the production, i.e. *pre-consumer waste*, or after use by consumers or companies in the service sector, i.e. *post-consumer waste*. The pre-consumer waste may be fibre, yarn or fabric scrap. It is generally considered to be more easy to recycle since it is a material of known composition and quality from the production of textiles (Bartl et al. 2005). In this thesis, post-consumer waste was used, however, textiles of rather known quality.

There are a number of different methods to produce both recycled products of a higher or equal value, *up-cycling*, and products of lower value, *down-cycling*. Textile recycling techniques is commonly divided into two distinct methods: *mechanical recycling* and *chemical recycling* (Leonas (2017); Vadicherla and Saravanan

¹ Reprinted from Waste Management, vol. 39, M. Gharfalkar, R. Court, C. Campbell, Z. Ali, G. Hillier, Analysis of waste hierarchy in the European waste directive 2008/98/EC, 9 pages, (2015), with permission from Elsevier.

(2014); Collier et al. (2007); Karayannidis and Achilias (2007)). These approaches will be introduced in the following sections of this chapter.

2.1 MECHANICAL RECYCLING

In terms of textiles, mechanical recycling refers to the disintegration of the textile material by mechanical action back to a fibrous form. This process is also referred to as *shredding*. Shredded material may be used for the formation of non-woven materials. Depending on the application, the homogeneity in terms of fibre mixture and colour may be of less importance. Since shredded textiles are commonly used as bulk material, e.g. padding, inside new products, with a virgin outer material, it has no impact on the performance. Mechanical recycling may lead to a down-cycled material of mixed fibres. An interesting fraction, when discussing mechanical recycling of post-consumer waste, is denim fabric or garments, which is fairly easy to identify in textile waste sorting. It may be mechanically recycled into various products (Collier et al. 2007). There are several jeans companies, such as G-star and Nudie jeans that use post-consumer denim waste in their products (Luiken and Bouwhuis 2015). Esteve-Turrillas and de la Guardia (2017) has found that mechanical recycling of pre-consumer industrial fabrics, with a small addition of post-consumer waste, could be made into yarns by open-end yarn spinning technique at an industrial spinning mill. The Spanish mill behind this technology, Hilaturas Ferre, has worked with recycling industrial scrap into yarn for over 70 years. Nowadays their recycled yarns with the brand name Recover[®] are used in products of several companies such as H&M, Zara, Primark and Puma. In cooperation with H&M and I:CO, the aim is to develop a system to use post-consumer waste in the process (Nieder 2015). This type of mechanical recycling described above is suitable for any type of fabric, yarn and/or fibre waste. However, one problem with this type of recycling for yarn spinning, especially when using post-consumer waste, is the loss in fibre length. The length of the fibres is an essential parameter in yarn spinning. It may be significantly reduced by the harsh mechanical treatment to obtain fibres from fabrics. Therefore it is common that recycled fibres, sometimes referred to as reclaimed fibres, need to be blended with a proportion of virgin fibres to obtain a high quality yarn (Gulich 2006). The mechanical action in combination with the detergent's wear on the chemical structure during laundering decrease the *degree of polymerization*, DP, of cellulose in cotton textiles (Vaeck 1966). Lowered DP directly affects the polymer strength (Walker 2001) and thereby the fibre strength, and in addition to a reduction in fibre length this may cause difficulties during the manufacturing of new yarns using mechanically recycled fibres.

Another category of mechanical recycling, is the reprocessing of thermoplastic polymers, from plastic waste, to form new filaments or other types of products (Leonas 2017). Many types of thermoplastic polymers can be re-melted in this way but the most well-known example of commercial success for textile applications is the processing of polyester bottles into new polyester fibres (Vadicherla and Saravanan 2014). However, the number of possible recycling cycles is limited due to the degradation induced by the thermo-mechanical treatment during reprocessing (Badía et al. 2009).

2.2 CHEMICAL RECYCLING

Chemical recycling involves chemical processing of the polymers of the fibres, e.g. *depolymerizing* or *dissolving*. Chemical recycling of synthetic polymers, also referred to as *feedstock recycling* may depolymerize waste plastics into high purity, polymerization grade, monomers. The purity and quality of the monomers obtained after recycling depend on various factors such as presence of additives and chemicals used in the polymerization process. *Pyrolysis*, sometimes named *thermolysis*, is referring to the thermo-chemical processes to decompose polymers. Pyrolysis is conducted at various temperatures, pressure levels and with presence of catalysts or reactive gases. It is common that pyrolysis yield mixtures of liquids and gases that vary with the input waste material. So far, pyrolysis processes are only economically viable for certain polymers e.g. polyamide 6. (Scheirs 2006)

For other synthetic polymers used in textile industry, other processes are used. Chemical recycling of polyester, which is in focus in this project, has been quite extensively studied. However, very few studies have been published using polyester fibre waste (Shukla and Harad (2005); Shukla and Kulkarni (2002)). Most of the published work has been conducted on soft-drinking bottle waste (Al-Sabagh et al. (2016); Park and Kim (2014); Bartolome et al. (2012); Venkatachalam et al. (2012); Sinha et al. (2010); Karayannidis and Achilias (2007); Paszun and Spychaj (1997)). The processes mainly studied in literature for depolymerisation of polyester include *glycolysis*, *hydrolysis* and *metanolysis*. These processes depolymerize the polyester in glycol, water and methanol respectively. The aim of all of these processes is to cleave the functional ester group in polyester, and depending on the reaction, different monomers or oligomers are obtained. These products could be used to synthesize new polyester for the production of virgin textile fibres. Polyester bottles have in this way been recycled into new polyester used to spin new yarns for textile applications (Koo et al. (2013); Upasani et al. (2012)). The Japanese company Teijin has worked many years in collaboration with their customers to chemically recycle returned polyester garments into monomers that is re-polymerized and made into new fibres (Gullingsrud 2017).

Dissolution is the other approach to chemically recycle polymers. In fact, cotton linters, a cotton rest product from the ginning process, was used extensively to produce viscose fibres (Seymour and Porter 1993) and is still used for dissolving pulps as well as for various specialty applications in the chemical and paper industry (Sczostak 2009). However, using other cellulose sources e.g. used cotton textiles to produce man-made cellulosic fibres did not receive any real attention until the last ten years. The main solvent systems that could be used are NMMO (lyocell process) and ionic liquids (Collier et al. 2007). In a press-release from February 2017, Europe's most prominent manufacturer of man-made cellulosic fibres, Lenzing AG, launched a new fibre trademark in their TENCEL® family. The fibre named Refibra™ is produced with a pulp made from wood and cotton scrapings. The cotton leftovers are claimed to come from the textile production process i.e. pre-consumer waste (Lenzing AG 2017). Researchers from Aalto University and University of Helsinki in Finland, have filed a patent (Michaud et al. 2014) for a process of using ionic liquids to produce cellulose shaped articles such as textile fibres. The same research group, Asaadi et al. (2016), recently published an article that studies

how to chemically recycle 100% cotton hospital bed sheets with their process. This was achieved by the means of direct dissolution in [DBNH]OAc, an ionic liquid. The dope of dissolved cellulose where then dry-jet wet spun into filaments. Tensile tests show this new man-made cellulosic fibre from cotton waste has significantly higher tenacity compared to virgin cotton, both in dry (conditioned) and wet state.

The Swedish company re:newcell have patented a technology (Henriksson and Lindström 2013) for producing a cellulose raw material from old cotton textiles. Lyocell fibres produced of re:newcell recycled cotton show equal quality to TEN-CEL® fibres regarding several important properties such as dye absorbency and abrasion resistance (Aronsson and Björquist 2015). The Sourcing Journal ranks the investment in upscaling of re:newcell’s technology as the number one on a top-ten-list of sustainability moments in 2016 (Scarano 2016). The US company EvRnu have applied for a patent (Flynn and Stanev 2016) for a process of isolating cellulose in cellulose-containing material e.g. post-consumer textile waste. The patent comprise a multiple step process with pre-treatment, pulping stage and finally an extrusion process of the cellulose material to regenerate fibres.

Chemical recycling is very promising once technologies are developed to make better reuse of energy, water and chemicals during the process (Vadicherla and Saravanan 2014). Whilst mechanical recycling has already been efficiently adopted by industry for recycling of single fibre materials, chemical recycling is expected to be more suitable for large-scale recycling of blended materials. For blends of cellulosics with man-made synthetics, some researchers are showing promising results in separating the fibres by selective dissolution or degradation (Leonas 2017). This opportunity, with a focus on separating cotton and polyester from each other, will be discussed in the next section.

2.3 SEPARATION OF COTTON AND POLYESTER IN BLENDS

In order to recycle cotton and polyester from polycotton textiles, the materials must first be separated or disintegrated from each other. There are two main ways to achieve this, dissolution and degradation i.e. depolymerisation. Depending on whether these approaches are applied to cotton or polyester, four main routes for recycling polycotton textiles are possible, see Figure 2.

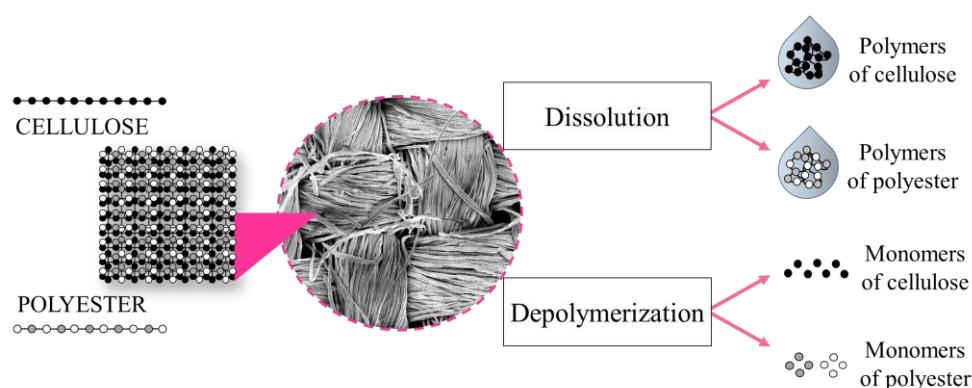


FIGURE 2 ILLUSTRATION OF INTIMATELY BLENDED WOVEN TEXTILES AND THE SCHEMATIC OVERVIEW OF DIFFERENT APPROACHES IN ORDER TO SEPARATE COTTON AND POLYESTER

Even if individual staple fibres are consisting of one polymer type only, in intimately blended textiles, the fibres are intermingled in a random manner. Thus, only chemical methods could lead to a complete separation of the materials of the complex network illustrated in Figure 2.

Dissolution of cellulose in cotton is one of the methods that could be used. De Silva et al. (2014) investigated the separation of intimately blended polyester and cotton yarns by means of ionic liquids. The recovered polyester show no change in melting temperature compared to untreated 100% polyester samples which is vital for mechanical reprocessing. However, the NMR and FTIR spectra show that a small amount of cellulose may be present in the separated polyester. No attempts were documented on fibre melt spinning of the recovered polyester fraction. The dissolved cellulose, on the other hand, was regenerated to films and filaments using water as coagulating medium to prove the concept of recycling the cotton fraction. At the American Chemical Society's conference this April (2017), the researchers behind the Ioncell-F process cited in the previous section (Michaud et al. 2014), presented their work on separation of polyester and cotton in waste textiles. By dissolving the cotton part in ionic liquid, polyester could be filtered off. Although they underline that many challenges still exist, they have been able to spin both man-made cellulosic fibres and polyester fibres from the separated fractions. The cellulose filaments were indeed possible to draw to produce very fine staple fibres for yarn manufacturing. A prototype in form of a women's top was also presented to show that the technology works on lab scale. The SaXcell initiative named after the Saxion University in the Netherlands is working on recycling polycotton blended textiles (Luiken and Bouwhuis 2015). The researchers have filed a patent for a process where waste textiles containing both cellulosic and synthetic fibres are treated with a cellulose solvent. The synthetic material is removed from the cellulose solution that is used to produce regenerated fibres (Brinks et al. 2014).

The second approach would be to dissolve the polyester (Serad (1994); Sidebotham et al. (1977)) but no process has gained any commercial success so far. UK based company Worn Again is working together with big brand names such as Nike and H&M to commercialize their technology of separating polyester from polycotton blends (Gullingsrud 2017). Their first patent application describe a method for extraction of polyester from any article, using a solvent system for the polyester. By solvent system, the inventor refers to any homogenous or heterogeneous mixture of solvents with the formulae stated in the pending patent (Walker 2014). The more recently filed application defines a procedure for extracting polyester from packaging material but also from fabric (Walker 2016). The multi-stage process is suitable for polyester extraction from garments containing one or more dyes.

Another method for separating the cotton and polyester, to reuse the polyester part solely, includes destruction of the cotton component (Sankauskaitė et al. 2014). Jaihanipour et al. (2010) are first using the approach to dissolve cellulose of polycotton fabric in NMMO to separate the materials. The authors thereafter perform enzymatic hydrolysis and fermentation of the cellulose to produce ethanol or digesting it to biogas. Ouchi et al. (2010) describe a two-step method for recycling of polycotton fabrics using an acid pre-treatment followed by mechanical action of

the textiles. The method is claimed to efficiently remove the cotton as a powder from the polyester part.

An approach that would preserve also the cellulose in cotton is to depolymerize the polyester. Negulescu et al. (1998b) use alkaline hydrolysis to depolymerize polyester in fabric pieces mixed with cotton fabrics in the solution. The cotton was further dissolved in NMMO and spun to lyocell filaments. Alkaline hydrolysis was also used by Palme et al. (2017) and pure raw materials of polyester monomers as well as a cotton residue was produced from new hospital sheets containing cotton and polyester.

Other concepts of recycling to preserve the value in polycotton textiles investigated are composite manufacturing (Ramamoorthy et al. 2014) and dyestuff production (Shukla et al. 2009).

There is yet no commercial large scale recycling of polyester and cotton blended textiles. Therefore, this thesis aims to further develop the concept of chemical recycling of these textiles using alkaline hydrolysis to depolymerize the polyester. This approach is interesting for several reasons. Firstly, both cotton and polyester fibres are affected by laundering (IFI 1995; Vaeck 1966) which has an effect on the mechanical recyclability. Thus, a complete depolymerization of polyester in old textiles is preferred in order to produce new high quality products, since monomers are generated that could be re-polymerized into virgin quality polyester. Secondly, solutions of sodium hydroxide are used as steeping lye in pre-aging and steeping steps of the viscose process (Mozdyniewicz et al. 2013). Therefore, it would be possible to integrate the recycling of old polycotton textiles as one step in the process chain of viscose fibre manufacturing. By developing an efficient recycling process of polycotton textiles, a large amount of worn out textiles, generated from hotels or hospitals could be recycled into man-made cellulosic fibres. The next two following chapters aim to give a further understanding of both polyester and cellulose respectively.

3. POLYESTER

Poly(ethylene terephthalate), abbreviated *PET*, is one of the most commonly used plastics (see repeating unit in Figure 3). Due to good thermal, mechanical and chemical properties, PET is favoured for many applications including food packages and soft drink bottles. In textile industry, PET is referred to as *polyester*. Polyester is used extensively to produce filaments and staple fibres for both technical and apparel applications (Karayannidis and Achilias 2007). This chapter aims to give a brief overview of the synthesis and hydrolysis of polyester.

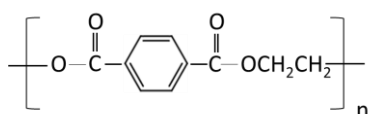


FIGURE 3 REPEATING UNIT OF PET

Generally, the synthesis of polyesters is described as a reaction of a diol and a dicarboxylic acid. In the 1940's, polyester for textile fibre production was synthesized for the first time using terephthalic acid (TPA), shown to the left in Figure 4, and its' dimethyl ester in reaction with ethylene glycol (EG), seen to the right in Figure 4.

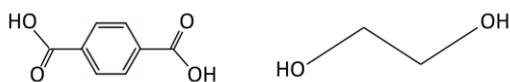


FIGURE 4 CHEMICAL STRUCTURE OF TPA, LEFT, AND EG, RIGHT

The challenge was for a long time to produce pure TPA (East 2005). The more easily producible dimethyl terephthalate (DMT) was used as a starter for polyester synthesis. However, since 1960's TPA has been readily available on the market and the polycondensation reaction between TPA and EG has become the major route for polyester synthesis in industry (Koyikkal 2013; Thomas and Visakh 2011). Hydrolysis of polyester waste, resulting in the monomers TPA and EG, may therefore be a solution to the problem of recycling polyester waste. This will be discussed in the next section.

3.1 HYDROLYSIS OF POLYESTER

Hydrolysis refers to any chemical reaction where the addition of water is leading to cleavage of the chemical bonds in a compound. The general descriptive formula of a hydrolysis reaction is seen below:



Hydrolysis of polyester may be performed in either an acid, neutral or alkaline environment. The reaction lead to depolymerisation of polyester into the monomers TPA and EG. Acid hydrolysis is commonly performed in concentrated sulfuric acid although other strong mineral acids could be used. Steam or hot water is used to promote the depolymerisation in neutral hydrolysis processes (Karayannidis and Achilias 2007). For processes performed in acid environment, a substantial amount of acid is needed. Materials present in the process also need to withstand the very low pH. Acid hydrolysis is thus not a suitable pathway to degrade polyester in polycotton textiles due to the long known sensitivity of cellulose to acids (Pacsu 1947). Since cellulose is relatively unreactive in alkaline environment, alkaline hydrolysis may be a good option for depolymerisation of polyester in order to maintain the cotton residue as unaffected as possible. Additionally, the consumption of water and energy in an alkaline process will be lower than for neutral hydrolysis.

Alkaline hydrolysis of polyester is often performed in aqueous solutions, 4-20 wt% of potassium hydroxide or sodium hydroxide. Partial alkaline hydrolysis has in fact been successfully adopted by fibre industry for limited degradation of polyester to achieve a proper molecular weight distribution for fibre spinning. Many factors are influencing the hydrolysis process efficiency: time, temperature and alkali concentration. As seen in Figure 5, polyester is degraded by sodium hydroxide, which leads to formation of sodium terephthalate salt and EG (Sinha et al. 2010).

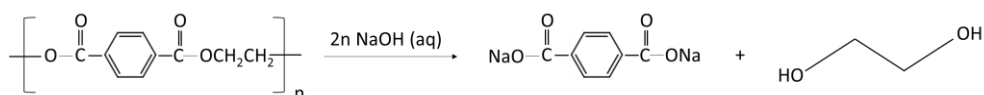


FIGURE 5 ALKALINE HYDROLYSIS OF PET BY SODIUM HYDROXIDE RESULTING IN DISODIUM TEREPHTHALATE SALT AND EG

When the hydrolysis solution is acidified using sulfuric acid, or another strong mineral acid, pure TPA will precipitate (see Figure 6). The solid TPA can be filtered off from the liquor.

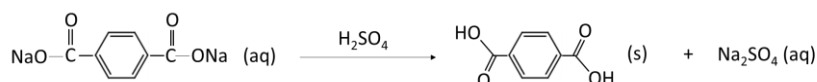


FIGURE 6 PRECIPITATION OF TPA BY ACIDIFICATION OF THE SOLUTION CONTAINING DISODIUM TEREPHTHALATE SALT BY ADDITION OF SULFURIC ACID

Alkaline hydrolysis may be performed in several temperature ranges and for several time intervals and pressure levels (Mark 1985) and high purity TPA could be obtained after subsequent acidification and filtration (Karayannidis et al. 2002).

4. COTTON AS CELLULOSE SOURCE

Cotton has been an appreciated natural fibre for centuries due to its excellent properties in terms of comfortability, moisture absorption and good dyeing properties (Mather and Wardman 2015). Although, the cotton fibre has been subjected to criticism due to that the farming of cotton requires large volumes of water and pesticides. Additionally, cotton production takes up arable land which could be used to grow food on. Therefore the man-made cellulosic fibres, having similar properties, are predicted to raise their share on the future fibre market (Haemmerle 2011).

The cotton fibre contains around 90% of cellulose. Compared to other plants it is thereby one of the most pure cellulose sources in nature. The non-cellulosic materials of native cotton are proteins, waxes, pectins, inorganic and other compounds. The amount of non-cellulosics vary depending on the plant type, farming conditions and stage of maturing of the fibre (Huwlyer et al. 1979; Meinert and Delmer 1977). The primary fibre wall contains only 30% cellulose or less but the secondary wall, on the other hand, contains almost 100% cellulose (Hsieh 2006). This chapter aims to give a brief introduction to cellulose chemistry in order to understand this thesis.

4.1 CELLULOSE

Cellulose is the most abundantly available natural polymer since cellulose is one of the main building blocks in all plants (Ciechańska et al. 2009). Regardless of the source of cellulose, the polymer is built up by several anhydroglucose units, as shown in Figure 7. Two such units, with an alternating 180° configuration around the chain axis, are forming the repeating unit of cellulose referred to as the cellobiose unit. Each anhydroglucose unit has three hydroxyl groups that contribute to various properties of the cellulose e.g. the hydrophilicity and reactivity. Cellulose

polymers in fibres such as cotton are organized in complex structures from the molecular to micro level of fibrils.

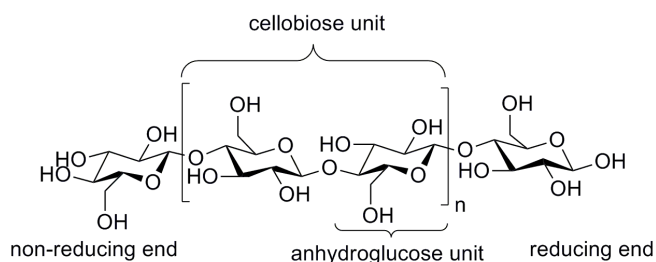


FIGURE 7 MOLECULAR REPRESENTATION OF THE CELLULOSE POLYMER

The ends of the cellulose macromolecule have different character - a reducing and a non-reducing end. Chemical alterations of the cellulose chains are induced by a few main reactions and generally takes place in the amorphous regions of the polymer or at the surface of the cellulose fibrils (Heinze 2016). *Peeling* reactions of cellulose occur in strong alkali solutions at the reducing ends. *Auto-oxidation* may cleave the chain if oxygen is present (Sjöström 1993) which could lead to a drastic drop in chain length.

One, in particular, important factor of cellulose for man-made fibre spinning is the DP, *degree of polymerization* i.e. the number of repeating cellobiose units in the chain length. The DP affect both the processing ability of the dope during fibre spinning as well as the final fibre properties (Morton 1996). As reported by Wilkes (2001), the DP of the cellulose of dissolving pulps used for manufacturing of man-made cellulosic fibres are usually 750-850. In viscose processing, the chain length need to be shortened yet it must be long enough to produce fibres of acceptable tensile properties. For production of normal viscose staple fibre quality, the DP is reduced to around 270-350 during the pre-aging step. However, as will be explained in the following paragraph, relating the DP to the actual material properties is not always an easy task.

Cellulose, like other polymers, give rise to specific fluid properties in specific solvents. These fluid properties is related to the polymer weight distribution and as well as the average DP. The DP of dissolving pulps is generally estimated by dissolving material samples into a specific solvent and measuring the flow rate of the polymer solution through a thin capillary. The *intrinsic viscosity*, η , could be calculated and be related to the DP using the Mark-Houwink equation (Gruber 2006). Although this relationship between intrinsic viscosity and DP have been questioned (Morton (1996); Evans and Wallis (1989)) it was not taken into account in this thesis since no conversion to DP was made. The measured values of intrinsic viscosity should be compared to the values of dissolving pulps for viscose products measured by similar procedures which is about 450-500 ml/g (Sixta 2008).

5. MATERIALS

The textiles in this study were provided by Textilia and comprised white sheets with a blue print on a minor part of the area and white pillow cases. The sheets were woven with plain weave technique and the pillow cases had large stripes of a satin weave construction. According to the supplier, the sheets contained 50% cotton and 50% polyester as new. This ratio was unknown for the pillow cases.

5.1 NEW SHEETS

Non-used and non-laundered, new sheets, hereafter referred to as *Sheets 0*, since they have been laundered zero times, were included in the study. The sheets were divided in four categories: *bulk* (major part of area without print), *selvedge*, *blue print* and *sewing thread*, see Figure 8, for characterization. Only the bulk area was used in the separation process.



FIGURE 8 NEW SHEET OF COTTON AND POLYESTER MATERIAL

5.2 OLD SHEETS

Old sheets, used at Swedish hospitals, referred to as *Sheets 18; 48; 49; 51; 52; 54; 56* respectively, representing the number of launderings measured by washable RFID tags, were also included in this study, see Figure 9. Laundering had been performed industrially by Textilia at a maximum temperature of 84°C using an alkaline detergent, Clax Hellux free 3EP3 (JohnsonDiversey Sverige AB). After laundering, the sheets were centrifuged and tumble dried. Despite being laundered, the sheets occasionally had small and very light stains of unknown matter. These parts of the bulk area were not excluded from the study. On a large area of *Sheet 54*, a type of wax finish was noted to be present. This part was excluded from the experiments. No attempts were made to characterize it further in this study.



FIGURE 9 OLD SHEET, LEFT, COMPARED TO NEW SHEET, RIGHT

5.3 OLD PILLOW CASES

Pillow cases, see Figure 10, washed approximately 100 times or more, according to experienced staff at Textila, were included in the study. Several holes could be detected. The pillow cases were laundered and dried with the same detergent and procedure as described for the sheets, see section 5.2.



FIGURE 10 SATIN WEAVE CONSTRUCTION, OLD SHEETS

5.4 CHEMICALS

The following analytical and reagent grade chemicals were used without further purification: sodium hydroxide (pellets), glacial acetic acid, sulfuric acid (95-98%), ammonium hydroxide (aq. 28-30%) and cupriethylenediamine (CED) solution (1M).

6. METHODS

This section include the methods used in the project. The separation experiments were performed in a heated glass reactor system, using 500 grams of hydrolysis solution. First, an overview of the separation process and characterization methods is presented. Secondly, the procedures for the separation experiments and the precipitation of TPA are described. Finally the characterization methods used to analyse the materials are presented.

6.1 OVERVIEW

This first section aims to give an overview of the process in order to facilitate the understanding of the methods used in the separation experiments. Figure 11 shows the procedure used throughout the laboratory work.

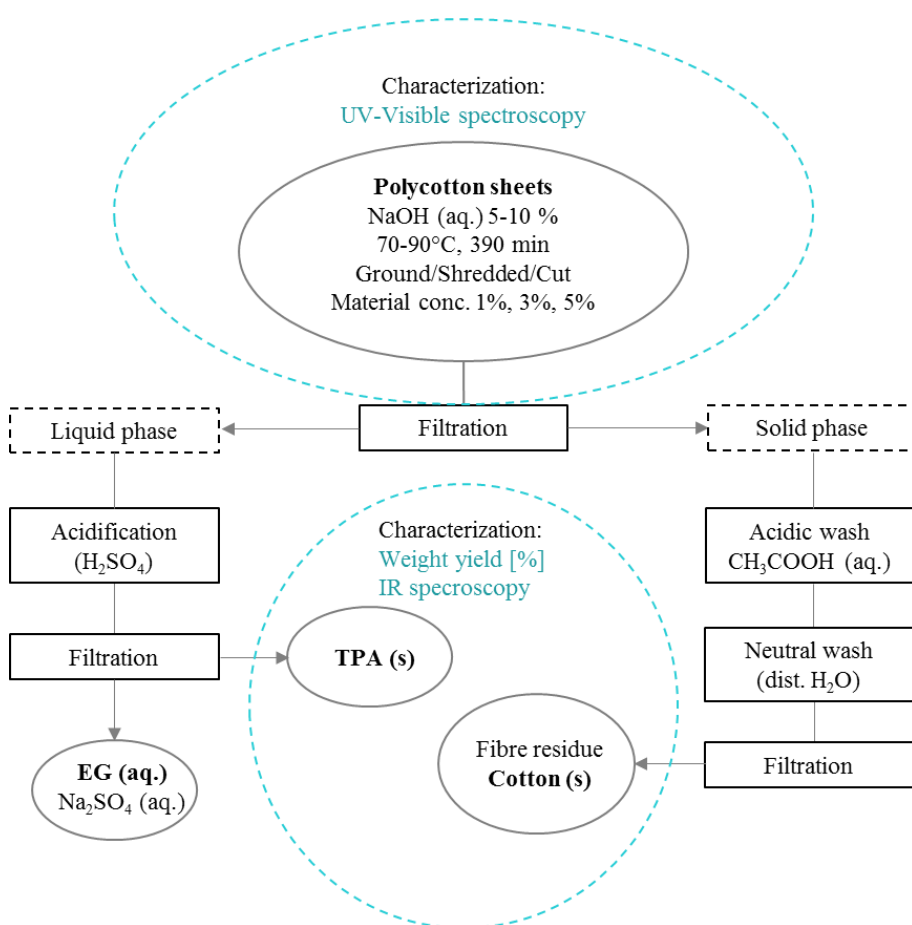


FIGURE 11 SCHEMATIC OVERVIEW OF THE SEPARATION OF COTTON AND POLYESTER

6.2 MECHANICAL PRE-TREATMENT

Three categories in terms of material fineness for *Sheets 0* were used in the separation process, henceforth referred to as *ground*, *shredded* and *cut*, seen in Figure 12.



FIGURE 12 GROUND, SHREDDED AND CUT SHEETS

The sheets were cut randomly and then *ground* to a powder using a Wiley mill, sieve 1 mm, or cut to ca. 2 cm² pieces and *shredded* to threads using sieve 10 mm. The *cut* material was obtained by cutting approximately 1 cm² pieces with a pair of scissors.

6.3 SEPARATION EXPERIMENTS

For each experiment, polycotton material was added to heated sodium hydroxide solution, and the hydrolysis was performed for 390 min. After the experiment was finished, the solid fibre residue was separated from the liquid phase and treated in a number of washing steps.

A certain wt% of polycotton material to solution, *material concentration*, 1%, 3% and 5%, was used. The wt% used were grams oven dry (o.d.) material. Aqueous sodium hydroxide solutions of concentrations 10wt%, 7.5wt% and 5wt% were prepared. Before starting the experiments, a sample of approximately 1.5 ml from the solution was always removed to run the background in the UV-Vis measurements.

The experiments were performed in a heated glass reactor with a reflux condenser to prevent evaporation. Aluminium foil was used around the reactor to keep the temperature as constant as possible. The experiments were performed at 70 °C, 80 °C and 90 °C and the temperature was controlled via an external digital thermometer. An anchor stirrer with a stirring speed of 150 rpm was used. When the experiments with 3% and 5% material to solution were performed, a specially adapted plug around the anchor stirrer at the centre, shown in Figure 13, was used in order to prevent loss of solution through evaporation. This adaptation was made since it had been noted in the earlier experiments that evaporation could occur.

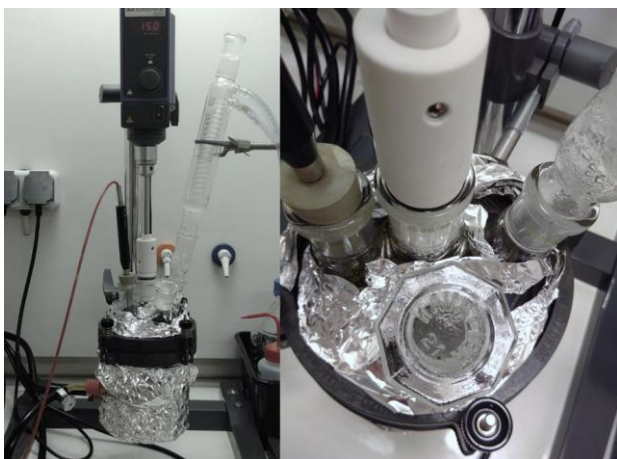


FIGURE 13 PROCESS SET-UP AND LID WITH CENTRE PLUG

During the process, approximately 1.5 ml of solution was withdrawn from the reactor at the times 120; 180; 240; 300; 360 and 390 min. The sample liquid was filtered with a syringe and filter with a 45 μm GHP membrane and saved in a small tube.

When the experiment was finished, the solid and liquid phase was separated by filtration using vacuum suction and a GF/A type glass microfiber filter, see scheme of the process in Figure 11. The fibre residue was directly put in a large beaker with 1L of 2% aqueous solution of acetic acid for 10 minutes. The fibre residue was then separated from the wash liquor by filtration using a new glass fibre filter. A neutral wash was performed by leaving the residue in 1L of distilled water for at least 10 minutes. The fibre residue was finally filtered through a new pre-weighed glass microfiber filter and air-dried at room temperature for at least 48 h. The mass as well as the moisture content of the fibre residue was determined in order to calculate the cotton yield.

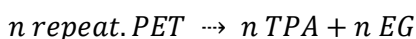
6.4 PRECIPITATION AND WEIGHT YIELD OF TPA

The liquid phase, separated from the fibre residue, was acidified using concentrated sulphuric acid (95-97%). The acidification was carried out until the pH of the solution reached 2.00, measured with a pH-meter, Metrohm 827 pH lab. The solid TPA was filtered through a pre-weighed GF/A type glass microfiber filter. The last filtrate, containing EG and solution, was not further analysed in this project. The TPA was dried in an oven at 105 $^{\circ}\text{C}$ for at least 6 hours, see Figure 14, before weighing.



FIGURE 14 PRECIPITATED AND DRIED TPA

The TPA yield was calculated from the total mass balance of the depolymerisation of PET, see Figure 5 and 6 in chapter 3. The number of moles PET, n_{PET} , is generating an equal amount of moles TPA and EG:



Thus, n_{TPA} equals n_{PET} and is calculated:

$$n_{TPA} = n_{\text{repeat. PET}} = \frac{m_{PET \text{ input}}}{M_{PET}}$$

The mass of polyester in grams, $m_{PET \text{ input}}$, was calculated by multiplying the total weight of polycotton material used in the experiment with the determined polyester ratio. The molar mass of one repeating unit of polyester, M_{PET} , used in these calculations was 192.16 g/moles.

The theoretical mass of terephthalic acid generated in grams, $m_{TPA \text{ theoret. output}}$, was then calculated:

$$m_{TPA \text{ theoret. output}} = n_{TPA} \times M_{TPA}$$

The molar mass of terephthalic acid, M_{TPA} , used in these calculations was 166.13 g/moles. The mass of precipitated terephthalic acid, $m_{TPA \text{ output}}$, was used to calculate the TPA yield in per cent for the experiments:

$$TPA \text{ yield } [\%] = \frac{m_{TPA \text{ output}}}{m_{TPA \text{ theoret. output}}}$$

The TPA was weighed immediately after it had been removed from the oven. The moisture content of the TPA was not considered in this study.

6.5 CHARACTERIZATION

Several techniques were used to characterize both the original materials as well as the raw materials generated from the separation process.

6.5.1 ATR FTIR SPECTROSCOPY

The new sheets and the old pillow cases were analysed using a PerkinElmer FTIR spectrophotometer with a mounted ATR device, GladiATR from Pike Technologies. The measurements were performed in air at room temperature using 20 scans per samples between wavelengths of 4000 to 400 cm^{-1} . Additionally, pure TPA was analysed as well as fabric samples of 100% cotton and 100 % polyester.

6.5.2 FIBRE RATIO DETERMINATION

For all materials in this study, the proportion of cotton and polyester in the bulk area was determined using ISO 1833-11:2006. For each material, three samples of approximately 1 gram of ground material were analysed to obtain a mean value. Each sample was dried in an E-flask of known weight, for minimum 4 h and maximum 16 h in a ventilated oven at 105°C. Before removing the samples from the oven, the flask cap was put on. The flasks with samples were immediately transferred to a desiccator. The flasks were left to cool for at least 2 h and then weighed to give the exact dry mass of the sample. The standard procedure was then followed using 75 wt% of aq. solution of sulphuric acid to degrade the cellulose for

one hour at 50°C. The sample was filtered through a pre-weighed glass filter crucible to remove the solvent. The residue, containing the polyester, was then washed several times with fresh acid solution, distilled water, aqueous ammonium hydroxide and finally by distilled water according to the standard method. The glass filter crucible was dried and weighed as described previously in this section to obtain the polyester weight. The purity of the polyester residue was verified by ATR FTIR spectroscopy.

6.5.3 UV-VIS SPECTROSCOPY

The absorbance of the background solution and solution samples withdrawn at different times was measured using Analytikjena spectrophotometer Specord 205 at the wavelength 242 nm. According to Lambert-Beer law, the concentration of TPA in the hydrolysis solution is directly proportional to the measured absorbance (Lampman 2010):

$$A = \epsilon cl$$

Absorbance, A , equals the product of the molar extinction coefficient, ϵ , the concentration of TPA, c , and the length of the UV-Vis sample cuvette, l . The molar extinction coefficient was determined using pure TPA from previous studies (Palme et al. 2017) at known concentrations, 0.25wt%, 0.5wt% and 1wt% of TPA dissolved in the background.

6.5.4 SCANNING ELECTRON MICROSCOPY

Selected samples of materials and fibre residues were prepared for SEM analysis. A small cut piece of samples were attached to the sample holder with a carbon tape. The samples were placed in a sputter chamber to obtain a gold coating. The thickness of the coating was 300Å. The SEM images were captured using high resolution SEM, LEO Ultra 55.

6.5.5 INTRINSIC VISCOSITY

The limiting viscosity number of the pure cotton residue for the old sheets was determined using ISO/FDIS 5351:2009 (E) standard. An o.d. sample weight based on the expected intrinsic viscosity was wetted during 3 min of shaking with 25 ml of dist. water in a sample bottle. Further 25 ml of 1M CED-solution was added followed by 5 min shaking. Air was pressed out of the bottle and the cap was sealed to ensure as little oxygen present as possible. The bottle was conditioned in a 25°C water bath for 30 minutes. Three efflux times were measured for each sample using a capillary viscometer. For each fibre residue that was measured, two samples were taken. The test data was used to calculate the limiting viscosity number reported in nearest 10 ml/g.

7. RESULTS AND DISCUSSION

In this section, the results from the experiments are presented. Figures and diagrams are explained and the interpretations of the results are discussed. In the last section of this chapter, the results from this thesis are put into a wider context, by discussing the effect the findings may have on the industry in a larger perspective.

7.1 MATERIAL CHARACTERIZATION

The materials were characterized using ATR FTIR and the results in transmittance of the different materials at wavelengths 400 cm^{-1} to 4000 cm^{-1} are shown in Figure A, B and C in Appendix I. The C-O and C=O bonds in the 100% polyester sample give rise to bands in the spectrum at wavelengths around 1250 cm^{-1} and 1750 cm^{-1} (Lampman 2010). This may be compared to the 100% cotton spectra which do not exhibit such bands. By comparing the different areas of the sheets to the 100% cotton and 100% polyester samples, with a focus of the $1100\text{-}1800\text{ cm}^{-1}$ region of the spectra, it was shown that all areas of the sheets contain both cotton and polyester and no other materials. The selvedge and bulk material of the sheets have the same transmittance pattern. The printed area has a very similar pattern but not identical. Some very slight bands are seen in the wavelength interval 1450 cm^{-1} to 1600 cm^{-1} and are unique for this material. The sewing thread matches with the 100% polyester spectrum.

In the separation experiments, only bulk material was used. However, the results of the IR characterization indicate that an integrated recycling, without removal of seams and selvedge, for sheets of this or similar character may be possible. The brightness of dissolving pulps is important for producing regenerated fibres of good quality (Gruber 2006). Thus, removal of the dye of the print could be necessary since the IR spectra show traces of the dye in the blue printed area.

7.2 COTTON-POLYESTER RATIO

The cotton-polyester fibre ratio was investigated, in new as well as old sheets. The plot of the mean values for new and laundered sheets are presented in Figure 15.

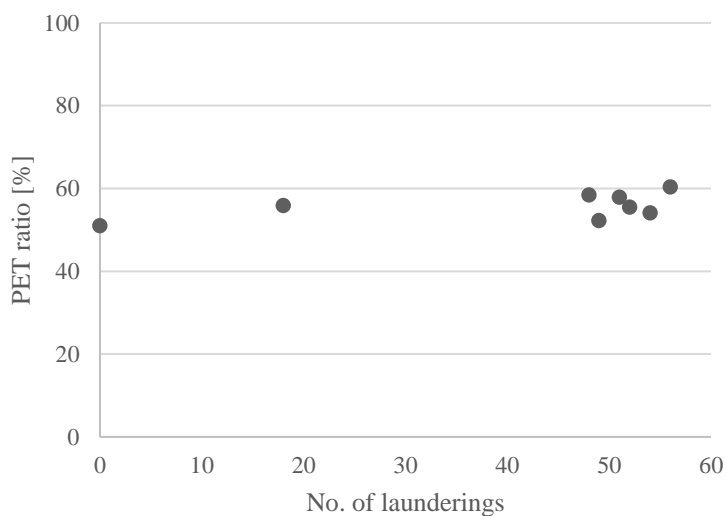


FIGURE 15 MEAN RATIO OF POLYESTER IN NEW AND LAUNDERED SHEETS

The result confirm that the cotton/polyester ratio in new sheets is around 50/50%. The mean value of fibre ratio for Sheets 0 was 51.1% polyester. The sheets laundered 18 times contain 55.9% polyester. The polyester content in the sheets laundered around 50 times was between 52.3% (Sheets 49) and 60.4% (Sheets 56). On average, the sheets laundered around 50 times contain 56.4% polyester which means that there is still 43.6% cotton left in old sheets.

The same method was also used to determine the cotton-polyester ratio in the old pillow cases. The mean value for the fibre ratio of the pillow cases was 57.5% cotton and 42.5% polyester. The ratio from the beginning was unknown.

A general view, amongst representatives in the laundering and textile service sector, is that the cotton ratio in sheets after repeated laundering would decrease to a very large extent. Even though the cotton per cent decrease in the old sheets included in this study, there is not a major difference between sheets laundered 18 times and around 50 times. Thus, sheets laundered around 50 times, regarded as discarded by Textilia, still contain a substantial amount of cotton that could be recycled. Furthermore this study show that the standardized method could be used in order to determine the cotton/polyester ratio in textiles, such as the pillow cases, where this information is unknown.

7.3 PROCESS PARAMETERS

The separation of cotton and polyester was characterized using UV-Vis spectroscopy, TPA weight yield and ATR FTIR spectroscopy of the cotton residue.

7.3.1 ALKALI CONCENTRATION

Three different concentrations of sodium hydroxide were investigated: 5%, 7.5% and 10%. The experiments were performed at 70°C and the material was ground material of Sheets 0. The result of the increase in TPA concentration, expressed as the increase in absorbance, during the experiments is shown in Figure 16.

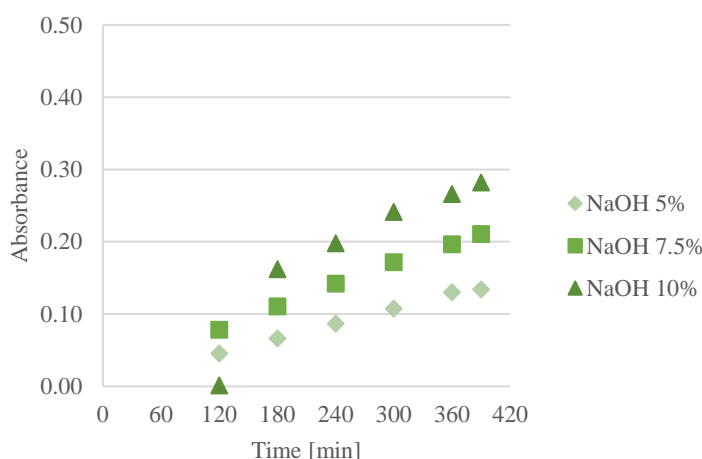


FIGURE 16 THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE DEPOLYMERISATION RATE OF POLYESTER IN NEW SHEETS AT 70°C

The TPA concentration in the solution with 10% concentration of sodium hydroxide is increasing with a higher rate than at in the experiments of 5% and 7.5% sodium hydroxide. However, none of the graphs fully reach an equilibrium where the absorbance is levelled out.

In Figure 17, the results from the TPA yield from the experiments using different sodium hydroxide concentration are shown.

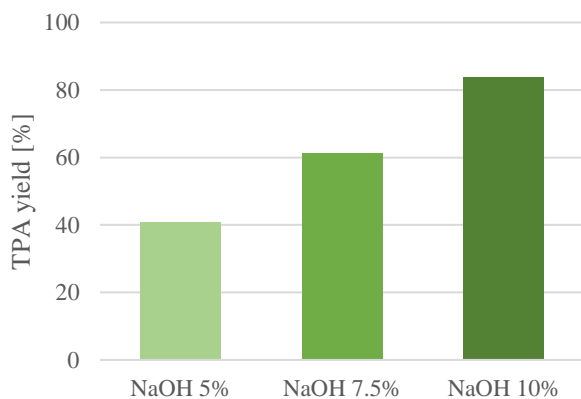


FIGURE 17 THE EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE TPA YIELD AFTER PROCESSING NEW SHEETS AT 70°C

The large impact of sodium hydroxide concentration on the depolymerisation rate of polyester was further confirmed by the results in TPA yield. The experiments performed in 5% and 7.5% sodium hydroxide concentration generate far from 100% yield. The experiment performed with 10% sodium hydroxide concentration generated the highest yield, 83.6%. The IR spectra of all of the fibre residues from these experiments, Figure D in Appendix I, show traces of polyester.

7.3.2 TEMPERATURE

Separation experiments performed at three different temperatures, 70°C, 80°C and 90°C were carried out in order to investigate the effect of the temperature. The experiments were performed using ground material of Sheets 0 and the sodium hydroxide concentration was 10% concentration. The experiment performed in 80°C was excluded from the results since the data of absorbance was incomparable to the

data from the other experiments performed at 70°C and 90°C. The influence of temperature on the hydrolysis rate is shown in Figure 18.

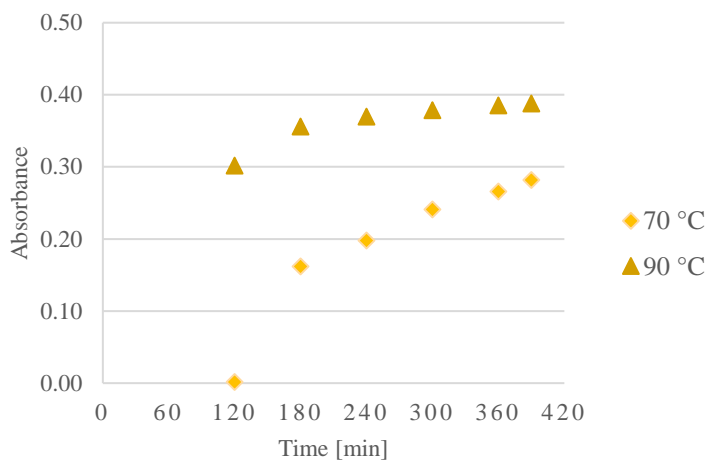


FIGURE 18 THE EFFECT OF TEMPERATURE ON THE POLYESTER DEPOLYMERISATION RATE IN NEW SHEETS WITH 10% SODIUM HYDROXIDE CONCENTRATION

The graph show that the temperature has a major effect on the depolymerisation rate. The experiment performed at 90°C reach an equilibrium although the levelling out of the absorbance is not complete. Since evaporation during the process was noted to occur, this could be an explanation of this phenomena.

The TPA yields from the experiments performed at different temperatures, are shown in Figure 19.

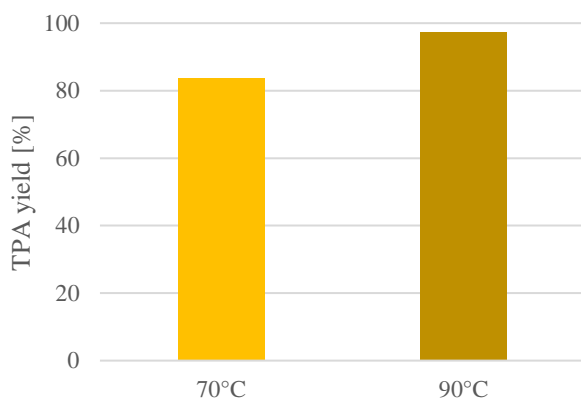


FIGURE 19 THE EFFECT OF TEMPERATURE ON TPA YIELD AFTER PROCESSING NEW SHEETS WITH 10% SODIUM HYDROXIDE CONCENTRATION

The TPA weight yield from the experiment performed at 90°C was 97.3%. This result correlates with the trend of high TPA concentration in the solution toward the end of the process time, see Figure 18. The IR spectra of the fibre residues generated from the experiments performed at different temperatures are seen in Figure E. in Appendix I. The IR spectra for the fibre residue from the experiment performed at 90°C confirms that the sample is pure cotton compared to the non-pure sample from the experiment performed at 70 °C.

7.3.3 MATERIAL FINENESS

The effect of the mechanical pre-treatment i.e. the material fineness was investigated by performing experiments with ground, shredded and cut material of Sheets 0. The experiments were performed at 90°C, using 10% concentration of sodium hydroxide. Figure 20 shows the effect of material fineness on the TPA concentration in the solution during the experiments.

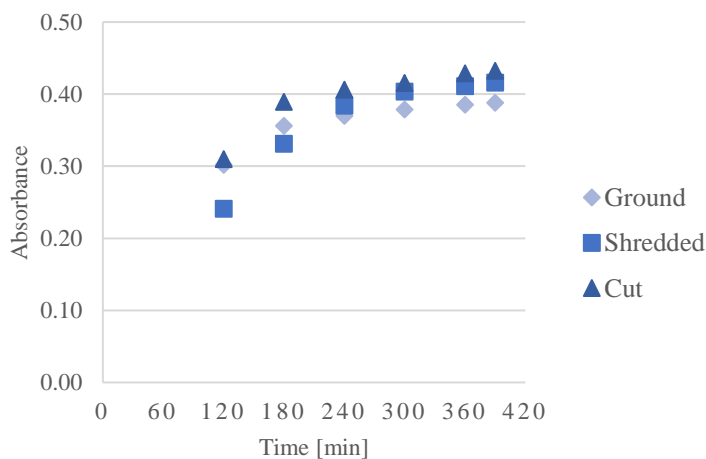


FIGURE 20 THE EFFECT OF MATERIAL FINENESS ON POLYESTER DEPOLYMERISATION RATE IN NEW SHEETS AT 90°C USING 10% SODIUM HYDROXIDE CONCENTRATION

The increase of TPA concentration in the solution during the process is equal, regardless of the material fineness. As noted during the experiments run at higher temperatures, 80°C and 90°C, evaporation was occurring. The absorbance does not level out completely for any the experiments performed using different material fineness at the end of the process time. Thus, it could not be excluded that evaporation was occurring also during these experiments.

The TPA yield from the three experiments performed with ground, shredded and cut material are presented in Figure 21.

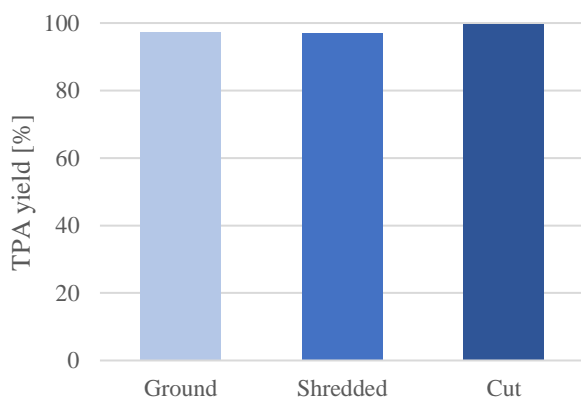


FIGURE 21 THE EFFECT OF MATERIAL FINENESS ON TPA YIELD AFTER PROCESSING NEW SHEETS AT 90°C USING 10% SODIUM HYDROXIDE CONCENTRATION

The TPA yield was high for all of the experiments, regardless of the material fineness. The yield from the experiment performed with cut material resulted in a very high yield of 99.88%. The cut material was easy to add to the heated solution when starting the experiment. Furthermore, the filtration was easy to carry out using the cut pieces of the sheets. The IR spectra of the fibre residues generated in the experiments using different mechanical pre-treatment are shown in Figure F. in Appendix I. The spectra confirm that the samples contain only cotton.

It has earlier been shown that the depolymerisation rate of polyester in flakes increases with decreasing particle size (Karayannidis and Achilias 2007). However, the woven structure used in this study has essentially only two dimensions compared to the three dimensional polyester flakes, since it is presumed that the polyester staple fibres in the yarn have the same length and fineness throughout the entire yarn. Thus, this might explain that the depolymerisation of polyester in these samples was as equally efficient regardless of the mechanical pre-treatment. It cannot be determined that the grinding significantly increase the surface area compared to the already large surface area of the very fine polyester staple fibres. The effect of parameters such as fabric construction, yarn structure and the linear density of the polyester fibres on depolymerisation of polyester in polycotton textiles, could be a focus in future research. Although nor the linear density of the yarns nor the cover factor was determined for the fabrics in the sheets it should be noted that, from the results of this study, alkaline hydrolysis is a promising route for depolymerising polyester in staple fibres in this type of woven structure without mechanical pre-treatment.

7.3.4 MATERIAL CONCENTRATION

The effect of material concentration, wt% o.d. material to solution, was investigated using cut material of laundered sheets. Two experiments were performed using 1% material concentration of two different combinations of old sheets, 48/52/56 and 49/51/54. The increase in TPA during the process is shown in Figure 22.

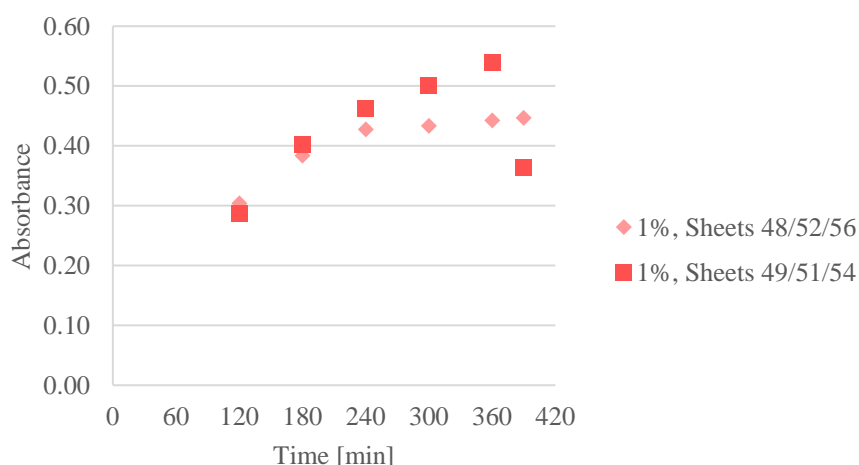


FIGURE 22 THE EFFECT OF MATERIAL CONCENTRATION ON POLYESTER DEPOLYMERISATION RATE IN OLD SHEETS AT 90°C USING 10% SODIUM HYDROXIDE CONCENTRATION

These results further confirm that evaporation of water was a problem with the reactor set-up. This was in particular noted in the 1% experiment using sheets 49/51/54, see Figure 22, where the absorbance values indicate that something went wrong during this specific experiment. Thus, there was a need for an adaptation of the set-up at this stage to prevent evaporation in further experiments.

Two experiments were performed with cut material of 3% and 5% material concentration using a mix of all old sheets laundered around 50 times. In these experiments a specially adapted plug was used in order to prevent evaporation, see Figure 13 in section 6.3. Due to this adaptation, the TPA concentration during the process could be calculated from the absorbance values obtained at the different times by Beer-Lambert law, see section 6.5.3. The increase of TPA concentration is shown in Figure 23.

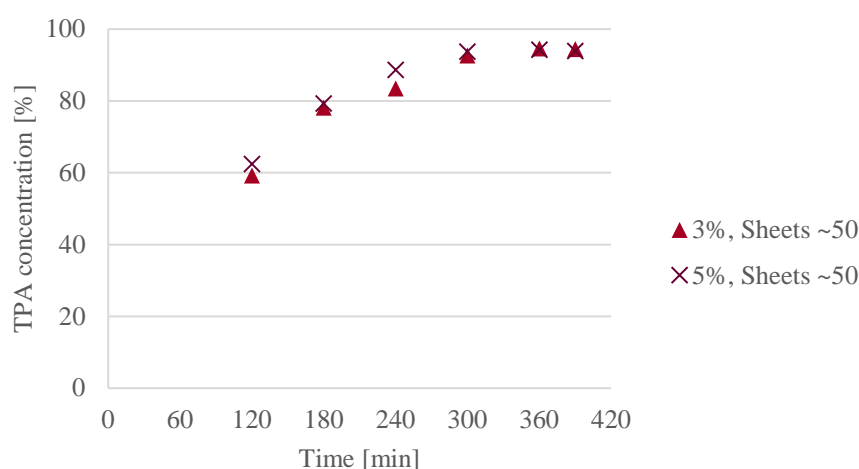


FIGURE 23 THE EFFECT OF MATERIAL CONCENTRATION ON POLYESTER DEPOLYMERISATION RATE IN OLD SHEETS AT 90°C USING 10% SODIUM HYDROXIDE CONCENTRATION

The TPA concentration was levelled out at the end of the process time for both experiments. At the times, 360 and 390 min, the TPA concentration was steady at between 93.9% and 94.7% for both experiments. Thus, it was concluded that the adapted plug prevented evaporation.

The effective TPA yield from these experiments are shown in figure 24.

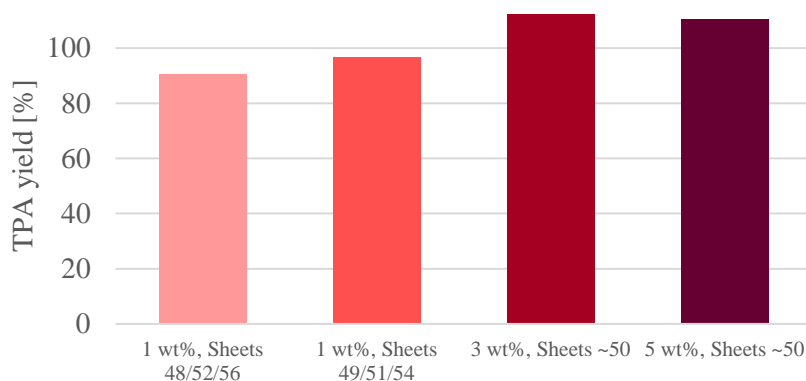


FIGURE 24 THE EFFECT OF MATERIAL CONCENTRATION ON TPA YIELD AFTER PROCESSING OLD SHEETS AT 90°C USING 10% SODIUM HYDROXIDE CONCENTRATION

The experiments using 1% of material concentration using old sheets generated 90.4% and 95.6% TPA yield respectively. As previously discussed, the graphs of absorbance, see figure 22, show that the TPA concentration of these two experiments differed from each other during the process due to evaporation of water from the solution. It is therefore difficult to draw any solid conclusions of the effect of using different combination of sheets. The IR spectra from these experiments are shown in Figure G. in appendix I. This characterization confirms that the fibre residues from the experiments of 1% material concentration contain only cotton.

The experiments performed with all sheets laundered around 50 times and with higher concentration of material, 3% and 5%, generate more than 100% of the theoretical output of TPA, seen in Figure 24. The stirring in these experiments was more difficult than in the 1% experiments. It should be further noted that the filtration of the precipitated TPA was very difficult for these experiments. Since much more TPA was produced the filtration had to be performed in several steps using multiple pre-weighed glass microfiber filters. Although this would be presumed to lead to a decrease in the effective TPA yield, the results show the contrary. From the IR spectra, Figure G. Appendix I, it is possible to see that the fibre residue of the 3% experiment generate a pure cotton residue. The residue from the 5% experiment on the other hand, indicate that the sample is not pure. However, by comparing the spectra with that of 100% TPA, it was found that the fibre sample contain TPA and not polyester. The -COOH groups of TPA give rise to bands in transmittance in the region of $1700\text{-}1725\text{ cm}^{-1}$ (Kice and Marvell 1971) that matches with the bands of the sample. TPA could neither be present in the original material nor be contaminated by the equipment. Thus, the reason for the presence of TPA in the fibre residue is interesting to discuss. The fibre residue is filtered to remove the liquid phase containing disodium terephthalate salt and ethylene glycol. The TPA is recovered after an acidification to pH 2.00, as described schematically in figure 11, section 6.1, and in detail in section 6.4. Due to the high moisture regain of cotton, the fibre residue, even after filtration using vacuum suction, could contain as much as 90wt% of solution. The fibre residue is treated in 1L of 2% solution of acetic acid (with an estimated pH of around 3). This step is performed in order to neutralize the alkali to prevent cellulose degradation. Thus, this acidic wash may lead to

precipitation of the TPA dissolved in the solution already at this stage. During experiments using a lower material concentration in the process, the filtered fibre residue cake, was smaller. This might explain why this phenomena was not seen in the initial experiments using a low material concentration. Thus, it is probable that the experiment with 5% material concentration also led to full removal of polyester, as implied by Figure 23.

7.4 COTTON YIELD

For the experiments investigating the effect of material fineness as well as material concentration, the cotton yield (o.d.) was determined. The cotton yield from the experiments using new sheets and different material fineness is presented in Table 1.

TABLE 1 EFFECT OF MATERIAL FINENESS ON COTTON YIELD

Material fineness	Cotton yield [%]
Ground	96.3
Shredded	93.7
Cut	93.3

As reported by Palme et al. (2017) the cotton yield was low as below 90% for grounded materials hydrolysed for 360 min at 90°C with 10% sodium hydroxide concentration and 1% material concentration performed without phase transfer catalyst. From the same study, experiments was also performed at the same conditions for 240 min using a catalyst. These yield are just below 90%.

Table 2 present the values of cotton yield from the experiments performed at the same conditions using different material concentrations and cut material from the combination of old sheets.

TABLE 2 EFFECT OF MATERIAL FINENESS ON COTTON YIELD

Material concentration	Cotton yield [%]
1%, Sheets 48/52/56	99.9
1%, Sheets 49/51/54	93.2
3%, Sheets ~50	101.3
5%, Sheets ~50	105.7

The cotton yield was 93.2% and 99.9% respectively for the experiments performed using 1% material concentration of cut material of old sheets. Regarding the higher material percentages, 3% and 5%, the cotton yield was above 100% of the theoretical value.

To weigh the mass of the input material used in the various experiments, an o.d. mass of polycotton material was used. The mean value of the cotton ratio was determined empirically, results presented and discussed in section 7.2. The fibre ratio was taken into account for the calculations of the theoretical output of cotton and TPA. Since only three samples for each material were used to estimate the cotton/polyester fibre ratio, it is difficult to state that the mean is representative for the true fibre ratio of the materials. Other methods e.g. thermal methods for fibre ratio determinations could also be considered (Negulescu et al. 1998a). Another factor

that could influence the results in cotton yield is the measurement of moisture content. Pieces of material were randomly sampled from the air-dried fibre residue and the moisture content was measured. However, variations in moisture content could vary within the sample, in particular in the fibre residues from the experiments using higher material concentrations where a higher amount of residue was generated. The fact that TPA was present in the fibre residue of the 5% material concentration experiment might also explain that the effective yield was above 100% of the theoretical value. However, it is presumed that the amount of TPA in the sample was little, thus, not enough to show a yield almost 6% above the theoretical output. Therefore, is hard to draw solid conclusions about the process by means of the cotton yields from these experiments.

Generally, it should be noted that in all experiments were the cotton yield was calculated, the yield was as low as around 93%. This decrease in cotton weight after the process is explained by reactions that takes place along the cellulose chain in strong alkali under oxidative conditions. Palme et al. (2014) found that the intrinsic viscosity of 100% cotton sheets, and thereby the DP, was significantly reduced by use and repeated laundering with alkaline detergents. No laundering systems is free of oxygen and this oxidative environment causes chain scission that is presumed to be the main reason for the drop in DP. In fact, this type of oxidative depolymerisation of cellulose is adopted in the viscose process to obtain a pre-aged raw material of suitable DP (Wilkes 2001). However, the reduction of DP in the pre-aging step of the viscose process is controlled by adapting time, temperature and oxygen content. With the reactor set-up used in this study an oxygen-free environment could not be ensured. The presence of oxygen under these alkaline conditions explain the loss of cotton weight after the experiments.

7.5 SEM CHARACTERIZATION

The results of the SEM characterization are presented in this section. Selected images are discussed in context of the previous characterization results.

Figure 25a and 25b show the plain weave structure of new and old polycotton sheets respectively. Figure 25c show the structure of a pure cotton residue after performing the separation process.

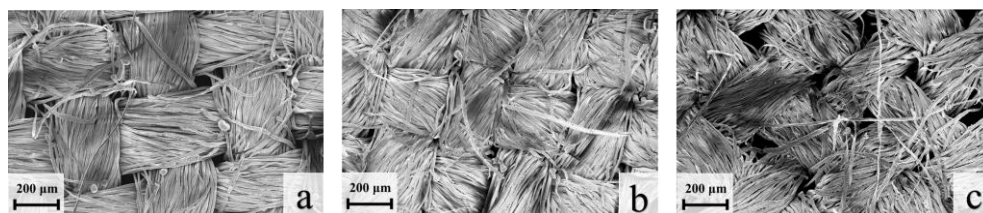


FIGURE 25 WOVEN STRUCTURE OF NEW SHEETS IN IMAGE A, OF OLD SHEETS IN IMAGE B, AND OF PURE COTTON RESIDUE IN IMAGE C, AT A MAGNITUDE OF 200 TIMES

The images show that the new sheets have a more open weave structure compared to the old sheets. Thus, the yarns were more densely packed in the laundered sheets due to the mechanical action during laundering that cause material shrinkage. This could have an effect on the separation but was not investigated. As previously discussed in section 7.3.3, the polyester staple fibre fineness rather affect the polyester

depolymerisation to a larger extent than the weave structure. It can further be noted from the micrographs that the weave of the cotton residue after separation from polyester have a more open weave structure due to the degradation of the polyester fibres.

Figure 26a and 26b show the comparison of new and old sheets at a magnitude of 2000 times. The smooth and regular polyester fibre are seen next to the twirled cotton fibre in both new and old sheets.

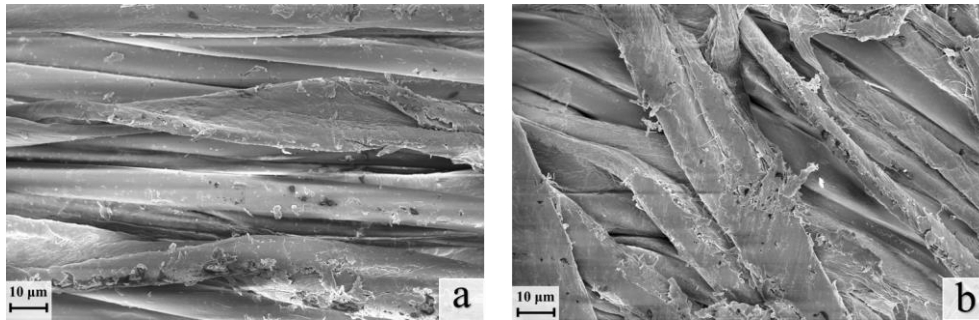


FIGURE 26 COTTON AND POLYESTER FIBRES IN, NEW SHEETS, A, AND OLD SHEETS, B, AT A MAGNITUDE OF 2000 TIMES

The polyester fibres was not much affected by laundering, see Figure 27a of fibres in new sheets at a magnitude of 30 000 times and Figure 27b of fibres in new sheets at a magnitude of 20 000 times. However, note the difference in magnitude.

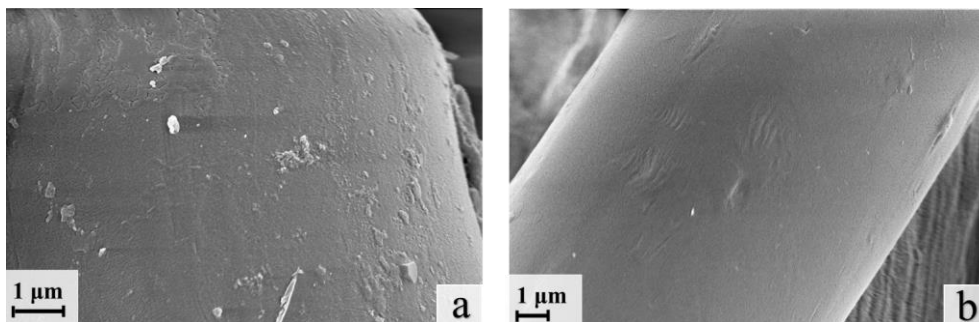


FIGURE 27 POLYESTER FIBRE SURFACE IN NEW SHEETS AT A MAGNITUDE OF 30 000 TIMES, A, AND IN OLD SHEETS AT A MAGNITUDE OF 20 000 TIMES, B

Even in new sheets, it was noted that the cotton fibres were damaged due to the mechanical processing of the fibres in yarn and fabric manufacturing. However, during the capturing of the micrographs, it was seen that the cotton fibres in the used and laundered sheets were significantly more damaged, see Figure 28a and 28b. It was seen that the primary wall of the cotton fibres was highly damaged.

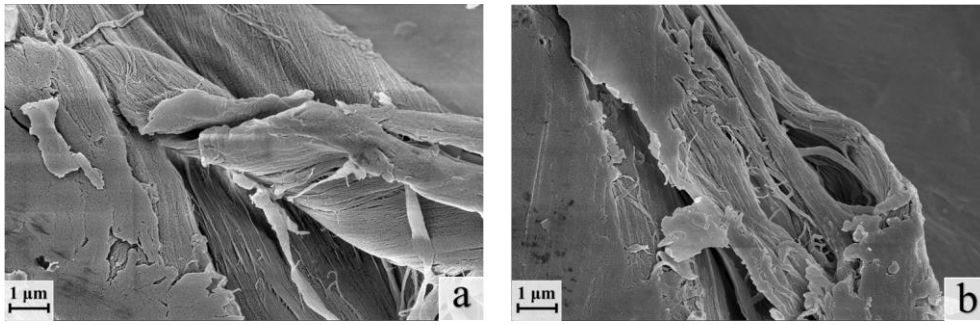


FIGURE 28 DAMAGED COTTON FIBRES IN OLD SHEETS AT A MAGNITUDE OF 20 000 TIMES

SEM images was also used to characterize the fibre residues generated from selected separation experiments. Figure 29a show the fibre residue from the 3% material concentration experiment, by the means of IR measurements characterized as pure cotton. Figure 29b, show the image of the fibre residue from the 5% material concentration experiment. This fibre residue was not characterized as pure. ATR FTIR spectroscopy showed that the residue contained traces of TPA.

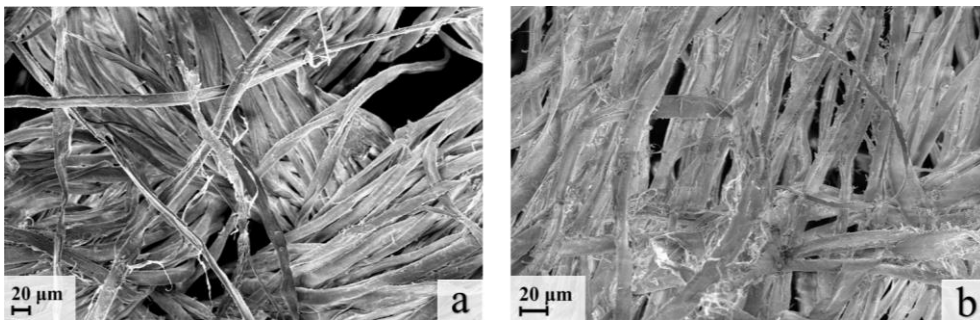


FIGURE 29 FIBRE RESIDUES FROM EXPERIMENTS USING DIFFERENT MATERIAL CONCENTRATION, 3% EXPERIMENT AT A MAGNITUDE OF 500 TIMES, A, AND 5% EXPERIMENT AT A MAGNITUDE OF 700 TIMES, B

As discussed in section 7.3.4, the acidic wash of the fibre residue cake led to precipitation of TPA. As earlier observed in the same section, the TPA concentration, calculated from the absorbance values, levelled out at the end of the process time during the 5% material concentration experiment indicating that all polyester was depolymerised. The SEM characterization further strengthen the conclusion that all polyester in fact was removed. The sample was examined at different magnitudes and no polyester fibres could be seen.

Overall, it was seen that the structure of the weave was effected of both laundering and the hydrolysis of polyester, Figure 25a-c. The surface of the polyester fibres was not affected by laundering. The primary wall of the cotton fibres on the hand was highly damaged. Since other substances than cellulose are present in the primary wall while the secondary wall contain almost 100% cellulose (Hsieh 2006), laundered cotton textiles could possibly be a raw material for cellulose derivatives. Nevertheless, it is not only the cellulose content that determines if such a raw material could be used to produce new textile fibres. Dissolving pulps are well engineered raw materials for man-made cellulosic fibres. Numerous factors influence the chemical properties of dissolving pulps e.g. DP, molecular weight distribution, alkali resistance, optical brightness (Sixta 2008). Thus, such properties would be

interesting to investigate in future studies in order to develop the process industrially. As a first attempt to further characterize the cotton residue from old sheets generated in this study, the intrinsic viscosity was measured.

7.6 INTRINSIC VISCOSITY

Intrinsic viscosity measurements were made on one of the pure cotton residues that was produced from the process using 1% material concentration and a mix of sheets 48/52/54. The mean value of the intrinsic viscosity number was 460 ml/g with a standard deviation of 0.71 for the two samples of the residue. However, it is not possible to determine the value before the process, due to the fact that the cellulose is blended with polyester. Thus, it is difficult to draw solid conclusions about the drop in DP. The value could however be compared to the values of intrinsic viscosity of 100% cotton textiles, used and industrially laundered, reported by Palme et al. (2014). By comparing the results from this study to the previous study, it is clear that the alkaline conditions needed to depolymerize polyester significantly reduced the intrinsic viscosity. However, the mean value of intrinsic viscosity of the cotton residue of sheets laundered around 50 times included in this master thesis, show that the residue could be a potential raw material for viscose staple fibres. Sixta (2008) reported that an appropriate intrinsic viscosity of dissolving pulps for standard viscose fibres is in the range of 450-500 ml/g. Furthermore, as already discussed the process set-up used in this thesis could not ensure an oxygen-free environment since air was present in the reactor during the process. The DP of the cotton fibre residue could be higher, resulting in higher intrinsic viscosities and cotton yields, if the oxidative reactions could be prevented. Therefore, a system that ensures an oxygen free environment and no evaporation should be investigated in order to maintain the cellulose as unaffected as possible.

7.7 DISCUSSION ON INDUSTRIAL AND ENVIRONMENTAL IMPACT

This section aims to put the results of this thesis in a larger context by discussing the effect this process may have on the industry.

The service sector textiles, including work wear, bedlinen and towels from e.g. hospitals and hotels, are commonly polycotton material. These textiles need to be substituted with new products before reaching their end-of-life in performance due to stains. The old sheets included in this study had indeed stains and were discoloured due to staining of the print to the bulk area in the laundering process. It is presumed unlikely that these textiles could be reused due to the lowered quality induced by laundering and use. Mechanical recycling could be considered, however, it is mostly carried out on pre-consumer waste due to the more homogenous quality of industrial scrap compared to the stained and discoloured service textiles. The next step of the waste hierarchy would thus be chemical recycling. The results from this thesis show that it is possible to upcycle stained and worn-out textiles to generate chemical raw materials, TPA and EG, as well as a high cellulose containing material for the manufacturing of regenerated textile fibres. Thus, the process investigated in this thesis could lead to a more circular flow of these types of textile products. The polyester could potentially be recycled endlessly since the depolymerisation lead to removal of all history of the material i.e. monomers are obtain

which could be used to synthesize virgin polyester. This type of chemical recycling, in terms of environmental impact, could be more beneficial compared to mechanical reprocessing that lead to thermal degradation, highly affecting the material properties and limiting the number of recycling cycles for the polyester. The intrinsic viscosity of the cotton residue obtained from old sheets show that this residue could be suitable for producing regenerated fibres. However, the DP of the cellulose is significantly reduced during the viscose process, thus, another loop of recycling the cellulose for fibre manufacturing would not be possible. The viscose fibres produced of the cotton residue must after their end-of-life be recycled by other means or reused in other applications e.g. composites.

In this particular study, it was proven that the depolymerisation of polyester could be performed with cut material in the process. This would reduce the amount of energy needed in a mechanical pre-treatment process. It was also shown that the process could be performed using a higher material concentration. With another reactor design, allowing better stirring or movement of the liquor, and another washing procedure, even higher concentrations of material could be used in the process. This would make this method more economically viable. The reason why higher material concentrations is presumed to work is that there is an excess of sodium hydroxide at 10% concentration. Thus, one of the current bottle necks for the process efficiency and thereby the impact for the industry, is the process set-up. The method must be tested further at a larger scale, in a reactor ensuring the presence of as little oxygen as possible and a good liquor flow. This is important for other processes in textile industry e.g. dyeing processes where the flow rate is well controlled to ensure good dyeing results. Similarly, this chemical process needs to be further optimized in order to be commercially interesting for the industry. Such an optimization could lead to better use of water, chemicals and energy which directly influences the environmental impact of the technology. The main drawback with the process found at this point, is the spent sodium hydroxide that could not be recovered. Hence, LCA studies must be carried out in order to map the environmental impact of this particular recycling technology in comparison to other recycling options as well as to the current waste handling of these textiles which is incineration.

Finally, one of the main advantage of this process for the chemical recycling of the materials included in this study is that all parts of the sheets could be recycled in an integrated process without removal of any parts. If the process could be further integrated in a parallel line in a viscose spinning mill, it could have a major impact on recycling of polycotton textiles.

8. CONCLUSIONS

The aim of this thesis was to further develop the separation process of cotton and polyester in textiles using alkaline hydrolysis to depolymerize the polyester. The main focus was the effect of the key parameters: alkali concentration, time, temperature and material concentration. Characterization of old hospital textiles, in terms of fibre content, was also carried out.

This study showed that the polyester ratio in old textiles increase after repeated use and industrial laundering. Nevertheless, it may be concluded that old polycotton textiles from the service sector still contain a large proportion of cotton that could be recycled to man-made cellulosic fibres. On average, the cotton ratio only decreased to 44% after 50 laundings, compared to the originally 50% cotton ratio.

The separation process was performed on new sheets with a material concentration of 1% using different alkali concentrations, temperature and material fineness. From these experiments it was concluded that the polyester is fully depolymerized without a catalyst at 90°C using 10% sodium hydroxide concentration after a process time of 390 min. The study show that these conditions could be used with good results in TPA yield regardless the material fineness i.e. using ground, shredded or cut material in the process. The fibre residue was characterized as pure cotton and the cotton yield was above 96% for all of the experiments.

The process was further performed with old sheets, laundered around 50 times, with a material concentration of 1%, 3% and 5% of cut material. It was concluded that the processes performed mixing three different types of sheets with a material concentration of 1% led to full depolymerisation of the polyester. A pure cotton residue with a cotton yield of above 93% was generated, using the same conditions as established for the new sheets. Further experiments with old sheets, laundered around 50 times and using the same process conditions, showed that even higher material concentrations could be used in the process. However, to ensure a pure cotton residue of high yield, a reactor ensuring better stirring or flow of the hydrolysis solution must be used as well as a different washing procedure to treat the fibre residue after the process.

In this work, pure cotton residue with an intrinsic viscosity of the same level as dissolving pulps used in viscose fibre spinning was produced from old hospital sheets containing both cotton and polyester from the beginning. This is a promising result that suggest that a separation of cotton and polyester using alkaline hydrolysis to depolymerize the polyester is an interesting technology for recycling old cotton and polyester textiles.

9. FUTURE WORK

The recycling of textiles have become an interesting area of research. Attempts to solve the problem of recycling textile waste more efficiently, is carried out both in industry and academia. Several processes are currently studied on how to recycle blended textile waste - including cotton and polyester blends.

The aim of this thesis was to investigate alkaline hydrolysis of polyester as a potential route for recycling of old polycotton material. Several questions need yet to be answered regarding the process. The characterization of the fibre ratio in the sheets using chemical methods need to be determined with a higher number of samples to ensure an accurate estimation. Other characterization methods than degradation of the cellulose using sulfuric acid could be considered in order to provide a better estimation of the true fibre ratio in the materials.

The design of the system used for the separation process should be further developed to prevent evaporation and ensure an environment free of oxygen. The cotton yield in relation to this should be in focus. The washing procedure also needs to be further evaluated, especially in order to use higher material concentrations in the process.

Since all textiles either have some kind of print and/or finishing or are dyed, the effect of this on the depolymerisation of the polyester and on the raw materials generated after the separation need to be investigated. An integrated recycling of hem, with sewing thread, and selvedge of the sheets is another interesting approach.

In this study, it was found that the process could be performed in a more efficient way e.g. using cut material instead of a more fine material. In order for the process to reach an industrial scale, the method must be further developed. LCA studies must also prove the economic and environmental benefits of such a process. The process must be investigated in a large scale with reactors that enables continuous processing.

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APPENDIX I

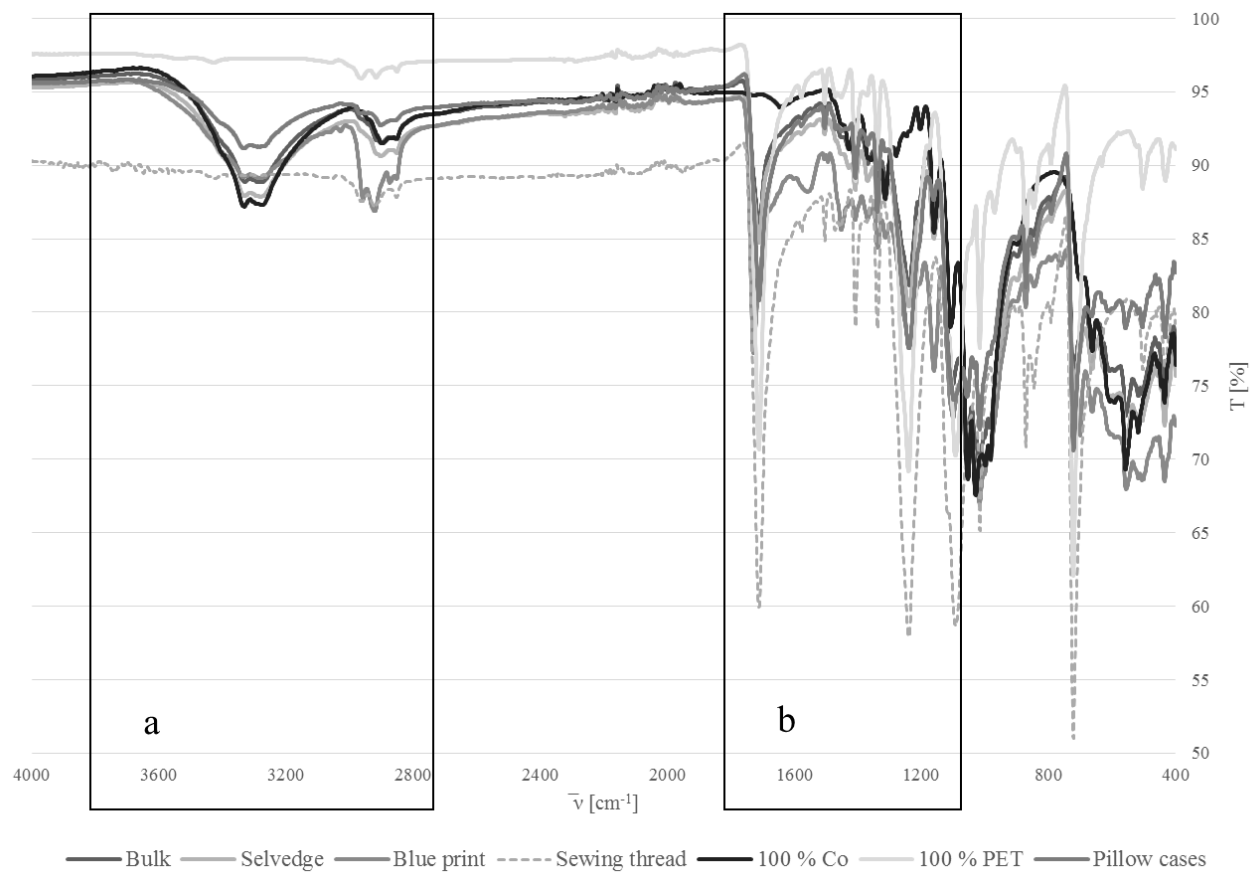
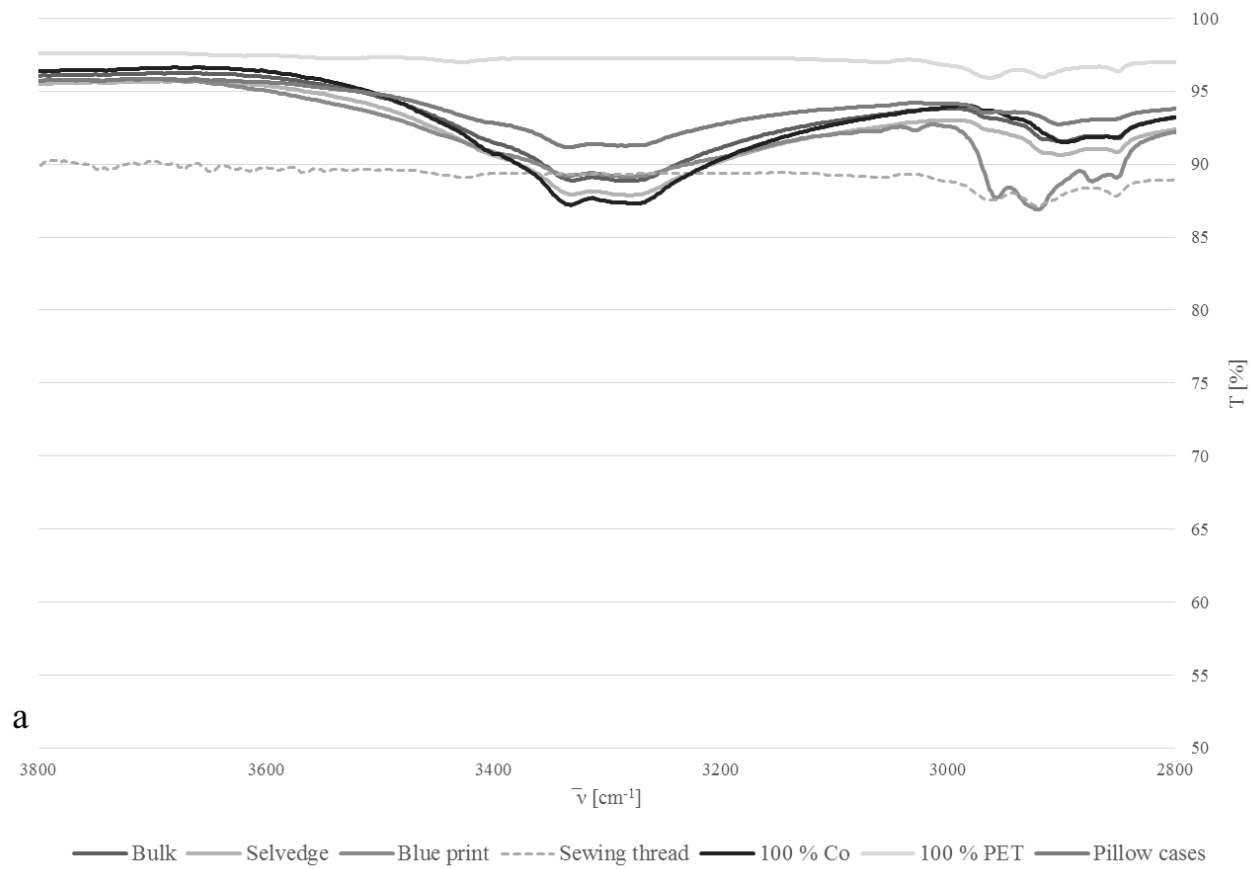


FIGURE A. IR SPECTRA OF THE CHARACTERIZED MATERIALS, WITH A AND B REGIONS



a

FIGURE B. REGION A OF THE IR SPECTRA FOR THE CHARACTERIZED MATERIALS

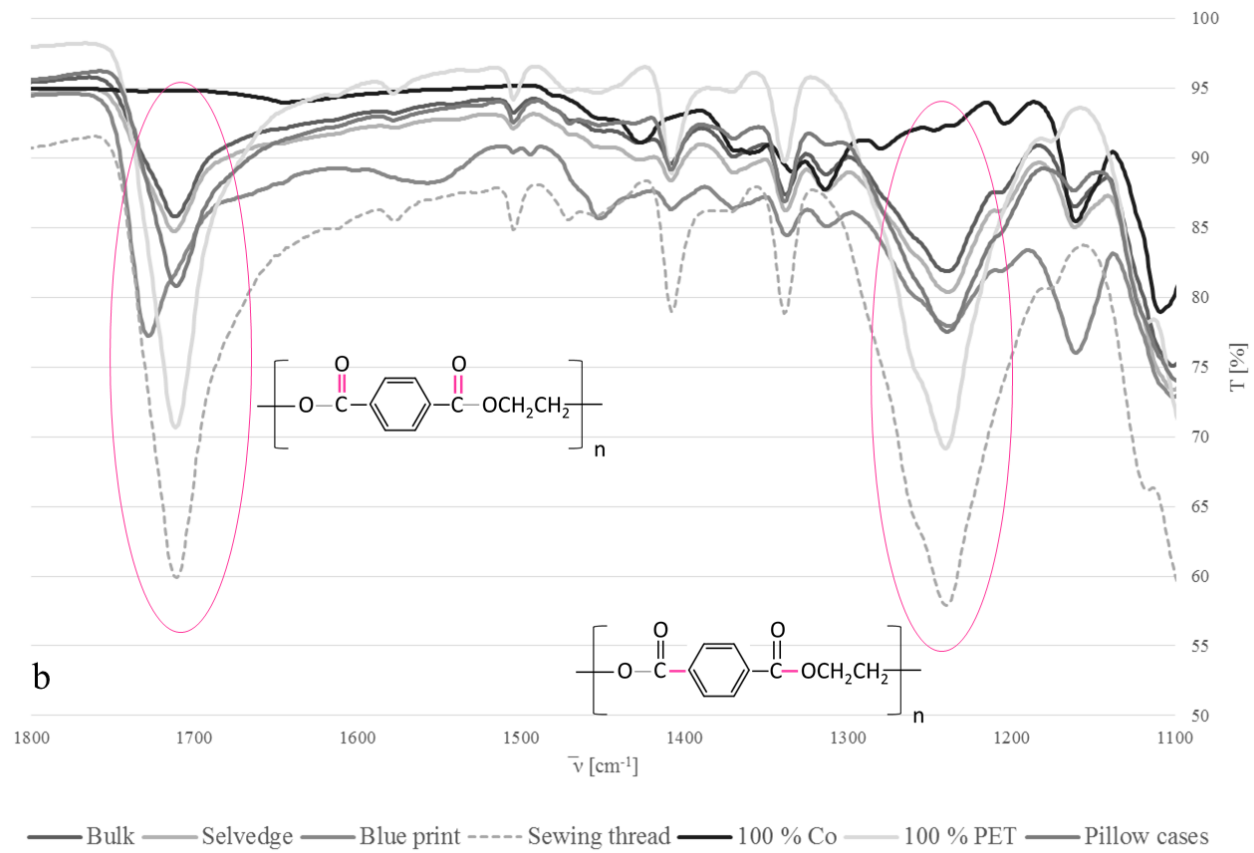


FIGURE C. REGION B OF THE IR SPECTRA FOR THE CHARACTERIZED MATERIALS

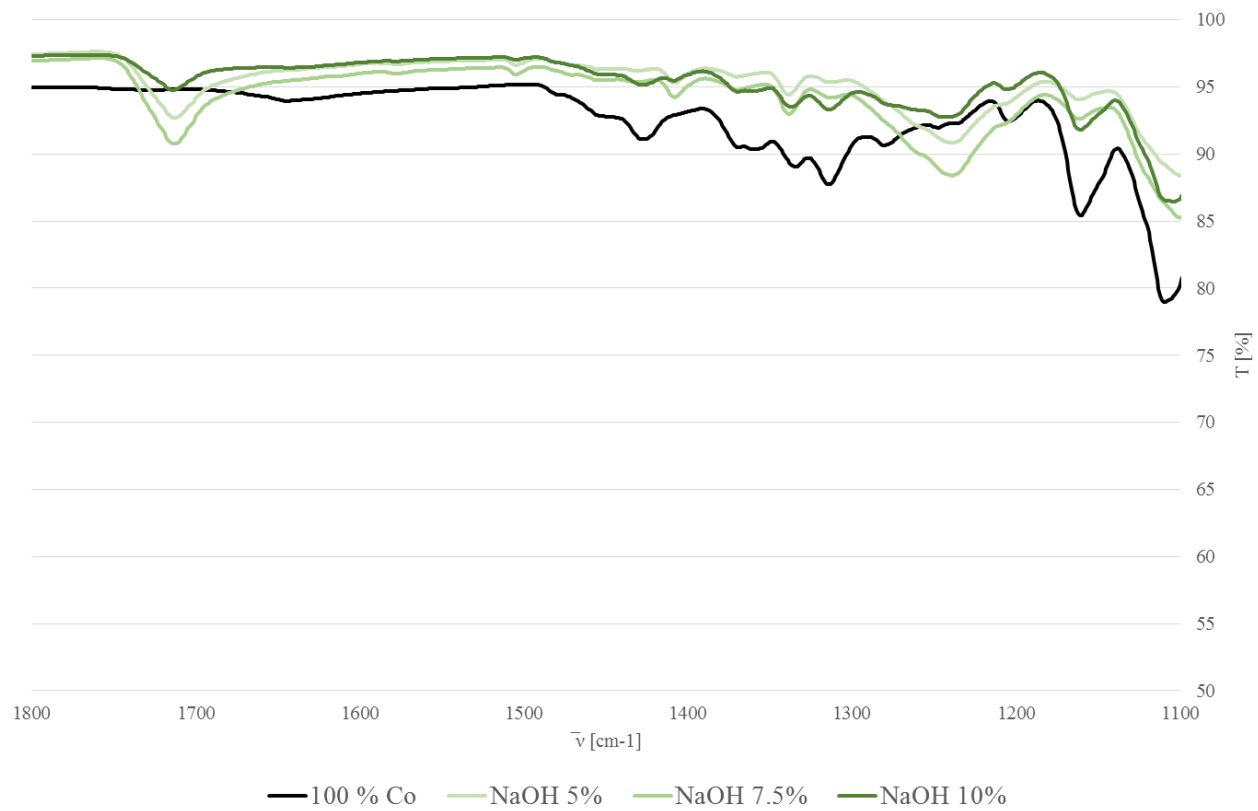


FIGURE D. IR SPECTRA OF THE FIBRE RESIDUES FROM EXPERIMENTS USING DIFFERENT SODIUM HYDROXIDE CONCENTRATIONS

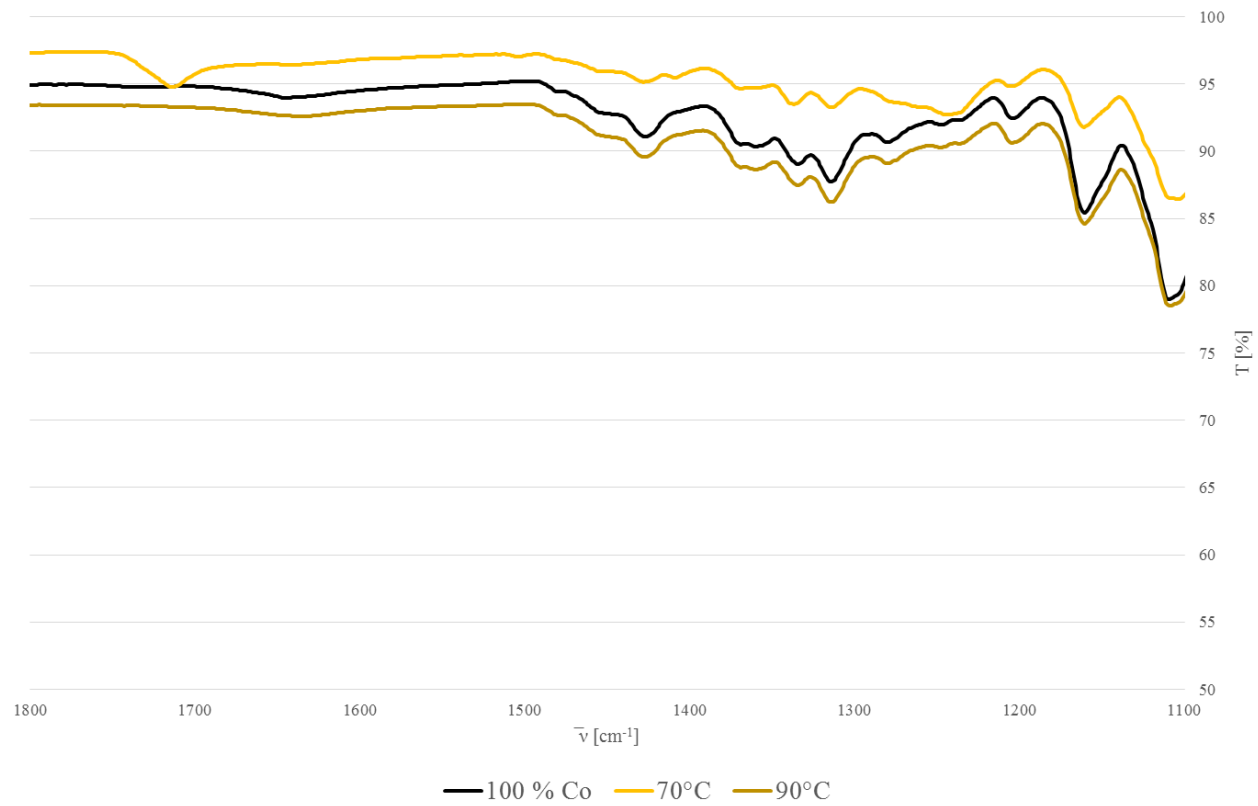


FIGURE E. IR SPECTRA OF THE FIBRE RESIDUES FROM EXPERIMENTS USING DIFFERENT TEMPERATURES

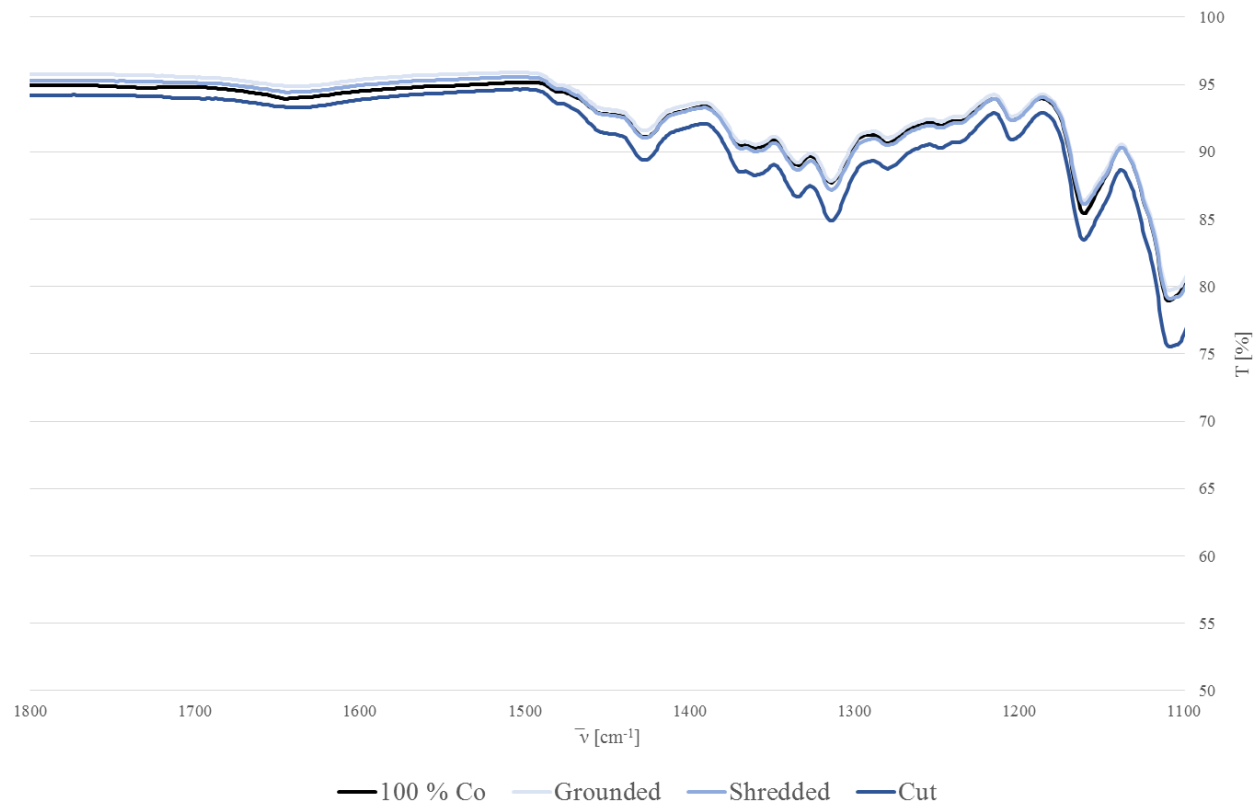


FIGURE F. IR SPECTRA OF THE FIBRE RESIDUES FROM EXPERIMENTS USING DIFFERENT MATERIAL FINENESS

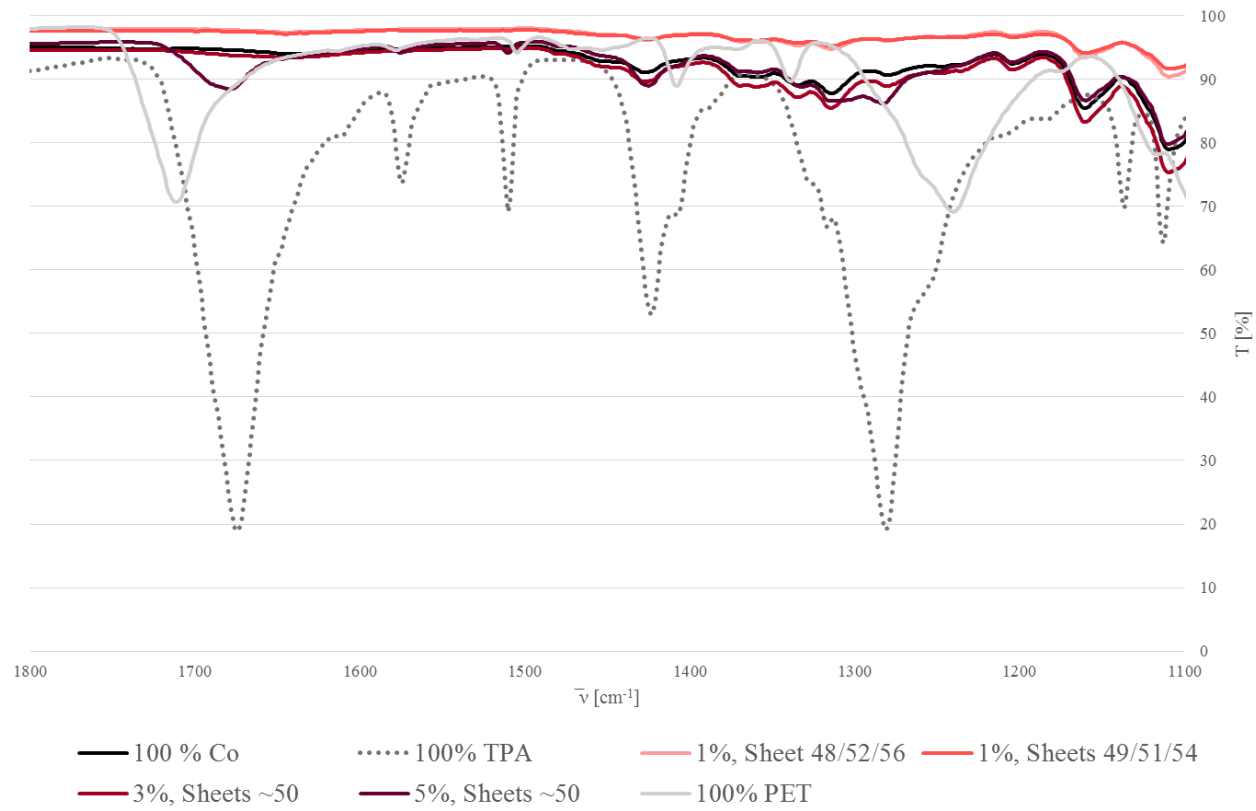


FIGURE G. IR SPECTRA OF THE FIBRE RESIDUES FROM EXPERIMENTS USING DIFFERENT MATERIAL CONCENTRATIONS