Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemical Engineering

Chaitanya Doifode

Chemical Recycling of Elastane and Elastane Blends

Master's thesis in Polymer Technology
Supervisor: Edd Blekkan
Co-supervisor: Zengwei Guo
July 2023

NTNU
Norwegian University of
Science and Technology

Chaitanya Doifode

Chemical Recycling of Elastane and Elastane Blends

Master's thesis in Polymer Technology
Supervisor: Edd Blekkan
Co-supervisor: Zengwei Guo
July 2023

Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemical Engineering

NTNU
Norwegian University of
Science and Technology

Abstract

The global environmental landscape has been significantly impacted by the accumulation and improper management of post-consumer polymers. With a significant rise in the use of polymeric textile fibres, and the massive amount of textile waste generated every year, there is an immediate need to find sustainable processes for handling this waste. Chemical recycling is an auspicious approach that involves the conversion of waste polymers into useful monomers, fuels, or chemicals. However, the chemical recycling of primary polymer components typically results in the degradation or loss of secondary polymer components due to their multi-component characteristics and comparable chemical activities. Every year, elastane, one such polymeric textile fibre, renders roughly 2Mt of textile waste unrecyclable globally. Even though the average content of elastane in any blended fabric is low (~ 10%), it has a significant impact on the recycling of polyester fibres. Hence, there is a need for a sustainable and economically feasible technology to deal with this massive textile waste other than incineration. In this master's thesis, the chemical recycling of elastane and its blend with polyester was studied. The aim was to understand the depolymerization of elastane using two methods, methanolysis and glycolysis, to obtain Poly(tetramethylene ether)glycol (PTMG) and grasp how basic parameters such as temperature, catalyst, etc. affects the processes and the recycled products. The polyester/elastane blends were also depolymerized to obtain Bis(2-hydroxyethyl) terephthalate (BHET), with the hope of understanding the effect of increasing elastane content on the recycled products. Vital data was obtained, and the recycled products were analysed using characterization methods like Fourier-transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and Differential Scanning Calorimetry (DSC).

Keywords: Chemical recycling, Elastane, PET, Methanolysis, Glycolysis, BHET, PTMG

Contents

Abbreviations

Chemicals –

PTMG - Poly(tetramethylene ether)glycol

BHET - Bis(2-hydroxyethyl) terephthalate

PET - Polyethylene terephthalate

EG – Ethylene glycol

DMT - Dimethyl terephthalate

TPA - Terephthalic acid

PTFE - Polytetrafluoroethylene

DIW – Deionized water

KAc – Potassium acetate

NaAc – Sodium acetate

ZnAc – Zinc acetate

MnAc – Manganese acetate

NaMeO – Sodium methoxide

TiMeO – Titanium methoxide

Na2CO3 – Sodium carbonate

Nomenclature – (G = Glycolysis ; M = Methanolysis)

M240 – Methanolysis at 240 °C

G240 – Glycolysis at 240 °C

MKAc – Methanolysis using KAc as catalyst

GNoC – Glycolysis using no catalyst

PPol. – Pure polyester blend

1%B – Blend with 1% elastane content

1. Introduction

Plastics are among the biggest challenges that the world confronts today, evidenced by the fact that it is predicted that by the year 2050, there will be more plastic particles in our seas than fish by weight[1]. This 'plastic problem' is a major cause of concern for our entire civilization and needs immediate attention. Textiles are among the largest and most prevalent uses for synthetic polymers, and the widespread and growing use of plastics in clothing presents a significant environmental concern. There is a need to recycle these plastics to create valuable products. However, the rate of textile recycling is not particularly great. Aside from the frequently cited cause of the insufficient public desire to participate in recycling, economics, and lack of technologies are major factors in the adoption of other waste disposal methods[2]. There are just a handful of economically feasible textile recycling techniques. The development of technologies to convert textile wastes to raw materials for the production of new textile fibres is a key problem for the textile industry. This master's thesis addresses such a process: chemically separating polyester and elastane fibres and depolymerizing the polyester/elastane blend using methanolysis or glycolysis to respective monomers and polyols. The polyols may subsequently be utilised to make elastane fibres, while the polyester monomers might be used as raw materials or re-polymerized into fresh polyester. The aim of this introductory chapter is to provide the reader with an overview of the thesis project. The background, problem description, motivation, objective, scope, and limitations of the thesis are presented in this chapter.

1.1 Background

The worldwide need for textile products is continually growing at a very rapid rate. As the world population grows and living conditions improve, consumption also increases. The quick shift of fashion trends, along with relatively low clothing prices, also contributes to the rise in consumption and has also reduced the life cycle of textile products, resulting in greatly increased textile waste[3]. So far, approximately 8.3 billion tonnes of synthetic polymers and plastics have been produced, with only about 9% of these having been recycled[4]. This is mostly owed to unsolved technological hurdles and the comparative prices of recycled and virgin materials[5]. Textiles are one of the most common applications for synthetic polymers, and the widespread and expanding usage of plastics in clothing is causing considerable waste generation. In 2021, 113 million tonnes of textile fibres were produced globally. Global fibre output nearly doubled in the last 2 decades, from 58 million tonnes to 113 million tonnes, and is predicted to exceed 149 million tonnes in 2030 if current trends continue. The majority of these fibres, 69%, are man-made and include both synthetic and cellulosic fibres. Yet in 2021, pre-and post-consumer recycled textiles accounted for less than 1% of the global fibre market[6].

Blended textile materials account for more than one-third of post-consumer textile waste. But if trimmings like sewing thread and labels are considered, it is likely much more prevalent[7]. Because of their distinct properties, blended fabrics are frequently made and widely utilized. They have a range of complexities that provide them with the desired properties. However, as these fabrics reach their end of life, their variety and complex structures make them very hard to recycle[8]. The most popular elastane-containing fibre blends have a polyester, polyamide, or cotton base. Certain applications involving wool may also contain elastane in the blends. Elastane is predicted to expand at the fastest rate of volume growth over the next decade, at 66%, as opposed to 39% for polyester fibres[9]. Elastane's entire market share is expected to increase from 0.7 to 1% by 2030. Although this amount appears insignificant, elastane stands out as a specific issue because, despite being a minority fibre, it is used in an increasing number of garments. Elastane now accounts for around 20% of the theoretically recyclable textile waste, an amount that might climb to 29% by 2030[10].

1.2 Problem

Currently, some fibre blends are being recycled on an industrial scale, but the processes have yet to be demonstrated at scale in terms of both technology and operating expenses. As a result, the vast majority of post-consumer textile waste is either burnt for energy recovery or discarded in landfills[11]. Recycling of wool-, denim- and cotton-based textile products is currently achievable to some extent. Polyester recycling to secondary raw material for PET manufacture is already in place and may be utilised to supply smaller amounts of sustainable building blocks into the pre-existing textile value chain[12]. The existence of elastane in the textile blends results in the destruction of 0.1 Mt of already accessible, collected, and potentially useful recyclable material in Northwestern Europe and roughly 2 Mt globally[10]. This is mainly because elastane acts as an impurity in the recycling process of textile blends. The structure of elastane is relatively unreactive due to the mixture of multiple types of linkages, no enzymatic system has been found to be successful at biodegrading elastane[13]. Mechanical separation and melt separation also prove to be a challenge when it comes to elastane blends. During melt separation, the elastane tends to degrade which makes it very hard to separate from the base fibre and hence ends up contaminating the desired textile. Similarly, as the fraction of elastane in most textile blends is low, it is very complicated to separate it mechanically. Hence, chemical recycling is the most suitable and research worthy path toward finding a suitable technology for elastane blend recycling.

This master’s thesis explores the chemical recycling of pure elastane and elastane blends. Polyester/elastane blend is one of the most common and highly utilised textile blends.

A process that chemically separates elastane and polyester in blended fabrics to address the difficulty of recycling blended textiles is investigated in this thesis work.

1.3 Motivation

Of the total waste stream, textile waste is still a minor fraction of it, but from a lifecycle viewpoint, textile waste is among the most severe climatic implications. The manufacturing of new textiles produces around 15 kg of CO_2 each kilo of textile produced, as well as a large quantity of water, energy, and chemicals are required for the same. Because textile materials are typically manufactured in low-wage nations with lax environmental regulations, costs are maintained cheap, and the expense of environmental harm is not incurred by the customer. As a result, using virgin products is more cost-effective than recycling[14]. Most of the industry currently lacks technologies that allow the utilisation of waste textiles to manufacture new high-quality fibres. An effective recycling chain must be capable of collecting, sorting, and regenerating high-quality fibres. It is estimated that, regardless of its utilization as a minor fraction of a textile blend and small total quantity, elastane currently renders approximately 16 million tonnes of textile waste very hard or even unable to recycle, which could increase to 50 million tonnes by 2030. This highlights the complexity of recycling blends of elastane. Elastane caused the buildup of 300 Mt of non-recyclable garbage between 2000 and 2020, a figure that is expected to rise to 500 Mt by the year 2030[15]. As stated earlier, textile fibre recycling is a complex issue, yet the environmental advantages of a functioning textile fibre recycling chain are immense. Thus, developing a technology that allows to chemically separate the fibres and bring back the recycled products in the value chain, is of great importance. To treat the textile waste stream, novel technology must be created, as well as knowledge in this field must be significantly improved.

1.4 Purpose

The purpose of writing this master's thesis is to examine and evaluate the potential of chemical recycling processes as a sustainable and viable solution for handling elastane and elastane blend waste. The goal is to maximise the efficiency with which material resources are used and to re-route material resources back into the loop in the value chain. The working of the processes and then optimizing the processes so they are sustainable and economically viable. To get a full grasp of the chemical properties of elastane and its blend, including structure, composition, and properties. This understanding will serve as a basis for developing efficient recycling systems. Also, to understand the degradation mechanisms of elastane and its blend under various conditions. This investigation will aid in the identification of the most efficient depolymerization procedures and conditions for the effective recovery of crucial monomers or other chemical compounds. Evaluate the efficiency and efficacy of some processes among all the processes that can be used, such as hydrolysis, methanolysis, glycolysis, pyrolysis, etc. This assessment will examine whether it is feasible to recycle elastane waste into valuable resources with high yields and purity. This master thesis should contribute to the advancement of sustainable waste management and provide valuable data and findings on the recycling of elastane and elastane blends. The findings will provide valuable insights for future work to be done in this field. Ultimately this thesis seeks to encourage a circular and sustainable approach to elastane waste management, so assisting in the transition to a more sustainable and resource-efficient textile sector.

1.5 Objective

As illustrated in the above section, the main objective of this thesis is to increase the scientific knowledge regarding recycling of elastane and its blend. Following the purpose described, the following were the objective of this thesis project -

- Investigate the recycling of pure elastane by methanolysis and glycolysis.
- Compare the two processes based on efficiency and reaction conditions to choose the most viable process.
- Using the most suitable process among the two processes and then investigating recycling of polyester/elastane blend using that process.
- Optimizing the processes.
- Characterization of the products obtained after recycling.
- Analysing the data of the materials and the products.

1.6 Scope and Research Questions

Based on the purpose and objectives described above, the scope of this thesis was to select the most viable and effective process for recycling of elastane and elastane blend, optimise the process and collect valuable data. This was achieved by investigating the following parameters –

- Varying the reaction conditions for both methanolysis and glycolysis.
- Changing the temperature of the process keeping all other parameters constant, hence checking the dependence of temperature on both the processes.
- Testing different catalysts and checking their efficiency at the most suitable temperature.
- Investigating different polyester/elastane blend ratios, i.e., varying percentage of elastane in the blend.

The following are the research questions that this thesis project hopes to answer and were considered throughout the project –

I. What is the decomposition mechanism of elastane under various chemical recycling process conditions, and how do these mechanisms impact the recovery of important products?
II. What are the ideal conditions for effective depolymerization and recovery of important components, and how may glycolysis, and methanolysis be used as chemical recycling processes for elastane and elastane blends?
III. What is the efficiency and selectivity of various chemical recycling processes for elastane waste, and how do they compare in terms of yield and purity of the recovered products to conventional recycling methods?

1.7 Limitations

Chemical recycling by processes such as methanolysis and glycolysis for plastics and synthetic fibres can have high energy requirements and harsh reaction conditions that could harm the material components which is especially problematic when separating out a minor constituent like elastane from a blend. Furthermore, the unspecific breaking of bonds in polymer backbones hinders further separation and purification which can be very problematic if the whole process is to be economical and sustainable. The other significant limitation of this thesis project was the lack of information and available literature. Given the rapid rise in production of elastane and its blends over the last couple of decades, the research seems to lack behind and not in conjuncture. There is a research gap and hence there is not much published research on chemical recycling of elastane or its blends. Also, the time required for the process (from depolymerization to purification) could also be said as a limitation, as this limits the number of experiments that can be done in the allowed timeframe. Choices made regarding the project have thus been compelled to take all this into consideration, such as investigating and selecting which recycling process to focus on and what process conditions are more suitable.

The subsequent section of the thesis includes an overview of the fundamental structure, whereby Chapter 2 explores the relevant theoretical framework and literature review conducted for this particular research project. Chapter 3 subsequently illustrates the methodologies and procedures utilized for this thesis work. Chapter 4 of the thesis encompasses a comprehensive presentation and detailed discussion of the data derived from the conducted characterization techniques. Chapter 5 of the manuscript presents the conclusions derived from the research findings. Subsequently, chapter 6 outlines potential avenues for further research on this particular topic.

2. Theory

2.1 Textile fibres

The market offers a diverse array of textile fibre varieties. These textile fibres exhibit not only diverse chemical compositions but also a broad range of physical properties, hence demonstrating their extensive use across several domains. The selection of textile fibre is dependent upon several factors, including the intended application, economic considerations, environmental implications, and desirable characteristics of the ultimate product. The continuous development of technology has led to an expansion in the variety of fibres that are now accessible, therefore providing novel solutions to address the numerous needs faced by the textile industry[16].

There are fundamentally two types of textile fibres, natural fibres, and man-made fibres.

2.1.1 Natural fibres

A natural textile fibre refers to a fibre that either occurs naturally or is derived from natural sources[17]. Natural textile fibres are frequently biodegradable, and their manufacture typically does not cause significant harm to the environment. They have the ability to thrive in many climatic conditions and possess the capacity to efficiently recycle carbon dioxide. Textile fibres of natural origin may be categorized into three distinct classes based on their source: vegetable, animal, and mineral. Various types of plant fibres can be obtained, such as cotton, banana, jute, flax, hemp, and others[18].

They are of three types based on their chemical classification –

- Cellulosic fibres
- Protein fibres
- Mineral fibres

Cellulosic fibres that are widely employed in the textile sector encompass cotton, linen, flax, hemp, and jute. Various types of natural textile fibres derived from animals encompass silk, wool, cashmere, and other similar materials. Asbestos the only know naturally occurring mineral fibre[19].

Natural textile fibres are commonly distinguished by their key characteristics, including air permeability, hygroscopicity, moisture release capability, absence of harmful substances or allergenic reactions, biodegradability, and reduced flammability relative to synthetic fibres[20].

They also have a diverse array of physical, mechanical, and chemical qualities, which distinguish them from one another. The physical and mechanical properties of a material encompass various characteristics such as dimensions (length, width, cross-sectional shape, and diameter), colour, lustre, surface contour, strength, flexibility, abrasion resistance, handle or feel (e.g., softness in cashmere, coarseness in coir, crispness in linen), moisture absorbency, and electrical properties. Significant chemical characteristics encompass fire resistance, chemical reactivity, resistance to various substances such as acids, alkalis, solvents, light, etc., and antibacterial capabilities[21].

2.1.2 Man-made fibres

Man-made fibres are produced by the process of extrusion, wherein a polymer is melted or dissolved and then forced through the narrow apertures of a spinneret. This method enables the production of both filament yarns, which consist of a single continuous fibre, and spun yarns, where shorter fibres are cut and spun together[16]. Man-made fibres can be characterized into three types as shown in Figure 1.

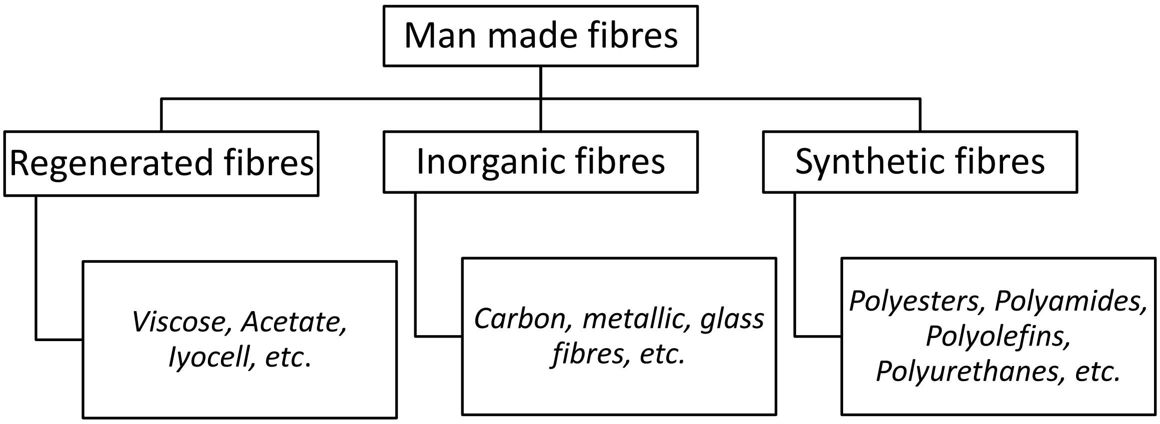


Figure 1 - Types of man-made fibres[22]

The classification of man-made fibres can be based on their composition, dividing them into two categories: organic and inorganic. Organic man-made fibres may be classified into two main categories: regenerated fibres and synthetic fibres. Synthetic fibres are derived from polymers that are chemically produced. Polyester, acrylic, and polyamide fibres are highly recognized in the fashion and clothing industries due to their extensive range of uses[22].

Synthetic textile fibres have shown a substantial increase in their utilization within the textile industry, becoming prominent raw materials. These fibres find application in a wide range of common items, either in their pure form or in combination with other fibres such as cotton. They consist of polymers and exhibit a lack of decomposition in natural environments. Synthetic textile fibres are manufactured by the process of extrusion, wherein a polymeric substance of synthetic nature is forced through a spinneret into either air or water. Synthetic fibres are commonly derived from these polymers from petrochemical sources, and hence are typically classified as fibre-forming polymers[23]. These textile fibres provide several notable characteristics, such as high tensile strength, exceptional durability, inherent elasticity, prolonged crease retention, resistance to a wide range of chemicals, and low moisture absorption, hence facilitating accelerated drying processes. These materials exhibit resistance to insects, fungi, and decay, and they retain their original dimensions even after undergoing washing. They are extensively utilized in both the garment and industrial sectors[24].

Polyester is the favoured synthetic fibre commonly used in a blend of cotton and wool. In addition to their utilization in the production of clothes, these materials find application in various home furnishings, including but not limited to curtains, carpets, draperies, sheets, covers, and upholsteries. Polyesters are extensively utilized in a diverse range of products, including tire cords, belts, ropes, nets, hoses, sails, automotive upholstery, as well as fibre fillings for various items such as cushions and furnishings[25].

One of the main challenges encountered within the synthetic textile fibre production industry refers to the degradation of the environment, with the concurrent increase in the need for environmentally sustainable fibres. The environmental pollution caused by synthetic polymers may be attributed to several factors, including the release of carbon dioxide (CO_2) during their life cycle, the depletion of finite fossil resources, and their detrimental effects on aquatic and wildlife habitats. Extensive research has been conducted to explore biological methodologies for the degradation of synthetic fibres as a means of addressing this issue. Various types of microorganisms have been investigated in order to identify organisms capable of incorporating synthetic fibres into their metabolic processes. The manufacture of sustainable synthetic fibres is a crucial response to the aforementioned difficulties[26].

In order to have a comprehensive understanding of the potentialities and obstacles associated with textile recycling, it is necessary to develop a profound comprehension of textile fibres. This section aims to offer a more comprehensive understanding of polyester and elastane fibres. The mentioned fibre types are given prominence due to their significant production quantities and significant future growth, resulting in their overwhelming presence in the textile waste stream and rendering a large fraction of recyclable waste very difficult to recycle. In order to comprehend degradation processes, polymerization, depolymerization, and potential recycling procedures, it is important to possess knowledge regarding molecular structure, crystal structure, and chemical resistance of the fibres, all of which will be discussed below.

2.1.3 Polyester fibres

Polyester, being the most widely utilized synthetic fibre globally, finds extensive application across several domains, including both traditional textile products and specialized technical fabrications. Polyethylene terephthalate (PET) is the prevailing form of polyester. It is a linear polyester composed of organic compounds characterized by the presence of repeated ester groups. Among all synthetic textile fibres, PET fibre is the most extensively manufactured. The polymer has a chemically uniform structure characterized by a restricted degree of flexibility in its macromolecules. The majority of the elementary units comprise a phenylene ring and two ester groups[27].

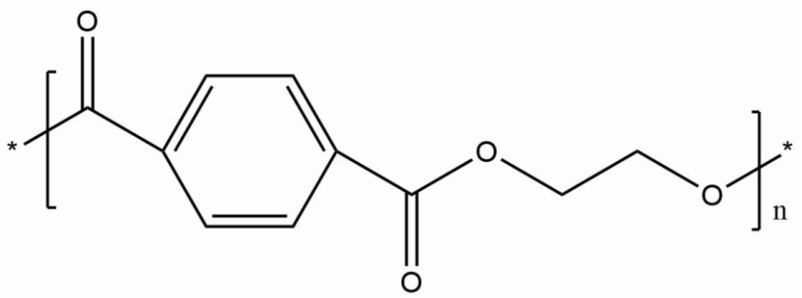


Figure 2 - Structure of Polyethylene terephthalate (PET)

In the commercial context, the use of aromatic polyester involves the utilization of ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA) to synthesize polyethylene terephthalate. PET is produced for commercial use using two distinct manufacturing processes: the dimethyl terephthalate (DMT) technique and the terephthalic acid (TPA) method. The DMT technique entails the use of DMT, which is subjected to a reaction with mono ethylene glycol (EG) in the presence of a catalyst, commonly a metal oxide, at temperatures ranging from 150 to 200°C. This process yields the monomer diethylene glycol terephthalate (DGT). The DGT compound subsequently undergoes poly-condensation polymerization in the presence of a catalyst, often a metal acetate, at a temperature ranging from 265 to 285 °C and a pressure of 1mm Hg, resulting in the formation of PET polymer. The TPA technique involves the reaction of terephthalic acid with ethylene glycol under the influence of metal oxides acting as catalysts, in a temperature range of 250–290°C, resulting in the formation of the monomer BHET. Polycondensation polymerization is employed in the production of PET polymer through the process of DGT[22,28]. PET fibres have remarkable physical and chemical properties, including exceptional dimensional stability, durability, bulk elasticity, resistance to chemicals, and great resistance to abrasion. Additional attributes are stability exhibited by thermoset creases, elevated levels of light and heat resistance, as well as the enduring nature of PET fabrics. PET fibres have the ability to dry quickly as a result of their low water absorption. The material has a favourable reaction to prolonged stress, demonstrating resilience in both creep and fatigue conditions. Additionally, the acceleration of creep damage is observed under these conditions[29]. It is widely utilized as the primary polyester for the manufacturing of fibres. This is primarily attributed to its favourable end-use characteristics and cost-effectiveness. Moreover, PET exhibits a high degree of adaptability through physical and chemical modifications, which allow for the elimination of undesirable features and the enhancement of those that are advantageous. PET fibres have the inherent capability to be simply changed and conveniently textured. The extent of strength reduction resulting from environmental factors is contingent upon the specific degradation process at play. PET fibres exhibit several unfavourable qualities, including limited water absorption, high susceptibility to pilling, static electrification, and challenges in achieving dyeability[28,30]. These fibres are often employed in a wide range of applications, encompassing both the textile and industrial sectors. A diverse range of fibres are available in the market, including multi-filament, textured yarn, staple fibre, mono-filament, and chopped fibre. They are extensively utilized in the field of technical textiles, finding application in many goods including but not limited to tire cords, belts, ropes, hoses, airbags, car seats, geo-textiles, fishing nets, and non-woven fabrics[31].

2.1.4 Elastane fibres

Elastane fibres are often recognized by their commercial names such as Lycra or Spandex. Elastane is a synthetic fibre of biological origin that was developed in Germany in 1937. One of the notable characteristics of this substance is its exceptional flexibility, which is not typically observed in natural materials. The fibres exhibit a tensile strain of more than 200% at the point of fracture and demonstrate a prompt restoration of their original state upon the removal of tension. Elastane fibres have rubber-like characteristics, with a notable capacity for reversible extension reaching levels as substantial as 400-800%. The aforementioned materials exhibit superiority over rubber due to their enhanced strength, reduced weight, and heightened versatility. One notable benefit of elastane fibres in comparison to rubber yarns is their inherent ability to be easily spun into thin fibres, rendering them highly appropriate for many textile applications[32].

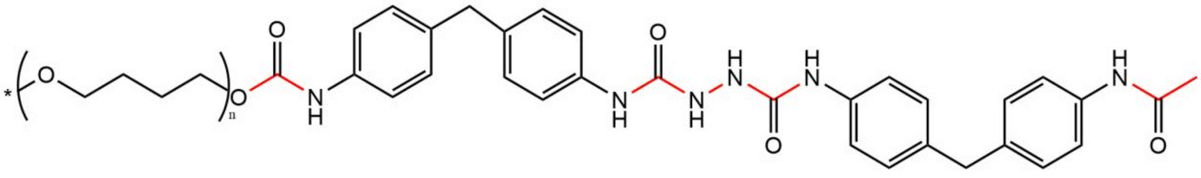


Figure 3 - Structure of elastane

Elastane is produced using elongated synthetic polymers mostly composed of segmented polyurethanes. Elastane may be described as a synthetic linear macromolecule composed of a lengthy chain consisting of a minimum of 85% segmented polyurethane. This chain is characterized by the presence of alternating hard and soft segments that are connected by urethane bonds, namely NH - CO - O. The elastane fibres are composed of polymeric chains that consist of alternating blocks of hard and soft segments. Soft chain segments provide elasticity to the elastane fibres and can be composed of either polyethers or polyesters. In the condition of relaxation, the structures of the soft segments are characterized by a loose arrangement. However, with the extension of the fibre, these segments undergo unwinding and exhibit a greater alignment with the axis of the fibre. Upon the removal of tension, the segments undergo a transition back to their initial condition. In contrast, the hard segments of the material consist of hard aromatic structures that contribute to molecular interactions, imparting strength, and long-term stability to the fibre. The interaction between individual hard segments is primarily facilitated by hydrogen bonding, allowing for intermolecular interactions with nearby polymeric chains. Hence, the elastomeric fibre exhibits a robust interconnected structure, hence preventing the occurrence of slippage between neighbouring chains. The determination of the characteristics of the fibre is dependent upon the equilibrium between the relative proportions of soft and hard segments. Insufficient stretch may result if the intermolecular interactions among polymeric chains are very strong. If the interaction is insufficient, the chains will slide relative to one another, and the fibre will not recuperate correctly after being stretched. However, effective management of the composition and dimensions of each segment, as well as the proportion of rigid to flexible segments, may yield precise control over the resulting mechanical characteristics. The elastane fibre has a high degree of compatibility with several commonly used fibres such as nylon, polyester, acetate, polypropylene, acrylic, cotton, wool, rayon. Consequently, it may be effectively blended with these fibres during the spinning process, resulting in the creation of distinctive textiles that possess combined features of both fibres. Elastane, because of its lightweight nature, soft texture, smooth surface, and non-constraining properties, finds predominant application in sporting apparel. The thermal characteristics of elastane at low temperatures are mostly determined by the properties of the soft segments. The thermal behaviour at elevated temperatures is contingent upon several factors, including the composition of the hard segment matrix, the molecular weight, the kind of chain extension, and the orientation of the hard segment. At temperatures over 170°C, a discernible thermal degradation of the fibre occurs, resulting in observable yellowing and a decline in elastic characteristics. The compound exhibits solubility in solvents with high polarity, such as DMF and dimethylacetamides[16,33,34].

2.2 Textile recycling

Textiles can be considered complex materials. To begin with, it is pretty common practice to incorporate fibre blends in the composition of several fabrics in order to achieve certain desired characteristics, which cannot be achieved by a single fibre type. These blended textiles are dyed and undergo chemical treatment to produce certain qualities, such as fire resistance or water repellence. Hence, these textile production processes involve significant use of chemicals, and it is possible for residues from these chemical operations to remain in the textile. Buttons, zippers, and prints serve as additional components that contribute different materials to the overall composition of the product. All these are some of the factors that make textiles so complicated, hence, making their recycling even harder. Textile recycling can be done either by mechanical recycling or by chemical recycling.

The focus of this thesis work was on chemical recycling of textile fibres. In case of elastane blends, mechanical recycling is not feasible as discussed in the previous section. Hence, chemical recycling was the chosen method.

2.2.1 Chemical recycling

Chemical recycling is the process that includes the utilization of chemical techniques for treating the polymers present in fibres, such as depolymerization or dissolution. The process of chemical recycling involves the depolymerization of synthetic polymers, with the aim of producing monomers of exceptional purity suitable for polymerization purposes. The purity and quality of the monomers acquired by recycling are influenced by several aspects, including the presence of additives and chemicals employed during the polymerization procedure[35]. There are many types of chemical recycling processes that are used for recycling textile waste as shown in figure 4. For the recycling of the polymeric textiles is focus, there is much literation on the processes that can be used to treat polyester, but the recycling of elastane lacks such research. Since, elastane is 85% or more segmented polyurethane, along with the available literature on elastane, polyurethane recycling was also reviewed to understand the basic mechanism of depolymerization. The process of methanolysis and glycolysis will be discussed for both the recycling of polyester and elastane.

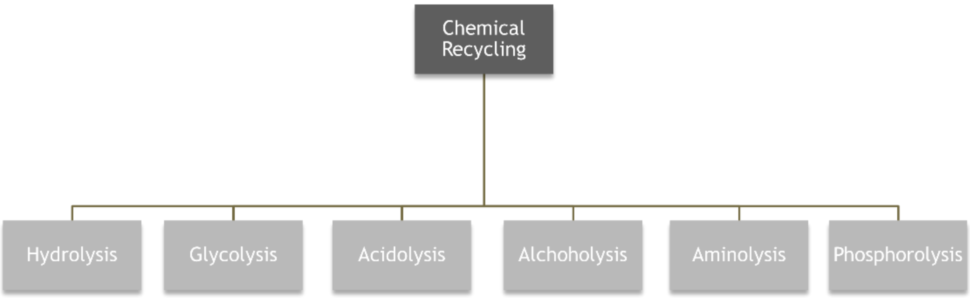


Figure 4 - Types of chemical recycling for textile waste

2.2.2 Recycling of polyester fibres

The production of polyester fibre is associated with several environmental challenges, including the depletion of non-renewable resources such as petroleum. Additionally, the production process requires significant amounts of energy, further exacerbating environmental concerns. Furthermore, the disposal of polyester at the end of its life cycle poses additional environmental issues. Given these factors, recycling polyester emerges as a crucial and necessary solution. Recycling procedures are the most effective means of economically mitigating the accumulation of PET waste. In contrast, although the cost of raw PET fibre stays consistent, the emergence of novel and more cost-effective PET recycling processes offers a distinct advantage to the recycling sector, as it enables access to comparatively less expensive PET materials. The utilization of recycled polyesters derived from post-consumer waste has been seen to yield significant environmental advantages in comparison to virgin polyester. Recycled PET exhibits distinctive properties such as molecular weight, inherent viscosity, carboxyl end-group concentration, colour readings, thermal stability, and other relevant factors. Findings of a comprehensive literature review indicate that there is a correlation between molecular weight and the percentage of recycled PET, where a rise in the latter leads to a decrease in the former. Furthermore, the viscosity of recycled polymer decreases with an increase in the presence of -COOH groups. In order to increase characteristics and useful advantages recycled fibres are frequently combined with virgin polyester fibres, organic cotton, flax, and elastomeric fibres[36,37].

Chemical recycling processes result in the production of monomers, as well as petroleum liquids and gases. The monomers undergo a process of purification by distillation and drying, which is then followed by their use in the production of polymers. Polyester fibres are considered to be extremely suitable for chemical recycling due to the existence of a polar sp2-hybridized carbonyl bond (C=O), which is prone to nucleophilic reactions. Polyethylene terephthalate (PET) fibre has ester groups with functional properties that may be cleaved by several reagents, including water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis), and amines (aminolysis). Recycled polyethylene terephthalate (PET) finds predominant application in many forms such as fibres, films, foams, sheets, and bottles[38,39].

Glycolysis is a frequently employed process in the chemical recycling of PET fibres, which has significant importance in commercial applications[40]. The process of glycolysis involves the molecular breakdown of PET polymer by the use of glycols, facilitated by trans-esterification catalysts, primarily metal acetates. This reaction results in the cleavage of ester linkages within the polymer, which are then substituted with hydroxyl groups. The breakdown of PET fibre is commonly performed using several substances such as ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol, among others. The procedure is carried out within a broad temperature range of 180–250℃, for a duration spanning from 0.5 to 8 hours[41]. Typically, a catalyst of 0.4-0.6% by weight, commonly zinc acetate, is included in proportion to the polyethylene terephthalate PET content. The glycolyzed products find many applications in industries such as the manufacturing of unsaturated polyester resins, polyurethanes, epoxy resins, vinyl esters, polymer concretes, textile dyes, and plasticizers. In addition to its inherent flexibility, glycolysis is regarded as the least intricate and most well-established pathway for PET recycling[38].

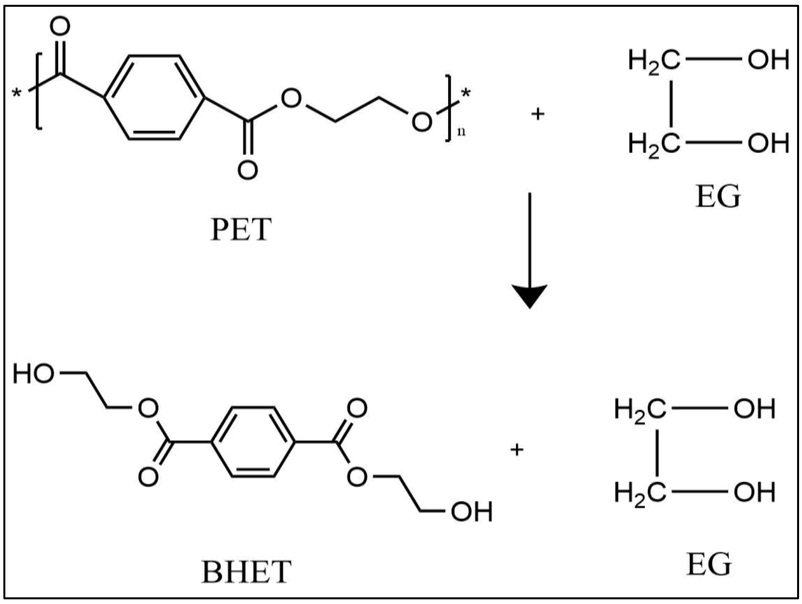


Figure 5 - Glycolysis of PET[41]

In the process of methanolysis, there is a breakdown of PET fibre by the utilization of methanol at elevated temperatures and under conditions of high pressure. The primary outputs of PET methanolysis encompass dimethyl terephthalate (DMT) and ethylene glycol (EG), both of which serve as essential constituents for the synthesis of this specific polymer. Catalysts, including zinc acetate, magnesium acetate, etc. have been found to augment the process. Among these catalysts, zinc acetate is the most frequently employed[42]. Methanolysis often involves the use of comparable key parameters, such as pressures ranging from 2 to 4 MPa and temperatures ranging from 180 to 280℃. Polymer breakdown occurs concurrently with the liberation of ethylene glycol. Following the conclusion of the reaction, it is imperative to inactivate the catalyst. Alternatively, during the following steps of the procedure, it is conceivable for losses of DMT to occur due to transesterification with ethylene glycol. The DMT is precipitated from the post-reaction mixture following its subsequent cooling, followed by undergoing centrifugation and crystallization. One notable benefit of this approach is that the resulting DMT exhibits an equivalent product quality to that of virgin DMT. Furthermore, the recovery and recycling of ethylene glycol and methanol may be achieved with relative ease[43].

One of the drawbacks of this approach is the significant expense involved in the separation and purification of the mixture of reaction products, which consists of glycols, alcohols, and phthalate derivatives. In the event that water disrupts the process, it has the potential to adversely affect the catalyst and give rise to a range of azeotropes. The incorporation of DMT generated during hydrolysis into TPA significantly increases the expenses associated with the methanolysis procedure. The lack of assistance in the recovery of dimethyl terephthalate (DMT) has resulted in the end of the use of the methanolysis process for PET fibres[44].

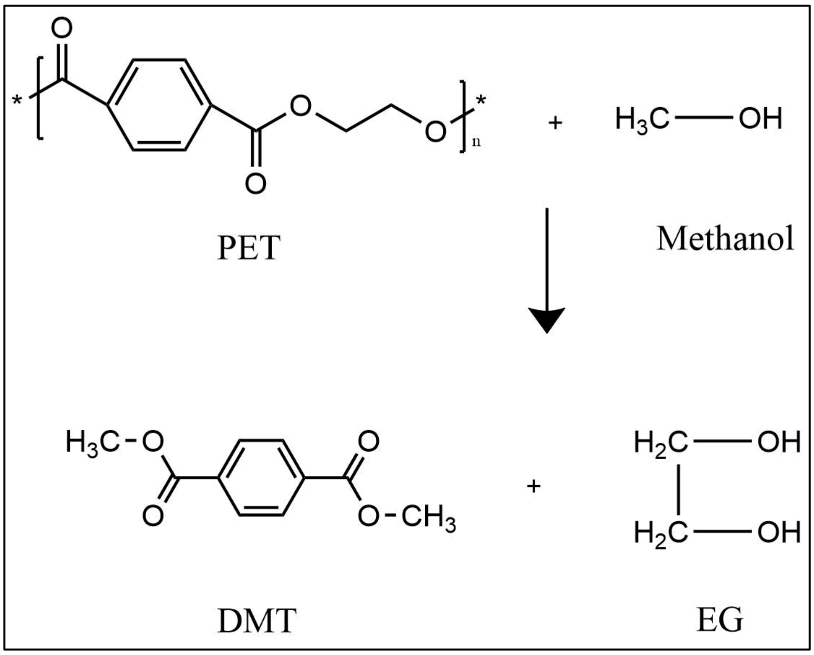


Figure 6 - Methanolysis of PET[41]

2.2.3 Recycling of elastane fibres

As already discussed in the sections above, the chemical recycling of elastane is a significant yet scarce topic of research. This can be due to many reasons, one important out which is the complexity of elastane. Some work on polyurethane or specifically polyurethane elastomer can be analogous to the recycling on elastane. Methanolysis of segmented thermoplastic polyurethane elastomer was done in supercritical methanol (T > 240 °C)[45]. It characterizes the recycled polyols that can be very similar to the Poly(tetramethylene ether)glycol (PTMG) polyol obtained from the depolymerization of elastane. The recycling of elastane can be done in many ways. Thermal separation was studied for elastane and nylon blend[46] and the work done by et. al Emanuel Boschmeier[47] on the thermal behaviour of elastane explains the thermal decomposition and the thermal characteristics of elastane. Selective dissolution of elastane is one more method than can be used to separate or remove elastane from the blended textile, for its further recycling. However, this method has major drawbacks like the economic feasibility as the solvents that are able to dissolve elastane are very expensive, and the toxicity of these solvents, which can be a big hurdle if the process is to be scaled up in the future[48,49].

In a work done by et. al. Wen-Hao Xu[50], polyester, and polyester/elastane blends where depolymerized using a two-step process, which can be seen in figure 7.

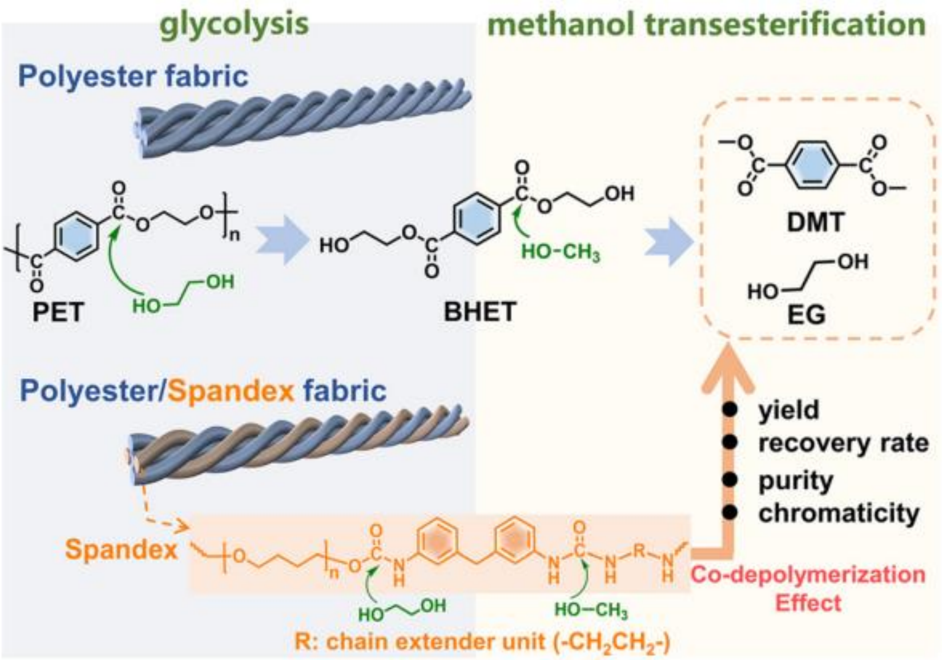


Figure 7 - Depolymerization of polyester/elastane blend

In the process used by et. al. Wen-Hao Xu, the first step involves the glycolysis of the blend followed by the transesterification by methanol. It can be understood by this work that the depolymerization process is very complex. Referring to figure 3, we can see the possible sites for a nucleophilic attack by the alcohol group.

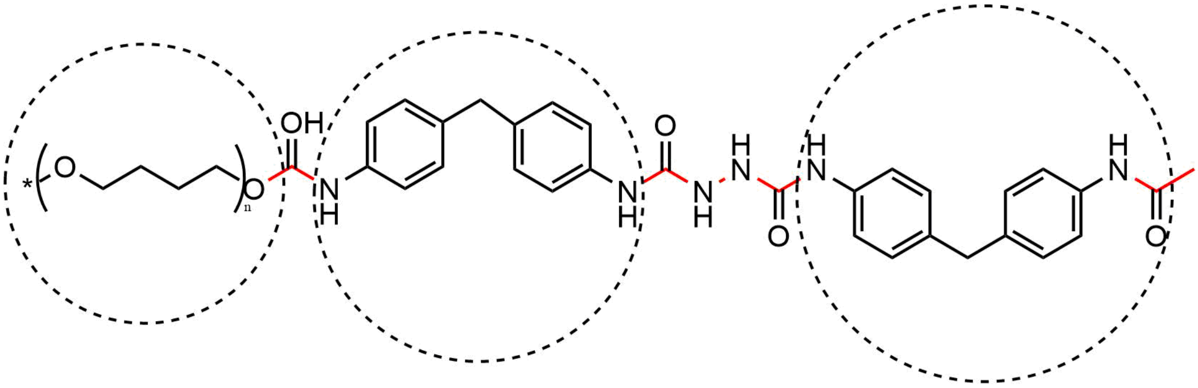


Figure 8 - Possible cleaving of bonds after attack by nucleophile

From figure 8 we can comprehend a little about the number of possibilities of bond cleavage and hence the number of different compounds that can be formed after the depolymerization of elastane.

3. Materials and Method

3.1 Materials

Pure elastane fibres, pure polyester fibres, and 10% Polyester/Elastane commercial blend were all obtained from the industry. Methanol, Ethylene glycol (EG), Ethanol, Diethyl ether, Dimethylacetamide (DiMAc), Dimethylformamide (DMF), and Tetrahydrofurfuryl alcohol (THFA) were all ordered and obtained from Sigma-Aldrich Sweden AB. All the catalysts used in the project, Sodium methoxide, Titanium methoxide, Potassium acetate, Sodium acetate, Zinc acetate dihydrate, Manganese acetate tetrahydrate, and Sodium carbonate were all acquired from Sigma-Aldrich Sweden AB. Filter paper was obtained from Whatman GE Healthcare. Deionized water used for purification and a 7:3 Methanol:Water mixture (M:W mixture) was obtained in-house.

3.2 Methods

The experimental work was conducted in three parts –

1. Temperature study (Elastane)
2. Catalyst study (Elastane)
3. Blend study (Polyester/Elastane blend)

The first two studies involved the examination of temperature effects and catalyst effects on pure elastane fibres, utilizing two distinct recycling methods, namely methanolysis, and glycolysis. The objective of this study was to enhance understanding of the impact of both processes on the depolymerization of elastane. The primary goal was to gather fundamental data on the influence of temperature and various catalysts on both processes. Ultimately, the purpose was to identify a more feasible and appropriate technique for the polyester/elastane blend. Furthermore, the third investigation was conducted employing an optimized methodology to enhance the understanding of the impact of increasing the elastane content in polyester/elastane blend on recycled products.

Table X presents the parameters and desired products in order to enhance comprehension of the experimental study.

Table 1 - Experimental parameters

<table>
<tr><th colspan="2">Temperature Study</th><th colspan="2">Catalyst Study</th><th colspan="2">Blend Study</th></tr>
<tr><td>Methanolysis</td><td>Glycolysis</td><td>Methanolysis</td><td>Glycolysis</td><td colspan="2">Glycolysis</td></tr>
<tr><td colspan="2">Reaction parameters –</td><td colspan="2">Reaction parameters –</td><td colspan="2">Reaction parameters –</td></tr>
<tr><td colspan="2"><i>Temperature -> Variable</i></td><td colspan="2"><i>Temperature -> 200</i> °C</td><td colspan="2"><i>Temperature -> 200</i> °C</td></tr>
<tr><td colspan="2"><i>Catalyst -> Sodium methoxide</i></td><td colspan="2"><i>Catalyst -> Variable</i></td><td colspan="2"><i>Catalyst -> Potassium acetate</i></td></tr>
<tr><td colspan="2"><i>Time -> 2 hours</i></td><td colspan="2"><i>Time -> 2 hours</i></td><td colspan="2"><i>Time -> 2 hours</i></td></tr>
<tr><td colspan="2"><i>Fibre:Solvent -> 1:5</i></td><td colspan="2"><i>Fibre:Solvent -> 1:5</i></td><td colspan="2"><i>Fibre:Solvent -> 1:5</i></td></tr>
<tr><td colspan="2"><i>Desired product -> PTMG</i></td><td colspan="2"><i>Desired product -> PTMG</i></td><td colspan="2"><i>Desired product -> BHET</i></td></tr>
<tr><td colspan="2">Temperature studied –</td><td colspan="2">Catalysts studied –</td><td colspan="2">Blends studied –</td></tr>
<tr><td colspan="2">180°C</td><td>NaMeO</td><td>TiMeO</td><td>1%</td><td>10%</td></tr>
<tr><td colspan="2">200°C</td><td>KAc</td><td>Na_2CO_3</td><td>2%</td><td>20%</td></tr>
<tr><td colspan="2">220°C</td><td>NaAc</td><td>MnAc</td><td>5%</td><td>30%</td></tr>
<tr><td colspan="2">240°C</td><td>ZnAc</td><td>No Catalyst</td><td>8%</td><td>No elastane</td></tr>
</table>

3.2.1 Washing of textile fibres (Pre-treatment)

i. The textile fibres to be cleaned were taken in a big glass beaker.
ii. Enough Ethanol (for cleaning) was added to the beaker so that all the fibres submerged in the cleaning solvent.
iii. The fibres were then thoroughly washed in the cleaning solvent for a few minutes to ensure that all the surface finishes and additives are removed.
iv. The fibres were then drained and kept for drying in an oven overnight.
v. The dried fibres were then taken out from the oven and stored in a dry container for further use in depolymerization.

3.2.2 Depolymerization process

i. One end of the high-pressure cylindrical reactor (shown in figure 9[a]) was sealed with PTFE tape wound screw cap.
ii. X g of pure elastane fibres (or polyester/elastane blend fibres) and Z g (4%) of Sodium methoxide (or other catalysts) was weighed and added to the reactor.
iii. Then, Y mL of Methanol (for methanolysis) or Ethylene glycol (for glycolysis) was added to the reactor.
iv. The reactor was then purged using N_2 gas for 2–3 minutes to rid the reactor of oxygen to prevent oxidation.

v. The reactor was then immediately sealed using the other PTFE wound screw and placed in the high temperature oven (already set at the desired temperature) containing a rotating stand for the reactor (shown in figure 9[b]).
vi. The oven was then closed, and the reaction was carried out at a temperature T for 2 hours.
vii. At an interval of 30 minutes each, the oven was checked to see if the reactor was rotating to ensure homogenous reaction conditions.
viii. After the reaction was completed, the reactor was quenched to halt the reaction.
ix. The reaction mixture was then transferred to a centrifuge tube: 10 mL of cold 7:3 Methanol:Water mixture for pure elastane and 20 mL boiling hot DIW for Polyester/Elastane blend, was added to the reactor to clean and get everything out and transferred to the centrifuge tube.
x. Finally, the reaction mixture was centrifuged at 2500 RPM for 4 minutes and then kept in the freezer overnight: at -16°C for pure elastane and at 4°C for Polyester/Elastane blend for further purification and recovery of the desired products.

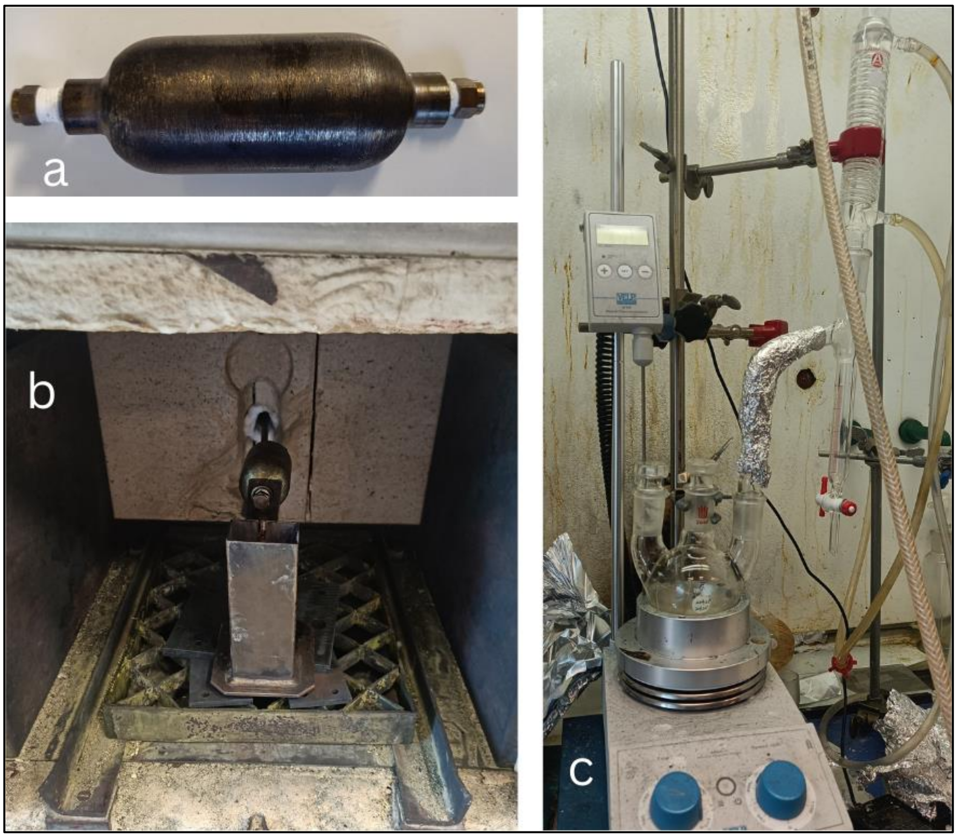


Figure 9 - [a] High pressure reactor sealed by PTFE tape; [b] High temperature oven with rotating stand; [c] Distillation setup for purification of PTMG

3.2.3 Purification and recovery of PTMG polyol by distillation

i. The centrifuge tube was taken out from the freezer and centrifuged at 2500 RPM for 4 minutes and the supernatant was discarded. The contents of the centrifuge tube were then washed with 20 mL cold methanol:water mixture 2 times with centrifugation for 4 minutes between each wash. This was done so any small oligomers would wash away.
ii. After washing, Diethyl ether was added to the tube till 20 mL mark and shaken well to dissolve the polyol in the ether.
iii. Then the tube was centrifuged for another 4 minutes. The supernatant was then transferred to a 3 necked round bottom flask. Care was taken as to not let any solid part in the round bottom flask.
iv. The round bottom flask was then heated at 100°C in a distillation setup (shown in figure 9[c]). The ether was evaporated and removed from the round bottom flask using vacuum pumps.
v. After all the ether was evaporated, the round bottom flask was removed from the setup and transferred to the freezer for cooling overnight. The polyol obtained in the flask was then measured and stored for further characterization by FTIR, TGA, and DSC.

3.2.4 Purification and recovery of BHET by crystallization

i. The centrifuge tube was taken out from the freezer and centrifuged at 4000 RPM for 4 minutes.
ii. The floating solidified polyol on the top was then taken out using a spatula and stored.
iii. The remaining content of the centrifuge tube was then transferred to a glass beaker, then 50 mL boiling hot water was added to the tube to get everything out to the beaker.
iv. After transferring everything, the beaker was heated on an induction till it started boiling and the content of the beaker turned transparent.
v. The mixture was then filtered using vacuum filtration; the white solid was collected on the filter paper and the filtrate (First) in the Buchner flask was transferred to the same glass beaker.
vi. Then, the filtrate (First) was again filtered through the same filter paper. The final filtrate (Second) was then transferred to a fresh glass beaker and kept in the freezer at 4°C overnight for crystallization .
vii. The next day, the crystals formed in the beaker was mixed well with spatula to get them off the walls and base of the beaker.
viii. The contents were then filtered again using vacuum filtration, and the crystals were collected on a filter paper.

ix. The filter paper was then kept in an oven at 65°C for drying, after which the crystals were weighed and stored for further characterization by FTIR, TGA, and DSC.

Figure 10 shows the recycling process for blend depolymerization and purification.

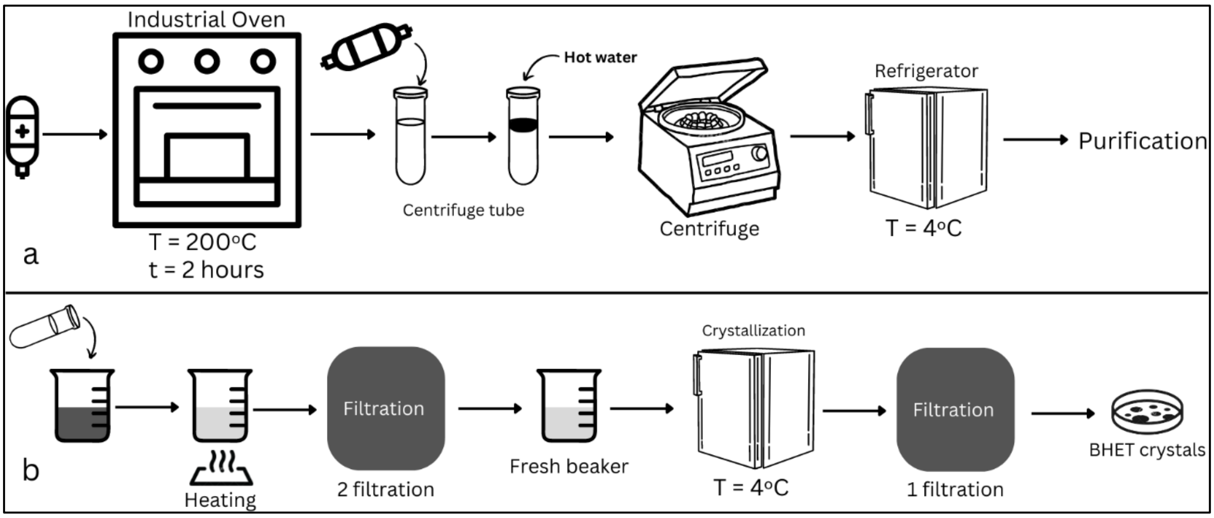


Figure 10 - [a] Depolymerization of blend; [b] Purification to obtain BHET crystals

4. Results and Discussion

In this section, all the results from the different analysis techniques and characterizations done in this thesis project are presented and discussed. This is done using various tables and figures and the observations from these are listed. These observations are then discussed in detail along with the interpretations and the effect of the findings in this project on the industry.

There were 3 studies performed in this thesis, first the temperature study to understand the effect of different temperatures on PTMG polyol after depolymerization, then to understand the effect of different catalysts on PTMG, catalyst study was done (these two were done on pure elastane), and then finally different blends with increasing elastane content were studied in the blend study to understand the effect of increasing elastane content (in polyester/elastane blend) on the BHET produced from depolymerization.

4.1 Temperature study of pure elastane

4.1.1 Yield of PTMG polyol

The yield of PTMG polyol from the depolymerization of pure elastane fibres via both methanolysis and glycolysis is presented. As described in section 3.X, for both methanolysis and glycolysis processes, the effect of temperature was studied over 3 or more independent runs at the same temperature, keeping all other parameters constant. The yield of PTMG was calculated by the following equation for both, the temperature study, and the catalyst study -

$$\%\ Yield = \frac{Weight\ of\ polyol}{Weight\ of\ elastane\ fibres} \times 100$$

The main aim of this thesis project was the recycling of elastane and its blends by depolymerization, and then bringing back the products from the depolymerization process like monomers, oligomers, and polyols back in the loop, i.e., back in the value chain. As these monomers and polyols are the desired products, their yield is of great significance as it directly reflects the effectiveness and efficiency of the recycling process. It is a direct quantitative measure of the conversion of elastane and polyester textile waste into recycled products. The yield data plays an important role in process optimization. Understanding all the variables that influence yield, such as reaction conditions or catalysts, gives crucial information to improve the recycling process for optimal results. This data also has practical implications as it can be used to effectively scale up the process for the industry. The yield also has a direct effect on the general quality and performance of recycled monomers and polyols. A higher yield may indicate that the recycling process retains the key characteristics desired in the products whereas a lower yield may indicate potential degradation or unwanted side reactions. This is true for the yields of both the products studied in this thesis work, PTMG from pure elastane (discussed in sections 4.1.1 and 4.2.1) and BHET from polyester/elastane blend (discussed in 4.3.1).

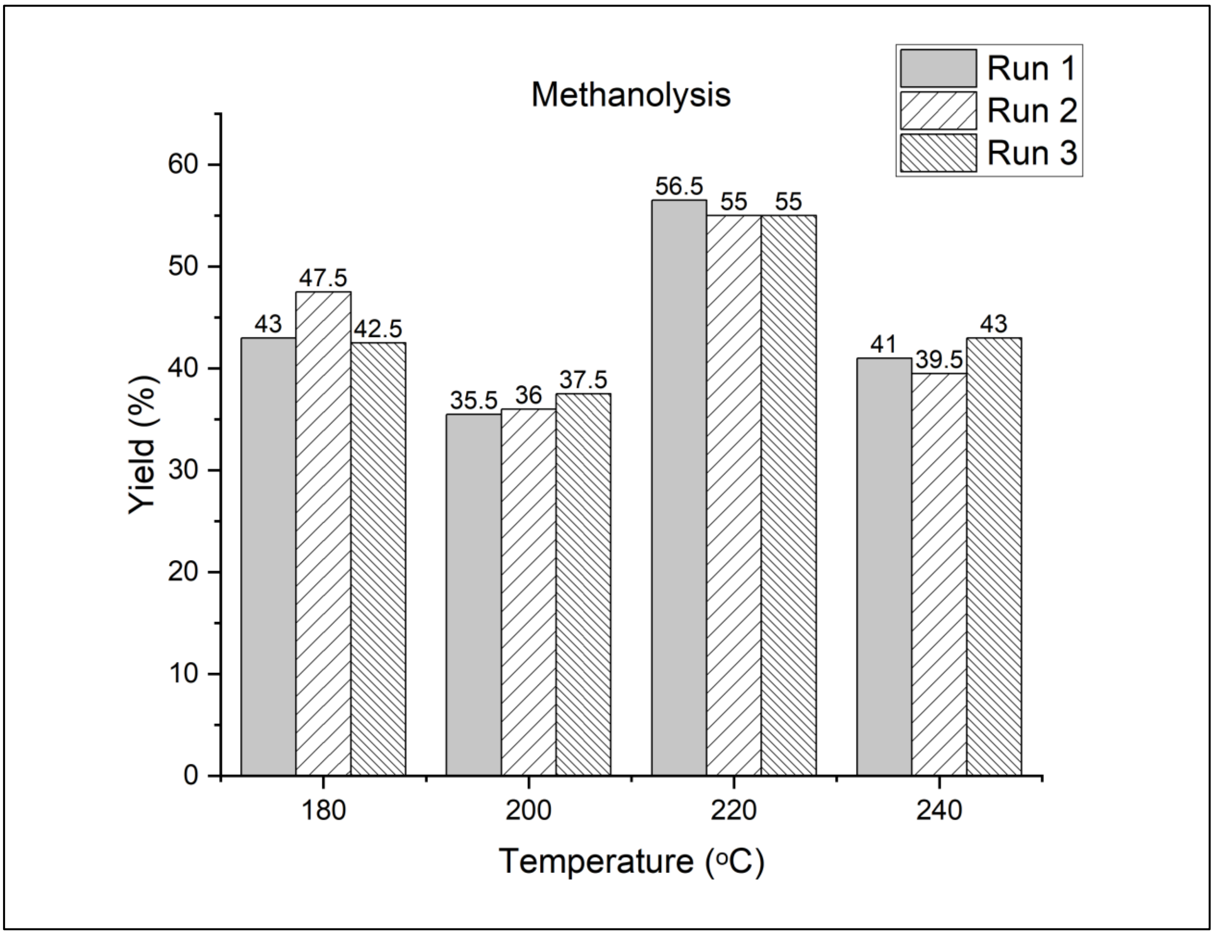


Figure 11 - Yield of PTMG over 3 runs by methanolysis

In Figure 11, the yield of PTMG at each temperature for methanolysis is displayed and compared. It can be seen that the yield does not exhibit any discernible trend and that the yields across the three experimental runs are comparable. Table 2 displays the average yields of a methanolysis temperature study.

Temperature (°C)	Average yield (%)
180	44
200	36
220	55.5
240	41

Table 2 - Average yield of methanolysis temperature study

The yield was highest at 220 °C and lowest at 200 °C as shown by the data presented above. It can be observed that the yield at 180 °C and 240 °C have similar values.

As for glycolysis, Figure 12 reveals that there are no yield data at 180 °C and that the yields for other temperatures, particularly 220 °C, are inconsistent. Both at 200 °C and 220 °C, there is a 9% difference between the highest and lowest yields, which cannot be disregarded.

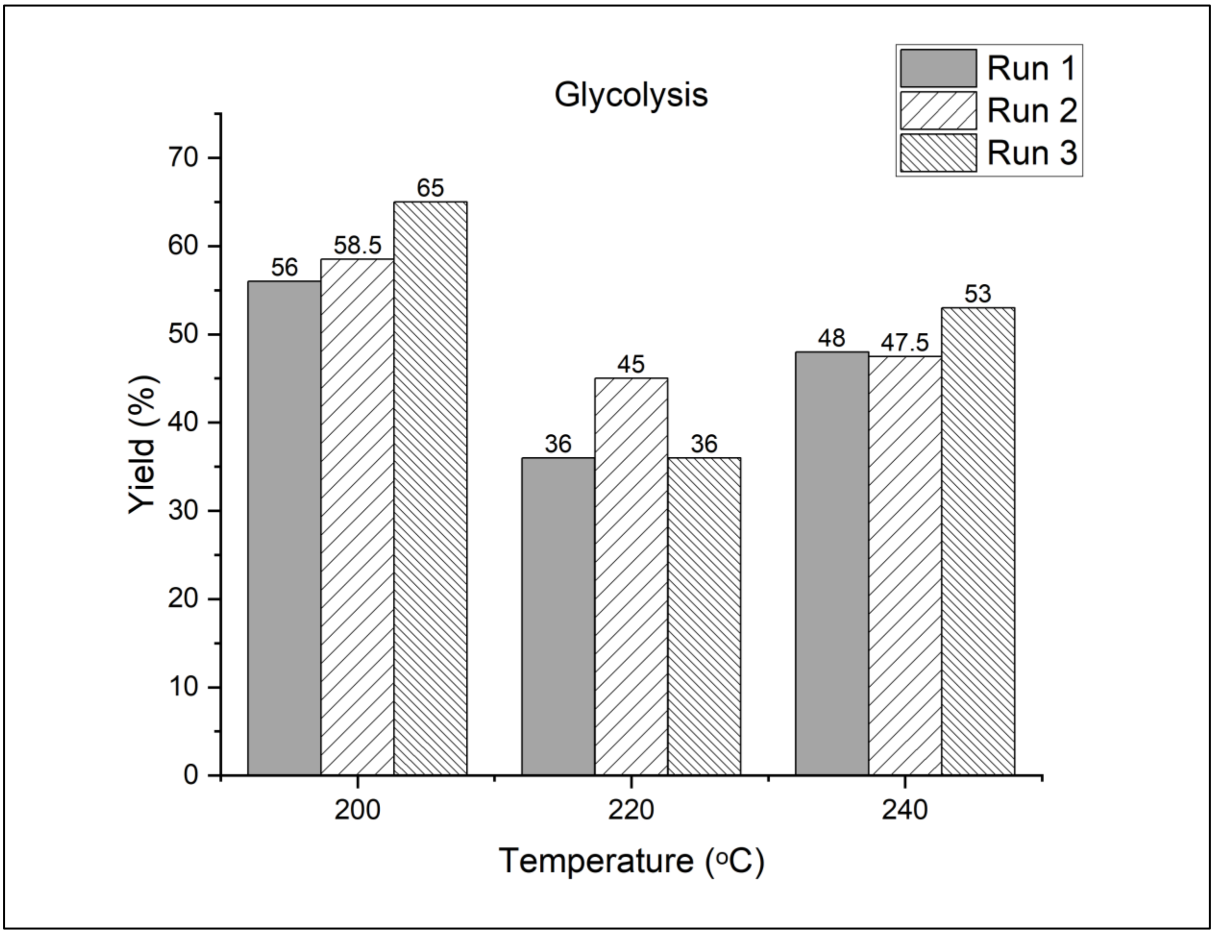


Figure 12 - Yield of PTMG over 3 runs by glycolysis

Table 3 shows the average yield of glycolysis temperature study. It can be seen in the table that, at 200 °C, the average yield of PTMG is highest for glycolysis compared to any other temperature. The lowest yield can be observed at temperature 220 °C, exactly opposite of what was observed for methanolysis, where the yield was highest at that temperature.

Temperature (°C)	Average yield (%)
180	-
200	60
220	39
240	49.5

Table 3 - Average yield of glycolysis temperature study

From the above observations, we can conclude that there was no linear relationship between yield and temperature for methanolysis. It was anticipated that the yield would either increase or decrease as the temperature rose. This was primarily due to the fact that as temperatures increase, so does the reactivity of methanol[51]. Consequently, it can be stated that elastane depolymerization should also be increased, which can result in higher yields, or even lower yields if the degradation is excessive and the polyol depolymerizes further into oligomers. The temperature range of 220 °C –240 °C is regarded as the subcritical temperature range for methanol, while 239.5 °C is regarded as the critical temperature (Tc) of methanol[52]. Therefore, the higher yield at 220 °C could be due to the onset of methanol's subcritical region. In this region, the methanol group's attack on the elastane fibres increases considerably, resulting in a higher yield. Also, at 240 °C, the significant decrease in yield (even lower than at 180 °C) may be primarily attributable to the degradation of polyol to oligomers, as at this temperature the methanol is in the supercritical region and has higher activity for reactions. Although, the significant decrease in yield going from temperature 180 °C to 200 °C could not be fully understood.

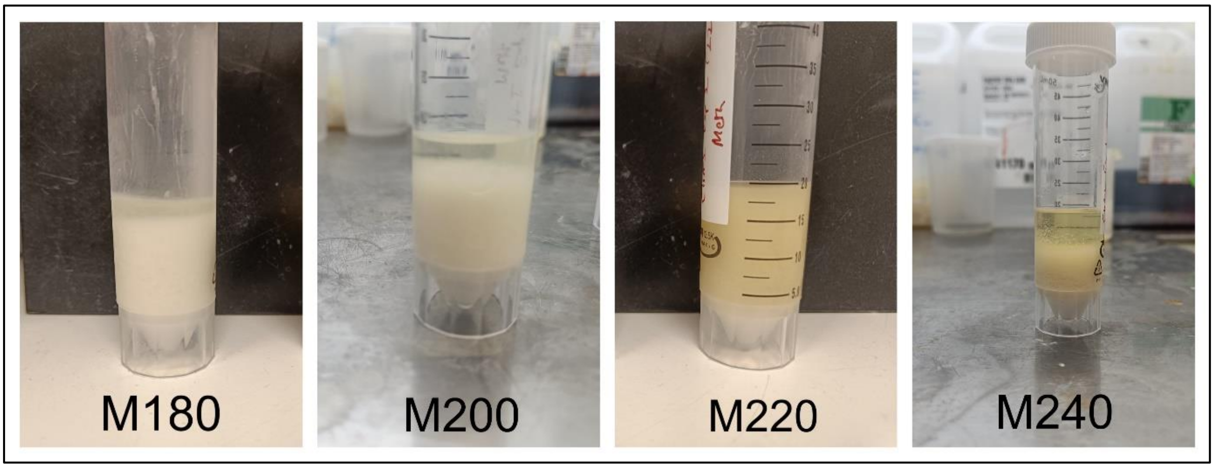


Figure 13 - Colour change for methanolysis after depolymerization

There was a visible colour change after depolymerization as the temperature increased, as shown in figure 13. The colour of the depolymerized solution was white at 180 °C, like the pure elastane fibres. The colour can be seen to become more and more yellow as the temperature increased to 240 °C, where the depolymerized solution can be seen to be visibly yellowish.

When considering the observations for glycolysis as shown above, there is a general but non-linear decrease in yield with increasing temperature. At 180 °C, the elastane fibres did not depolymerize even after 2 hours of reaction time. The fibres did not break down and were in the state in which they were when put in the reactor. This shows that this temperature is too low for any kind of activity of ethylene glycol on the fibres. The highest yield was observed at 200 °C, which was significantly higher than at higher temperatures. This could be due to rapid increase in the activity of glycol molecules at higher temperatures, hence increasing their reactivity. At 200 °C, the temperature could be coincidently optimal for the depolymerization to PTMG polyol and hence the higher yield. This also extends to higher temperatures as the yield decreases, which could be caused by further depolymerization of polyol to smaller oligomers or molecules. We can conclude here that the lower yield at high temperatures is not because of lower efficiency but because of higher activity of the ethylene glycol.

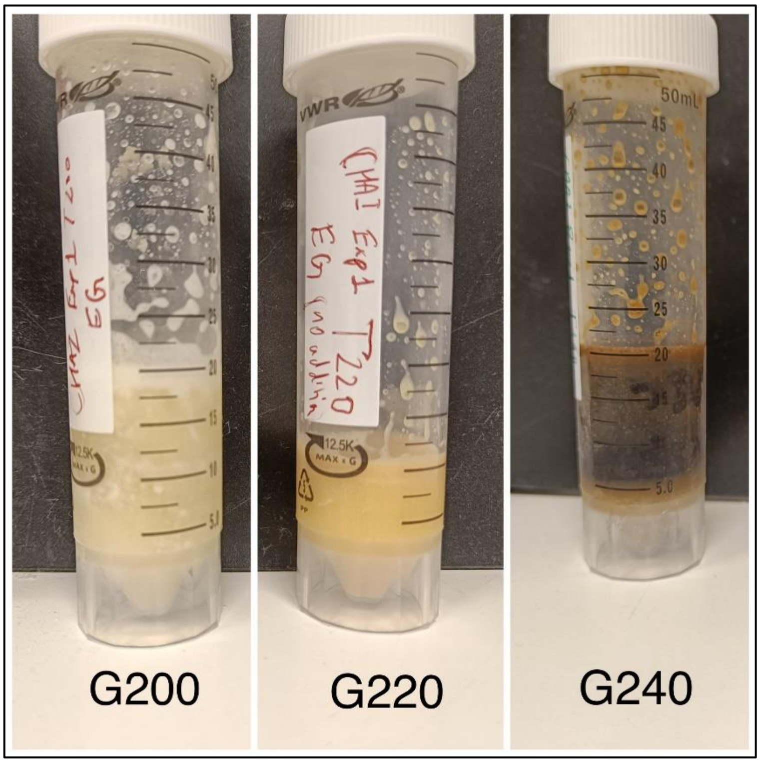


Figure 14 - Colour change for glycolysis after depolymerization

This could also be evident, as shown in figure 14, in the colour change of the depolymerized solution. The solution can be seen as light yellowish at 200 °C, but there is a very drastic colour change when going to 240 °C as the solution turns dark brown or even blackish. The solution at 220 °C also seems to be yellow. This colour change could also be the effect of higher activity as already said above.

We know, higher yield of any product usually suggests that the process is efficient, while a low yield often signifies inefficiency and loss during the process. Higher yield is also directly related to better economic viability and resource utilization, as it implies cost savings. Although higher yield does not always mean higher quality products, this is because there could be presence of impurities and undesired products, like hard segments, aromatic products, etc.

4.1.2 FTIR

ATR-FTIR provides important information regarding the molecular structure of recycled products. It permits the identification and characterization of functional groups, which may assist in the comprehension of the chemical changes that occurred during depolymerization. It is sensitive to various kinds of chemical bonds (such as C-H, C=O, and C=C), allowing us to evaluate the retention or formation of particular bonds during recycling. Changes in the position and intensity of these characteristic peaks can reveal changes in the chemical structure of a material. In addition, it can identify impurities in recycled monomers or polyols, casting light on potential sources of contamination in the recycled material. It can be used as a tool for ensuring the consistency and integrity of recycled products. By monitoring particular peaks, it is possible to confirm that the recycled materials satisfy the chemical requirements for the intended applications. It can also be used to validate proposed chemical degradation reactions during the recycling process.

In this study, FTIR spectroscopy was utilized to analyse all samples for both recycling processes, namely methanolysis, and glycolysis. Figure 15 shows the FTIR spectra for elastane fibres. First it is necessary to talk about the virgin fibre before going to its recycled product. Here we can see the different transmission peaks for elastane, with a few important ones marked in the figure. The presence of a distinctive band in the stretching vibration region at around 1100 cm^{-1} indicates the sample tested as polyurethane with an ether-based polyol, which is elastane[53]. The peak at 3317 cm^{-1} indicates the N-H stretching from the urethane bonds. The sharp peaks at 2941 cm^{-1} and 2856 cm^{-1} are from the C-H stretching and can be seen in most fibrous polymers[54]. Further, the two peaks at 1730 cm^{-1} and 1705 cm^{-1} are due to the presence of C=O of free group and C=O of the H-bonded group[55]. Finally, the 1600 cm^{-1} and 1539 cm^{-1} are indicative of the N-H bending[56,57].

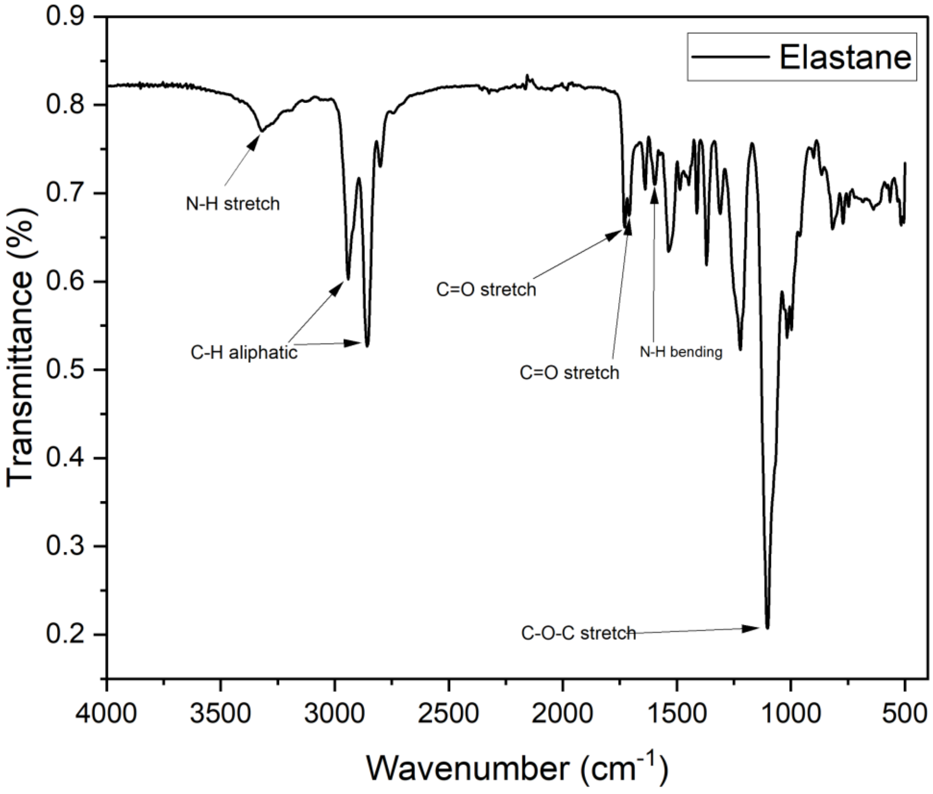


Figure 15 - FTIR spectra of elastane

Now, if we compare the FTIR spectra of elastane and PTMG, as shown in figure 16, we can see confirm the depolymerization, and formation of the polyol. It can be seen that the N-H stretching that was observed in elastane at around 3317 cm^{-1} is absent in PTMG spectra. The carbonyl C=O peaks between 1750 cm^{-1} and 1700 cm^{-1} are also not present in the PTMG curve. The important observation is also the retention of C-O-C stretching that can be observed at around 1100 cm^{-1}.

Figure 17 displays the FTIR spectra obtained from three experimental runs conducted at a temperature of 200 °C using the glycolysis process. The spectra for all other temperatures were also displayed and can be found in Appendix 1. This was done due to the little disparity seen between the samples subjected to depolymerization at identical temperatures. The transmission spectra of the three samples, namely 200-1, 200-2, and 200-3, exhibit a high degree of similarity, as seen in Figure 17. Therefore, the primary objective of this discussion will be to compare the different temperatures and their impact on the resulting PTMG.

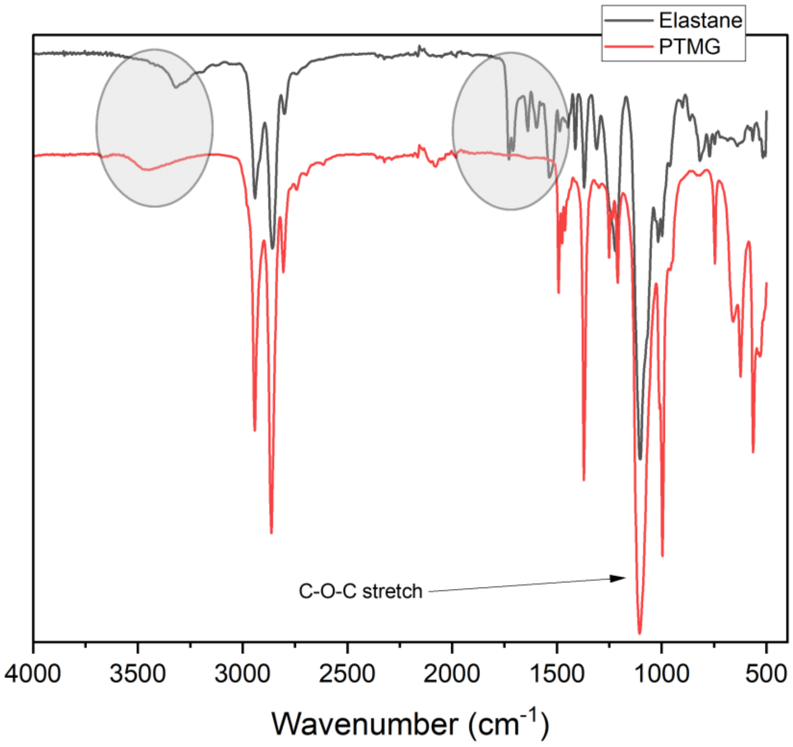


Figure 16 - Comparison of FTIR spectra of Elastane vs. PTMG

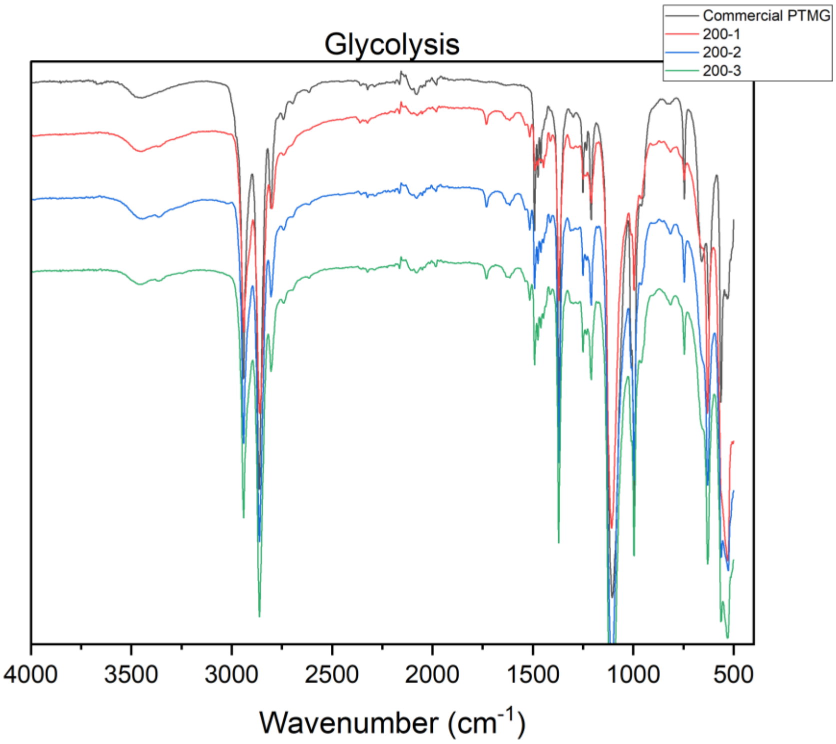


Figure 17 - PTMG FTIR spectra for glycolysis at 200 °C

Based on the observations made in figure 17, it can be inferred that the spectra of the recycled PTMG samples exhibit a high degree of similarity. This suggests that the depolymerization experiment demonstrated repeatability, indicating that the reaction conditions remained consistent across all three runs and that experimental error was minimized.

Figure 18 shows the FTIR spectra of the PTMG samples from the methanolysis process at different temperatures. The main observation that can be made here is that the spectra for all the samples are identical to the spectra of commercial PTMG like in figure 18. This confirms that the polyol that was obtained after depolymerization was PTMG. The main region that differs and is of importance is between 2000 cm^{-1} and 1500 cm^{-1}.

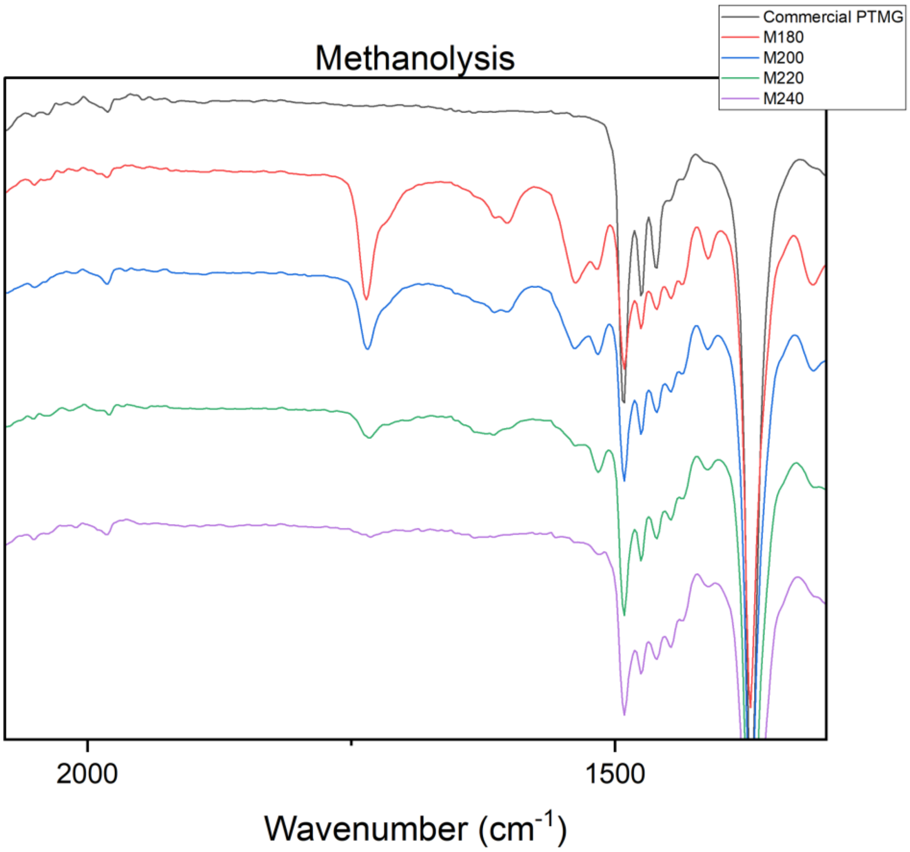


Figure 18 - PTMG FTIR spectra for methanolysis at different temperatures

It can be seen in figure 18 that compared to commercial PTMG, all other spectra show peaks at 1730 cm^{-1}, 1620-1600 cm^{-1}, 1539 cm^{-1}, and 1515 cm^{-1} unlike the former. The peak at 1730 cm^{-1} indicates the presence of a free carbonyl group. It can be seen that as the reaction temperature increases, the intensity of this peak decreases[58]. The other observable peaks in this region are mostly indicative of aromatic presence in the recycled PTMG. The primary distinguishing feature of the C–H out of plane bending vibration in 1,4-disubstituted aromatic rings is the vibration of the C=C bond at a frequency of 1,597 cm^{-1} as can be seen in the spectra[59]. These medium to weak signals in the region from 1625 cm^{-1} to 1440 cm^{-1} are indicative of the presence of these aromatic C=C which are not present in the commercial PTMG and hence can be considered as an impurity in the recycled PTMG[60]. It can also be seen that the presence of these impurities is nearly absent in the M240 sample, and hence can be said that even if the yield is low at this temperature, the purity of the sample is higher.

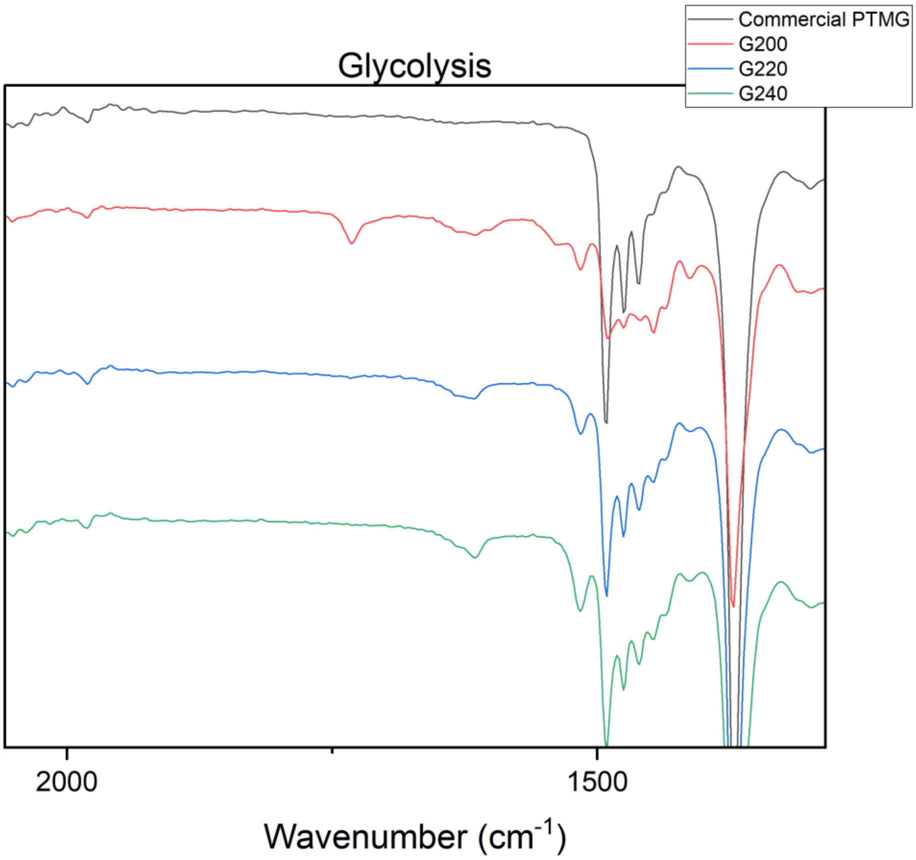


Figure 19 - PTMG FTIR spectra for glycolysis at different temperatures

Figure 19 shows the FTIR for glycolysis at different temperature. Here, it can also be seen that similar to methanolysis, there is presence of impurities and also carbonyl signal around 1730 cm^{-1}. This carbonyl is most likely from the aromatic impurity and hard segment that is present in the polyol.

4.1.3 TGA

Thermogravimetric analysis (TGA) facilitates the assessment of the thermal stability of fibres and their recycled counterparts. It presents data on the temperature range in which substantial weight loss is seen, hence revealing the thermal stability of the materials under various recycling conditions. It also aids in comprehending the degradation characteristics of recycled materials. TGA frequently shows a multitude of degradation phases that are linked with various constituents within the recycled product. This data may also be employed to enhance the recycling process through the identification of optimal temperatures or conditions that maximize material yield or preserve desirable material qualities.

In figure 20 we can see the thermal degradation curve of virgin elastane fibres. We can see that there is an initial weight gain that is visible in the curve. The observed increase in weight can be attributed to the convection phenomena resulting from the upward movement of hot gases emanating from the walls of the furnace, which subsequently induces a downward airflow inside the central region of the furnace where the sample pan is positioned. At elevated temperatures, an increase in weight is attributed to buoyancy effects. As the temperature rises, the gas around the sample pan undergoes a decrease in density, resulting in a reduction in the buoyant lift experienced by the pan[61]. We can also see that there is no water or other volatiles that are present as there is no apparent weight loss initially. This can also be due to the decrease in buoyancy around the pan. We can see that the weight loss starts at around 185°C.

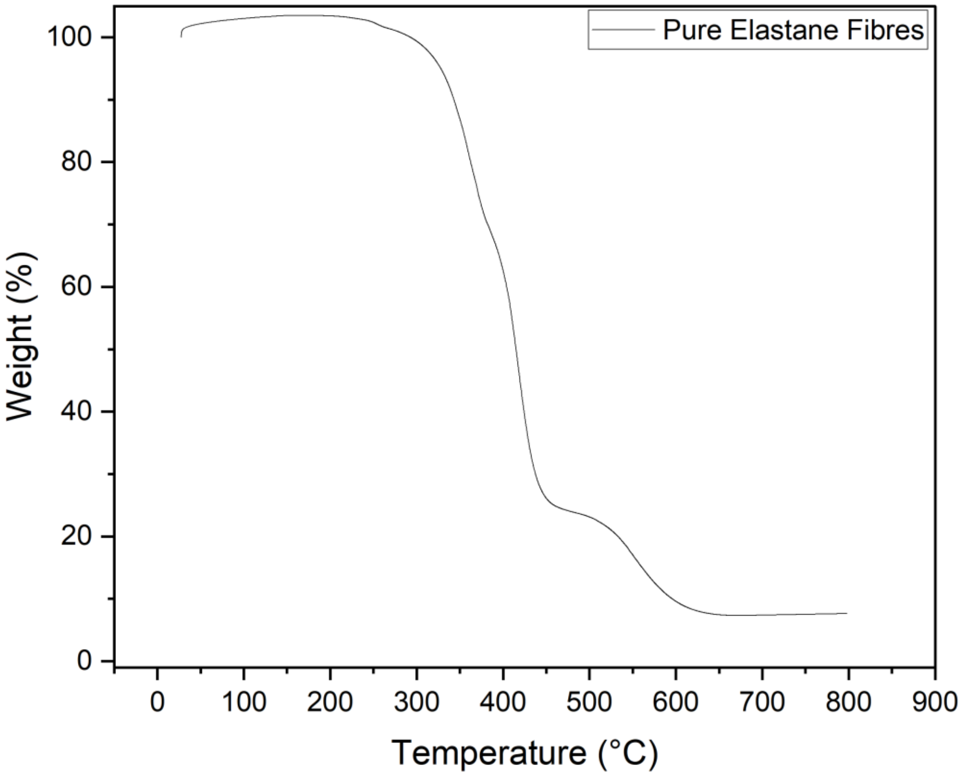


Figure 20 - TGA curve of virgin elastane fibres

We can see here that the degradation occurs in a multi-stage process. This is also apparent in the DTG of the same sample show in figure 21. The initial stage of degradation occurring involves a depolycondensation mechanism, which is closely linked to the urethane hard segment. The degradation process of the second stage is characterized by the degradation of the soft segment by polyol depolycondensation[62]. Finally, the last stage can be due to combustion to ashes.

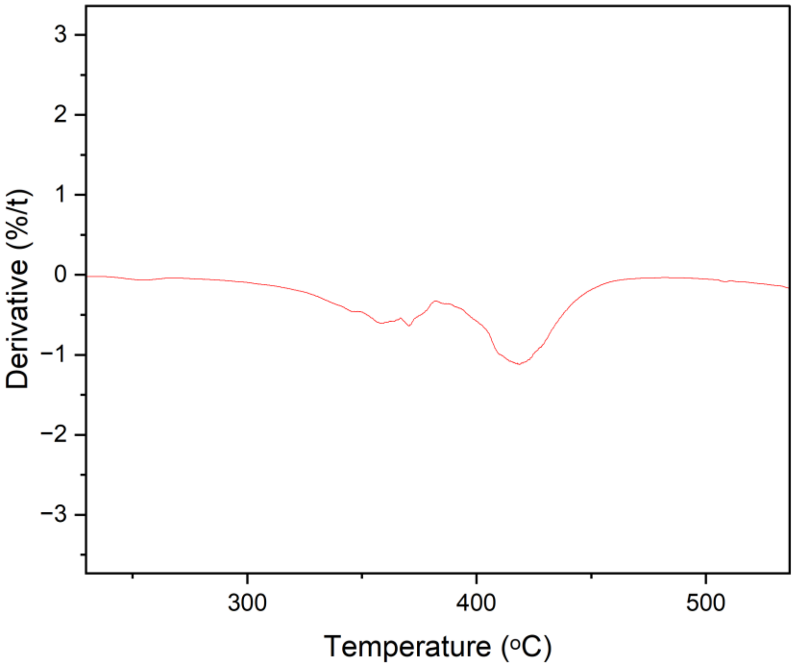


Figure 21 - DTG graph for virgin elastane fibres

In a similar fashion, the degradation curves of methanolysis and glycolysis at different temperatures are shown in figure 22 and figure 23 respectively. It can be seen from these figures that the degradation of commercial PTMG is a single stage process. We can observe, unlike commercial PTMG we can see more than one stages of degradation for both methanolysis and glycolysis. This can be mainly due to the presence of aromatic hard segments in the recycled PTMG, which was also apparent in the FTIR of both methanolysis and glycolysis[63] . In figure 22 for methanolysis we can see that the onset of weight loss is higher than commercial PTMG for all the samples by 40-60°C and from figure 23 we can see that the onset temperature for glycolysis is higher than 60-90°C. This difference in the onset temperature for both the processes is quite high and hence significant. This can be because of increased thermal resistance due to presence of aromatic hard segment[64]. This result also supports our claim regarding the presence of hard segments and impurities. As it was said in the previous section that for methanolysis at 240 °C, the FTIR was identical to commercial PTMG and hence it had less or no impurities. This cannot be completely true as seen in the TGA graph for methanolysis.

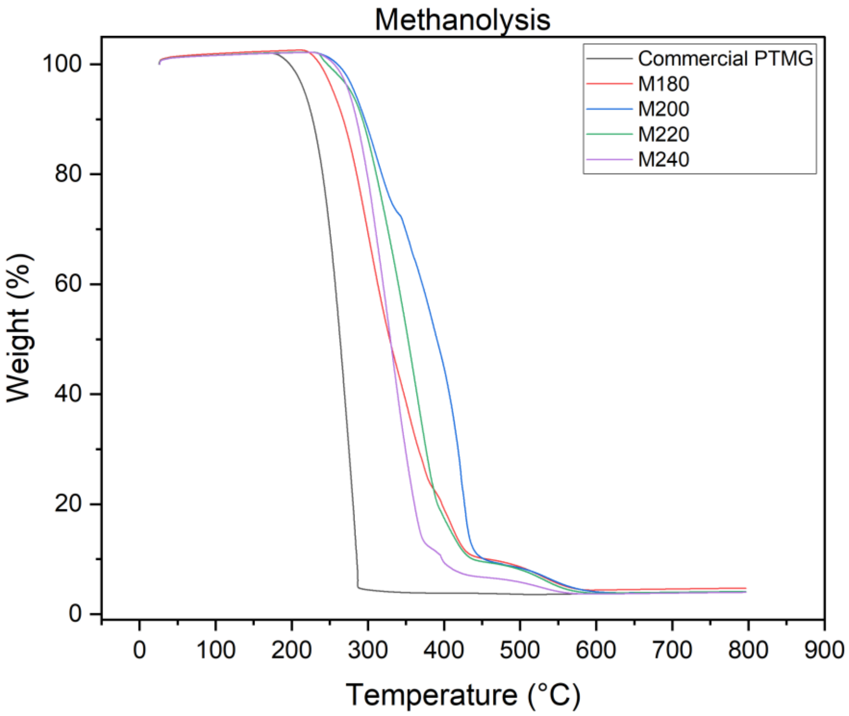


Figure 22 - TGA curve of methanolysis at different temperatures

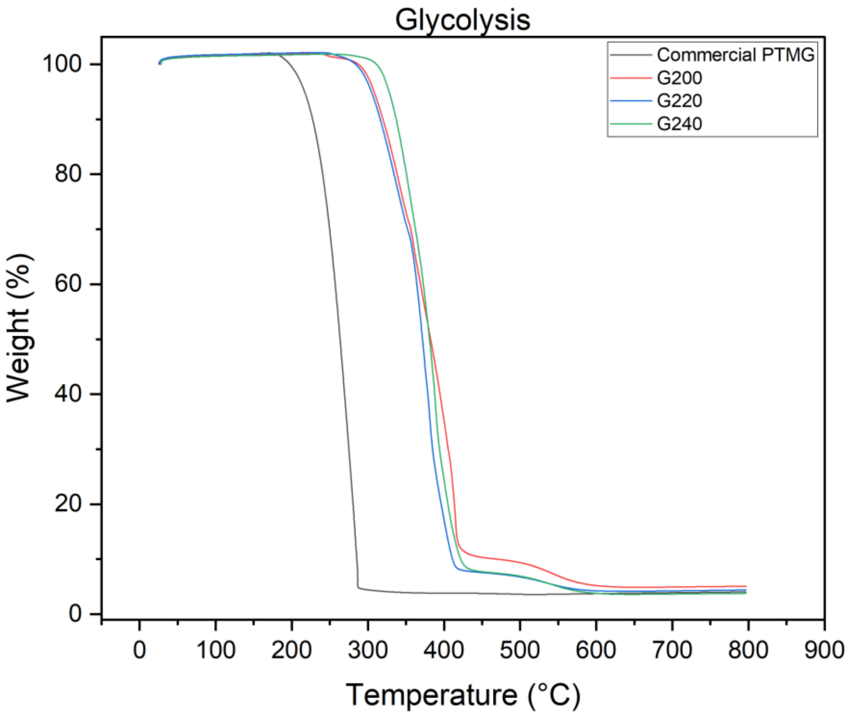


Figure 23 - TGA curve of glycolysis at different temperatures

4.1.4 DSC

Differential scanning calorimetry (DSC) is a technique that enables the identification and characterization of several thermal transitions, including the glass transition and melting processes of recycled products. The mentioned transitions play a pivotal role in interpreting the response of the material to varying temperature conditions and can significantly influence its mechanical and physical characteristics. The utilization of DSC data enables the optimization of the recycling process through the identification of the optimal temperature and heating rate that effectively preserves the desired thermal characteristics.

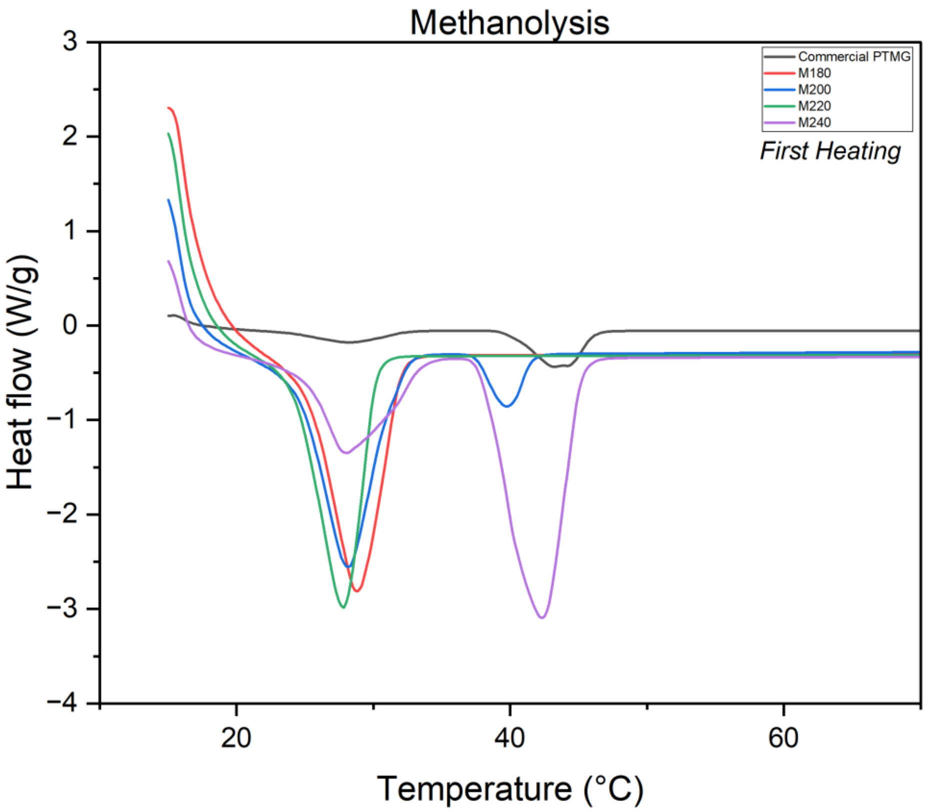


Figure 24 - Methanolysis First heating curve for different temperatures

For both methanolysis and glycolysis samples, it was observed that the cooling cycle and the second heating cycle were a straight line. These straight lines indicated that there were no significant thermal transitions occurring in these cycles. Among the many reasons for this, the one that is most likely for PTMG is the that the crystallization has already occurred during the first heating cycle and overlaps with the glass transition step, making it harder to interpret both of these transitions[65]. The glass transition temperature of PTMG is -84 °C and melting temperature is 35 °C from literature[66].

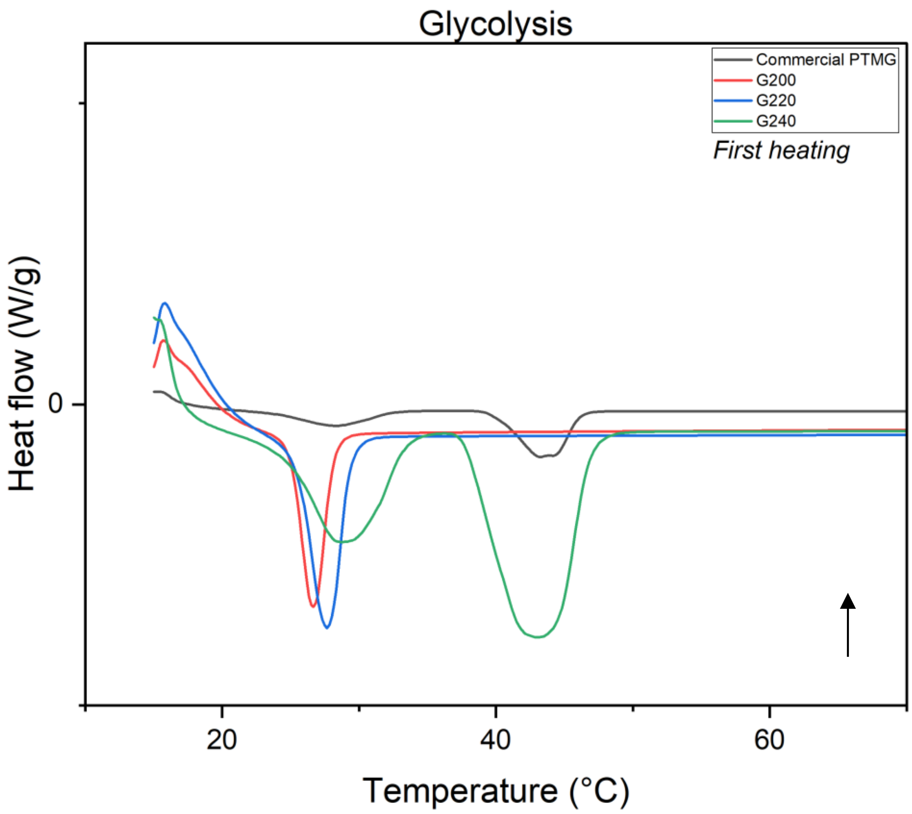


Figure 25 - Glycolysis First heating curve for different temperatures

Figure 24 and figure 25 shows the first heating curve obtained by DSC for methanolysis and glycolysis at different temperatures respectively. In both the graphs it can be seen that there are two endothermic peaks. This can be due to the presence of two phases or two different components in the sample. In case of commercial PTMG, the first peak is very weak and can be effect of presence of volatiles. In case of recycled PTMG, for both glycolysis and methanolysis, the peaks have high intensity, indicating higher heat absorption which could be due to the presence of hard segments. Although, for some samples such as M180, M220, G200, and G220, the second endothermic peak was absent and the reason for which was inconclusive. This shows that the DSC results were very vague and to fully understand and interpret these results, other characterizations such as X-ray diffraction can be very useful.

4.2 Catalyst study of pure elastane

This study investigated the impact of using various catalysts in both the methanolysis and glycolysis techniques. Seven distinct catalysts were employed and are documented in section 3.1. Several findings in this section exhibit similarities to the prior research, mostly due to the same nature of the resulting product.

4.2.1 Yield of PTMG polyol

The different yields of PTMG for methanolysis can be seen in Figure 26. Titanium methoxide shows negative yield compared to no catalyst being used for methanolysis of pure elastane. The average yields obtained from different catalysts are shown in Table 4.

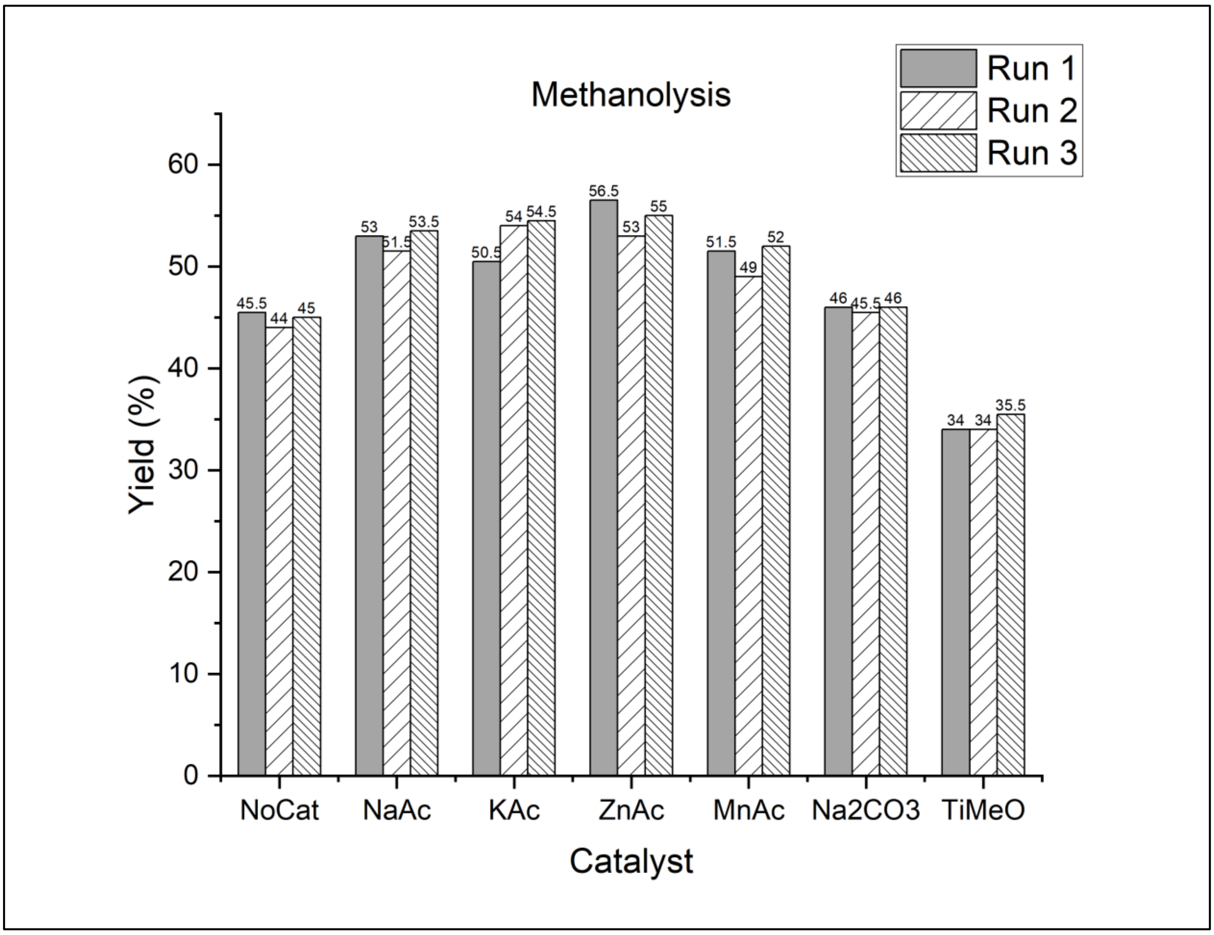


Figure 26 - Yield of PTMG over 3 runs by methanolysis

It can be seen here that the yield obtained by using no catalyst is lower than all other catalysts, except Sodium carbonate (almost similar) and Titanium methoxide (lower). The highest average yield was obtained by ZnAc, although the average yields from KAc, MnAc and NaAc are not so far from the same.

Catalysts	Average yield (%)
No catalyst	45
NaAc	53
KAc	53
ZnAc	55
MnAc	51
Na_2CO_3	46
TiMeO	34.5

Table 4 - Average yield of methanolysis catalyst study

For the glycolysis process, the yields are plotted for different runs and shown in Figure 27. Like all other PTMG yield mentioned above, the yields do not show any observable trend. All catalysts have higher yield than no catalyst in the process. Among all the catalysts, ZnAc and MnAc did not show any yield data as they did not depolymerize the elastane fibres when used in glycolysis. This could be due to the presence of water of crystallization in these two catalysts which hindered the depolymerization process.

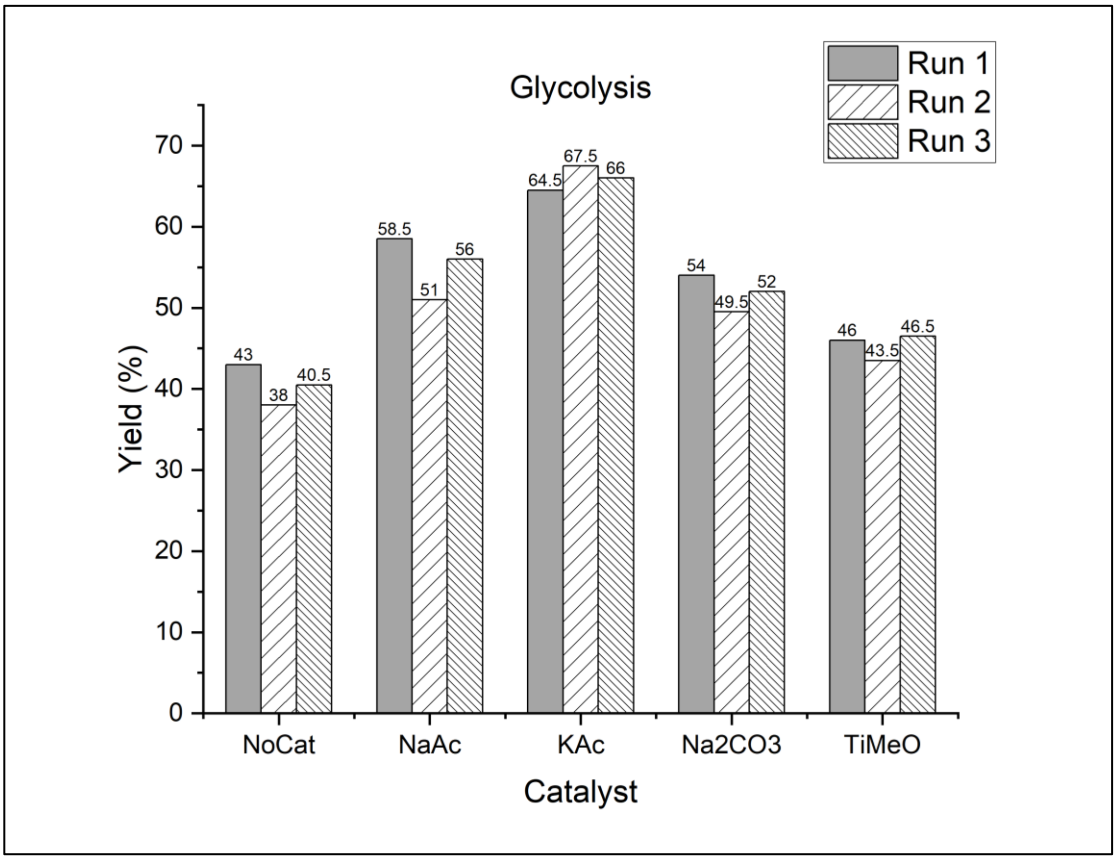


Figure 27 - Yield of PTMG over 3 runs by glycolysis

Table 5 shows the average yield for the glycolysis with different catalysts. Potassium acetate is seen to have the highest average yield compared to other catalysts. Unlike glycolysis, methanolysis seems to be compatible with most of the catalysts and was more consistent.

Catalysts	**Average yield (%)**
No catalyst	40.5
NaAc	55
KAc	66
Na_2CO_3	52
TiMeO	45

Table 5 – Average yield of glycolysis catalyst study

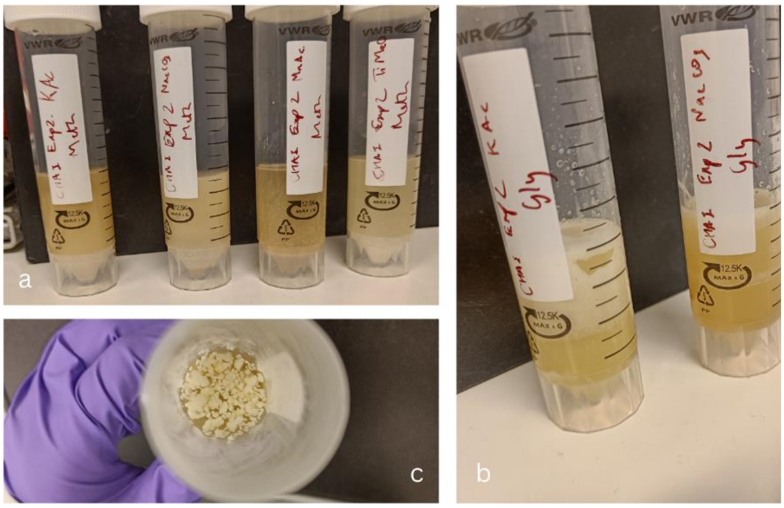


Figure 28 – Samples from different catalysts (a) Methanolysis; (b) Glycolysis; (c) PTMG from TiMeO catalyst

Figure 28 shows some depolymerized samples from both the processes. It can be observed that there is yellowing in all the samples with the intensity of the colour change being the difference. It also seen that for Potassium acetate the yellowing was more intense in methanolysis than glycolysis. Among all the catalysts, Titanium methoxide was evidently the least suitable for either of the processes. In addition to the low yields, it can be seen in figure 28 (c) that the PTMG formed was very grainy even after freezing overnight which made it really hard to purify.

4.2.2 FTIR

Figure 29 shows the FTIR spectra for different runs glycolysis using Potassium acetate as catalyst. Such spectra were plotted for all other catalysts and are presented in Appendix 1. Similar to section 4.1.2, it can be seen here that the spectra for all the runs are almost identical and hence can be said that the experiment showed repeatability.

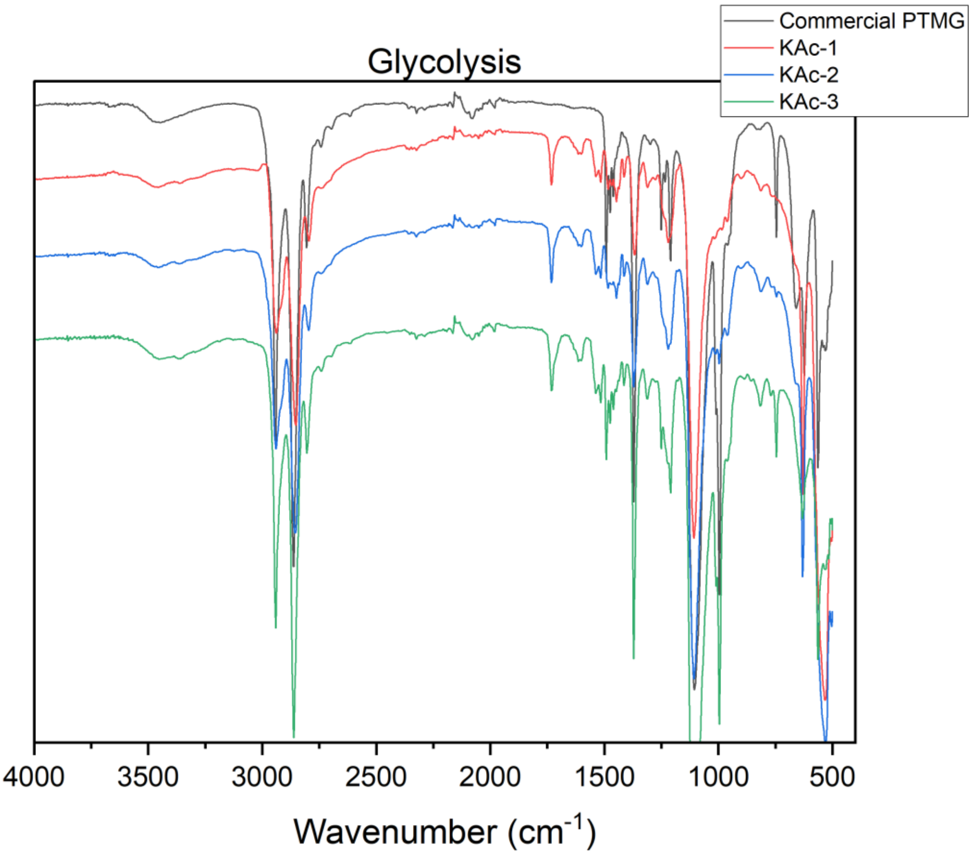


Figure 29 - PTMG FTIR spectra for glycolysis using KAc

We can observe the FTIR spectra of PTMG from methanolysis using various catalysts in figure 30. It can be seen here that all samples have the presence of the carbonyl group at 1730 cm^{-1} and the aromatic signals between 1400 cm^{-1} and 1600 cm^{-1} but with varying intensity, of which KAc showed the lowest intensity followed by NaAc. The spectra of sample from TiMeO can be clearly seen to be significantly varied with sharp peaks 3330 cm^{-1} which are indicative of N-H stretching, and sharp peaks of carbonyl stretching unlike others. It is very clear from this that TiMeO is not a suitable catalyst for methanolysis of elastane.

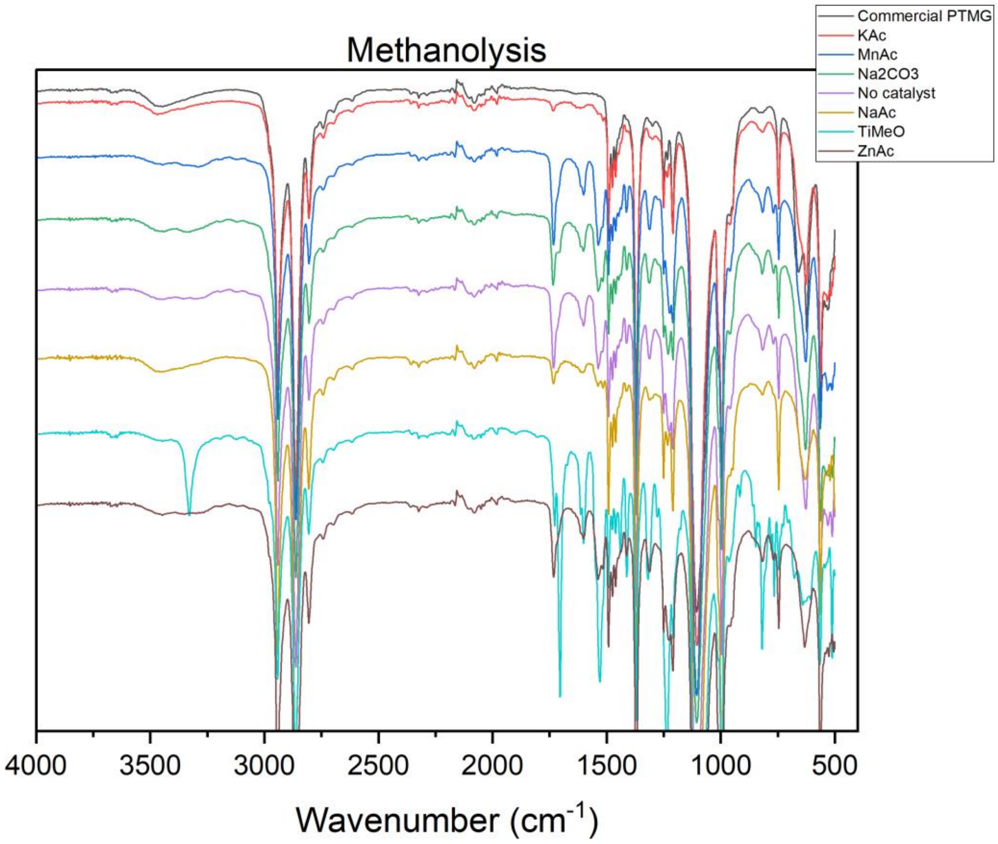


Figure 30 - PTMG FTIR spectra for methanolysis using different catalysts

In case of glycolysis, it can be inferred from its FTIR peak shown in figure 31 that the polyol obtained after using a catalyst yields a better polyol than no catalyst. Here, it is true for even TiMeO as its spectra is very similar to other samples. We can see the presence of impurities and aromatic hard segments in the obtained polyol, but the intensities of the peaks vary for all the catalysts. KAc, NaAc, and Na_2CO_3 can all be considered as good catalysts for glycolysis of elastane fibres.

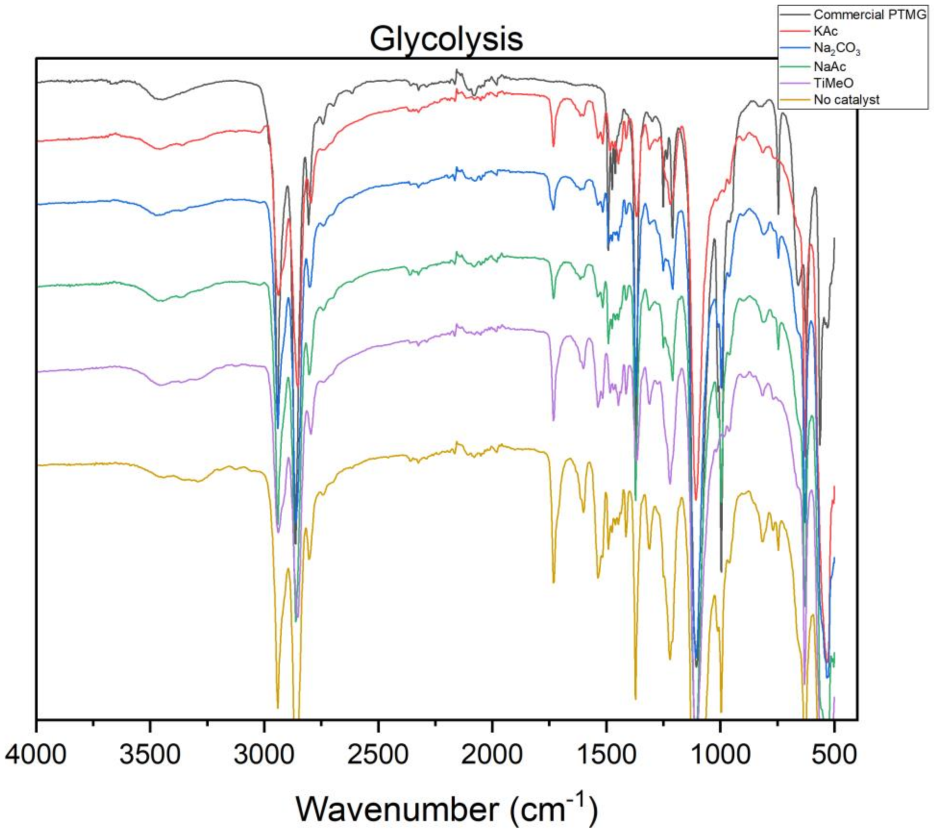


Figure 31 - PTMG FTIR spectra for glycolysis using different catalysts

4.2.3 TGA

Figure 32 shows the TGA decomposition curves for samples of PTMG obtained from methanolysis using different catalysts. These curves and data are mostly identical to the data already discussed in section 4.1.3. The main observation here is the difference in onset temperature of weight loss compared to the commercial PTMG. KAc showed the least temperature difference of 35 °C and Na_2CO_3 with the difference of around 60 °C. This difference is significant and can be evidence to the presence of impurities, especially in sample from Na_2CO_3 as the rate of degradation is slower than others and can be said because of the broader peak followed by a rapid weight loss rate. Moreover, there is also the presence of multi-stage decomposition in all the samples except the commercial PTMG, the possible reason for which is already discussed.

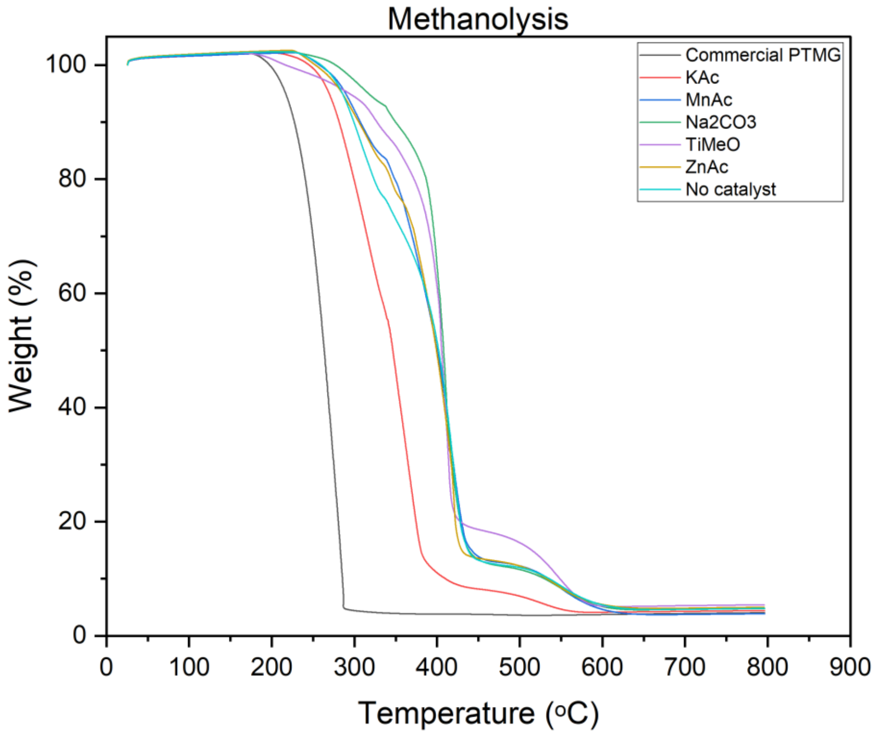


Figure 32 - TGA curves for methanolysis using different catalysts

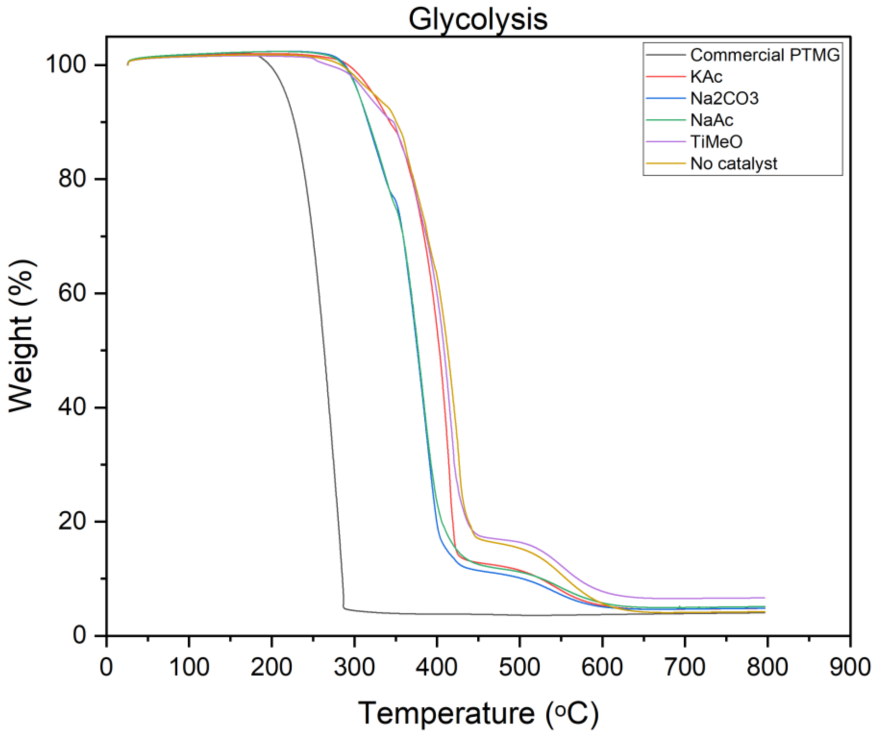


Figure 33 - TGA curves for glycolysis using different catalysts

In case of the glycolysis, it can be seen in the figure 33 that the onset temperature is almost similar for all the recycled samples. These samples show varied decomposition rate, and hence varied thermal stability. It can also be said that the recycled samples are more thermally resilient than commercial PTMG, which could also be a positive characteristic for certain applications.

4.2.4 DSC

Like in the temperature study, all the samples in the catalyst study also had the similar straight line cooling cycle curve and second heating cycle curve for the DSC analysis. Hence, the data from the DSC measurement for PTMG was not very useful on its own due to the inherent characteristics of this polyol.

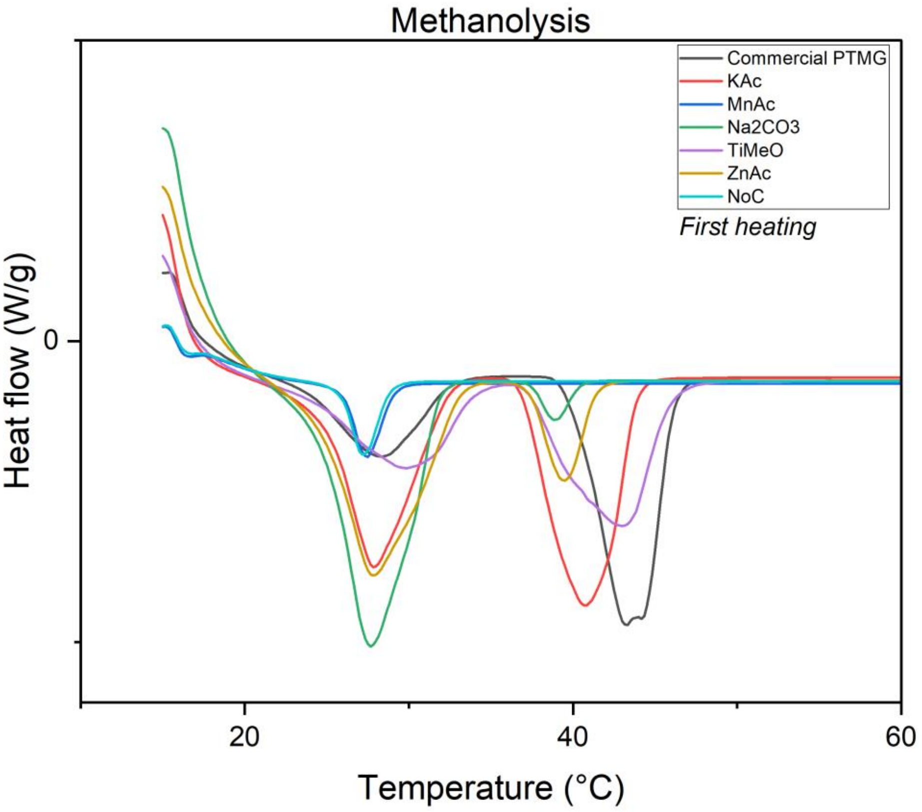


Figure 34 - DSC thermogram for methanolysis using different catalysts

From the DSC curve for methanolysis shown in figure 34, we can see that samples from almost all catalysts show two endothermic peaks with similar intensity to that of the commercial PTMG. Also as inferred in the above section, this could be due to the presence of different constituents in the recycled polyol. Other than that, this could also be due to the semi-crystallinity of the polyol.

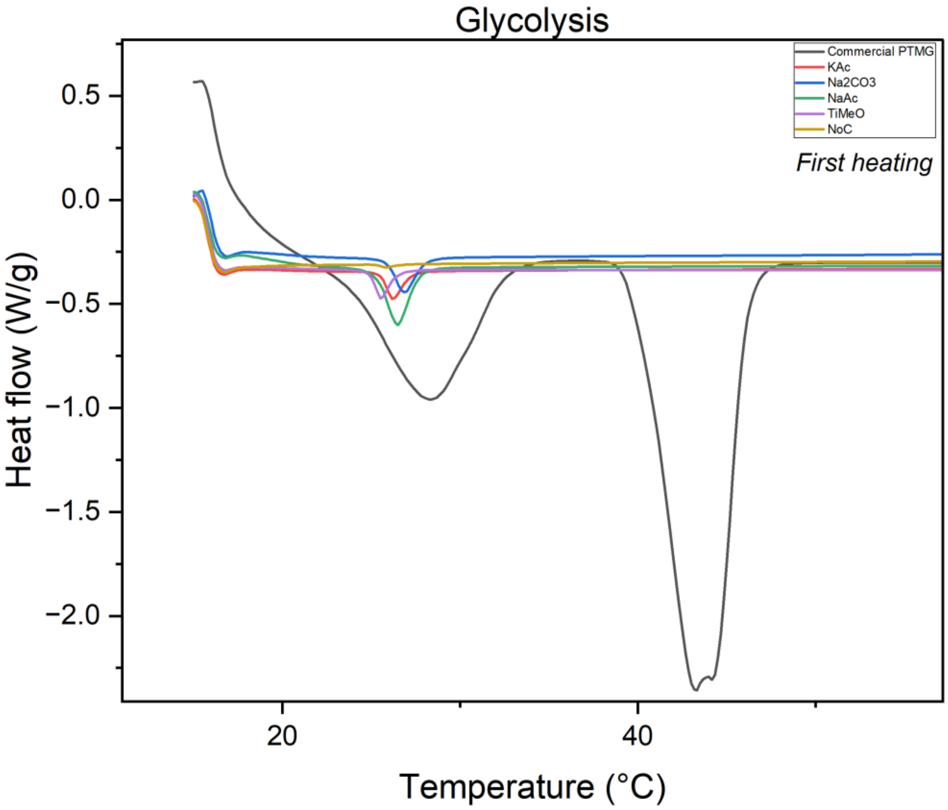


Figure 35 - DSC thermogram for glycolysis using different catalysts

The DSC curve is shown for glycolysis in the figure 35. Here we see that the intensity of the peaks in very low compared to any sample discussed above and the commercial PTMG. The reason for this could be because of the thermal stability of the recycled polyol. This also matches with the inference made in the section above about the TGA of glycolysis using different catalysts, which showed broader peak indicating slow decomposition rate, and hence increased thermal stability of the recycled PTMG.

4.3 Blend study of polyester/elastane blends by glycolysis

In this study of the project, based on the initial data and observations of the temperature and the catalyst study, the most suitable process and process parameters were selected. The aim of this study, as already discussed was to understand the effect of elastane content in the depolymerization process of the polyester/elastane blend. For this, the elastane content was started with 0% (Pure polyester fibres) and was increased as high as 30% (Polyester:Elastane = 7:3, keeping all other reaction parameters constant. The desired product was the BHET crystals obtained from the polyester. The depolymerization product from the elastane was not the focus of this study, mainly due to two reasons –

1. As the elastane content was as low as 1%, on a lab scale it was not possible to collect this depolymerized PTMG as it was a very small fraction and would mostly stick to the walls of the centrifuge.
2. Even if the PTMG was collected for higher percentage of elastane, due to its low quantity it was not feasible to purify it for all the experiments done, as the only thing affected of the PTMG was the colour change, and all the analysis showed similar results as the previous two studies.

Now, the depolymerization was performed using the process of glycolysis. This was the preferred process over methanolysis mainly because the purification of the depolymerized products is harder and more energy consuming than it is for glycolysis products. As already mentioned in section 2, after depolymerization, the glycolysis products form three phases with the top phase being the polyol, making it easier to separate. This is not the case for methanolysis, in which the polyol requires dissolution in Diethyl ether, which could affect the BHET crystals. Additionally, according to literature already discussed in section 2, glycolysis has many advantages over methanolysis and from the data of the previous two studies of this thesis, glycolysis was more consistent and easier to handle.

4.3.1 Yield of BHET crystals

The yield of the BHET crystals from the depolymerization of polyester/elastane blend via glycolysis is presented. Similar to the previous two studies, more than three experimental runs were performed for each blend composition keeping all the parameters constant.

The yield of BHET was calculated by the following equation –

$$\%\,Yield = \ (moles\ of\ BHET/initial\ moles\ of\ PET\ ) \times 100$$

Figure 36 shows the yield of the recycled BHET over three different experimental runs. The average yield for this data is tabulated in table 6.

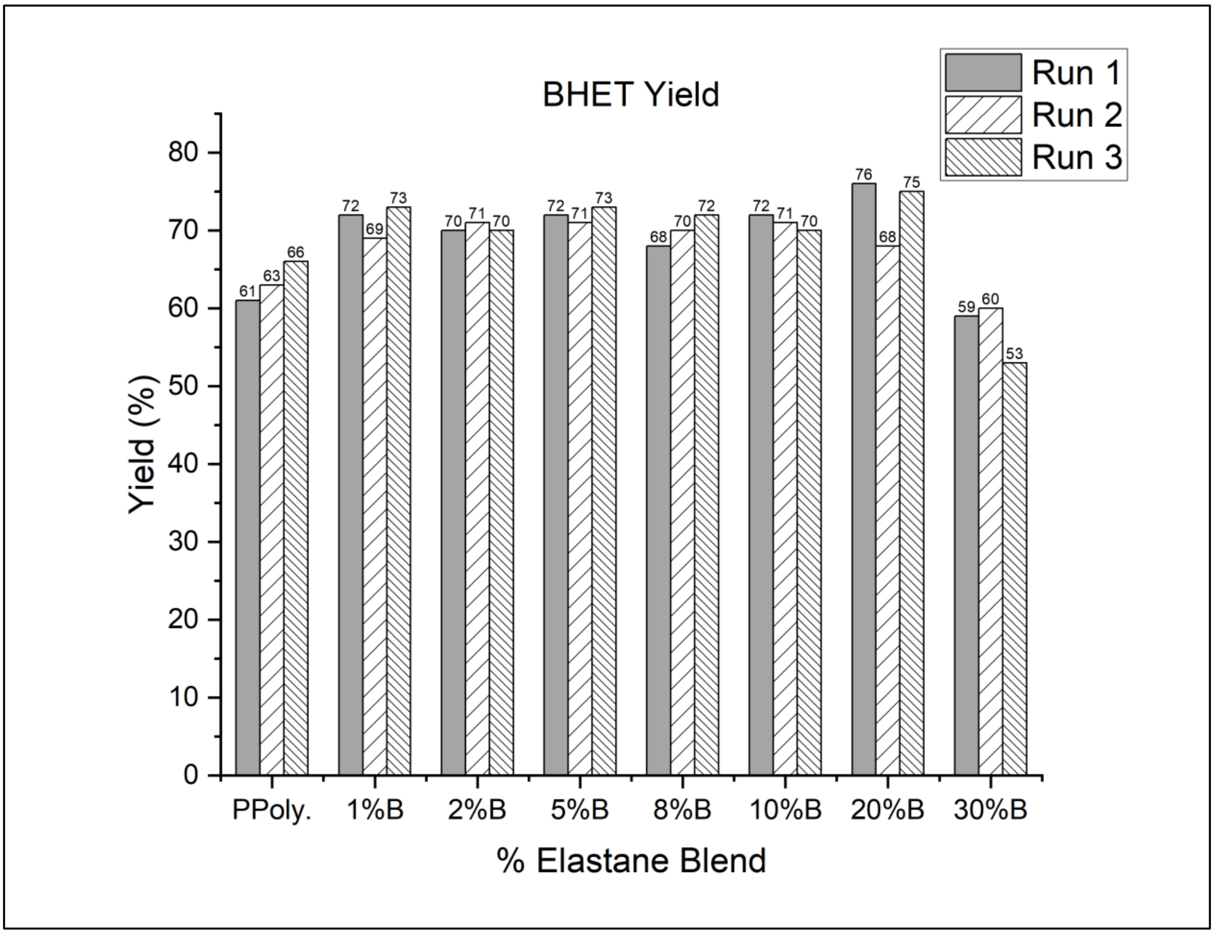


Figure 36 - BHET yield for different blend compositions

Table 6 - Average yield of different blend compositions

% Elastane in blend	Average yield (%)
Pure Polyester	63
1 %	71
2 %	70
5 %	72
8 %	70
10 %	71
20 %	73
30 %	57

From the figure 36, we can see that the yield of BHET from pure polyester fibres is lower than from any other blend (except 30% blend). This can be also seen in the average yield data, the average yield for all blend percentage is almost similar. For 30% blend composition, the average yield was the lowest. From the data presented here, the increase in yield of BHET with the introduction of elastane contradicts the fact that elastane negatively affects the depolymerization of blends. From literature review, it is confirmed that the increase in elastane content, the depolymerization becomes harder and the products are worse compared to depolymerization of pure fibres. Based only on the yield data, we cannot say if the depolymerization was improved or degraded.

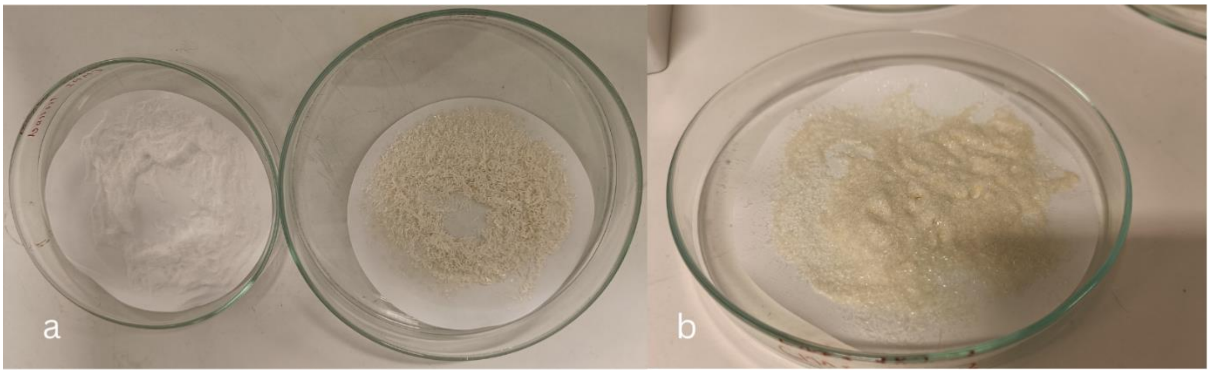


Figure 37 - Recycled BHET crystals; (a) BHET from pure polyester(Left) and 20% blend(Right) (b) BHET from 5% blend

From figure 37 (a), we can see that the BHET crystals obtained from the depolymerization of pure polyester fibres is white like snow. In comparison to that the crystals obtained from 10% blend is yellowish and the crystals are not properly formed. From figure 37 (b), we can see the crystals from depolymerization of 5% blend. We can see that the crystals have formed but they have changed colour. Now if we look at figure 38 (a), we can see that the BHET obtained for 30% blend looks like a powder rather than crystals and its colour is brownish. Also, we can

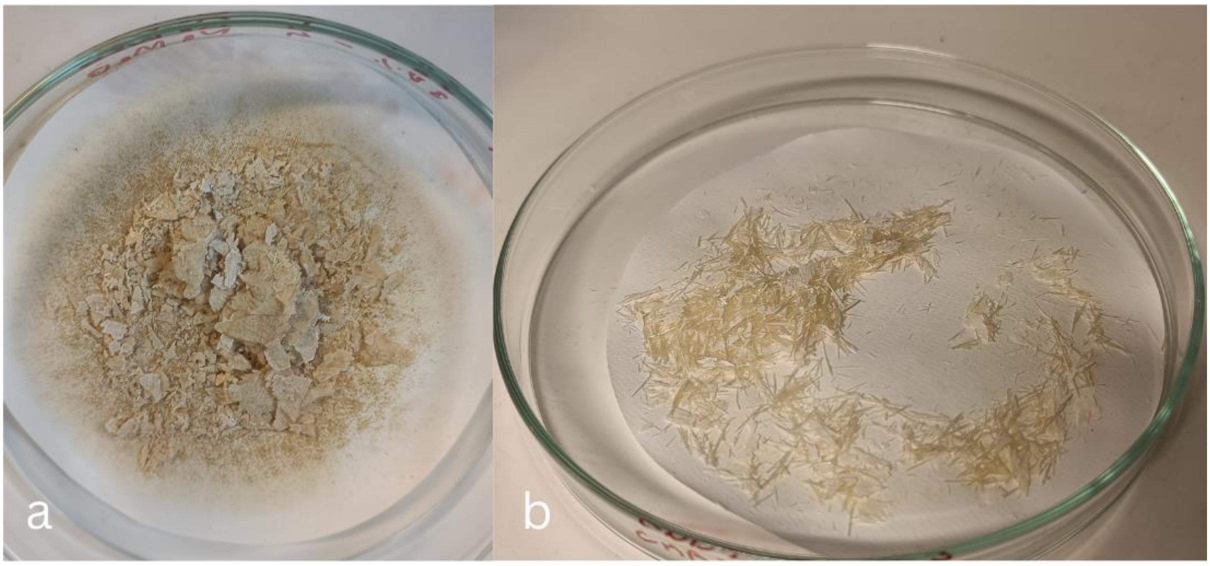


Figure 38 - (a) BHET from 30 % blend and (b) BHET from 20 % blend

see in figure 36 (b), for 20% blend, long yellowish crystals are formed along with white flakes. This shows that even if the yield comes out to be high for the blends, the presence of elastane has adverse effects on the quality of the BHET crystals.

4.3.2 FTIR

For the FTIR analysis of the BHET crystals, first FTIR of the virgin PET fibres was done and compared with spectra of BHET, as shown in figure 39. It can be seen from the spectra that the main difference between the two apparent in region from 3500 cm^{-1} to 2800 cm^{-1}. We can clearly see that for PET fibres, the small peak at around 2970 cm^{-1} is for the symmetrical -CH stretch[67]. In case of the BHET crystals, the presence of two peaks observed at 1282 cm^{-1} can be attributed to the C–O–C bond stretch. The presence of the C=O bond is responsible for the observed peak at 1730 cm^{-1}. The presence of a prominent peak at 3447 cm^{-1}, accompanied by two adjacent peaks at 2931 cm^{-1} and 2879 cm^{-1}, suggests the presence of an alcoholic functional group. The intensity of the peak seen at 3430 cm^{-1} and 3280 cm^{-1} is much higher compared to the PET spectra, which can be attributed to the increase of the O–H bond within the HO-CH2-CH2– group[68].

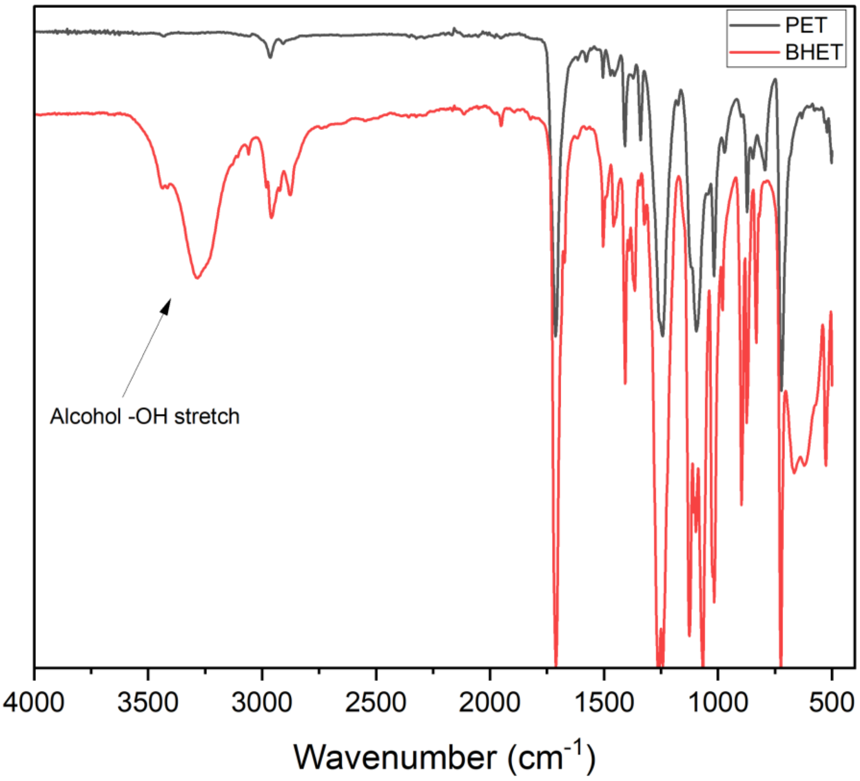


Figure 39 - FTIR spectra of PET and BHET

From figure 40, we can see that most of the blends have the same spectra when compared to commercial BHET, except 30%. But this was not the case for the experimental runs. These spectra show the most ideal FTIR spectra for all samples.

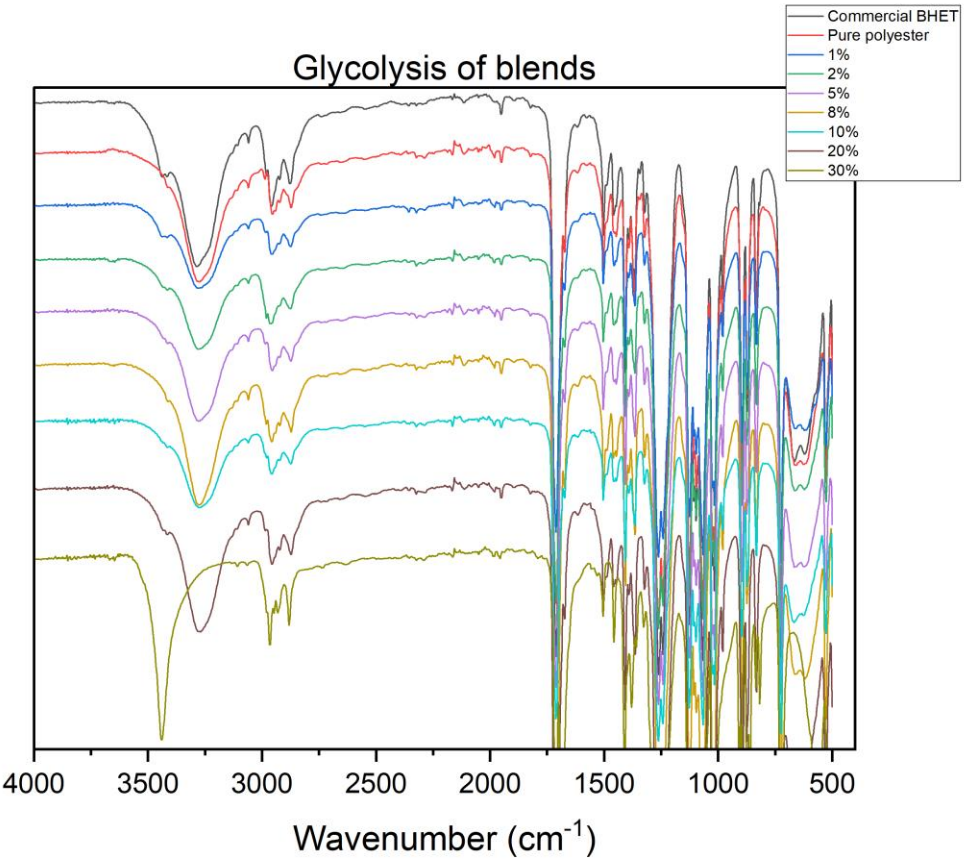


Figure 40 - FTIR spectra for different blend compositions

If we consider the spectra shown in figure 41, in which the FTIR analysis was run two times for the same sample, we can clearly see that the spectra are quite different. One matches the commercial BHET while the other shows an extra peak at around 3500 cm^{-1}. This was apparent in all other blends and can be seen in Appendix 1. The reason for this can be the presence of impurities from the N-H stretch from the elastane. However, this was observed even in the pure polyester depolymerization. Due to this we can say that the peaks are both for the -OH stretch, the only difference is its environment, or crystal structure[69].

If we observe the figure 42 (b) carefully, we can see that for the same sample, there are crystals of BHET (Sample 20%-1 in figure 41) and a white powdery substance (Sample 20%-2 in figure 41). The spectrum for the crystal is identical to the commercial BHET and for the white powder there is difference of one peak as discussed above.

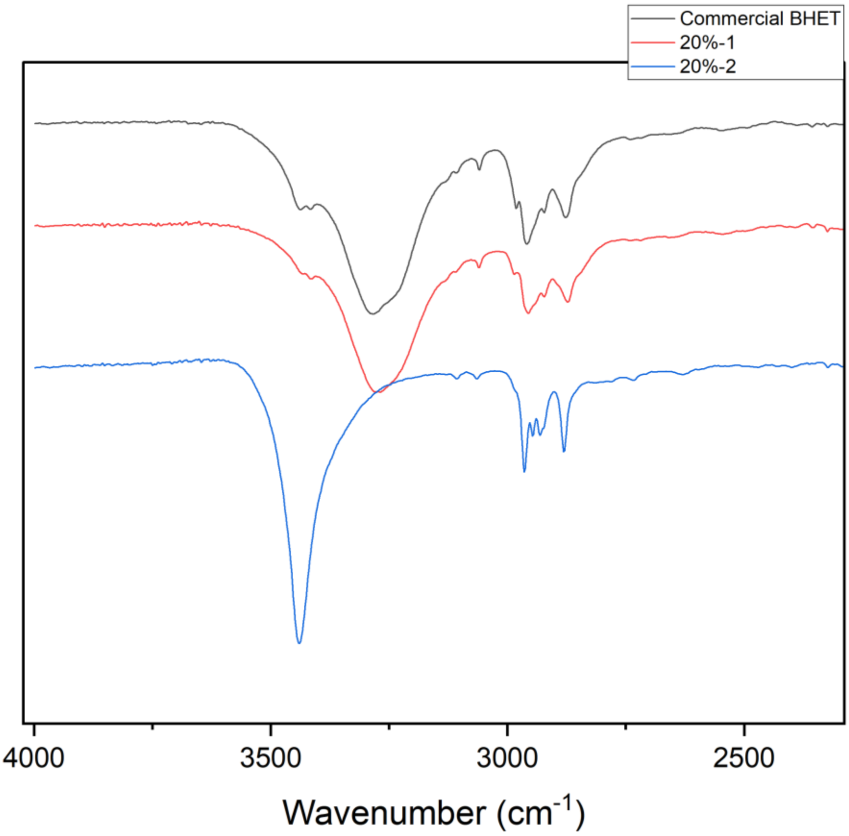


Figure 41 - FTIR spectra of 20% blend run twice

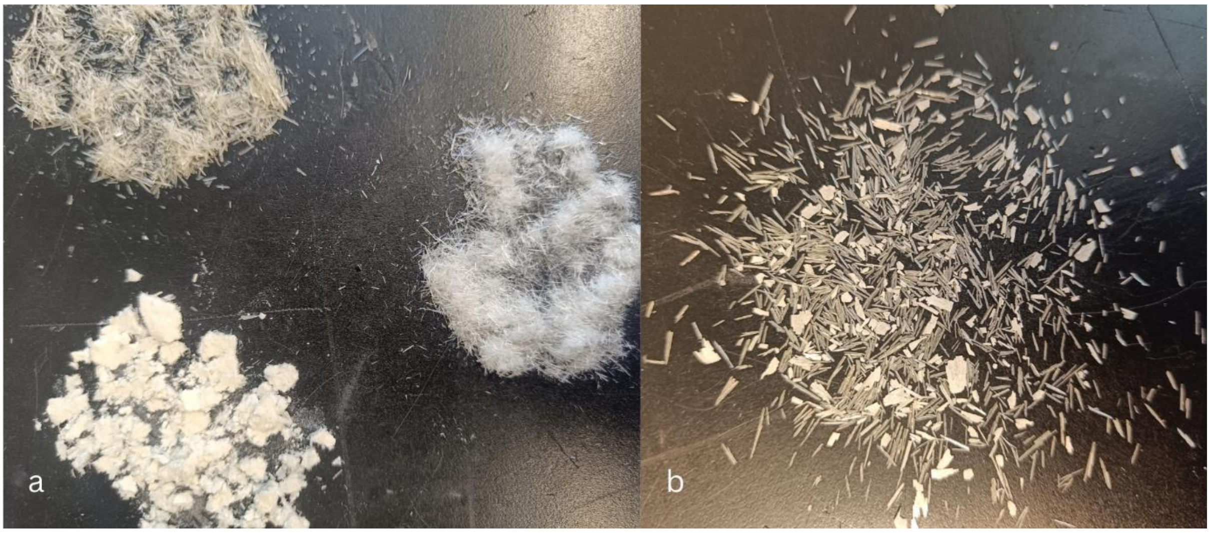


Figure 42 - (a) Different BHET crystals (b) BHET crystals and white flakes observed in 20% blend

4.3.3 TGA

From figure 43, we can see that the PET fibres are thermally stable till 340 °C, which is the onset of weight loss. This can also be seen in the figure 44, which shows the DTG of the PET fibres for the same sample.

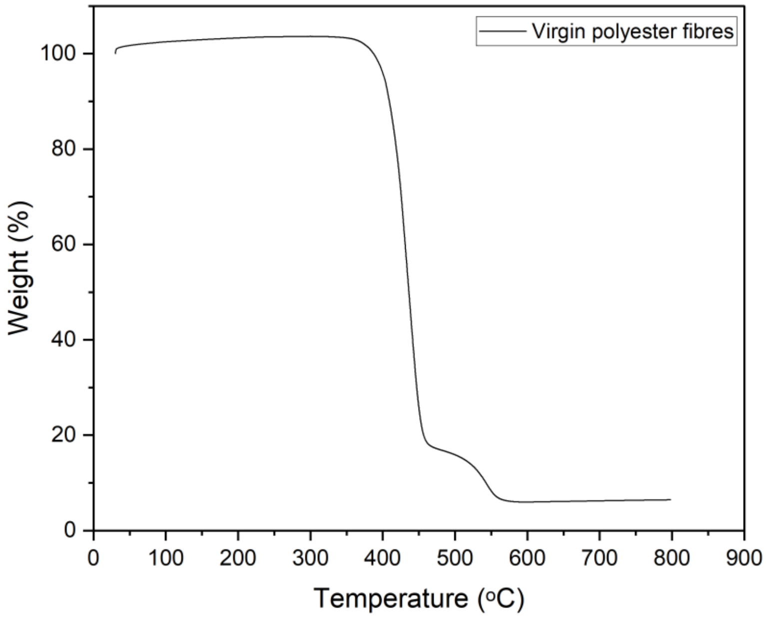


Figure 43 - TGA curve for virgin PET fibres

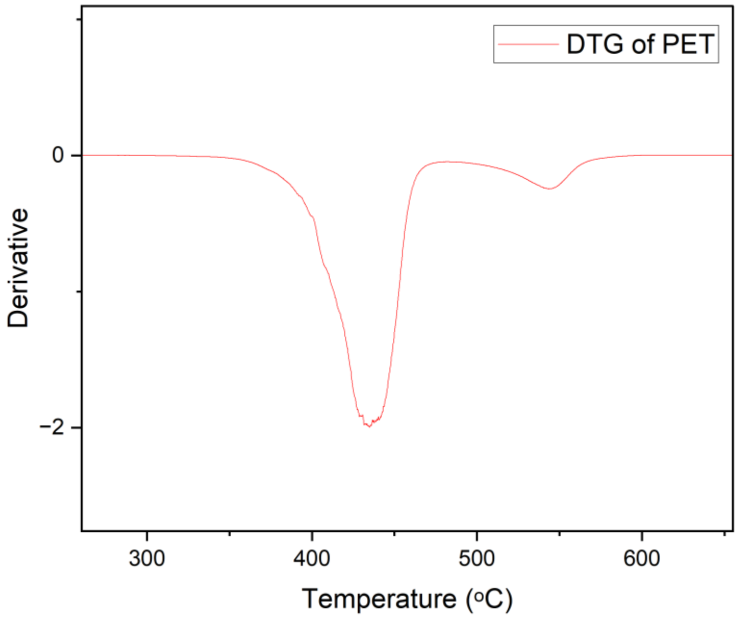


Figure 44 - DTG of PET fibres

For PET, the TGA should be a one stage decomposition process[67], but we can see here in the DTG that there is a small peak. This can be due to some additives or can be due to combustion due to air.

Figure 45 shows the TGA curve for different blend composition. We can clearly observe here that the curves of all the samples show a similar two stage thermal decomposition like commercial BHET. They also have similar thermal stability at around 205 ºC. The first weight loss corresponds to the thermal breakdown of BHET, while the second weight loss is attributed to the thermal decomposition of PET that has undergone repolymerization throughout the heating process conducted in the TGA investigation[70].

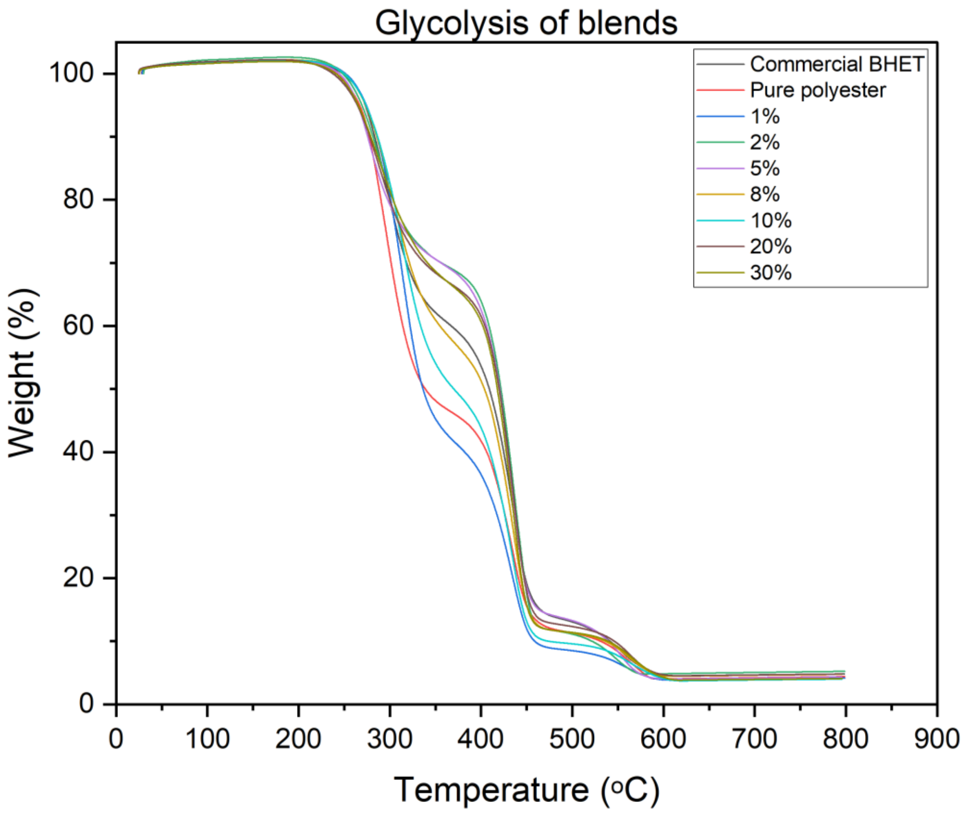


Figure 45 - TGA from different blend composition

The final change in rate could be due to combustion in air.

4.3.4 DSC

Figure 46 shows the first heating curve for different blend compositions. As can be seen here, there is almost no difference between the endothermic peaks for the blends. The endotherms for all the samples have a distinct peak around 109.7, which aligns with the reported melting temperature of BHET. The cooling and second heating curves of samples, presented in Appendix 3, have similar peaks as commercial BHET for most blends. Hence, as they show similar peaks, no further quantifiable work was done for the two curves.

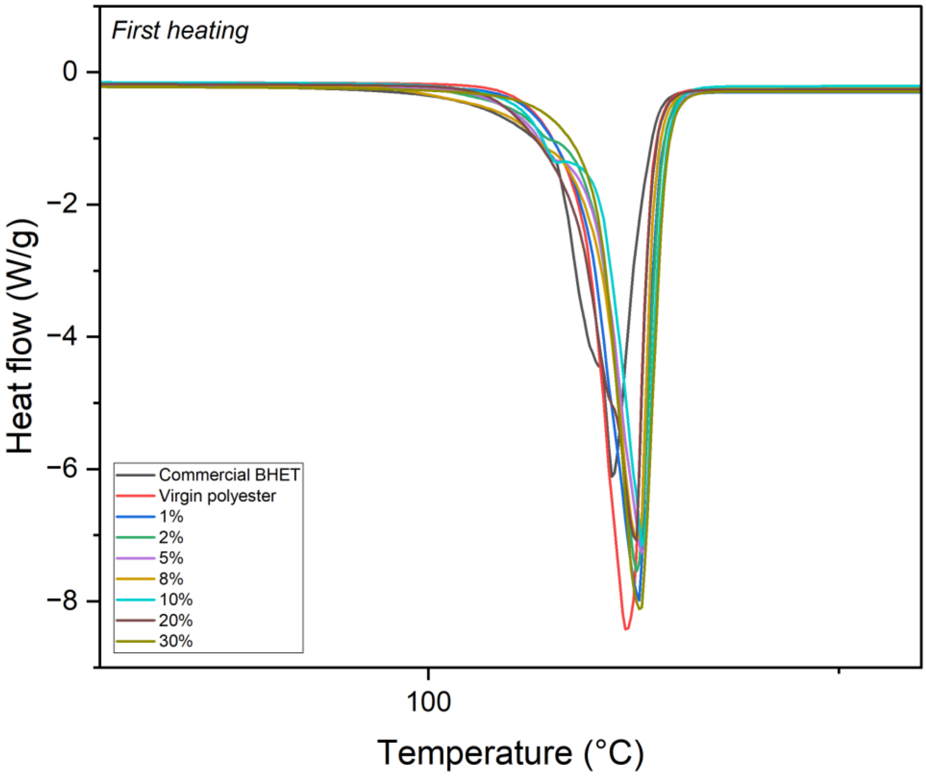


Figure 46 - First heating curve for different blend composition

5. Conclusion

Currently, the majority of industries lack the necessary technological advancements to utilize post-consumer waste textiles as a viable source for producing high-quality fibres. The recycling technologies need a rapid revamp in order to sustain the future load of textile, which is on the rise every minute. Synthetic textiles made from polymers, like polyesters, polyamides, etc. pose a great threat for the environment, and there is a need to find sustainable technologies to recycle these polymeric fibres and bring them back in the loop. In this master thesis, the problem of one such synthetic textile fibre, elastane, was studied and an effort was made to understand its effect on other fibres. Elastane renders quite a big fraction of the textile waste of the world useless as it makes it very hard and economically not feasible, leaving incineration the only viable option. Hence, to gain a fundamental understanding of the behaviour of elastane depolymerization and its effect on polyester/elastane blend was the main focus of this work.

Two processes were studied, namely methanolysis and glycolysis to depolymerize the elastane fibres and the polyester/elastane blend. The effect of temperature and different catalysts was first studied on the depolymerization of elastane and its recycled product, PTMG. The effect of elastane content in the blend was examined to see how the recycled product, BHET, is affected. Both these recycled products were analysed using various characterization techniques. The yield results showed that in most cases, with increasing yield, the impurity also increased. It was also observed that, since it's a recycled product, 100% purity is nearly impossible, and there will always we some impurity. This is one of the reasons that even if a recycled product is brought back in the value chain, it is always used in fraction with pure raw materials to form a product. From the FTIR analysis of both PTMG and BHET, it was evident that the depolymerization product was in fact the desired product. Comparing with the virgin fibres, we could clearly see the evidence for depolymerization. FTIR analysis also confirmed the presence of aromatic impurities from the hard segment of elastane. The products were also tested for thermal properties using TGA and DSC. The data from the TGA showed the increase in the thermal stability of the recycled products, which could primarily be due to the presence of impurities. The DSC curves did not provide any significant information regarding the recycled products. For PTMG, along with the melting temperature, it showed the presence of two endotherms which could be due to multiple constituents or the crystallinity. This can not be conclusive based solely on DSC data.

The lack of published research made it harder to understand the process. This thesis gave only the initial understanding of the depolymerization process and further research is needed to fully grasp the mechanism of the process and the characteristics of the recycled products.

6. Future work

The work done in this master's thesis can be used as an initial steppingstone to further research on this topic, at least that was the aim while performing this work. As stated earlier, there is lack of published research on this topic, hence even the results from a minor change in any parameter can be vital.

The process itself can be optimized in many aspects, like the use of a different reactors, the process can be purged continuously throughout the reaction, using different solvents for washing of the recycled product. The parameters that are studied in this work can be further tested with a greater number of experiments. Other parameters like time and different fibre:solvent ratio can also be tested. Also, the recycled products can also be used in the synthesis of new products to understand the effect on their properties Comprehensive mechanistic experiments can also be conducted to gain a thorough understanding of the chemical processes and degradation pathways that occur during the recycling procedure.

Examination of the potential for scaling up the chemical recycling process from laboratory-scale to industrial-scale operations can also be done. Also, an extensive life cycle evaluation of the chemical recycling procedure for elastane and elastane blends in order to analyse its environmental ramifications in relation to other recycling techniques and disposal alternatives should be conducted along with a comprehensive cost-benefit analysis of the chemical recycling process, considering many elements like the initial capital outlay, ongoing operating expenses, and possible revenue generated from the sale of recovered goods.

Acknowledgements

I want to express my deepest gratitude to everyone who has helped me finish my master's thesis. This study could not have been done without their constant help and heartiest efforts.

First of all, I'd like to say that I'm very thankful to my supervisor Zengwei Guo for his help, advice, and support. This thesis could not have been possible without you. Your thoughtful comments, patience, and hard work helped me shape this thesis and improve the way I do research. I also want to thank Edd Blekkan for agreeing to be my supervisor and helping me throughout. I want to thank my examiner Torbjorn Pettersson for providing the opportunity to do the master thesis on the topic of "Chemical recycling of Elastane and its blends", and the valuable comments on planning thesis. Further, I want to thank Anna Peterson and Richard Sott for helping me in the lab and guiding me during the meetings.

I want to thank the researchers at RISE for helping me in small yet important things during my experiment. I also want to thank my friends for being so helpful, sharing ideas, and making this whole process a lot easier. I want to thank Parul, Anish, Ahmed, and Sumant for bearing with me and helping me whenever things got hard.

I want to thank NTNU and RISE for giving me the opportunity do this study and get my master's degree.

Last but not least, I want to thank my parents very much. You are the most important people in my life, and I can't say enough good things about you. When I study abroad, I don't feel lonely because you give me mental support.

Everyone, thanks.

Bibliography

1. Ellen MacArthur Foundation and World Economic Forum. The New Plastics Economy: Rethinking the future of plastics. *Ellen MacArthur Found.* 120 (2016).

2. Wang, Y. *Recycling in textiles*. *Recycling in Textiles: A Volume in Woodhead Publishing Series in Textiles* (2006). doi:10.1533/9781845691424.

3. Lu, J. J. & Hamouda, H. Current status of fiber waste recycling and its future. *Adv. Mater. Res.* **878**, 122–131 (2014).

4. Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, 25–29 (2017).

5. Gibb, B. C. Plastics are forever. *Nat. Chem.* **11**, 394–395 (2019).

6. Textile Exchange. Preferred Fiber & Materials: Market Report 2022. 1–118 (2022).

7. Ward, G. D., Hewitt, A. D. & Russell, S. J. Fibre composition of donated post-consumer clothing in theUK. *Proc. Inst. Civ. Eng. Waste Resour. Manag.* **166**, 29–37 (2013).

8. Kahoush, M. & Kadi, N. Towards sustainable textile sector: Fractionation and separation of cotton/ polyester fibers from blended textile waste. *Sustain. Mater. Technol.* **34**, (2022).

9. Jönsson, C. *et al.* Biocatalysis in the Recycling Landscape for Synthetic Polymers and Plastics towards Circular Textiles. *ChemSusChem* **14**, 4028–4040 (2021).

10. Fibersort. Manual Sort of Post-Consumer Textiles in North-West Europe. (2018).

11. Sandin, G. & Peters, G. M. Environmental impact of textile reuse and recycling – A review. *J. Clean. Prod.* **184**, 353–365 (2018).

12. Ljungkvist, H. Critical aspects in design for fiber-to-fiber recycling of textiles Mistra Future Fashion View project. (2016).

13. Cregut, M., Bedas, M., Durand, M. J. & Thouand, G. New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process. *Biotechnol. Adv.* **31**, 1634–1647 (2013).

14. Jung, S. Miljöbedömning samt kartläggning av verksamhetsavfall som del av Uppsala kommuns avfallsplan 2014- 2022. (2014).

15. Gschwandtner, C. Outlook on Global Fiber Demand and Supply 2030. *Lenzinger Berichte* **97**, 11–19 (2022).

16. Mather, R. R. & Wardman, R. H. *The Chemistry of Textile Fibres*. *The Chemistry of Textile Fibres* (2015). doi:10.1039/9781782626534.

17. Kozłowski, R. M. & Mackiewicz-Talarczyk, M. Introduction to natural textile fibres. *Handb. Nat. Fibres Second Ed.* **1**, 1–13 (2020).

18. Nayak, R., Houshyar, S., Khandual, A., Padhye, R. & Fergusson, S. *Identi fi cation of natural textile fi bres 14*. (2020).

19. Ahmed, F. & Mondal, M. I. H. *Introduction to natural fibres and textiles*. *Fundamentals of*

Natural Fibres and Textiles (2021). doi:10.1016/B978-0-12-821483-1.00001-2.

20. Ivanova, N. *et al.* We are IntechOpen , the world ' s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %. *Intech* **i**, 13 (2016).

21. Objectives, L. PROPERTIES : WHAT IS A. 3–27 (2015).

22. Deopura, B. L. & Padaki, N. V. *Synthetic Textile Fibres: Polyamide, Polyester and Aramid Fibres*. *Textiles and Fashion: Materials, Design and Technology* (Elsevier Ltd, 2015). doi:10.1016/B978-1-84569-931-4.00005-2.

23. Romakkaniemi, I. Teknillinen Tiedekunta Biodegradation of Synthetic Textile Biodegradation of Synthetic Textile. (2018).

24. Shioya, M. & Kikutani, T. Synthetic Textile Fibres: Non-polymer Fibres. *Text. Fash. Mater. Des. Technol.* 139–155 (2015) doi:10.1016/B978-1-84569-931-4.00007-6.

25. Bhalla, S. Toxicity of Synthetic Fibres & Health. *Adv. Res. Text. Eng.* **2**, (2017).

26. Karthik, T. & Rathinamoorthy, R. *Sustainable synthetic fibre production*. *Sustainable Fibres and Textiles* (2017). doi:10.1016/B978-0-08-102041-8.00008-1.

27. Perepelkin, K. E. Physicochemical nature and structural dependence of the unique properties of polyester fibres. *Fibre Chem.* **33**, 340–352 (2001).

28. Militky, J. The chemistry, manufacture and tensile behaviour of polyester fibers. *Handb. Tensile Prop. Text. Tech. Fibres* 223–314 (2009) doi:10.1533/9781845696801.2.223.

29. Manufacture of polyester yarns. 62–96 (1987) doi:10.1016/B978-1-84569-298-8.50003-1.

30. Le Clerc, C., Bunsell, A. R. & Piant, A. Influence of temperature on the mechanical behaviour of polyester fibres. *J. Mater. Sci.* **41**, 7509–7523 (2006).

31. Matsuo, T. Fibre materials for advanced technical textiles. *Text. Prog.* **40**, 87–121 (2008).

32. Senthilkumar, M., Anbumani, N. & Hayavadana, J. Elastane fabrics - A tool for stretch applications in sports. *Indian J. Fibre Text. Res.* **36**, 300–307 (2011).

33. Hu, J., Lu, J. & Zhu, Y. New developments in elastic fibers. *Polym. Rev.* **48**, 275–301 (2008).

34. Elija M. Hicks, Jr., Arnoldus J. Ultee, J. D. Spandex Elastic Fibers Coalesced multifil (Lycra). *Science (80-.).* **147**, 373–379 (1965).

35. Damayanti, D., Wulandari, L. A., Bagaskoro, A., Rianjanu, A. & Wu, H. S. Possibility routes for textile recycling technology. *Polymers (Basel).* **13**, (2021).

36. Nautiyal, H., Shree, V., Khurana, S., Kumar, N. & Varun. *Recycling potential of building materials: A review*. *Environmental Footprints and Eco-Design of Products and Processes* (2015). doi:10.1007/978-981-287-643-0_2.

37. Awaja, F. & Pavel, D. Recycling of PET. *Eur. Polym. J.* **41**, 1453–1477 (2005).

38. Malik, N., Kumar, P., Shrivastava, S. & Ghosh, S. B. An overview on PET waste recycling for application in packaging. *Int. J. Plast. Technol.* **21**, 1–24 (2017).

39. Payne, J. & Jones, M. D. The Chemical Recycling of Polyesters for a Circular Plastics Economy: Challenges and Emerging Opportunities. *ChemSusChem* **14**, 4041–4070 (2021).

40. Yasir, A. H., Khalaf, A. S. & Khalaf, M. N. Preparation and Characterization of Oligomer from Recycled PET and Evaluated as a Corrosion Inhibitor for C-Steel Material in 0.1 M HCl. *Open J. Org. Polym. Mater.* **07**, 1–15 (2017).

41. Sinha, V., Patel, M. R. & Patel, J. V. Pet waste management by chemical recycling: A review. *J. Polym. Environ.* **18**, 8–25 (2010).

42. Yang, Y., Lu, Y., Xiang, H., Xu, Y. & Li, Y. Study on methanolytic depolymerization of PET with supercritical methanol for chemical recycling. *Polym. Degrad. Stab.* **75**, 185–191 (2002).

43. Achilias, D. S. & Karayannidis, G. P. The chemical recycling of PET in the framework of sustainable development. *Water, Air, Soil Pollut. Focus* **4**, 385–396 (2004).

44. Park, S. H. & Kim, S. H. Poly (ethylene terephthalate) recycling for high value added textiles. *Fash. Text.* **1**, 1–17 (2014).

45. Liu, L., Wu, Y. & Zhu, Z. Internal structure and crystallinity investigation of segmented thermoplastic polyurethane elastomer degradation in supercritical methanol. *Polym. Degrad. Stab.* **140**, 17–24 (2017).

46. Lv, F. *et al.* Recycling of waste nylon 6/spandex blended fabrics by melt processing. *Compos. Part B Eng.* **77**, 232–237 (2015).

47. Boschmeier, E., Archodoulaki, V. M., Schwaighofer, A., Lendl, B. & Bartl, A. A novel quantification tool for elastane in textiles using thermal treatment. *Polym. Test.* **118**, 107920 (2023).

48. Phan, K. *et al.* A Combined Experimental and Theoretical Study on Textile Recycling: the Dissolution of Elastane. (2020).

49. Wang, L., Huang, S. & Wang, Y. Recycling of Waste Cotton Textile Containing Elastane Fibers through Dissolution and Regeneration. *Membranes (Basel).* **12**, (2022).

50. Xu, W. H. *et al.* New insights into urethane alcoholysis enable chemical full recycling of blended fabric waste. *Green Chem.* **25**, 245–255 (2022).

51. Liu, L., Tang, L., Wu, Y., Ni, Y. & Zhu, Z. Degradation process investigation of thermoplastic polyurethane elastomer in supercritical methanol. *Polym. Degrad. Stab.* **98**, 2520–2528 (2013).

52. Liu, L., Zhu, Z. & Wu, Y. Depolymerization kinetics for thermoplastic polyurethane elastomer degradation in subcritical methanol. *Polym. Degrad. Stab.* **140**, 126–135 (2017).

53. Zhang, B. *et al.* Latest development on ceramics and titanium alloy materials welded by SPS. *Naihuo Cailiao/Refractories* **51**, 157–160 (2017).

54. Marjo, C. E., Gatenby, S., Rich, A. M., Gong, B. & Chee, S. ATR-FTIR as a tool for assessing potential for chemical ageing in Spandex/Lycra®/elastane-based fabric collections. *Stud. Conserv.* **62**, 343–353 (2017).

55. Yuan, Q. *et al.* Hydrogen bond breaking of TPU upon heating: Understanding from the viewpoints of molecular movements and enthalpy. *RSC Adv.* **5**, 31153–31165 (2015).

56. Głowińska, E., Datta, J., Rodríguez Romero, J. F., Simón Herrero, D. & Carmona, M. Novel cast polyetherurethanes based on dispersed polymeric polyols. *Polym. Test.* **68**, 340–349 (2018).

57. Lei, W. *et al.* Morphology and thermal properties of polyurethane elastomer based on representative structural chain extenders. *Thermochim. Acta* **653**, 116–125 (2017).

58. Electronic Supplementary Material (ESI) for RSC Advances . This journal is © The Royal Society of Chemistry 2014 Table 2 . Characteristic FTIR transmittance peak and their assignments [wave no . (cm -1)] Sample name C = O Functional groups C = C. 2014 (2014).

59. Tang, Q. & Gao, K. Structure analysis of polyether-based thermoplastic polyurethane elastomers by FTIR, 1H NMR and 13C NMR. *Int. J. Polym. Anal. Charact.* **22**, 569–574 (2017).

60. Mohrig, J. R.; Hammond, C. N.; Schatz, P. F. Techniques in Organic Chemistry. Freeman: New York. 1–6 (2006).

61. Cassel, R. B. Determining Volatiles in Polyethylene Terephthalate Using the Q5000 IR Thermogravimetric Analyzer. *TA Instruments Appl. Br.* 1–6 (2005).

62. Wang, X., Chen, H., Chen, C. & Li, H. Chemical degradation of thermoplastic polyurethane for recycling polyether polyol. *Fibers Polym.* **12**, 857–863 (2011).

63. Boschmeier, E., Archodoulaki, V. M., Schwaighofer, A., Lendl, B. & Bartl, A. A novel quantification tool for elastane in textiles using thermal treatment. *Polym. Test.* **118**, 107920 (2023).

64. Kim, B. K., Seo, J. W. & Jeong, H. M. Morphology and properties of waterborne polyurethane/clay nanocomposites. *Eur. Polym. J.* **39**, 85–91 (2003).

65. Raftopoulos, K. N., Janowski, B., Apekis, L., Pielichowski, K. & Pissis, P. Molecular mobility and crystallinity in polytetramethylene ether glycol in the bulk and as soft component in polyurethanes. *Eur. Polym. J.* **47**, 2120–2133 (2011).

66. Jenkins, M. J., Cao, Y. & Kukureka, S. N. The effect of molecular weight on the crystallization kinetics and equilibrium melting temperature of poly(tetramethylene ether glycol). *Polym. Adv. Technol.* **17**, 1–5 (2006).

67. Charles, J. & Ramkumaar, G. R. FTIR and thermal studies on polyethylene terephthalate and acrylonitrile butadiene styrene. *Asian J. Chem.* **21**, 4389–4398 (2009).

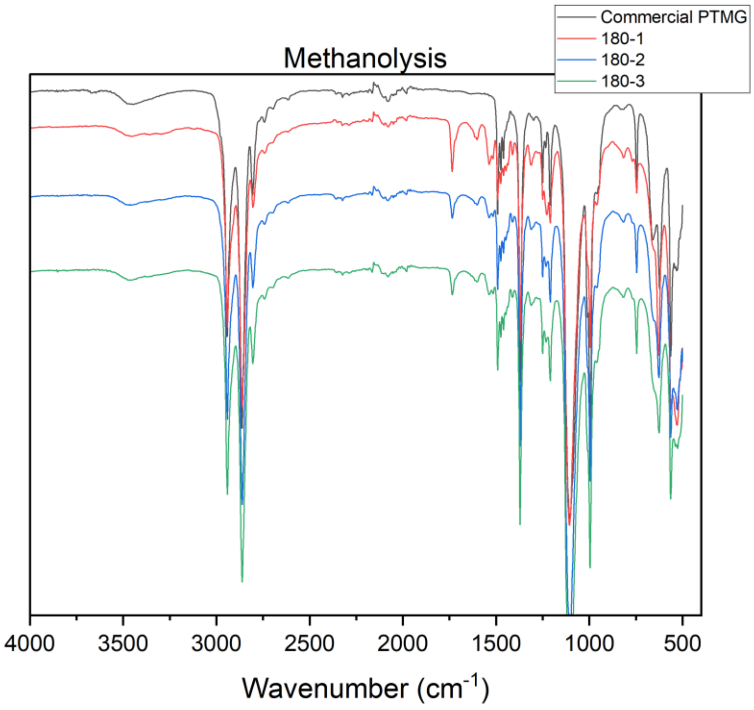
68. Zhou, X., Lu, X., Wang, Q., Zhu, M. & Li, Z. Effective catalysis of poly(ethylene terephthalate) (PET) degradation by metallic acetate ionic liquids. *Pure Appl. Chem.* **84**, 789–801 (2012).

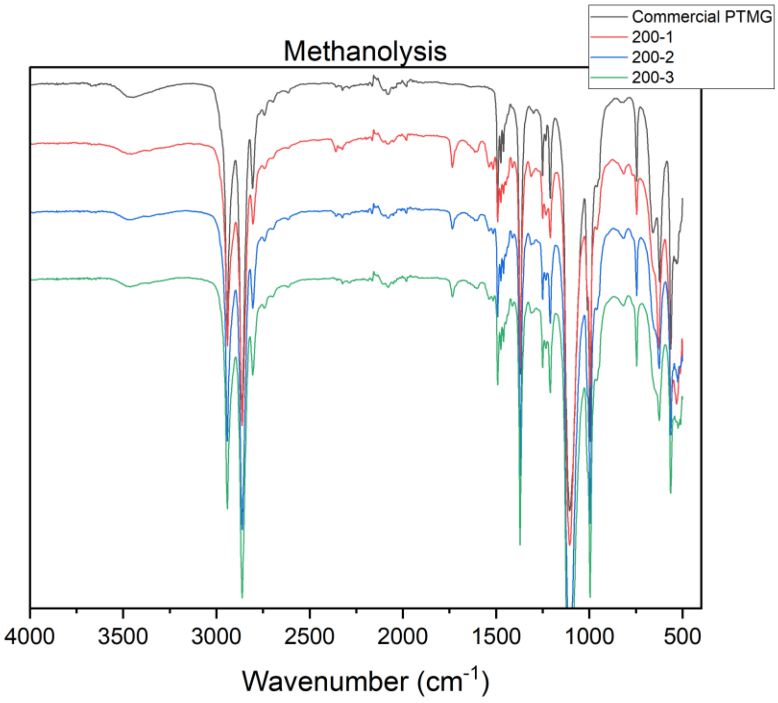
69. Charles, J. & Ramkumaar, G. R. Qualitative analysis of high density polyethylene using FTIR spectroscopy. *Asian J. Chem.* **21**, 4477–4484 (2009).

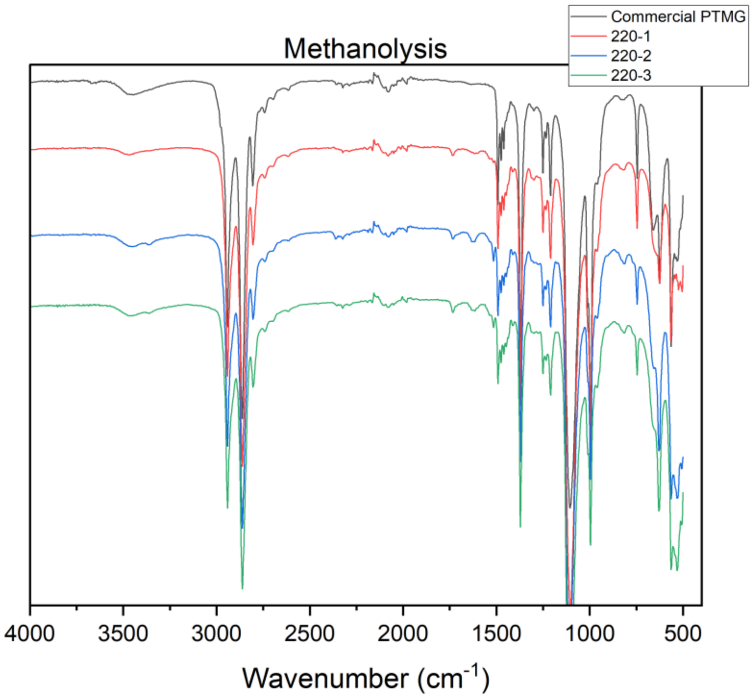
70. Scé, F. *et al.* Comparing conventional and microwave-assisted heating in PET degradation mediated by imidazolium-based halometallate complexes. *New J. Chem.* **43**, 3476–3485 (2019).

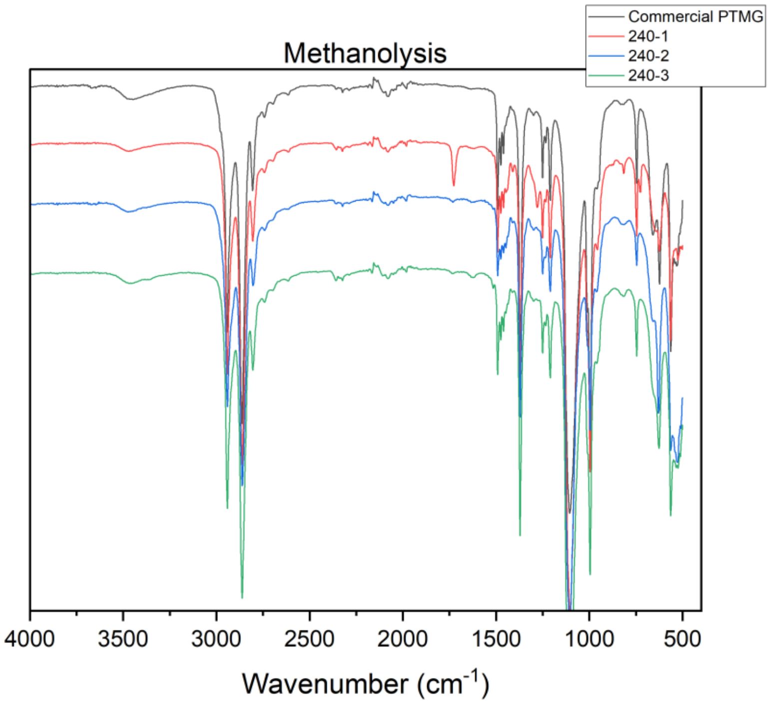
Appendix 1

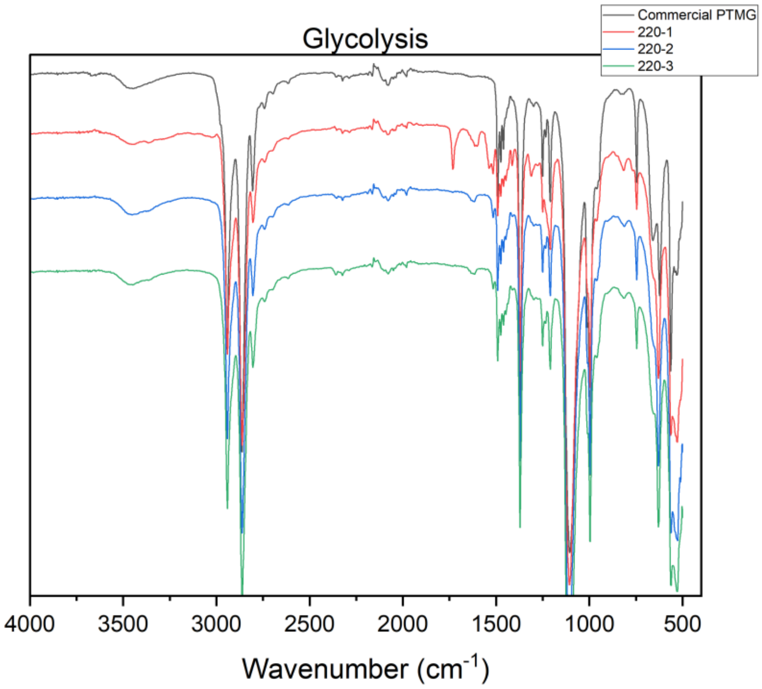
FTIR graphs of Temperature study

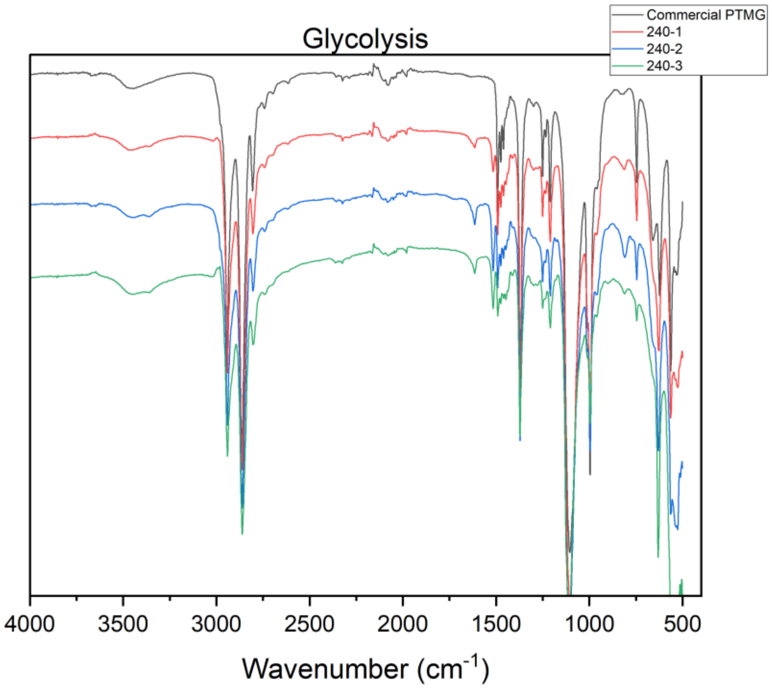




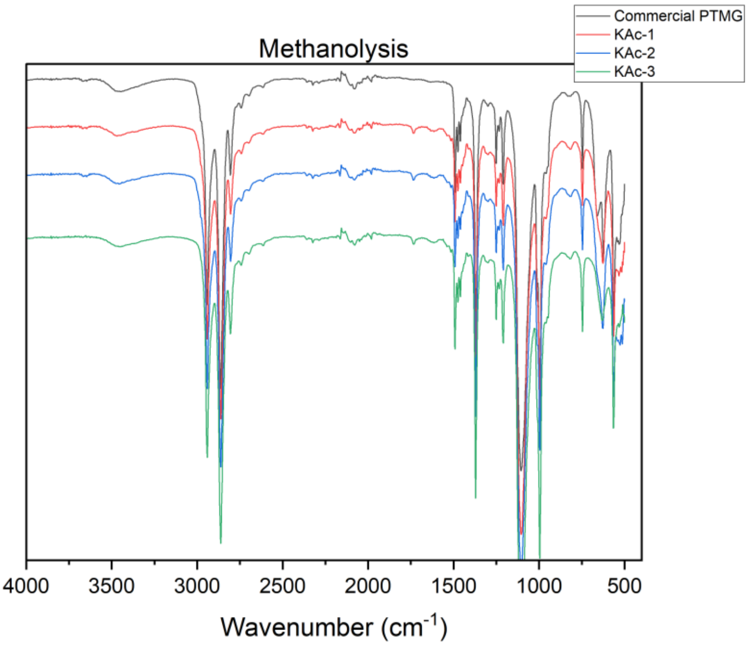

Methanolysis
Commercial PTMG
220-1
220-2
220-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

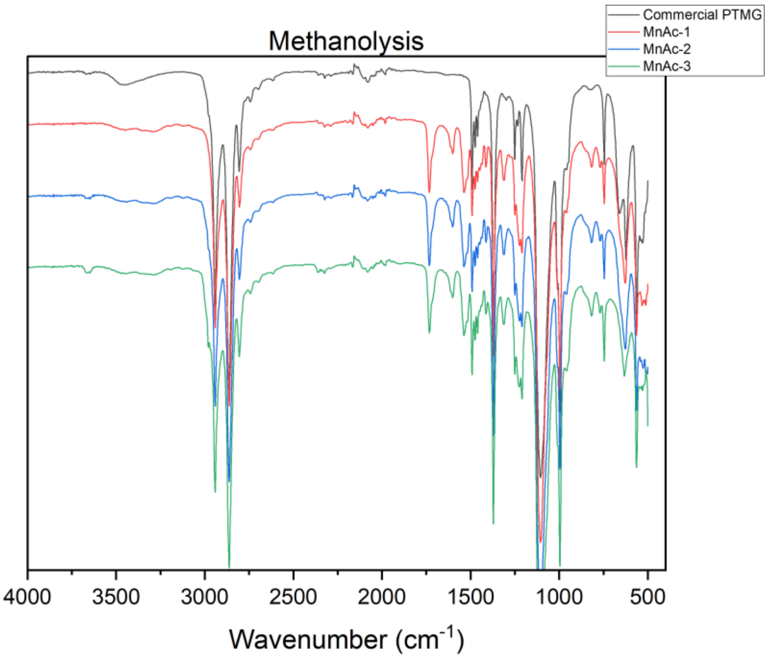

Methanolysis
Commercial PTMG
240-1
240-2
240-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

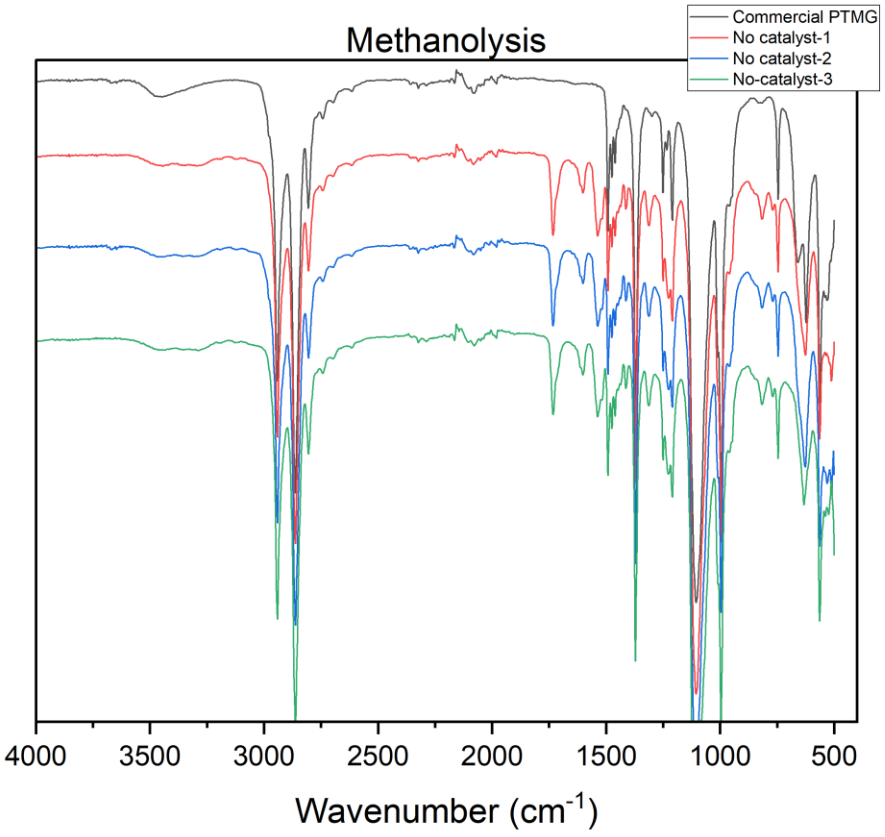

Glycolysis
Commercial PTMG
220-1
220-2
220-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

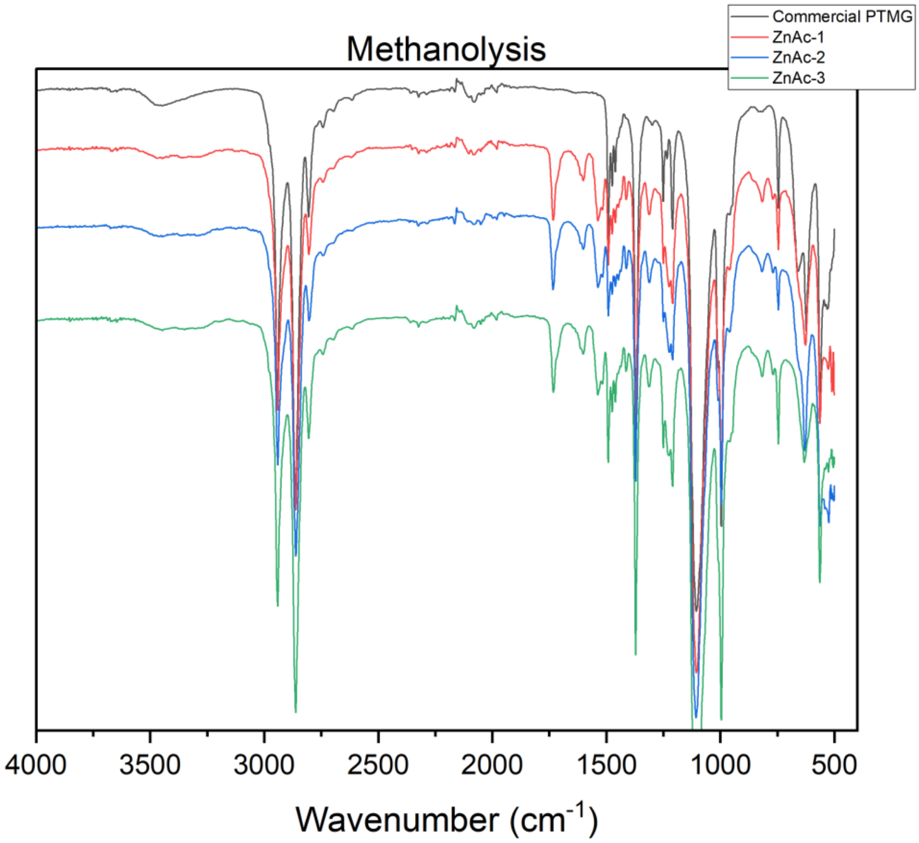

Glycolysis
Commercial PTMG
240-1
240-2
240-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

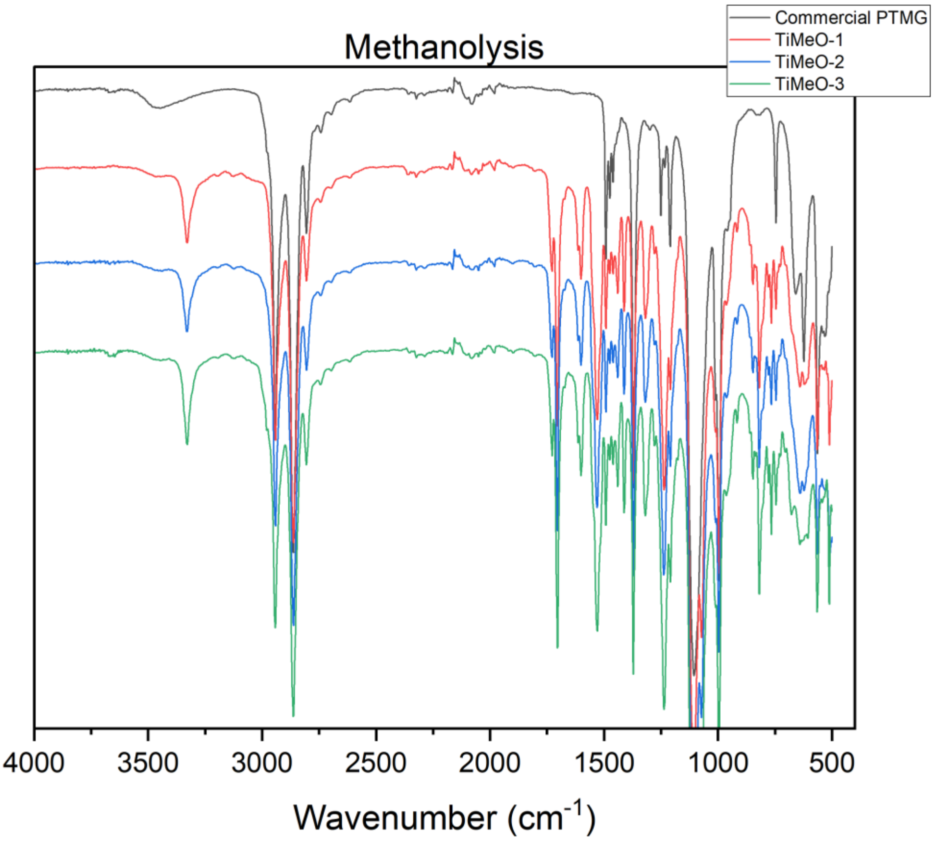
FTIR graphs of Catalyst study

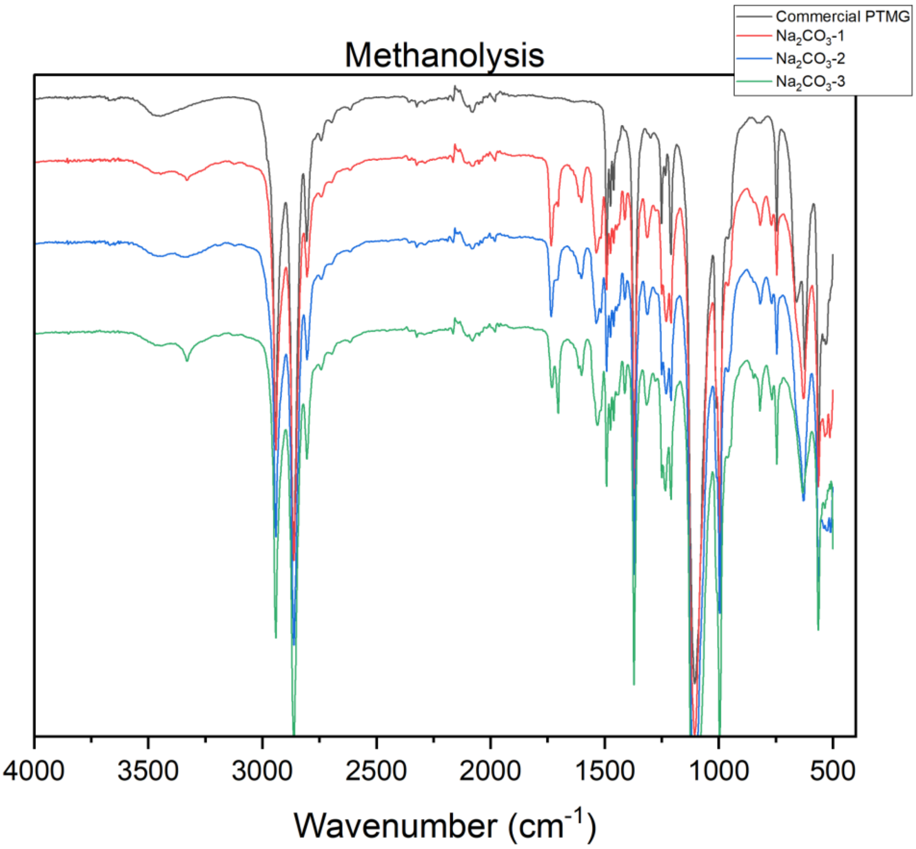


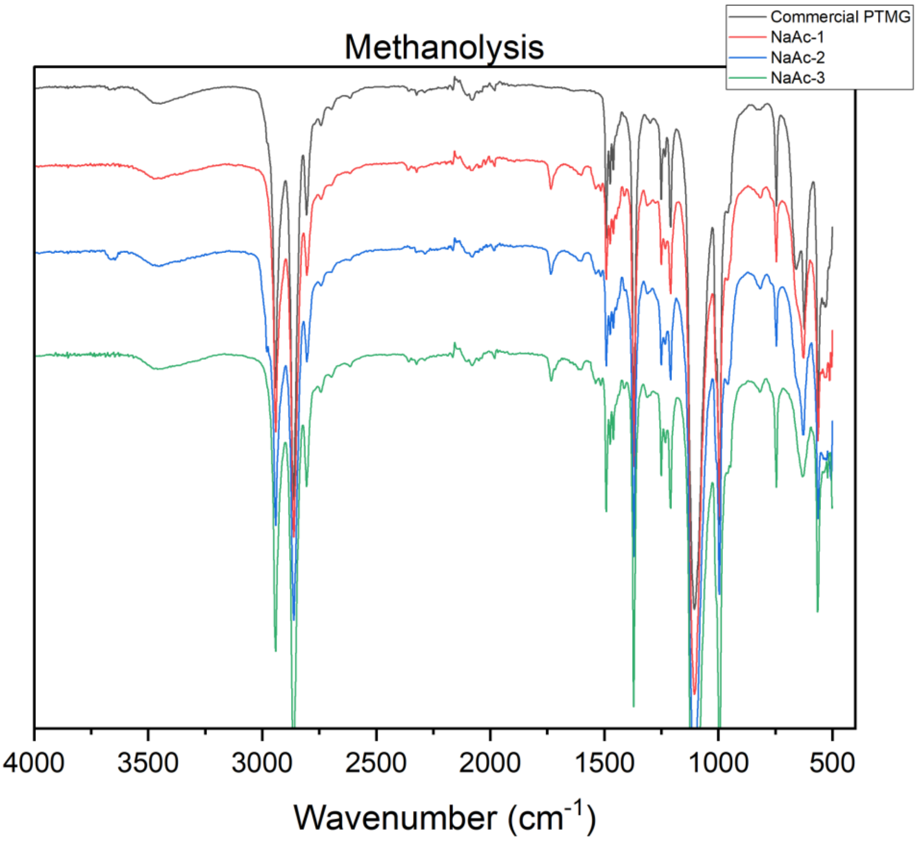


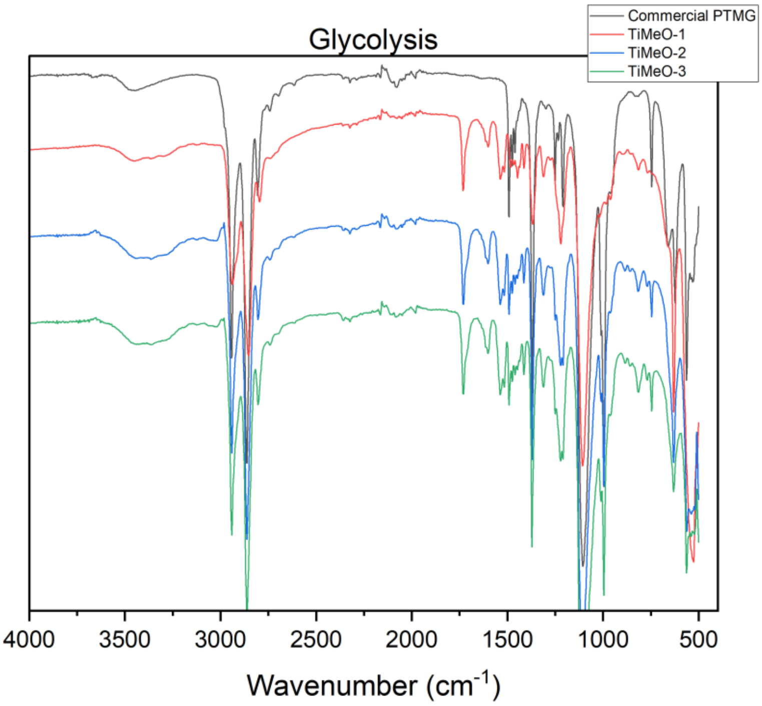

Methanolysis
Commercial PTMG
No catalyst-1
No catalyst-2
No-catalyst-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

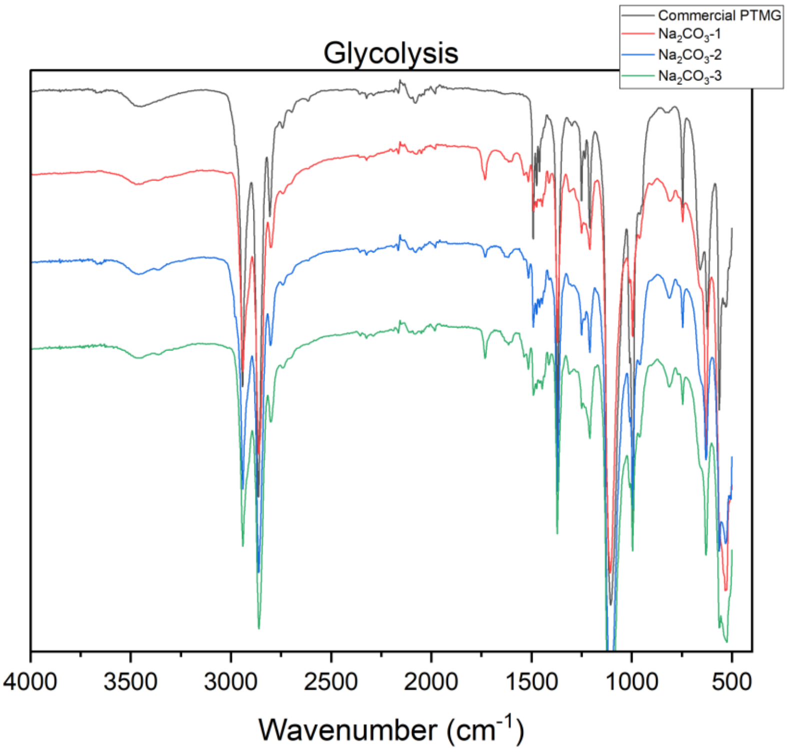

Methanolysis
Commercial PTMG
ZnAc-1
ZnAc-2
ZnAc-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

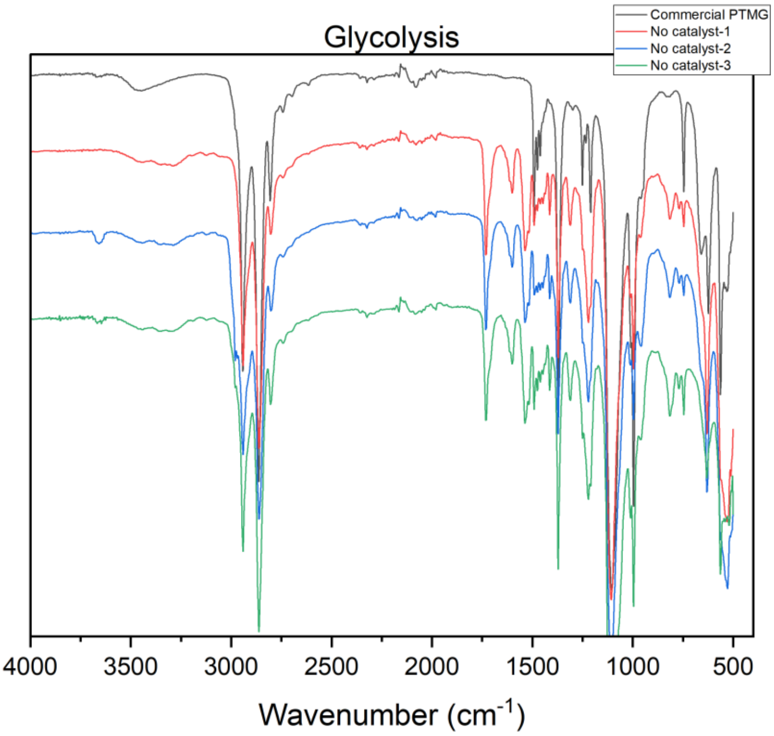

Methanolysis
Commercial PTMG
TiMeO-1
TiMeO-2
TiMeO-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

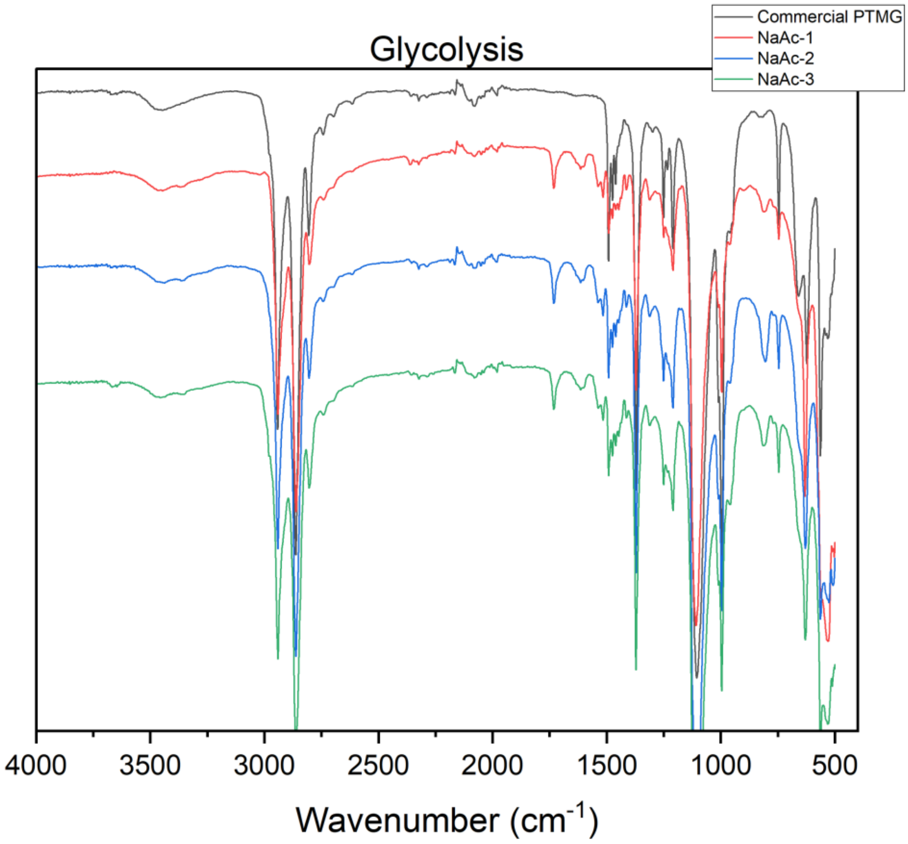

Methanolysis
Commercial PTMG
Na_2CO_3-1
Na_2CO_3-2
Na_2CO_3-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


Methanolysis
Commercial PTMG
NaAc-1
NaAc-2
NaAc-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

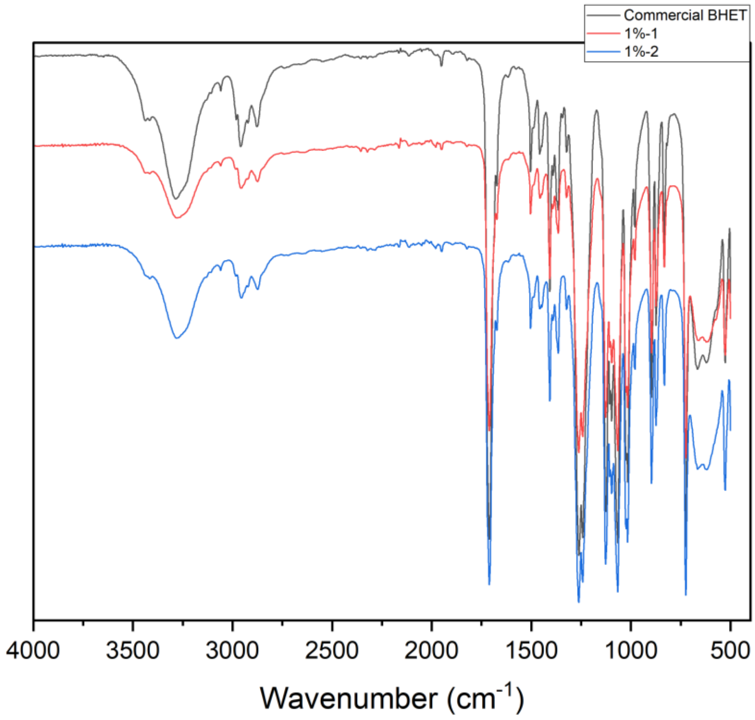

Glycolysis
Commercial PTMG
TiMeO-1
TiMeO-2
TiMeO-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

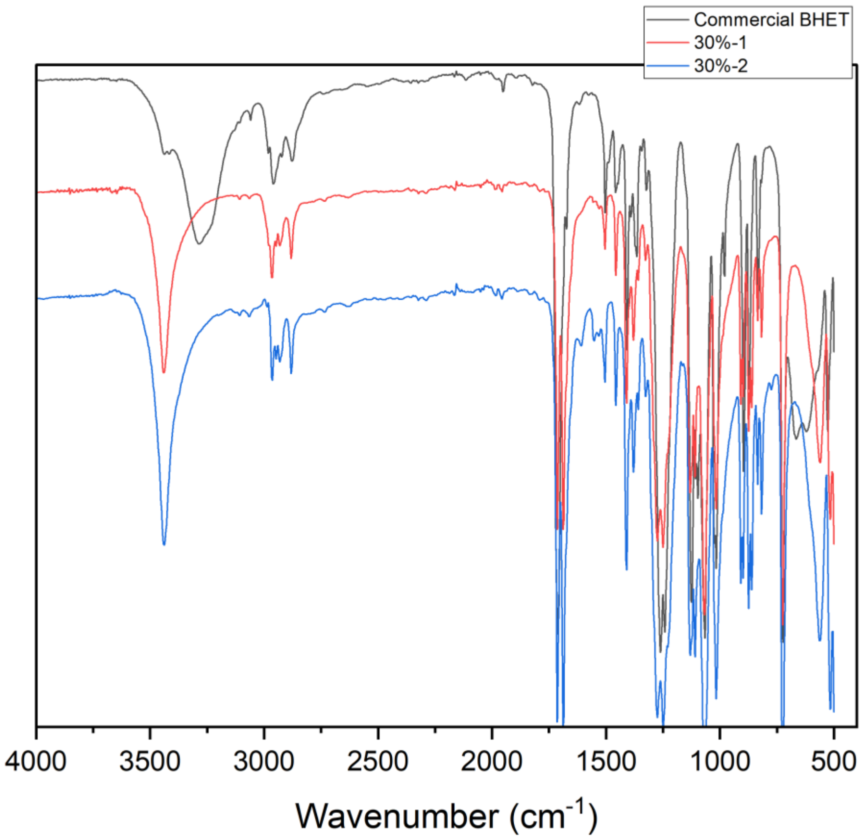

Glycolysis
Commercial PTMG
Na_2CO_3-1
Na_2CO_3-2
Na_2CO_3-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

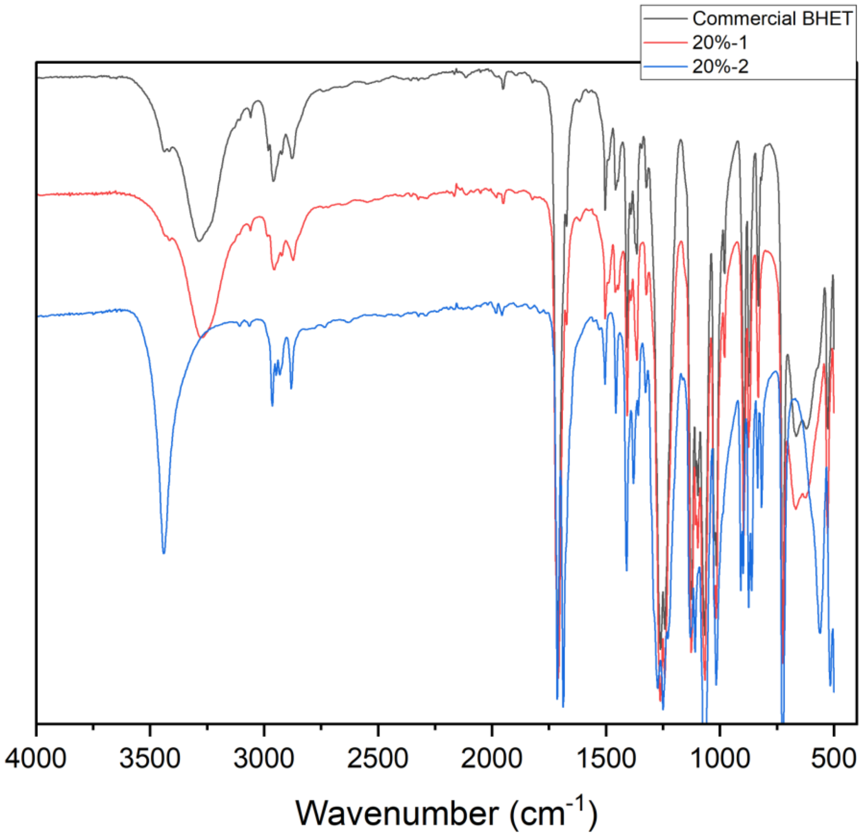

Glycolysis
Commercial PTMG
No catalyst-1
No catalyst-2
No catalyst-3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

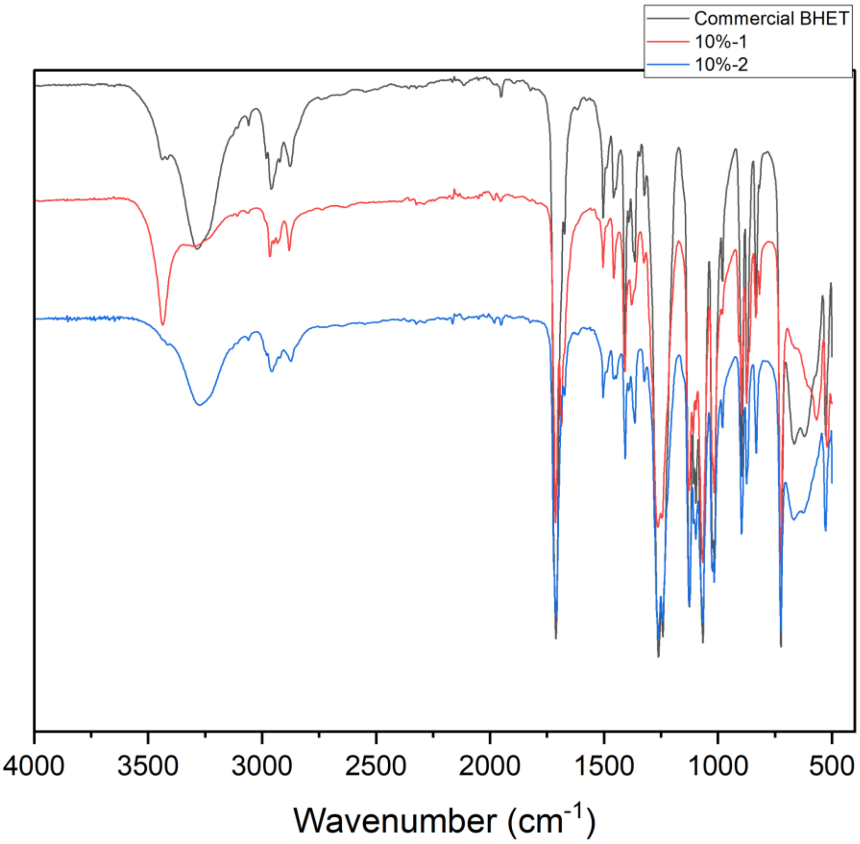


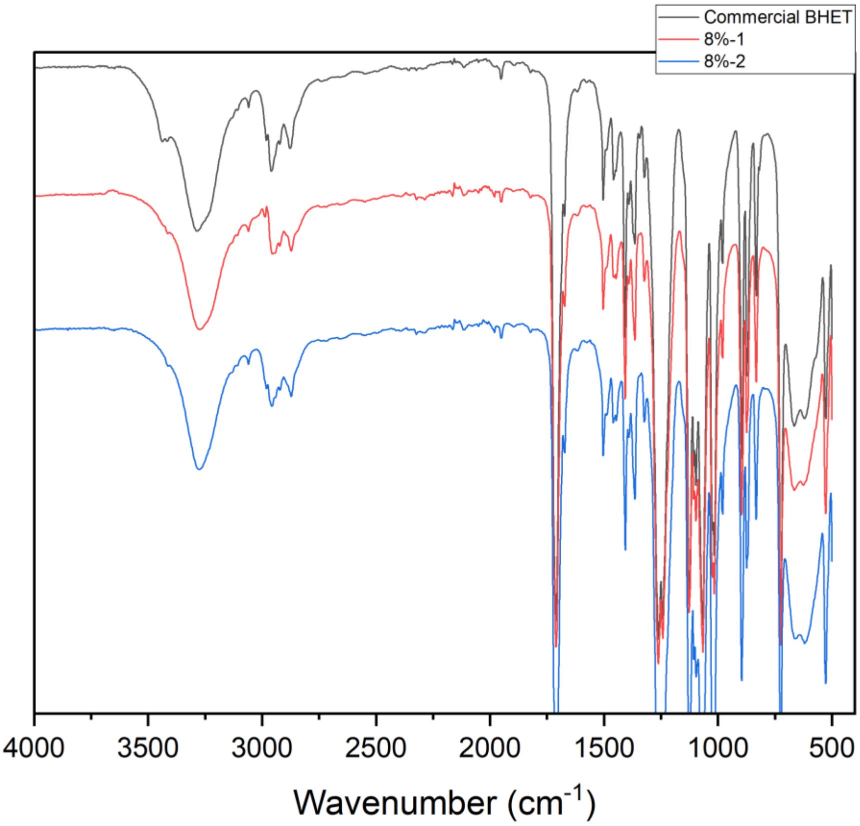
FTIR graphs of blend study

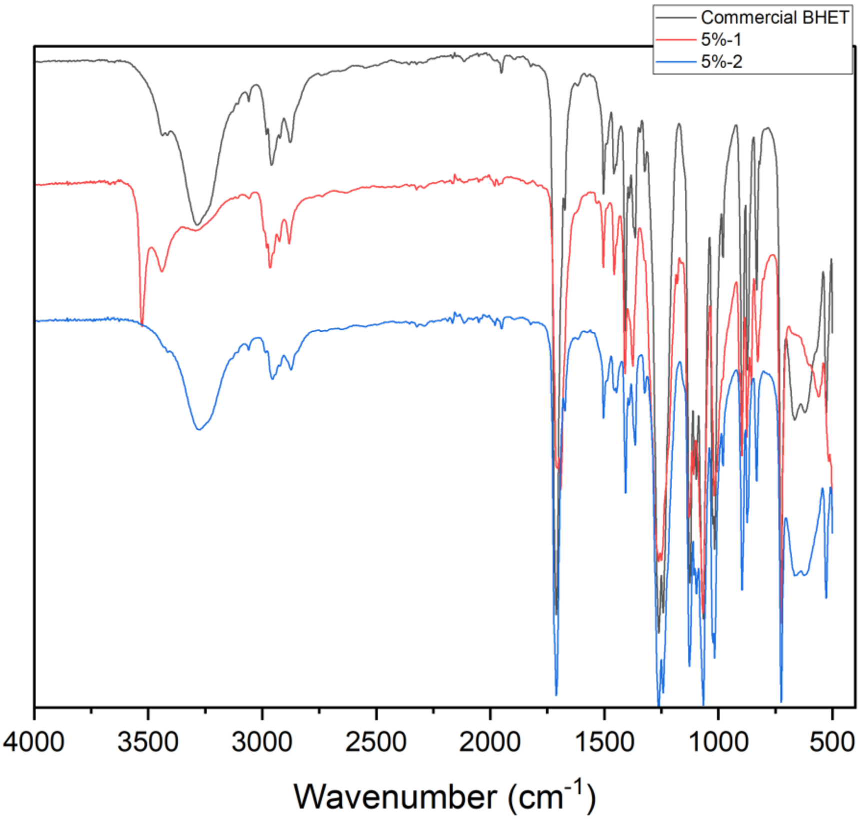


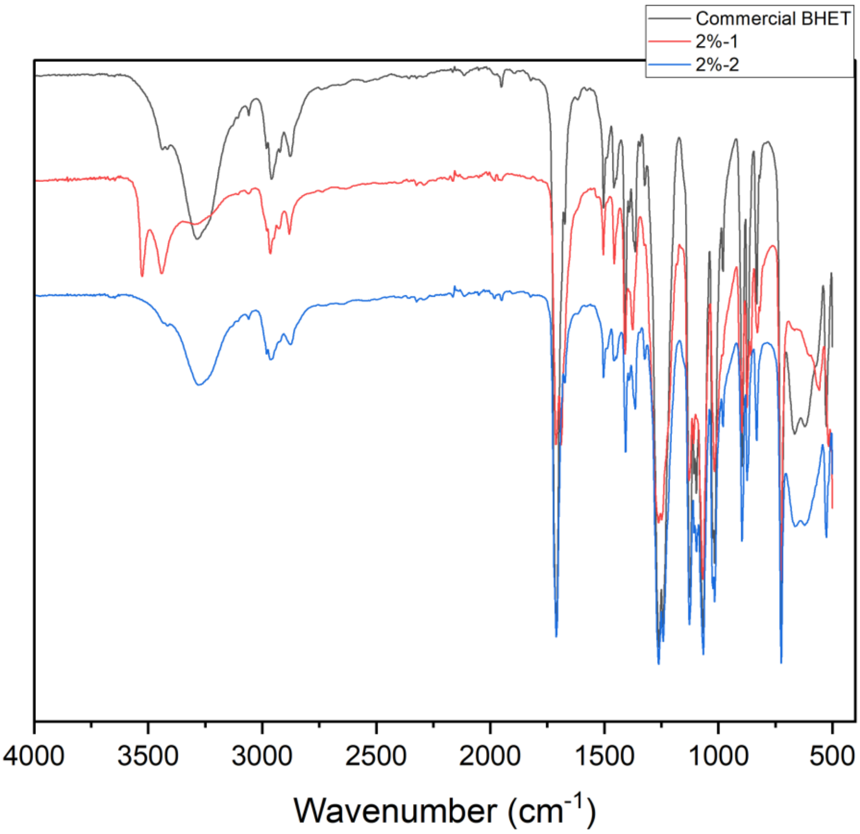

Commercial BHET
30%-1
30%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


Commercial BHET
20%-1
20%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


Commercial BHET
10%-1
10%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

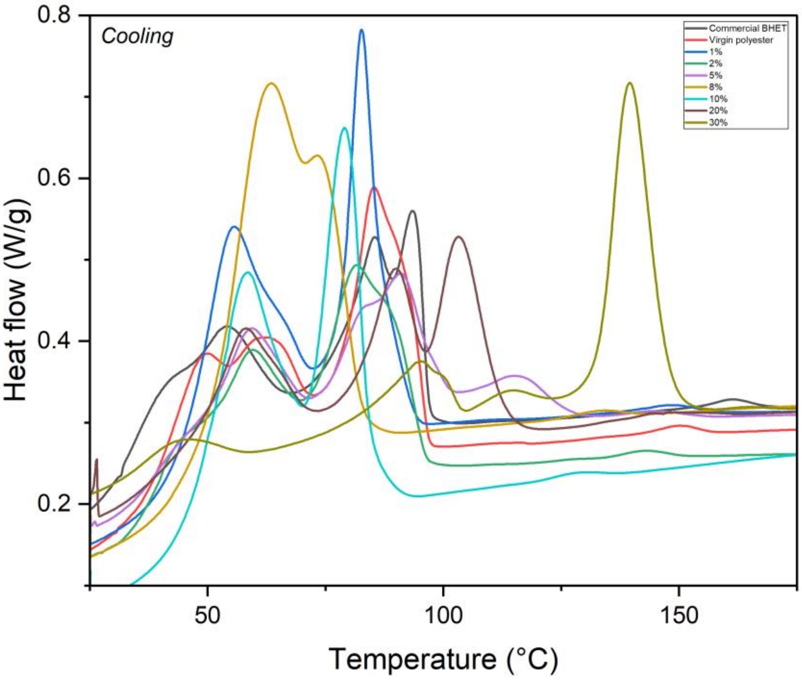

Commercial BHET
8%-1
8%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

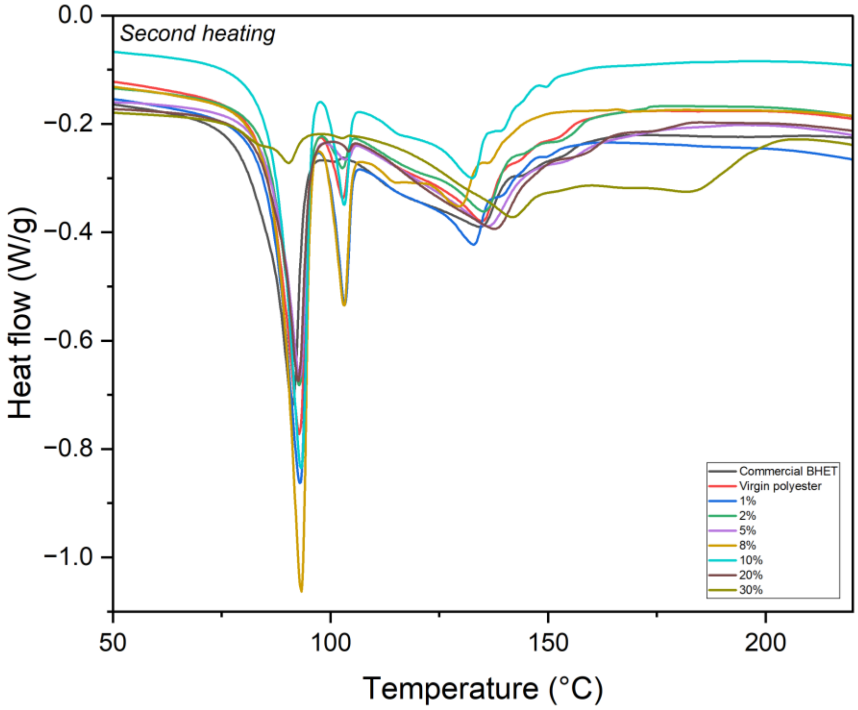

Commercial BHET
5%-1
5%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


Commercial BHET
2%-1
2%-2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Appendix 2

Cooling and 2nd heating graphs for blends




Second heating
Heat flow (W/g)
Temperature (°C)
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
50
100
150
200
Commercial BHET
Virgin polyester
1%
2%
5%
8%
10%
20%
30%

NTNU

Norwegian University of
Science and Technology