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Exploring the Compatibility of Dope-Dyed Polyester Textiles in Chemical Recycling

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KTH Makromolekylära Materials	Examensarbete TRITA-CBH-GRU 2024:XXX **Undersökning av kompatibiliteten hos dopfärgade polyestertextilier i kemisk återvinning** Aakriti Mohanty

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Sammanfattning

Textilindustrin ökar fokuset på att hitta hållbara sätt att minska dess miljöpåverkan genom att använda olika metoder för att återvinna textilavfall. Konventionella färgningstekniker för PET ger dock ofta råvaror som inte är optimala för produktion av nya textilier. Behovet är produktion av ofärgad råvara, som är BHET, i processen för glykololysering - en kemisk depolymerisationsprocess för återvinning av PET, är målet att producera en icke-färgad råvara, särskilt BHET.

Dispergerade färgämnen, som vanligtvis används vid färgning av PET, bryts ned under den kemiska återvinningsprocessen, vilket resulterar i missfärgade monomerer (BHET). En alternativ metod, dopfärgning, är en lovande väg på grund av dess minskade vatten- och kemikalieanvändning och dess potential för mindre missfärgning av monomeren. Vissa färger tenderar dock att finnas kvar i BHET, vilket komplicerar återvinningsprocessen.

Denna avhandling syftar till att förstå varför vissa färger, som röda och gula, finns kvar i BHET medan andra, som blågrå, inte gör det. Studien går ut på att utvärdera de kemiska och fysikaliska egenskaper som skiljer dessa färger åt.

Fyra färger - Blå, Grå, Röd och Gul - valdes ut för en omfattande analys. Egenskaperna hos varje färg, inklusive deras utbyte genom den kemiska återvinningsprocessen, termiska egenskaper och kemiska strukturer utvärderades noggrant. För att få exakta analytiska mätningar isolerades färgämnena och analyserades med hjälp av avancerade tekniker som ICP och FT-IR. Dessa tekniker hjälpte till att avkoda materialens slutliga strukturer och gav insikter om skillnaderna i deras egenskaper och kompatibilitet med PET-återvinning.

Genom att förstå dessa skillnader syftar denna forskning till att förbättra återvinningsprocessen och förbättra kompatibiliteten mellan olika färgämnen och PET-återvinning. Resultaten syftar till att ge en grund för att optimera återvinningsmetoder och välja färgämnen som minimerar monomermissfärgning och därigenom bidra till produktionen av återvunna textilier av högre kvalitet

Nyckelord

Textilåtervinning, PET, BHET, Depolymerisering, Dopefärgning, Glykolys, ICP, FTIR, Färgämnesstruktur

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Abstract

The textile industry is increasing its focus on finding sustainable ways to reduce its environmental footprint by adopting various methods to recycle textile waste. A major challenge in recycling PET is that conventional dyeing techniques often result in discolored raw materials, suboptimal for the production of textiles.During glycolysis - a chemical depolymerization process of recycling PET, the goal is to produce a non-colored raw material, specifically BHET.

Disperse dyes, commonly used in dyeing PET, degrade during the chemical recycling process, resulting in discoloured monomers (BHET). An alternative method, dope dyeing, is a promising avenue due to its reduced water and chemical usage and its potential for less discolouration of the monomer. However, certain colours tend to persist in the BHET, complicating the recycling process.

This thesis aims to understand why certain colours, like reds and yellows, remain in the BHET while others, like blue-greys, do not. The study involves evaluating the chemical and physical properties that differentiate these colours.

Four colours- Blue, Grey, Red and Yellow - were selected for a comprehensive analysis. The properties of each colour, including their yield through the chemical recycling process, thermal properties and chemical structures were thoroughly assessed. To obtain precise analytical measurements, the colourants were isolated and analyzed using advanced techniques such as ICP and FT-IR. These techniques helped decode the final structures of the materials and provided insights into the differences in their properties and compatibility with PET recycling.

By understanding these differences, this research seeks to enhance the recycling process and improve the compatibility of various dyes with PET recycling. The findings aim to provide a foundation for optimizing recycling practices and selecting dyes that minimize monomer discolouration, thereby contributing to the production of higher-quality recycled textiles.

Keywords:

Textile Recycling, PET, BHET, Depolymerisation, Dope Dyeing, Glycolysis, ICP, FTIR, Dye chemical structure

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Nomenclature

Abbreviations

ATR	Attenuated Total Reflectance
DSC	Differential Scanning Calorimetry
FTIR	Fourier-Transform Infrared Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
BHET	bis(2-hydroxyethyl) terephthalate
DMSO	dimethyl sulphoxide
DPP	diketopyrrolopyrrole
EG	ethylene glycol
PBT	polybutylene terephthalate
PET	polyethylene terephthalate
TPA	terephthalic acid

Contents

Chapter 1

Introduction

The textile industry is a significant contributor to global environmental challenges, with its production and waste generation posing substantial threats to sustainability. The need for textile recycling has emerged as a critical solution to address the environmental impact of this industry. Textile waste has reached alarming levels, with millions of tons being discarded annually, leading to pollution, resource depletion, and landfill overcrowding. However, the rate of textile recycling is not particularly great, with less than 1% of the materials that have been used in textile production getting recycled into textiles. [1] 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, 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. Add to that the problem of removing the dyestuff from these textiles to ensure we get similar coloured clothes as virgin PET. This master' s thesis addresses such a process: chemically recycling polyester using glycolysis, followed by subsequent characterisation of the dyestuff to investigate which classes of colourants used in dope dyeing are more compatible with chemical recycling.

1.1 Background

With the rise in fast fashion and the shortening of fashion cycles, the consumption and demand for textiles is on the rise. This has also led to an increase in textile waste. Only about 25% of textile waste is collected in the EU, annually.

In 2018 alone, 17 million tons of textile municipal solid waste were produced in the United States, with over 100 billion garments manufactured annually, leading to significant environmental consequences [2] . This waste not only occupies landfill space but also contributes to pollution and consumes vast amounts of power and water. The environmental impact of textile production is substantial, with the fashion industry being one of the largest polluters globally, second only to the oil industry.[3, 4] Textile production requires extensive resources, such as water and land, with estimates suggesting that producing a single cotton tshirt can consume 2,700 litres of fresh water, enough to meet the drinking needs of one person for 2.5 years [5]. Furthermore, the textile sector is a major source of water pollution and land use, further exacerbating environmental issues. Textile waste also contributes to water pollution, with textile production accounting for about 20% of global clean water pollution from dyeing and finishing products. The release of microplastics from synthetic textiles during washing poses a significant threat to aquatic ecosystems and human health, as these microplastics can enter the food chain and accumulate in the environment.

In addition, the fashion industry is a significant emitter of greenhouse gases, responsible for approximately 8.1% of the total global greenhouse gas emissions. In the EU alone, textile purchases in 2020 generated approximately 270 kg of CO2 emissions per person, totalling 121 million tonnes of greenhouse gas emissions from textile consumption. [5]

1.2 Problem

Currently, a majority of PET textiles are conventionally dyed using disperse dyes. However, the problem with using such dyes is that they degrade at higher temperatures. The introduction of dope dyeing brought the promise of dyeing fabrics using fewer resources such as chemicals and water. Dope dyes are more thermally stable. While the recycling of dope-dyed polyester to its monomers is an established process, it has not been sufficiently studied, particularly in the context of dye adhesion. Notably, there is a variation between colours in how strongly they adhere to the monomer, which poses a significant challenge for chemical recycling.

Figure 1.2.1: Dispersed dye fabrics compared to their depolymerised monomers[6]

***Problem Statement**: What classes of colours are more compatible with the recycling of dope-dyed PET textiles and why is that so? Can we categorize these dyes into categories that are more or less suitable for recycling?*

1.3 Purpose

This thesis aims to explore various methods to identify which dyes are more compatible with the recycling of dope-dyed textiles. It will focus on understanding the composition of dyes used in textile manufacturing, particularly in dope dyeing. By examining these methods, the thesis seeks to offer insights into how we can better determine the classes of dyes to recycle in polyester textiles. Ultimately, this research aims to improve recycling processes, promoting sustainability in the textile industry.

1.4 Goal and Objective

The goal of this degree project is to identify and evaluate the compatibility of various classes of dope dyes with the recycling of PET textiles and to develop effective methods to determine the composition of these dyes. Through systematic investigation, the project aims to enhance the recycling process and promote sustainability within the textile industry.

This was achieved by:

1. Comprehensive analysis of different classes of dope dyes used in PET textiles.
2. Evaluation of the stability and removability of these dyes during glycolysis.
3. Recommendations for recycling companies on implementing suitable chemical methods for analyzing dye compositions.
4. A report describing the findings, methodologies, and recommendations generated from the project.

1.5 Benefits, Ethics and Sustainability

The implementation of sustainable practices in textile manufacturing and recycling stands to benefit various stakeholders, including recycling companies, environmental organizations, policymakers, and manufacturers. Recycling companies, for instance, can enhance their operational efficiency and accuracy by gaining insights into dye compositions, thereby improving sorting and recycling processes. Simultaneously, environmental organizations can utilize project findings to advocate for eco-friendly practices within the textile industry, contributing to broader efforts toward environmental sustainability. However, ethical concerns may arise concerning the disclosure of chemical compositions by manufacturers, potentially hindering safety measures for textile workers and environmental protection. These concerns often stem from the protection of intellectual property rights, as manufacturers may be reluctant to disclose proprietary information about their dye compositions. Moreover, chemical methods employed for dye composition analysis may pose health risks if not handled properly, highlighting the need for stringent safety measures and worker training. Additionally, the disposal of chemicals used in dye analysis can have adverse environmental consequences, prompting ethical considerations in managing chemical waste responsibly to minimize harm to ecosystems.

The project also makes significant contributions to resource conservation and waste reduction. By improving recycling efficiency and enabling more targeted recycling processes through enhanced dye composition analysis, the project aids in the conservation of resources and reduces waste generation. This supports the transition towards a circular economy model, where materials are reused and recycled, thereby minimizing reliance on virgin resources and reducing environmental impact. In addition, the promotion of eco-friendly practices, such as dope dyeing, further advances sustainability efforts in the textile industry. Dope dyeing methods significantly reduce water consumption and chemical discharge compared to traditional dyeing processes, aligning with broader goals of environmental preservation and resource efficiency.

1.5.1 Alignment with Sustainable Development Goals (SDG)

The project aligns with several SDGs including

- **SDG 9: Industry, Innovation, and Infrastructure:** By improving the recycling processes, this project contributes to building resilient infrastructure and fostering innovation within the textile industry.
- **SDG 12: Responsible Consumption and Production:** This project promotes sustainable practices in the textile industry by enhancing recycling processes, reducing waste, and encouraging the use of eco-friendly dyeing methods.
- **SDG 14: Life Below Water:** Dope dyeing methods that reduce chemical discharge help protect aquatic ecosystems by minimizing pollution and safeguarding marine life.
- **SDG 15: Life on Land:** Improved chemical waste management and reduced environmental impact contribute to the preservation of terrestrial ecosystems and biodiversity.

1.6 Delimitations

This study confines its examination solely to glycolysis as a method for recycling polyester materials, excluding consideration of alternative recycling or depolymerization techniques. Furthermore, it restricts its analysis to the use of a specific catalyst, namely Mg-Al mixed oxides, for all reactions investigated.

The study was solely operated on a small scale in a laboratory, without conducting any large-scale testing, thus limiting insights into the scalability and practical application of the glycolysis process on an industrial level. The study also refrains from delving into a comprehensive life cycle assessment of the recycled monomer compared to virgin petroleum-based material, thus restricting the assessment of the overall environmental impact and sustainability implications of glycolysis-based polyester recycling.

These delimitations are essential for maintaining the focus and manageability of the study while providing valuable insights into the specific aspects of glycolysis-based polyester recycling within the defined parameters.

1.7 Outline

In subsequent chapters of the thesis, the focus shifts towards an in-depth exploration of the relevant theoretical framework and comprehensive literature review. Methodologies and procedures utilized in the research are detailed, followed by comprehensive analyses in the conclusions and discussions sections. Additionally, potential avenues for further research are identified and discussed.

A flowchart of the entire process is given below

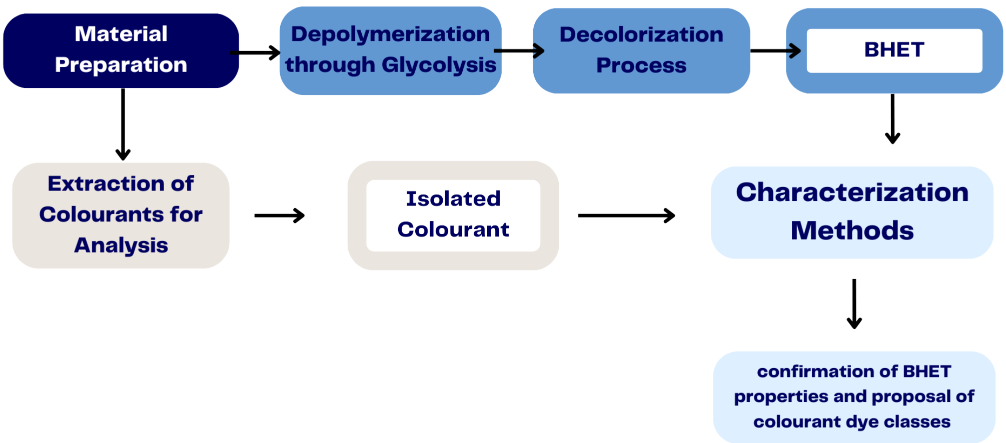


Figure 1.7.1: flowchart depicting entire process

Chapter 2

Theoretical Background

2.1 Textiles

The textile industry has undergone significant transformations since its inception, with a growing focus on sustainability. The drive to close the loop and reduce environmental impact has led to innovations in recycling and eco-friendly practices. [7]

2.1.1 Synthetic Textiles

Synthetic textiles, also known as man-made textiles, are fabrics produced from chemically created fibres like polyester, nylon, acrylic, and spandex. [8] These textiles offer various advantages such as durability, affordability, and ease of maintenance. Synthetic fibres are derived from petroleum-based compounds and are manufactured through chemical processes, making them distinct from natural fibres like cotton or wool. The production of synthetic textiles has significantly increased over the years, with polyester being the most widely used synthetic fibre globally. While synthetic fabrics provide benefits like durability, wrinkle resistance, and stretch, they also have environmental impacts due to their manufacturing processes involving chemicals and non-renewable resources. Despite these drawbacks, synthetic textiles continue to dominate the textile market due to their performance advantages, low price and versatility in various applications like clothing, upholstery, and carpeting

2.2 PET fibres

Poly(ethylene terephthalate) (PET) is one of the most widely used thermoplastic polymers in our daily lives. Its durability, water-repellent properties and lightweight nature make it a popular choice for various applications. PET consumption is around 63 million tons per year worldwide, with a market share of 54% in global fibre production in 2022. [9, 10]

Polyethylene terephthalate (PET) is a type of polyester that exhibits a semi-crystalline form when stable. PET is widely used in numerous applications, including fibres for carpets and clothing, containers for food and beverages, automotive parts, films, sheets, strapping, and industrial items like geotextiles and roof insulation[11] Recycled PET, known as rPET, is commonly used in these applications, offering a cost-effective and environmentally friendly alternative to virgin PET.[12] It has been deemed non-toxic and poses no threats to human health, making it a versatile and safe material for various applications.

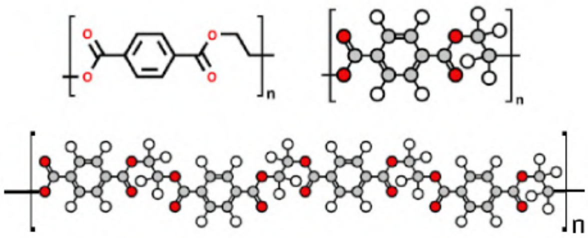


Figure 2.2.1: PET[13]

2.3 Recycling of PET

Increased environmental awareness, legislative measures, and public demand for environmental sustainability are leading to an increased interest in plastic recycling. [14] PET accounts for 8% by weight and 12 % by volume of the world's total solid waste. [15]

The mechanical recycling of PET is relatively simple, requires low investments, utilizes established equipment, is flexible in terms of feedstock volume, and has little adverse environmental impact.

But it also presents several disadvantages: PET loses colour and clarity, and if not properly dried, it degrades easily due to residual moisture. The presence of coloured PET results in an undesirable hue in the rPET. [16]The thermal and oxidative degradation can also cause yellowing and diminished mechanical properties of the materials. There are high costs related to the collection, sorting and separation of the PET waste.[17] The recycling of complex and contaminated PET wastes mechanically is challenging, often yielding in recycled PET with low and varied intrinsic viscosity values.

Chemical recycling is an accepted PET recycling method that follows the principle of "sustainable development"[18]. The chemical recycling of PET involves breaking down the polymer into its original components, such as monomers, and then repolymerizing them to produce high-quality plastics. This method excels in handling mixed or degraded waste streams and yields materials with properties closely resembling virgin PET. Thermomechanical recycling is more efficient and environmentally friendly, although it requires a much cleaner, high-quality feedstock.[19]Chemical recycling can be done through various methods, including methanolysis, glycolysis, hydrolysis, ammonolysis, and aminolysis. These methods can produce a wide range of products, including monomers, fine chemicals, and carbon materials.

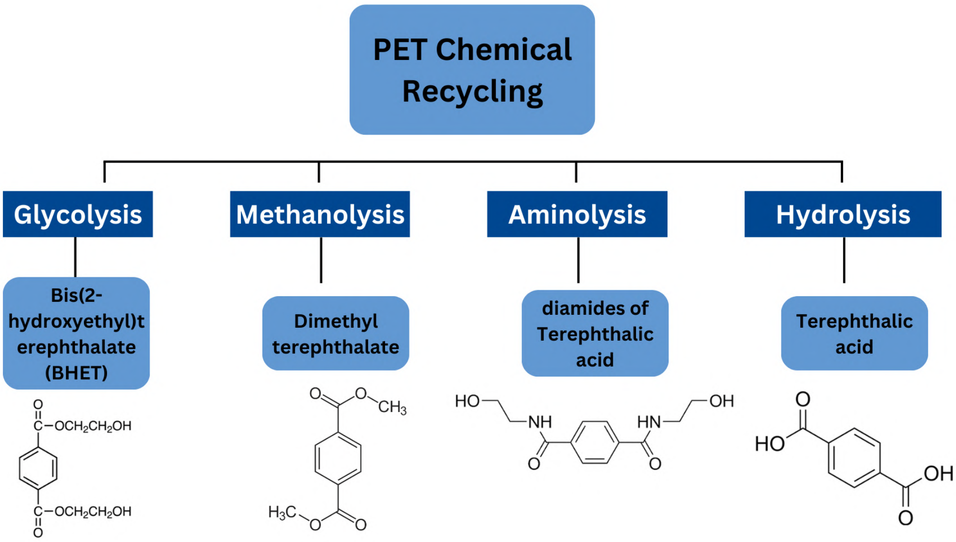


Figure 2.3.1: Different methods to recycle PET chemically

2.3.1 Glycolysis

Chemical recycling of polyethylene terephthalate (PET) through glycolysis presents a promising method for the efficient and sustainable recovery of PET from post-consumer waste. Glycolysis involves the reaction of PET with ethylene glycol (EG) in the presence of a catalyst, resulting in the formation of bis(2-hydroxyethyl) terephthalate (BHET), a valuable monomer that can be reused to produce new PET products.

$$n\,\text{BHET} \rightleftharpoons (\text{PET})_n + (\text{n-1})\,\text{EG}$$

2.4 Dyes

Textile colouring matter, commonly referred to as dyes, plays a pivotal role in the textile industry, imparting colour to fibres, yarns, and fabrics. Dyes can be classified based on various parameters, including their chemical structure, application method, and desired colour fastness. The classification of dyes is crucial for practical purposes and can be categorized according to their application or chemical constitution. Application-wise classification is particularly significant, distinguishing between synthetic dyes, natural dyes extracted from plants or animals, and insoluble colourants like vat and azoic pigments used in textile printing. The chemical structure of dyes is diverse, with various functional groups such as anthraquinone, azo, phthalocyanine, sulfur, indigo, and nitro defining different dye types[20, 21]. Additionally, dyes must possess specific characteristics like absorbing light in the visible spectrum, containing chromophores and auxochromes, and exhibiting resonance of electrons to maintain their colour. Understanding the classification and properties of textile dyes is essential for achieving desired colour outcomes and ensuring the quality and performance of dyed textiles in various applications within the textile industry.

2.4.1 Dope Dyed Textiles

Soluble Dye

A soluble dye is a colourant that is soluble in a solvent, typically water or another liquid. Soluble dyes are usually organic compounds that can be dissolved in a solvent to produce a coloured solution. They are commonly used in textile dyeing and printing processes. Soluble dyes have the following characteristics:

- Solubility: Soluble dyes are soluble in water and other solvents.
- Particle size: The particles of soluble dyes are smaller than those of pigments.
- Light resistance: Soluble dyes are more prone to losing colour, brightness, or spark when exposed to heat, light, or air.
- Applications: Soluble dyes are used in textile dyeing and printing, as well as in various industrial and commercial applications.

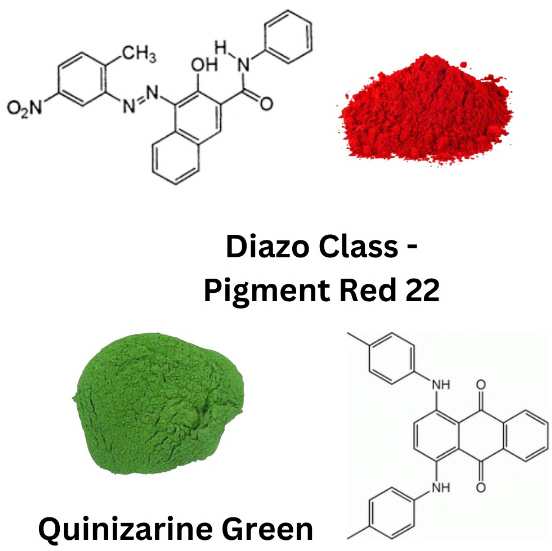


Figure 2.4.1: Soluble dye examples [22–24]

Organic Pigment

Organic pigments are colourants typically made from carbon-based compounds and may contain metallic salts or oxides. They are insoluble in solvents and are more opaque with larger particles compared to soluble dyes. They are commonly used in paints, coatings, and other industrial applications. Organic pigments have the following characteristics:

- Solubility: Organic pigments are soluble in organic solvents or water, depending on chemical structure.
- Particle size: The particles can be large or small depending on the dye type.
- Light resistance: Organic pigments have varied light resistance
- Applications: Organic pigments are used in textiles, papers and other industrial applications.

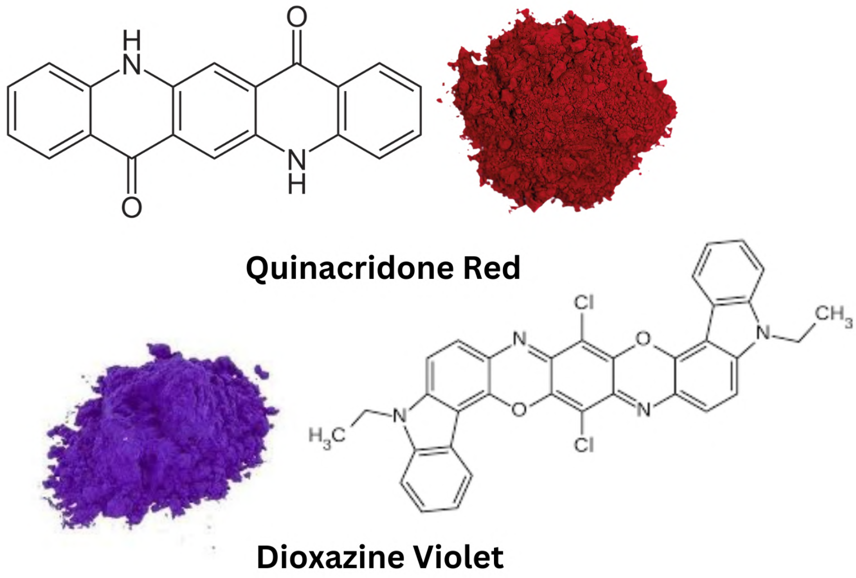


Figure 2.4.2: Organic pigment examples[25–27]

Inorganic Pigments

Inorganic pigments are a class of pigments that are insoluble in solvents and are typically made from metallic salts or oxides. They are more opaque and have larger particles than soluble dyes. Inorganic pigments are commonly used in paints, coatings, and other industrial applications.

- Solubility: Inorganic pigments are insoluble in water, soluble in solvents or dispersible in media.
- Particle size: The particles of inorganic pigments are larger than those of soluble dyes and organic pigments
- Light resistance: Inorganic pigments are highly resistant to light.
- Applications: Inorganic pigments are used in paints, coatings, and ceramics.

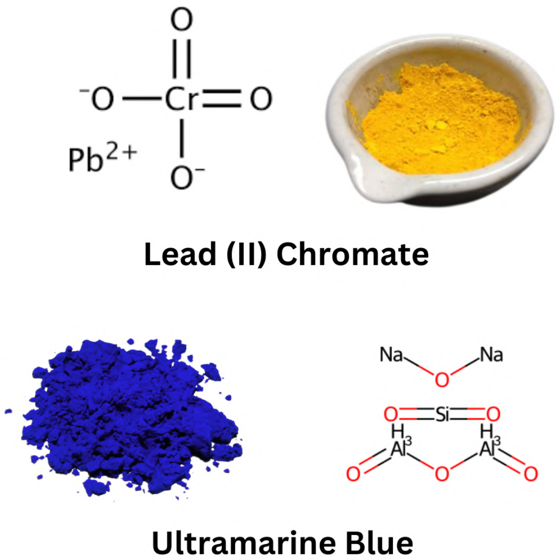


Figure 2.4.3: Inorganic pigment examples[28–31]

2.5 Analytical Techniques

2.5.1 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique used to identify organic, polymeric, and sometimes inorganic materials by analyzing their infrared spectra. In FTIR analysis, infrared radiation is passed through a sample, with some radiation being absorbed and some transmitted. The absorbed radiation is converted into rotational and vibrational energy by the sample molecules, producing a unique spectral fingerprint that represents the molecular composition of the sample. FTIR spectroscopy is widely employed in quality control for industrial materials, aiding in material analysis by identifying unknown substances, characterizing contamination, detecting additives, and investigating issues like oxidation or decomposition. FTIR is a valuable tool for both qualitative and quantitative analysis, providing insights into the chemical composition and structure of various materials.

2.5.2 DSC

Differential Scanning Calorimetry (DSC) is a thermal analysis technique that measures the heat flow into or out of a sample in relation to temperature or time, providing insights into various material characteristics. DSC analysis is crucial for understanding material properties like glass transitions, crystallization, phase changes, melting, cure kinetics, and oxidative stability. It plays a vital role in research, quality control, and production applications, offering a comprehensive assessment of materials. DSC involves subjecting a sample to controlled temperature changes

Figure 2.5.1: FTIR instrument[32]

while quantifying heat exchange with the surroundings, allowing for the observation of phase transitions and chemical reactions. This technique is widely used in industrial settings for quality control due to its ability to evaluate sample purity and thermal behaviour

Figure 2.5.2: DSC instrument[33]

2.5.3 Colour Analysis

LAB colour analysis, based on the CIELAB colour space, involves evaluating colours using three coordinates: L* for lightness, a* for red-green value, and b* for blue-yellow value. This colour space was developed to provide a uniform and perceptually accurate representation of colours, allowing for precise measurement and comparison of all perceivable colours. LAB colour values offer a standardized way to communicate and locate colours, essential for various industries like manufacturing, design, and quality control. By utilizing LAB colour analysis, differences between colours can be accurately identified, aiding in preventing rejects and rework in production processes

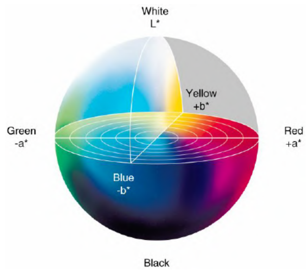


Figure 2.5.3: CIE-Lab colour space[34]

2.5.4 ICP

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a powerful analytical technique that utilizes an inductively coupled plasma to ionize a sample, followed by mass spectrometry to detect and quantify the ions produced. ICP-MS is renowned for its ability to detect metals and non-metals in liquid samples at very low concentrations, making it a valuable tool in various fields like environmental analysis, medical diagnostics, and industrial monitoring. This technique offers high speed, precision, and sensitivity compared to other analytical methods like atomic absorption spectroscopy. ICP-MS can detect different isotopes of the same element, providing versatility in isotropic labelling applications. Despite its advantages, ICP-MS may introduce interfering species like argon from the plasma and contaminants from the environment, necessitating careful calibration and quality control measures for accurate results

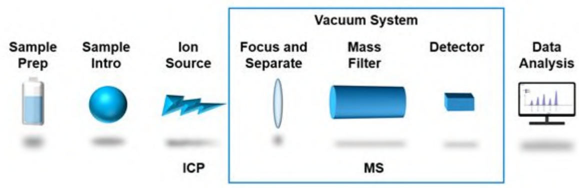


Figure 2.5.4: ICP main components[35]

Chapter 3

Methodology

3.1 Materials

For this study, an in-house synthesized MgO-Al$(OH)_3$ catalyst with an average active surface area of 0.11 m^2/g was employed.

PET pellets were dyed in-house, using the masterbatch addition method, where the colourants - M PBT Fire Red, M PBT Blue, M PBT Yellow and M PBT Grey, which were dispersed in PBT, sourced from Color-Service GmbH & Co. KG. were mixed with the PET in 3% by weight and extruded and pelletized together to get a coloured fibre. These pellets then went through glycolysis. A list of reagents is in 3.1.2.

Sr. No	Colour	Masterbatch Pellets	PET Pellets
1	M PBT Fire Red		
2	M PBT Blue		
3	M PBT Yellow		
4	M PBT Grey		

Table 3.1.1: Table showing PET colours

Chemical	Supplier	CAS Number
Ethylene Glycol	Acros Organics	107-21-1
1-Butanol	Sigma Aldrich	71-36-3
n-Hexane	Merck	110-54-3
Toluene (anhydrous,99.8%)	Sigma-Aldrich	108-88-3l
Dimethyl sulphoxide	VWR Chemicals	67-68-5
Ethyl Acetate,99.5%	Thermo Scientific	141-78-6
Sodium Hydroxide,98%, flakes	Thermo Scientific	1310-73-2
Acetone	VWR Chemicals	67-64-1

Table 3.1.2: Table showing reagents

3.2 Depolymerisation through Glycolysis

PET pellets dyed with masterbatch were depolymerized using glycolysis. Quadruplicates of all colors were carried out. PET Pellets of all 4 colours were stored at room temperature.

.Glycolysis was carried out in stainless-steel reactors with pre-weighed amounts of PET pellets (10g), EG (50 ml) and catalyst (11 mmol). The reactors, along with EG, PET, catalyst and ceramic balls were then placed in an oven with a rotating attachment for 70 minutes at 230 °C. Upon completion of the glycolysis reaction of PET, the reactors were rapidly quenched with cold water. Then 75 ml of boiling water was slowly added into the reactor. Then the whole reactor mixture was quickly filtered using Whatman Filter 5 *(pore size=2.5 microns)*and a vacuum filtration setup.

The first filtration done at a boil (labelled Date-of-experiment_A1 / B1) removed contaminants, dyestuff, hetero-materials, and any oligomers present. The second filtration at around 70°C (labelled Date-of-experiment_A2 / B2) removes dimers. The samples collected on the filter paper were dried in the oven until the constant weight was recorded and then analyzed using DSC, and FTIR. The filtrates were stored in the refrigerator for over 12 hours to ensure complete crystallisation of BHET. The crystallised BHET was then collected on filter paper and dried to record its constant weight.

The supernatant fluid from post-crystallisation BHET filtration was disposed of.

PET conversion was calculated using the following equation.

$$\text{PET Conversion, } X = \frac{m_{\text{PET}_{\text{initial}}} - m_{\text{PET}_{\text{residual}}}}{m_{\text{PET}_{\text{initial}}}} \times 100\% \tag{3.1}$$

where $m_{PET,initial}$ is the initial mass of PET in gram, $m_{PET,residual}$ is the mass of incompletely depolymerized PET in gram after glycolysis reaction is complete.

The BHET yield was calculated using the following equation.

$$\text{BHET Yield, } Y = \frac{m_{\text{BHET}} \,/\, M_{\text{BHET}}}{m_{\text{PET}} \,/\, M_{\text{PRU}}} \times 100\% \tag{3.2}$$

where $m_{PET,0}$ is the initial weight of PET in grams, m_{BHET} is the weight of BHET crystals collected in grams, M_{BHET} is the molecular weight of BHET (254 g/mol) and M_{PRU} is the molecular weight of PET repetition unit (PRU) (192 g / mol) [10]

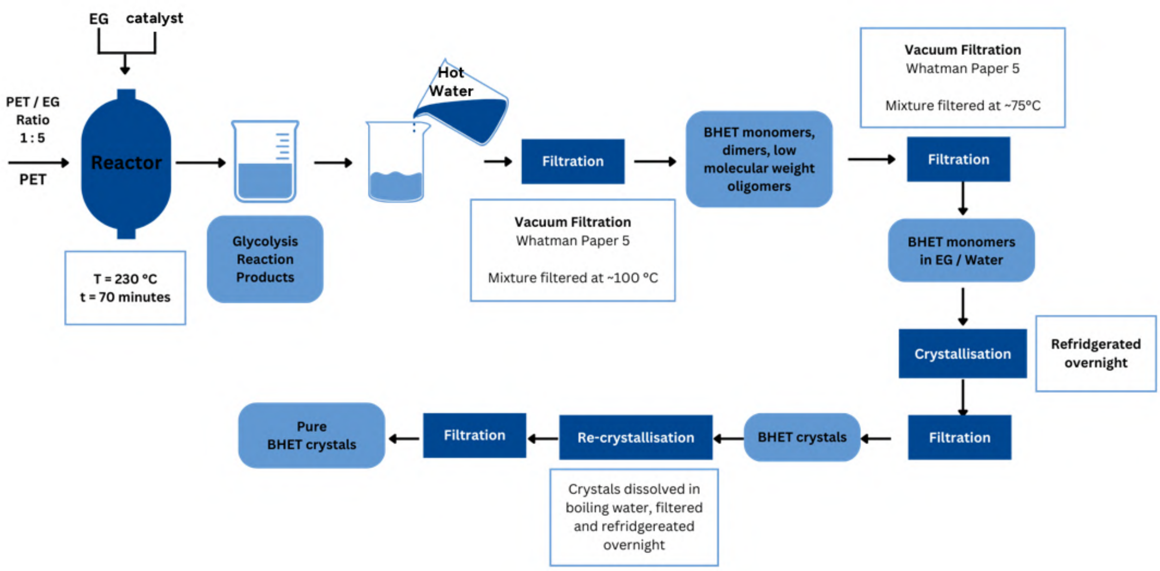


Figure 3.2.1: Glycolysis process overview

3.3 Decolorisation

In the case of colour removal, a physical method using active carbon was used. 5 grams of the BHET was taken with 1% of active carbon and heated up to 70°C for 3 hours. The dye pigments were adsorbed onto the active carbon. The active carbon was then filtered off, and the BHET was recrystallised.

3.4 Extraction of Colourants for Analysis

The masterbatches received did not include information on the chemical structure of the colouring matter. To gain a better understanding of the chemical composition and structure of the pellets, various methods were employed to isolate the colouring matter from the carrier, PBT (polybutylene terephthalate).

3.4.1 Hydrolysis followed by Liquid-Liquid Extractions

Hydrolysis of PBT masterbatch pellets was carried out in a 2-necked round-bottom flask using 2 g of PBT, 40 mL of NaOH, and 0.3 g of a catalyst. The reactants were heated to 90°C for 3 to 5 hours. Following the hydrolysis, liquid-liquid extractions were performed with the reaction mixture using various solvents, including ethyl acetate, toluene, hexane, and butanol. The hydrolysis setup and the liquid-liquid extractions can be seen in A.0.5-A.0.9 Hexane was finalised for further isolation of colourants since it has the lowest boiling point amongst all reagents.

3.4.2 Dissolution in DMSO

The master batch was dissolved in DMSO to facilitate the extraction of the colourants. The pellets were heated in DMSO up to 170°C for 3 hours to ensure complete dissolution of the PBT pellets into the solvent. After dissolution, various solvents, including acetone, ethanol, ethyl acetate and water, were added to leach the colours out of the respective solvent mixtures as seen in A.0.10. Water caused precipitation of both PBT and colourant. Further, extraction with hexane resulted in a coloured hexane solution with suspended PBT particles. The hexane mixture was centrifuged at 2000 RPM for 2 minutes to separate the coloured hexane from the PBT particles. The process is shown in A.0.11

3.5 Characterisation methods used for BHET

3.5.1 DSC

Differential scanning calorimetry (DSC) is employed to investigate the thermal properties of glycolysis products. The BHET crystals were analyzed using DSC to ensure they were pure BHET and to identify any potential impurities. The DSC analysis was conducted under a 120 ml/min nitrogen flow.

The Mettler Toledo DSC 1 Star System was employed for the DSC experiments. Samples, weighing approximately 7-8 mg each, were placed in aluminum pans sealed with lids. Heating occurred at 10°C/min.

The DSC analysis involved heating the BHET samples from room temperature to 150°C, followed by cooling back to room temperature, and then reheating to 300°C, to check whether any impurities were present other than BHET. This thermal cycle allows for the observation of both melting and crystallization behaviours, as well as the detection of any exothermic or endothermic transitions. The first heating cycle erases the thermal history of the material, while the second shows us the actual thermal properties of the material and checks whether there are any impurities present.

For the filter cake, the samples were heated from room temperature to 280°C and cooled back to room temperature.

3.5.2 FTIR

FTIR spectroscopy was employed to characterize the BHET obtained from coloured PET. The FTIR spectra of BHET were acquired using the Bruker Tensor 27 FTIR Spectrometer, with industrial-grade BHET serving as the reference material.

The FTIR measurements were conducted using the ATR attachment with a Germanium crystal over a spectral range spanning from 500 to 4000 cm^{-1}, providing comprehensive coverage of molecular vibrations relevant to the BHET compound. A spectral resolution of 4 cm^{-1} was employed and 16/32 scans were performed per measuring point to ensure detailed spectral features were captured with high precision. A background scan was carried out before initiating the scanning of all samples.

This analytical technique allows for the identification of functional groups present in the BHET samples, aiding in the assessment of their chemical composition and structural characteristics.

3.5.3 Colour Analysis

The KONICA MINOLTA CM-3600A Spectrophotometer was employed for this analysis. The BHET produced at each step was crushed into a powder form and subsequently analyzed using the spectrophotometer. The CIE Lab values were then recorded, and compared to those of Industrial-grade BHET.

3.6 Characterisation Methods for Colouring Matter

3.6.1 TGA

Thermal Gravimetric Analysis(TGA) is employed to investigate the presence and quantity of fillers, additives and other components in the colouring matter. TGA was carried out for both the masterbatch and the isolated pigments. The analysis was conducted under a nitrogen flow of 120 ml/min.

The Mettler Toledo TGA 1 Star System was employed for the TGA experiments. Each sample was carefully inserted into the TGA apparatus at an initial temperature of 30°C. Subsequently, the samples were heated gradually under a nitrogen atmosphere, with the temperature ramping up to 550°C. This allowed for the observation of the thermal degradation and decomposition behaviour of the sample under an inert atmosphere.

Upon reaching 550ºC, the atmosphere within the TGA chamber was then changed to an oxygenated one. This ensured the complete oxidation of any organic components present in the sample. The temperature was increased to 850°C under the oxygenated atmosphere to facilitate thorough combustion and oxidation of organic materials.

3.6.2 FTIR

KBr pellets of both reference and each isolated colour were prepared using The Specac Manual Hydraulic Press and an Evacuable Pellet Die. The FTIR measurements were conducted in the Transmission mode with the help of a universal window aligner over a spectral range spanning from 500 to 4000 cm^{-1}. A spectral resolution of 4 cm^{-1} was employed and 16 scans were performed per measuring point to ensure detailed spectral features were captured with high precision. A background scan was carried out before initiating the scanning of all samples.

3.6.3 ICP-MS

Each isolated colouring matter was sent to ALS Scandinavia for ICP Analysis. Trace elements were quantified through 18 scans across the mass range, with a total measurement time of 300 seconds. The reported concentrations for most elements were within ±30% of the measured values.

Chapter 4

Results and Discussion

For the analyses pertaining to BHET, including Fourier Transform Infrared Spectroscopy (FTIR) of BHET, Differential Scanning Calorimetry (DSC), and colour analysis, all colours will be discussed together. This comprehensive approach enables the comparison and identification of overarching trends and patterns across the different colour categories. However, for isolated colour analysis, such as individual colourant characterization and properties, the discussion will be conducted colour-wise. This targeted approach ensures a thorough examination of the specific characteristics and behaviors exhibited by each colour component within the masterbatch samples.

In this thesis, a comprehensive analysis was conducted on four distinct colours: Blue, Grey, Red, and Yellow. Each colour underwent rigorous examination to assess its specific properties and characteristics. The results and discussions presented herein are organized according to these colour categories, allowing for a focused and detailed exploration of the unique attributes associated with each hue. By examining the data colour-wise, a deeper understanding of the variations and intricacies within the analyzed samples can be elucidated.

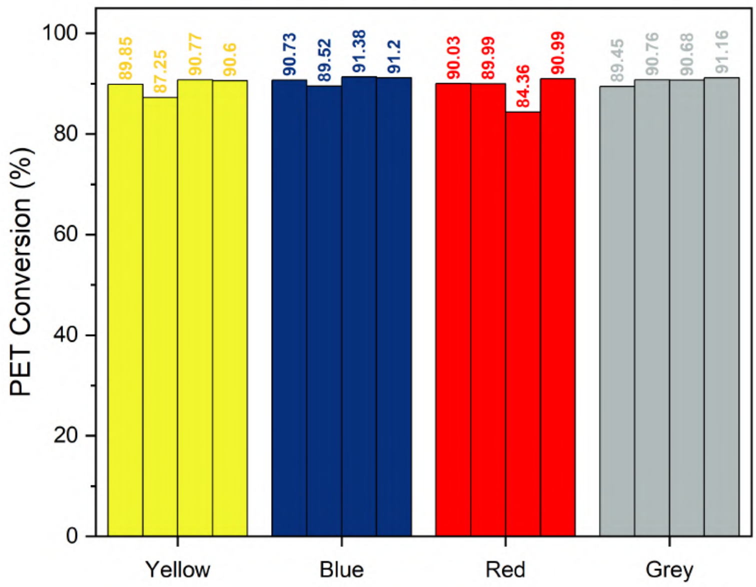
4.1 Overall Analysis of BHET

4.1.1 shows us an overview of the glycolysis results, separated by each colour.

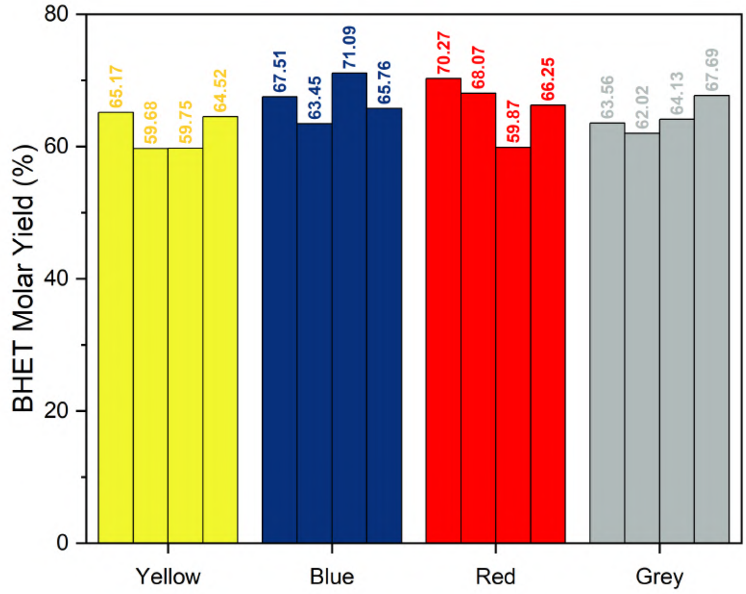
Figure 4.1.1: Overall Result of the Glycolysis

4.1.1 Yields from Glycolysis

The molar yield and mass conversion of the dope-dyed PET pellets and the reference PET are shown in 4.1.2.



(a) PET Conversion



(b) Molar Yield

Figure 4.1.2: Overall conversion and molar yield of the reaction.

All colours give as high yields as 70 mol %. No specific differences were seen among different colours. These results show that dope-dyed PET can be depolymerised into BHET, regardless of the colour. Any differences seen in final yield can be attributed to random and human errors.

From the above observations, we can conclude that there is no relationship between the colour and the resulting yield of BHET. Hence, the dye structure does not play a role in affecting yield during glycolysis.

No distinct colour change was observed for the glycolysed reaction mixture. It could be attributed to the fact that the glycolysis was performed at 230°C, a temperature at which the pigments are thermally stable. Disperse dyes on the other hand, are not as thermally stable and undergo degradation.

4.1.2 Thermal Property Confirmation of BHET

4.1.3 shows the DSC scans of pure crystalline BHET. All BHET curves show sharp endothermic peaks at approximately 111°C which agrees with the well-known melting point of BHET. Hence, we can confirm that the glycolysis of dope-dyed PET resulted in formation of BHET.

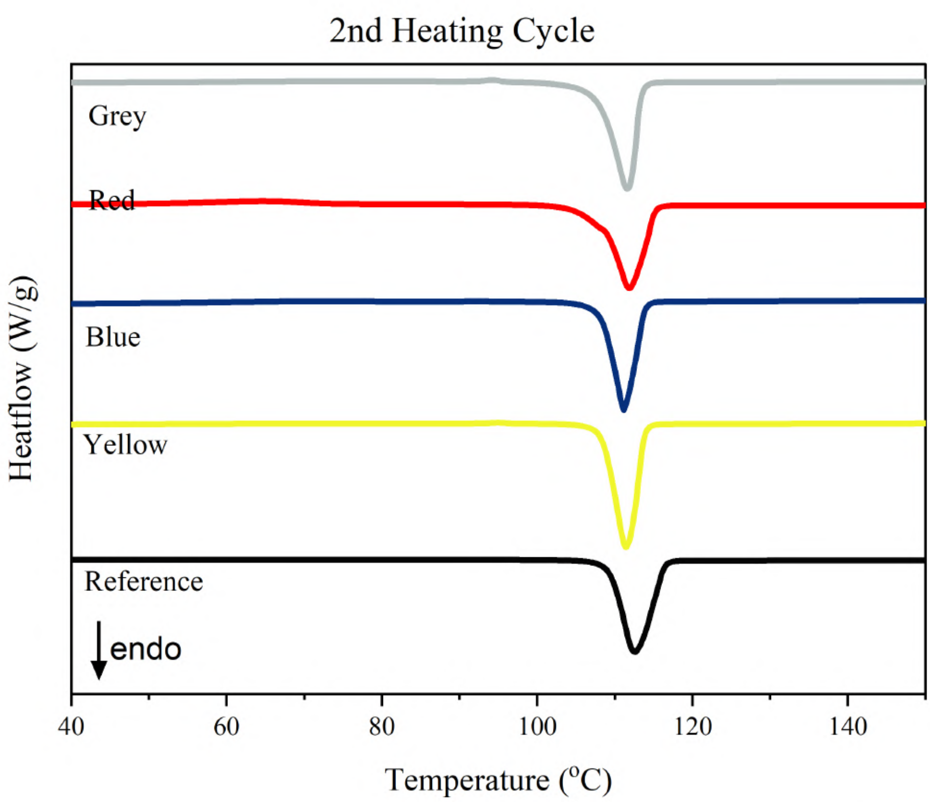
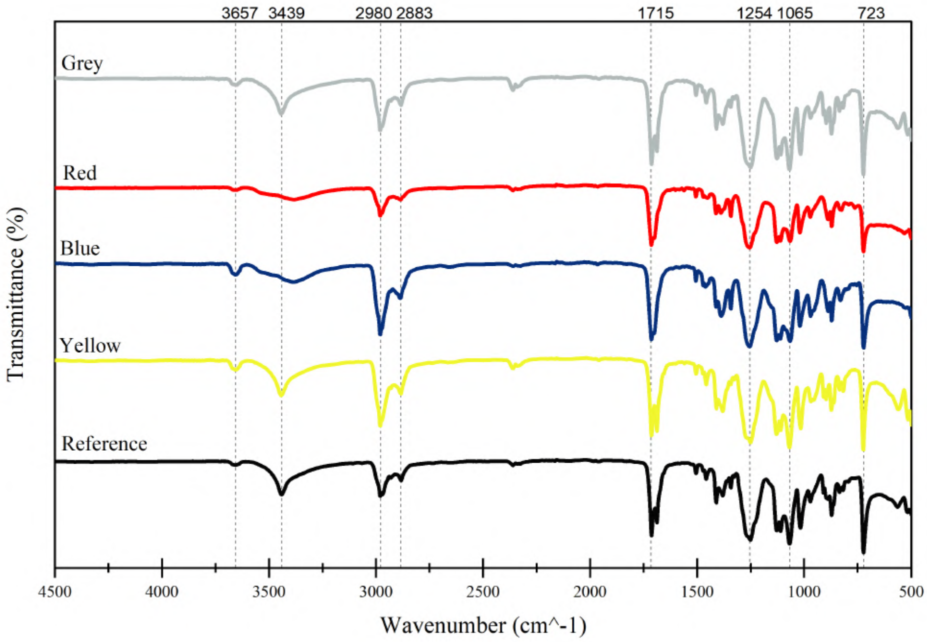


Figure 4.1.3: DSC of BHET from each colour and Reference BHET

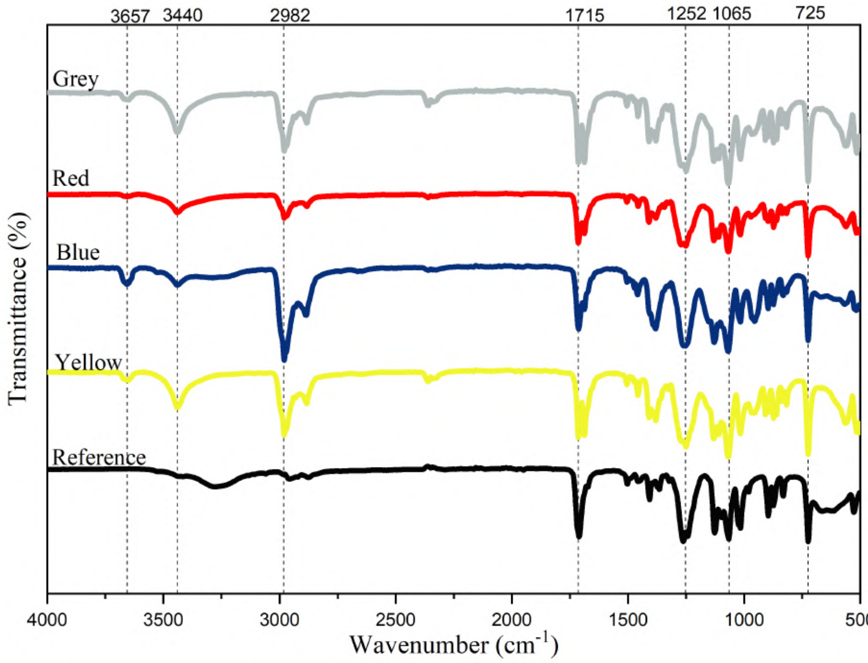
While differences can be observed in the DSC graphs, they are not consistently significant across the triplicate runs to draw definitive conclusions regarding the relationship between the colour of the sample and the corresponding DSC curve.

4.1.3 Chemical Structure Confirmation of BHET

FTIR of the First Filtration Filtercake and BHET are shown in 4.1.4. Notable peaks include a strong peak at 1715 cm^{-1} which can be allocated to C=O stretching, CH_3 and CH_2 asymmetric vibrations between 2800 cm^{-1} and 3000 cm^{-1}, C–H rocking vibration at 725 cm^{-1}, C-O stretching at 1252 cm^{-1} indicating an aromatic ester. [36] All spectra show that the filter cake and BHET are polyesters with terephthalate. No discernible differences among colours were observed in the FTIR plots.



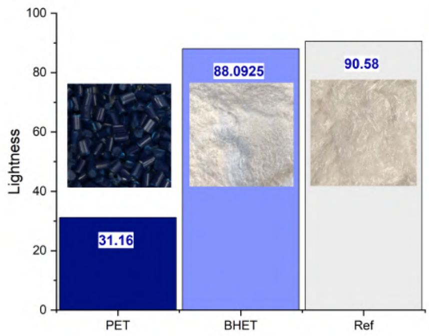
(a) 1st Filtration Filtercake



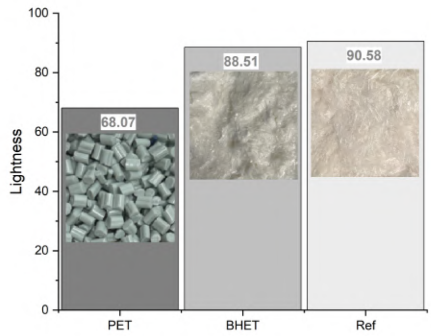
(b) BHET

Figure 4.1.4: FTIR

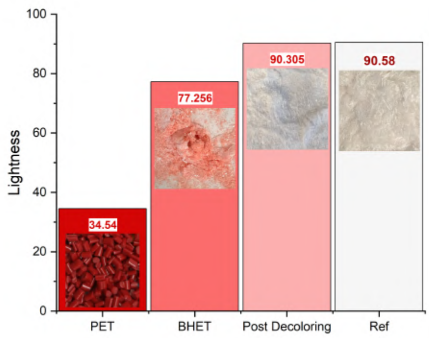
4.1.4 Comparison of BHET Colour with Industrial Standards



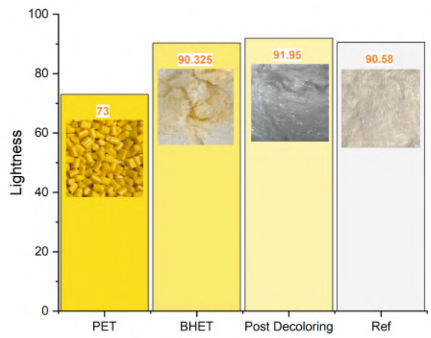
(a) Blue



(b) Grey



(c) Red



(d) Yellow

Figure 4.1.5: L values comparison

A significant improvement in the L* values for all colours was observed, which is comparable to the L* value of 90.58 observed in industrial BHET. As compared in BHET colours as seen through A.0.1b-A.0.4, it is seen that the Reds and Yellow samples tend to stay with the BHET and hence decolourisation was carried out for them. Notably, the decolourisation process by active carbon led to further improvements in the L* value for the Red and Yellow samples, which can also be seen visually. This suggests that the decolourisation process was effective in removing unwanted colours, and improved the optical properties of the recycled BHET, making it more comparable to industrial standards.

4.2 Blue Colourant Analysis

4.2.1 Chemical Structure Analysis

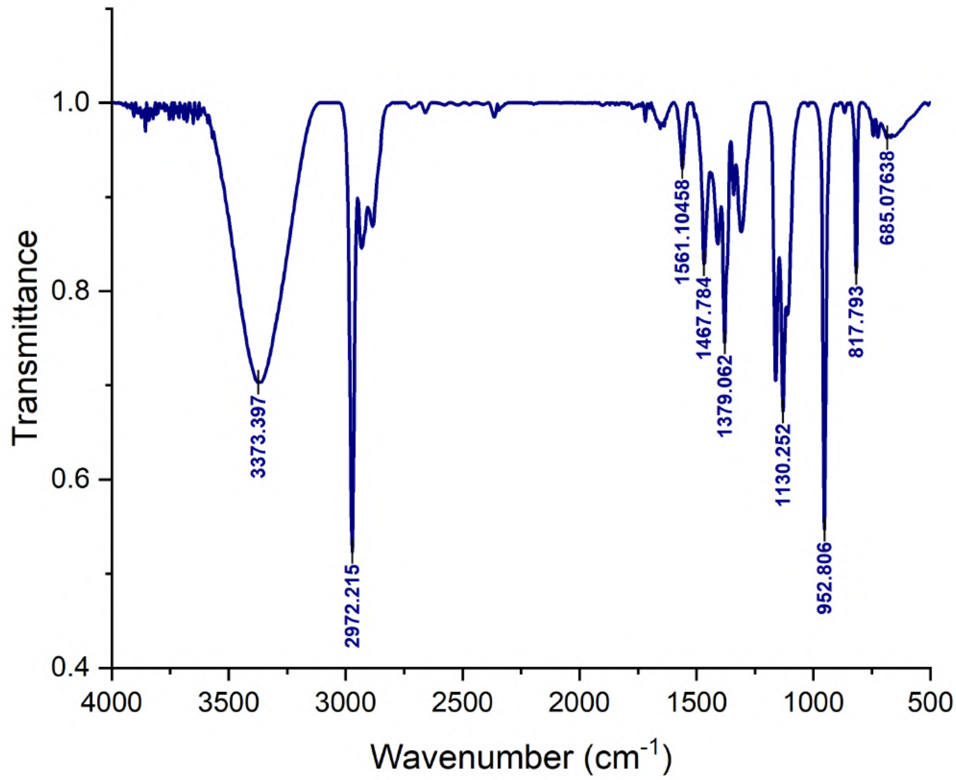


Figure 4.2.1: FTIR of Isolated Blue Pigment

Wavelength	Vibration Type	Assignment
3373.397	O-H stretching	Alcohol
2972.215	C-H stretching	Alkane
1467.2	C-H bending	Alkane
1379.8	O-H bending	Alcohol
1130.252	C-O stretching	Tertiary Alcohol
817.793	C-H bending	Alkene

Based on the observed peaks, the blue pigment could consist of alcohols, alkanes and alkene derivatives, along with other additives or stabilisers. This could potentially be a phthalocyanine blue pigment.[37] Phthalocyanine has tertiary amine groups (R_3N) which show no peaks in the IR region. [38]

4.2.2 Elemental Analysis

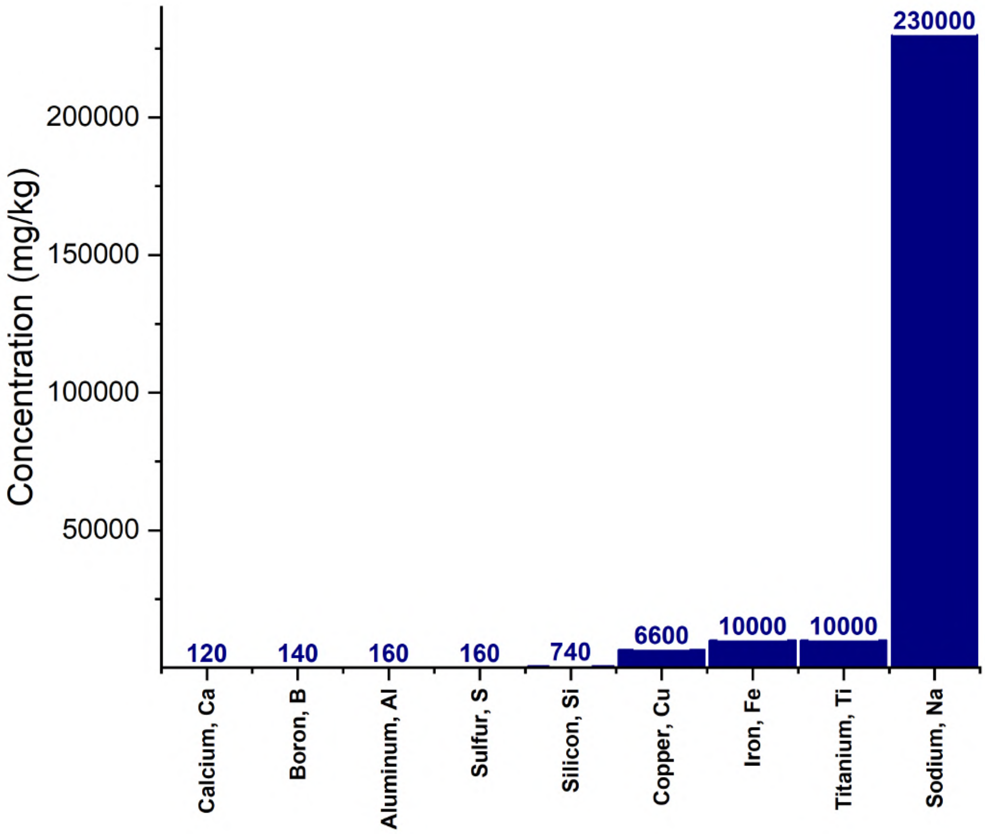


Figure 4.2.2: ICP of Isolated Blue Pigment

The high sodium content could indicate the presence of sodium-based compounds or additives. It may also be present as an impurity from the hydrolysis method. The presence of titanium and iron in the pigment is consistent with the composition of phthalocyanine blue pigments. Titanium may be present as titanium dioxide, which helps enhance colour intensity and opacity.[39] The presence of copper is also consistent with phthalocyanine blue pigments, as copper pthaolcyanine is the main component of these pigments.

Proposed Chemical Class of the Blue Colourant: Phthalocyanine Blue

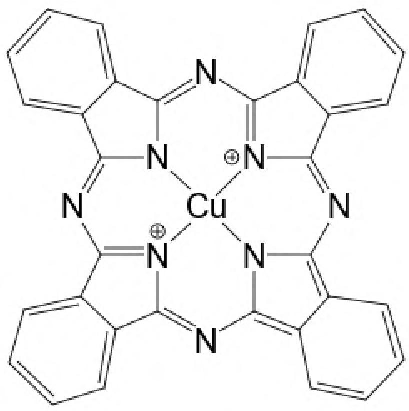


Figure 4.2.3: phthalocyanine blue

4.3 Grey Colourant Analysis

4.3.1 Chemical Structure Analysis

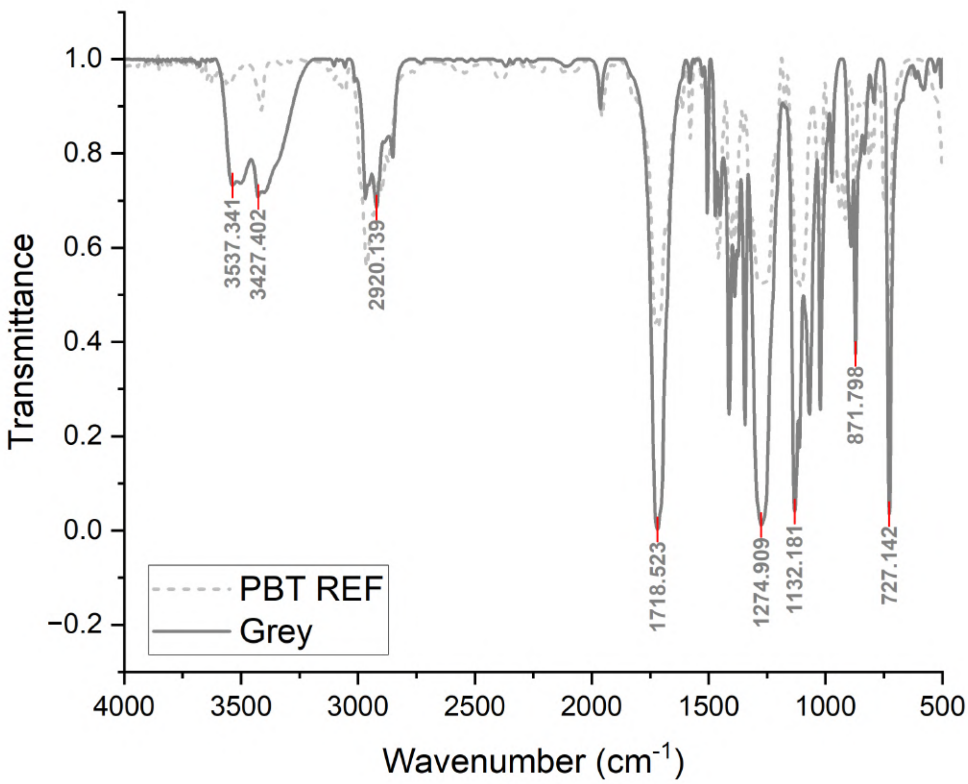


Figure 4.3.1: FTIR of Isolated Grey Pigment

Wavelength	Vibration Type	Assignment
3537.341	O-H stretching	Alcohol
3427.402	O-H stretching	Alcohol
2920.138	C-H stretching	Alkane
1718.523	C=O stretching	α,β-unsaturated ester
1274.909	C-O stretching	Aromatic Ester
1132.181	C-O stretching	Tertiary Alcohol
727.142	C-H bending	Alkene

The Grey Pigment shows O-H stretching vibrations suggesting the presence of alcohol functional groups within the pigment. Alkanes and unsaturated ester functional groups are also present. These may be the remnant peaks of PBT, since some peaks of PBT and the isolated grey pigment overlap. Hence it is difficult to infer any particular structure from just the FTIR of Grey.

4.3.2 Elemental Analysis

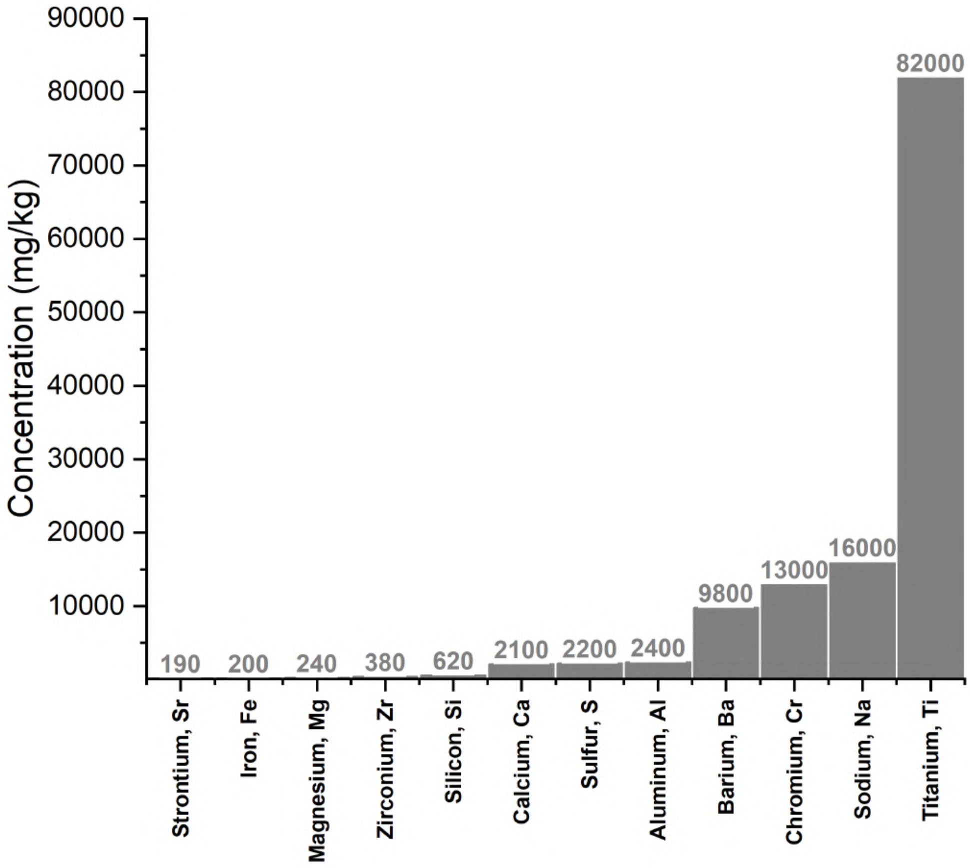


Figure 4.3.2: ICP of Isolated Grey Pigment

High presence of Titanium suggests the presence of Titanium Dioxide, Sodium could be present as an impurity, Chromium, Barium, Aluminium, Sulfur, and Calcium may also be impurities or additives.

4.4 Red Colourant Analysis

4.4.1 Chemical Structure Analysis

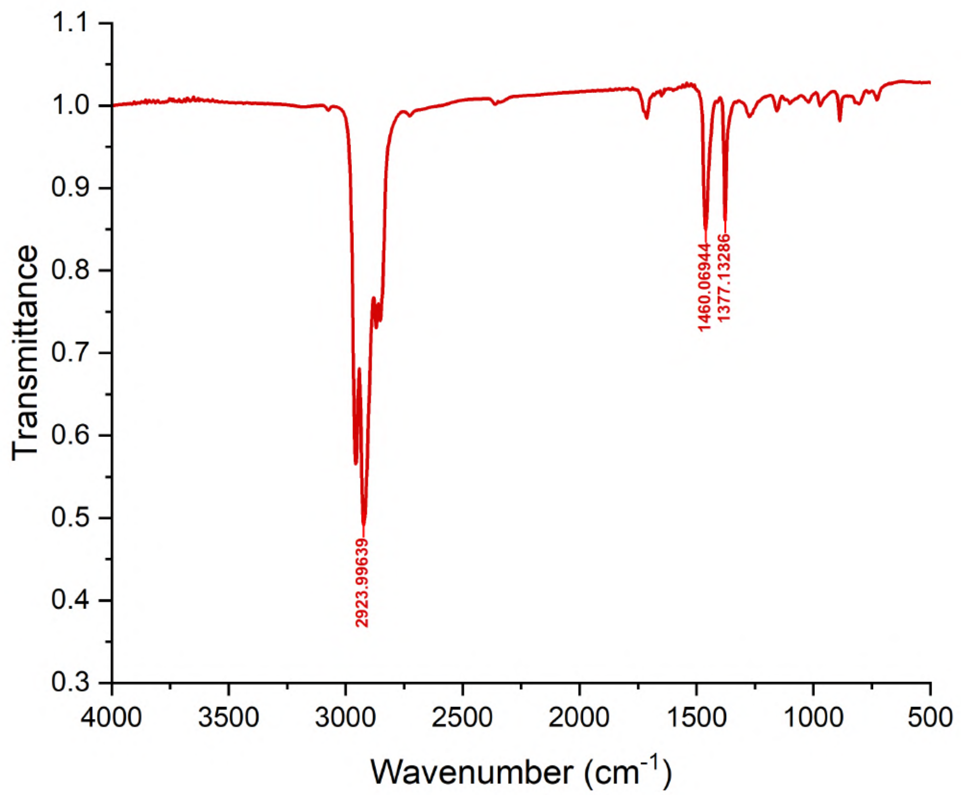


Figure 4.4.1: FTIR of Isolated Red Pigment

Wavelength	Vibration Type	Assignment
2923.99639	C-H stretching	Alkane
1718.523	C=O stretching	Aliphatic Ketone
1377.13256	C-H bending (in-plane)	methyl or methylene

4.4.2 Elemental Analysis

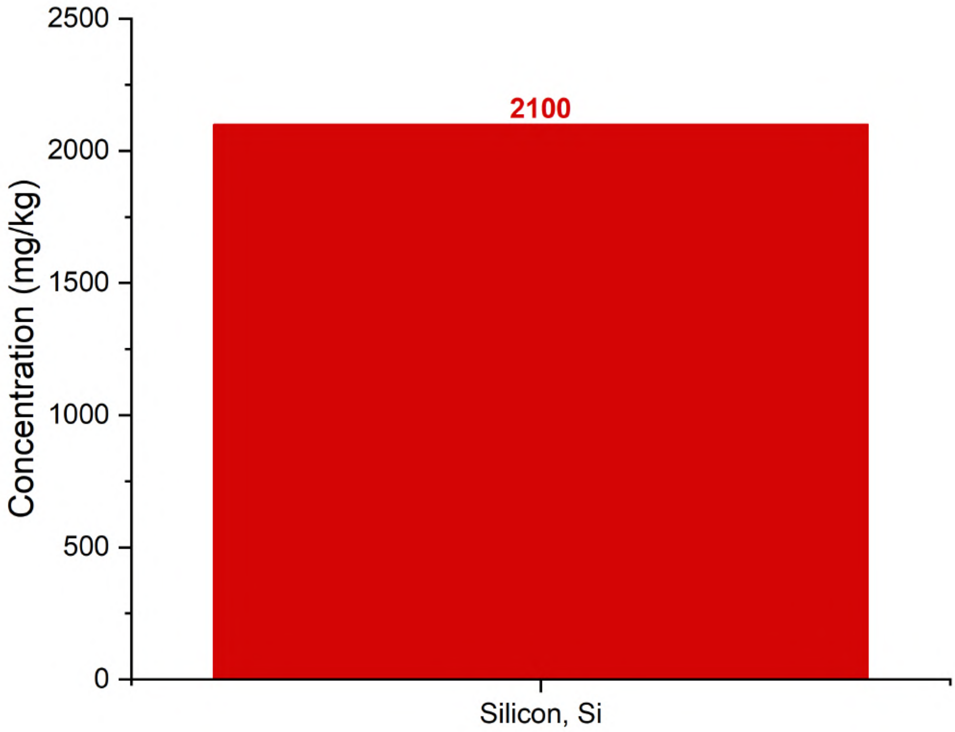


Figure 4.4.2: ICP of Isolated Red Pigment

The detection of silicon in the ICP suggests the presence of silicon-containing compounds in the pigment formulation. Silicon, present as silica SiO_2 , is a common additive in red pigments.[40] Based on the information from the FTIR and ICP, we can speculate the red pigment may contain organic pigments with aliphatic ketone groups and alkane chains, combined with silicon-containing compounds, such as an organo-silicon pigment. It could be a diketopyrrolopyrrole (DPP).

This conclusion is further strengthened by our observation that the red pigment undergoes degradation during alkaline hydrolysis. DPP is thermally stable but does not react well with acid and base.

Proposed Chemical Class of the Red colourant: DPP

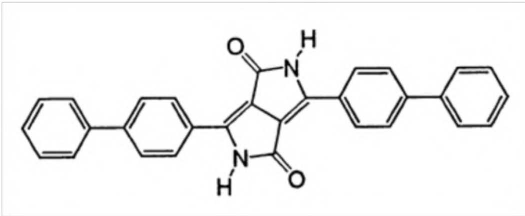


Figure 4.4.3: DPP - pigment red 264[41]

4.5 Yellow Colourant Analysis

4.5.1 Chemical Structure Analysis

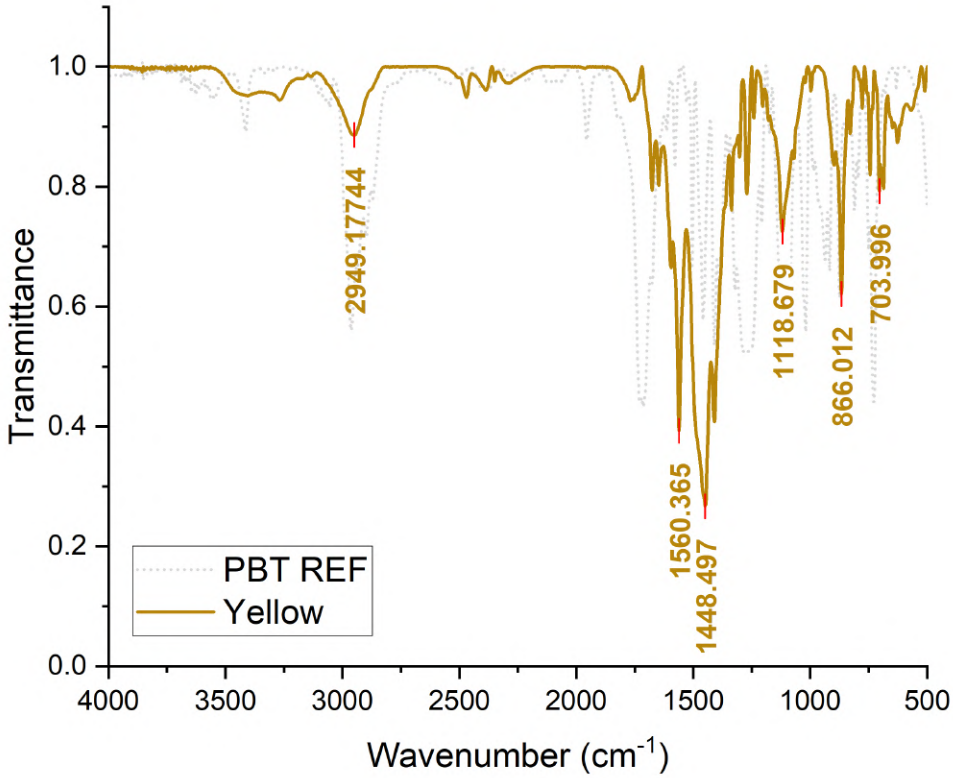


Figure 4.5.1: FTIR of Isolated Yellow Pigment

Wavelength	Vibration Type	Assignment
2949.17744	C-H stretching	Alkane
1448.497	C-H bending	Alkane
1118.679	C-O stretching	Ether
866.012	C-H bending	Aromatic Ring

The yellow pigment contains aliphatic hydrocarbons, ether linkages and aromatic rings in their chemical structure.

4.5.2 Elemental Analysis

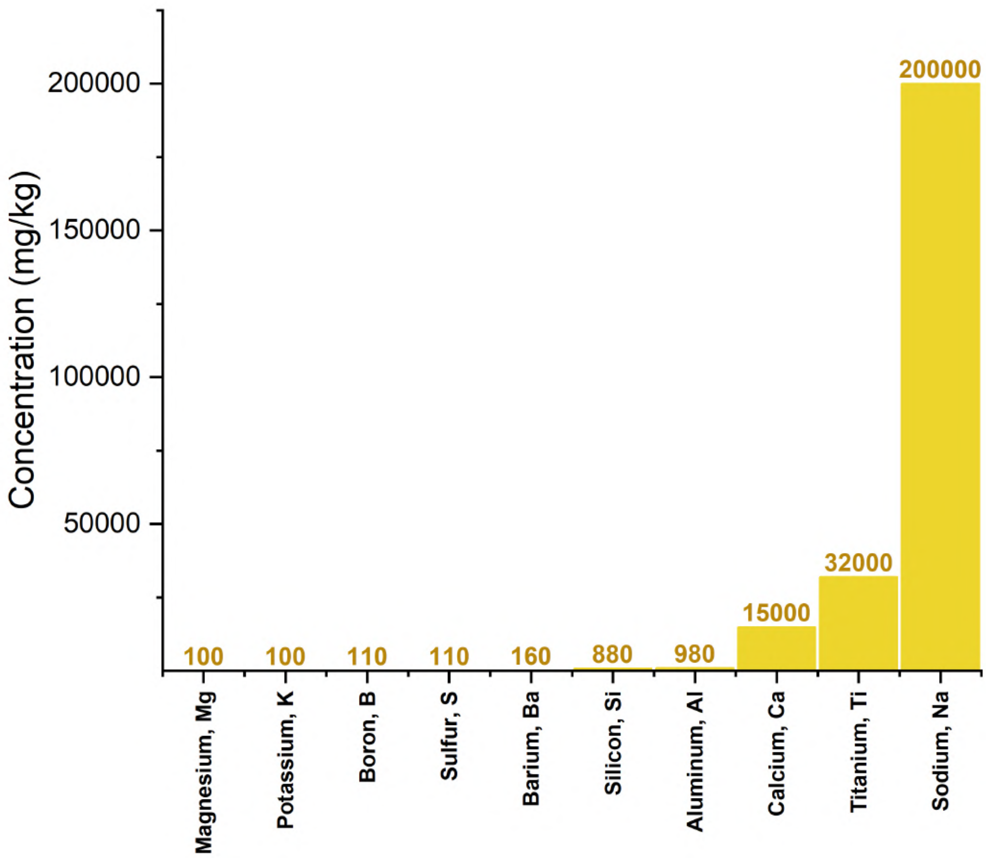


Figure 4.5.2: ICP of Isolated Yellow Pigment

ICP suggests the presence of Titanium which could indicate the potential use of titanium dioxide (TiO2) as an inorganic pigment or additive in the yellow pigment formulation.

While further analysis would be needed to confirm the exact pigment composition, azo pigments or mixtures containing azo pigments along with titanium dioxide could be potential candidates based on the inferred data.

Proposed Chemical Class of the Yellow Colourant: Azo Pigment

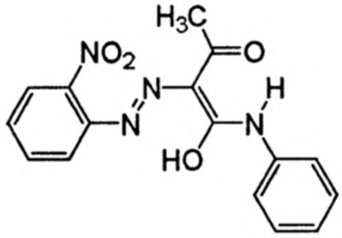


Figure 4.5.3: DPP [22]

4.6 Comparison of Chemistries

DPP (red) and phthalocyanine (blue) are organic pigments, Azo can be found both as pigments and liquid dyes.

Assuming that it is DPP and phthalocyanine that are seen for the red and blue, respectively, several investigations can be made regarding their recycling behaviours. If the recycling could be attributed to a physical property such as particle size, it would be expected that both red and blue should be filtered off. However, red persists. This could be due to the difference in chemical properties of DPP and phthalocyanine.

DPP is known to be more polar compared to phthalocyanine, and this polarity could facilitate hydrogen bonding with BHET (Bis(2-hydroxyethyl) terephthalate). This suggests that DPP might be dissolved in BHET or form strong intermolecular connections, preventing it from being filtered off as easily as phthalocyanine.

When treated with carbon black, the red colourant appears to be adsorbed onto the carbon black particles. This adsorption mechanism can be attributed to the interactions between the aromatic rings of DPP and the aromatic structures in carbon black, leading to the red pigment being effectively removed from the solution.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

A comprehensive analysis was conducted on the four distinct colours (Blue, Grey, Red and Yellow). It yielded valuable insights into their chemical composition and properties. The glycolysis process effectively depolymerized the PET pellets into BHET, with high yields observed across all colours, indicating the viability of dope-dyed PET as a feedstock for BHET production. However, no significant differences were observed in the yield of BHET among the different colours, suggesting that the dye structure does not influence the glycolysis process.

DSC analysis confirmed the formation of pure crystalline BHET from the glycolyzed PET pellets, with characteristic endothermic peaks consistent with BHET melting points. FTIR spectroscopy revealed the presence of polyester with terephthalate in both the filter cake and BHET, indicating successful depolymerization of PET into BHET.

Colour analysis demonstrated significant improvements in the L* values of all colours, indicating enhanced optical properties comparable to industrial-grade BHET. The decolourization process further improved the L* values for the Red and Yellow samples, highlighting the effectiveness of colour removal and the enhancement of optical properties in the recycled BHET.

The FTIR and ICP analyses provided insights into the chemical composition of the isolated pigments. The presence of specific functional groups and elements suggested potential pigment compositions, such as phthalocyanine blue for the blue pigment and organosilicon pigment for the red pigment.

5.2 Future Work

Future research endeavours could focus on further optimizing the glycolysis process to enhance BHET yields and purity, potentially through the modification of reaction conditions or catalyst formulations. Investigating the influence of different dye structures on the glycolysis process could also provide valuable insights into the factors affecting BHET production from coloured PET pellets.

Extracting dyes from the filter cakes for potential reuse in textile dyeing processes represents a promising avenue for future research and application. Once the dyes are successfully extracted, their performance and compatibility with different textile substrates could be evaluated through dyeing experiments.

Additionally, deeper investigations into the chemical structures and properties of the isolated pigments could be conducted using advanced analytical techniques, such as NMR spectroscopy or mass spectrometry. This would enable a more comprehensive understanding of the molecular composition and functional groups present in the pigments, facilitating their characterization and potential applications in various industries.

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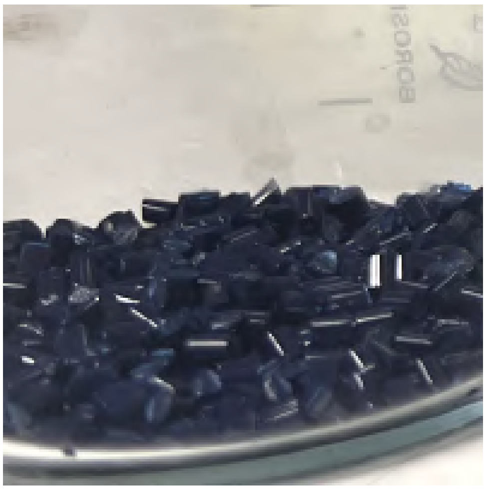
Chapter A

Appendices



(a) Blue PET

(b) BHET from glycolysis of Blue PET

Figure A.0.1: Images showing PET and corresponding BHET

(a) Yellow PET

(b) BHET from glycolysis of Yellow PET

Figure A.0.2: Images showing PET and corresponding BHET

(a) Red PET (b) BHET from glycolysis of Red PET

Figure A.0.3: Images showing PET and corresponding BHET

(a) Grey PET (b) BHET from glycolysis of Grey PET

Figure A.0.4: Images showing PET and corresponding BHET

Figure A.0.5: Image showing the hydrolysis setup

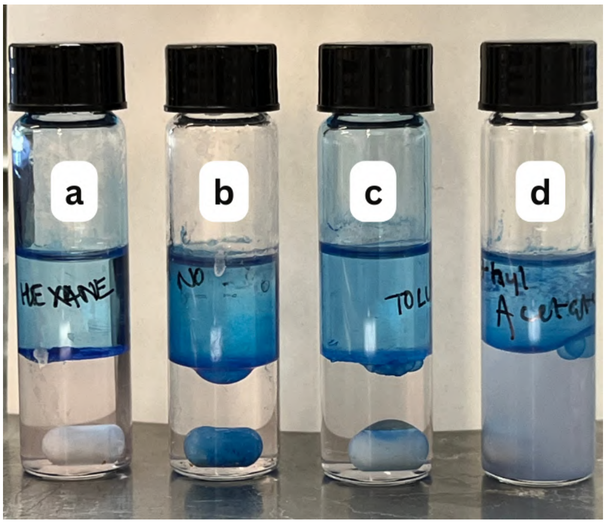


Figure A.0.6: Images showing liquid liquid extraction of hydrolysed masterbatch pellets product with a) hexane , b) butanol, c) toluene and d) ethyl acetate

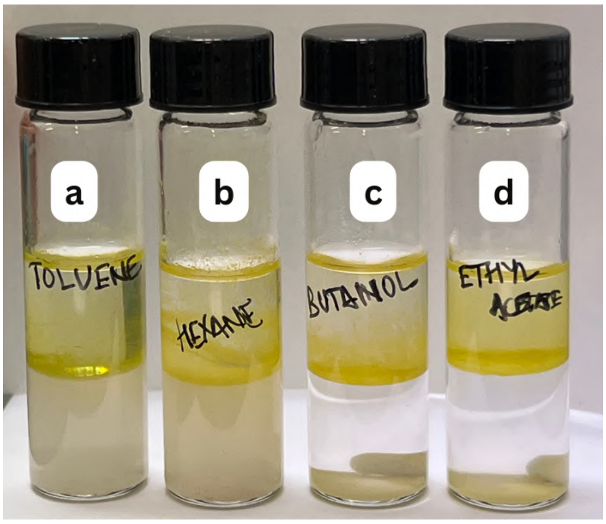


Figure A.0.7: Images showing liquid liquid extraction of hydrolysed masterbatch pellets product with a) toluene , b) hexane, c) butanol and d) ethyl acetate

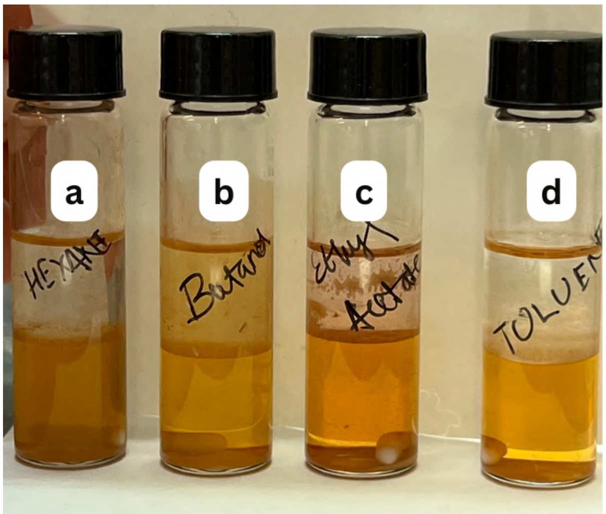


Figure A.0.8: Images showing liquid liquid extraction of hydrolysed masterbatch pellets product with a) hexane , b) butanol , c) ethyl acetate and d) toluene

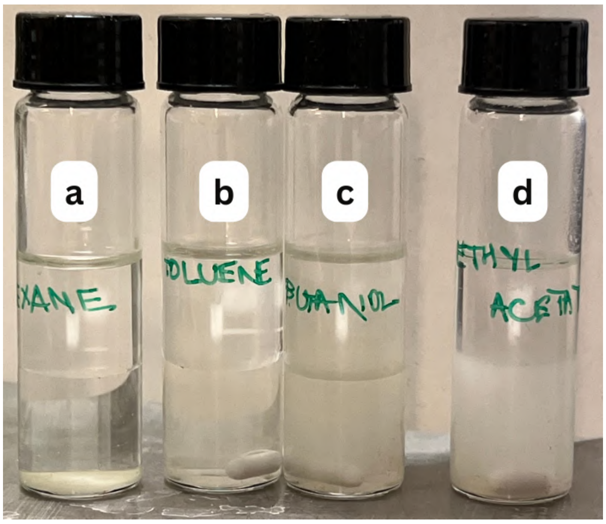


Figure A.0.9: Images showing liquid liquid extraction of hydrolysed masterbatch pellets product with a) hexane , b) toluene, c) butanol and d) ethyl acetate

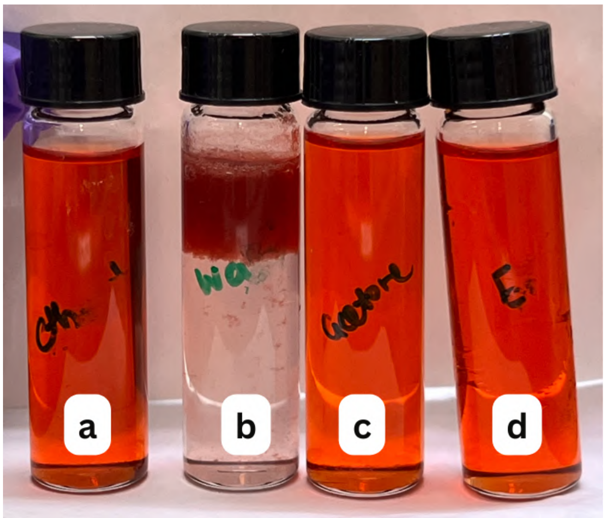


Figure A.0.10: Images showing efforts to leach colorants out of DMSO using a) ethanol , b) water, c) acetone and d) ethyl acetate

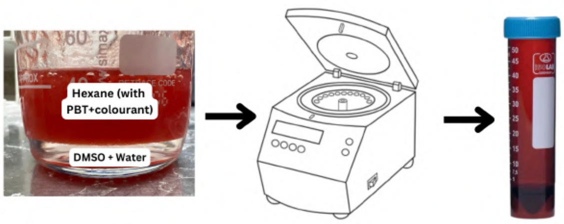


Figure A.0.11: Images showing DMSO dissolution process

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