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Chemical Recycling of All-Polyester Vehicle Interior Solutions

Investigating the Recyclability of PET and PBT Mixes, Including a Polyester Based Vehicle Interior Flooring Solution by Glycolysis

Master's Thesis in Materials Chemistry

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Abstract

Increased circularity in the plastic industry is key to decrease oil-dependence and find more sustainable solutions. In addition to the most widely used method, mechanical recycling, others are possible which could enable more complex material streams to be recycled. One such route is chemical recycling where depolymerisation yields monomers of virgin quality, which can be used to synthesise new polymer chains.

Typical vehicle flooring solutions results in waste consisting of various different polymeric fibres and foams adhered together, resulting in low recyclability and the waste is either incinerated or sent to landfills. In response to the low recyclability of conventional soulutions, new solutions based on polyester and comonomers have been developed, as the most commonly used polyester, poly(ethylene terephthalate) (PET), has good recyclability. However, the recyclability of an all-polyester solution, containing different polyesters and comonomers has not been investigated and that will therefor be done in this project. In the project, PET, poly(butylene terephthalate) (PBT), polyester based components for vehicle flooring, and a complete all-polyester vehicle flooring solution were depolymerised by glycolysis.

Analyses showed that the components in the polyester based vehicle flooring consisted mainly of either PET or PBT. Glycolysis of neat PBT gave a crystallised yield of 38 mol% of bis(2-hydroxyethyl)terephthalate (BHET), PET monomer, compared to 79 mol% from neat PET. Several of the components yielded similar amounts as neat PET, whilst lower yields were obtained from components which consisted mainly of PBT, where co-polyester glue appeared most challenging. The glycolysis of the full vehicle flooring solution yielded white crystalline BHET with a purity above 97 % and a crystallised yield of 60 mol% confirming that the product is recyclable.

The origin of the low yield of BHET crystals from PBT, compared to PET, was further studied using HPLC. It was shown that the yields of BHET in the reaction solution was significantly higher compared to the crystallised yield after workup. This indicates that for the flooring, and other PBT containing mixes, the separation process needs adjusting as compared to that used for neat PET, likely due to additional byproducts forming. The results showed that the polyester based vehicle flooring solution, and PET and PBT blends, can be chemically recycled by glycolysis to BHET which could help close the material loop as a more circular solution.

Keywords: chemical recycling, depolymerisation, glycolysis, polyester, PET, PBT, BHET, vehicle interior.

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Karin Nilsson, Gothenburg, August 2023

List of Acronyms

Listed below are the acronyms used in this thesis, presented in alphabetical order.

ACN	Acetonitrile
ATR	Attenuated total reflectance
BD	1,4-butanediol
BHBT	Bis(4-hydroxybutyl)terephthalate
BHBT dimer	*O,O*'-(butane-1,4-diyl)bis(2-hydroxyethyl)diterephthalate
BHET	Bis(2-hydroxyethyl)terephthalate
BHET dimer	*O,O*'-(ethane-1,2-diyl)bis(2-hydroxyethyl)terephthalate
DEG ester	2-hydroxyethyl[2-(2-hydroxyethoxy)ethyl]terephthalate
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
EG	Ethylene glycol
ESI	Electrospray ionisation
FTIR	Fourier transform infrared
HBHET	4-hydroxybutyl(2-hydroxyethyl)terephthalate
HBHEET	4-hydrobutyl(2-(2-hydroxyethoxy)ethyl)terephthalate
HPLC	High-performance liquid chromatography
MHBT	4-((4-hydroxybutoxy)carbonyl)benzoic acid
MHET	Mono(2-hydroxyethyl)terephthalic acid
MS	Mass spectroscopy
PBT	Polybutylene terephthalate
PET	Polyethylene terephthalate
PU	Polyurethane
TGA	Thermogravimetric analaysis
TPA	Terephthalic acid
UV	Ultra violet

Contents

1

Introduction

In order to lessen the oil-dependence of the plastic industry and find more sustainable solutions, more circular processes are key. To achieve this from the current largely linear production where most plastic waste goes to incineration for energy recovery, or to landfills, more material needs to be recycled [1]. In addition to the most commonly used method mechanical recycling, other methods are possible such as chemical recycling.

Polyethylene terephthalate (PET) is a commonly used polymer for both textiles and packaging applications, but is also used in the transportation industry. PET can be chemically recycled through different processes which all depolymerise the polymeric chain into smaller fragments which can be utilised as new feedstock. The most widely researched process route for this is the solvolysis reaction glycolysis, which has also been applied commercially in several facilities. Through this process the monomer bis(2-hydroxyethyl)terephthalate (BHET) is obtained, which is traditionally synthesised from petroleum based feedstock. BHET can be used for polymerisation of new PET or used as feedstock for other reactions.

Whilst, glycolysis of PET is well-known, both from scientific literature and industrially, reports on glycolysis of other types of polyester are scarce. Still, polyester mixes are becoming more abundant and an increased knowledge on the joint depolymerisation of different polyesters and co-polyesters is needed. One of the few articles is Wang et al. (2021), showing that glycolysis can also be used for depolymerisation of mixes of PET and polybutylene terephthalate (PBT) to the monomer BHET [2]. The study of several different zeolitic imidazolate framework composites as catalysts showed that BHET could be yielded from a 50:50 mass ratio of PET and PBT.

In regards to plastic waste from vehicles the majority is incinerated, whilst the rest goes to landfills [3]. At the end-of-life of a vehicle, it is dismantled and spare parts are collected whilst the rest is fragmented. The plastic part of the fragmented waste could be of interest for chemical recycling. Moreover, if the plastic waste was collected separately during dismantling a higher purity could be assured, which might make it of interest for both chemical and mechanical recycling. The possibility for either type of recycling of the plastic vehicle waste would depend on the composition of the material, as well as the additives used in the plastic. The specific composition of polymeric materials are often the intellectual property of the manufacturer, which is a further challenge for the recycling [4].

Typical vehicle flooring solutions result in waste consisting of various different polymeric fibres and polyurethane (PU) foams, with low recyclability [5]. Other material options with higher recyclability but maintained or improved performance have therefore been investigated. Polyester based solutions, most commonly based on PET, have been developed since PET has good recyclability. However, whilst the recyclability of polyester and neat PET fibres are generally described as an advantage for its use, literature does not investigate or show the recyclability of polyester-based vehicle interior solutions.

1.1 Aim

The aim of this project is to investigate the recyclability of an all-polyester vehicle flooring solution through a glycolysis process. The behavior of neat PET, neat PBT and polyester based vehicle flooring components in glycolysis will be investigated. Moreover, the depolymerisation through glycolysis of the components assembled together into a vehicle flooring solution will be studied. This will provide useful information regarding the recyclability of a high-end vehicle product solution using glycolysis, and how different parts of the vehicle flooring design will affect the recycling process.

1.2 Limitations

This study focuses on glycolysis and no other recycling or depolymerisation methods is studied. One catalyst is utilised for all the glycolysis reactions, a Mg-Al mixed oxides catalyst. The materials used are virgin materials intended for the interior use of vehicles and components made from blends of these materials. No end-of-life waste is used for depolymerisation. All reactions are performed in laboratory scale and no large scale testing is done. The sustainability of the recycling process itself in regards to, for example, the carbon-footprint of the recycled monomer in comparison to virgin petroleum based material falls outside the scope of this master's thesis.

1.3 Specification of Issue Under Investigation

This study investigates how the yield of glycolysis varies between different components in a vehicle flooring solution such as bicomponent staple fibre, co-polyester glue, co-polyester film and polyester primary backing. The study aims to give answers regarding which components might decrease the yield of the depolymerisation of the vehicle flooring solution as a whole, and where in the process alterations might be required to improve its efficiency. Furthermore, the components used in the vehicle flooring solution are characterised to correlate the composition to the behavior in the glycolysis reaction, whilst also giving an indication of the ease of identifying differences in the materials in relation to the challenges they could cause for a recycling process. Additionally, the byproducts formed in the glycolysis of the

different materials will are analysed to identify differences between the materials.

2
Theory

2.1 PET

PET is a semi-crystalline polymer that is commonly used for the production of fibres, bottles, food packaging and films, among other things [1, 6]. PET has good mechanical and thermal properties and also exhibits a high permeability to both moisture and oxygen.

The production of PET is done in several steps [7]. Firstly, through either transesterification of ethylene glycol (EG) with dimethyl terephthalate (DMT) or direct esterification of terephthalic acid (TPA). Both routes result in the formation of BHET. Next, BHET is used as the monomer in polycondensation yielding PET. EG is continuously removed as the equilibrium constant for this reaction is low. The most commonly used process for PET production is based on TPA as feedstock [8]. The reaction steps from EG and TPA to PET are illustrated in Figure 2.1.

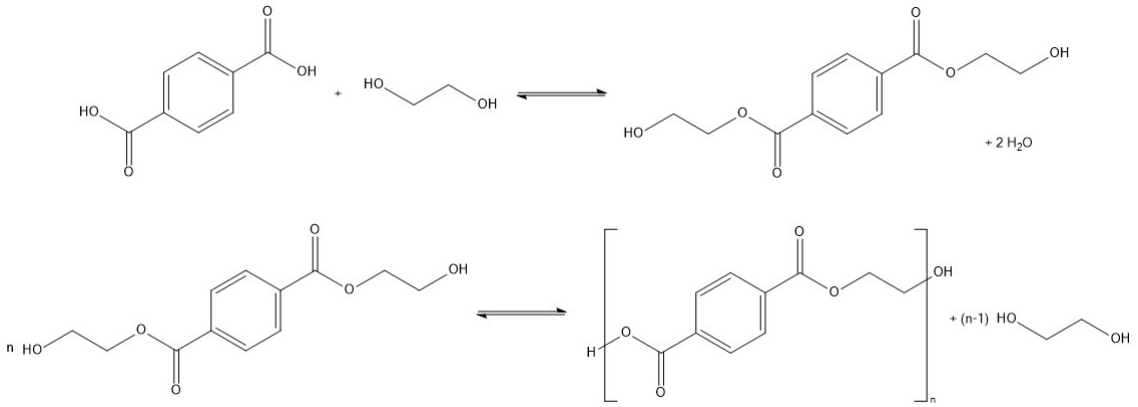

Figure 2.1: Reaction steps for polymerisation of PET from TPA and EG, via BHET.

The most common use of PET is the manufacture of textile fibres [9]. By introduction of comonomers in the PET polymer chain it can also be used to produce fibres with lower melting temperatures which can be used to make nonwoven materials [10]. Additionally, PET can be used for bicomponent fibres where two polymers are spun together into one fibre. In the textile industry PET, often referred to simply as polyester, is the most commonly used fibre [11]. The majority of textile waste goes to either landfills or is incinerated. These methods result in resources being lost from the value chain and can have negative environmental effects. In

order for a more circular system to be possible, recycling processes are needed to turn low-value PET product waste into high-value virgin-quality material.

2.1.1 Recycling of PET

Recycling of PET can be done by several different methods but the most commonly used one is mechanical recycling [12]. Mechanical recycling is a process where the material is put through mechanical operations such as the material being cut, crushed and melted after which it can be used to make new products. However, after repeated cycles, the strength of the material decreases and the brittleness increases, leading to decreased quality and downgrading.

Another method for recycling PET is through chemical recycling where monomers or oligomers are produced by depolymerisation, the controlled degradation of polymers [12]. Compared to mechanical recycling, in which the material is downgraded successively, chemical recycling can generate high quality feedstock [4]. It also gives the potential for up-cycling waste as higher-value chemicals can be produced. Additionally, chemical recycling has the potential to recycle more contaminated material streams and complex plastic waste, such as multi-layer systems [1].

A key factor, enabling chemical recycling, is the presence of a cleavable bond in the backbone of the polymer [4]. In the case of PET these are the ester linkages since the carbonyl bond is highly polar and susceptible to nucleophilic attack. Several different methods can be used to chemically recycle PET, and the main ones are glycolysis, methanolysis and hydrolysis [12]. These different methods for depolymerisation result in the production of different monomers: BHET, DMT and TPA, respectively.

Glycolysis of PET is done by the transesterification of the ester groups in PET by a diol [13]. The diol is in excess, and the most commonly used diol is EG, the use of which yields BHET as a monomer. The recovered BHET can then be used in the polymerisation of new PET or for other uses such as foams, coatings and resins. The flexibility in the use of the monomer is a financial advantage of the glycolysis method. Furthermore, the reaction can be done under relatively mild conditions, and does not require the use of strong acids or alkalis that PET hydrolysis requires, nor the supercritical methanol sometimes used in methanolysis. However, glycolysis does generally require the presence of a catalyst to increase the rate and prevent larger oligomers from forming during the glycolysis.

The mechanism for the catalysed glycolysis of PET is shown in Figure 2.2 where a positively charged metal ion from the catalyst forms a complex with the carbonyl carbon [14]. This facilitates a nucleophilic attack from the EG on the ester group and a covalent bond is formed between the hydroxyethyl group of the EG and the carbonyl carbon. Thereby, the polymer chain is severed into shorter chains and eventually oligomers and then BHET is formed.

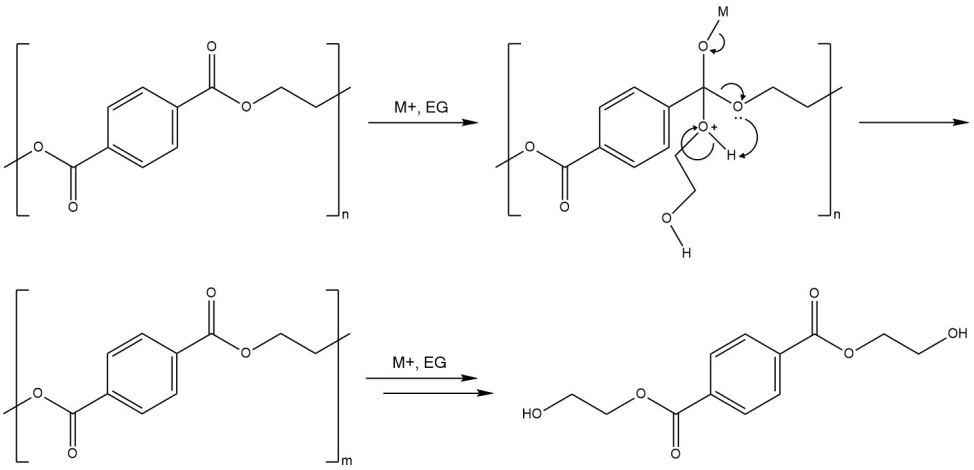

Figure 2.2: Reaction schematic with mechanism of metalsalt catalysed depolymerisation of PET through glycolysis, into oligomers, into BHET. M^+ is a positively charged metal ion from the catalyst and n>m.

2.2 PBT

Another semi-crystalline thermoplastic polyester is PBT, which is similar to PET but differs in that it has four methylene groups in the repeating unit instead of two [9]. The structure of the repeating unit of PBT is shown in Figure 2.3. The additional methylene groups increase the mobility of the polymer chain and also the ability for the chains to crystallise. PBT also has minimal moisture absorption, good chemical resistivity, high toughness and strength, as well as low creep at elevated temperatures [15]. These properties makes it useful in a number of applications such as in the automotive and electronic industries. PBT can also be used as an elastic textile fibre [10]. It recovers very well from elongation under low loads which makes it useful as a fibre for clothing.

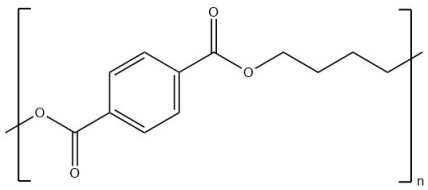

Figure 2.3: Structure of the repeating unit of PBT, were n is the number of repeating units.

2.3 Vehicle Flooring Solutions

The flooring solution in a vehicle needs to serve several functions [16]. In addition to the aesthetics of vehicle flooring solutions, acoustic and barrier properties are vital, whilst remaining as lightweight as possible. To achieve this and more the vehicle flooring system is generally made up of several layers, each consisting of several components. The surface layer typically consists of a polyamide or polyester carpet. Below the surface layer is a substrate layer which works as either barrier, lightweight

sound absorption or both and it is typically made of a rubber or polymeric base which is stuffed with calcium carbonate or barium sulphate. Lastly, the decoupler is in contact with the car body in white and decouples sound and vibrations, for which PU foam is often used. Solutions utilising other materials, with increased recyclability have been investigated [5]. Polyester, and most prominently PET, is of interest due to important properties such as a good durability to price ratio, but also because it has good recyclability. A vehicle flooring solution is illustrated in Figure 2.4, which shows one similar to the that investigated in this project.

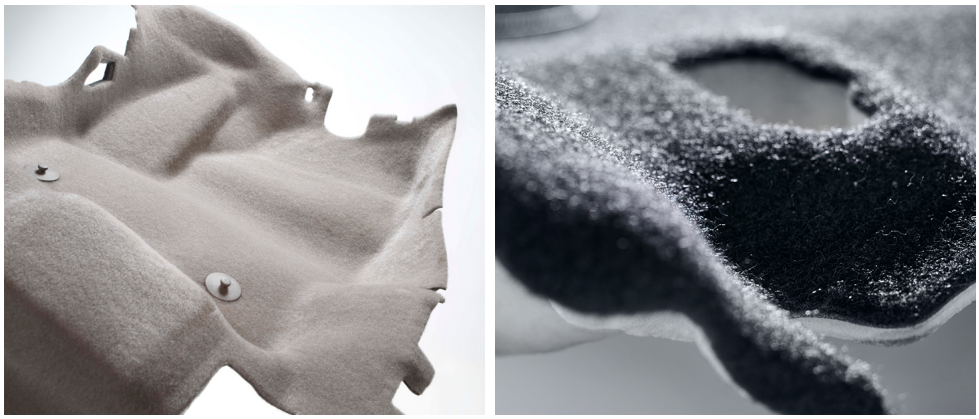

Figure 2.4: Vehicle interior flooring solution from Autoneum (Di-Light) [17], similar to that investigated in this project.

2.4 Analytical Techniques

In this section several analytical techniques will be presented. These have been used to characterise either the polymeric materials or the compounds resulting from the depolymerisation reactions.

2.4.1 ATR-FTIR

A useful technique for the characterisation of polymeric materials is Fourier transform infrared spectroscopy (FTIR), in which the material is subjected to infrared electromagnetic radiation [18]. The material's absorption of the radiation causes distinctive changes in the vibrations and rotations of the molecular bonds. Based on this, polymers and other substances can be identified. Attenuated total reflectance (ATR) is a low-penetrating FTIR technique where a high-refractive-index crystal is used to internally reflect the IR radiation and only the material in direct contact with the crystal is affected by the radiation.

2.4.2 DSC

The thermoanalytical technique differential scanning calorimetry (DSC) measures the enthalpy changes of a sample as the temperature is either changed or kept constant [18]. As the samples undergo thermal events such as glass transition, melting and crystallisation, heat is emitted or absorbed. The temperatures at which

such events occur can be determined, as well as other properties of the material such as degree of crystallinity.

2.4.3 TGA

Another thermoanalytical technique is thermogravimetric analysis (TGA) [18]. In TGA the weight of a sample is measured as thermal events such as volatilisation and decomposition of components in the sample occur as a function of temperature and time. The measurement is done in the flow of gas, which is either inert or reactive. Different polymers have different typical decomposition temperatures, which are also dependent on the heating rate.

2.4.4 HPLC-MS and -UV

High performance liquid chromatography (HPLC) is a technique where compounds in a liquid matrix are separated as they elude with the liquid mobile phase through a column [19]. The column is typically packed with porous silica particles which constitute the stationary phase. Different interactions between the stationary phase and the different analytes result in different elution times. The elution of the compounds out of the column can be detected by a variety of detection techniques, two of which are ultraviolet (UV) absorption and mass spectroscopy (MS). Several different ionisation techniques can be used in LC-MS. For polar molecules electrospray ionisation (ESI) is the most commonly used ionisation technique, where positive or negative adducts between the analyte molecule and ions are observed. Some common adducts for positive ionisation mode are presented in Table 2.1. The formed ions from the analyte (M) and the corresponding ion mass as a function of the molecular weight (MW) of M are presented.

Table 2.1: Common adducts in LC-MS from positive ionisation, where M is the analyte molecule and MW is the molecular weight of that molecule.

Ion Formation	Ion Mass [u]
$[M+H]^+$	MW+1.0073
$[M+Na]^+$	MW+22.9892
$[M+K]^+$	MW+38.9632
$[M+NH_4]^+$	MW+18.03382

3
Materials and Methods

The materials and methods used in this project will be presented in the following sections.

3.1 Materials

The polymeric materials that were subjected to characterisation and depolymerisation are presented in Table 3.1. Images of these materials are shown in Appendix 1. PET staple fibre was only used for one set of glycolysis testing and was not further characterised. If nothing else is specified PET refers to the PET pellets.

Table 3.1: Polymeric materials subjected to characterisation and depolymerisation. Specifying notation throughout this report, material name, form, color and, when possible, manufacturer.

Notation	Material name	Form	Colour	Manufacturer
PET	PET	pellet	white	Invista
PET fibre	PET staple fibre	staple fibre	white	-
PBT	PBT (Ultradur® B 4500)	pellet	white	BASF
Bicomponent fibre	Bicomponent staple fibre	core/sheath staple fibre	white	-
Backing	Polyester primary backing	nonwoven	black	-
Glue	Co-polyester glue	pellet	white	-
Film	Co-polyester film	film	transparent	-
Yarn	PET yarn	yarn	black	-
Transition fibre	Transition polyester fibre	staple fibre	black	-
Felt	Flooring felt layer	substrate layer	black	Autoneum
Surface	Flooring surface layer	surface layer	black	Autoneum
Flooring	Full flooring solution	carpet	black/grey	Autoneum

The felt layer in the flooring solution consists of transition polyester fibre and bicomponent staple fibre. The surface flooring layer is what is seen in the finished vehicle and it contains transition fibre, bicomponent fibre, polyester primary backing and co-polyester glue. The composition of the full vehicle flooring solution is illustrated and the flooring is shown in Figure 3.1. It is made up of the surface layer, the backing, the substrate layer, which is the felt layer, and an additional layer of transition polyester fibre and bicomponent staple fibre as a decoupler layer. All layers have been adhered together with co-polyester glue.

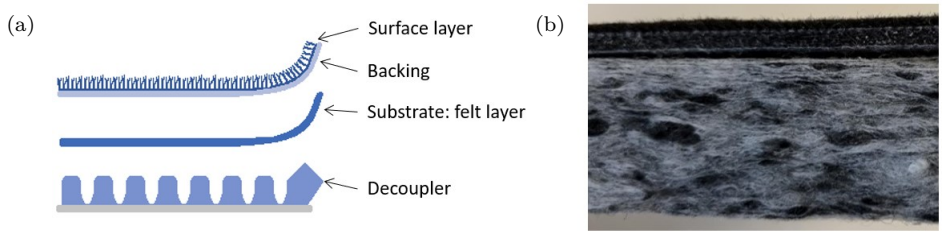

Figure 3.1: Vehicle flooring solutions shown as (a) an illustration showing the different layers and (b) an image.

EG of technical grade with a purity of ⩾98 % from VWR was used for all glycolysis reactions. MgO-$Al(OH)_3$-catalyst with an average active surface area of 0.14 m^2/g, synthesised in-house, was used.

3.2 Depolymerisation of Materials

The standard conditions and procedure was as follows and these were used unless otherwise specified. Duplicate reactions were done for all materials. Solutions were prepared by the addition of 10 g of material into a 250 mL metal reactor, followed by 0.11 wt% of MgO-$Al(OH)_3$-catalyst, corresponding to an active surface area of approximately 0.14 m^2 catalyst/g PET. For all materials that were not in pellet or fibre form, pieces of around 1x1 cm were cut to enable them to fit into the reactor and to increase the surface area. 50 mL EG was then added giving a ratio between PET:EG of 1:5 (g:mL), corresponding to a molar ratio of approximately 1:17.2. Three ceramic balls were added into the reactor to facilitate mixing. Two reactors were placed in a rotating rig in an oven at 230 °C for 70 min. The reactors were not preheated and the reaction mixture was therefore not at the given temperature for the entire reaction time. The full process, from glycolysis of polyester polymer to workup to purified BHET, is illustrated in Figure 3.2.

After 70 min the reactors were quenched in cold water. The content of the reactor was emptied and rinsed with 75 mL of boiling water. The mixture, at a temperature of 95-100 °C, was vacuum filtered and the filter cake was rinsed with boiling water. The filtrate was then filtered again, at a temperature of 70-75 °C. The filtrate was then set in a refrigerator at 5 °C to recrystallise for at least 16 h. The recrystallised mixture was filtered and the filter cake was redissolved in boiling water and set to

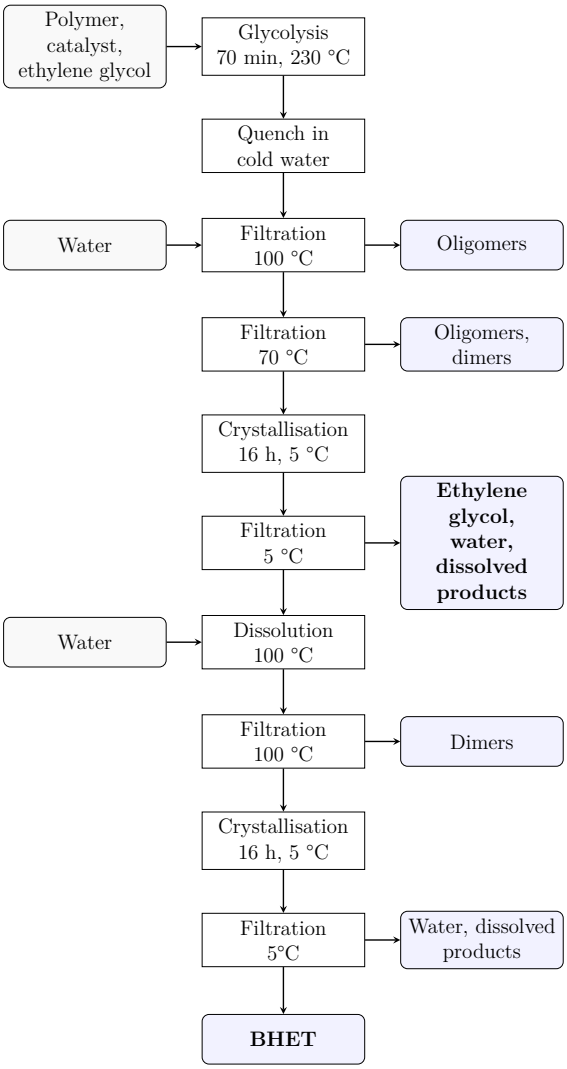

Figure 3.2: Flowchart illustrating the glycolysis and workup process from polyester polymer to BHET. Marked in bold are the streams that were further analysed, both the filtrate after the first crystallisation, and the BHET product.

recrystallise again. A final filtration was preformed after a minimum of 16 h at 5 °C and the dried crystals were considered the product of the process, from which the yield was calculated. Molar yield of BHET (254.24 g/mol) was calculated for each reaction based on the molar mass of the monomeric unit mass of PET (192.17 g/mol), or PBT (220.23 g/mol). The monomeric unit mass of PBT was used for materials that characterisation showed mainly consisted of PBT and the monomeric mass of PET was used in all other cases. The calculation for yield is shown in Equation 3.1, where Y is yield, m is mass, M is molar mass and n is the amount of substance.

$$Y_{BHET} = \frac{m_{BHET}/M_{BHET}}{m_{polymer}/M_{monomeric\ unit}} = \frac{n_{monomeric\ unit}}{n_{polymer}} \tag{3.1}$$

Mass conversion was calculated based on the solid material collected from the filtrations at 100 and 70 °C following the reaction, as shown in Equation 3.2, where

X is conversion.

$$X_{polymer} = 1 - \frac{(m_{filtercake1} + m_{filtercake2})}{m_{polymer}} \tag{3.2}$$

3.2.1 Catalyst and EG Dependence for Glycolysis of PET

Glycolysis reactions with varying amounts of catalyst and EG, respectively were performed according to the method previously described apart from the one varied parameter. For the catalyst experiments PET pellets were used and the amount of catalyst was varied to 0.07, 0.10, 0.14 and 0.28 m^2 catalyst/g PET. For the experiments where the amount of EG was varied, PET staple fibre was used and the EG volumes used were 50 and 100 mL, giving ratios between PET:EG of 1:5 and 1:10 (g:mL), respectively.

3.2.2 Glycolysis of PET and PBT

PET pellets, PBT pellets and mixtures of both were used in glycolysis reactions. The ratios and amounts used for these reactions are presented in Table 3.2.

Table 3.2: Molar ratio and amounts of PET and PBT used in glycolysis reactions in terms of moles of monomeric unit (mmol) and weight (g).

Molar ratio PET:PBT	PET (mmol)	PBT (mmol)	PET (g)	PBT (g)
100:0	52.2	0	10.0	0
75:25	37.7	12.5	7.24	2.76
50:50	24.3	24.3	4.68	5.34
75:25	11.8	35.2	2.26	7.75
0:100	0	45.4	0	10.0

3.2.3 Glycolysis of Polyester Based Components and Vehicle Flooring Solution

For all of the component materials and the vehicle flooring solution, except the film and glue, the glycolysis was carried out using the amounts previously specified, and without being mixed with other materials. The film was depolymerised at half the amounts as the others with the same ratio due to constrictions in material availability. For the glue component PET and glue mass ratios were varied to 100:0, 90:10, 50:50 and 0:100 of PET:glue.

3.3 Thermal and Chemical Analyses

This section presents the thermal and chemical analyses used to characterise the materials used for depolymerisation, as well as the products from the depolymerisation reactions.

3.3.1 FTIR of Materials and Products

FTIR spectroscopy was used to characterise the materials that were then depolymerised and, the BHET products from the depolymerisation. For these analyses a Bruker Tensor 27 was used and the absorbance was measured using attenuated total reflectance (ATR) with a diamond crystal.

3.3.2 DSC Analysis of Materials and Products

DSC analysis was carried out by the use of a DSC 1 STAR^e System from Mettler Toledo. A heating and cooling rate of 10 K/min and an inert nitrogen atmosphere with a flow of 50 mL/min was used. For the analyses of the polyester materials the first and second heating were done from -20 to 300 °C, with a cooling in between. Samples of 3-4 mg were used. These analyses aimed to identify the polymer(s) present in the materials. Furthermore, the solid products from the depolymerisation reactions were analysed with DSC. For analysis of the final monomer product the first heating was done from 25 to 150 °C, cooling to 25 °C and second heating to 300 °C. The lower top temperature of the first heating was used to avoid temperatures where the material could start to polymerise. The higher temperature of the second heating was used to determine if any long chained species remained in the product.

3.3.3 TGA of Materials

TGA was done on the polyester materials to identify the degradation temperatures and if several components were present in the materials. This was done using a STARe System TGA/DSC 1 from Mettler Toledo. Sample weights of around 10 mg were used. The samples were heated in nitrogen from 30 to 650 °C at 5 K/min, then the atmosphere was changed to air and 650 °C was held for 15 min, followed by a heating to 850 °C and lastly another isothermal step for 15 min.

3.3.4 HPLC-MS and UV Analyses of Filtrates and Products

The crystalline product was analysed with HPLC-MS and HPLC-UV. Filtrates were analysed with only HPLC-MS. HPLC-MS was used for qualitative analysis, whilst HPLC-UV was used for quantitative analysis. In each case one of the duplicates of each reaction was analysed. The HPLC analyses were done with a HPLC-ESI-MS 1200 series/6420 Triple Quad LC/MST from Agilent Technologies. Reverse phase columns of the type Kinetex C18 (150*4.6 mm u.d., 2.6 µm particle size) were used. The conditions used were injection volumes of 5 µL for UV and 5 µL for MS, column temperature of 25 °C and flow rate of 0.6 mL/min. Two mobile phases were used: solution A (10 mM ammonium acetate containing 0.1 % formic acid) and solution B (acetonitrile (ACN)). The same linear gradient method was used for all chromatography analyses and it was programmed according to Table 3.3. UV detection was done at the wavelength 254 nm. The ESI-interface parameters used were drying gas flow of 11 mL/min at 150 °C, nebuliser gas pressure of 35 psi and capillary voltage of 4 kV. The MS was done in positive mode, scanning interval of

100-550 m/z, the fragmentor voltage was 50 V and the ion source temperature was 100 °C. Method based on the work of Lindqvist et al. (2021) [20].

Table 3.3: Gradient program for the mobile phases A (10 mM ammonium acetate containing 0.1 % formic acid) and B (ACN) for HPLC analyses.

Time (min)	A (%)	B (%)
6	80	20
13	40	60
20	40	60
22	10	90
24	10	90
26	80	20
35	80	20

3.3.4.1 Purity of BHET

The purity of BHET in the crystallised product was calculated based on the area percentage of the peaks obtained from the HPLC-UV analyses. The purity was calculated according to Equation 3.3, where I is intensity at each retention time.

$$purity_{BHET} = \frac{\int I_{BHET}\, dt}{\sum \int I_{substance}\, dt} \tag{3.3}$$

3.3.5 Semi-Quantitative HPLC-UV Analysis

The quantity of BHET in four reaction mixtures were measured by use of an external standard and HPLC-UV measurements. The analysis was done for PET, PBT, bicomponent fibre and flooring. Samples were prepared through glycolysis reactions of conditions previously described, but after quenching the reactors were placed in an oven at 105 °C for at least 30 min, to ensure the content was liquid. The content was then emptied into a beaker and heated to above 100 °C to make the solution homogeneous, after which 100 µL was collected and diluted in 5 mL ACN. 150 µL of each solution was then diluted with 4850 µL ACN and 5000 µL H_2O yielding a total volume of 10 mL. A standard curve was created through double injection of samples prepared as shown in Table 3.4 using BHET from glycolysis of PET.

Table 3.4: Preparation of external standard were sto,1 is a stock solution of 50:50 ACN:H_2O and sto,2 is the solution creating from the first disolutution step.

BHET [mg]	$V_{sto,1}$ [mL]	C_1 [mg/mL]	$V_{sto,2}$ [mL]	$V_{tot,2}$ [mL]	C_2 [mg/mL]
100	100	1	200	10	0.02
100	100	1	400	10	0.04
200	100	2	300	10	0.06
200	100	2	400	10	0.08

4

Results and Discussion

4.1 Material Characterisation

In this section, characterisation of PET and PBT reference materials, as well as the different polyester based components for vehicle flooring solutions, are presented. The results from the FTIR, DSC and TGA analyses are presented here along with a short discussion of what that indicates for the composition of the materials. This is done since the precise content of the composition materials are unspecified, as is often the case with materials from producers.

4.1.1 FTIR Analyses of Materials

FTIR spectra of the material surfaces are shown in Figure 4.1. All materials show great similarities in the yielded FTIR spectra. Furthermore, the great similarities to PET and PBT shows that all materials are terephthalate containing polyesters. However, some differences can be observed between the materials, often correlated to differences seen between PET and PBT. PET shows an absorbance peak at 1339 cm^{-1}, as does yarn, transition fibre, backing and bicomponent fibre. This corresponds to the O-C-H bending of the trans conformation which is typical of PET [21]. However, no peak can be seen at that wavelength for PBT, glue or film. The opposite is true for the absorption peak around 1389 cm^{-1} which only appears for PBT, glue and film, but not the other materials. This peak corresponds to the CH_2 wagging of PBT [22].

The FTIR spectra show that the yarn, transition fibre and backing consist of mainly PET. The bicomponent fibre yields a spectrum similar to PET but with some slight differences, the main of which is a shift from 972 cm^{-1} for PET to 980 cm^{-1} and an increase in relative absorbance of that peak for bicomponent fibre. The film appears to consist of PBT, whilst the glue is similar to PBT with some deviations, such as a peak at 1234 cm^{-1}, instead of 1249 cm^{-1}.

4.1.2 Thermal Analyses of Materials

Thermal analyses with DSC and TGA was done to further characterise the materials. The second heating of the DSC analyses are shown in Figure 4.2. The first heating removes the thermal history of the material and the second is only dependent of the material composition. PET displayed an endothermic peak at 257 °C and yarn, transition fibre and backing showed endothermic peaks between 243-248 °C.

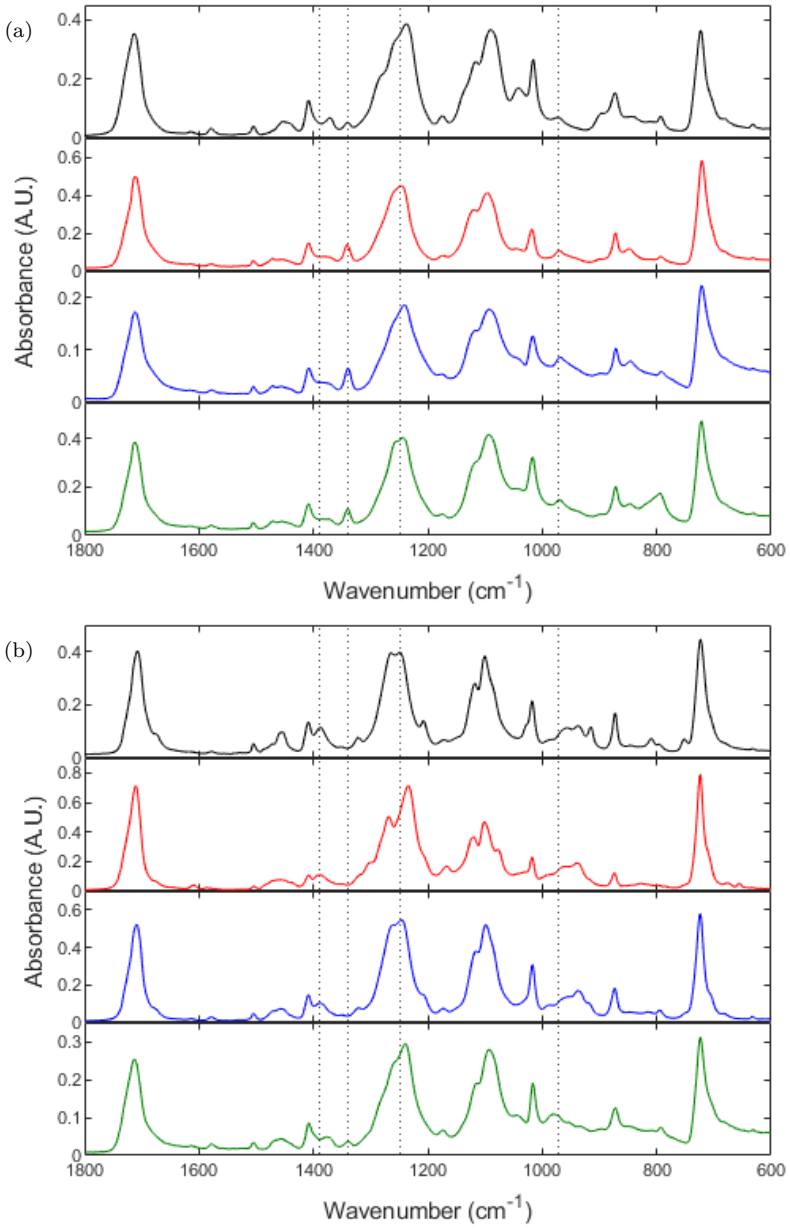

Figure 4.1: FTIR spectra in the wavelength interval 600-1800 cm^{-1} of (a) PET (black), yarn (red), transition fibre (blue), backing (green) and (b) PBT (black), glue (red), film (blue), bicomponent fibre (green). Dashed lines mark wavelengths 1389, 1339, 1249 and 972 cm^{-1}, respectively.

Both PBT and the film had endothermic peaks at 223 °C, whilst the film also displayed an additional endothermic peak at 213 °C. The bicomponent fibre had two separate endothermic peaks at 76 and 237 °C, which likely corresponds to the different components in the core and the sheet, where one of the components could contain comonomers to alter the melting behavior. Moreover, the melting of the glue is over wider temperature intervals with endothermic peaks centered around 19 and 127 °C.

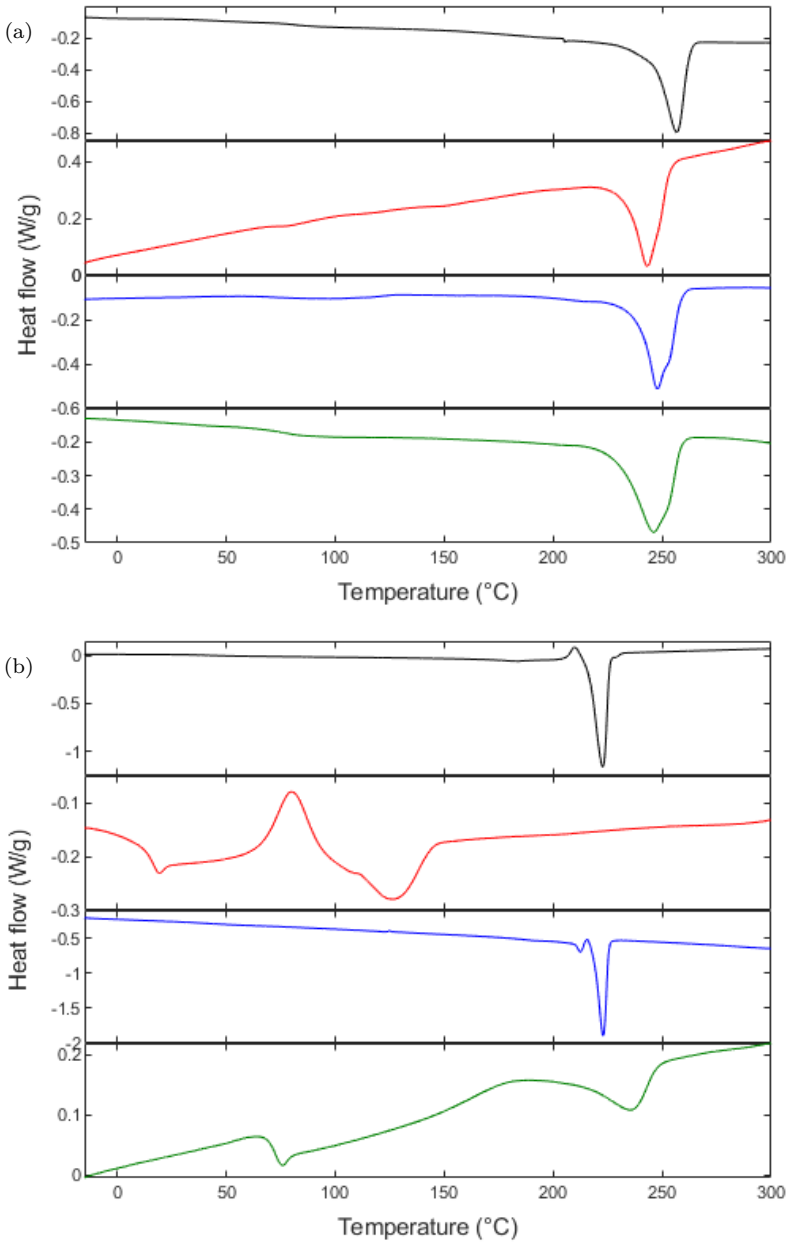

Figure 4.2: DSC thermograms of the second heating between -20 to 220 °C showing from top to bottom that of (a) PET (black), yarn (red), transition fibre (blue), backing (green) and (b) PBT (black), glue (red), film (blue), bicomponent fibre (green). Exothermic up and endothermic down.

The degradation profiles of the materials are shown in Figure 4.3, and those of

PET, transition fibre and yarn were all similar with midpoint temperatures of 434-437 °C. PBT, glue and film also show similar degradation behaviors and the midpoint temperatures are lower compared to PET, in these cases 401-402 °C. The degradation of backing and bicomponent fibre occurs at temperatures between that of PBT and PET, with midpoint temperatures of 433 and 429 °C, respectively.

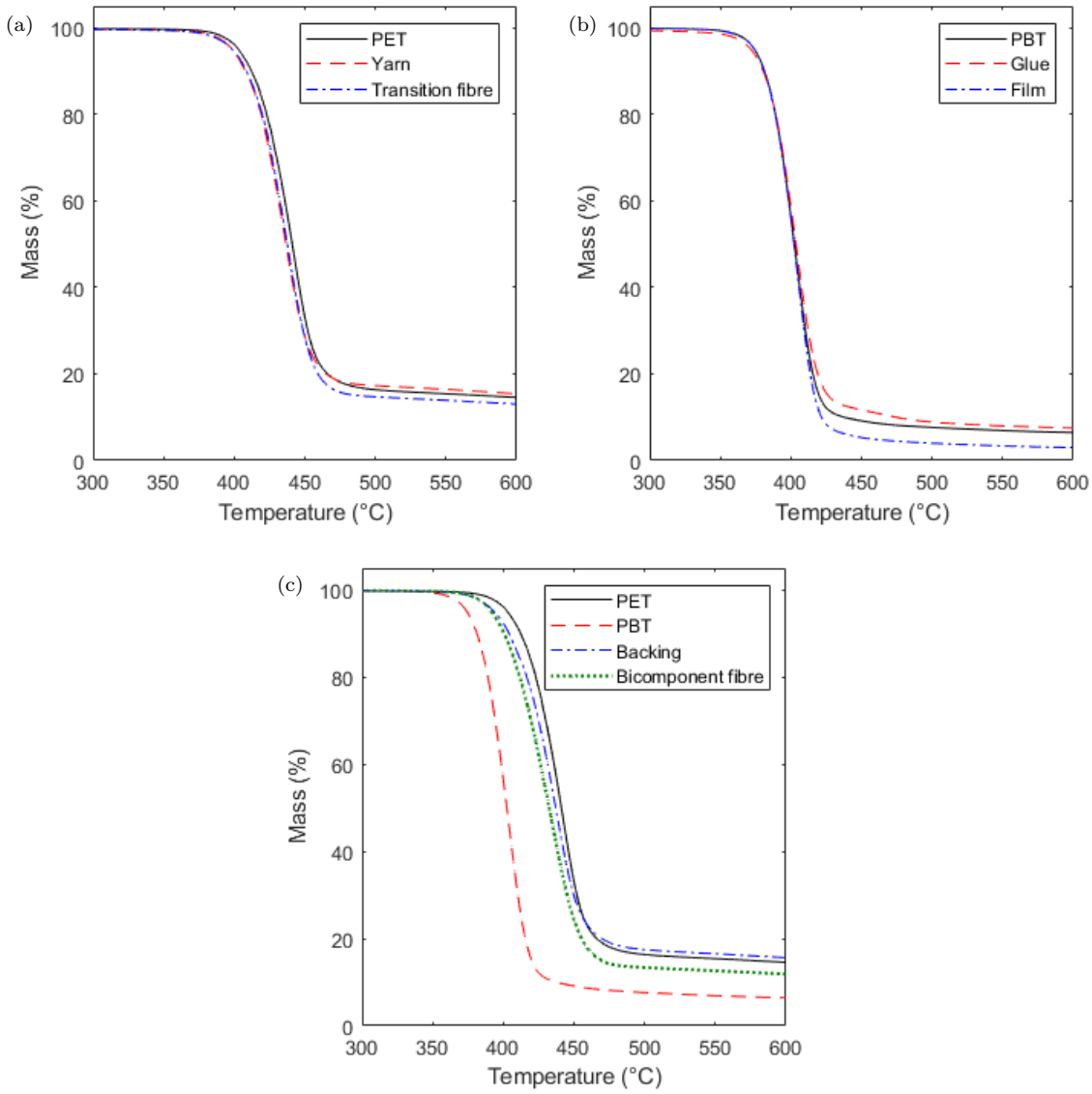

Figure 4.3: TGA thermogram over the temperature interval 300-600 °C in nitrogen atmosphere of of (a) PET (black), yarn (red), transition fibre (blue), (b) PBT (black), glue (red), film (blue), (c) PET (black), PBT (red), backing (blue), bicomponent fibre (green).

The thermal analyses coincide well with the results from the FTIR analysis and combined they give a more substantiated view of the material composition. The yarn and transition fibre consist of PET and the film of PBT. The glue contains PBT but has been modified in a way that alters melting behavior. The main component of the bicomponent fibre is PET and some other comonomer is present that is effecting

melting behavior, for example by disturbing the regularity of the polymer chain. The primary backing mainly consists of PET with some alteration that causes the degradation to begin at a somewhat lower temperature compared to neat PET.

4.2 Depolymerisation Reactions

Molar yields and mass conversion from each glycolysis reaction are presented in this section. The molar yields from the glycolysis reactions are based on how much BHET was retrieved through the separation steps and crystallisation. This shows how much product is obtained. The mass conversion is a measure of how much of the polymeric material remains as insoluble products after the depolymerisation. These two quantities will be presented together to illustrate both the efficiency of depolymerisation and to what degree the desired product, BHET monomer, has been formed.

Additionally, the characterisation of the reaction products are presented, including both the purity of the yielded products and identification of byproducts. Lastly, the semi-quantitative HPLC-analysis of reaction solutions is showed and compared to the findings of crystallised yield.

4.2.1 Reaction Parameters for Glycolysis of PET

Two parameters of the glycolysis reaction were varied independently and the resulting molar yields and mass conversion are shown in Figure 4.4. The change in the ratio of EG:PET, between 1:5 and 1:10 (g:mL), did not change the yield of the reaction product, as it was around 78 % for both ratios. Mass conversion appeared to increase for the higher EG ratio, from 92 to 96 %. Hence, larger parts of PET are converted to soluble species when a higher EG:PET ratio is used. However, since no more BHET was yielded from the process when using more EG it does not appear to warrant the use of more solvent, which in turn would increase the energy needed for the process.

Variation of catalyst amount, and thereby active area per mass of PET of 0.07, 0.10, 0.14 and 0.28 m^2/g, did not show any clear trends. Both yield and conversion appeared unaffected by variation of catalyst for the investigated interval. However, the standard deviation was larger for the samples where less catalyst was used.

The same mass ratio between polyester material and catalyst (0.14 m^2 cat/g polyester) and EG (1 g polyester:5 mL EG), respectively, was used for the glycolysis of all materials. Therefore, it is of interest that the variation in catalyst and EG:PET ratio did not have any significant effect on the yield. The higher molecular weight of the repeating unit of PBT ($(CH_2)_4$) compared to PET ($(CH_2)_2$), means that the molar ratio of EG:PBT will be larger compared to PET at the same mass loading. Therefore, more EG per mol polyester is available for depolymerisation in the PBT reaction. Furthermore, in a recycling process of mixed polyester materials

the precise amount of each polyester type would likely not be known, as in the case of the component materials and the vehicle flooring solution used in this project. In that sense the stability under the varied conditions of 1:5 and 1:10 (g:mL), could be positive and makes it less likely that the consistent amount of EG effects different mixes of PET and other polyesters differently.

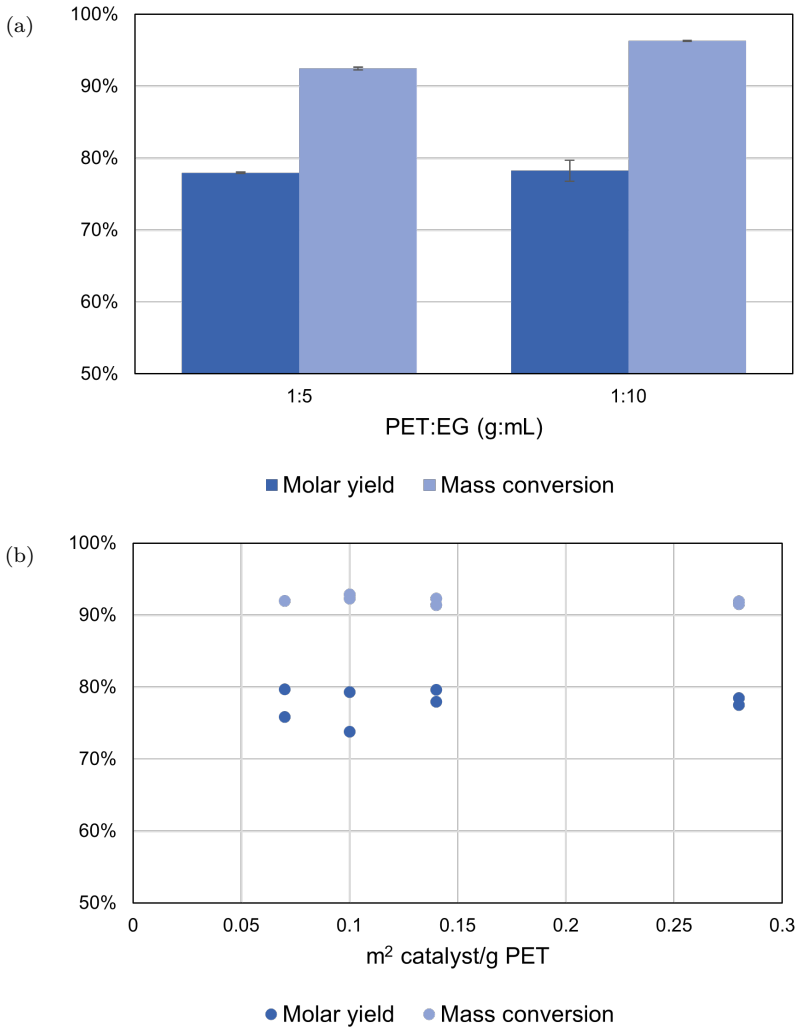

Figure 4.4: Molar yield and mass conversion for (a) comparing 1:5 and 1:10 (g:mL) ratios between PET and EG, and (b) as a function of catalyst area (m^2) per amount of PET (g).

4.2.2 Yields from Glycolysis of PET and PBT

Glycolysis reactions were done to depolymerise both neat PET and neat PBT, both on their own, as well as mixes of the two materials. The molar yield of BHET and mass conversion of varying the molar ratio between PET and PBT are shown in Figure 4.5. A clear linear trend can be seen in the yield depending on the ratio, with neat PBT only yielding around 38 mol% whilst PET yields around 79 mol%. It is clear that PBT, both pure and together with PET, decreases the amount of crystallised product that is recovered from the reaction. This could be due to less

product being generated, effects on the purification process or a combination of both.

Moreover, no ratio dependence can be seen for the mass conversion, so the depolymerisation of PBT is also to be taking place. Glycolysis of PET only requires the transesterification to take place where the depolymerisation is occurring to result in BHET, since the monomeric unit already has the same side group ($(CH_2)_2$) as that formed in the glycolysis with EG. That is not the case for PBT for which a transesterification must occur at both carboxylic groups, not just the one enough for depolymerisation, in order for BHET to form. This could be one reason that the used reaction conditions are not as efficient for the BHET formation from PBT as from PET.

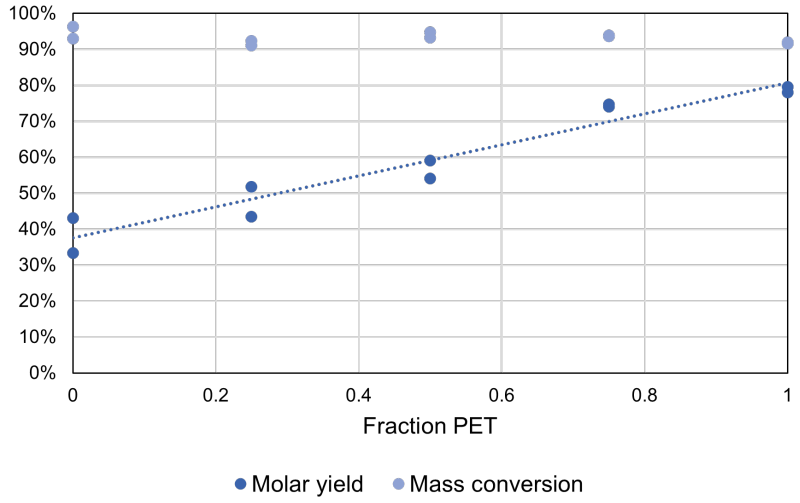

Figure 4.5: Molar yield and mass conversion varying molar ratios of PET:PBT from 0:100 to 100:0. Linear equation: Yield=0.432*(n_{PET}/(n_{PET}+n_{PBT}))+0.376, R^2-value: 0.936.

4.2.3 Yields from Glycolysis of Vehicle Flooring Solution

The molar yield and mass conversion of the polyester based components yarn, transition fibre, bicomponent fibre, backing and film, as well as the neat PET, are shown in Figure 4.6 (a). The neat PET is shown as a reference for what is possible to achieve from the process with the equipment at hand. The molar yield and mass conversion of glue, and neat PET when mixed with glue, are shown in Figure 4.6 (b).

Several of the components give approximately as high yields as PET (79 mol%), namely yarn and transition fibre with 76 and 78 mol% respectively. These are also the components that the material analysis showed were PET. The backing, which appeared to be PET but the onset of degradation occurred at a slightly lower temperature, gives a lower yield of 69 mol%. The same is true for bicomponent fibre, which the material analysis showed contains PET and additional unknown modifications, where the yield was 65 mol%.

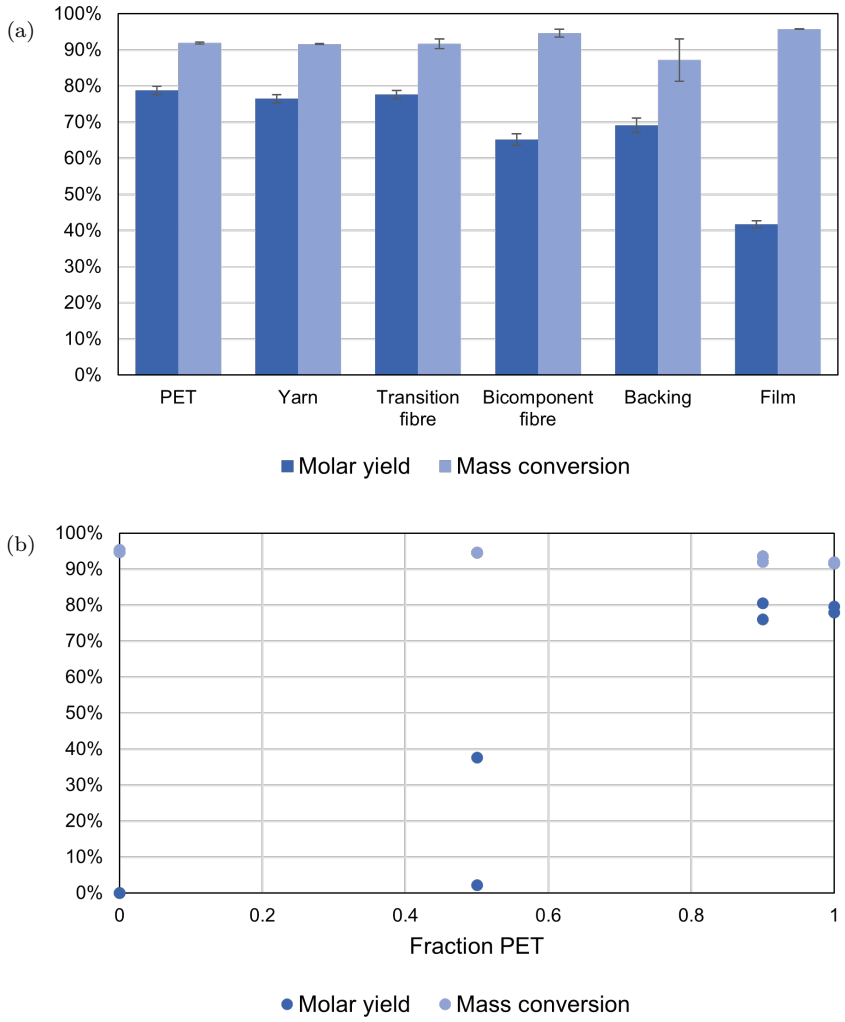

Figure 4.6: Molar yield and mass conversion for (a) polyester based components for interior vehicle solutions with PET as a reference for what is possible to achieve in the process with the specified workup, and (b) the glue in varying mass ratios with PET from 0:100 to 100:0 PET:glue for which molar yield, apart from the glycolysis of 100 % glue, is based on the amount of PET, excluding glue.

The film gives a significantly lower yield than the other components at 42 mol%, based on the monomeric weight of PBT as the material analysis showed that the film consists of PBT. The molar yield is also comparable to that of PBT (38 mol%). The mass conversion does not follow the trends of the BHET yield and shows only small differences. This means that the PBT has been depolymerised into soluble species that did not crystallise as BHET.

The polyester based glue component, that based on material analyses contains PBT, did not yield any crystallised BHET. Since no BHET was recovered from glycolysis of glue, mixes of glue and neat PET were used to investigate if the glue would interfere with the glycolysis of PET. The yield shown in Figure 4.6 (b) are based only on the amount of neat PET, not glue. Mixing PET with glue in small amounts (10 weight%) did not affect the BHET yield at 78 mol%. However, 50

weight% glue greatly decreases the BHET yield from PET to an average under 40 mol%, and causes very large variation between the sample duplicates. Therefore, it appears that a lower fraction of the glue, such as 10 weight% in a composition would not interfere with the depolymerisation and recovery of BHET, but a larger fraction, such as 50 weight%, could.

These results shows that even if a material is a polyester and contains PBT, which can be depolymerised into BHET, the glycolysis process does not necessarily yield BHET. Either because the glycolysis reaction, the separation steps, or a combination of both, are affected by other chemical or polymeric components that are present in the material or formed during reaction. The mass conversion of glue, and 10 and 50 % glue with PET (based on total mass of material), is similar to that of the other materials, at 92-95 weight%, which shows that a depolymerisation occurs for the glue as well, even though no BHET could be recovered.

The yield from the felt and surface vehicle flooring layers (see Figure 3.1), made up of the polyester components, as well as the full vehicle flooring solution are shown in Figure 4.7. The yield from the felt and surface layers differ and was 66 and 49 mol%, respectively. One explanation could be that the surface layer contains glue and the felt layer does not, but also general differences in composition. The full vehicle flooring solution gave a crystallised yield of 60 mol%, showing that it is possible to recover BHET from the product as a whole. For the felt and surface layers and the full vehicle flooring solution the mass conversion of 92-94 weight% is comparable to that of PET. However, for the surface layer some solid pieces remained. The same was not observed for the flooring where the surface layer is only a fraction of the whole.

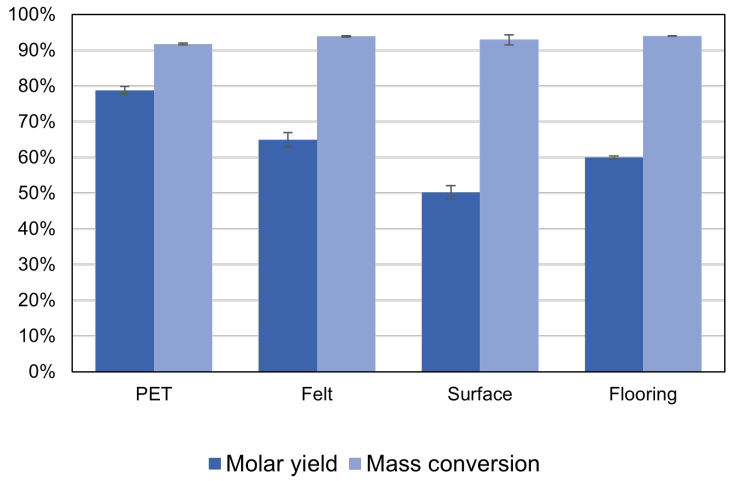

Figure 4.7: Molar yield and mass conversion for vehicle flooring solution layers and full vehicle flooring solution, made up of the polyester based components. PET is also included as a reference for what is possible to achieve in the process with the specified workup.

4.2.4 Analyses of Filtrates and Products

The analyses of filtrates and product are presented in this section. These analyses were done to verify the identity of the product as the monomer BHET and the purity of BHET, from the different materials. Moreover, the analyses aimed to identify what byproducts were formed in the glycolysis reactions and whether they were separated from the BHET monomer in the purification process. Firstly, a summary of molecules identified in the HPLC analyses is shown. Next, the analysis of the crystallised BHET product by HPLC, and subsequently by DSC, are presented. Followed by a discussion regarding the colouration of crystallised BHET. Lastly, HPLC analysis of the filtrates are presented.

Table 4.1: Compounds detected in HPLC with molecular weights, MW (Da), identified based on molecular ions detected in HPLC-MS and retention times, t_R (min). (-) indicates that the ion was not detected.

	Chemical name	t_R (min)	MW (Da)	Molecular ion (m/z)			
				$[M+H]^+$	$[M+NH_4]^+$	$[M+Na]^+$	$[M+K]^+$
MHET	4-((2-hydroxyethoxy) carbonyl)benzoic acid	5.7	210	211	-	233	249
BHET	Bis(2-hydroxyethyl) terephthalate	7.2	254	255	272	277	293
DEG ester	2-(2-hydroxyethoxy) ethyl(2-hydroxyethyl) terephthalate	8.7	298	299	316	321	337
MHBT	4-((4-hydroxybutoxy) carbonyl)benzoic acid	11.8	238	239	277	261	-
HBHET	4-hydroxybutyl (2-hydroxyethyl) terephthalate	12.4	282	283	300	305	321
HBHEET	4-hydroxybutyl (2-(2-hydroxyethoxy) ethyl) terephthalate	12.7	326	327	344	349	365
BHBT	Bis(4-hydroxybutyl) terephtalate	14.0	310	311	328	-	349
BHET dimer	*O,O*'-(ethane-1,2-diyl) bis(2-hydroxyethyl) diterephthalate	15.2	446	447	464	469	485
BHBT dimer	*O,O*'-(butane-1,4-diyl) bis(2-hydroxybutyl) diterephthalate	16.3	474	475	492	497	513

The identified compounds in products and filtrates based on the HPLC-MS are presented in Table 4.1 and the molecular structures are shown in Appendix 2. The identification was done based on the glycolysis reactions with the reference

materials PET and PBT. The compounds identified from the depolymerisation of PET (MHET, BHET, DEG ester and BHET dimer) correspond well with that found in the literature [20]. The degradation products identified from the depolymerisation of PBT were identified from HPLC-MS analysis. Additional compounds detected in the HPLC analysis have not been identified, and the presence of these will be indicated as unidentified in the following sections.

4.2.4.1 Purity of BHET

The purity of BHET and presence of other substances, obtained from the HPLC-UV at the wavelength 254 nm, are presented in Table 4.2. HPLC-UV spectra of BHET from PET, PBT and the full vehicle flooring solution are shown in Figure 4.8. The analysis shows that the main product of the glycolysis of all the materials is BHET. In several cases the purity is close to that of BHET obtained from PET at 98.5 %. The lowest purities are seen for BHET from PBT and PET:glue mix, but all are above 94 %.

Table 4.2: The area percentage of different substances in the final product based on HPLC-UV, measured at the wavelength 254 nm. (-) indicates that the substance was not detected.

Material	MHET (%)	BHET (%)	DEG ester (%)	HBHET (%)	BHET dimer (%)	BHBT dimer (%)	Unident. (%)
PET	0.2	98.5	0.2	-	1.2	-	-
PBT	0.3	94.5	-	3.1	1.3	0.4	0.5
Bicomponent fibre	0.1	95.8	-	1.4	1.8	1.0	-
Backing	0.1	97.5	0.1	0.7	1.1	0.1	0.3
Film	0.6	96.0	-	1.6	1.1	0.4	0.3
PET:glue	0.2	94.4	0.1	2.9	1.8	0.4	0.2
Yarn	0.1	98.3	0.2	0.2	1.2	-	-
Transition fibre	0.2	98.3	0.2	0.1	1.2	-	-
Felt layer	0.1	95.0	0.2	1.4	2.4	0.7	0.2
Surface layer	0.2	97.0	0.1	0.4	2.2	0.1	-
Flooring	0.3	97.3	0.6	0.1	1.3	0.4	0.1

The purity of BHET from the full vehicle flooring solution is 97.3 %, which is comparable to the purity of BHET from neat PET. It is also comparable to that obtained from earlier projects at RISE where BHET was obtained from PET packages, textiles from production waste and industrial polyester waste [20, 23]. The BHET from glycolysis of production and industrial waste of similar purity could be repolymerised into PET, which was possible to melt-spin into PET multifilaments. This indicates that the purity of BHET from the full vehicle flooring solution is to be considered high and that the purity would not be a limitation for the use of BHET from the chemical recycling of the full vehicle flooring solution.

The analysed BHET was of high purity of 94.4-98.5 %, but a few contaminants were detected, related to degradation of PET and PBT. Low amounts of MHET and DEG ester are present at 0.1-0.6 and 0-0.6 %, respectively. BHET dimer is overall the most prominent contaminant at 1.1-2.4 % and it therefore appears that the last 100 °C filtration step, which aimed to remove dimers, was not entirely successful. However, the purity is still relatively high and depending on the end-use of the BHET ,such as chemical feedstock or spinning to fibre, a low amount of BHET dimer might be tolerable.

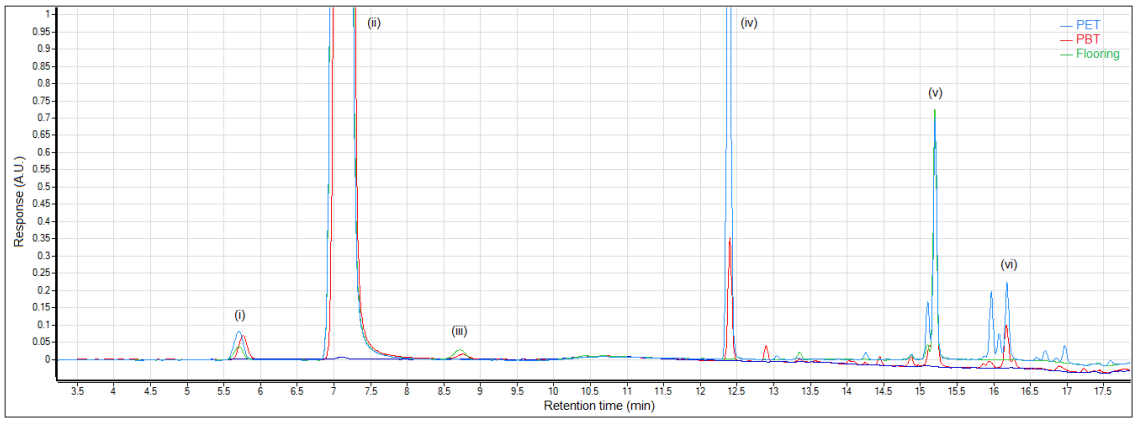

Figure 4.8: Spectra from HPLC-UV at 254 nm of BHET from PET (blue), PBT (red) and the flooring (green). Peaks identified as (i) MHET, (ii) BHET, (iii) DEG ester, (iv) HBHET, (v) BHET dimer and (vi) BHBT dimer.

In the PBT containing materials HBHET is also prominently present in the product. HBHET is detected in the product from all materials except for PET at varying amounts of 0.1-3.1 %. HBHET could introduce butyl chain segments into a new polymer chain. BHBT dimer, present in the product of all the materials, except PET, yarn and transition fibre, at 0.1-1.0 %, could possibly cause similar problems. Therefore, the effect of these contaminants on the polymerisation process need to be investigated. If these contaminants affect the polymer properties additional purification of the product could be required.

Based on the other substances found in the BHET product, it appears that some amount of PBT monomer has been present in all of the component materials, since HBHET can be found in all products except that from neat PET. In the product from yarn and transition fibre the amounts are very low, coinciding with the highest yields of BHET of 76-78 mol%, which were comparable with PET. This shows that low amounts of PBT, which may originate from, for example, the masterbatch used for dying, do not decrease BHET yield. However, in the product from bicomponent fibre and backing, more HBHET and some BHBT dimer were present. Furthermore, the glycolysis of these components resulted in lower yields (65-69 mol%). One possible reason could be that PBT monomers are present in the materials, likely to alter the melting behavior. The experiments with mixtures of PET and PBT (Figure 4.5) showed that the presence of PBT decreases the yield of BHET. However, other comonomers in the polymeric chains could also be present

but were not specifically identified by the methods used where only PET and PBT were used as references.

4.2.4.2 DSC analysis of BHET

The results from the second heating of the DSC analysis of the crystallised product from glycolysis of PET, PBT, bicomponent fibre and the full vehicle flooring solution are shown in Figure 4.9. The crystalline products from the glycolysis reactions were analysed by DSC. The peak melting temperature at approximately 111 °C, seen in the figure, could be observed in the analysis of all BHET samples, except for one of the 50:50 PET:glue duplicates. The results from the depolymerisation experiments with 50:50 PET:glue were not consistent (see Figure 4.6 (b)). The higher yielding reaction resulted in product which was confirmed to be BHET with a melting peak around 111 °C with DSC and by HPLC. However, the product from the low yielding reaction of 50:50 PET:glue did not melt around 111 °C and is therefore of other origin.

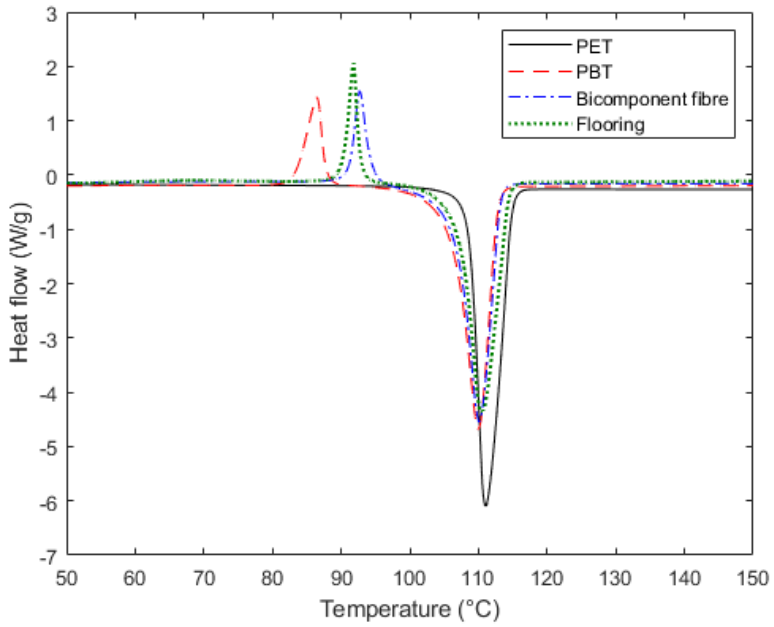

Figure 4.9: DSC thermogram of the second heating of BHET from glycolysis of PET (black), PBT (red), bicomponent fibre (blue) and vehicle flooring solution (green).

Furthermore, the samples from PBT, film, bicomponent fibre, backing, 50:50 PET:glue, as well as the felt layer, surface layer and full vehicle flooring solution all showed an additional exothermic peak at around 86-93 °C before melting, which was only observable in the second heating, not the first. This is consistent with the products where BHBT dimer was observed and it is therefore possible that it might be involved in an exothermic event, such as cold crystallisation. None of the product samples show any other melting peaks such as those from PET, PBT or oligomers of such, indicating that these were successfully separated in the filtration steps.

4.2.4.3 Colouration of BHET

Another property of BHET that is important for its usefulness is the colour. White pr uncoloured BHET is ideal since it can be used for a wide range of applications. Images of BHET from the glycolysis of each material are shown in Appendix 1. For most of the materials the yielded BHET was white, including the black backing and yarn. The product solutions from the glycolysis of backing and yarn were black, but the filtration steps removed the carbon black and uncoloured BHET could be crystallised.

On the other hand, the glycolysis of some materials resulted in coloured BHET, most prominently transition fibre. For this material the black colour was removed in the filtration similarly to the backing and yarn. However, some colour remained and the crystallised BHET varied in colour, either blue or purple. This shows that some colourants can remain and that the presence of such need not be apparent from visual inspection of the material. Furthermore, BHET from glycolysis of both the felt and surface layer had a pink colour. This likely originated from the transition fibre, since that is present in both and the other components did not yield coloured BHET.

The BHET from the glycolysis of the full vehicle flooring was white. However, since some colouration could be seen from the felt and surface layers and the colouration of BHET from transition fibre varied, it is likely that BHET from the flooring could also be coloured. This could need to be considered when manufacturing materials since colours that are not visible in the full vehicle flooring solution could be visible in the BHET monomer. Overall, the resulting colour of BHET showed that the purification process worked very well in removing colour used in the polymeric material. Thereby, BHET could be obtained which could yield products that could easily be coloured to a variety of shades, as is not not always the case for recycled materials.

4.2.4.4 Qualitative Analysis of Filtrate Content

The compounds identified in the filtrates after the first crystallisation are shown in Table 4.3. Additionally, all filtrates contain some compounds that have not been identified in the crystallised BHET product. The filtrates were only analysed with HPLC-MS and the data presented is therefore only qualitative. BHET was detected in all filtrate, showing that not all of it had crystallised and hence BHET is lost in the separation steps. Furthermore, the presence of BHET in the filtrate from the glycolysis of glue shows that even though BHET was recovered from the solution, some BHET was formed in the reaction.

MHET, DEG ester and HBHET, which were also found in the products, are detected in the filtrates. Since the amounts of MHET and DEG ester in the products were low, the purification has worked well for these byproducts. In case of PBT, bicomponent fibre and film, DEG ester was only detected in the filtrates not the products.

MHBT is formed from PBT and film. The same applies for HBHEET which also formed from bicomponent fibre. In the filtrates from these three, glue and surface layer, BHBT was also detected. The purification has worked well also for these byproducts since no MHBT, HBHEET or BHBT was detected in any product. Even so, the formation of byproducts will still lead to a decrease in the yield of desired product.

Table 4.3: Compounds present in filtrates detected by HPLC-MS. (X) indicates the compound was present, (-) indicates that it was not.

Material	MHET	BHET	DEG ester	MHBT	HBHET	HBHEET	BHBT
PET	X	X	X	-	-	-	-
PBT	X	X	X	X	X	X	X
Bicomponent fibre	X	X	X	-	X	X	X
Backing	X	X	X	-	X	-	-
Film	X	X	X	X	X	X	X
Glue	X	X	-	-	X	-	X
PET:glue	X	X	X	-	X	-	X
Yarn	X	X	X	-	X	-	-
Transition fibre	X	X	X	-	X	-	-
Felt layer	X	X	X	-	X	-	-
Surface layer	X	X	X	-	X	-	X
Flooring	X	X	X	-	X	-	-

The presence of BHBT, as well as HBHET, is one explanation for the mass conversion of PBT being as high as for PET whilst the yield is lower. PBT has been depolymerised, and since BHET has formed, the catalyst is successfully replacing the butyl chain-segments with ethyl groups. However, this has not occurred in all cases and molecules with one or two butyl groups also remain. To increase the yield of the depolymerisation reaction some reaction parameters would need to be modified in order to improve the process for PBT specifically, and to push the equilibrium between BHET and byproducts further towards BHET. Since EG is already in great excess and variation of EG and active catalyst area showed no effect on neat PET, it could be of interest to further study the effect of some other reaction conditions such as time and temperature.

In addition to lowering the yield of the reaction itself it is also possible that the byproducts formed from PBT have other effects on the process. The solution which BHET is crystallising from differs in chemical and physical properties for the the different materials due to the formation of diverse byproducts profiles. Additionally, a lower yield from the reaction would mean that the BHET concentration would be lower which might also affect the crystallisation. Because

of these differences it could be possible that the workup to retrieve BHET is more or less successful. To investigate if that was the case, reaction mixtures of four materials were analysed with HPLC-UV.

4.2.5 Semi-quantitative Analysis of Reaction Solutions

The reaction solutions from glycolysis of PET, PBT, bicomponent fibre and the full vehicle flooring solution were analysed with HPLC-UV to investigate if the differences in yield of crystallised BHET after workup, coincided with a lower BHET concentration in the reaction solutions. The quantification was done using an external standard, and the calibration curve from the BHET standard is shown in Figure 4.10.

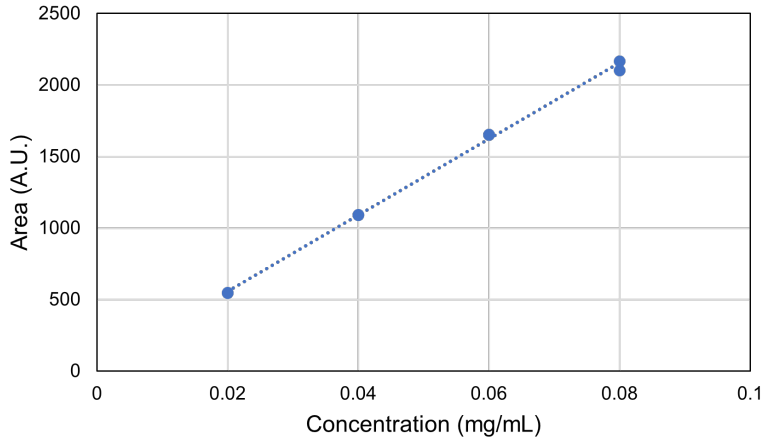

Figure 4.10: Calibration curve for BHET concentration (C) based on area (A) of the peak measured with HPLC-UV at the wavelength 254 nm. Based on double injections. Linear equation: A=26630*C+25, R^2-value: 0.998.

The concentrations of BHET in the reaction solutions were calculated based on the calibration curve from the external standard. Moreover, the molar yield in the reaction solution was calculated and the results are shown in Table 4.4. Since the sampling was done directly out of the reactors, without further workup, the results are consider semi-quantitative.

Table 4.4: Resulting data from semi-quantitative HPLC-UV analysis showing area of the BHET peak, C_{sample} which is the corresponding concentration based on the calibration curve, as well as the total amount that corresponds to in the 50 mL reaction solution and the yield in solution. The crystallised yield is the average value from the full process as previously presented.

Material	Area	C_{sample} (mg/mL)	m_{tot} (g)	n_{tot} (mmol)	Yield (mol%)	Crystallised yield (mol%)
PET	1735	0.064	10.7	42	81	79
PBT	1215	0.045	7.4	29	64	38
Bicomponent fibre	1626	0.060	10.0	39	76	65
Flooring	1426	0.053	8.8	34	66	60

The molar yield of BHET in solution from PET is only slightly higher than what was crystallised after workup, at 81 compared to 79 mol%. For the reaction solutions other than PET the molar yields of BHET in solution are higher compared to what was measured through crystallisation.

When measured in the reaction solution, the molar yield of BHET from PBT of 64 mol%, was 79 % of what was yielded from PET. Contrasting to BHET yield from crystallisation, which for PBT at 38 mol%, was 48 % of that from PET. This shows that the glycolysis of PBT produces substances that affect the crystallisation of BHET. For example, 1,4-butanediol will be generated when BHET is produced from PBT, in comparison to EG being generated when BHET is produced from PET. The HPLC also showed a number of additional byproducts being formed from PBT compared to PET, which could possibly interfere with the BHET recovery.

The analysis of the reaction solution of bicomponent fibre showed that the yield of the reaction was higher, at 76 mol%, than the 65 mol% retrieved through the workup. Bicomponent fibre thereby yielded almost as much BHET as PET which was 81 mol%. It therefore appears to be something interfering with the crystallisation, similar to the PBT glycolysis but not as pronounced.

The full vehicle flooring solution showed less of a difference, at 66 mol% in solution compared to 60 mol% crystallised yield, indicating that the reason for the lower yield from it compared to PET could more likely be improved through altering the parameters of the glycolysis reaction. However, the full vehicle flooring solution was also the least homogeneous reaction solution as it contained carbon black particles, amongst other things, which were not dissolved. Therefore, it is possible that this effected the sampling of this solution.

Since the BHET yield in solution was significantly higher than the crystallised BHET yield for PBT, bicomponent fibre and the flooring, the separation steps are an important consideration for optimising the process. It could therefore be of interest to investigate the crystallisation further to optimise the ratio of EG and water for crystallisation, and to see if evaporation of some of the water added during workup could increase the amount of crystallised BHET. Here a balance between high enough BHET concentration, but still enough of the anti-solvent water would need to be found. The effect of time and temperature for crystallisation could also be of interest to investigate. Additionally, specifically investigating the effect of some of the byproducts, such as HBHET, BHBT and 1,4-butanediol, on the crystallisation behavior of BHET, could be of interest. On the other hand the yield from BHET is still lower in the solution as well, and the reaction specifications could also need to be adapted.

5

Conclusion

This project has investigated the recyclability of an all-polyester based vehicle flooring solution, by glycolysis, to the PET monomer BHET. The polyester components of the vehicle flooring solution were found to consist of mainly PET or PBT, and the glycolysis of neat PET and neat PBT have also investigated.

The glycolysis of neat PBT resulted in BHET as product, but of lower molar yield (38 mol%) than from neat PET obtained through the same process (79 mol%). HPLC analysis of the reaction mixtures showed both that the yield from the glycolysis reaction was lower, and more BHET was lost in the separation steps when PBT was used as the starting material, compared to PET. BHET yielded from PBT had a purity of over 94 %, compared to BHET from PET with a purity over 98%. The BHET product contained several additional byproducts, including HBHET and BHBT dimer. Glycolysis of mixes of PET and PBT indicated a linear dependence of the molar yield on the molar ratio, increasing with the fraction of PET.

FTIR, DSC and TGA show that all the polyester based components (bicomponent fibre, backing, glue, film, yarn and transition fibre) mainly consisted of either PET or PBT. All components yielded BHET from the glycolysis and workup, except for the glue, which had been identified as mainly PBT, but proved more challenging. The purity of the BHET was above 95 % for all components, except for the glue. Moreover, the colour of the crystalline BHET product were white from all investigated component materials except for transition fibre and in all cases the black colour was removed. The efficient removal of carbon black particles during workup is promising as a white or colorless product is much preferred by users of recycled feedstock.

HPLC analysis of products and filtrates showed that glycolysis of all components resulted in some byproducts, such as HBHET, which were also detected when PBT was depolymerised, but not PET. This indicated that PBT was present in all materials, in some case in too low amounts to detect with the used analyses. However, for yarn and transition fibre, which were identified as mainly consisting of PET, the low content of another polyester than PET did not reduce the yields (76-78 mol%), as they were comparable to that from neat PET (79 mol%). Whereas, for the other components that diverged more from PET in the FTIR and thermal analyses, the BHET yield was decreased compared to PET. Out of the investigated layers in the vehicle flooring solution, the surface layer appeared most

challenging, yielding 49 mol%. This was likely due to the presence of glue, given that the glue did not yield BHET, and when present in high amount (50 weight%) it also reduced the BHET yield from neat PET.

Optimisation of both the glycolysis reaction and separation steps would be of interest to increase the yield, and thereby the sustainability and economic viability of the recycling process. Alterations to process conditions need to be investigated further to find an optimum for the glycolysis of PBT where BHET is even more favored in comparison to byproducts such as HBHET. Since the formation of additional byproducts also alter the chemical and physical properties of the solution which BHET crystallises from, parameters for the separation also need investigating, such as EG:water ratio.

It was concluded that BHET can be yielded from the glycolysis of the full vehicle flooring solution and BHET was recovered at a yield of 60 mol%. This shows that it is possible to recycle the full vehicle flooring product through glycolysis. Hence the recyclability of all-polyester based vehicle flooring solutions has been confirmed. Furthermore, the BHET that was yielded had a high purity of above 97 % and was white in color.

This project has shown that chemical recycling is a useful route for recycling all-polyester based vehicle interior solutions that are usually incinerated for energy recovery at best. A key point is that the flooring solutions are designed for recyclability, where the all-polyester solution mostly consisting of two very similar polymers enables the use of glycolysis for the full solution. Chemical recycling of all-polyester solutions can be used to obtain high quality monomer for the production of the new polymers, enabling increased circularity for vehicle flooring solutions.

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A

Appendix 1

In the following section images of the materials used for glycolysis and BHET produced from each material are shown.

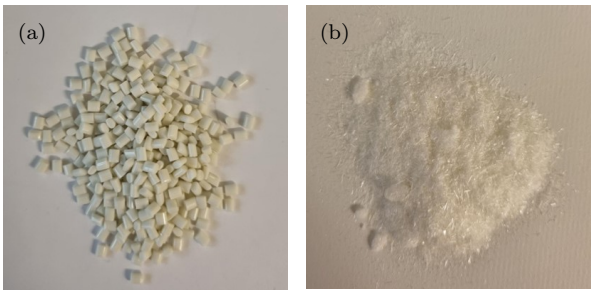

Figure A.1: Images showing (a) PET and (b) BHET from glycolysis of PET.

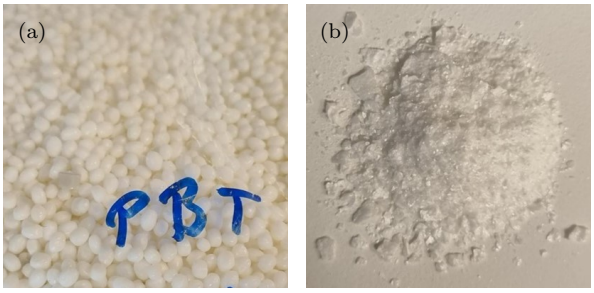

Figure A.2: Images showing (a) PBT and (b) BHET from glycolysis of PBT.

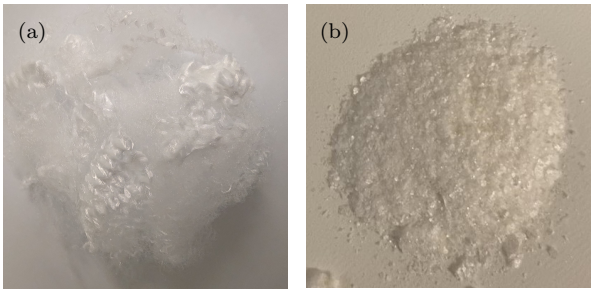

Figure A.3: Images showing (a) bicomponent fibre and (b) BHET from glycolysis of bicomponent fibre.

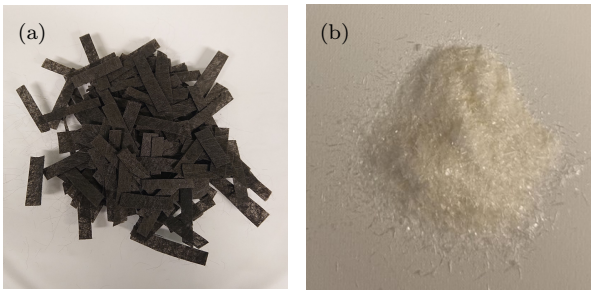

Figure A.4: Images showing (a) (cut pieces of) backing and (b) BHET from glycolysis of backing.

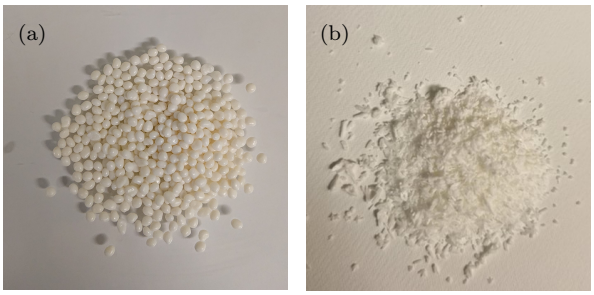

Figure A.5: Images showing (a) glue and (b) BHET from glycolysis of 50:50 PET:glue.

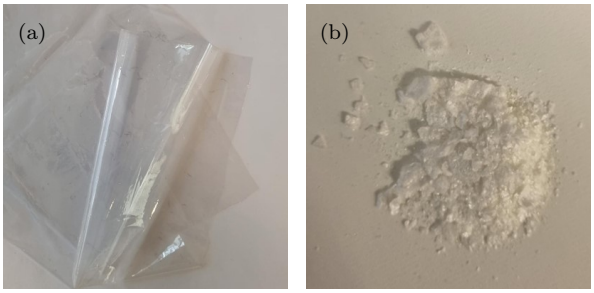

Figure A.6: Images showing (a) film and (b) BHET from glycolysis of film.

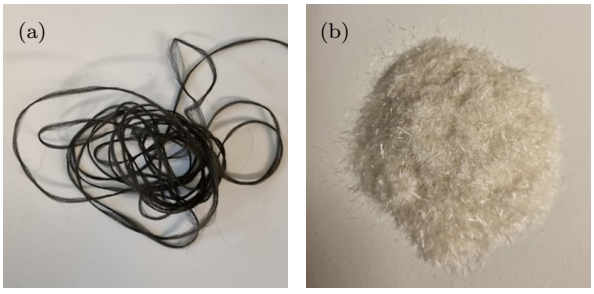

Figure A.7: Images showing (a) yarn and (b) BHET from glycolysis of yarn.

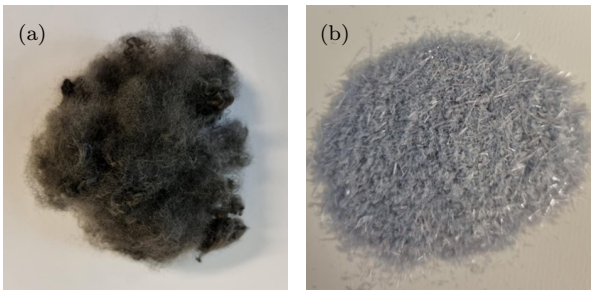

Figure A.8: Images showing (a) transition fibre and (b) BHET from glycolysis of transition fibre.

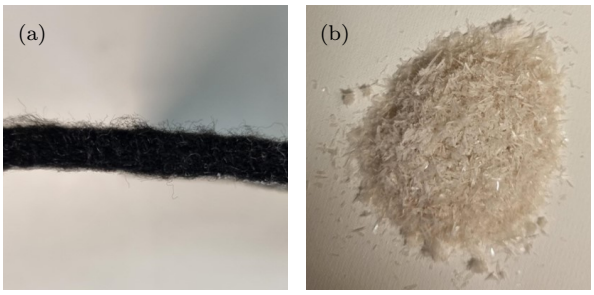

Figure A.9: Images showing (a) the felt layer and (b) BHET from glycolysis of the felt layer.

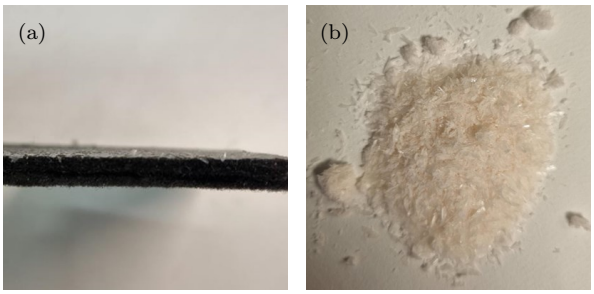

Figure A.10: Images showing (a) the surface layer and (b) BHET from glycolysis of the surface layer.

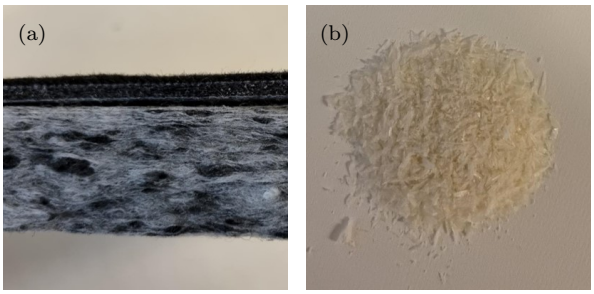

Figure A.11: Images showing (a) the full vehicle flooring solution and (b) BHET from glycolysis of the full vehicle flooring solution.

B

Appendix 2

Shown below are the molecular structures of the compounds identified with HPLC-MS as presented in Table 4.1, in order of retention time.

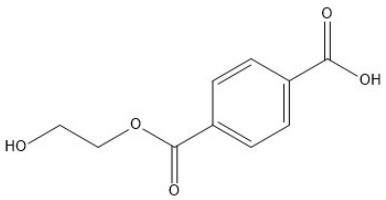

Figure B.1: Molecular structure of 4-((2-hydroxyethoxy)carbonyl)benzoic acid, MHET.

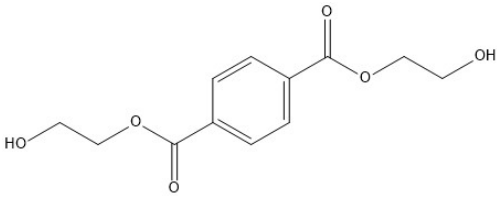

Figure B.2: Molecular structure of bis(2-hydroxyethyl) terephthalate, BHET.

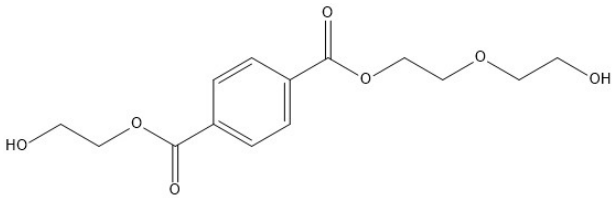

Figure B.3: Molecular structure of 2-(2-hydroxyethoxy)ethyl(2-hydroxyethyl) terephthalate, DEG ester.

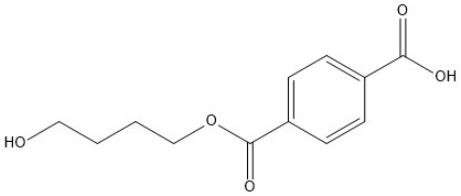

Figure B.4: Molecular structure of 4-((4-hydroxybutoxy)carbonyl)benzoic acid, MHBT.

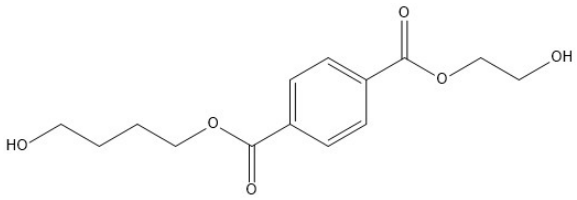

Figure B.5: Molecular structure of 4-hydroxybutyl(2-hydroxyethyl) terephthalate, HBHET.

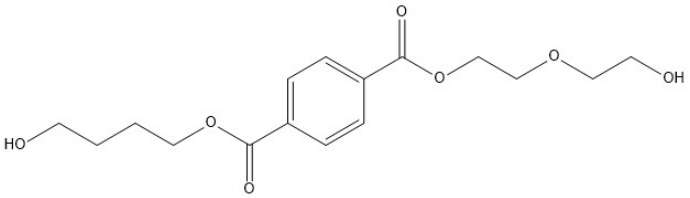

Figure B.6: Molecular structure of 4-hydroxybutyl(2-(2-hydroxyethoxy)ethyl) terephthalate, HBHEET.

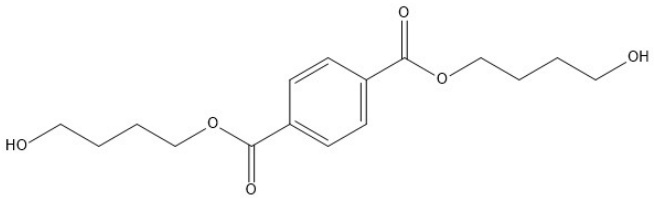

Figure B.7: Molecular structure of bis(4-hydroxybutyl) terephthalate, BHBT.

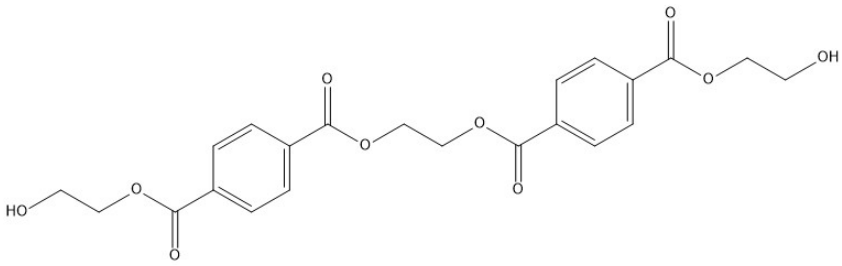

Figure B.8: Molecular structure of *O,O*'-(ethane-1,2-diyl)bis(2-hydroxyethyl) diterephthalate, BHET dimer.

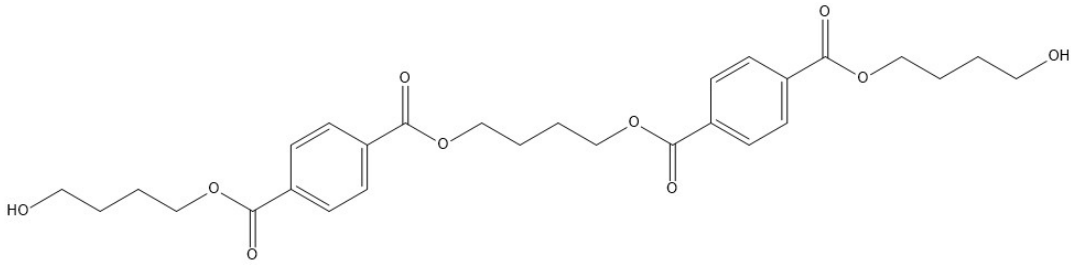

Figure B.9: Molecular structure of *O,O*'-(butane-1,2-diyl)bis(2-hydroxybutyl) diterephthalate, BHBT dimer.

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