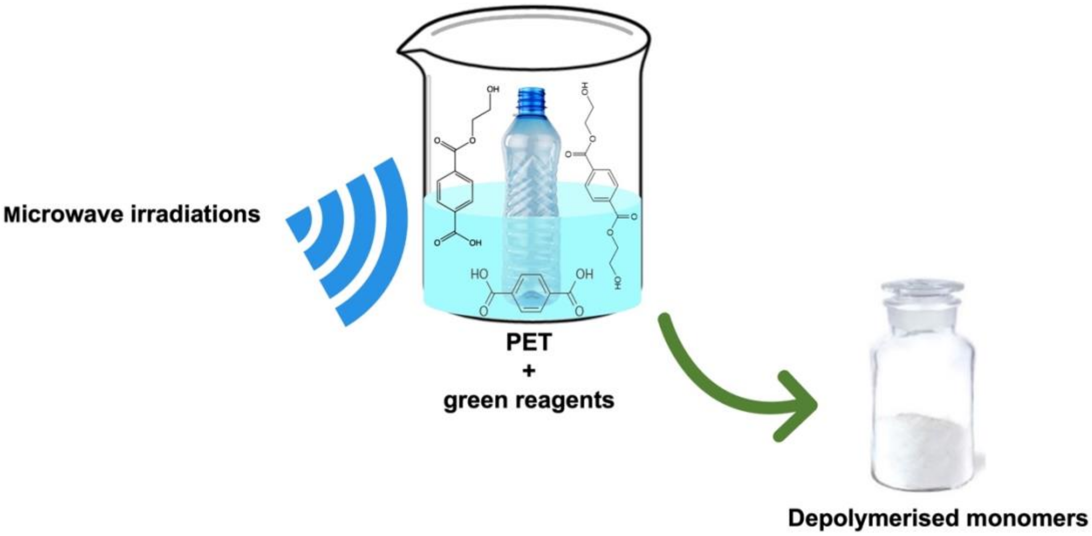
Deep Eutectic Solvents and Green Reagent Based Processes for Polyethylene Terephthalate Depolymerisation



Deep Eutectic Solvents and Green Reagent Based Processes for Polyethylene Terephthalate Depolymerisation

A thesis submitted for the degree of
Doctor of Philosophy
to the
Technological University of the Shannon
By
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Based on the research carried out under the supervision of
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PRISM Research Institute,
Technological University of the Shannon,
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Declaration

I hereby declare that this thesis submitted to the Technological University of the Shannon for the degree of Doctor of Philosophy, is a result of my own work and has not in the same or altered form, been presented to this institute or any other institute in support for any degree other than for which I am now a candidate.

19/09/2023

Muhammad Azeem

Date

"As a researcher, it's my duty to push the boundary of human knowledge forward."

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List of Abbreviations

PET	Polyethylene terephthalate
ANOVA	Analysis of Variance
DESs	Deep eutectic solvents
MW	Microwave
BHET	Bis(2-hydroxyethyl)terephthalate
EG	Ethylene glycol
TPA	Terephthalic acid
DEG	Diethylene glycol
ChCl	Choline chloride
MHET	mono-(2-hydroxyethyl) terephthalate
BBD	Box-Behnken Design
DEA	Diethanolamine
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
R^2	Coefficient of Determination
ICP-MS	Inductively coupled plasma-mass-spectrometry
KOH	Potassium hydroxide
APHA	American public health association
NMR	Nuclear magnetic resonance
FTIR	Fourier transform infrared
HPLC	High-performance liquid chromatography
TGA	thermogravimetric analysis
DSC	Differential scanning calorimetry
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
ASTM	American Society for Testing and Materials
Pt.Co	Platinum-Cobalt
DMAc	Dimethylacetamide
SDGs	Sustainable Development Goals
UN	United Nations

Abstract

Polyethylene terephthalate (PET) is a ubiquitous thermoplastic polymer which has numerous industrial applications including textile, construction, and packaging applications due to its versatile nature, transparency, strength, and barrier properties. According to recent studies, the production of PET is increasing at a growth rate of 8% per annum with of plastic waste rising to 8 million tons every year. It is therefore imperative to develop sustainable and scalable plastics recycling methodologies to reduce plastic waste accumulations stockpiles.

Recently enzymatic treatment methodologies have emerged as promising and environment-friendly techniques for efficient PET depolymerisation. Higher selectivity of desired monomers is achievable due to specific targeting enzymes. Considerable further research and development is required to overcome the enzyme costs, sensitivity limitations and long reaction times to become amenable to industrial-scale production. Chemical recycling of PET has advantages over other recycling techniques due to increased efficiency while utilising a wide range of PET waste products and converting them into primary building blocks that could be used in repolymerisation to make virgin PET. However, the usage of harsh solvents and longer reaction conditions restrict their large-scale applications. Therefore, it is important to develop a most efficient and industrial applicable PET depolymerisation techniques.

Deep eutectic solvents (DESs) are mixtures of different compounds with many applications in organic, analytical, and polymer chemistry fields. Recently, DESs were proposed as green catalysts in plastics chemical recycling and have shown remarkable potential as catalysts in PET depolymerization reactions. Microwave (MW) technology has been investigated as an efficient method for fast PET depolymerization reactions. The rapid heating achievable via MW while utilising DESs as model catalysts has allowed significant shortening of reaction times while delivering acceptable monomers conversion yields.

As there is insufficient knowledge in this area, this thesis aims to address PET waste pre-treatments and depolymerisation reactions under new and instant MW technology coupled with DESs. Three studies were carried out to investigate DESs based MW depolymerisation technology and are detailed in the appended papers. As this research work explores the ultra-green and sustainable depolymerisation methodologies for PET, **Paper I** demonstrates combined ultra-green chemical and biocatalytic depolymerization of PET using DES-based MW treatment followed by enzymatic hydrolysis. A green DES with a triplet composition of choline chloride, glycerol, and urea was selected for PET depolymerization under MW irradiation without the use of additional depolymerization agents. Under the optimized conditions of 20 mL DES volume, 260 W MW power, and 3 min MW irradiation time, a significant increase in the carbonyl index and PET percentage weight loss was observed. The combined MW-assisted DES depolymerization and enzymatic hydrolysis of the treated PET residue using LCC variant ICCG resulted in a total monomer conversion of ≈16% (*w/w*) in the form of terephthalic acid, mono-(2-hydroxyethyl) terephthalate, and bis-(2-hydroxyethyl) terephthalate. **Paper II** illustrates combined green and fast glycolysis-hydrolysis depolymerization of PET under MW with excellent efficiencies. In MW-assisted glycolysis of PET, the catalytic activity of two DES based on (choline chloride-urea (DES 1)) and (choline chloride-thiourea (DES 2)) was evaluated and compared. Optimised glycolysis conditions were determined using Box Behnken Design (BBD) to attain maximum weight loss of PET, low crystallinity and increased carbonyl index of residual PET.

DES volume of 4 mL, 5.5–6 mL of ethylene glycol, and 0.5 min MW irradiation time resulted in a prominent rise in PET weight loss and carbonyl index of residual PET. DES 2 showed an improved catalytic activity than that of DES 1 which is associated to its stronger interaction with EG and PET polymer chains during the course of the reaction. Residual PET obtained post glycolysis reaction was further depolymerized using MW assisted hydrolysis in the presence of weakly basic Na_2CO_3 and EG. Within 3-minute, the proposed sequential depolymerization technologies facilitated ≈99% conversion of PET to terephthalic acid (TPA), monohydroxyethyl terephthalate (MHET), and bis (2-hydroxyethyl) terephthalate (BHET) monomers produced at a yield of 62.79–80.66%, 17.22–34.79% and 0.54–0.59% respectively.

Paper III explains a highly efficient 2-step microwave-based (MW) degradation of PET. Initially, a MW-assisted pre-treatment was evaluated using glycerol as a non-toxic reagent for the conversion of PET into a modified form that makes it easily depolymerized. Box Behnken Design was employed to determine the optimised pre-treatment conditions attaining maximum PET weight loss and favourable crystallinity and carbonyl indices for the residual PET. Glycerol of 12 ml volume and 3 min of 182W MW irradiation resulted in 11% PET weight loss at onset temperature of degradation and gave rise to carbonyl index up to 4.22 and 33% crystallinity of residual PET. MW assisted hydrolysis of the pre-treated PET was then performed in the presence of sodium bicarbonate and ethylene glycol as depolymerizing agents. Within 3 min, the proposed depolymerisation methodology provided 99.9% conversion of PET into 79.1% terephthalic acid (TPA), 17.6% monohydroxyethyl terephthalate (MHET), and 1.8% bis (2-hydroxyethyl) terephthalate (BHET). The obtained TPA was separated from the monomers mixtures and its purification was evaluated via different characterization techniques against a standard TPA. A purity of 95%, 82.4 APHA colour value, 645.3 mgKOH/g acid number and acceptable heavy metal content indicated that the purified TPA can be repolymerized as virgin PET. Hence, MW-assisted DES technology is validated as an efficient process for boosting the depolymerisation of PET in an ultrafast and eco-friendly manner.

Key words: Depolymerization, Microwave, Deep eutectic solvent, Polyethylene terephthalate, Monomers, Recycling

Publication and Dissemination Record

List of Appended publications

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Azeem, M., Attallah, O. A., Tas, C. E., & Fournet, M. B. (2023). All Green Microwave Assisted 99% Depolymerisation of Polyethylene Terephthalate into Value Added Products via Glycerol Pre-treatment and Hydrolysis Reaction. *Journal of Polymers and the Environment*. https://doi.org/10.1007/s10924-023-02979-8

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Ferrero, P., Attallah, O. A., Valera, M. Á., Aleksic, I., **Azeem, M.**, Nikodinovic-Runic, J., & Fournet, M. B. (2022). Rendering Bio-inert Low-Density Polyethylene Amenable for Biodegradation via Fast High Throughput Reactive Extrusion Assisted Oxidation. *Journal of Polymers and the Environment*, *30*(7), 2837–2846. https://doi.org/10.1007/s10924-022-02400-w

Nikolaivits, E., Pantelic, B., **Azeem, M.**, Taxeidis, G., Babu, R., Topakas, E., Brennan Fournet, M., & Nikodinovic-Runic, J. (2021). Progressing Plastics Circularity: A Review of Mechano-Biocatalytic Approaches for Waste Plastic (Re)valorization. *Frontiers in Bioengineering and Biotechnology*, *9*(June), 1–31. https://doi.org/10.3389/fbioe.2021.696040

Pantelic, B., Araujo, J. A., Jeremic, S., **Azeem, M.**, Attallah, O. A., Slaperas, R., Mojicevic, M., Chen, Y., Fournet, M. B., Topakas, E., & Nikodinovic-Runic, J. (2023). A novel Bacillus subtilis BPM12 with high bis(2 hydroxyethyl)terephthalate hydrolytic activity efficiently interacts with virgin and mechanically recycled polyethylene terephthalate. *Environmental Technology & Innovation*, 103316. https://doi.org/https://doi.org/10.1016/j.eti.2023.103316

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Buckley, J., Araujo, J. A., Aribilola, I., Arshad, I., **Azeem, M.**, Buckley, C., Fagan, A., Fitzpatrick, D. P., Garza Herrera, D. A., Hyland, T., Imtiaz, M. B., Khan, M. B., Lanzagorta Garcia, E., Moharana, B., Mohd Sufian, M. S. Z., Osterwald, K. M., Phelan, J., Platonava, A., Reid, C., … Zainol, I. (2023). How transparent are quantitative studies in contemporary technology education research? Instrument development and analysis. *International Journal of Technology and Design Education*. https://doi.org/10.1007/s10798-023-09827-9

Conference Proceedings

Azeem, M. ’Adly A. O. ’Fournet, M. (2022). Enhanced Biodegradation of Polyethylene Terephthalate (PET) via Microwave-Assisted Green Bio-Based Deep Eutectic Solvent Pre-Treatment Technique . *2nd International Electronic Conference on Catalysis Sciences*. https://doi.org/10.3390/ECCS2021-11181

Attallah, O. ’ J. A. **’Azeem, M**. ’Fournet, M. (2022). Ultrafast, Optimized Hydrolytic Depolymerization of Polyethylene Terephthalate Using a Dissolution/Degradation Approach. *2nd International Electronic Conference on Catalysis Sciences*. https://doi.org/10.3390/ECCS2021-11111

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Azeem, M., Adly, Olivia, Fournet, M. B., Devine, D., (2023). In a sustainable way, we can cut the plastic away! In: TUS Athlone Research Day. Athlone, Ireland.

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Awarded grant to participate in one week training on “Circular Design with Plastics’ 2nd Edition in **2022**” at Polytechnic of Cávado and Ave, in Portugal.

Awarded grant to attend 5th Training School in **2023**, funded by the COST action CA18112 funding – “Scaling-up mechanochemistry in batch and by continuous flow mode” Max-Planck-Institut für Kohlenforschung, Mülheim, Germany.

Awarded grant to attend prestigious “green chemistry postgraduate school” in 2023, Venice, Italy.

Chapter 1. Introduction

1.1 Thesis Structure

This thesis comprises six chapters, starting with an introductory chapter, that offers a concise summary of the research challenge and proposed solution. The introduction section (Chapter 1) contains the overall context to the thesis and outlines the research aim, questions, and objectives. The literature review section (Chapter 2) presents the background of relevant research which underpins this study. Chapter 3-5 constitute the appended papers of this thesis (Figure 1-1). These chapters contain works from the following three published articles:

Attallah, O. A[#]., **Azeem, M**[#]., Nikolaivits, E., Topakas, E., & Fournet, M. B. (2022). Progressing ultragreen, energy-efficient biobased depolymerization of poly(Ethylene terephthalate) via microwave-assisted green deep eutectic solvent and enzymatic treatment. In *Polymers* (Vol. 14, Issue 1). https://doi.org/10.3390/polym14010109

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Azeem, M., Fournet, M. B., & Attallah, O. A. (2022). Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation. *Arabian Journal of Chemistry, 15*(7), 103903. https://doi.org/10.1016/j.arabjc.2022.103903

Azeem, M., Attallah, O. A., Tas, C. E., & Fournet, M. B. (2023). All Green Microwave Assisted 99% Depolymerisation of Polyethylene Terephthalate into Value Added Products via Glycerol Pre-treatment and Hydrolysis Reaction. *Journal of Polymers and the Environment*. https://doi.org/10.1007/s10924-023-02979-8

Chapter 3-5 comes with a preface section which is used to link the chapters and provide a summary of each chapter. Finally, in the conclusion section (Chapter 6), an overall summary of the research achievements is presented. It also presents the limitations and future considerations for advancing explorations in this research area. The contribution of the candidate to the appended papers is determined below;

- Conceptualization
- Methodology
- Software
- Formal analysis
- Investigation
- Data curation
- Writing—original draft preparation

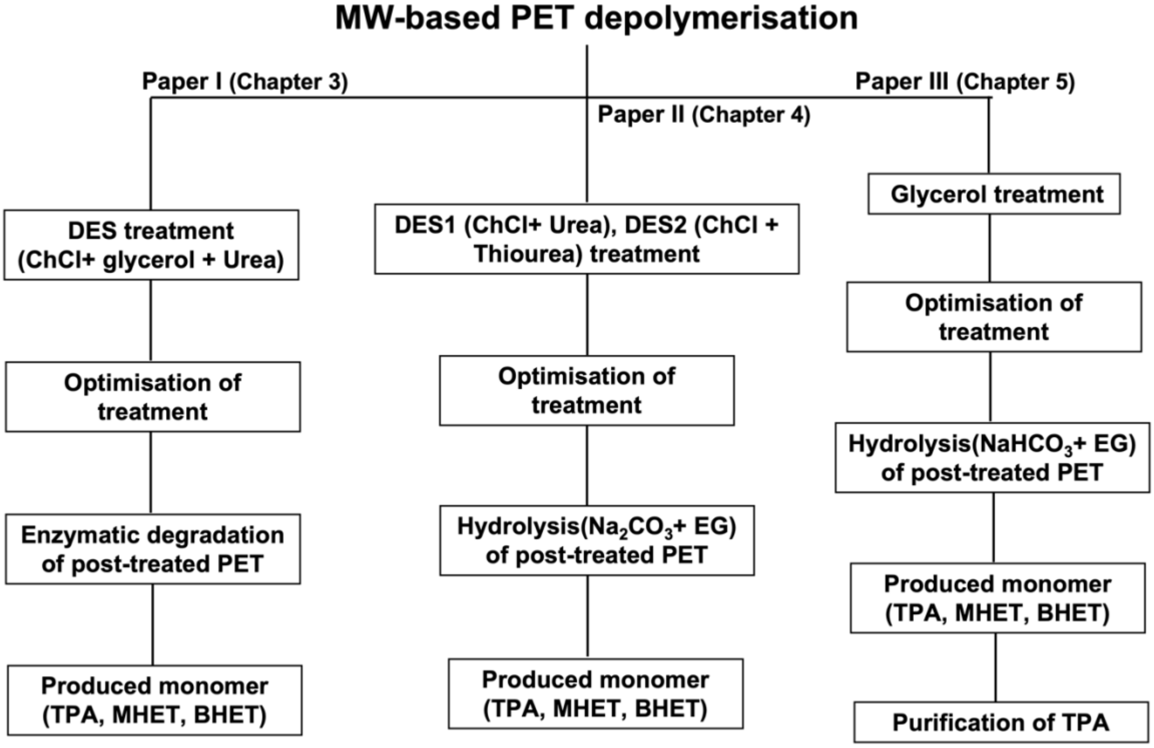

Figure 1-1 The proposed layout of the research.

1.2 Research Challenge

The prosperity of planet Earth is recognized as the foundation for the well-being of its populations. Global resource consumption rates are currently increasing to degrees that would require the equivalent of almost three planets to sustain current lifestyles by 2050. Resource extraction and processing produce almost half of current greenhouse gas emissions and are responsible for more than 90% of biodiversity loss and water stress. This coincides with predictions that global waste production is to increase by 70%. Plastic, which is primarily processed from fossil fuel resources, is a ubiquitous and indispensable material in the world economy and our daily lives, providing both high-performance energy-saving benefits along with alarming pollution and waste stockpiles.

Polyethylene terephthalate is a high-performance thermoplastic polymer with excellent physical and chemical properties. The global production of PET was approximately 74 million tonnes by the end of 2020, with the largest part of its production being used for water bottles and food or drink packages(Danso et al., 2018) . Specifically, more than 480 billion bottles were produced worldwide in 2015, a number that is predicted to exceed 580 billion by 2021(Choudhary et al., 2019). Despite the fact that PET is a fully recyclable polymer, less than 28% of PET bottles were recycled in the United States in 2018, while 57% of the produced bottles were disposed of in landfills (Worch & Dove, 2020).

It is now widely recognized that changing from linear consumption and transitioning to sustainable growth models is essential to safeguard the planet and its populations. The development of new regenerative technologies is essential to eliminate the indelible imprint of pervasive plastic, to deliver plastics circularity, and to secure the future prosperity of the planet and its inhabitants.

Therefore, it is imperative to develop innovative, ultra-green, and sustainable recycling technologies to enable PET plastic circularity.

1.3 Solution Proposed

In order to tackle the challenges of recycling waste PET plastic, which is one of the most consumed plastics, a green solvent based depolymerization approach is proposed which dramatically accelerates the depolymerization process from hours to minutes. This new class of green solvents encompasses deep eutectic solvents (DESs) and ultra-green reagents which were assessed under microwave irradiation to initiate instantaneous glycolysis/hydrolysis of PET. This was greatly enhanced by the excellent microwave absorption properties of these solvents facilitating green and ultrafast PET depolymerization into its monomers TPA, MHET, and BHET. The evaluation of these solvent systems was carried out to address microwave-based efficient PET pre-treatment/chain scissions challenges under milder reaction conditions to make PET amenable to enzymatic degradation or chemical depolymerization. The yield of the produced monomers was optimized using the Box-Behnken design which is an experimental design used to optimize the process response that depends on several variables or factors. Moreover, separation/purification of monomers was carried out to ensure that they could be used in the repolymerization of virgin PET or other bioproducts. This will help in preserving precious fossil fuel resources that are currently used in plastic production and mitigate PET plastic imprints from the environment. This research will have a great impact on achieving plastic circular economy targets, as it focuses on the combined ultra-green chemical and biocatalytic depolymerisation of polyethylene terephthalate using recently emerged biodegradable and unique biologically compatible solvent-based low-energy microwave treatments followed by enzymatic/chemical hydrolysis.

1.4 Research Aim

This research aimed to demonstrate how PET plastic waste can be efficiently transformed into value added monomers/products by developing effective pre-treatment processes based on microwave technology.

1.5 Research questions

The determination of the effect of MW based PET pre-treatments in the presence of DESs and other green reagents could have a great impact on the recycling of plastics. The monomers (TPA, MHET, BHET) produced through these efficient and eco-friendly methods could be utilised in the repolymerisation of virgin PET and other bioproducts. This thesis aims to explore sustainable and environmentally friendly options for PET recycling, therefore, the following research questions were identified and addressed:

RQ1. Can new DES formulations act as optimised energy-efficient and greener solvents for plastic pre-treatments?

RQ2. Can new innovative green pre-treatment processes facilitate efficient biocatalytic depolymerisation?

RQ3. Can high recovery of monomers or lower molecular weight compounds from depolymerisation be used as feedstocks to generate new high-performance polymers or bioproducts?

1.6 Research objectives

In an effort to address the above-motioned questions and achieve the research aim, the research work of this thesis proposed the following:

1. Designing and developing green DESs and to assess and enhance their efficiency in plastic pre-treatments for depolymerization reactions.

2. Establish optimized MW-assisted DES pre-treatment methodologies for improved biocatalytic depolymerization using selected enzymes.

3. Recovery of monomers and lower molecular weight products from optimized pre-treatment/depolymerization reaction systems and purification of depolymerized products to form feedstocks for the regeneration of PET and for the generation of new high-performance polymers or bioproducts.

Chapter 2. Literature Review

2.1 Recycling and its types

The recycling of plastics can reduce waste, conserve natural resources, and reduce the environmental impact of plastic production on the environment. For a sustainable future, it is crucial to recycle plastic products and to support recycling initiatives. PET recycling can be classified into four major approaches; which are: primary, secondary, tertiary, and quaternary approaches(Singh et al., 2017a), as shown in Figure 2-1.

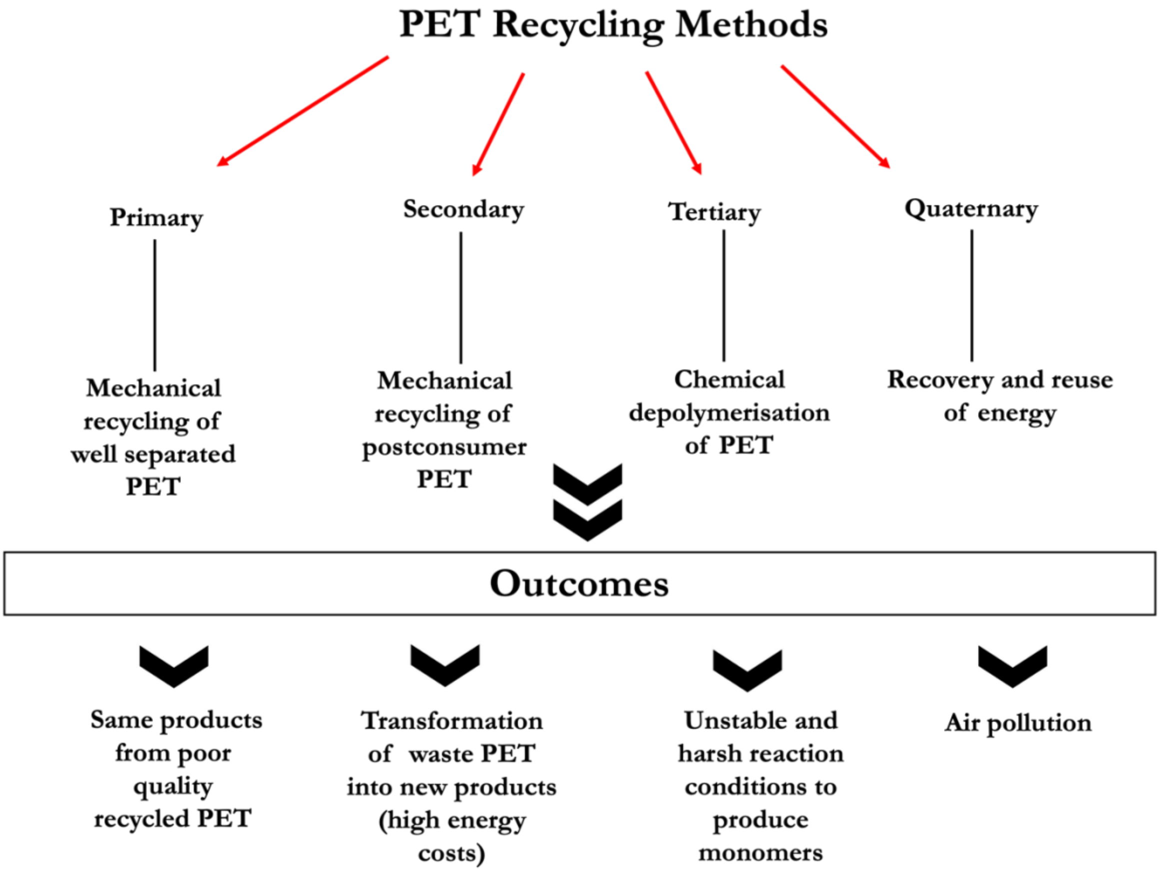

Figure 2-1 Classification of PET recycling.

Recently, Biological recycling has achieved several breakthroughs for enzymatic treatments particularly the depolymerization of PET into basic monomers which is discussed in more depth in the following section (Bio recycling). Each recycling methodology has its own pros and cons. Typically after recycling processes, polymer materials tend to lose some of their characteristics like transparency, wear resistance, and mechanical strength. The following section elaborates some of the above-mentioned recycling techniques.

2.1.1 Primary recycling

This type of recycling is also called re-extrusion (Al-Salem et al., 2009) which is the oldest recycling methodology. This technique also known as closed loop processing, in which single kind of uncontaminated polymers are recycled(Sachin Kumar Achyut K. Panda, 2011). The utilisation of scrap plastics having similar characteristics to those of their initial products is a key factor in this type of recycling(Singh et al., 2017a). This is only feasible with when clean or semi-clean scrap is effectively separated out from contaminations. The simplicity, low cost, and ease of using this technique, coupled with the ability to convert plastic waste into original quality products, makes it favourable among different manufacturers(Kosloski-Oh et al., 2021).

2.1.2 Secondary recycling

Primary and secondary recycling methods are connected to mechanical recycling which involves recycling via mechanical means(Mastellone, 1999).Both are largely applied and commercialised techniques(Al-Salem et al., 2010). However, in secondary recycling, the conversion of materials into low grade or fewer demanding products is carried out by mechanical means(Sachin Kumar Achyut K. Panda, 2011). After separating the polymer and contaminants, the polymers are reprocessed into granules. The typical steps involved in secondary recycling include pre-washing and drying to remove glued contaminants. Then, size reduction, sorting, and contaminants separations are carried out. After these preliminary steps, one type of material is extruded by heat and reformed to get a granulated form. Further, the final product is collected and used in the production of low-stream products after the addition of certain additives and pigments (Aznar et al., 2006) (Clark et al., 1999), (Al-Salem et al., 2009).Click or tap here to enter text. Certain limitations of secondary recycling include heterogenous nature of plastics waste and the gradual decrease in the quality of the product due to application of high temperature in extrusion process which develops mechanical stresses and photooxidation reactions which could lead to decline product’s characteristics.

2.1.3 Tertiary recycling

Primary and secondary recycling methods are industrially well established and developed methods. However, identification and sorting of materials can be challenging sometimes. Similarly in order to make primary and secondary recycling efficient, getting decontaminated polymers and homogenous plastic waste makes the whole recycling process difficult (Sadat-Shojai & Bakhshandeh, 2011). Furthermore, these recycling techniques do not fulfil the criteria of sustainable developments. Tertiary recycling which is often referred to chemical recycling is a well-established method of recycling and only one which is completely aligned with goals of sustainable development, as it enables the generation of main building block monomers from postconsumer plastics waste that could be used again to synthesize same polymers(Achilias & Karayannidis, 2004).& Karayannidis, 2004).

Tertiary recycling involves various recycling methods including gasification, pyrolysis, cracking and chemolysis. Recycling involves recovery of monomers via depolymerization process. Chemical and thermal recycling are subcategories of tertiary recycling in which means of depolymerization reaction is chemical based (solvolysis) or heat based (thermolysis)(Singh et al., 2017b).

2.1.4 Quaternary recycling

After going through a number recycling cycles via primary, secondary, and tertiary recycling, plastics properties gradually deteriorate. Herein, quaternary recycling is employed as an alternative to landfills, which demonstrate recovery of energy from waste plastics by incineration(Subramanian, 2000). This technique helps to reduce waste volumes, where remaining residue can be disposed of through landfilling. However, this recycling technique involves emissions of hazardous gases and air pollutants that could potentially damage the ecosystem. Therefore, certain methods like membrane filtration, flue gas cooling, addition of activated carbon, and acid neutralization are used to overcome emissions of pollutants(Yassin et al., 2005).

2.2 Chemical recycling of polyesters (PET) in general

Chemical recycling has been extensively studied and well-established method for the depolymerisation of polyesters that contain carbonyl bonds which can be easily targeted by nucleophilic attack that yield smaller molecules of amides or esters. PET (Figure 2-2) is the most commonly used polyester with overall 38% consumption of the total plastics packaging production worldwide reported in 2015(Rabnawaz et al., 2017).

In a typical industry, PET is synthesized in a four stages process. In the first stage process, bis(2- hydroxyethyl) terephthalate (BHET) is generated by esterifying ethylene glycol (EG) with terephthalic acid (TPA). The second and third stages involve pre-polymerization of PET and then melt condensation to produce lower number average molecular weight which could be used in applications of PET fibers(Payne & Jones, 2021). In the final stage, solid state polymerisation is employed to get high number average molecular weight PET which could be used in applications of drinking bottles(Pavel & Awaja, 2005).

Conventionally, TPA and EG are derived from petroleum which are used as feedstock in the synthesis of PET. Recently biobased PET synthesis has drawn attention towards circularity but process complexations in extracting EG from biomass restrict large scale production of 100 % bio-PET(Lamberti et al., 2020).

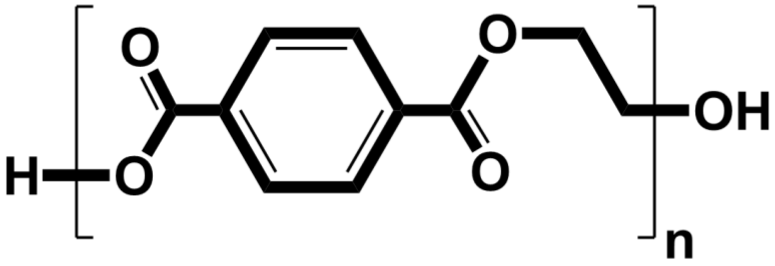

Figure 2-2 Structure of PET polymer.

Chemical recycling seems a viable solution to sustainable routes with considerable benefits over conventional recycling methods for the achievement of circular economies for PET. This technology has the potential to produce original monomers in total depolymerisation and other value added products or oligomers in partial depolymerisation and reduce dependance on petroleum-based feedstocks(George & Kurian, 2014). When carbonyl group of PET is exposed to certain reagents, The cleavage in carbonyl group can be carried out in the presence of reagents such as alcohols, glycols, water, acids and amines(Carta et al., 2003).

Three reversible reactions are involved in depolymerisation of PET. Initially, the carbonyl oxygen in PET polymer chain is converted into a second hydroxyl group due to rapid protonation. Then, protonated carboxyl carbon atom is attached by hydroxyl oxygen (from the newly added hydroxyl containing molecule). Finally, the carbonyl oxygen which was converted to hydroxyl group in the first step along with proton are removed which results in the formation of a simple alcohol or water and the catalytic proton(Patterson et al., 2007). As illustrated in Figure 2-3, PET depolymerisation can be classified in five main types which depend on the solvent system used in reaction.

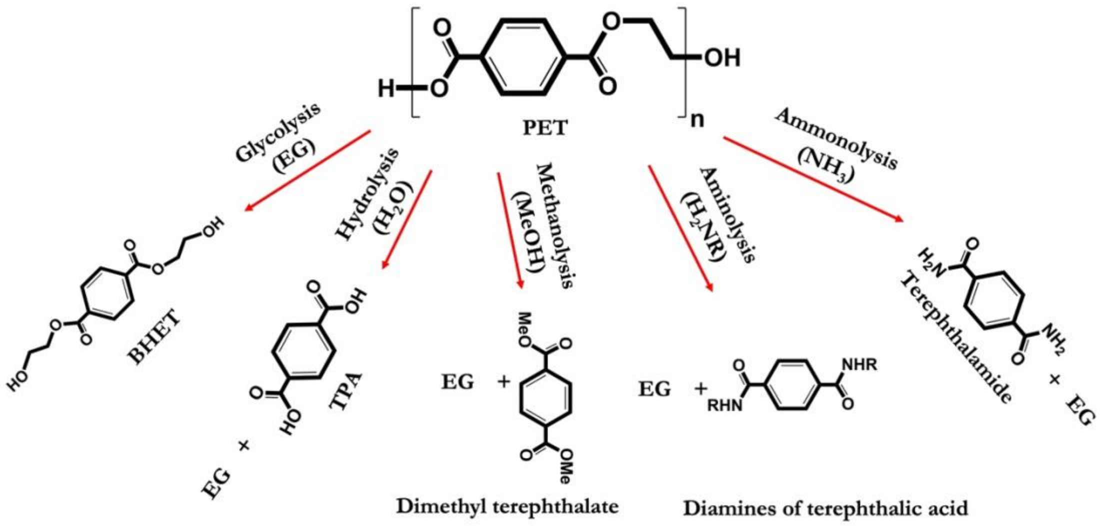

Figure 2-3 Various PET depolymerization techniques under chemical recycling.

Method involving glycols as solvent is termed as glycolysis and BHET is produced as a depolymerisation product of PET. Similarly, methanol and water solvents-based methods are called methanolysis and hydrolysis which produce dimethyl terephthalate and TPA respectively(Azeem et al., 2022a)(Bartolome et al., 2012). Several research publications have been carried out on the advancement in these chemical recycling methods. We will be focusing on evaluating the catalysts systems and technologies in terms of reactions times and selectivity.

2.2.1 Ammonolysis

In PET ammonolysis, liquor ammonia is employed at a certain temperature (70-180^{0}C) and pressure (2 MPa) in the presence or absence of a catalyst such as zin acetate(Sinha et al., 2010). The primary depolymerization products are terephthalamide (1,4-benzene dicarboxamide) and EG. Low pressure ammonolysis can also be conducted using ammonia coupled with EG in the presence of 0.05% zinc acetate. By utilising a ratio of 1:6 of PET/NH_3, 87% yield of terephthalamide was obtained(Sinha et al., 2010). This recycling method could not gain much success due to harsh reaction conditions and commercial scaleup limitations.

2.2.2 Aminolysis

Currently, there are no industrial applications observed for PET aminolysis. However, this recycling technique is employed to enhance PET properties such as coloration of fibers in fiber production with certain processing characteristics(El Mejjatti et al., 2014). Aminolysis can be carried out with or without adding a catalyst. Aqueous solutions of primary amine including methylamine, ethanolamine, anhydrous n-butylamine, and ethylamine are used commonly in aminolytic chain scission reaction producing diamines of TPA and EG. The reaction conditions of aminolysis are milder as compared to ammonolysis(Payne & Jones, 2021). Aminolysis of PET has broad range of applications including utilization in antibacterial drugs, polyurethane foams, and adhesion accelerators(George & Kurian, 2014)(Spychaj et al., 2001).et al., 2001).

2.2.3 Methanolysis

In methanolysis recycling method, PET is depolymerized into dimethyl terephthalate and EG. This technique is promising and ideal as the end product (dimethyl terephthalate) can be used again to generate raw virgin PET and solvent used (methanol) can be recycled. PET

methanolysis reactions requires elevated temperature (18-280^{0}C) and pressures (2-4 MPa) conditions to produce dimethyl terephthalate and EG(Payne & Jones, 2021).
Limitations to this recycling method include difficulties in separating and purifying reaction products mixtures. Moreover, water contamination could poison catalyst used and generate different azeotropes. Therefore, most of the companies are encouraged to produce TPA instead of dimethyl terephthalate(Al-Sabagh et al., 2016).

2.2.4 Glycolysis

The PET glycolysis recycling method is conducted with a glycol such as EG to generate BHET and some other intermediate products. The generated BHET by glycolysis can be used with virgin BHET to produce PET. These depolymerised products can be used to synthesise polyurethane foams, polyesters, acrylic coatings, and hydrophobic dyes(Bartolome et al., 2012). A number of well-known and prominent companies including Shell, Eastman Kodak, and Dupont has been already using PET glycolysis(George & Kurian, 2014). Some other important reagents such as di/triethylene glycol(Öztürk & Güçlü, 2004)(Nikje & Ghamary, 2015), 1,4-butane-diol(Kulkarni et al., 2004), and propylene/dipropylene glycol(Vaidya & Nadkarni, 1988) may be used in PET glycolysis, and propylene/dipropylene glycol(Vaidya & Nadkarni, 1988) may be used in PET glycolysis.

Previously reported studies on PET glycolysis kinetics (Table 2.2-2.4) have shown that reaction performance is too slow and incomplete depolymerisation occurs without adding any catalysts(J. Chen & Chen, 1999). Sometimes end products contain mixture of oligomers which makes it challenging to separate them from each other. Therefore, it is essential to resolve issues related to toxicity, leftover impurities in BHET, and environmental impact by developing advanced catalytic systems. The most common catalytic systems used for glycolysis reaction are mentioned below;

Table 2-1 Metal catalyst-based PET glycolysis conditions.

Catalyst	EG: PET ratio	Time	Temperature (ºC)	Catalyst weight %	BHET yield (%)	PET conversion (%)	Reference
Zinc acetate	5 (w/w)	180 min	196	0.01	85.6	-	(Xi et al., 2005)
Manganese acetate	2:1 w/w)	2.5 h	190	2.5	-	100	(C. H. Chen, 2003)
Sodium carbonate	6 (mol/mol)	480 min	190	0.005	61.5	-	(Shukla & Kulkarni, 2002)
Cobalt acetate	2:1 w/w)	1.5 h	190	2	65.72	-	(CHEN & C.-Y CHEN, YU-WEN LO, CHING-FENG MAO, 2001) (C. Chen et al., 2001)

Table 2-2 Heterogenous catalysts-based PET glycolysis conditions.

Catalyst	EG: PET ratio	Time	Temperature (ºC)	Catalyst weight %	BHET yield/selectivity (%)	PET conversion (%)	Reference
β-Zeolite	6:1	8 h	196	1	66	-	(Shukla et al., 2008)
γ-Zeolite	6:1	8 h	196	1	65	-	(Shukla et al., 2008)
Ostrich eggshells	15:1	2 h	192	1	76.41/isolated yield	-	(Yunita et al., 2019)

Table 2-3 Nano-catalysts-based PET glycolysis conditions.

Catalyst	EG: PET ratio	Time	Temperature (ºC)	Catalyst weight %	BHET yield (%)	PET conversion (%)	Reference
Magnesium oxide on silica nanoparticle	11 (mol/ mol)	80 min	300	0.005	~85	-	(Imran et al., 2010)
Zinc oxide on silica nanoparticle					>90		
Titanate Nanotubes Modified with Zinc	4:1	180 min	196	0.3	87/ isolated yield	>99%	(Lima et al., 2019)

2.2.5 Hydrolysis:

Hydrolysis involves the recovery of TPA and EG from PET depolymerisation under neutral, acidic, and alkaline environment which can be repolymerise again to synthesise virgin PET. In addition, this technique can also be employed to produce more valuable chemicals like oxalic acid(Yoshioka et al., 2003). Hydrolysis usually requires harsh operating conditions (higher temperature and pressure). Another difficult is the recovery and separation of TPA from other products which requires additional steps to get the desired purity of TPA monomer. Acid hydrolysis is typically carried out with acids such as concentrated H_2SO_4, HNO_3 and H_3PO_4(George & Kurian, 2014)(Sinha et al., 2010)(Haith, 2005). One significant limitation of acid hydrolysis is generation of high corrosions and bulk quantities of aqueous and inorganic wastes. In alkaline hydrolysis, PET depolymerisation is conducted in a solution of NaOH or KOH to from corresponding disodium or dipotassium salts of TPA and EG(Sinha et al., 2010) followed by precipitation of TPA or neutralisation of disodium or dipotassium salts by quenching of reaction with strong acid such as HCL and H_2SO_4. This is also called aqueous alkaline hydrolysis due to presence of alkaline aqueous solutions. Non-aqueous, hydrolysis of PET relies on ether solvents (dioxane , tetrahydrofuran) in combination with methanol(Shukla & Mathur, 2000), ethanol, EG(Oku et al., 1997) , and methyl cellosolve(Karayannidis et al., 2002). This approach is useful in handling highly contaminated waste PET such as metallised PET. The main advantage of using these kinds of solvents in this method for PET depolymerisation significantly reduce the operating temperatures (60-80 °C) as compared to typical glycolysis reaction temperature (>150 °C).

Neutral hydrolysis of PET is carried out in steam or water in the presence or absence of a transesterification catalyst such as metal salts(Paszun & Spychaj, 1997). This process involves high pressure and/or temperature conditions. This method addresses problems associated with equipment corrosions using alkaline hydrolysis. However, extra purification steps for desired purity of TPA, increase the process cost and make it complex. This process involves high pressure and/or temperature conditions. This method addresses problems associated with equipment corrosions using alkaline hydrolysis. However, extra purification steps for desired purity of TPA, increase the process cost and make it complex. The most common catalytic systems used for hydrolysis reaction are mentioned in Table 2-4;

Table 2-4 PET hydrolysis conditions using different solvents.

Catalyst	Time	Catalyst to PET ratio	Temperature (°C)	Pressure	TPA yield (%)	Reference
Zinc acetate	30 min	1.5%	240	3.2 MPa	90.5	(Y. Liu et al., 2012)
$ZnCl_2/H_2O$	8 h	70%	180	-	98.31	(Y. Wang et al., 2019)
$[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$	2 h	7 wt%	145	-	100	(L. Zhang et al., 2013)

2.2.6 Bio recycling

The biodegradation of PET is the most studied of all the recalcitrant polymers. One of the first reports on microbial PET degradation was in 1982 by surgeons who noticed the loss of tensile strength and decrease of molecular mass in bacterial-infected PET implants from patients(Gumargalieva et al., 1982). Since much progress has been made in the discovery of microorganisms and enzymes that can efficiently hydrolyse PET. Kawai et al. differentiated PET-hydrolysing enzymes to PET-modifying and PET-degrading enzymes(Kawai et al., 2019). This is an important categorization, as not all PET-hydrolysing enzymes can be used for the complete degradation of PET into its monomers.

Enzymes that can modify PET's surface are very useful as catalysts, particularly for the textile industry and enhancing the properties of polyester fabrics (Kanelli et al., 2015)(Araújo et al., 2007)(J. Zhang et al., 2004). Surface hydrolysis is the desirable outcome, in order to generate functional groups, without affecting the bulk properties of the polymer.

In the early years of PET-biodegradation research, cutinases were identified as key enzymes that were suitable for this challenging task(Ronkvist et al., 2009), since these enzymes' natural action is to degrade the plant polyester cutin. Cutinases are serine esterases of the α/β hydrolase family, with their nucleophilic serine exposed to the solvent (unlike lipases) and a flexible active site(Nikolaivits et al., 2018).

Up until 2015 the arsenal of cutinases and other esterases that were able to degrade PET had become richer, comprising of bacterial and fungal enzymes, most deriving from the actinomycete genus *Thermobifida* (Zimmermann & Billig, 2011)(Kawai et al., 2014) (Table 2-5). In 2016, however, Yoshida et al. reported the discovery of a bacterium originating from a PET-contaminated site, which could assimilate the material after depolymerizing it(Yoshida, 2016). Most recently, Tournier et al. developed LCC variants which showed breakthroughs in PET degradation on an industrial scale. Influenced from this literature, LCC variant ICCG enzyme was selected for enzymatic degradation of PET(Tournier et al., 2020).

Table 2-5 Enzymes involved in polyethylene terephthalate (PET) degradation. Reaction conditions and effect on specific materials are reported for each enzyme(Nikolaivits et al., 2021)**.**

Enzyme	**Origin**	**GenBank/ PDB ID**	**Material**	**Reaction conditions**	**Weight loss (%)**	**Ref.**
TfH		ALF04778.1	PET-GF* film (Goodfellow, UK) 250 μm thick (crystallinity 2.3% by (Wei et al., 2019a))	65 °C, 1.5 mL 1 M Tris pH 8.5, 10 mM $CaCl_2$, 2 d (108 mg film/mL reaction) 2.5 nmol enzyme/mg film or 0.4 nmol enzyme/cm^2 film	13	(Then et al., 2015)
TfCut2					12.6	
TfCut2 variant				70 °C, 1.5 mL 0.5 M HEPES pH 8, 2 d	25	(Then et

(D204C-E253C-D174R)		4CG1	(crystallinity 9.8% by (Barth et al., 2015))	(30 mg film/mL reaction) 35 μmol enzyme/mg film or 0.5 mmol enzyme/cm^2 film		al., 2016)
TfCut2 expressed in *Bacillus megaterium*				70 °C, 1.8 mL Phosphate pH 8, 5 d (25 mg film/mL reaction) 0.03 nmol enzyme/mg film or 1 nmol enzyme/cm^2 film	97	(Wei et al., 2019 b)
			PET-CP, post-consumer Carton Pack (Carton Pack Srl, Rutigliano, Italy) Crystallinity 4-6%	70 °C, 1.8 mL Phosphate pH 8, 7 d (17 mg film/mL reaction) 0.05 nmol enzyme/mg film or 1 nmol enzyme/cm^2 film	23.9-56.6	
			PET-AP, post-consumer Agripack (Groupe Guillin, Ornas, France) Crystallinity 4-6%	70 °C, 1.8 mL 1 M Phosphate pH 8, 7 d (15 mg film/mL reaction) 0.04 nmol enzyme/mg film or 1 nmol enzyme/cm^2 film	8.2-50.5	
TfCut2			Low crystallinity PET sheets (NOACRYSTAL-V) 200 μm thick 3-5% crystallinity Coated with C_{12}-$N(CH_3)_3^+$ surfactant	65 °C, 0.5 mL 0.15 M Bicine pH 9, 10 mM CaCl$_2$, 2 d (15 mg film/mL reaction) 0.07 nmol enzyme/mg film or 0.8 nmol enzyme/cm^2 film	30	(Furukawa et al., 2018)
TfCut2 variant (G62A/F209A)				65 °C, 1 mL 0.15 M Bicine pH 9, 10 mM CaCl$_2$, 1.25 d (7.5 mg film/mL reaction) 0.13 nmol enzyme/mg film or 1.7 nmol enzyme/cm^2 film	100	
LCC	Uncultured bacterium	4EB0	PET film from plastic package	50 °C, 1 mL 0.5 M Tris pH 8, 1 d (20-25 mg film/mL reaction) 8 pmol enzyme/mg film or 3.6 nmol enzyme/cm^2 film	6.5	(Sulaiman et al., 2012)
			PET-GF* film (Goodfellow, UK) 250 μm thick crystallinity 7%	70 °C, 3 mL 0.5 M HEPES pH 8, 2 d (30 mg film/mL reaction) 3 mmol enzyme/cm^2 film	95	(Shirke et al., 2018 a)
LCC-glycosylated					95	

Cut190*	*Saccharomonospora viridis*	4WFK	PET-S from package 600 μm thick	63 °C, 1 mL 0.1 M Tris pH 8.2, 50 mM $CaCl_2$, 24% glycerol, 3 d (20-25 mg film/mL reaction) 11 nmol enzyme/mg film	27	(Kawai et al., 2014)
			PET-GF* film (Goodfellow, UK) 250 μm thick T_g=76 °C		14	
HiC	*Humicola insolens*	4OYY	PET-GF* film (Goodfellow, UK) 250 μm thick (crystallinity 7%) T_g=75 °C	70 °C, 3 mL 1 M Tris pH 7.5, 10% glycerol, 4 d 13 nmol enzyme/ cm^2 film	97	(Ronkvist et al., 2009)

[a] Enzyme concentration per film area is calculated considering that both sides of the film are accessible to the enzyme molecules.

A lot of effort has been made in order to discover or engineer thermostable PET hydrolases; and for good reason. Due to the nature of its aromatic building block, PET shows inert stiffness, which results in high melting temperature (>230 °C) and glass transition temperature (T_g) of over 70 °C. It has been proven that at temperatures above T_g, the amorphous regions of the polymer become very flexible and prone to enzymatic attack. Lower thermostability, slower reaction times restricts large scale applications of enzymatic degradation. Regardless of these limitations, a solution to complete depolymerization of crystalline PET could be the combination of chemical with enzymatic treatment. Such process can lead to high purity TPA and EG that could be recovered and used as a feedstock in whole-cell processes for the production of high added-value compounds as described later in the text.

2.3 Microwave technology

Microwaves are a type of electromagnetic radiations, characterised by wavelengths (λ) of a range between 1 mm to 1 m and frequency range between 0.3 and 300 GHz(Figure 2-4). Microwaves fall between infrared irradiation and radio waves in the electromagnetic spectrum. To prevent interference, typical commercial MW ovens operate at a frequency of 2.45 GHz at a specified wavelength (λ=12.2 cm).

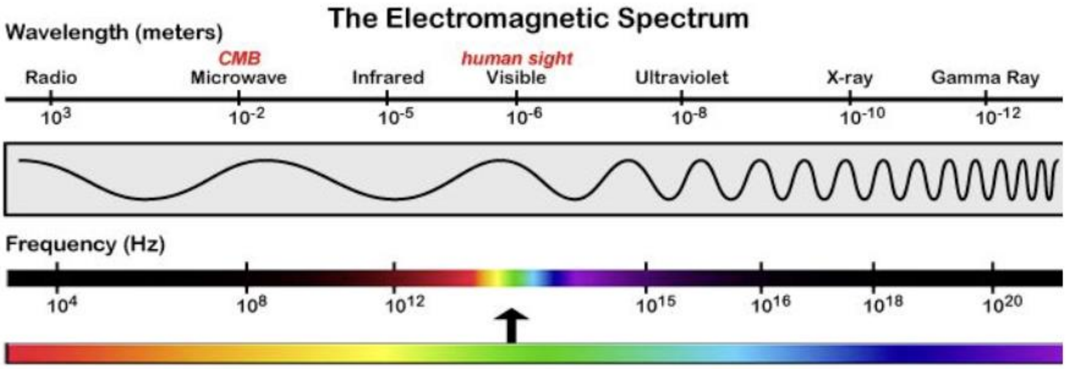

Figure 2-4 Electromagnetic spectrum(Kot et al., 2014)**.**

Microwave radiation, like all forms of electromagnetic radiation, comprises a magnetic field as well as an electric field component. The electric field component plays an important role in the process of dielectric heating in molecules, which occurs through two distinct mechanisms: conductivity and dipolar polarization. In the dipolar polarisation mechanism, heating requires the presence of molecules with dipolar moment. The dipole shows sensitivity to an external electric field and struggles to align itself with this field, making the dipole rotating. In microwaves, the frequency of the alternating electric field causes atoms from the dipole to vibrate, and the frequency is too high for the dipole to rotate and align entirely with the field. The vibrations of the dipole produce heating by friction with other neighbouring species.

The conductivity mechanism also follows the same principle, but the vibrating species are ions. Therefore, ionic and/or polar solvents are required for microwave heating. Solvents that possess polar and ionic species, the conductivity mechanism is dominant. Microwave (MW) technology has been investigated as an efficient method for fast PET depolymerization via glycolysis and hydrolysis reactions. The rapid heating achievable via MW while utilising greener solvents with higher MW absorbing capabilities as model catalysts has allowed significant shortening of reaction times while delivering acceptable monomers conversion yields. This could be attributed to the heating behaviour and MW absorption properties of these solvents when considered for catalysing depolymerisation reactions under MW irradiation. Therefore, solvents with strong MW absorbing capabilities are highly desirable for efficient PET depolymerisation using MW technology.

2.3.1 Advantages of MW heating over conventional heating

MW heating differs from conventional heating because it operates by converting electromagnetic energy into thermal energy instead of involving heat transfer. This phenomenon involves delivering MW energy directly to materials at the molecular level interactions with the electromagnetic field. Since microwaves supply energy by penetrating the material, heat can be uniformly generated uniformly across the entire volume of the material, causing volumetric heating. As compared to conventional heating methods, MW heating provides additional advantages, including non-contact heating, rapid heating, ability to selectively heat materials, less waste and equipment size, and the capability to treat waste *in situ*(J. Sun et al., 2016).

2.3.2 Microwave-based glycolysis of PET

After the optimised selection of environmentally friendly catalysts for PET glycolysis, research is extending towards the utilisation of non-conventional heating sources, such as MW radiation. In MW-assisted glycolysis, MW radiation is employed as the energy or heating source for PET depolymerisation. By employing MW as the heating source, the glycolysis reaction of PET was remarkably reduced from 8 h to 35 min(Pingale & Shukla, 2008). Chen et al. studied the glycolysis of PET in the presence of EG and zinc acetate. After optimising the parameters for glycolysis reactions, 78% yield of BHET was achieved in 35 min of MW irradiations at 196°C(F. Chen et al., 2013). Alnaqabi et al. investigated combination of ionic liquid (1-butyl-3-methyl imidazolium bromide ([bmim]Br)) and microwave technology in glycolysis of waste PET. Under optimised conditions, almost 100% PET conversion with 64% BHET yield was achieved within 1.75-2 h reaction time and temperature range of 170 °C-175 °C (Alnaqbi et al., 2015). Similarly, Achilias et al. studied the reaction kinetics of microwave radiation on PET glycolysis in combination with diethylene glycol. By varying the MW energy, complete depolymerisation was achieved within 2-5 min. while in conventional heating sources, it take at least 4 h to complete PET depolymerisation(Yang et al., 2010).Click or tap here to enter text..

Although, microwave technology has shortened the reaction times, still much research is required to increase the production yield of BHET and complete PET depolymerisation.

This may be attained by adding further pre-treatment steps or using simultaneous glycolysis/hydrolysis steps.

2.3.3 Microwave-based hydrolysis of PET

Recently, MW-assisted hydrolysis of PET has gained attention owing to its efficient and scalable depolymerisation reactions. Liu et al. studied the neutral hydrolysis of PET under microwave irradiation using a temperature/pressure-monitored reactor. After optimising the parameters, it was observed that the pressure, temperature, and water-to-PET ratio played a key role in PET conversion and TPA yield(L. Liu et al., 2005). Complete depolymerisation of PET into TPA, EG, and diethylene glycol (DEG) was attained at 20 bar pressure and 90-120 min reaction time.

Siqqiqui et al. significantly shortened the PET hydrolytic depolymerisation reaction time. They explored MW-based alkaline hydrolysis of PET using a MW reactor. Complete depolymerisation of PET and the recovery of TPA and EG was carried out within 30 min at 180 ^oC and 46 W MW power. Furthermore, usage of phase transfer catalyst produced similar results at lower temperatures(Siddiqui et al., 2010).

Similarly, Ikenaga et al. investigated the hydrolytic depolymerisation of PET under microwave irradiation in a high-pressure reactor. At a certain reaction condition of pressure (2.3-3.0 MPa) and temperature (223-232^{o}C), complete depolymerisation was achieved within 30 min of MW irradiation. They claimed that MW treatment facilitated an increase in PET depolymerisation due to high diffusion of water into the PET polymer matrix. Moreover, the addition of 1 wt% HCL, further decreased the reaction time from 30 min to 15 min for the complete depolymerisation of PET(Ikenaga et al., 2016). Click or tap here to enter text..

Mohsin et al. also studied the *in situ* hydrolysis of PET under microwave irradiation. Hydrolysis of PET was carried out using sodium methoxide in the presence of dimethyl sulfoxide and methanol. The maximum TPA yield (51.6) was achieved under the optimised conditions of time (5 min), temperature (60 ^{o}C), and solvent ratio (2:3) of methanol and dimethyl sulfoxide.

In conclusion, MW technology has enormous potential for accelerating glycolysis and hydrolysis depolymerisation of PET, at shorter reaction times, making it significantly scalable and economically viable.

2.4 Deep eutectic solvents (DESs)

DESs are a new class of solvents that have emerged as green alternatives possessing characteristics like those of ionic liquids. Typically, they are obtained by interaction of two or more components which are classified as hydrogen bond donor (HBD) and a hydrogen bond accepter (HBA). Complexation of a quaternary ammonium salt (HBA) with a metal salt/ hydrogen bond donor (HBD) generates a mesh-like connected molecule via hydrogen bonding, termed DESs. The formation of DESs mixtures at lower melting points compared to the individual components could be attributed to charge delocalisation taking place through hydrogen bonding. For example, hydrogen bond donor and halide ion is the reason of lower meting point as compared to melting point of individual components(Smith et al., 2014).

Abbot et al. heated zinc chloride with a number of quaternary ammonium salts and measured the freezing points of the formed solutions. Choline chloride (ChCl), as an ammonium salt, gave lowest melting point (23-25^{o}C)(Abbott et al., 2001). Following the initial research work, further research has developed a range of liquids from eutectic mixtures of HBD and salts(Smith et al., 2014). Then these liquids were called deep eutectic solvents in order to distinguish them from ionic liquids which only contain discrete ions. For a mixture to be classified as DES, its components should form a eutectic mixture that should remain in the liquid state at a temperature lower than the freezing points of individual components.

2.4.1 Classification of DESs

A number of DESs can be prepared with a range of customised physiochemical properties which can play a significant role in depolymerisation reactions. Their easy preparation, readily availability, and low cost make them advantageous over ionic liquids. DESs have potential for large scale application because they are easy to prepare. For example, HBD and HBA components are mixed at a moderate rate which reduces the capital cost compared to conventional solvents.

Based on the complexing agent employed as the component moiety, DES are classified into four main types (Table 2-6)(Smith et al., 2014).

Table 2-6 Classification of DESs(Smith et al., 2014).

Type	General formula	terms
type I	$Cat^{+}X^{-}zMCl_{x}$	M = Zn,[1,5,6] Sn,[7] Fe, Al,[8] Ga,[9] In[10]
type II	$Cat^{+}X^{-}zMCl_{x}\cdot yH_{2}O$	M = Cr,[11] Co, Cu, Ni, Fe
type III	$Cat^{+}X^{-}zRZ$	Z = $CONH_2$,[12] COOH,[13] OH[14]
type IV	$MCl_x + RZ = MCl_{x-1}^{+}\cdot RZ + MCl_{x+1}^{-}$	M=Al, Zn and Z=$CONH_2$, OH

The general formula to describe deep eutectic solvents is given below;

Cat+ X- zY (2-1)

Where Cat+ could be a sulfonium, phosphonium or ammonium cation, and ion X is generally a halide anion. Complex mesh-like anionic species are developed between either a Brønsted or lewis acid Y (z= no. of Y molecules that interact with anion) and X−. DESs are formed from quaternary ammonium salts and MClx , type I can be taken as similar type of metal halide/ imidazolium salt systems. This type contains non-hydrated metal salts which restricts its applications whereas type II contains choline chloride and metal hydrated salts. Type II is widely used in industrial applications due to its slower moisture/air sensitivity and due to lower cost of hydrated metal salts. Eutectics of type III are formed between HBD and ChCl and are widely known because of their capability to dissolve transition metal species as well as oxides and chlorides)(Abbott et al., 2003, 2006). The physical properties can be tailored by the hydrogen bond donor and adjustable according to the end application.

Abbot et al. extended their research on inorganic cations and developed ambient temperatures eutectics incorporated with transition metals. These are referred to as type IV DESs. Overall physio-chemical properties of DESs depend on water content, molar ratio and type of HBD/HBA used for the synthesis.

2.4.2 DES assisted glycolysis of PET in the presence of MW irradiation

Several studies have been carried out to evaluate DES based glycolysis of PET in the presence of MW irradiation. Another study by Choi et al. implicated the use of glycerol/choline chloride DES to depolymerise PET in blend fabrics in the presence of sodium hydroxide (NaOH) under MW irradiation. A 38 to 61% weight loss of PET was achieved in less than 100 s, under different NaOH concentrations (S. Choi & Choi, 2019). Cho et al. investigated non aqueous glycolysis of PET using alkali conditions under MW irradiation. Within 120 s of MW irradiation and 0.1% concentration of NaOH, glycolyzed PET showed high hydrophilicity. The MW treatment reduced the treatment time from 1-2 h (traditional dyeing machine) to 180 s(Cho et al., 2013). Chen et al. carried out the glycolysis of PET using zinc acetate and excess EG under MW irradiation. After optimising the parameters, it was concluded that at a 1%weight ratio of catalyst to PET, 5 weight ratio of EG/PET, at 196 ^{o}C of temperature, 35 min of MW irradiation, yielded 78% BHET(F. Chen et al., 2013).

2.4.3 DES assisted hydrolysis of PET in the presence of MW irradiation

For MW assisted hydrolysis reactions, Choi et al. performed an alkaline hydrolysis reaction of PET in MW using urea/choline chloride DES as a catalyst. Enhanced hydrophilicity of the PET fabric and minimal hydrolysis products were observed within 1 min of the reaction time (H. M. Choi & Cho, 2016). In another study, Cho et al. converted PET into a more hydrophilic structure using EG-ChCl based DES in combination with NaOH and MW irradiation. Within 60 s of MW irradiation and 0.5% NaOH content, the PET fabric rapidly demonstrated a highly hydrophilic surface(Cho et al., 2016).

2.4.4 DES assisted glycolysis of PET in the absence of MW irradiation

Wang et al.(Q. Wang et al., 2015) investigated the effect of a DES of urea and metal salt for catalysing the glycolysis of PET waste. The results showed fast reaction rates and high conversions (up to 100%) of PET to BHET within 30 min at 170 ^{o}C. In a study by Liu et al. 1,3-dimethylurea based DESs were evaluated for the glycolysis depolymerisation of PET with the active sites of urea, which play a critical role in the conversion of PET to

BHET (82%) at 190 °C in a 20 min reaction time (B. Liu et al., 2019). Sert et al. studied PET glycolysis under catalysed reaction conditions using urea and urea derivative based DESs such as urea/choline chloride and dimethyl urea/choline chloride, increasing the conversion of PET into BHET to 55-60% at 180°C temperature and a reaction time of 5 h. (Sert et al., 2019b). Choi et al. used ChCl-EG based DES solvent in combination with NaOH and MW irradiation to identify PET in a composition of PET/cotton blend. The results produced smaller yields of TPA and BHET along with higher content of oligomers within 120~140 s (S. Choi & Choi, 2021)

2.4.5 Choice of solvent systems

Based on the literature review, different solvents were selected to obtain the maximum degradation of PET under microwave irradiation. For example, in Paper I, Ternary DES based on the triplet composition of choline chloride, glycerol, and urea was selected for PET depolymerisation under MW irradiation without the use of additional depolymerisation agents. In a previous study, this unique combination of DES showed maximum absorption properties among different DES compositions under MW irradiation. Therefore, this DES solvent system was chosen for the MW treatment as described in Chapter 3. Similarly, Tournier et al. developed LCC variants which showed breakthroughs in PET degradation on industrial scale applications. Influenced from this literature, LCC variant ICCG enzyme was selected for the enzymatic degradation of PETin the second step (Tournier et al., 2020). In Paper II, a hybrid depolymerisation technique involving simultaneous glycolysis-hydrolysis was adopted. By considering the unique combination of urea and its derivatives with ChCl and their effect in depolymerization reactions, ChCl-urea and ChCl-thiourea based DESs were employed for PET depolymerisation(H. M. Choi & Cho, 2016; Q. Wang et al., 2012a).In the PET hydrolysis step , Na_2CO_3 in EG was proposed as a potential environment-friendly PET depolymerising agent.

In Paper III, the approach of combining all green and ultrafast MW-reagent-based PET pre-treatments to depolymerise PET efficiently was implemented. MW-assisted pre-treatment was conducted in the presence of glycerol. Glycerol was selected as solvent because of its efficient MW absorption properties and increased thermal heating response under MW irradiation which could also result in improved catalytic performance in different depolymerisation reactions(González-Rivera et al., 2020)(González-Rivera et al., 2021). In the second step of PET hydrolysis, $NaHCO_3$ in EG was used as a green PET depolymerising agent because it has shown great potential for glycolysis and hydrolysis recycling of PET under shorter reaction times.

Chapter 3. Progressing Ultra-green, Energy-Efficient Biobased Depolymerization of PET via MW-Assisted Green DES and Enzymatic treatment

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3.1 Preface

In this study, an all-green, environmentally friendly sequential PET depolymerization approach was employed comprising treatment of PET using MW-assisted DES technique without the use of additional depolymerization agents followed by enzymatic hydrolysis using a variant of LCC cutinase. A green DES of ternary composition of choline chloride, glycerol, and urea was selected for PET treatment in the presence of MW irradiation. Recently, BBD has been utilized in many studies for the optimization of reaction processes(Didaskalou et al., 2018; Marichamy et al., 2020). In this work, optimized MW treatment conditions were determined using BBD with respect to MW irradiation time, MW power, and volume of DES**.** The crystallinity index, carbonyl index, and weight loss of residual PET were used as the studied responses for BBD. Residual PET resulting from the optimized MW treatment process was further exposed to a four-day hydrolysis process by a thermostable polyesterase, and the total depolymerization efficiency was evaluated. The success of the combined techniques proposed in this study is expected to provide a green, environmentally friendly approach for plastic recycling.

3.2 Introduction

All-green routes to continuous circular material and commodity production, unmaking and remaking in a manner analogous to nature’s many resource cycles, remain largely elusive for plastics(Gómez et al., 2019). Polyethylene terephthalate (PET) plastic value chain is a pertinent example of many current linear mine, use, and dispose economic processes. PET is highly recalcitrant and widely used in the manufacturing of packaging materials, beverage bottles, and synthetic fibers due to its high mechanical and thermal properties, nontoxicity, and excellent transparency (George & Kurian, 2014). The unabated increase in the demand for PET production is a grave environmental concern given the poor degradation rates of PET in soil and air (Rorrer et al., 2019). Mechanical and chemical processing are the current mainstay approaches for PET recycling, with each having considerable limitations(Singh et al., 2017b) Loss of transparency of mechanically recycled

PET and the presence of traces of reactive antimony catalyst restrict the application of recycled PET in food and beverage packaging(Filella, 2020; Singh et al., 2017a).

3.2.1 Chemical recycling of PET

On the other hand, chemical recycling, which comprises glycolysis, methanolysis, aminolysis, and hydrolysis to depolymerize PET into its monomers (W. Chen et al., 2021; Khoonkari et al., 2015; Rubio Arias & Thielemans, 2021; Q. Wang et al., 2015; Yue et al., 2013), requires long reaction times, large volumes of non-green solvents for reaction, and several product purification processes(Nikolaivits et al., 2021). Recently, a number of alternative techniques are being explored for PET depolymerization, including the incorporation of efficient catalytic systems in depolymerization reactions(Barnard et al., 2021; Musale & Shukla, 2016), supercritical technology(Imran et al., 2010), and microwave-assisted methods(Attallah, Janssens, et al., 2021; S. Choi & Choi, 2019). However, despite the achievement of increased reaction rates, the need for harsh reaction conditions and use of non-green solvents remain a considerable challenge(Kawai et al., 2019; Park et al., 2021). Recently, plastic biodepolymerization has been proposed as an environmentally friendly and promising technology for PET recycling(Attallah, Mojicevic, et al., 2021). Greener approaches for PET recycling, such as complete solubilization of PET in natural deep eutectic solvents and thin-layer film synthesis from PET polymer waste for nanofiltration, have also been employed recently as sustainable routes for PET recycling(Park et al., 2021; Pestana et al., 2021; Wei & Zimmermann, 2017).

3.2.2 Simultaneous glycolysis-hydrolysis

Herein, a novel multistep approach that echoes nature’s sequential depolymerization steps for naturally occurring polymers, namely weathering, arthropodal digestion, and microbial and enzymatic degradation, is presented. A MW-assisted DES technique was combined with enzymatic hydrolysis to obtain enhanced PET depolymerization compared with enzymatic hydrolysis alone. Such a recycling methodology would be advantageous due to its low energy requirements and operation under mild conditions during plastic degradation/depolymerization(Kawai, 2021). A series of impeding factors, namely the need for low physical dimension preparations of the polymer as suitable substrates, slow catalytic activity, enzymatic thermal degradation at high processing temperatures(Wei et al., 2019b), low interaction levels with the chemical structures of linear polymers(Ali et al., 2021), and high polymer crystallinity and hydrophobicity(Donelli et al., 2009), serve to hinder the efficiency of biobased plastic recycling. Assisting techniques designed to overcome these barriers, which can render the plastic more amenable to bio depolymerization/biodegradation and augment the probability of depolymerization events using biobased agents, are required to progress towards sustainable plastic resource cycling. Recently, new combinations of physiochemical treatment techniques have been applied to overcome existing hindrances to bio depolymerization(Falkenstein et al., 2020). For instance, Falah et al.(Falah et al., 2020) proposed several sequential physiochemical treatments, including ultraviolet, high temperature, and nitric acid solvent treatment, prior to exposing PET for enzymatic degradation. The authors observed the development of cracks on the PET surface after treatment, which led to some enhancement in the enzymatic degradation of PET. (Quartinello et al., 2017) et al. used a sequential chemoenzymatic treatment to facilitate depolymerization of PET from textile waste under mild conditions. The chemical treatment was performed under neutral conditions (pressure = 40 bar and temperature = 250 °C) to depolymerize PET into high-purity terephthalic acid (TPA) and small oligomers with a total monomer conversion of 85% within 90 min. Enzymatic hydrolysis was then performed using Humicola insolens cutinase to yield 97% pure TPA. Furthermore, Gong et al.(Gong et al., 2018) used a combination of alkaline hydrolysis and microbial strains (T = 37 °C, pH = 12, time = 48 h) and found enhanced conversion of PET into its functional monomers as a result of faster microbial growth and reduction in particle size of PET.

3.2.3 Deep eutectic solvents

Deep eutectic solvents (DESs) are a new class of ionic liquids that are becoming prominent for plastics depolymerization due their unique characteristics(Gómez et al., 2019). The use of DESs as catalysts in depolymerization reactions can make reaction conditions milder and decrease reaction times(B. Liu et al., 2019a). Recently, these solvents have been utilized as catalysts in microwave (MW)-assisted PET depolymerization reactions due to their strong MW heating characteristics and the synergic hydrogen bond formation of these solvents with PET polymer chains(W. Chen et al., 2021; S. Choi & Choi, 2019). Different compositions of DESs have been employed and evaluated for the enhancement of PET depolymerization under mild conditions, as elaborated in Table 3-6. To the best of our knowledge, the combination of MW-assisted DES technique and enzymatic hydrolysis to obtain enhanced PET depolymerization compared to enzymatic hydrolysis alone has not been previously explored and presents a strong progress towards the achievement of all-green permanent resource circularity in tandem with nature. Noticeably, treating PET in DESs under MW irradiation can increase PET chain flexibility and change the physicochemical properties of the polymer(Khoonkari et al., 2015). Thus, such MW-assisted DES treatment can provide an enhanced monomer conversion yield upon PET depolymerization.

3.2.4 Proposed Methodology

In this study, an all-green, environmentally friendly sequential PET depolymerization approach was employed comprising treatment of PET using MW-assisted DES technique without the use of additional depolymerization agents followed by enzymatic hydrolysis using a variant of LCC cutinase. A green DES of ternary composition of choline chloride, glycerol, and urea was selected for PET treatment in the presence of MW irradiation. Recently, the Box–Behnken design (BBD) has been utilized in many studies for the optimization of reaction processes(Didaskalou et al., 2018; Marichamy et al., 2020). In this work, optimized MW treatment conditions were determined using BBD with respect to MW irradiation time, MW power, and volume of DES**.** The crystallinity index, carbonyl index, and weight loss of residual PET were used as the studied responses for BBD. Residual PET resulting from the optimized MW treatment process was further exposed to a four-day hydrolysis process by a thermostable polyesterase, and the total depolymerization efficiency was evaluated. The success of the combined techniques proposed in this study is expected to provide a green, environmentally friendly approach for plastic recycling.

3.3 Materials and Methods

3.3.1 Materials

PET granules were purchased from Alpek Polyester UK Ltd. (Lazenby, UK) and converted into micron-sized fine powder using a centrifugal miller (Retsch Verder Scientific, Haan, Germany). Glycerol (99%), choline chloride (98%, ChCl), and urea (98%) were purchased from Sigma-Aldrich (Dorset, UK). All other chemicals were obtained from Aldrich (Darmstadt, Germany) and were of analytical grade and readily available to use without any purification.

3.3.2 Preparation of DES

The synthesis of the ternary DES was based on the method provided by(Kadhom et al., 2017). Prior to the preparation of DES, ChCl was dried overnight at 65 °C in the oven. A DES of triplet composition based on urea/glycerol/ChCl was synthesized with 1:1:1 molar ratio by continuously mixing and heating at 80 °C until a homogeneous, clear, and transparent liquid was formed within 10 min.

3.3.3 MW Treatment Experiments

The MW treatment experiments were carried out by mixing 1 g of powdered PET in varied volumes of synthesized DES while stirring for 15 min. The prepared suspensions were then exposed to MW irradiation at specified MW power and time. After MW treatments, residual PET was filtered and washed three times with distilled water to obtain clean residual PET, and DES was regenerated. The PET residues were then dried in an oven at 70 °C overnight and kept in sealed containers for further analysis.

3.3.4 Experimental Design

A three-factor, three-level Box–Behnken design (BBD) (Design Expert Stat-Ease Inc., Minneapolis, MN, USA) was implemented for optimization of the proposed MW-assisted DES technique. A total of 15 runs with three center points were set up to study the following three factors: MW irradiation time (min) (X_1), microwave power (W) (X_2), and volume of DES (ml) (X_3). The responses were concluded as the weight loss (%), carbonyl index, and crystallinity index of residual PET. The chosen values for the studied factors were constructed using reported literature and preliminary experiments (Table 3-1).

Table 3-1 Variables and levels in Box–Behnken experimental design for PET pre-treatment.

	Level			
Independent Variables	**−1**	**0**	**1**	**Constrains**
X_1: MW time (min)	1	2	3	In the range
X_2: MW power (W)	100	250	400	In the range
X_3: Volume of DES (mL)	20	35	50	In the range

3.3.5 Enzymatic Hydrolysis of PET Materials

For the enzymatic depolymerization, LCC variant ICCG (LCCv) was used(Tournier et al., 2020). The coding sequence of LCCv was codon optimized for expression in *E. coli* and cloned into pET26b(+) vector (GenScript Biotech B.V., Leiden, the Netherlands). The expression and purification of the recombinant protein was performed as described previously(Djapovic et al., 2021). The purity of the resulting enzymatic preparation was checked on SDS-PAGE electrophoresis (12.5% (w/v)), and protein concentration was determined by measuring the absorbance at 280 nm based on the calculated molar extinction coefficient.

MW-treated PET samples used for enzymatic depolymerization were washed twice with ultrapure water in order to remove residual monomers that could potentially inhibit enzymatic action. Reactions took place in 10 mL of 100 mM potassium phosphate buffer, pH 8, containing 100 mg of PET residue and 4 µM of enzyme. Control reactions without the addition of enzyme were also realized. All reactions were incubated at 55 °C under shaking for 4 days. After that, 0.1% (v/v) of 6M HCl was added in each reaction and centrifuged at 4000× *g* at 10 °C. Supernatants were collected and analyzed by HPLC (Perkin Elmer, Boston, Massachusetts, USA)(Djapovic et al., 2021) in order to determine the concentration of the resulting water-soluble degradation products. The remaining material was washed 3 times with ultrapure water, freeze-dried, and weighed. Experiments were run in triplicates, and the standard deviation was estimated.

3.3.6 Instrumental Characterization

A domestic 1200 W MW oven was used for all experiments. Glass beakers were used to expose suspensions containing PET to MW irradiation at a certain MW power and time. The PET samples before and after MW-assisted DES treatment were analyzed by FTIR spectroscopy (Perkin Elmer, Washington, MA, USA) at a spectral region of 4000–600 cm^{-1}. The carbonyl index was determined based on the obtained results using the baseline method. Ratios of ester carbonyl peak intensity at 1713 cm^{-1} to that of the normal C–H bonding mode at 1408 cm^{-1} in PET were calculated as follows(Chelliah et al., 2017):

$$\boldsymbol{Carbonyl\ index} = \frac{\boldsymbol{Absorption\ at\ 1713\ cm^{-1}}}{\boldsymbol{Absorption\ at\ 1408\ cm^{-1}}} \qquad \textbf{(3-1)}$$

The thermal behavior of the samples was evaluated by a DSC Perkin Elmer 4000 (Perkin Elmer Washington, MA, USA) with Pyris Software version 13.3.1 (Perkin Elmer Washington, MA, USA) under an inert nitrogen stream. About 10 mg of specimen was sealed in an aluminum pan. The DSC scans were recorded while heating from 30 to 275 °C at a heating rate of 10 °C min^{-1} and then cooled to 30 °C. The crystallinity index was calculated according to the following equation(Li et al., 2017):

$$\boldsymbol{Crystallinity\ index = (\Delta H_m/W\Delta H_{m0}) \times 100} \qquad \textbf{(3-2)}$$

where ΔH_m (Jg^{-1}) is the heat of fusion of the PET sample, ΔH_{m0} is the heat of fusion for completely crystalline PET (140 Jg^{-1}) (Fosse et al., 2019), and W(g) is the weight fraction of residual PET in the samples.

The percentage weight loss of PET was determined at onset temperature of degradation (T_0) using a thermogravimetric analyzer Pyris TGA (Perkin Elmer, Washington, MA, USA). The polymer samples were placed in a standard aluminum pan and heated from 30 to 600 °C at the rate of 10 °C min^{-1} under nitrogen flow of 50 mL min^{-1}. The PET weight loss (%) was calculated as follows:

$$\boldsymbol{PET\ weight\ loss\ (\%) = (100 - weight\ percent\ of\ PET\ at\ T_0)} \qquad \textbf{(3-3)}$$

3.4 Results

3.4.1 Properties of DES

Ternary DES has been reported as a new type of DES to widen the range of DES applications owing to the extra functionality provided by their components. One pertinent area where ternary DESs were recently applied is CO_2 capture, which demonstrates that DESs have great flexibility in terms of synthesis, forms, and applications(Kadhom et al., 2017). In the current study, we selected a green ternary DES with ChCl as a hydrogen bond acceptor and glycerol and urea as hydrogen bond donors to provide an initial depolymerization of PET when coupled with MW irradiation and to facilitate PET enzymatic hydrolysis. A schematic diagram of the proposed interactions of DES with PET is demonstrated in Figure 3-1. The advantage of this DES lies in its components being green, inexpensive, and largely available with the capacity to provide synergistic effects on PET depolymerization(S. Choi & Choi, 2019; Quartinello et al., 2017; Tournier et al., 2020; Yue et al., 2013). As shown in Figure 3-1, depolymerization of PET is postulated to involve a form of glycolysis reaction due to the presence of glycerol within the ternary DES(S. Choi & Choi, 2019). It is also known that a quaternary ammonium compound, such as ChCl and DES itself, could act as a catalyst in mild glycolysis(W. Chen et al., 2021; S. Choi & Choi, 2019; Falah et al., 2020; Yue et al., 2013). Simultaneously, the H-bond action between glycerol and urea is expected to change the charge density of the hydroxyl (OH) group in glycerol and increase the electronegativity of the oxygen atom in the glycerol OH group. Hence, the nucleophilicity of the oxygen becomes stronger, thereby supporting preferential attack to the carbon of the ester group in PET (Alomar et al., 2016; Q. Wang et al., 2012a). Based on previous reports, DESs with high pH values and low viscosity can contribute to the catalytic activity and influence the reaction rate(Sert et al., 2019a; Q. Wang et al., 2012a). The pH and density values of the proposed ternary DES were found to be 9.95 and 1.16 g/mL, respectively, giving rise to a suitable pH for depolymerization reaction to occur. Moreover, the employment of MW irradiation in the current depolymerization technique led to the production of expeditious heating, in particular with DES due to its high electric conductivity(H. M. Choi & Cho, 2016). Therefore, initial depolymerization of PET can be achieved very efficiently due to the synergistic effects of MW irradiation, glycolysis due to glycerol, and the catalytic activities of ChCl, urea alone, and in DES.

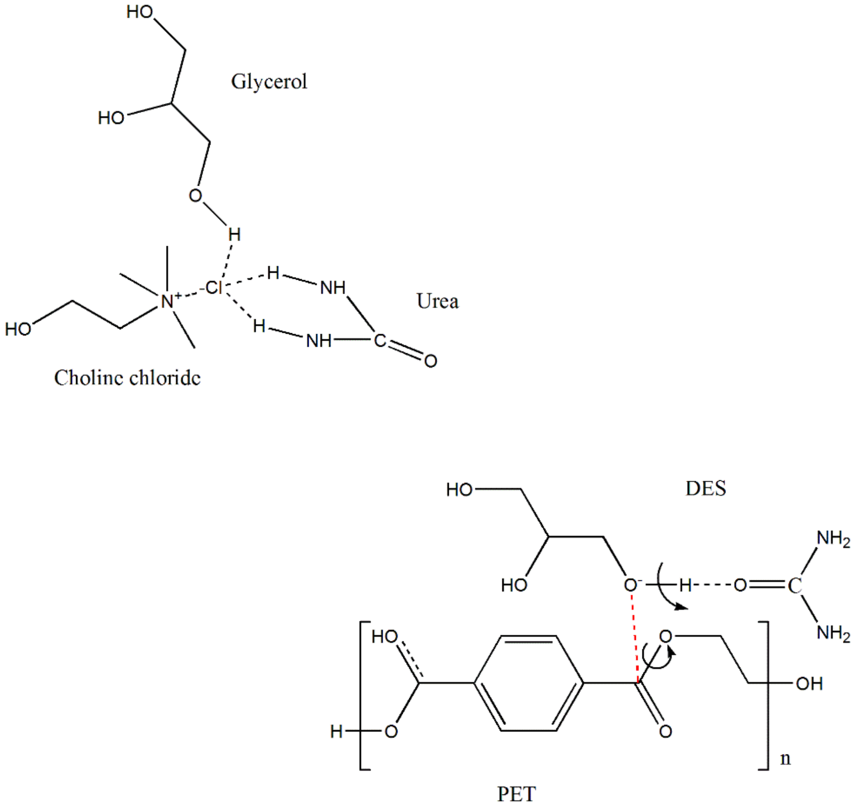

Figure 3-1 Schematic diagram for the proposed interactions of DES (composed of choline chloride/urea/glycerol in the ratio of 1:1:1) with PET via hydrogen bonding.

Prior to the depolymerization process, the prepared DES was also characterized using FTIR, as shown in Figure 3-2. In the typical FTIR spectrum of pure urea, the characteristic C=O, N–H and C–N stretching peaks appeared at 1677, 3427, and 1459 cm^{-1}, respectively, while the N–H deformation peak appeared at 1590 cm^{-1}. Pure glycerol's spectrum showed a C–O stretching peak at 1043 and 1111 cm^{-1} and O–H stretching peak at 3339 cm^{-1}. The FTIR spectrum of pure ChCl had O–H and C–H stretching peaks at 3220 and 3006 cm^{-1}, respectively, and the asymmetric and symmetric stretching peaks of C–N linkage were observed at 954 and 892 cm^{-1}, respectively. The FTIR spectrum of the prepared DES showed the formation of new bonds at 1668 and 1624 cm^{-1} compared to the FTIR spectra of pure urea, glycerol, and ChCl. The C=O linkage frequency peak at 1677 cm^{-1} of urea was shifted to lower side at 1668 cm^{-1}, indicating the formation of more hydrogen bonds, and the N–H stretching frequency of urea at 3427 cm^{-1} was masked by the O–H stretching peak(Çabuk et al., 2019). The C–O stretching peak of glycerol at 1043 cm^{-1} was also shifted to higher wavenumber in the DES, indicating the successful formation of DES.

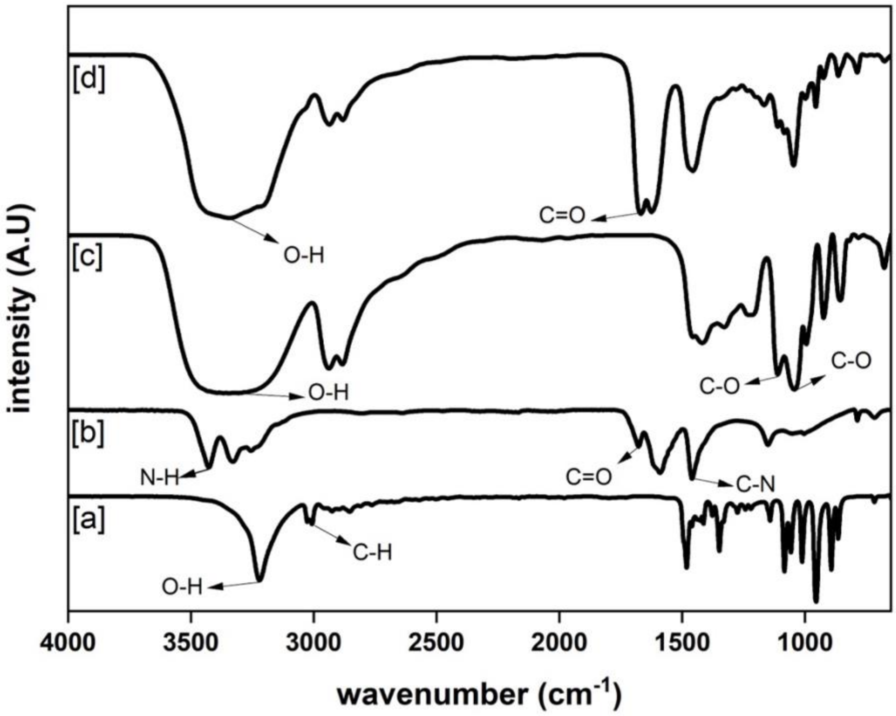

Figure 3-2 FTIR spectra of: (a) choline chloride, (b) urea, (c) glycerol, and (d) DES (choline chloride/urea/glycerol in the ratio of 1:1:1).

3.4.2 Experimental Design Results

The model of PET MW treatment was studied using response surface methodology. In the current study, the experimental runs were carried out based on the design plan proposed for the studied parameters (MW irradiation time, MW power, and volume of DES). After each run, the crystallinity index, carbonyl index, and weight loss (%) at T_0 of degradation of treated PET were calculated. The results are presented as responses for each run in Table 3-2.

Table 3-2 Experimental matrix and observed responses for PET pretreatment in BBD.

	Independent Variable			**Dependent Variable**		
Run	**X_1 (min)**	**X_2 (W)**	**X_3 (mL)**	**Y_1**	**Y_2**	**Y_3(%)**
1	3	400	35	54.10	3.47	8.90
2	2	100	50	18.57	4.41	2.17
3	2	250	35	48.30	3.61	4.80
4	1	250	20	19.00	3.91	1.20
5	3	250	50	41.67	3.79	4.91
6	2	400	20	45.07	4.16	7.39
7	2	250	35	47.80	3.62	5.00
8	2	400	50	50.29	4.30	5.63
9	3	100	35	12.83	3.95	0.90
10	3	250	20	32.79	4.17	6.20
11	2	100	20	20.21	4.28	0.94
12	1	400	35	19.86	4.15	1.89
13	1	250	50	12.86	4.55	2.20
14	2	250	35	49.32	3.59	5.20
15	1	100	35	9.52	3.87	0.75

X_1: MW irradiation time, X_2: MW power, X_3: volume of DES, Y_1: crystallinity index, Y_2: carbonyl index, and Y_3: weight loss (%) at T_0 of degradation.

The studied responses were then tested against different regression models to determine the best-fitting mathematical model and the significance of varying the process parameters. The quadratic model was chosen as the best fitting model for the studied responses in comparison to the other models. The relationship between the crystallinity index (Y_1), carbonyl index (Y_2), and weight loss of PET at T_0 of degradation (Y_3) and the studied parameters of MW irradiation time (X_1), MW power (X_2), and volume of DES (X_3) is demonstrated in Table 3-3.

Table 3-3 Statistical analysis of measured responses for PET pre-treatment.

Fitting Model	**Factors**	**Coefficient**	***p*-Value**	**ANOVA**
PET crystallinity index (Y_1)	Intercept	48.47		*F* = 276.92, R^2 = 0.9944, Model *p*-value < 0.0001, *p*-value of lack of fit = 0.228
	X_1	10.02	<0.0001	
	X_2	13.52	<0.0001	
	X_3	0.79	0.1290	
	X_1X_2	7.73	<0.0001	
	X_1X_3	3.76	0.0017	
	X_2X_3	1.71	0.0385	
	X_1^2	−15.68	<0.0001	
	X_2^2	−8.72	<0.0001	
	X_3^2	−6.22	0.0002	
PET carbonyl index (Y_2)	Intercept	3.61		*F* = 461.34, R^2 = 0.9966, Model *p*-value < 0.0001, *p*-value of lack of fit = 0.355
	X_1	−0.14	<0.0001	
	X_2	−0.054	<0.0001	
	X_3	0.066	0.0005	
	X_1X_2	−0.19	0.0002	
	X_1X_3	−0.25	<0.0001	
	X_2X_3	2.5×10^{-3}	<0.0001	
	X_1^2	0.035	0.8048	
	X_2^2	0.22	0.0165	
	X_3^2	0.46	<0.0001	
Weight loss of PET at T_0 of degradation (Y_3)	Intercept	5.00		*F* = 264.71, R^2 = 0.9941, Model *p*-value < 0.0001, *p*-value of lack of fit = 0.537
	X_1	1.86	<0.0001	
	X_2	2.38	<0.0001	
	X_3	−0.10	0.2060	
	X_1X_2	1.72	<0.0001	
	X_1X_3	−0.57	0.0023	
	X_2X_3	−0.75	0.0007	
	X_1^2	−1.15	0.0001	
	X_2^2	−0.74	0.0008	
	X_3^2	−0.23	*0.0825*	

X_1: MW irradiation time, X_2: MW power, X_3: volume of DES, Y_1: crystallinity index, Y_2: carbonyl index, and Y_3: weight loss (%) at T_0 of degradation.

For the crystallinity index (Y_1), the coefficients of the quadratic model equation indicated that the increase in all the studied factors led to a significant increase in the crystallinity index of residual PET except for the volume of DES, where the *p*-value was more than 0.05. The interaction between MW irradiation time and volume of DES showed a positive effect on the crystallinity index as well revealed the significant effect both factors had on the PET residues. Moreover, the MW power interactions with both the MW irradiation time and volume of DES also showed a significant positive efficacy on the crystallinity index.

Such results indicate that all the studied factors and their interactions had positive effects on the crystallinity index of treated PET, with the increase in the studied factors leading to an increase in the degradation of PET and causing an increase in the crystallinity index of the treated samples(Beltrán-Sanahuja et al., 2020).

For the carbonyl index (Y_2), as demonstrated in Table 3-2, all treated PET residues had higher carbonyl index than that of the untreated PET (2.80). Both MW irradiation time and power showed a significant negative effect on the carbonyl index values, while the volume of DES showed a positive effect. The MW irradiation time interactions with both MW power and volume of DES also showed significant negative effects on the carbonyl index of PET residue. Thus, based on the obtained results and the carbonyl index of untreated PET, the increase in both MW irradiation time and power led to a degree of PET depolymerization, which was observed through the low values of the carbonyl index of the residual PET. On the other hand, high levels of DES volume with low levels of MW irradiation time and power caused a significant increase in the carbonyl groups on the surface of the PET as a result of surface oxidation rather than complete depolymerization of treated PET.

For PET weight loss at T_0 of degradation (Y_3), as elaborated in Table 3-3, the coefficients of the model equation showed that MW irradiation time and power and their interaction with each other had positive effect on PET weight loss. On the other hand, the volume of DES and its interactions with both MW irradiation time and power showed negative efficacy on PET weight loss at T_0 of degradation. These results indicate that increased levels of MW irradiation time and power and low levels of DES induce a decrease in thermal stability of treated PET, leading to a greater degree of PET depolymerization at the T_0 of degradation.

The adequacy of the proposed model to describe the crystallinity index, carbonyl index, and weight loss of treated PET at T_0 of degradation was evaluated, and the results are demonstrated in Table 3-3. Based on the statistics test, high coefficients of determination were observed for all responses. The adjusted R^2 values were calculated to be 0.9944 for the crystallinity index, 0.9966 for the carbonyl index, and 0.9941 for the percentage weight loss of PET at T_0 of degradation.

Analysis of variance (ANOVA) was also applied to determine the significance of the model at a 95% confidence interval. A model is said to be significant if the probability value (*p*-

value) is <0.05. The *p*-values demonstrated in Table 3-3 indicate that all the studied responses fitted the model well. From the lack-of-fit test. the response showed a highly desirable nonsignificant lack-of-fit ($p > 0.1$) with *p*-values of 0.228 for the crystallinity index, 0.355 for the carbonyl index, and 0.537 for the percentage weight loss of PET at T_0 of degradation.

3.4.3 Response Surface Analysis

Response surface graphical plots were generated between the responses obtained for PET MW treatment and the studied independent variables to estimate the effect of combinations of these variables on the studied responses. The 3D and contour plots for the crystallinity index, carbonyl index, and weight loss of PET at T_0 of degradation are demonstrated in Figures 3.3–3.5, respectively.

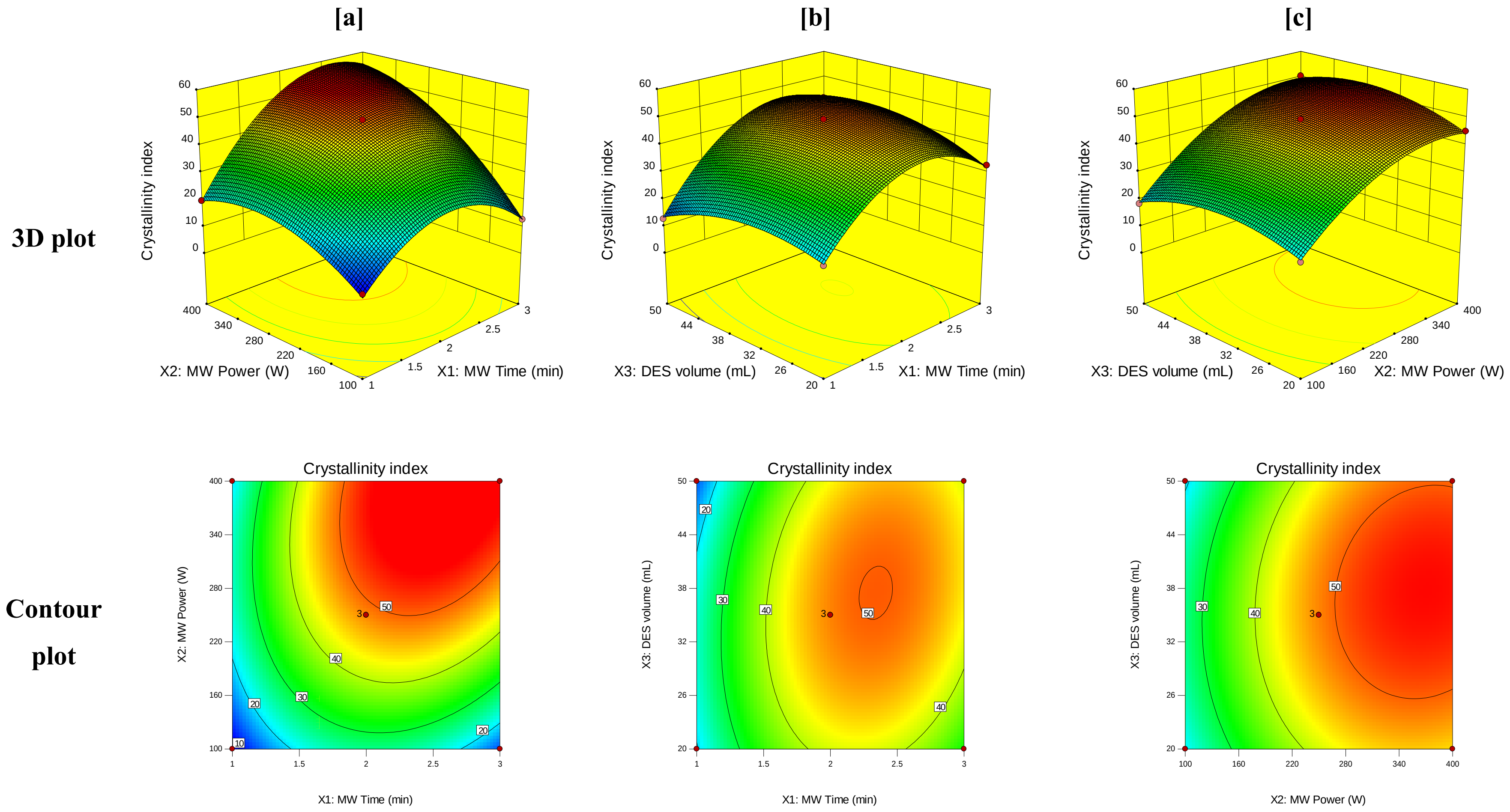

Figure 3-3 3D and contour plots of the effect of the interaction of (a) MW time (X_1) and MW power (X_2), (b) MW time (X_1) and volume of DES (X_3), and (c) MW power (X_2) and volume of DES (X_3) on the crystallinity index.

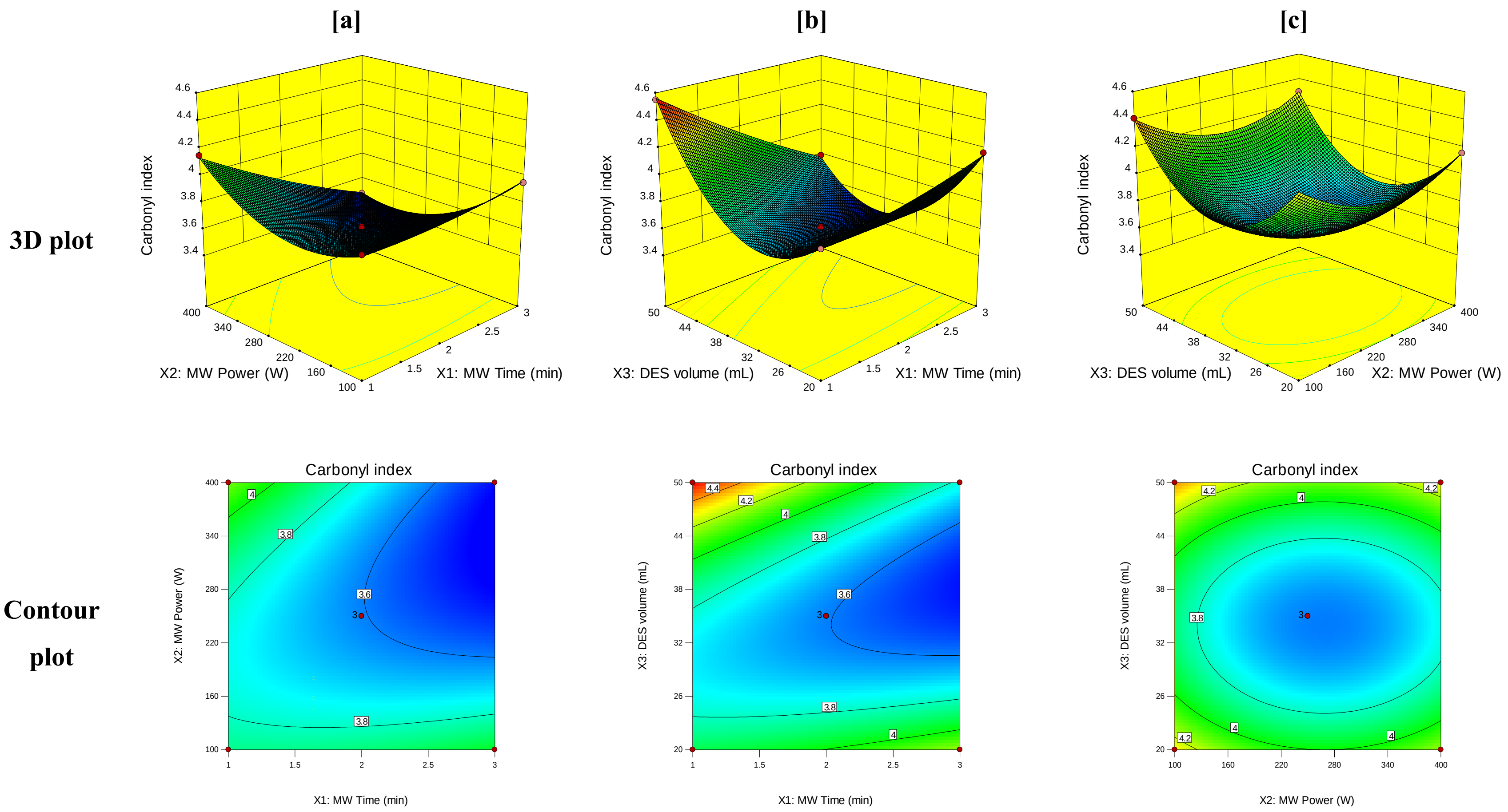

Figure 3-4 3D and contour plots of the effect of the interaction of (a) MW time (X_1) and MW power (X_2), (b) MW time (X_1) and volume of DES (X_3), and (c) MW power (X_2) and volume of DES (X_3) on the carbonyl index.

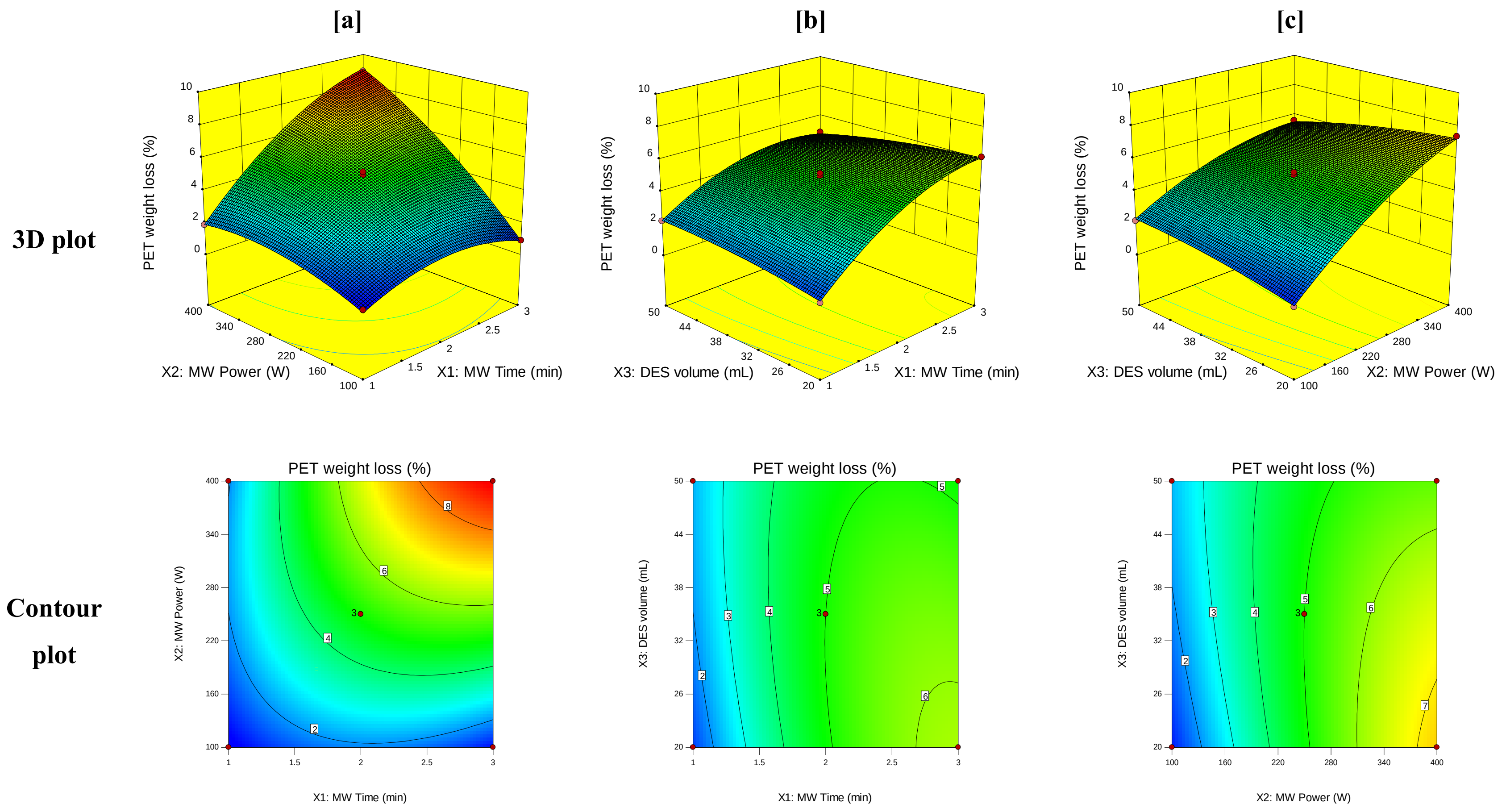

Figure 3-5 3D and contour plots of the effect of the interaction of (a) MW time (X_1) and MW power (X_2), (b) MW time (X_1) and volume of DES (X_3), and (c) MW power (X_2) and volume of DES (X_3) on PET weight loss (%).

As shown in Figure 3-3, high levels of both MW irradiation time and power caused an increase in the crystallinity index of PET residue. Such result can be attributed to the initial degradation of PET upon treatment with the MW-assisted DES technique, which usually occurs in the amorphous phase of PET, causing an increase in the overall crystallinity of the polymer(Beltrán-Sanahuja et al., 2020). A significant increase in the crystallinity index was also observed with the increase in DES volume until 35 mL. Further increase in DES volume did not show a profound effect on the crystallinity index, indicating that low volumes of DES are more effective in the initial depolymerization of PET using the proposed MW treatment technique.

The carbonyl index is considered one of the critical responses used in the evaluation of the hydrophilic nature of treated polymers. Hydrophilic polymers with high values of carbonyl index are more amenable for microbial depolymerization than hydrophobic ones. Figure 3-4 illustrates the dependence of the carbonyl index on the studied factors of MW irradiation time, MW power, and volume of DES. It can be observed that the increase in both MW irradiation time and power did not cause a significant increase in the carbonyl index of treated PET samples. Thus, it can be assumed that high levels of MW irradiation time and power result in PET depolymerization rather than surface oxidation, which is in accordance with the crystallinity index results. On the other hand, the interactions of high levels of DES volume with low levels of both MW irradiation time and power showed a significant increase in the carbonyl index, reaching a value of 4.55 and confirming the process of PET surface oxidation at these levels of the studied factors.

PET weight loss at T_0 of degradation is also an important response for assessing the initial depolymerization of PET. The higher the value of weight loss, the greater was the decrease in the thermal stability of the treated polymer, which confirmed the initial depolymerization of the treated PET samples. In Table 3-3, it can be observed that all the independent variables and their interactions influenced PET weight loss significantly (term p-value < 0.05) except for the volume of DES. As indicated in Figure 3-5, the interaction between MW irradiation time and MW power resulted in a significant increase in PET weight loss at T_0 of degradation to reach a value of 9%, whereas the value of weight loss of untreated PET was measured to be only 0.44%. In addition, it should be noted that low levels of DES volume showed higher PET weight loss percentage than high levels of DES volume, which means that initial depolymerization of PET occurs better at low volumes of DES. This might be due to more interactions between PET and DES, which can be observed at lower concentrations of the DES solvent.

3.4. Optimization of the MW-Assisted DES Technique

All three responses were optimized simultaneously using BBD optimization. Optimum MW treatment conditions were chosen with the aim of obtaining maximum initial depolymerization of PET and enhancing the biodegradation of residual PET after MW treatment. As previously described, maximum initial depolymerization of PET was observed with PET residues of increased percentage of weight loss at T_0 of degradation. Additionally, based on literature review, enhanced PET biodegradation can be achieved through low crystallinity and high carbonyl index of residual PET(Cho et al., 2016). Thus, the MW treatment conditions were adjusted to attain minimum crystallinity index and maximum carbonyl index and percentage weight loss of PET at T_0, as shown in Table 3-4. Based on BBD, a total of 63 optimized solutions were obtained. The selected solution was determined according to its success in attaining an acceptable desirability of >0.5 for the studied responses and in fulfilling the low carbon footprint goal with the lowest energy consumption concerning MW irradiation time and power. A batch experiment was carried out for PET MW treatment using the optimized conditions while keeping PET concentration at 1.0 g, and the three responses were evaluated to validate the predicted model factors and responses. The response values (predicted and observed) for the optimized conditions are recorded in Table 3-4. The model was proven to be validated as a fine agreement existed between the predicted and observed results. This indicates the success of BBD for the evaluation and optimization of the proposed PET treatment process.

Table 3-4 The optimized PET pretreatment process with observed and predicted response values.

Independent Variable		**Optimized Level**	
X_1: MW time (min)		3.0	
X_2: MW power (W)		260	
X_3: Volume of DES (ml)		20.0	
Overall desirability		0.59	
Dependent variables	Desirability	Expected	Observed
Y_1: PET crystallinity index	Minimize	33.39	32.98
Y_2: PET carbonyl index	Maximize	4.14	4.22
Y_3: PET weight loss (%)	Maximize	6.47	6.25

3.4.4 Enzymatic Depolymerization of PET Materials

Combination of green treatments with enzymatic hydrolysis as means for enhanced plastic recycling has been very limited within the literature. In this work, a multistep depolymerization process for PET comprising a green treatment process followed by enzymatic hydrolysis using a highly PET-active enzyme was performed. The total depolymerization of PET obtained after the optimized MW treatment and enzymatic hydrolysis was compared against that of untreated virgin PET biodegradation. The polymer's biodegradability was assessed based on the percentage weight loss of the material and the amount of the produced water-soluble monomers, namely TPA, mono-(2-hydroxyethyl) terephthalate (MHET), and bis-(2-hydroxyethyl) terephthalate (BHET), analyzed via HPLC (Figure 3-6).

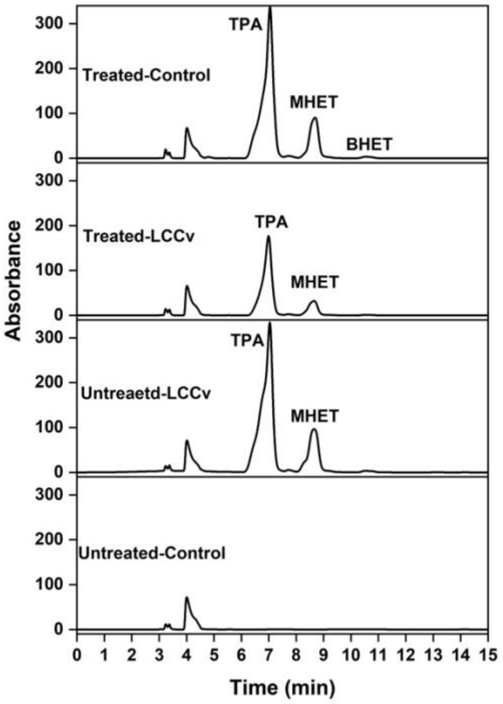

Figure 3-6 HPLC chromatograms of post-enzymatic hydrolysis products.

Following the MW treatment process, the optimized PET sample showed 20.2 ± 1.4% weight loss, and 15.76% (w/w) of the treated PET sample corresponded to a mixture of the released soluble monomers TPA, MHET, and BHET. Alternatively, the average percentage weight loss (%) for untreated and MW-treated PET samples was estimated to be 1.5 ± 0.3 and 1.8 ± 0.3%, respectively, after enzymatic hydrolysis. Such low percentage of weight loss can be attributed to the crystallinity of the materials where there are a few accessible amorphous regions for the enzyme to act on. Slightly higher weight loss percentage was observed for the MW-treated PET sample, which indicated the efficiency of MW treatment in enhancing the biodegradability of PET.

As detailed in Table 3-5, the total amount of monomers released after enzymatic hydrolysis was slightly higher for the virgin PET than for MW-treated PET residue (0.82 versus 0.55 mM). In both cases, 60–70% of the total products released was in the form of TPA and 30–35% as MHET, while only 1% remained as BHET. The higher product release for virgin PET could be explained by its slightly lower crystallinity index (31.40) compared to MW-treated PET residue (32.98), a factor that enhances enzyme action.

Moreover, the proposed multistep depolymerization approach resulted in the production of monomers during both the MW treatment and enzymatic hydrolysis processes, giving rise to an average PET weight loss of 22 ± 1.7% and a total monomer conversion of ≈16% (w/w). Thus, the obtained results for the suggested depolymerization protocol were considerably higher than the virgin PET undergoing enzymatic hydrolysis only. Similar literature on PET recycling using DESs and enzymes is presented in Table 3-6 and Table 3-7.

Table 3-5 Monomer concertation after a four-day incubation of LCCv enzyme with the untreated and treated PET materials.

Material	**TPA (µM)**	**MHET (µM)**	**BHET (µM)**
Untreated: Control	0.55 ± 0.04	0.00 ± 0.00	0.00 ± 0.00
Untreated: LCCv	521.13 ± 23.22	287.04 ± 7.63	7.07 ± 0.36
Treated: Control	0.83 ± 0.04	0.20 ± 0.00	0.00 ± 0.00
Treated: LCCv	384.79 ± 4.91	158.83 ± 4.52	4.21 ± 0.06

Table 3-6 Different compositions of DESs used in PET recycling.

DES composition			**Reaction conditions**			**Results**	**Reference**
HBA	HBD	Ratio (HBA:HBD)	Reaction time	Depolymerising agent	Temperature		
Choline chloride	Glycerol	1:2	80-100 s	Glycerol, NaOH	-	38-61% weight loss of PET	(S. Choi & Choi, 2019)
Choline chloride	Zinc chloride	1:1–1:3	30 min	Diethanolamine, ethanolamine	-	THETA, TPA, BHETA (82, 83 and 95 yield%)	(Musale & Shukla, 2016)
	Urea	1:2					
Potassium carbonate	Ethylene glycol,	1:6	2 h	ethylene glycol	180 °C	BHET (88 yield%)	(Sert et al., 2019a, 2019b)
Choline chloride	Urea, Dimethyl urea, Ethylene glycol, Glycerol	1:2					
Zinc chloride, zinc acetate, manganese acetate	Urea	1:12 to 1:6	30 min	ethylene glycol	170 °C	bis(hydroxyalkyl) terephthalate (83 yield%)	(Q. Wang et al., 2015)
1-methyl-3-butylimidazolium chloride	Zinc chloride, Manganese chloride	1:1	5.0 h	ethylene glycol	190 °C	BHET (83.8 yield%)	(Yue et al., 2013)
Choline chloride	Ethylene glycol	1:2	120 s	ethylene glycol, NaOH	144 °C	45.8% weight loss of PET	(Cho et al., 2016)

Table 3-7 Enzymatic depolymerization of PET under different conditions(Pasula et al., 2022)**.**

DES composition			**Reaction conditions**			**PET degradation**	**References**
Enzyme	Mutation	Physical form/crystallinity	Reaction time	pH	Temperature		
*Is*PETase	S238F/W159H	Film/13.3%	96h	7.2	30 °C	crystallinity decreased. Surface erosion observed in SEM.	(Austin et al., 2018)
DuraPETase	S214H/I168R/W159H/S188Q/	Film/30%	10 days	9.0	37 °C	15%	(Cui et al., 2021)
*Is*PETase	W159H/F229Y	Coca cola film/10%	24 h	9.5	40 °C	16.5%	(Meng et al., 2021)
LCC	glycosylated	Film/7%	48h	8.0	70 °C	95%	(Shirke et al., 2018b)

3.5 Conclusions

A stepwise depolymerization process for PET comprising an all-green, fast, low-energy, MW-assisted DES technique without the use of additional depolymerizing agents followed by enzymatic hydrolysis using LCCv enzyme was demonstrated. Compared to virgin PET biodepolymerization, the demonstrated combined approach was able to achieve increased PET depolymerization with a total of ≈16% (w/w) monomer conversion. The developed MW treatment process was optimized using BBD, where the volume of DES, MW power, and MW irradiation time were studied as independent variables. FTIR, TGA, and DSC spectra of the residual PET obtained after treatment with the MW-assisted DES technique showed a significant increase in residual PET carbonyl index and percentage weight loss at T_0 of degradation and maintenance of PET crystallinity percentage. Furthermore, optimum MW treatment was obtained at low DES volume (20 mL), 260 W MW power, and 3 min MW irradiation time. The enzymatic hydrolysis of treated PET demonstrated 1.8% weight loss and 0.55 mM monomers released after enzymatic hydrolysis, while 1.5% weight loss and 0.82 mM monomers were recorded for virgin PET. Analysis of the recycled monomers using HPLC confirmed the presence of TPA, MHET, and BHET as the monomers produced in the treated samples. The isolation of these monomers will be done in future work. The combination all-green treatments, which operated under mild, low-energy conditions without the use of additional depolymerization agents, produced an average PET weight loss of 22 ± 1.7% and a total monomer conversion of ≈16% (w/w). This MW-assisted DES followed by enzymatic hydrolysis methodology shows strong potential to achieve high conversion rates and is amenable to the incorporation of additional and sequential green approaches.

Moreover, large-scale applications of MW-assisted depolymerization in a continuous manner has recently shown great potential for recycling as it facilitates depolymerization of a large amount of materials in relatively mild conditions (lower temperature and frequencies)(Winter, 2013). Nevertheless, there are certain challenges with respect to high-cost reactor designs, emission of volatile degradation products, unequal irradiations due to hot spots, and nonuniform heating that still need to be resolved(Formela et al., 2019).

In conclusion, the promise of ultra-mild routes with no requirement for additional depolymerization agent is demonstrated herein for their capacity to play an instrumental role in highly sustainable degradation and depolymerization processes for PET and other polyesters, thus serving as a key step in delivering ultrasustainable all-green routes for circular plastic value chains.

Chapter 4. Ultrafast 99% PET depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation

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4.1 Preface

In the previous chapter, the development of green solvent-based MW PET pre-treatments and their effect on the enzymatic degradation of PET showed overall relatively low yields of depolymerized products. This occurred without using any additional depolymerizing agents. In order to increase yields and accelerate the reaction times, a hybrid depolymerisation technique involving simultaneous glycolysis-hydrolysis were adopted in this chapter. Glycolysis reaction was carried out in the presence of EG and urea derivatives based DESs(Urea, Thiourea) as catalysts and the optimization of the process was performed using Box Behnken design (BBD). Na_2CO_3 in EG was then used as depolymerizing agent in the hydrolysis of residual PET obtained post the optimized glycolysis processes to complete the depolymerization of the original PET sample. Characterization of the residual PET and the produced monomers was performed using DSC, FTIR and HPLC.

4.2 Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer with ideal physiochemical properties for a number of high consumption applications in particular fibers, packaging and bottles. PET product manufacturing has markedly increased and as the fourth largest produced polymer accounts for 12% volume of the world’s total solid waste (Chan & Zinchenko, 2021).

Chemical recycling has been recently proposed as one of the promising techniques for PET recycling where the waste plastics are broken down into monomers or other value-added products. Among the conventional chemical recycling techniques, glycolysis and hydrolysis are being explored for sufficient efficiency and feasibility for investment as industrial scale applications. In a typical glycolysis process for PET, ester linkages are replaced by hydroxyl groups generating feed stock monomer, bis (2-hydroxyethyl) terephthalate (BHET). In the hydrolysis of PET wastes, PET is depolymerised in the presence of steam, acid or base giving rise to ethylene glycol (EG) and terephthalic acid (TPA) monomer (Padhan & Sreeram, 2019a).

4.2.1 Hybrid glycolysis-hydrolysis step

The simultaneous application of glycolysis-hydrolysis, glycolysis-methanolysis and methanolysis-hydrolysis directed towards more efficient PET depolymerization have also been presented (Güçlü et al., 2003). Doerr *et al.* stated the reduction in PET molecular weight from 30,000 to 1000 by mixing small amounts of EG in an extruder with molten PET under a reaction temperature of 280 ^{0}C. In a subsequent hydrolysis reaction, the treated PET was converted to EG and TPA, with the glycolic pre-treatment step reducing the time required for the hydrolysis reaction from 45 to 15 min (Doerr, 1986). In Simon *et al.* patent initial glycolysis of PET to BHET, followed by a purification stage using adsorption and filtration and subsequent hydrolysis of BHET to yield TPA in a separate, glass-lined reactor at 200 ^{0}C and predetermined reaction time was presented (West, Simon, 1993).

A recent study by Güçlü *et al.* also introduced a simultaneous glycolysis and neutral hydrolysis of PET using constant amount of EG and increasing amounts of water, in the presence of xylene. The reactions were carried out at 170 and 190 ^{0}C to produce a highly pure monohydroxyethyl terephthalate (MHET) monomer of significant yield (Güçlü et al., 2003). Another study introduced a simultaneous hydrolysis-amino-glycolysis of PET waste by diethanolamine (DEA) in the presence of xylene as well. Depolymerised products containing carboxyl and hydroxyl end groups were obtained at reaction temperature of 170-220 ^{0}C and moderate pressure. It was postulated that the DEA during the glycolysis reaction led to the formation of piperazine and terephtalamide which upon further hydrolysis contributed to the production of carboxylic and hydroxylic groups. Thus, giving rise to carboxyl and hydroxyl end group intermediates (Is ̧ılAcar, 2011a).

Notwithstanding chemical recycling progress to date, the industrial implementation of these methods remains limited, due to slow reaction rates, bulk quantities of reactants, high volumes of solvents and high energy consumption during the depolymerization processes. Practically, the development of novel energy efficient methods including supercritical technologies and catalytic systems are currently the main focus in overcoming these drawbacks (Bartolome et al., 2014; Genta et al., 2010; Kazarian & Martirosyan, 2002).

Catalysts in depolymerization reactions have shown strong potential in converting PET and other plastics into their building block monomers or into high value intermediate products under mild reaction conditions (Ellis et al., 2021). This has paved the way for the current chemical recycling approaches designed to meet the demands of sustainability. The emergence of green catalysts that can upcycle and facilitate efficient PET depolymerisation are being new development. For example, the vital role of ionic liquids as purpose specific catalysts is vastly explored. Marullo *et al.* was able to convert PET into BHET via glycolysis reaction in the presence of cholinium-based ionic liquids. Under optimum conditions, 85% conversion of PET was achieved at 150 °C after 6 h (Marullo et al., 2021). Another study by Sun *et al.* investigated the use of cholinium phosphate as an ionic liquid catalyst for PET glycolysis reaction. At relatively low temperatures (120 °C, 3 h), approximately 100 % conversion of PET and 60.6 % yield of BHET were obtained (J. Sun et al., 2018).

DESs in contrast to ionic liquids, are mixtures of various compounds with numerous applications in organic, analytical, and polymer chemistry fields. Recently, DESs were proposed as green catalysts in plastics chemical recycling (Gómez et al., 2019; Martins et al., 2019). Urea based DESs in particular have shown remarkable potential as catalysts in PET depolymerization reactions. Wang *et al.*(Q. Wang et al., 2015) investigated the effect of a DES of urea and metal salt for catalysing the glycolysis of PET waste. The results showed fast reaction rates and high conversion (up to 100%) of PET into BHET within 30 min at 170 ^{0}C. In a study by Liu *et al.* 1,3-dimethylurea based DESs was evaluated for the glycolysis depolymerization of PET with the active sites of urea playing a critical role in the conversion of PET into BHET (82%) at 190 ^{0}C with a 20 min reaction time (B. Liu et al., 2019a). Sert *et al.* studied PET glycolysis under catalysed reaction conditions using urea and urea derivative based DESs such as urea/choline chloride and dimethyl urea/choline chloride, increasing the conversion of PET into BHET to 55-60% at 180^{0}C temperature and 5 h reaction time (Sert et al., 2019b).

4.2.2 Microwave technology

Microwave (MW) technology has been investigated as an efficient method for fast PET depolymerization via glycolysis and hydrolysis reactions. The rapid heating achievable via MW while utilising ionic liquids or DESs as model catalysts has allowed significant shortening of reaction times while delivering acceptable monomers conversion yields. This could be attributed to the heating behaviour and MW absorption properties of these solvents when considered for catalysing depolymerisation reactions under MW irradiation. Thus, solvents with strong MW absorbing capabilities are highly desirable (Attallah, Janssens, et al., 2021; González-Rivera et al., 2020, 2021). For instance, Rivera *et al.* investigated the MW heating response of different choline chloride based DESs and found that the MW absorption was mainly dependant on the intrinsic polarity and ionic behaviour properties of the DESs. A significant rise in MW absorption was observed in all DESs while choline chloride-glycerol based DES showed a maximum MW absorption capability due to the formation of hydrogen bond links and polarity enhancement under MW irradiations (González-Rivera et al., 2020). In our previous work for PET depolymerization using MW assisted DES/hydrolysis technique, it was also found that due to the strong MW absorption of the proposed DES catalyst of choline chloride and m-cresol, a PET conversion of 85% was achieved in 92 sec of MW irradiation (Attallah, Janssens, et al., 2021).

4.2.3 Catalyst systems for MW assisted PET depolymerisation

A series of studies of MW assisted glycolysis reactions comprising the use of ionic liquids as catalysts to evaluate the efficiency of PET depolymerization have also been reported. In one study, depolymerised products mainly constituting BHET monomer were obtained at a yield of 64% within 2 h at 175 ^{0}C temperature in a glycolysis reaction catalysed by 1-butyl-3-methylimidazolium bromide ionic liquid (Alnaqbi et al., 2015). In another study, PET glycolysis in MW while employing an oxalate-bridged binuclear iron(III) ionic liquid resulted in the conversion of PET into 80% BHET monomer yield within 3 h compared with 24 h under conventional heating (Cot et al., 2019). For MW assisted hydrolysis reactions, Choi *et al.* performed alkaline hydrolysis reaction in MW using urea/choline chloride DES as catalyst. Enhanced hydrophilicity of PET fabric and minimal hydrolysis products were observed within 1 min reaction time (H. M. Choi & Cho, 2016).

Another study by Choi *et al.* implicated the use of glycerol/choline chloride DES to depolymerise PET in blend fabrics in the presence of sodium hydroxide (NaOH) under MW irradiation. A 38 to 61% weight loss of PET were achieved in less than 100 sec, under different NaOH concentrations (S. Choi & Choi, 2019). In our previous work, MW assisted DES techniques for depolymerization of PET was also investigated. In one study, MW assisted DES/hydrolysis of PET was performed using DES of choline chloride and m-cresol in the presence of 10% NaOH. An overall 91.55% TPA yield was achieved within 92 sec of MW irradiation (Attallah, Janssens, et al., 2021). In another study, a 3 min, green MW assisted DES of choline chloride, urea and glycerol pre-treatment of PET followed by enzymatic hydrolysis was carried out and a total monomer yield of 16% (w/w) without adding any depolymerising agent was obtained (Attallah et al., 2022).

Moreover, trials at large scale are now being implemented to improve the sustainability of MW assisted depolymerization of PET. Practically, the use of high concentrations of caustic reagents such as NaOH can corrode the reaction vessels which poses a limitation for the MW assisted PET hydrolysis. Thus, the proposition of green PET depolymerizing agents is recommended to decrease the carbon footprint imposed by the current PET depolymerizing techniques.

Sodium carbonate (Na_2CO_3) is the disodium salt of carbonic acid having strong alkalinizing properties. It is found as a white powder that usually absorbs moisture from the air. Sodium carbonate is commonly used to make glass and as a water softener (Blackshaw, 2012). Recently, Na_2CO_3 has been proposed as a depolymerizing agent for hydrolysis reaction of PET. In one study, Weerasooriya *et al.* used Na_2CO_3 to depolymerize PET under the reaction time of 35 min and 170 ^{0}C operation temperature. The obtained yield of TPA was found to be 77.95% (Weerasooriya et al., 2011). López-Fonseca *et al.* studied the effect of Na_2CO_3 (0.06% (w/v)) as a catalyst in glycolysis of PET waste under excess EG. Within 1 h and around 196^{0}C temperature, 50% yield of BHET was achieved (López-Fonseca et al., 2010a). Another study by López-Fonseca *et al.* investigated the glycolysis of PET bottles using excess EG and Na_2CO_3 (0.45% (w/v)) as a depolymerising catalyst. Under optimised particle size (0.25 mm), 600 rpm stirring rate and 1 h reaction time, Na_2CO_3 efficiently catalysed PET conversion into BHET monomer and 80 % yield was obtained (López-Fonseca et al., 2011).

4.2.4 Proposed methodology

Noting the capacity of DESs as green catalysts and good MW absorbers in PET depolymerisation reactions and the proposition of Na_2CO_3 in EG as potential environmentally friendly PET depolymerizing agent. In this work, we present an ultrafast, green, sequential glycolysis-hydrolysis depolymerization of PET under MW irradiation to obtain value added monomers which can be reused in the production of commercial PET. Glycolysis reaction was carried out in the presence of EG and urea derivatives based DESs as catalysts and the optimization of the process was performed using Box Behnken design (BBD). Na_2CO_3 in EG was then used as depolymerizing agent in the hydrolysis of residual

PET obtained post the optimized glycolysis processes to complete the depolymerization of the original PET sample. Characterization of the residual PET and the produced monomers was performed using DSC, FTIR and HPLC.

4.3 Experimental

4.3.1 Materials

PET granules were obtained from Alpek Polyester UK Ltd. (UK) and were converted into micron sized fine powder using centrifugal miller. Ethylene glycol (EG) (99%), sodium carbonate (98%), choline chloride (98%, ChCl), thiourea (98%) and urea (98%) were purchased from Sigma Aldrich (UK). All other chemicals were of analytical grade and readily available to use without any purification.

4.3.2 Preparation of DESs

Prior to the preparation of DESs, ChCl was dried overnight at 65 ^{0}C in the oven. Two DESs of composition based on ChCl:urea and ChCl:thiourea were prepared with (1:2) molar ratio by continuously mixing and heating at 80 ^{0}C until homogeneous and transparent liquids were observed.

4.3.3 Sequential glycolysis-hydrolysis depolymerization of PET

MW assisted DESs/glycolysis of PET

The experiments were carried out by mixing one gram of powdered PET in varied volumes of ethylene glycol (EG) and the prepared DESs (ChCl:urea as DES 1 and ChCl:thiourea as DES 2) separately while stirring for 10 min. The prepared suspensions were exposed to MW irradiation of 350W power at specified MW irradiation times in a domestic 1200 W MW oven. After MW treatments, PET residues were collected by filtration, dried in an oven at 70 ^{0}C overnight and kept in sealed containers for further analysis by FTIR and DSC. Distilled water was then added to the filtrate and resultant BHET was precipitated by cooling overnight in the fridge at 2 ^{0}C. The DES/EG mixtures were regenerated by distillation to be ready for reuse.

Optimization of MW assisted DESs/glycolysis using BBD

Two BBDs (Design Expert, trial version 10.0.5.0, Stat-Ease Inc., Minneapolis, MN) were performed to optimize the proposed MW assisted PET glycolysis using DES 1 and DES 2 as catalysts. Fifteen runs were arranged for the designs to study volume of DES (mL) (X_1), volume of EG (mL) (X_2), and MW irradiation time (min) (X_3) as independent factors. Experiments were run in triplicates and the responses were determined as the carbonyl and crystallinity indices of residual PET and PET weight loss (%) (Table 4-1). Results were reported as the mean for triplicate measurements. BBD optimization was then used to optimize the studied responses.

Table 4-1 Variables and levels in Box-Behnken experimental design for MW assisted glycolysis of PET.

	level			
Independent variables	-1	0	1	Constrains
X_1: Volume of DES (mL)	4	5	6	In the range
X_2: Volume of EG (mL)	4	5	6	In the range
X_3: MW time (min)	0.50	1.25	2.00	In the range

MW assisted hydrolysis of residual PET obtained post glycolysis

The efficiency of MW assisted hydrolytic depolymerization of PET was evaluated using different PET samples including virgin PET (1.00 gm), residual PET of optimized MW assisted DES 1/glycolysis (0.85 gm) and residual PET of optimized MW assisted DES 2/glycolysis (0.82 gm). The PET samples were separately mixed in 10%(w/v) Na_2CO_3 in 20 mL EG and stirred for 10 min. The samples suspensions were then MW irradiated at 350 W in the MW oven for 3 min. Dissolved PET was precipitated by addition of distilled water. Finally, the obtained mixture was filtered, and the filtrate containing soluble monomers was analyzed by high performance liquid chromatography (HPLC). The residual PET samples were dried overnight at 70 ^{0}C. The depolymerization of PET was calculated using the following equation (Du et al., 2020a):

$$\text{Conversion of PET (\%)} = \left(1-\frac{\text{Weight of residual PET}}{\text{Weight of initial PET}}\right) \times 100 \qquad \textbf{(4-1)}$$

The selectivity of TPA, MHET and BHET was quantified by peak area normalization method from the HPLC chromatograms by taking ratio of the specific analyte's area to the total area of all the peaks, and the yield of TPA was calculated using the following equation (Du et al., 2020b):

$$\textbf{Yield of TPA (\%)} = \frac{(\textit{Conversion of PET}\ (\%) \times \textit{Selectivity of TPA}\ (\%))}{100} \quad \textbf{(4-2)}$$

Hydrochloric acid (HCl) (34%) of 2 mL was added to the cooled filtrate to precipitate the TPA monomer found as sodium terephthalate. The obtained TPA from each sample was then washed with water, dried overnight at 70 ^{0}C and kept in sealed bags for FTIR analysis.

4.3.4 Instrumental Characterization

The PET samples before and after MW assisted DES pre-treatment were analysed by FTIR spectroscopy (Perkin Elmer, UK) at a spectral region of 4000-600 cm^{-1}. Carbonyl Index was determined based on the obtained results using baseline method. Ratios of ester carbonyl peak intensity at 1713 cm^{-1} to that of the normal C-H bonding mode at 1408 cm^{-1} in PET were calculated as follows (Chelliah et al., 2017),

$$\textit{Carbonyl index} = \frac{\textit{Absorption at}\ 1713\ cm^{-1}}{\textit{Absorption at}\ 1408\ cm^{-1}} \quad \textbf{(4-3)}$$

The thermal behaviour of the samples was evaluated by a DSC Perkin Elmer 4000 (Perkin Elmer Washington, Ma, USA) with Pyris Software (Version 13.3.1) under an inert nitrogen stream. About 10 mg of specimen was sealed in an aluminium pan and the DSC scans were recorded while heating from 30 – 275 °C at a heating rate of 10 °C/min, and then cooled to 30°C. The crystallinity index was calculated according to the following Equation (Li et al., 2017),

$$\textbf{Crystallinity index} = (\Delta H_m / W \Delta H_{m0}) \times 100 \quad \textbf{(4-4)}$$

where ΔH_m (J/g) is the heat of fusion of the PET sample. ΔH_{m0} is the heat of fusion for completely crystalline PET (140 J/g) (Fosse et al., 2019) and W(g) is the weight fraction of residual PET in the samples.

The percentage weight loss of PET was calculated using following equation:

$$\textit{PET Weight loss}\ (\%) = (W_1 - W_2)/W_1 \times 100 \quad \textbf{(4-5)}$$

where W_1 was PET initial weight and W_2 was the weight of PET residual after MW assisted DESs/glycolysis technique.

Soluble monomers obtained from PET depolymerization were identified and quantified by HPLC (Alliance Waters, UK) with C-18 column (NUCLEODUR, Germany 4.6*250, 5 um) at 1.2 ml/min flow rate and 10 µl injection volume at 30 ºC. Standard TPA, MHET and BHET in 100% methanol were used as reference in the HPLC analysis. A mobile phase of acetonitrile and 10mM sulphuric acid in ultrapure water was employed with a UV detector at 254 nm. Total run time was 18 min. Retention times were TPA 7.9 min, MHET 9.6 min, BHET 11.7 min. Quantification of TPA, MHET and BHET was performed by constructing calibration curves with standard concentrations in the range of 0.01-1 mM.

4.4 Results and discussion

4.4.1 Properties of prepared DESs

The selected DESs; ChCl:urea as DES 1 and ChCl:thiourea as DES 2 are emerging as green and sustainable solvents that play a significant role in improving PET degradation reactions as elaborated in previous reports (B. Liu et al., 2019a; Sert et al., 2019b; Q. Wang et al., 2015). It is postulated that the amino and carbonyl groups in urea derivatives can efficiently enhance the catalytic activity of depolymerization reactions by interacting with both the depolymerizing agent and the carbon chain of the polymer to be degraded (Is ̧ılAcar, 2011b). This is in addition to the known catalytic activity posed by ChCl as quaternary ammonium compound in mild glycolysis reactions of PET (S. Choi & Choi, 2019; B. Liu et al., 2019a; Sert et al., 2019b; Q. Wang et al., 2015). Physical properties of the prepared DESs are illustrated in Table 4-2. The pH values of the DESs varied greatly where DES 1 had basic nature of pH 10.55 while DES 2 was acidic with a pH value of 3.02. Based on previous literature it is evident that acidic solvents enhance the dissolution of polymers making them amenable to substantial depolymerisation reactions (Tan et al., 2018). Additionally, by considering the optimum density and viscosity values of the DES that were used in literature for PET depolymerization (Sert et al., 2019a). The proposed DESs showed acceptable ranges of these properties for the catalysis of PET glycolysis reaction.

Table 4-2 Physical properties of the prepared DESs.

	DES 1	**DES 2**
pH	10.55	3.02
Density (Kg/m^3)	1.176	1.198
Viscosity (mPa.s)	1571	1862

*Values were measured at room temperature (25 ^{0}C)

Furthermore, the FTIR analysis of the prepared DESs (Figure 4-1) confirmed the presence of the expected functional groups together with some shifting in the peaks' frequency which indicated the new characteristics of the formed DESs. As illustrated in Figure 4-1[a] the spectrum of DES 1 showed the characteristic peaks of C–N, C=O and N–H functional groups of urea at 1446 cm^{-1}, 1670 cm^{-1} and 3432 cm^{-1} respectively. The shift of C – N stretching peak in urea from 1084 cm^{-1} to 1064 cm^{-1} and the appearance of the fingerprint region of ChCl in the DES 1 spectra also indicated the successful interaction between urea and ChCl to form the DES. In the FTIR spectrum of DES 2 (Figure 4-1[b]), characteristic peaks for asymmetric and symmetric stretching of N–H groups in thiourea were observed at 3364 cm^{-1} and 3254 cm^{-1}. Similarly peaks at 1465 cm^{-1} and 1097cm^{-1} corresponded to C–N asymmetric and stretching vibrations while C=S rocking vibrations were observed at 729 cm^{-1}. Formation of new bonds at 3107 cm^{-1} and 2060 cm^{-1} and shifting of N–H bending peak from 1610 cm^{-1} to 1593 cm^{-1} was also observed which depicted the new linkages between N-C-S and ChCl active sites(B. Liu et al., 2019b).

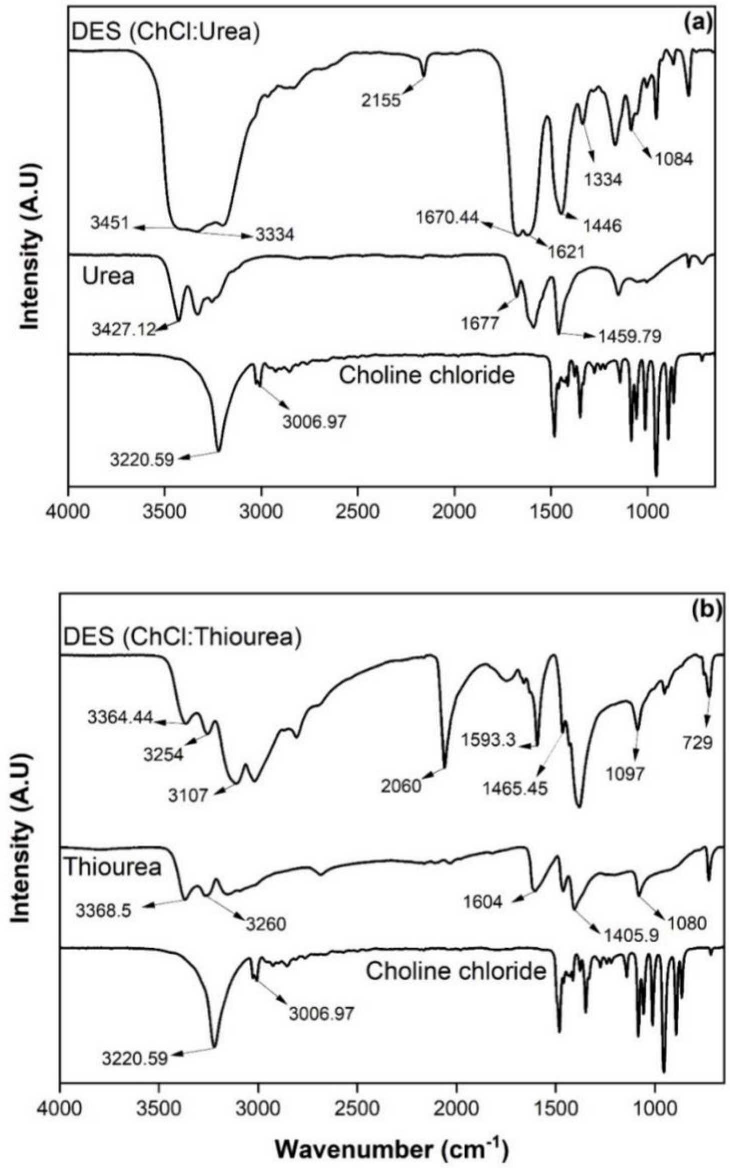

Figure 4-1 FTIR spectra of [a] DES 1 (Choline chloride:urea (1:2)) and [b] DES 2 (Choline chloride:thiourea (1:2)).

4.4.2 MW assisted DESs/glycolysis of PET experimental design

Response surface methodology was used to study the models of MW assisted glycolysis of PET using DES 1 and DES 2 as catalysts. Based on the designed plan by BBD for the studied parameters (DES volume, EG volume and MW irradiation time) the experimental runs were carried out. As recorded in Table 4-3, the studied responses comprising crystallinity and carbonyl indices of residual PET and PET weight loss (%) were determined after each run.

Table 4-3 Experimental matrix and observed responses for MW assisted glycolysis of PET in BBD.

	Independent variable			**Dependent variable**					
				DES 1			DES 2		
Run	X_1 (mL)	X_2 (mL)	X_3 (min)	Y_1	Y_2	Y_3(%)	Y_1	Y_2	Y_3(%)
1	6	5	0.5	3.63	26.83	13.97	3.87	26.00	11.86
2	6	4	1.25	3.43	28.02	11.20	3.84	38.32	9.76
3	5	4	2	3.46	34.96	22.38	3.16	29.22	26.18
4	5	6	0.5	4.59	27.09	19.36	3.85	24.65	15.35
5	6	6	1.25	3.38	33.71	27.50	3.90	42.02	1.22
6	4	4	1.25	3.19	31.09	15.00	3.91	36.23	1.00
7	4	5	0.5	4.15	26.41	16.87	4.65	27.68	20.76
8	4	5	2	3.15	35.27	13.51	3.69	35.38	20.07
9	5	4	0.5	3.48	25.93	18.40	3.72	26.47	16.37
10	5	5	1.25	3.81	28.69	7.41	3.70	34.01	7.41
11	5	5	1.25	3.78	28.77	6.85	3.69	34.20	6.68
12	5	6	2	3.06	36.99	31.10	3.50	40.65	28.71
13	6	5	2	3.23	37.27	32.38	3.90	39.13	31.35
14	5	5	1.25	3.75	29.12	5.45	3.70	34.80	6.62
15	4	6	1.25	3.92	27.62	9.51	4.32	42.02	7.63

X_1: volume of DES, X_2: volume of EG, X_3: MW irradiation time, Y_1:,Carbonyl index, Y_2: Crystallinity index and Y_3: Weight loss (%).

Different regression models were tested, and it was found that for both MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis techniques, the quadratic model was the best fitting model. The relationship between the carbonyl index (Y_1), crystallinity index (Y_2) and percentage weight loss of PET (Y_3) and the studied parameters; volume of DES (X_1), volume of EG (X_2), and MW irradiation time (X_3) are demonstrated in Table 4-4 and Table 4-5 for MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis, respectively.

Table 4-4 Statistical analysis of measured responses for MW assisted glycolysis of PET using DES 1.

Fitting model	Factors	Coefficient	P-value	ANOVA
PET Carbonyl index (Y_1)	Intercept	+3.78		F = 184.91, R^2 = 0.9916, Model P-value <0.0001, P-value of lack of fit = 0.352
	X_1	-0.092	0.0010	
	X_2	+0.17	< 0.0001	
	X_3	-0.37	< 0.0001	
	X_1X_2	-0.20	0.0001	
	X_1X_3	+0.15	0.0005	
	X_2X_3	-0.38	< 0.0001	
	X_1^2	-0.20	0.0001	
	X_2^2	-0.096	0.0045	
	X_3^2	-0.036	0.1253	
PET Crystallinity index (Y_2)	Intercept	+28.86		F = 442.16, R^2 = 0.9965, Model P-value = < 0.0001, P-value of lack of fit = 0.497
	X_1	+0.68	0.0005	
	X_2	+0.68	0.0005	
	X_3	+4.78	< 0.0001	
	X_1X_2	+2.29	< 0.0001	
	X_1X_3	+0.40	0.0212	
	X_2X_3	+0.22	0.1277	
	X_1^2	+0.73	0.0021	
	X_2^2	+0.52	0.0083	
	X_3^2	+1.86	< 0.0001	
Weight loss of PET (Y_3)	Intercept	+6.57		
	X_1	+3.77	< 0.0001	
	X_2	+2.56	0.0002	F = 214.20, R^2 = 0.9928, Model P-value = < 0.0001, P-value of lack of fit = 0.889
	X_3	+3.85	< 0.0001	
	X_1X_2	+5.45	< 0.0001	
	X_1X_3	+5.44	< 0.0001	
	X_2X_3	+1.94	0.0031	
	X_1^2	+2.80	0.0007	
	X_2^2	+6.43	< 0.0001	
	X_3^2	+9.81	< 0.0001	

Table 4-5 Statistical analysis of measured responses for MW assisted glycolysis of PET using DES 2.

Fitting model	Factors	Coefficient	P-value	ANOVA
PET Carbonyl index (Y_1)	Intercept	+3.70		F = 953.1, R^2 = 0.9984, Model P-value <0.0001, P-value of lack of fit = 0.107
	X_1	-0.13	< 0.0001	
	X_2	+0.12	< 0.0001	
	X_3	-0.23	< 0.0001	
	X_1X_2	-0.087	< 0.0001	
	X_1X_3	+0.25	< 0.0001	
	X_2X_3	+0.052	0.0006	
	X_1^2	+0.38	< 0.0001	
	X_2^2	-0.087	< 0.0001	
	X_3^2	-0.052	0.0007	
PET Crystallinity index (Y_2)	Intercept	+34.34		F = 311.78, R^2 = 0.9950, Model P-value = < 0.0001, P-value of lack of fit = 0.518
	X_1	+0.52	0.0173	
	X_2	+2.39	< 0.0001	
	X_3	+4.95	< 0.0001	
	X_1X_2	-0.52	0.0554	
	X_1X_3	+1.36	0.0013	
	X_2X_3	+3.31	< 0.0001	
	X_1^2	+3.56	< 0.0001	
	X_2^2	+1.76	0.0005	
	X_3^2	-5.84	< 0.0001	
Weight loss of PET (Y_3)	Intercept	+6.90		
	X_1	+0.59	0.1289	
	X_2	-0.050	0.8839	F = 170.28, R^2 = 0.9901, Model P-value = < 0.0001, P-value of lack of fit = 0.134
	X_3	+5.25	< 0.0001	
	X_1X_2	-3.79	0.1117	
	X_1X_3	+5.05	0.0001	
	X_2X_3	+0.89	0.0004	
	X_1^2	-1.32	0.0399	
	X_2^2	-0.68	0.2154	
	X_3^2	+15.43	< 0.0001	

For carbonyl index (Y_1) of MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis treatments, all treated PET residues had higher carbonyl index than that of the untreated PET (2.80). Both volume of DES and MW irradiation time showed a significant negative effect on the carbonyl index values while the volume of EG showed a positive effect. Nevertheless, the interactions of EG volume with both MW irradiation time and volume of DES showed significant negative effects on the carbonyl index of PET residue. Thus, it can be indicated that the increase in both MW irradiation time and DES volume led to some form of non-oxidative PET degradation which was observed through the low values of carbonyl index of residual PET. On the other hand, high levels of EG volume with low levels of MW irradiation time and DES volume caused a significant increase in the carbonyl groups on the surface of PET due to the hydrophilic nature of EG.

For crystallinity index (Y_2), the coefficients of the quadratic model equation in both treatments indicated that the increase in almost all the studied factors together with their interactions led to a significant increase in the crystallinity index of residual PET. Such results elaborate that the increase in the studied factors led to an increase in the degradation of PET which initially occurs in PET's amorphous phase (Beltrán-Sanahuja et al., 2020). Such behavior resulted in an increase in the overall crystallinity of treated samples and an elevation in PET's crystallinity index than that of virgin PET (31.4%) at high levels of studied factors.

For PET weight loss (Y_3), the coefficients of the model equations in both MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis showed that MW irradiation time and its interactions with DES volume and EG volume had positive effects on PET weight loss. Such results indicate that high levels of MW irradiation time allow more interaction between the PET chains and DES and EG leading to a greater degree of PET depolymerization and increase in its weight loss percentage.

As demonstrated in Table 4-4 and Table 4-5, the adequacy of the proposed model to describe the studied responses for MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis was evaluated and the obtained F-values of the quadratic model were large compared to other models' values. Hence, the proposed treatments can be modeled effectively. The statistics tests also showed high coefficients of determination for both MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis where the adjusted R^2 values for both treatments were higher than 0.99.

Moreover, based on the analysis of variance (ANOVA), the obtained *p*-values for both MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis indicated that all the studied responses fitted the model well with a probability value (p-value) < 0.05. Additionally, the lack-of-fit test performed on the studied responses showed a highly desirable non-significant lack-of-fit ($p>0.1$) with *p*-values ranging between 0.107 and 0.352 for crystallinity index, 0.497 and 0.518 for carbonyl index and 0.134 and 0.889 for percentage weight loss of PET.

4.4.3 Response surface analysis

Analysis of surface response was performed to determine the combinatorial effects of the studied variables on the responses resulting from MW assisted glycolysis of PET using DES 1 and DES 2. Contour plots of carbonyl index, crystallinity index and PET weight loss for MW assisted glycolysis using DES 1 and DES 2 are demonstrated in Figure 4-2, Figure 4-3, and Figure 4-4 respectively. The 3-D surface plots are provided in Figure 4-5, Figure 4-6 and Figure 4-7.

Figure 4-2 shows the carbonyl index (Y_1) dependence on the studied variables; volume of DES, volume of EG and MW irradiation time. Generally, carbonyl index is one of the important responses used to evaluate the extent of surface oxidation of the treated polymers. It can be observed that the increase in both volume of DES and MW irradiation time did not cause a significant increase in the carbonyl index of treated PET samples. Thus, it can be assumed that high levels of DES volume and MW irradiation time result in PET degradation rather than surface oxidation giving rise to slight increase in carbonyl index values. On the other hand, the interactions of high levels of EG volume with low levels of both DES volume and MW irradiation time showed a significant increase of carbonyl index confirming PET surface oxidation at these levels of studied factors.

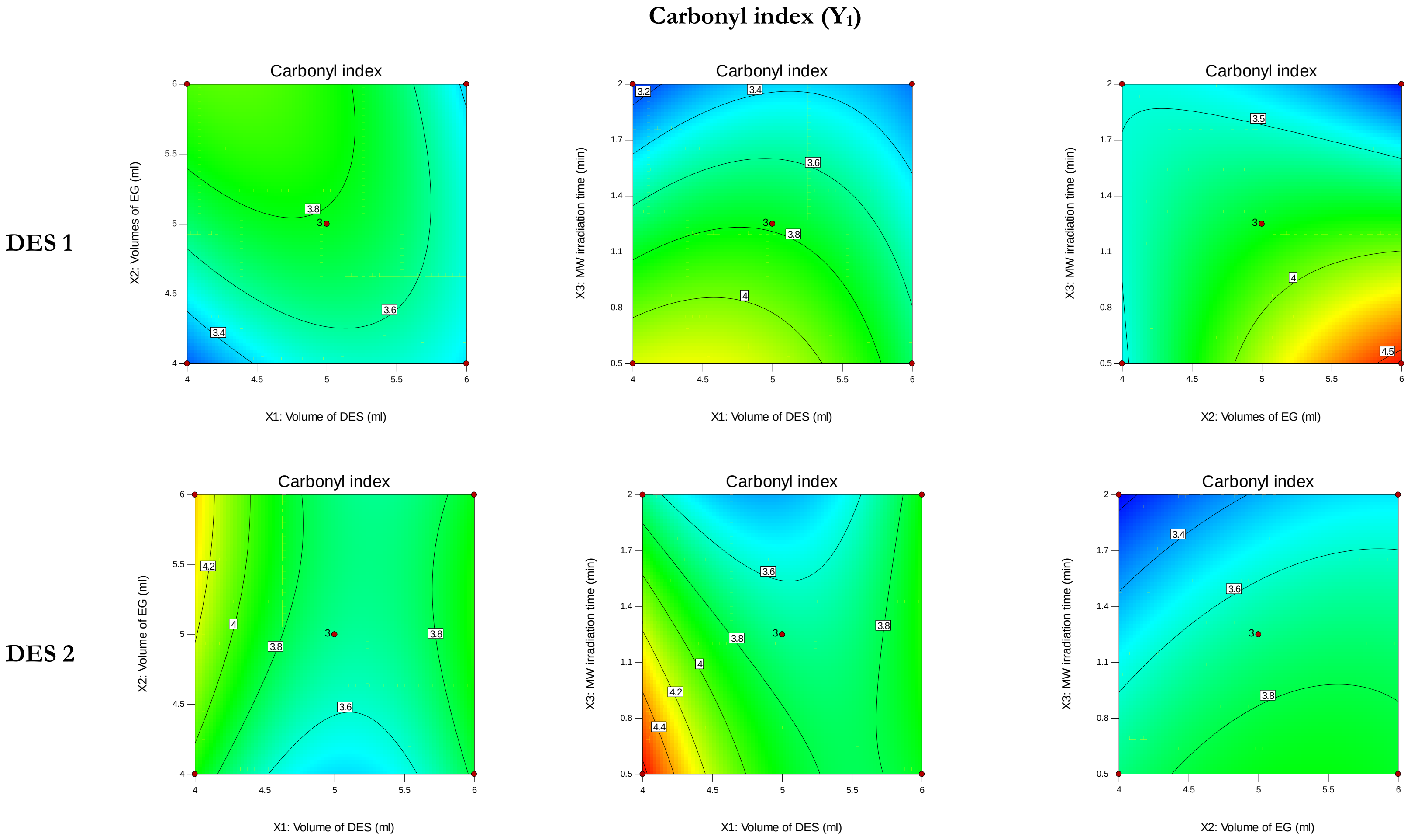

Figure 4-2 Contour plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on carbonyl index for MW assisted glycolysis of PET using DES 1 and 2.

Contour plots for crystallinity index (Y_2) are demonstrated in Figure 4-3. Noticeably, high level of MW irradiation time in combination with different levels of DES and EG volumes caused an increase in the crystallinity index of PET residue. Such result indicates that MW irradiation time has the upper hand in affecting the crystallinity of PET residue where increasing the reaction time led to the initial degradation of the amorphous phase of PET causing an increase in the overall crystallinity of the polymer (Cho et al., 2016). A significant increase in the crystallinity index was also observed at high levels of DES and EG volumes combinations especially in MW assisted glycolysis using DES 2. Hence, performing the MW assisted glycolysis of PET using the proposed DESs at high levels of all studied factors results in more effective initial degradation of PET and increased crystallinity of PET residues reaching 40%.

Crystallinity index (Y_2)

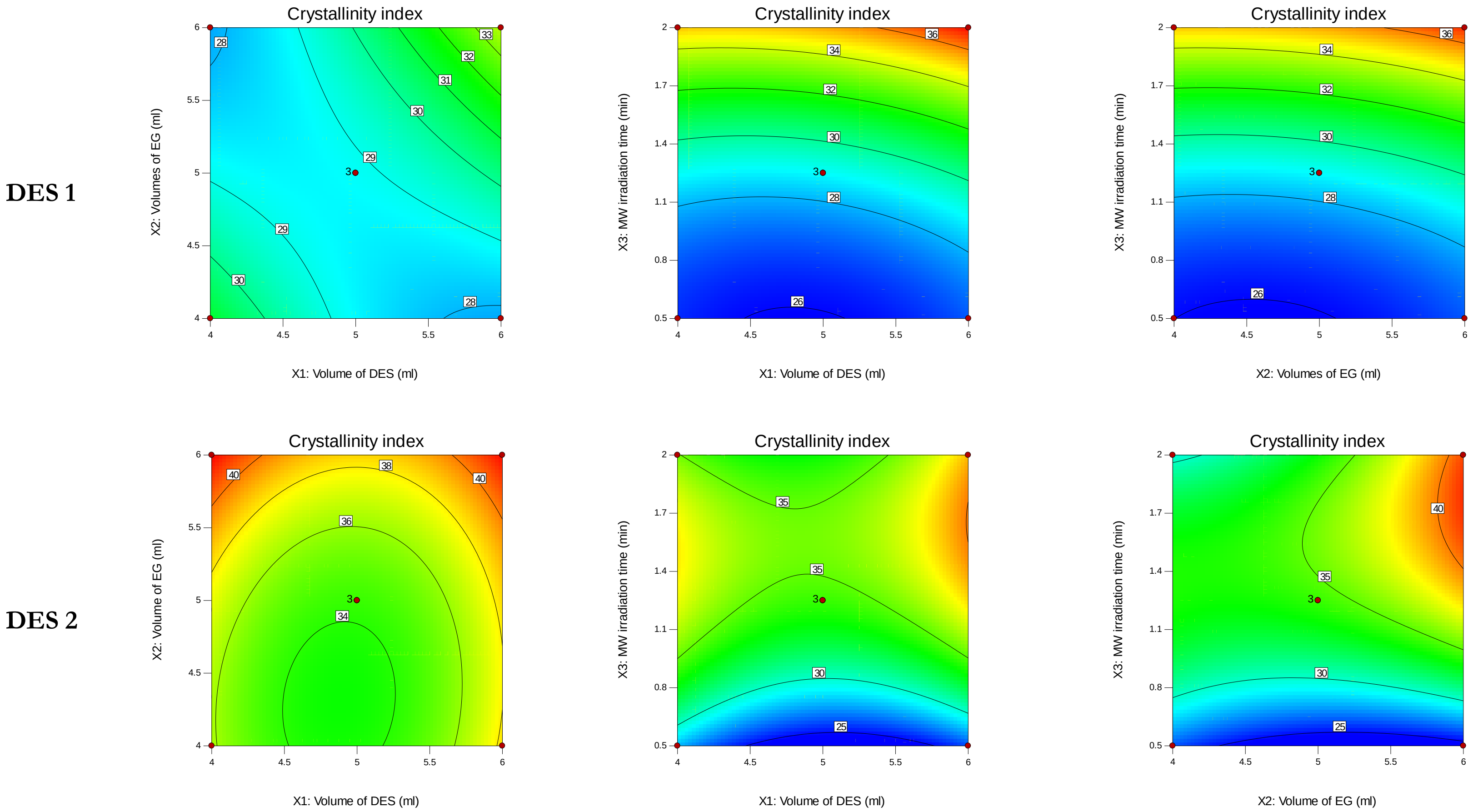

Figure 4-3 Contour plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on crystallinity index for MW assisted glycolysis of PET using DES 1 and 2.

PET weight loss is also considered one of the critical responses to assess initial degradation of PET. The higher the value of weight lost the greater the degree of initial degradation of the treated PET samples. As elaborated in Table 4-4 and Table 4-5, MW irradiation time and its interactions influenced PET weight loss significantly (term P-value < 0.05) which indicates that the reaction time in the MW has the upper hand in PET initial degradation. Such conclusion was also supported by the surface response results of MW irradiation time interactions with both DES and EG volumes. As shown in Figure 4-4, in the case of MW assisted glycolysis using DES 1, an increased PET weight loss was observed at the interactions of high levels of MW irradiation time and DES and EG volumes. Alternatively, in MW assisted glycolysis using DES 2, significant PET weight loss was observed at the interactions of high levels of MW irradiation times and all the levels of DES and EG volumes indicating the significance of MW irradiation time in the degradation process. These results come in accordance with those of crystallinity index indicating that the weight loss and crystallinity of PET are directly proportionally influenced by the studied independent variables.

Weight loss (%) (Y_3)

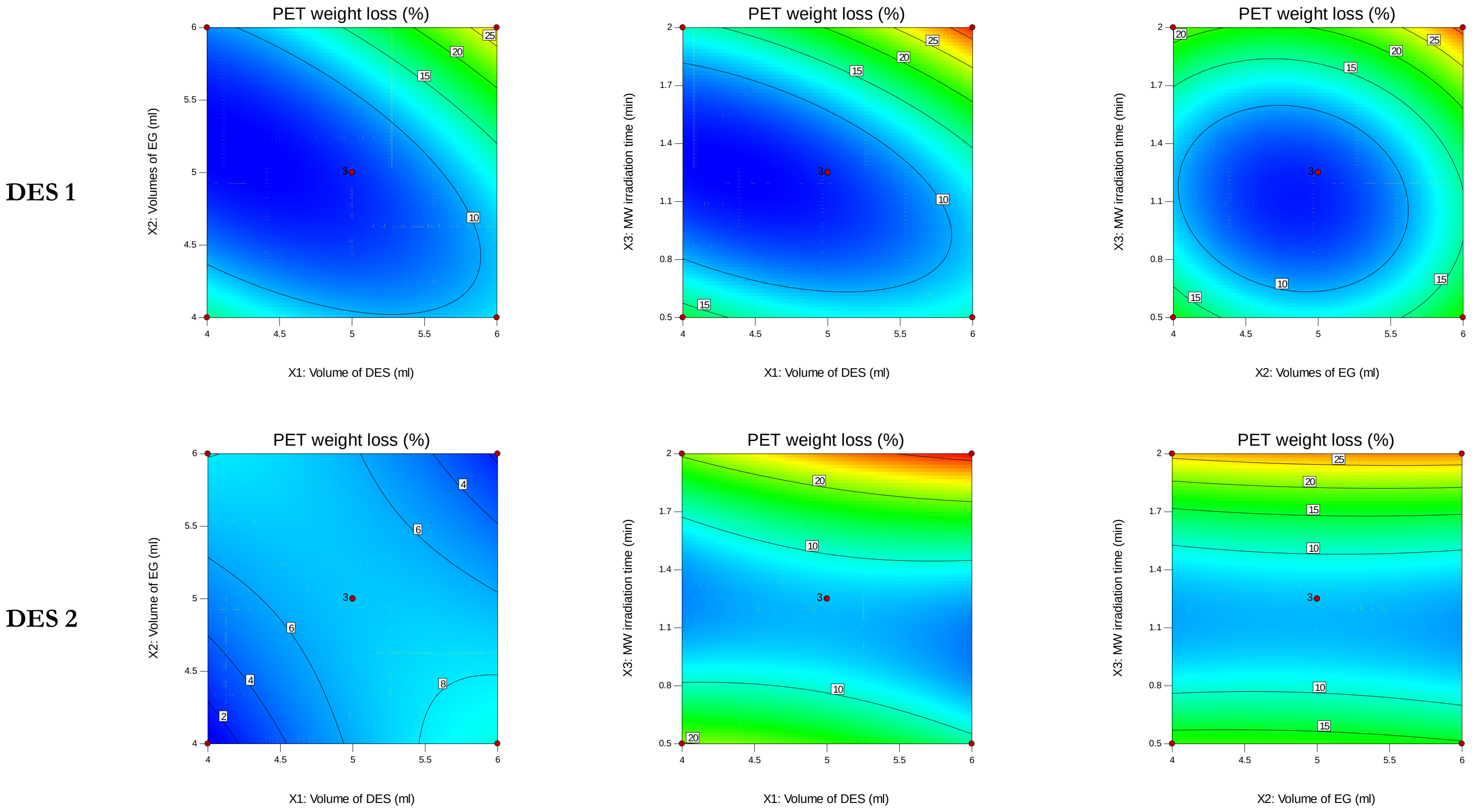

Figure 4-4 Contour plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on weight loss of PET (%) for MW assisted glycolysis of PET using DES 1 and 2.

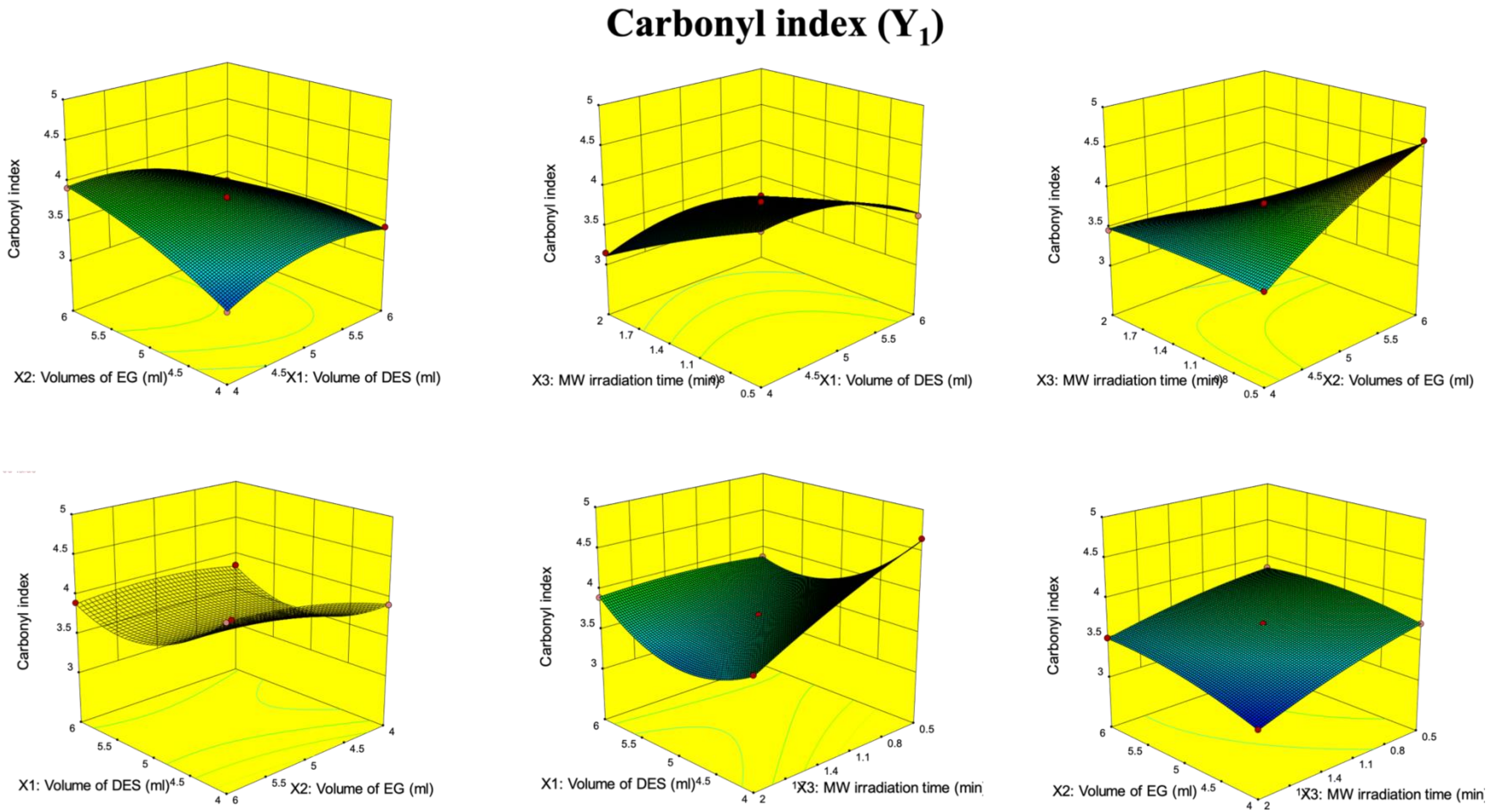

Figure 4-5 3-D plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on carbonyl index for MW assisted glycolysis of PET using DES 1 and 2.

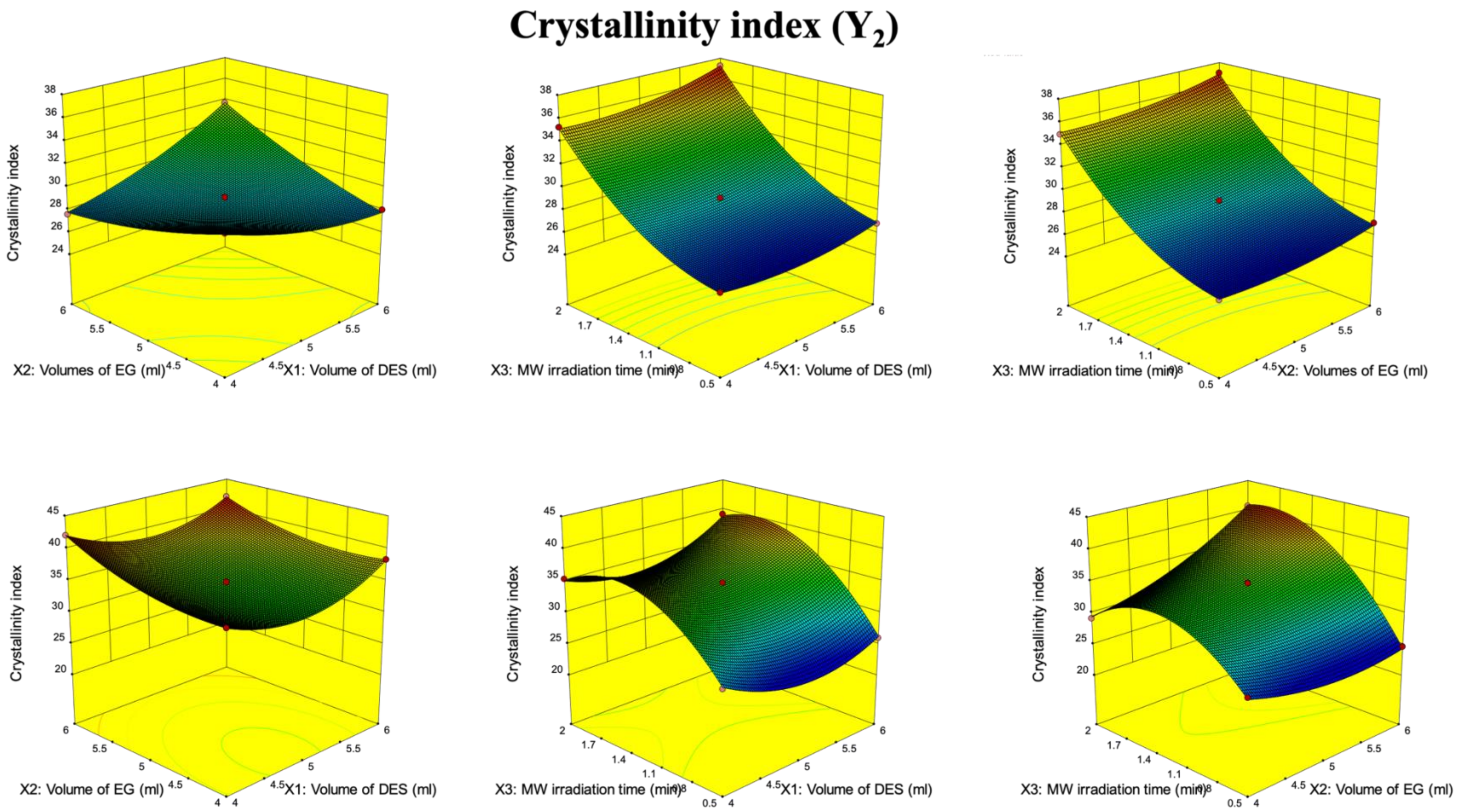

Figure 4-6 3-D plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on crystallinity index for MW assisted glycolysis of PET using DES 1 and 2.

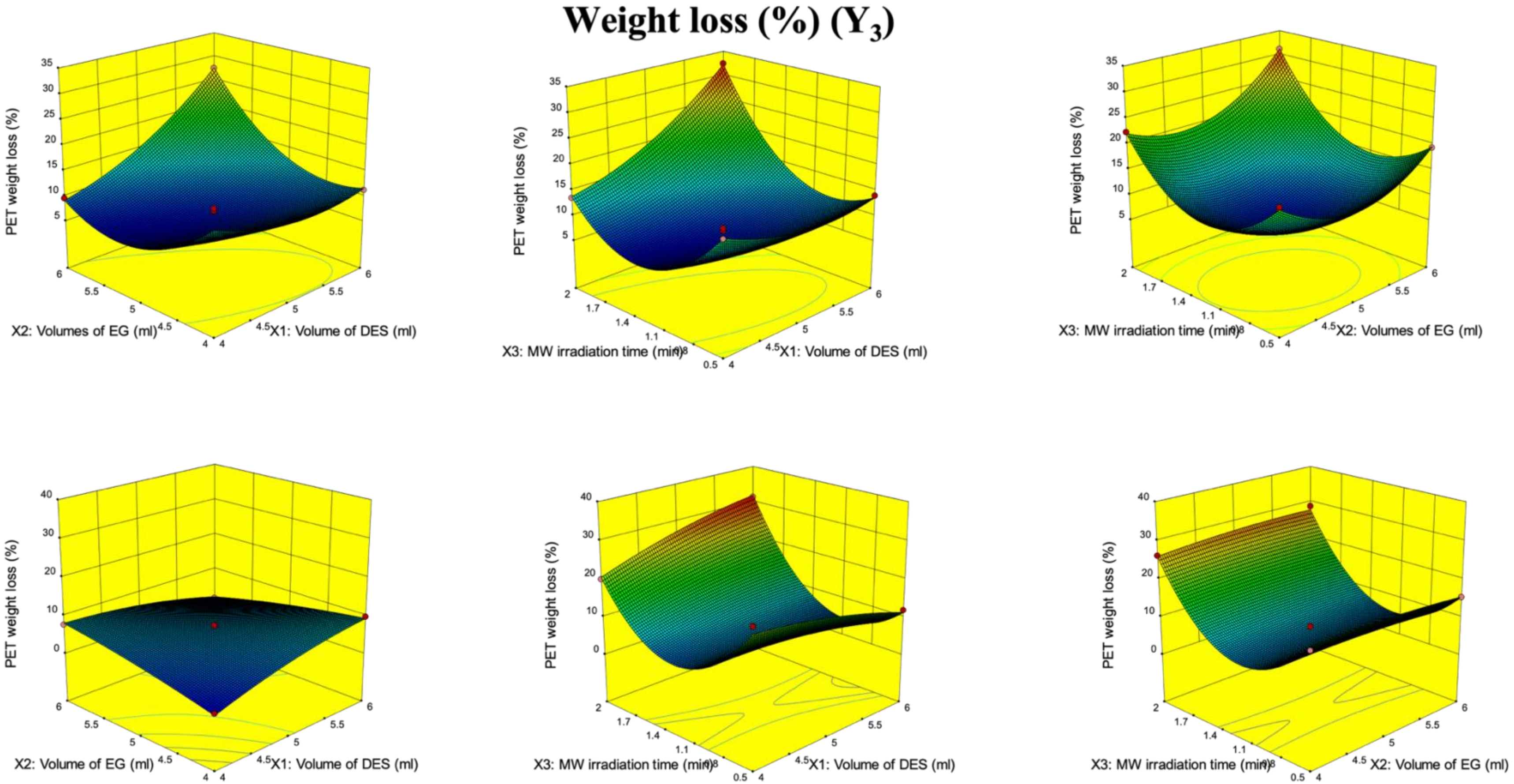

Figure 4-7 3-D plots of the effect of the interaction of [a] DES volume (X_1) and EG volume (X_2), [b] DES volume (X_1) and MW time (X_3) and [c] EG volume (X_2) and MW time (X_3) on weight loss of PET (%) for MW assisted glycolysis of PET using DES 1 and 2.

4.4.4 Optimization of MW assisted DES/glycolysis of PET

BBD optimization was performed on the studied responses and optimum conditions were chosen to obtain maximum initial PET degradation and residual PET characteristics that allow enhanced depolymerization in the MW assisted hydrolysis step. As previously discussed in the results, maximum initial PET degradation was observed with increased PET weight loss. Additionally, enhanced PET hydrolytic depolymerization can be achieved through low crystallinity and high carbonyl index of residual PET. Thus, the conditions of the MW assisted DES/glycolysis were adjusted to attain minimum crystallinity index and maximum carbonyl index of residual PET and maximum PET percentage weight loss. Two batch experiments were carried out at the optimized conditions for the MW assisted DES/glycolysis using DES 1 and DES 2. Typically, one gram of powdered PET was mixed with 5.5-6 mL EG and 4 mL of the prepared DES while stirring for 10 min. The prepared suspensions were exposed to MW irradiation of 350W power for 0.5 min. After MW treatments, PET residues were collected by filtration and dried. Excess distilled water was added to the filtrate and resultant BHET was precipitated by cooling overnight. As illustrated in Table 4-6**,** the studied responses values recorded a fine agreement between the observed and predicted results. Hence, the validity of the model was confirmed, and BBD proved its success in optimizing the proposed MW assisted DES/glycolysis technique for PET initial degradation. Precipitated BHET showed a percentage yield of 9.33 to 11.6% which confirmed the presence of some initial degradation of PET during the 0.5 min MW irradiation. Noticeably, MW assisted PET glycolysis using DES 2 as catalyst showed better results with respect to the studied responses than that of DES 1. This could be attributed to the enhanced catalytic activity of DES 2 where thiourea provided better interaction with EG and PET polymer. Lower C-S bond energy in thiourea which allowed the DES 2 to be more interactive with EG, thus, progressing enhanced PET chain cleavages. Such efficient catalytic activity gave rise to improved PET depolymerization which was manifested in the high PET weight loss percentage and increased crystallinity and carbonyl index of residual PET.

Table 4-6 The optimized MW assisted glycolysis of PET with observed and predicted response values.

Independent Variable		**Optimized level**			
		DES 1		DES 2	
X_1: Volume of DES (mL)		4		4	
X_2: Volume of EG (mL)		6		5.5	
X_3: MW time (min)		0.5		0.5	
Overall desirability		0.788		0.817	
Dependent variables	Desirability	DES 1		DES 2	
		Expected	Observed	Expected	Observed
Y_1: PET carbonyl index	Maximize	4.8	4.2	4.65	4.52
Y_2: PET crystallinity index	Minimize	25.07	28.65	27.95	29.32
Y_3: PET weight loss (%)	Maximize	18.61	16.75	21.45	18.66
Yield of BHET (%)	-	-	9.33	-	11.65

4.4.5 High PET conversion via MW assisted hydrolysis technique

Following the successful optimization of MW assisted DES/glycolysis conditions, virgin PET and residual PET obtained post glycolysis treatments underwent depolymerization via MW assisted hydrolysis using Na_2CO_3 in EG. The residual PET obtained was weighed and conversion of PET (%) was calculated. The reaction products dissolved in the cooled filtrate were analyzed by HPLC as shown in Figure 4-8. The effects of different PET treatments on the conversion of PET, the selectivity of BHET, MHET and the yield of TPA are illustrated in Figure 4-9. It was observed that the conversion of PET was only 66.80% when applying hydrolysis reaction on untreated virgin PET, and then rapidly increased to 98.62 and 99.31% when hydrolysing the treated residues of MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis respectively. Such significant increase in depolymerization efficiency with the MW assisted DES/glycolysis treated PET could be attributed to the new characteristics that the residual PET gained with respect to crystallinity, hydrophilicity, and weight loss upon treatment with MW assisted DES/glycolysis. These modifications in the PET residues increased the efficiency of their hydrolysis using Na_2CO_3 at only 3.0 min MW irradiation time. Moreover, the selectivity of MHET was much higher than that of BHET for all the treated samples as shown in Figure 4-9. It was also observed that the selectivity of BHET and MHET dramatically decreased while hydrolysing the PET residues obtained post glycolysis. Simultaneously, the yield of TPA increased from 34.28% for virgin PET sample to 63.67% and 81.23% for PET residues of MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis, respectively. Noticeably, the obtained results indicated that the formation of MHET was preferential to BHET and that the increased MW irradiation time and initial glycolysis step was beneficial to the yield of TPA.

It is also worth mentioning that the extent of hydrolytic depolymerization of PET residue obtained post MW assisted glycolysis using DES 2 into TPA was slightly higher than that using DES 1. Such finding confirmed that DES 2 as a catalyst resulted in a PET residue more amenable for efficient hydrolytic depolymerization using the weakly alkaline Na_2CO_3 in EG.

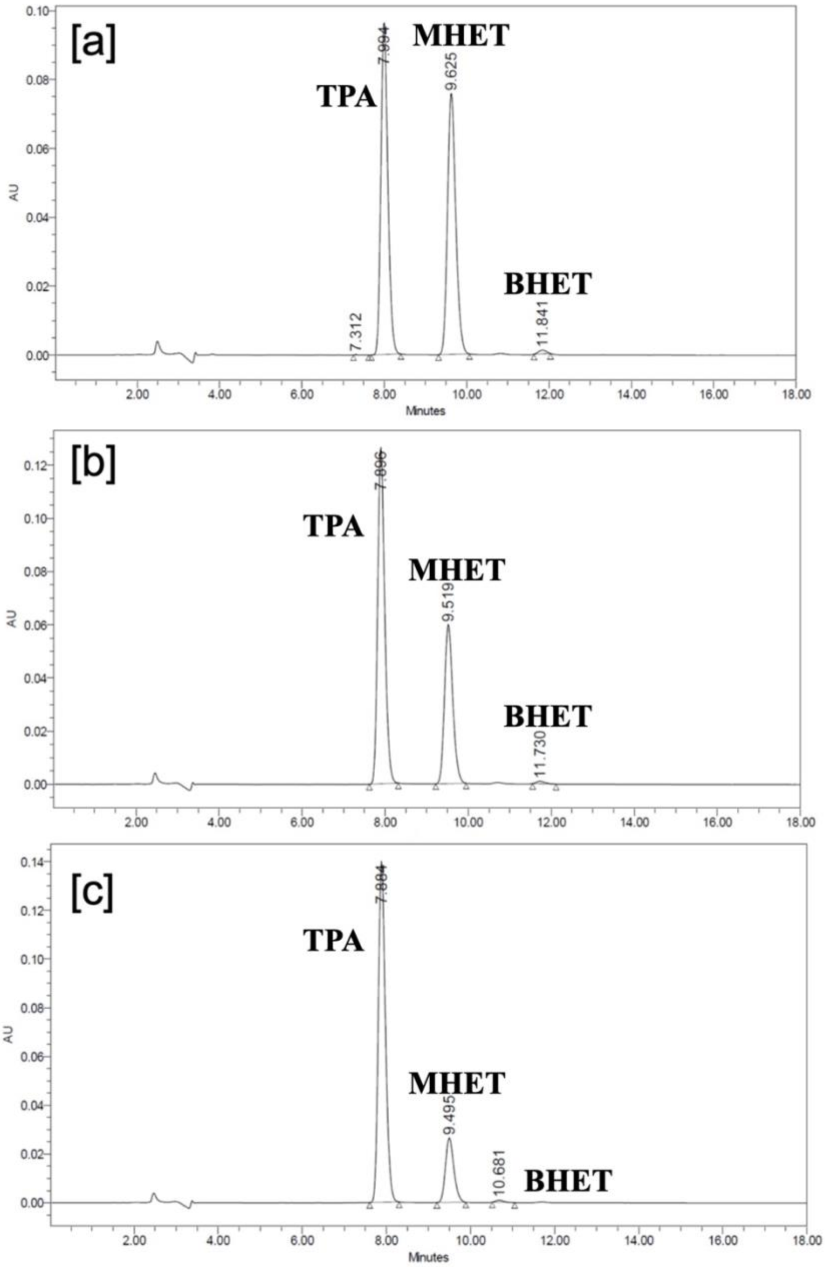

Figure 4-8 HPLC chromatograms of cooled filtrate of PET samples treated via: [a] MW assisted hydrolysis, [b] MW assisted hydrolysis post MW assisted DES 1/glycolysis and [c] MW assisted hydrolysis post MW assisted DES 2/glycolysis.

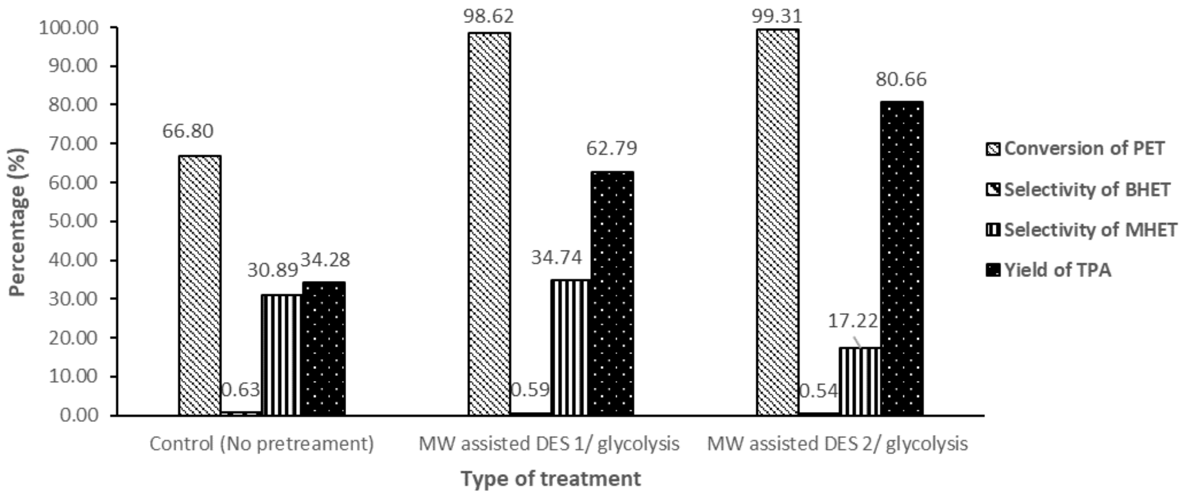

Figure 4-9 The effect of type of treatment on the conversion of PET and the selectivity of BHET, MHET and the yield of TPA.

The identity of the TPA white powder monomer precipitated post the MW assisted hydrolysis process was confirmed using FTIR analysis. Figure 4-10 demonstrates the FTIR spectra of precipitated TPA from all treated PET samples which showed great similarity to that of TPA standard. Carboxylic acid–OH was indicated by the peaks at 3064 cm^{-1}, acidic carbonyl group was indicated by 1673 cm^{-1} peak while the peak at 1280 cm^{-1} indicated the presence of ether C–O stretching (Musale & Shukla, 2016).

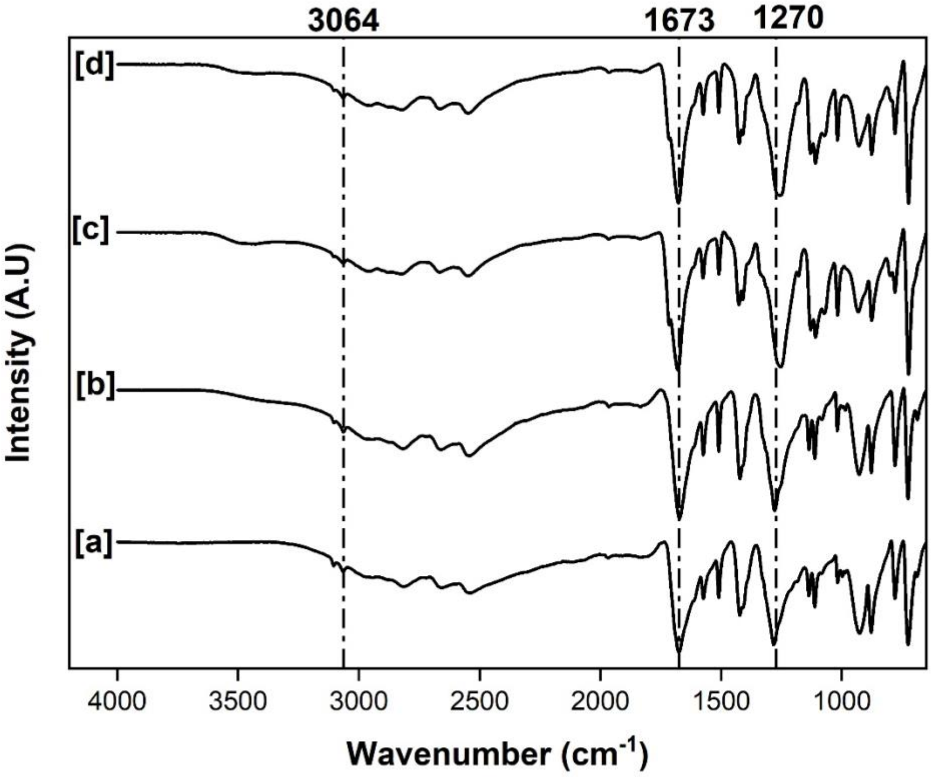

Figure 4-10 FTIR spectra of: [a] TPA standard, [b] TPA obtained from PET depolymerization via hydrolysis only, [c] TPA obtained from PET depolymerization via hydrolysis post MW assisted DES 1/glycolysis and [d] TPA obtained from PET depolymerization via hydrolysis post MW assisted DES 2/glycolysis.

4.4.6 Mechanism of the sequential glycolysis-hydrolysis of PET under MW irradiation

The sequential glycolysis-hydrolysis reactions and catalytic activity of DESs for PET depolymerization is explored in detail. A possible catalytic mechanism of the glycolysis of PET using DES 1 and 2 is presented in Figure 4-11. The H-bond actions between EG and the chloride of choline chloride and between EG and the urea (C=O) and thiourea (C=S) of DES 1 and 2 catalysts are expected to change the charge density of the hydroxyl (OH) group in EG and increase the electronegativity of the oxygen atom in OH group of EG. Hence, the nucleophilicity of the oxygen becomes stronger supporting preferential attack to the carbon of the ester group in PET (Q. Wang et al., 2012a). Under MW irradiation, PET treated with DES/EG initially changes to a more amorphous material, but with longer MW irradiation time, cleavage of the ester C-O bond and the formation of a new C-O bond with EG occur (Attallah, Janssens, et al., 2021; Q. Wang et al., 2012b). It is also worth mentioning that the enhanced catalytic activity of DES 2 as compared to DES 1 could be related to unique characteristic of lower C-S bond energy in thiourea which allowed the DES 2 to be more interactive with EG, thus, progressing enhanced PET chain cleavages (*Ohno A. (1977) Thiones. In: Oae S. (Eds) Organic Chemistry of Sulfur. Springer, Boston, MA. Https://Doi.Org/10.1007/978-1-4684-2049-4_5*, n.d.). Furthermore, difference in the electrochemical properties of DES 1 and DES 2 could also have a major impact on their catalytic performances. The higher conductivity offered by thiourea in DES 2 when compared to that of urea in DES 1 could have affected the heating rate of materials under MW irradiation and facilitated faster PET depolymerization (Boghosian & Howson, 1990; Hoppe et al., 2019).

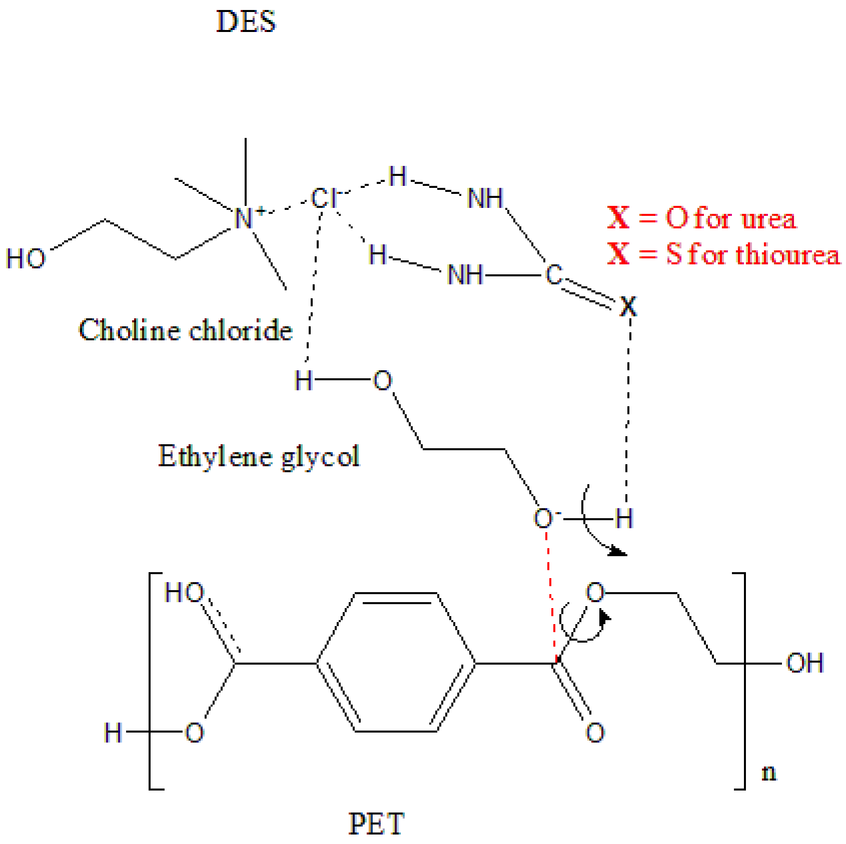

Figure 4-11 Schematic diagram for the interactions of DESs with EG and PET.

Based on previous reports for hybrid glycolysis/hydrolysis reactions (Güçlü et al., 2003; López-Fonseca et al., 2010b, 2011; Zanela et al., 2018), it is postulated that PET is converted to oligomers, and the oligomers are then converted to BHET and MHET and, finally, to TPA and EG. Figure 4-12 shows the proposed scheme for PET conversion to oligomers and ester hydrolysis of BHET producing TPA (a two-carboxylated compound) or MHET (a onecarboxylated compound). EG is formed in both cases. Technically, the water content causing BHET hydrolysis can be either produced during the reaction of PET with Na_2CO_3 in EG as previously reported by (Yoon et al., 1993) and (Güçlü et al., 2003) or could be due to moisture content from air.

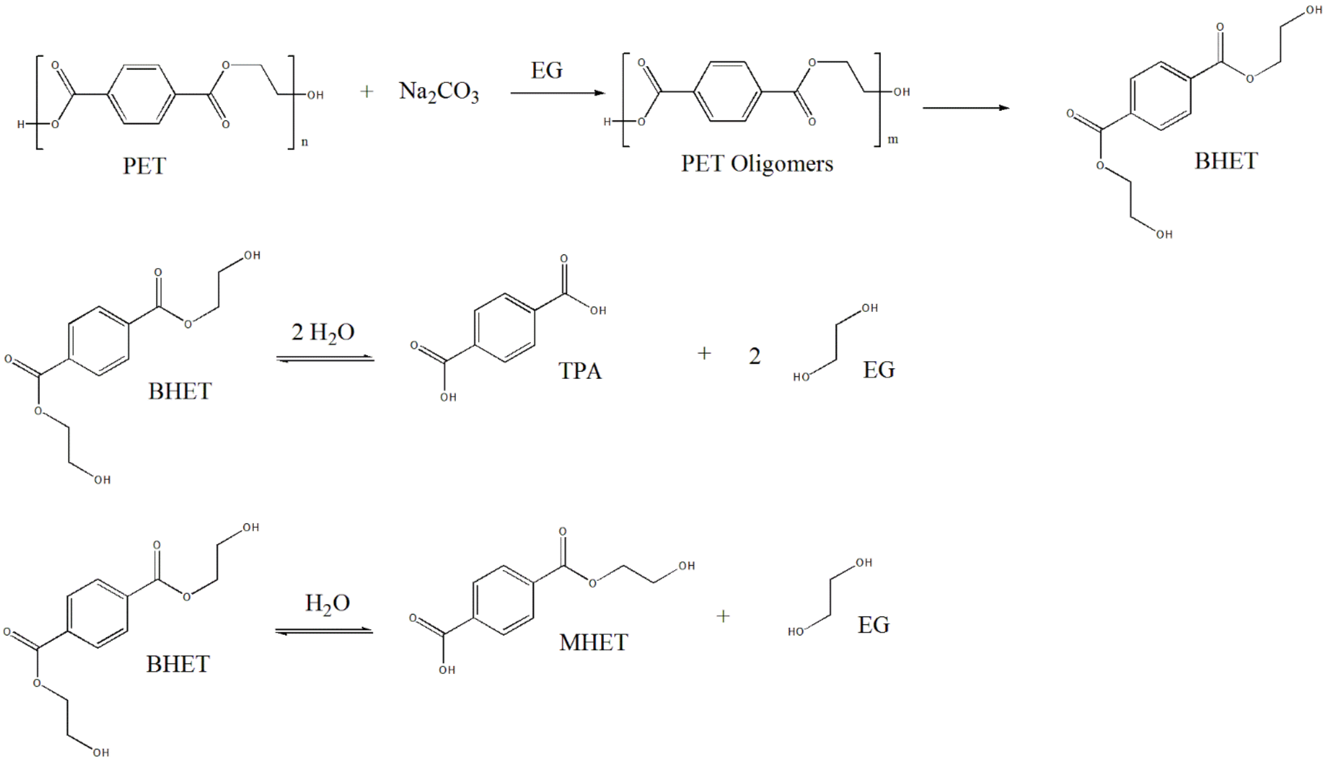

Figure 4-12 Suggestion mechanism for production of compounds during depolymerization of PET.

4.5 Application on postconsumer PET bottles

The efficiency of the proposed hybrid PET depolymerization technique involving MW assisted glycolysis followed by MW assisted hydrolysis was evaluated on post-consumer PET sample provided by SHABRA Plastics and Recycling ltd. (Ireland). The MW assisted DES/glycolysis was performed using the optimized conditions obtained from BBD (1 gm post-consumer PET, 4 mL DES, 6 mL EG and 0.5 min MW irradiation time). Residual PET samples obtained post glycolysis reaction were then mixed in 20 mL EG/10% (w/v) Na_2CO_3 and treated with MW irradiation for 3.0 min. Insoluble matter contents were separated, washed, dried and weighed. Percentage of PET conversion was calculated to be 96.77% and 98.25% for MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis, respectively. The yield of TPA obtained after precipitation with HCl was determined by HPLC and estimated to be 60.98% and 78.10% for

PET residues of MW assisted DES 1/glycolysis and MW assisted DES 2/glycolysis, respectively.

Based on the obtained results, it is postulated that the proposed hybrid depolymerization technique can achieve acceptable PET conversion percentages despite the presence of other additives or polymers in the post-consumer PET sample.

4.6 Evaluation of Performance

Practically speaking, for chemical recycling of plastics, it is noted that high ratios of solvents, harsh chemicals and longer reaction times significantly restrict its sustainable large-scale applications. Based on previous reports, it was found that a wide range of solvents to PET ratios of 4:1 to 50:1 are being used. Caustic chemicals such as NaOH, KOH, HCl and H_2SO_4 have also been selected as depolymerizing agents for hydrolytic depolymerization of PET. Reaction times ranging between 2 min to 8 h were set to complete the depolymerization reactions under conventional heating or MW irradiation while obtaining a monomer yield of 64% to 88%. Table 4-7 illustrates the reaction conditions and monomer yields of already established PET depolymerisation techniques using DESs as catalysts. Noticeably, the DESs proposed in the current study have proved themselves as efficient MW absorbers and PET depolymerization reaction catalysts owing to their unique properties. In the current work, the reaction time required for complete depolymerization of PET was only 3.5 min which is considerably short when compared to other studies presenting green approaches for PET degradation. Furthermore, the significant PET conversion (99%) and monomer yield reaching up to 80.66% can render the proposed technique ideal for PET depolymerisation and probably other polyesters from an industrial prospect.

Table 4-7 Comparison of DESs based PET depolymerization under various conditions.

DES composition			**Reaction conditions**			**PET conversion(%)**	**Monomer yield (%)**	**Reference**
HBA	HBD	Ratio (HBA:HBD)	Reaction time	Depolymerising agent	Temperature			
1,3-dimethylurea	$Zn(OAc)_2$	4:1	20 min	ethylene glycol	190 °C	100%	BHET (82)	(B. Liu et al., 2019a)
Choline chloride	Glycerol	1:2	1.3-1.6 min	Glycerol, NaOH	-	38-61%		(S. Choi & Choi, 2019)
Choline chloride	Zinc chloride	1:1–1:3	30 min	Diethanolamine, ethanolamine	-	-	THETA (82), TPA (83), BHETA (95)	(Musale & Shukla, 2016)
Choline chloride	m-cresol	1:2	1.5 min	NaOH	-	84%	TPA (91.55)	(Attallah, Janssens, et al., 2021)
Potassium carbonate	Ethylene glycol,	1:6	2 h	ethylene glycol	180 °C	-	BHET (88)	(Güçlü et al., 2003)
Choline chloride	Urea, Glycerol	1:1:1	3 min	-	-	1.8% weight loss	TPA, MHET, BHET 16 (w/w)	(Attallah et al., 2022)
Zinc chloride, zinc acetate, manganese acetate	Urea	1:12 to 1:6	30 min	ethylene glycol	170 °C	100%	bis(hydroxyalkyl) terephthalate (83)	(Q. Wang et al., 2015)
1-methyl-3-butylimidazolium chloride	Zinc chloride, Manganese chloride	1:1	5.0 h	ethylene glycol	190 °C	-	BHET (83.8)	(Yue et al., 2013)
Choline chloride	Ethylene glycol	1:2	2 min	ethylene glycol, NaOH	144 °C	45.8% weight loss of PET	-	(Cho et al., 2016)

Choline chloride	Urea,	1:2	3.5 min	sodium carbonate, ethylene glycol	-	98.62%	TPA (62.79), MHET (34.79), BHET (0.59)	This work
Choline chloride	Thiourea	1:2	3.5 min	sodium carbonate, ethylene glycol	-	99.31%	TPA (80.66), MHET (17.22), BHET (0.54)	This work

*** Hydrogen bond donor (HBD); hydrogen bond acceptor (HBA); (2-hydroxyethyl)-terephthalamide (THETA); Terephthalic acid: (TPA); bis (2-hydroxy ethylene) terephthalamide: (BHETA); bis(hydroxyethyl) terephthalate (BHET); sodium hydroxide (NaOH)**

4.7 Conclusion

A hybrid depolymerization process for PET comprising a fast, low energy MW assisted glycolysis-hydrolysis was presented. In comparison to reported MW assisted PET depolymerization approaches, the proposed hybrid technique achieved improved PET depolymerization with a total of ≈99% PET conversion under environmentally friendly operating conditions in only 3.5 min. The catalytic activities of urea derivatives based DESs for MW assisted glycolysis of PET were compared. DES 2 showed better results as catalyst with respect to the studied responses than that of DES 1 which was related to the enhanced interaction of thiourea of DES 2 with EG and PET polymer chains. The MW assisted hydrolysis of PET residue obtained post glycolysis reaction was then performed and a total of 99% weight loss of glycolytically treated PET in comparison to 67% weight loss of virgin PET undergoing only hydrolysis reaction was demonstrated. HPLC analysis of the reaction mixture filtrates obtained post hydrolytic depolymerization showed the presence of TPA, MHET and traces of BHET as the produced monomers. Application on Post-consumer PET sample also revealed very satisfactory results with 96.77-98.25% PET conversion rates and 60.98-78.10% yield of TPA.

Furthermore, taking into consideration the industrial scale depolymerization of PET with factors like plant installation and maintenance costs, skilled labour requirements and safety, the route demonstrated by the proposed technique can present an attractive economic and environmentally sustainable technology for PET and other polyester recycling and circularity.

Chapter 5. All green MW assisted 99% depolymerisation of PET into value added products via glycerol pre-treatment and hydrolysis reaction

Citation: **Azeem, M.**, Attallah, O. A., Tas, C. E., & Fournet, M. B. (2023). All Green Microwave Assisted 99% Depolymerisation of Polyethylene Terephthalate into Value Added Products via Glycerol Pre-treatment and Hydrolysis Reaction. *Journal of Polymers and the Environment*. https://doi.org/10.1007/s10924-023-02979-8

5.1 Preface

In the last two chapters, a deep understanding of the capabilities of MW-assisted green solvents for PET pre-treatments was developed. All green and ultrafast PET pre-treatments/depolymerisation efficiencies were evaluated. To build on this achievement, in this chapter, the approach of combining all green and ultrafast MW-reagent-based PET pre-treatments to depolymerise PET efficiently was implemented. The MW assisted pre-treatment was conducted in the presence of glycerol, and the process was optimised using Box-Behnken design. In the hydrolysis reaction, the pre-treated PET was exposed to MW treatment while using $NaHCO_3$ in EG to completely depolymerise PET into its value-added monomers. The TPA obtained from the depolymerisation process was then separated, purified and validated for repolymerisation into PET in terms of organic structure, metallic content, colour, and acid number.

5.2 Introduction

Polyethylene terephthalate (PET) belongs to the class of engineering polymers which have a broad range of applications because of their extensive corrosion resistance and thermal stability(Benyathiar et al., 2022). According to recent studies, the production of PET was doubled resulting in a growth rate of more than 5% per annum and the elevation of plastic waste up to 8 million tons every year(Padhan & Sreeram, 2019b)(Thiyagarajan et al., 2022)(Chan & Zinchenko, 2021)(Pudack et al., 2020).

5.2.1 Chemical recycling of PET

In recent years, there has been intensive care in the development of scalable and sustainable recycling methodologies to reduce plastic accumulation in nature to close the loop for a circular economy. Chemical recycling as one of these methodologies has shown great potential to produce polymers with higher quality and economic aspects. The importance of chemical recycling lies in its ability to convert polymers into their basic building blocks that can be repolymerised into virgin forms or upcycled into other useful products. There are two subcategories for chemical recycling which are distinguished based on the reaction systems involved such as transesterification-based and esterification-hydrolysis-based(Kirshanov et al., 2022)(Sadeghi et al., 2021). In general, commercial PET production from TPA as the monomer follows the production line, which consists of the extraction of raw materials (p-xylene) from petroleum/gas, and oxidation of p-xylene via a proper catalyst system. The oxidation reaction of p-xylene produces by-products such as p-toluic acid and p-formyl benzoic acid, resulting in the appearance of impurities in the TPA products. To overcome this problem, the manufacturing line also includes additional crystallisation/separation steps. Moreover, this production step involves harsh reaction conditions such as high pressure and temperature(*Organic Chemical Process Industry 6.11-1*, 2000).

In contrast, chemical recycling of post-consumer PET provides a strong way to produce monomers (such as TPA) by allowing them, to be converted directly from waste plastic as a source of raw material instead of oil. Thus, many commercial TPA production steps can be eliminated by instant and direct production through postconsumer PET. Therefore, chemical recycling of postconsumer PET significantly contributes to conserving resources, reducing waste, and developing an overall sustainable environment, because of the use of waste plastic as the raw material source and milder processing conditions(Frisa-Rubio et al., 2021). Among the different conventional chemical recycling techniques, glycolysis and hydrolysis appear feasible for large-scale applications(Azeem et al., 2022b). In the glycolysis of PET, bis (2-hydroxyethyl) terephthalate (BHET) monomer is produced as a result of replacing ester linkages of PET by hydroxyl groups(Gómez et al., 2019). In a typical hydrolysis processing of PET, terephthalic acid (TPA) and ethylene glycol (EG) are generated as depolymerised products in the presence of acid/base or steam(Sheel & Pant, 2019). Nevertheless, the implementation and practice of these chemical methods on a large industrial scale require further improvements due to their huge energy inputs, and slow reaction rates(Tang & Chen, 2019).

5.2.2 Microwave technology for PET recycling

Microwave (MW) technology has shown great potential for addressing the problems of energy loss and long reaction runs associated with the depolymerisation of PET. Several studies have been conducted to evaluate PET depolymerisation efficiency via MW-assisted glycolysis and hydrolysis reactions in combination or separately(B. Liu et al., 2019a). In one study, the PET glycolysis reaction time was decreased by 21 h from the original time (24 h) to 3h in the presence of an oxalate-bridged binuclear iron (III) ionic liquid under MW irradiation. The overall yield of monomer (BHET) was 80%(Cot et al., 2019). In another study, MW-assisted hydrolysis was conducted using deep eutectic solvent (DES) based on m-cresol and choline chloride (ChCl) in combination with different compositions of NaOH. The maximum yield of TPA monomer (91.55%) was achieved within 92 s of MW irradiation together with DES and 10% NaOH(Attallah, Janssens, et al., 2021). In our previous work we also studied the sequential glycolysis-hydrolysis depolymerisation of PET using ChCl-urea and ChCl-thiourea-based DESs and evaluated the conversion efficiency of PET into value-added monomers. Overall, 99% PET conversion into monomers was achieved within 3 min with a yield of TPA (80.66), MHET (34.79), and BHET (0.59)(Azeem et al., 2022b).

Nevertheless, MW assisted depolymerisation of PET as a promising and suitable for large-scale implementation still need constant developments to replace the caustic depolymerising agents which cause corrosion within reaction vessels with safer ones. Therefore, it is imperative to develop MW assisted depolymerisation treatments containing green depolymerising agents to improve the sustainability of PET recycling and reduce carbon footprints associated with conventional depolymerisation methodologies. For instance, Xie et al.(Xi et al., 2005) used zinc acetate to depolymerise PET into BHET. The resultant yield of the monomer (85%) was achieved under the reaction conditions of 196°C temperature, 3 h time, 1% weight ratio of catalyst to PET, and 5(w/w) weight ratio of EG to PET. In another study, sodium sulfate was used as a catalyst to depolymerise PET into BHET under an excess amount of EG. At 196°C temperature and reaction time of 8 h, 65% selectivity for BHET was achieved(Shukla & Harad, 2005). However, most of these conventional methodologies are performed under harsh conditions. Therefore, it is necessary to develop green reagents to improve the scalability and sustainability of recycling methods.

One of these suggested green reagents is sodium bicarbonate ($NaHCO_3$), a monosodium salt of carbonic acid with alkalising characteristics. It is white powder and crystalline, commonly known as baking soda, used to relieve acid indigestion(Fiore et al., 2016). Recently, $NaHCO_3$ has shown great potential for the glycolysis and hydrolysis recycling of PET. For instance, Dorin et al.(Ezeanu & Matei, 2021) used $NaHCO_3$ as a catalyst in the depolymerisation of waste PET via hydrolysis reaction. Within 150 min in a batch reactor, a 95 % TPA yield was achieved at 196°C temperature and 3 MPa reactor pressure conditions. In another study, Sun cong-hao et al.(C. hao Sun et al., 2018) implemented alcohol-alkali hydrolysis for the preparation of TPA from PET waste bottles in the presence of $NaHCO_3$. 94-

97% TPA was obtained with an overall 98% PET conversion under reaction times (60–75 min), temperature (170–180°C), mass ratio of $NaHCO_3$ to PET of 1:1.1; and different volume ratios of water to PET mass/EG to PET mass.

Glycerol on the other hand is also an inexpensive, green, biobased, organic molecule with a huge number of application in chemistry and PET depolymerisation reactions(Pagliaro et al., 2007)(Dzhabarov et al., 2020). For example, Dzhabarov et al.(Dzhabarov et al., 2020) used biodiesel wastes containing glycerol and potassium salts to study PET depolymerisation in a glass reactor. Complete conversion of PET was achieved at 190-195°C temperature within 90 min. In another study, glycerol-based DES also delivered exceptionally high PET conversion at short reaction times. The PET conversion achieved was 38-61% at 1.3-1.6 min(S. Choi & Choi, 2019). This could be associated with the efficient H-bond action between glycerol and urea that preferentially attacked the ester group in PET. Furthermore efficient MW absorption properties and increasing thermal heating response of glycerol under MW irradiations could also result in improved catalytic performance in the different depolymerisation reactions(González-Rivera et al., 2020)(González-Rivera et al., 2021).

5.2.3 Proposed methodology

Noting the effect of glycerol as efficient green MW absorbers and $NaHCO_3$ in combination with EG as green depolymerising agents. EG is used in the hydrolysis of PET as a reaction solvent to enhance the reaction rates. It provides hydroxyl groups which react with ester bonds, causing cleavage and the resulting depolymerisation of PET(S. Zhang et al., 2022). For example, Hu et al.(Hu et al., 1997) studied the depolymerisation of PET using NaOH in methanol in the presence and absence of dioxane. In the presence of dioxane (10 vol%), 96% depolymerisation was achieved at 60°C and 40 min of reaction time, whereas it took 7 h to achieve similar yield without dioxane. However, with the addition of EG (5 ml), the complete depolymerisation of PET into TPA was achieved within 15 min. This indicates that they can serve as good alternatives to conventional corrosive and harsh reagents which require longer times for PET depolymerisation reactions. In this research study, fast and all-green sequential PET depolymerisation technique comprising MW assisted pre-treatment followed by hydrolysis reaction was employed. The MW assisted pre-treatment was conducted in the presence of glycerol, and the process was optimised using Box-Behnken design. In the hydrolysis reaction, the pre-treated PET was exposed to MW treatment while using $NaHCO_3$ in

EG to completely depolymerise PET into its value-added monomers. The TPA obtained from the depolymerisation process was then separated, purified and validated for repolymerisation into PET in terms of organic structure, metallic content, colour, and acid number.

5.3 Experimental

5.3.1 Materials

PET polymer pellets were purchased from Alpek Polyester UK Limited and micronised into fine powder by using a centrifugal- ZM200 miller. Analytical grades of sodium bicarbonate (98%), glycerol (99%), ethylene glycol (99%), N,N-dimethyl acetamide (HPLC, ≥99.9%), ethyl alcohol (anhydrous, ≥99.5%) were obtained from Sigma Aldrich (UK).

5.3.2 MW assisted pre-treatment of PET

Experiments were performed by adding 1g of PET powder in different volumes ratios of glycerol. After stirring for 5 min, suspensions were kept under MW irradiation in a 1200 W domestic MW oven at specific MW irradiation powers and times. After MW exposure, the pre-treated PET was separated via filtration, followed by washing with distilled water prior to overnight oven drying at 65 °C. The MW assisted pre-treatment of PET was optimised using a three-level, three factor BBD (Design Expert,11.1.0.1, Stat-Ease Inc., Minneapolis, MN). Three factors; MW irradiation time (X_1) (min), MW power (X_2) (W), and glycerol volume (X_3) (ml) were studied by running 15 experiments in triplicates and mean data was reported. The responses were obtained as crystallinity index calculated from DSC data, weight loss % at onset temperature (T_0) of degradation from TGA results, and carbonyl index from FTIR spectra (Table 5-1).

Table 5-1 BBD levels and variables for PET pre-treatment process.

	level			
Independent variables	-1	0	1	Constrains
X_1: MW time (min)	2	3	4	In the range
X_2: MW power (W)	160	330	500	In the range
X_3: Volume of glycerol (ml)	8	12	16	In the range

5.3.3 MW-assisted hydrolysis of residual PET obtained after glycerol pre-treatment

Hydrolysis reaction of PET was carried out on both untreated and pre-treated PET to determine the necessity of the MW assisted pre-treatment step. Following the procedure developed in our previous work(Azeem et al., 2022b), untreated PET and pre-treated PET were mixed separately in 10%(w/v) $NaHCO_3$ in 20mL EG and stirred for 5 min. The prepared suspensions were then exposed to MW irradiations for 3 min in a MW oven at 350 W power. After MW treatment, dissolved contents of PET were precipitated by adding distilled water in the suspensions. Upon filtration, the filtrate consisting of soluble monomers was characterised by high performance liquid chromatography (HPLC). Pre-treated PET from both samples was dried at 65°C overnight. The precipitation of TPA from the filtrate was carried out using 2 mL hydrochloric acid (34%) followed by washing with distilled water and drying at 65°C overnight. Depolymerisation of PET was determined using the following equation(Azeem et al., 2022b):

$$\textbf{PET conversion (\%)} = \left(\mathbf{1} - (\boldsymbol{Residual\ PET\ weight})/(\boldsymbol{Initial\ PET\ weight})\ \times\ \mathbf{100}\right) \quad \textbf{(5-1)}$$

The selectivity measurement for the produced BHET, MHET, and TPA was extracted from HPLC chromatograms by quantifying peak area normalisation method and the following equation was used to calculate the yield of TPA(Du et al., 2020b):

$$\textbf{TPA yield (\%)} = \left(\ (\boldsymbol{PET\ conversion}\ (\%)\ \times\ \boldsymbol{TPA\ selectivity}\ (\%)\ )/\mathbf{100}\ \right) \quad \textbf{(5-2)}$$

5.3.4 Purification of the obtained TPA

Purification of the TPA precipitated from the monomers' mixture was carried out using a dissolution/crystallisation method with slight modifications(Wu et al., 2011a). For this purpose, 1 g of the precipitated TPA was dissolved in dimethyl acetamide (DMAc) at its boiling point. The hot solution was then filtered with filter paper to remove the insoluble parts from the solution system. The filtrate was directly inserted into an ice bath, and the formed TPA crystals were collected by filtration, washed with excess amount of ethanol to get rid of the DMAc residuals and finally dried in an oven at 80°C for 24h.

5.3.5 Instrumental characterisations

Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, UK) was used to analyse PET samples before and after microwave treatments and produced monomers within spectral range of 4000-600 cm^{-1} accumulating 16 scan cycles and a resolution of 4 cm^{-1}. The carbonyl index was extracted from obtained data by taking ratios of intensities of ester carbonyl peak (1713 cm^{-1}) to normal C-H bonding mode (1408 cm^{-1}) by using following equation(Attallah et al., 2022)(Chelliah et al., 2017);

$$\boldsymbol{Carbonyl\ index = \frac{Absorption\ at\ 1713\ cm^{-1}}{Absorption\ at\ 1408\ cm^{-1}}} \qquad \textbf{(5-3)}$$

The thermal characteristics of PET samples were attained by a differential scanning calorimetry (DSC)(Perkin Elmer 4000) under nitrogen flow. Each sample weighing between 5-6 mg were kept in aluminium pan and heated from 30-275°C at a rate of 10°C per min. The crystallinity index was calculated as follows(Li et al., 2017);

$$\boldsymbol{Crystallinity\ index = (\Delta H_m / W \Delta H_{m0}) \times 100} \qquad \textbf{(5-4)}$$

Where heat of fusion of PET samples is ΔH_m (jg^{-1}), weight fraction is W(g), and heat of fusion of completely crystalline PET(140 jg^{-1}) (Attallah, Janssens, et al., 2021)is denoted by ΔH_{m0}.

The weight loss % of PET was analysed by using thermogravimetric analyser (TGA). All the measurements were taken at onset temperature of degradation (T_o). The MW treated samples were kept in a standard pan and heated (30-600°C) at the rate of 10°C per min. The nitrogen flow of 50 mL per min was maintained for all the experiments. The following equation was used to calculate PET weight loss %;

$$\boldsymbol{Weight\ loss}\ (\%) = (\boldsymbol{100 - wieght}\ \%\ \boldsymbol{of\ PET\ at\ To}) \qquad \textbf{(5-5)}$$

Identification and quantification of soluble depolymerised products from PET was determined using HPLC (Alliance waters, UK) with a flow rate of 1.2 ml/min in a C-18 column (4.6*250, 5 um, Nucleodur, Germany). The injection volume for each specimen was 10ul at 30°C and all the standards (BHET, MHET, TPA) were prepared in 100 % methanol. Mobile phases containing acetonitrile, 10mM sulphuric acid, and ultrapure water was used with a UV detector of wavelength 254 nm. The total run time for each sample was 18 minutes. The quantification of the produced monomers was carried out by plotting calibration curves within the range of (0.01-1 mM) standard concentrations. NMR measurements of samples were carried out by a Bruker NMR advanced using the operating frequency of 600 MHz at 25°C in d-DMSO.

ICP-MS measurements were performed with Agilent 7800 ICP-MS instrument equipped with an SPS4 autosampler, MS40+ Foreline Pump, and G8481A re-circulating chiller. As the sample preparation for the test, 0.1 g of the sample was added to a beaker and digested with 5 mL of 67% Nitric Acid, 1.7 mL concentrated HCl, and 3.3 mL of water. The digestion process was carried out in a microwave at 230°C for 20 min. Finally, the prepared sample was rinsed and made up to 50 mL with water for ICP-MS analysis.

The acid number values of the products were determined with Eutech ION 700 pH/mV meter by following the ASTM standard D8031-16, the standard test method for the acid number of terephthalic acid by automatic potentiometric titration.

APHA colour values were determined based on a colour test by using Varian Cary 50 UV-Vis Spectrometer. As the sample preparation, 2.5 g of the sample was dissolved in 50 g of DMF (%5) by assisting with an ultrasonic bath. The measurements were performed with UV-Vis Calibrated at a low Range of 10-200 Pt-Co and a high Range of 50-500 Pt-Co. Samples were analysed by an appropriate calibration curve.

5.4 Results and Discussion

5.4.1 MW assisted pre-treatment of PET

In this study, green microwave technology was employed for PET pre-treatment using fully biobased, inexpensive and nontoxic glycerol solvent. Based on our previous work, a significant catalytic activity and increased reaction rate under MW irradiations was observed in solvents which possess high pH and low density values(Attallah, Janssens, et al., 2021)(Azeem et al., 2022b). For the glycerol solvent system, pH and density values were observed to be 8.6 and 1.21 g/cm^3 respectively(Wernke, 2014). The significant effect of glycerol solvent in its interaction with PET lies in its ability to raise the electron density and attraction between carbonyl oxygen of PET which tend to form single bond after rearranging electrons. Thus, electrostatic attraction between H and O can give glycol and forms ester C=O which facilitate producing monomers and other intermediate products with leftover glycol as presented in Figure 5-1 (Carta et al., 2003).

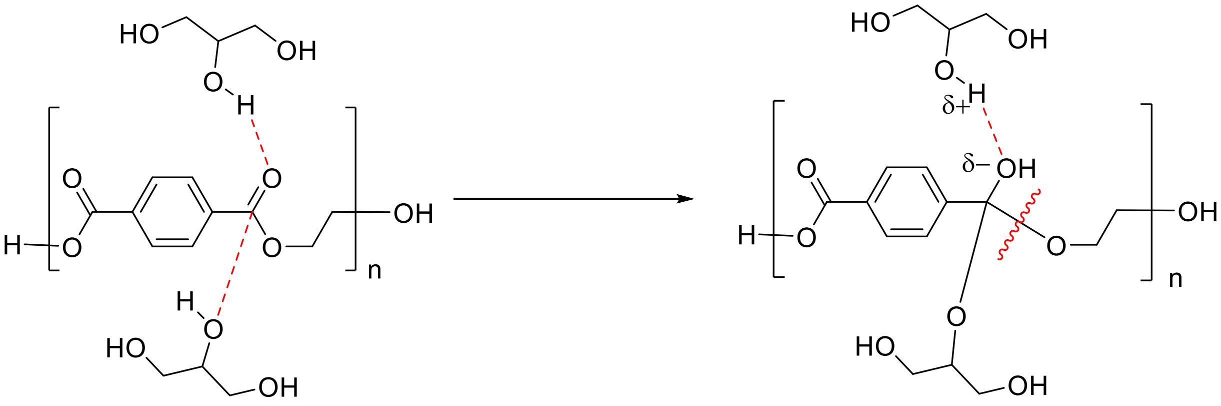

Figure 5-1 Proposed interaction mechanism between glycerol and PET in the MW assisted pre-treatment step.

5.4.2 Experimental design for MW-assisted PET pre-treatment

The response surface methodology was carried out to evaluate MW-assisted pre-treatment of PET best fitting model. In the current work, based on the BBD design for the studied parameters (MW irradiation time, volume of glycerol, and MW power), 15 experimental runs were performed. After each experiment, the crystallinity and carbonyl indices of PET residues, and weight loss % of PET at T_0 of degradation were determined and presented in Table 5-2.

The responses values obtained from the MW assisted pre-treatment of PET were tested against various statistical models and the quadratic model was found to be the best fitting one. As demonstrated in Table 5-6, The coefficient of determination of all the studied responses were within acceptable ranges and the obtained adjusted R^2 values were 0.9632, 0.9487, and 0.9206 for carbonyl index, weight loss at T_0 of degradation and crystallinity index respectively. High model F-values were also observed which implied that the quadratic model was suitable for the prediction of the studied responses. Analysis of variance (ANOVA) was performed to evaluate the curvature significance in the responses at a 95% confidence interval and showed that all the responses' probability values (*p*-value) were less than 0.05. The lack of fit test also demonstrated a highly desirable nonsignificant lack of fit ($p > 0.1$) where the carbonyl index, weight loss at T_0 of degradation and crystallinity index had *p*-values of 0.81, 0.74, and 0.90 respectively.

Table 5-2 Experimental runs and observed responses for treated PET in BBD.

	Independent variables			Dependent variables		
Run	MW time (min) X_1	MW Power (Watt) X_2	Volume of glycerol (mL) X_3	Carbonyl index Y_1	Crystallinity index % Y_2	Weight loss % at T_0 Y_3
Pure				2.80	31.4	0.44
1	3	350	12	3.41	54.65	11.918
2	3	500	8	3.75	55.70	9.013
3	3	160	16	4.43	40.08	5.082
4	4	350	8	2.98	55.04	7.719
5	3	350	12	3.36	62.86	9.524
6	3	160	8	3.66	42.55	2.275
7	2	160	12	3.63	31.55	2.339
8	2	500	12	3.30	57.28	12.10
9	4	500	12	3.22	43.40	10.202
10	4	160	12	3.58	44.52	7.51
11	4	350	16	4.01	41.57	10.75
12	3	500	16	3.92	49.66	8.604
13	2	350	8	3.43	50.69	10.82
14	3	350	12	3.12	55.1	8.476
15	2	350	16	3.68	51.66	9.673

X_1: MW irradiation time, X_2: MW power, X_3: volume of DES, Y_1: Carbonyl index, Y_2: Crystallinity index and Y_3: Weight loss (%) at T_0 of degradation.

Detailed results of the ANOVA for the response surface quadratic model and the significance of its regression coefficients are illustrated in Table 5-3, Table 5-4, and Table 5-5 for the carbonyl index, weight loss at T_0 of degradation and crystallinity index, respectively. The analysis of normal distribution of residual values which explain the difference between predicted values (model) and the observed values (experimental) is another critical diagnostic tool for evaluating the suitability of the fitted model to predict the studied responses. The data is said to be distributed normally if all the points fall close to the straight line. The normal probability plots of residual values of the carbonyl index, weight loss at T_0 of degradation and crystallinity index are illustrated in Figure 5-2 Normal probability plot of residuals for carbonyl index, weight loss at T_0 of degradation and crystallinity index of pre-treated PET. In each plot, the residual values for most of performed experiments were evenly distributed in space. Thus, the model can be accepted to describe the responses under study.

Table 5-3 Significance of regression coefficients of the carbonyl index of pretreated PET.

Source	Coefficient Estimate	df	Sum of Squares	F Value	p-value Prob > F
Model	3.30	9	1.88	14.54	0.0044
A-Time	-0.031	*1*	*7.813E-003*	*0.55*	*0.4934*
B-Power	-0.14	*1*	*0.15*	*10.75*	*0.0220*
C-Volume	0.28	*1*	*0.62*	*43.00*	*0.0012*
AB	-7.500E-003	*1*	*2.250E-004*	*0.016*	*0.9052*
AC	0.19	*1*	*0.15*	*10.62*	*0.0225*
BC	-0.15	*1*	*0.090*	*6.28*	*0.0541*
A^2	-0.14	*1*	*0.072*	*5.02*	*0.0751*
B^2	0.28	*1*	*0.28*	*19.55*	*0.0069*
C^2	0.37	*1*	*0.50*	*34.88*	*0.0020*
Residual		5	0.072		
Cor Total		14	1.95		

Table 5-4 Significance of regression coefficients of the weight loss at T_0 of degradation of pre-treated PET.

Source	Coefficient Estimate	df	Sum of Squares	F Value	p-value Prob > F
Model	9.97	9	120.15	6.44	0.0270
A-Time	0.16	*1*	*0.20*	*0.094*	*0.7715*
B-Power	2.84	*1*	*64.49*	*31.10*	*0.0026*
C-Volume	0.54	*1*	*2.29*	*1.11*	*0.3412*
AB	-1.77	*1*	*12.49*	*6.03*	*0.0576*
AC	1.04	*1*	*4.36*	*2.10*	*0.2065*
BC	-0.80	*1*	*2.59*	*1.25*	*0.3149*
A^2	0.78	*1*	*2.25*	*1.09*	*0.3450*
B^2	-2.72	*1*	*27.24*	*13.14*	*0.0152*
C^2	-1.01	*1*	*3.79*	*1.83*	*0.2343*
Residual		5	10.37		
Cor Total		*14*	*130.52*		

Table 5-5 Significance of regression coefficients of the crystallinity index of pretreated PET.

Source	Coefficient Estimate	df	Sum of Squares	F Value	p-value Prob > F
Model	57.54	9	996.11	10.26	0.0098
A-Time	-0.51	*1*	*2.08*	*0.19*	*0.6788*
B-Power	6.24	*1*	*311.38*	*28.87*	*0.0030*
C-Volume	-2.63	*1*	*55.18*	*5.12*	*0.0732*
AB	-7.35	*1*	*216.38*	*20.07*	*0.0065*
AC	-3.61	*1*	*52.13*	*4.83*	*0.0792*
BC	-0.89	*1*	*3.19*	*0.30*	*0.6101*
A^2	-5.62	*1*	*116.81*	*10.83*	*0.0217*
B^2	-8.37	*1*	*258.49*	*23.97*	*0.0045*
C^2	-2.17	*1*	*17.42*	*1.62*	*0.2597*
Residual		5	53.92		
Cor Total		*14*	*1050.03*		

The relationship between the studied responses and parameters of the MW assisted pre-treatment can be also demonstrated through the coefficient of determination for the quadratic equations as shown in Table 5-6. The carbonyl index (Y_1) of all pre-treated PET was increased when compared to that of virgin untreated PET (2.80). Both the MW power and irradiation time had a negative effect on the carbonyl index, whereas volume of glycerol had a significant positive effect. The interactions of both glycerol volume and irradiation time with MW power indicated a negative effect on pre-treated PET carbonyl index values. Thus, it can be predicted that high glycerol volumes with low MW power and irradiation time lead to an increase in carbonyl groups due to surface oxidation of the treated PET(Rouillon et al., 2016).

Moreover, the quadratic model equation coefficients showed an increase in crystallinity index of treated PET (Y_2) in all studied responses and their interactions. The preferential degradation of amorphous part of semicrystalline PET gave rise to an increased crystallinity index when compared to PET virgin counterpart (31.4%) at high levels of the studied factors(Azeem et al., 2022b)(Beltrán-Sanahuja et al., 2020). Positive effects were observed with MW power and irradiation time along with their interactions on PET weight loss (Y_3) while glycerol volume and its interactions with MW power and irradiation time had negative effect. This indicated that high levels of irradiation times and MW power coupled with low glycerol volume could lower the thermal stability of PET and facilitate initial depolymerisation of PET at its T_0 of degradation.

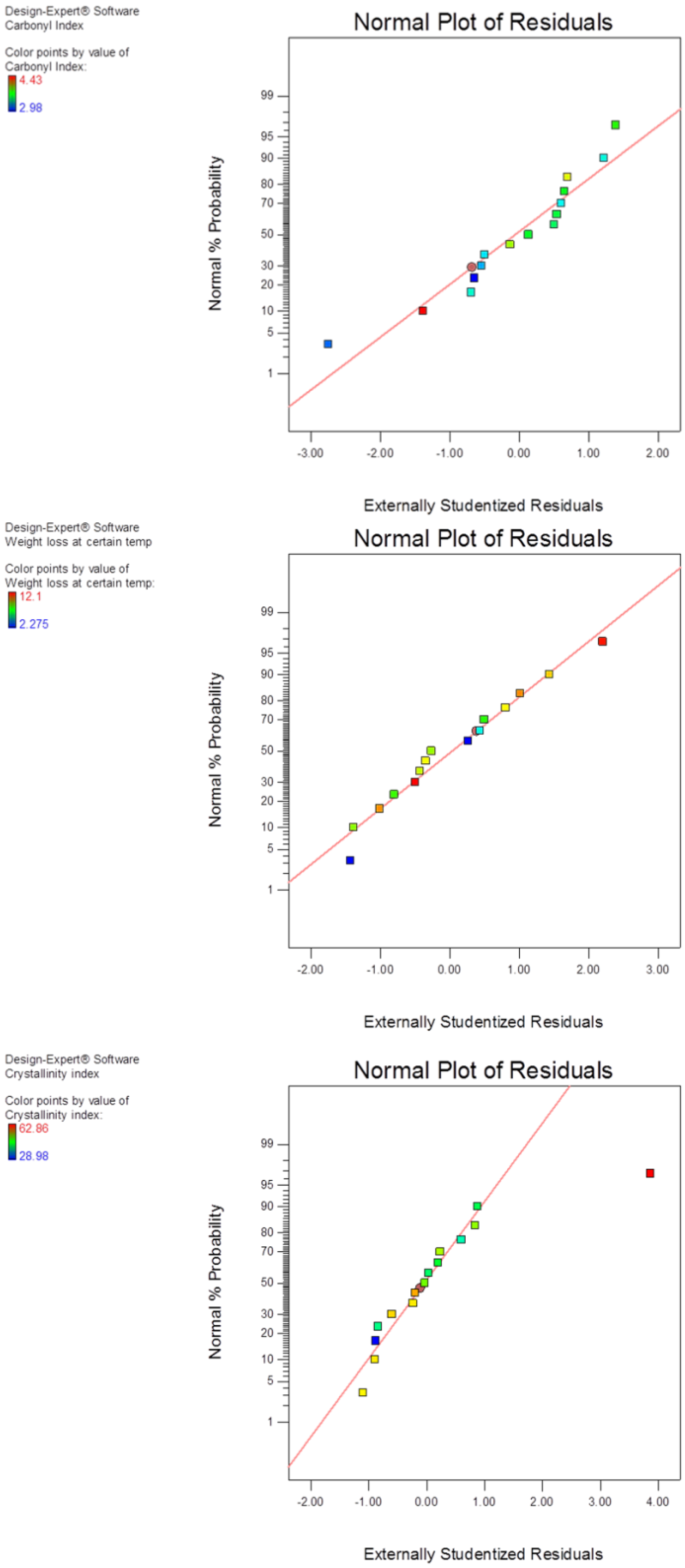

Figure 5-2 Normal probability plot of residuals for carbonyl index, weight loss at T_0 of degradation and crystallinity index of pre-treated PET.

Graphical plots of surface response analysis were generated between the studied variables, and responses were obtained to determine their effect in combinations. The 3D and contour plots for the, carbonyl index, crystallinity index and weight loss of PET at T_0 of degradation are shown in Figure 5-3, Figure 5-4, and Figure 5-5, respectively. The Carbonyl index is a critical parameter for evaluating the extent of surface modification of polymers after treatments. Figure 5-3 illustrates the carbonyl index (Y_1) and its dependence on MW time, power, and glycerol volume. It can be noticed that the interactions of high volumes of glycerol with low levels of MW power and time showed a significant rise in carbonyl index values up to 4.43 which confirmed the oxidation of the PET surface at these levels rather than complete depolymerisation(Appu et al., 2013).

As demonstrated in counter and 3D plots for crystallinity index (Y_2) in Figure 5-4, high levels of MW power and time led to the increase of crystallinity index of pre-treated PET. This result could be an indication of the initial degradation of the amorphous part of PET, which caused an increase in its overall crystallinity(Attallah et al., 2022)(H. M. Choi & Cho, 2016). Moreover, high values of crystallinity index were also observed in large volumes of glycerol up to a certain level, indicating that the intermediate levels of glycerol are relatively more effective for the pre-treatment of PET.

Table 5-6 Statistical analysis of the studied responses for the MW-assisted PET pre-treatment.

Fitting model	Factors	Coefficient	P-value	ANOVA
PET Carbonyl index (Y_1)	Intercept	3.30		F = 14.54, R^2 = 0.9632, Model P-value 0.0033, P-value of lack of fit = 0.8112
	X_1	-0.0313	0.4934	
	X_2	-0.1388	0.0220	
	X3	0.2775	0.0012	
	X_1X_2	-0.0075	0.9052	
	X_1X_3	0.1950	0.0225	
	X_2X_3	-0.1500	0.050	
	X_1^2	-0.1396	0.0751	
	X_2^2	0.2754	0.0069	
	X_3^2	0.3679	0.0020	
PET Crystallinity index (Y_2)	Intercept	57.54		F = 10.26, R^2 = 0.9487, Model P-value = 0.0098, P-value of lack of fit = 0.9039
	X_1	0.5100	0.050	
	X_2	6.24	0.0030	
	X_3	2.63	0.001	
	X_1X_2	7.35	0.0065	
	X_1X_3	3.61	0.0092	
	X_2X_3	0.8925	0.0001	
	X_1^2	-5.62	0.0217	
	X_2^2	-8.37	0.0045	
	X_3^2	-2.17	0.2597	
Weight loss of PET at T_0 of degradation (Y_3)	Intercept	9.97		
	X1	0.1561	0.001	F = 6.44, R^2 = 0.9206, Model P-value = 0.0270, P-value of lack of fit = 0.7475
	X2	2.84	0.0026	
	X3	-0.5352	0.3412	
	X1X2	1.77	0.0576	
	X1X3	-1.04	0.2065	
	X2X3	-0.8040	0.3149	
	X12	0.7810	0.3450	
	X22	-2.72	0.0152	
	X32	-1.01	0.2343	

X_1: MW irradiation time, X_2: MW power, X_3: volume of glycerol

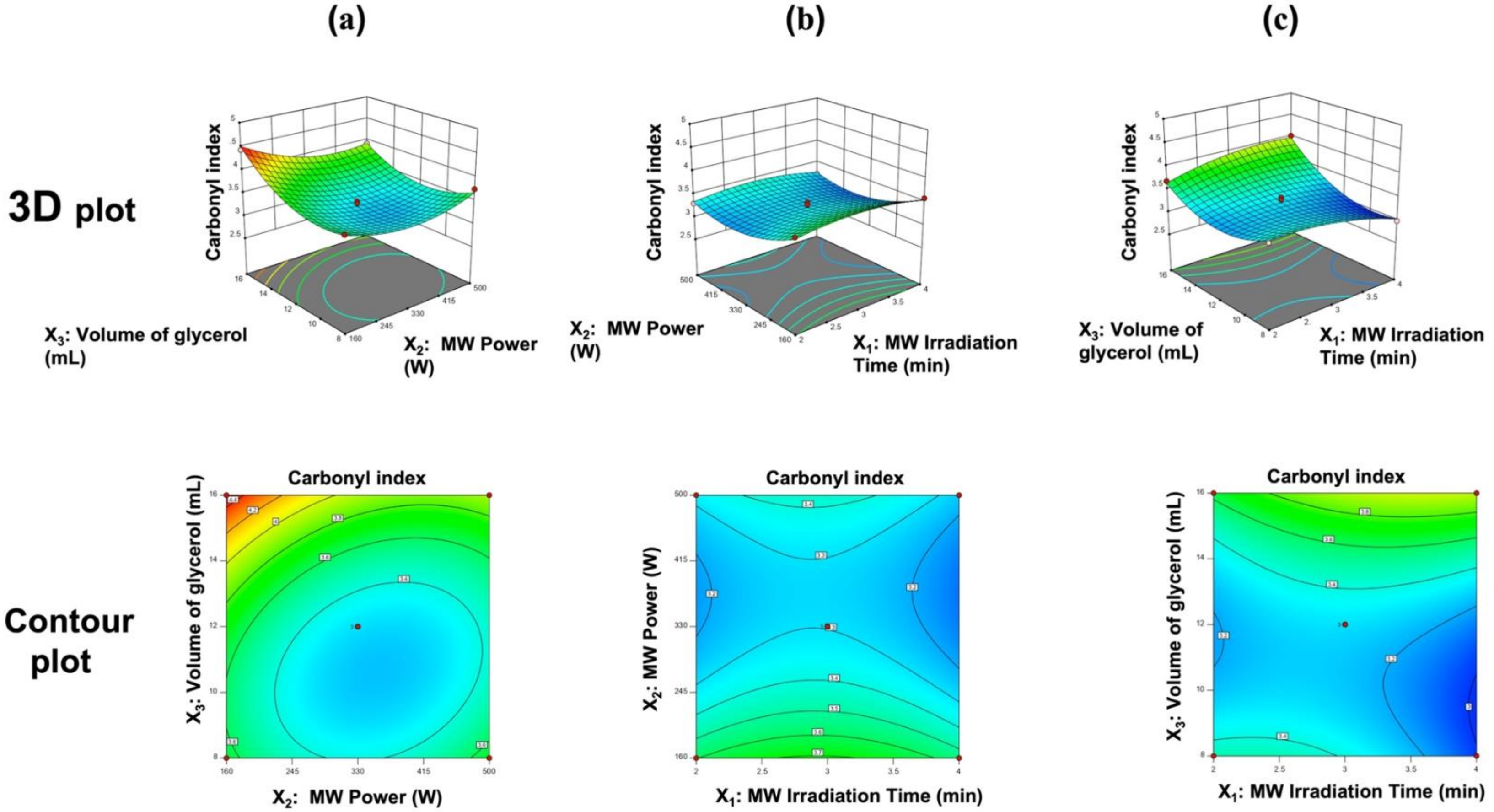

Figure 5-3 3D and contour plots of the effect of the interaction of [a] power (X_2) and glycerol volume (X_3), [b] time (X1) and power (X_2) and [c] glycerol volume (X_3) and time (X_1) on carbonyl index.

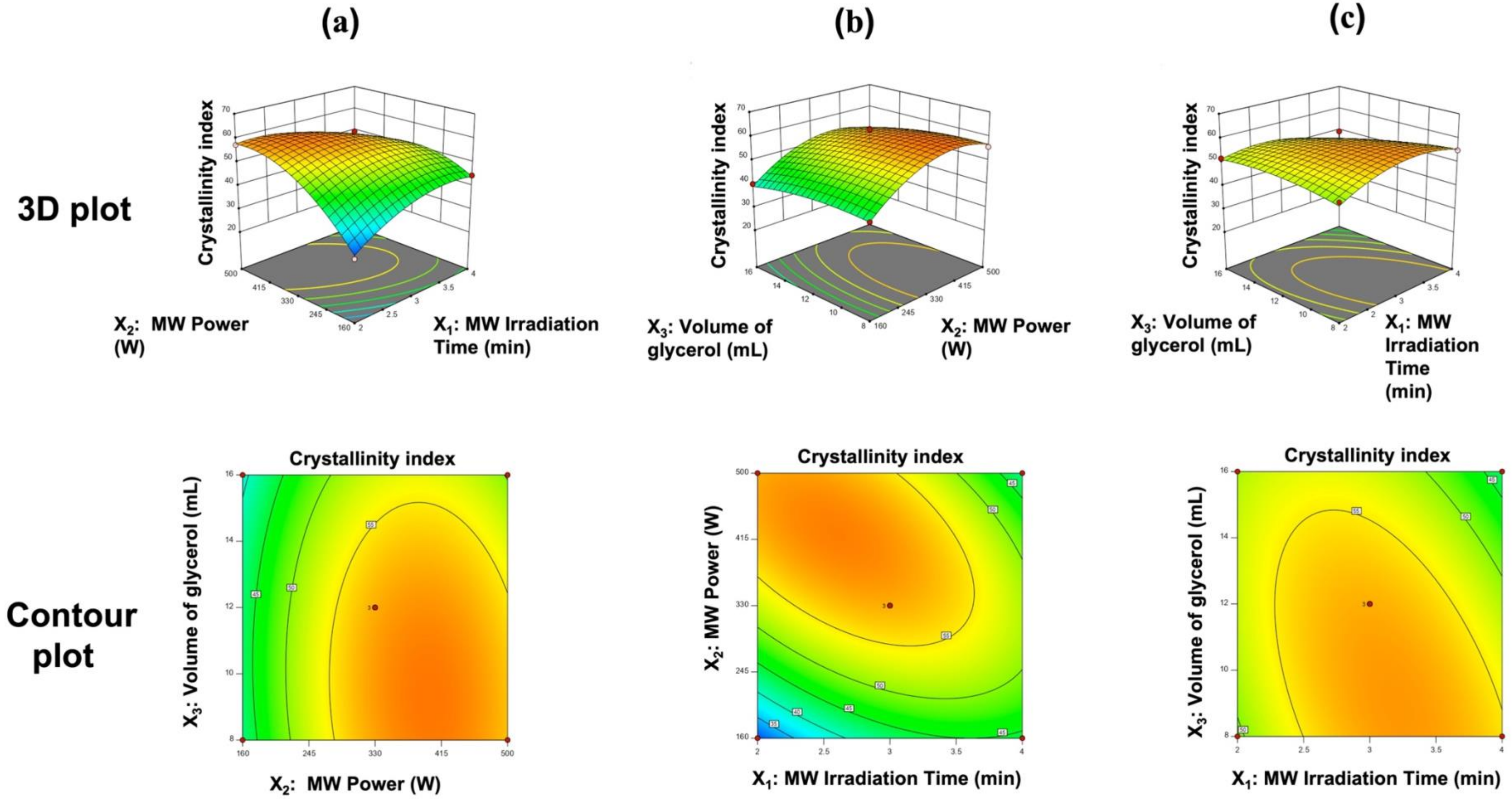

Figure 5-4 3D and contour plots of the effect of the interaction of (a) time (X_1) and power (X_2), (b) power (X_2) and glycerol volume (X_3), and (c) time (X_1) and glycerol volume (X_3) on the crystallinity index.

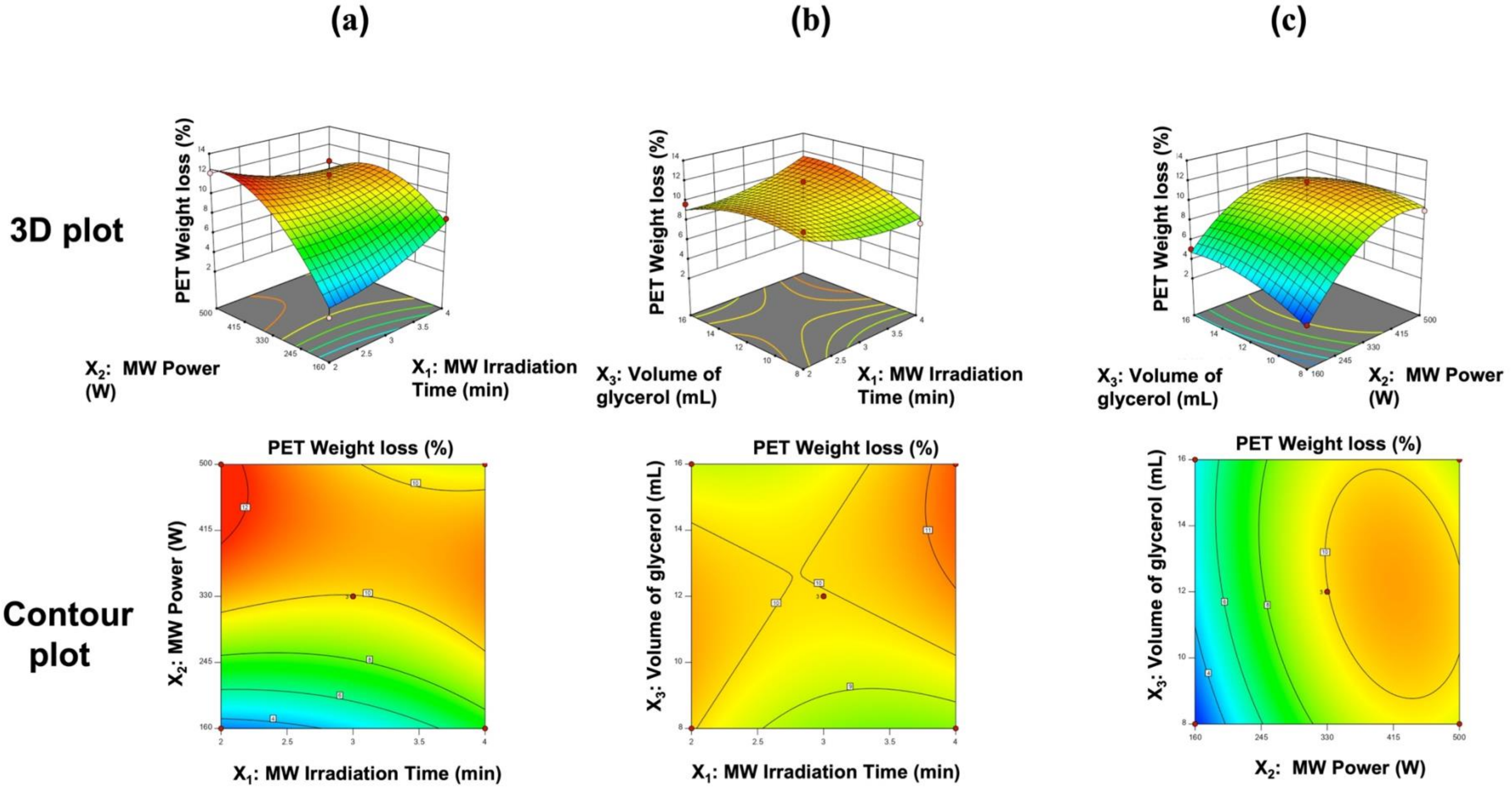

Figure 5-5 3D and contour plots of the effect of the interaction of [a] time (X_1) and power (X_2), [b] time (X_1) and glycerol volume (X_3) and [c] power (X_2) and glycerol volume (X_3) on PET weight loss (%).

The PET weight loss (%) at T_0 (Y_3) is also an influential variable for evaluating the initial degradation of PET through its thermal stability. High percentages of PET weight loss demonstrate a decreased level of thermal stability which validates initial degradation of PET. As shown in Figure 5-5, the interaction between MW power and time has positive effect on PET weight loss (%) at T_0 of degradation that reached up to 11.9% while pure PET weight loss had a value of 0.44%.

5.4.3 Optimisation of MW-assisted pre-treatment of PET

The BBD optimisation methodology was conducted in order to obtain maximum PET weight loss and desirable characteristics of pre-treated PET to accelerate the PET depolymerisation in the second step of MW assisted hydrolysis. Such pre-treatments might have a significant effect on PET conversion and crystallinity index, potentially enhancing efficient degradation/biodegradation in later stages. The MW assisted pre-treatment conditions were adjusted in such a way to get maximum weight loss (%) at T_0, maximum carbonyl index and minimum crystallinity index as shown in Table 5-7. A batch experiment was conducted by mixing 1 gm of PET with 12 ml of glycerol and exposing the mixture for 3 min to MW irradiation of 182W power. The predicted values for the optimised conditions showed fine agreement with the observed ones and that indicated a successful optimisation of the proposed PET pre-treatment process. The Optimised pre-treated PET had a 10.25% degradation % at T_0, an elevated carbonyl index of 4.22 and 33% crystallinity.

Table 5-7 The observed and predicted response values of optimized MW assisted pre-treatment of PET.

Independent Variable			Optimized level
X_1: MW time (min)			**3.0**
X_2: MW power (W)			**182**
X_3: Volume of glycerol (ml)			**12.0**
Overall desirability			**0.79**
Dependent variables	**Desirability**	**Expected**	**Observed**
Y_1: PET crystallinity index	**Minimize**	**35.45**	**32.98**
Y_2: PET carbonyl index	**Maximize**	**4.43**	**4.22**
Y_3: PET weight loss at T0 (%)	**Maximize**	**9.20**	**10.25**

5.4.4 MW assisted-hydrolysis of PET

Based on the optimised conditions of PET MW assisted pre-treatment, both virgin PET and pre-treated PET were hydrolysed under MW irradiations using $NaHCO_3$ in EG for 3 min. After the MW treatment, pre-treated PET was separated and PET conversion (%) was calculated. The produced monomers in the filtrate were also analysed by HPLC and the effects of various depolymerisation steps on selectivity of monomers (BHET, MHET), yield of TPA were determined as shown in Figure 5-6, and Figure 5-7. The observed conversion value of PET was only 61% after applying hydrolysis reaction on untreated virgin PET. On the other hand, a 99.9% PET conversion was achieved when the same hydrolysis reaction was applied to pre-treated PET obtained from the MW assisted pre-treatment step. Such improved efficiency of the hydrolysis reaction on the pre-treated PET could be associated to the structural modifications and new properties that were developed in such residual.

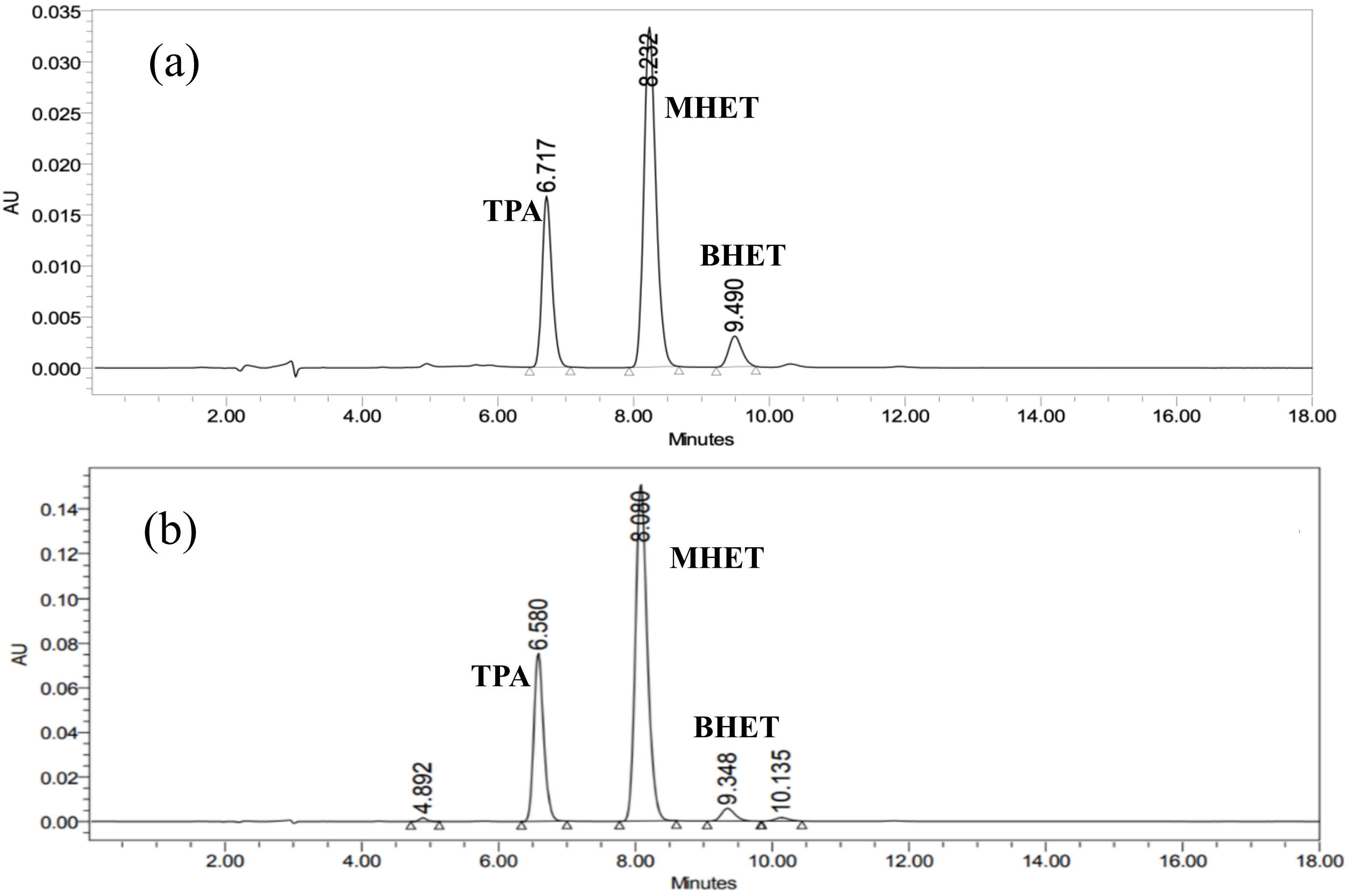

Figure 5-6 HPLC chromatogram of obtained monomers from (a) pure PET hydrolysis and (b)MW assisted hydrolysis of pre-treated PET.

Concerning the produced monomers analysis, a higher selectivity of MHET was observed as compared to BHET and TPA in hydrolysis step of untreated PET while TPA was the main monomer produced from the pre-treated PET residue. Additionally, the yield of TPA was increased from 12% for virgin PET to 79.1% in the pre-treated PET confirming the enhanced hydrolytic depolymerisation of PET upon applying the MW assisted pre-treatment step.

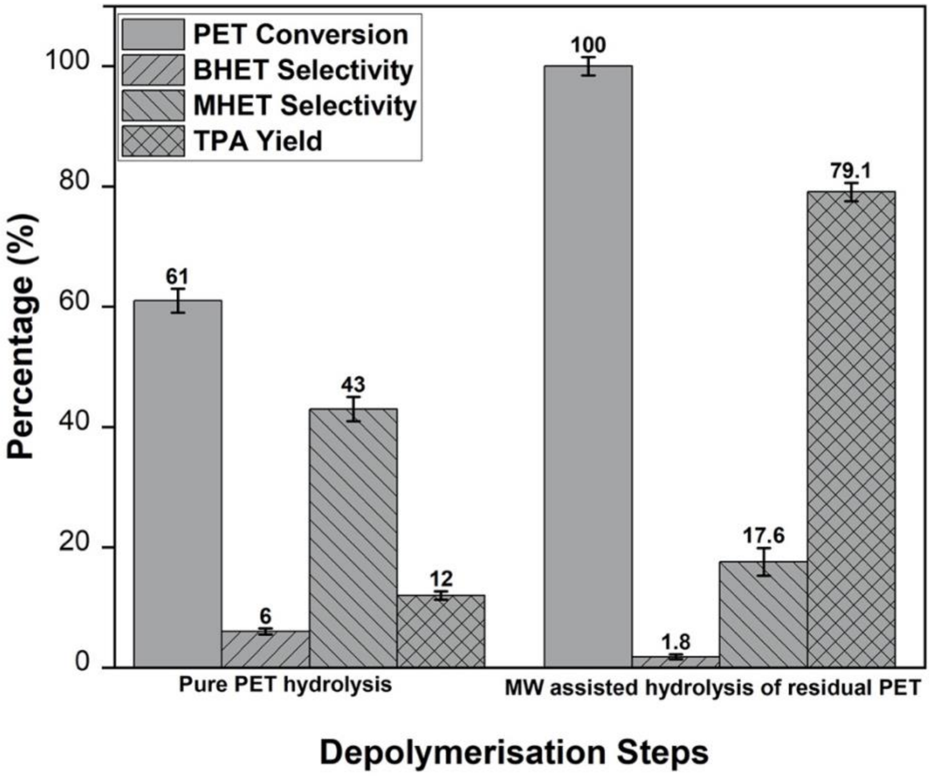

Figure 5-7 The percentage conversion of PET with different treatment methodologies, and the selectivity of obtained monomers (BHET, MHET) and the yield of TPA.

5.4.5 Purification and validation of obtained TPA for repolymerisation

A dissolution/recrystallisation purification approach was applied on the TPA produced from the pre-treated PET depolymerisation to remove any traces of monomers or impurities from it. The TPA before and after purification step were termed as precipitated TPA and recrystallised TPA respectively. As a result of the applied purification methodology, 72% of recrystallised TPA was recovered from the precipitated monomer mixture. This decreased recovery value could be attributed to the nature of purification via crystallisation since an amount of the desired compound might remain in the solvent system at the end of the heating-cooling process. Such drawback can be resolved by cooling the solvent system at lower temperatures. The recrystallised TPA purity was then confirmed using different characterisation techniques.

FTIR

The identity of the precipitated TPA monomer before and after purification was evaluated using FTIR. As illustrated in Figure 5-8, the TPA obtained from PET depolymerisation showed similar structural characteristics to that of standard TPA. The peaks at frequencies 3064 cm^{-1}, 1673 cm^{-1}, and 1280 cm^{-1} corresponded to carboxylic acid -OH, carbonyl group, and ether C-O stretching respectively. For the precipitated TPA, the extra peaks appearing in the fingerprint area which might be related to the MHET and BHET monomers present as impurities in the precipitated powder were successfully removed in the crystallised TPA. Thus, indicating its acceptable purity.

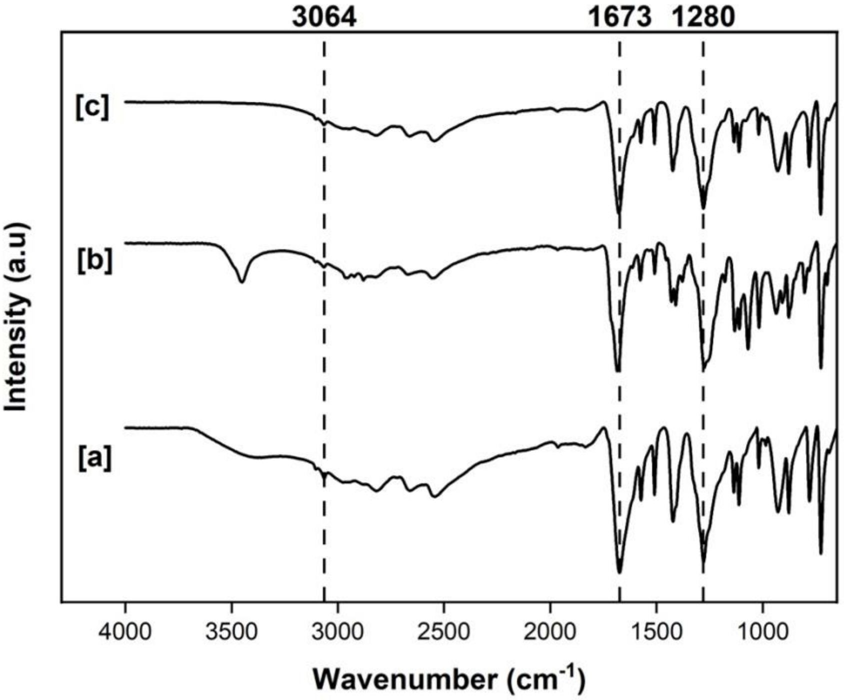

Figure 5-8 FTIR spectra of [a] Standard TPA, [b] Precipitated TPA, and [c] Crystallised TPA.

NMR

The structural confirmation of the TPA before and after purification was performed by NMR spectroscopy. The 1H and ^{13}C NMR spectra of the precipitated TPA product after PET depolymerization are presented in Figure 5-9[A] and [C], respectively. The signs labelled as "a" and "b" on the 1H NMR spectrum were assigned to acidic -OH, and -CH groups on the benzene rings at 13.34 (s, 2H) ppm and 8.09 (s, 4H), respectively. In addition to the NMR signals belonging to the TPA monomer, the signals assigned as "a^{I}" and "b^{I}", corresponding to the protons of the aromatic ring and acidic -OH, were attributed to the MHET monomer. Moreover, the signals arising from the MHET monomer (labelled as "c" and "d") appeared on the spectrum, corresponding to methylene linked to the -OH groups (δ_H = 3.71 ppm, m, 4H) and methylene linked to the -COO groups (δ_H = 4.32 ppm, t,4H), respectively. As to the signs around 2.5 ppm, these belonged to DMSO, while the ones at 3.3 and 2.0 ppm were referred to water residual and solvent contamination. As shown in Figure 5-9[C], the C NMR signals belonging to the TPA monomer are labelled as 1 (δ_C = 166.57 ppm), 2 (δ_C = 134.27 ppm), 3 (δ_C= 129.44 ppm) while the signals belonging to the MHET monomer and labelled as 1^{I} and 1^{II} (δ_C = 165.22 ppm and 165.47 ppm), 2^{I} (δ_C = 133.34 ppm), 3^{I} (δ_C = 129.46 ppm), 4 (δ_C = 66.92 ppm) and 5 (δ_C = 58.90 ppm) were assigned to the carbons of the chemical structure of both monomers(Lima et al., 2017)(Wu et al., 2011b).

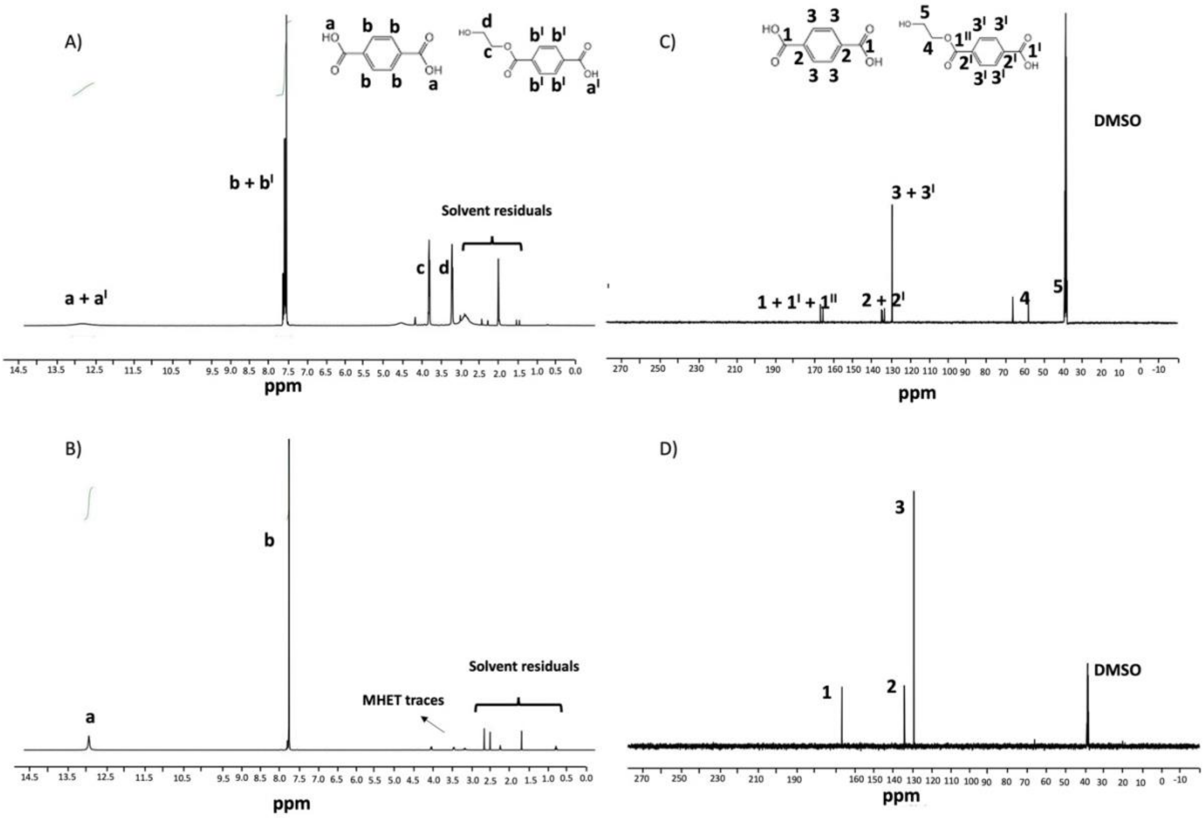

Figure 5-9 1H NMR spectrum of [a] Precipitated TPA and [b] crystallised TPA and 13C NMR of [c] Precipitated TPA and [d] crystallised TPA.

After the purification process, it was demonstrated that the crystallised TPA monomer was successfully separated from the monomers' mixture giving rise to pure peaks in both 1H and C NMR spectra. As presented in Figure 5-9[B], the ^{1}H NMR signs, 13.28 (s, 2H) ppm and 8.07 (s, 4H), corresponding to the TPA monomer structure were the most prominent signals remaining on the spectrum after the purification of the TPA monomer. Similarly, only peaks belonging to the TPA structure were observed on the ^{13}C NMR spectrum (Figure 5-9[D]), having the signals at 166.63 134.40, and 129.41 ppm and confirming that the TPA monomer was successfully extracted from the monomer mixture. These results also came in coordination with HPLC analysis of the crystallised TPA powder where a TPA yield of 94.88 % was obtained.

APHA colour value

The colour of TPA is one of the important physical parameters that should be considered for the re-polymerization step due to the fact that this colour is transferable to the PET product making it undesirable for industrial manufacturing. The colour of the obtained TPA was evaluated using a spectrophotometric methodology and its APHA colour value was determined(Taheri et al., 2019). As shown in Figure 5-10[a], the APHA value of the standard TPA was calculated as 7.71, while the precipitated TPA from PET depolymerization process had APHA value of 245.2.

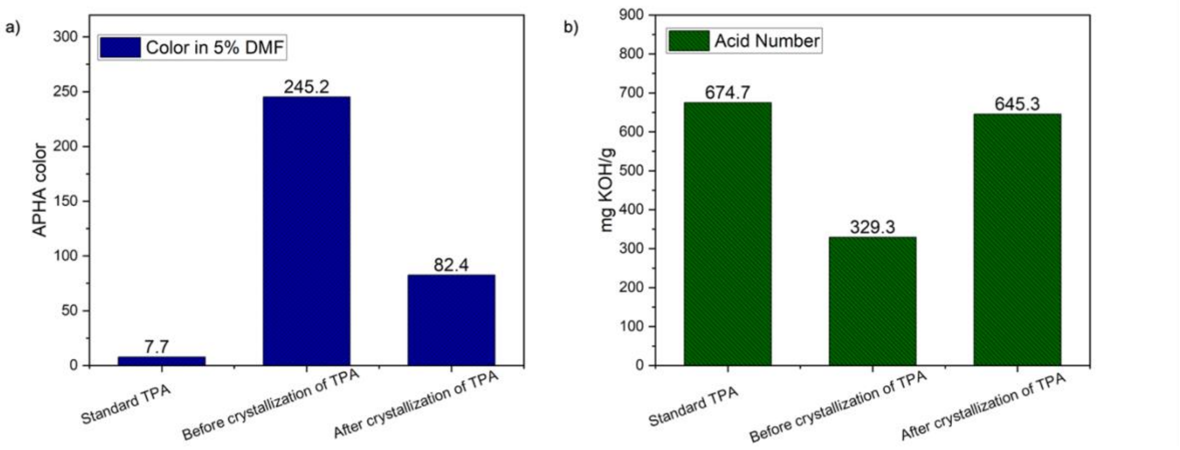

Figure 5-10 APHA colour values (a) and acid number (b) of the standard TPA, and the depolymerised product before and after the crystallisation of the TPA monomer.

This significantly high APHA colour value could be related to the contamination of the precipitated TPA by other organic compounds that were produced during the PET depolymerisation process. Noticeably, after the application of the dissolution and crystallisation procedure on the precipitated TPA, these organic compounds were removed and a crystallised TPA of 82.4 APHA value was obtained.

Acid number value

The acid number is defined as a number utilised to quantify the acidity of a chemical substance which is critical for the re-polymerisation of the TPA monomer in our case. As shown in Figure 5-10[b], standard TPA has an acid number of 674.7 mgKOH/g, while the precipitated TPA post PET depolymerisation had an acid value of 329.3 mgKOH/g. Such significantly low acid number could be attributed to the presence of MHET monomer and other residuals in the precipitated product resulting in the significantly low total acidity of the material. Upon purification of the precipitated TPA monomer, the acid number value was increased to 645.3 mgKOH/g, giving rise to a TPA monomer having sufficient colour and acid number values for re-polymerisation into PET material.

Heavy metal content

The heavy metal content of the TPA, which is the main monomer used for producing PET, should be within an acceptable range to avoid contaminating the PET product and to keep the polymerisation reaction efficient. Bearing this in mind, the precipitated TPA, before and after purification was analysed by ICP-MS to determine its heavy metal content. As listed in Table 5-8, it was found that the precipitated TPA post the depolymerisation process had a slightly higher metallic content than that of the standard TPA. On the other hand, the crystallised TPA possessed almost similar heavy metal content in comparison with the standard TPA, thus, making it suitable for the production of PET.

Table 5-8 Heavy metal trace analysis of the samples.

Heavy metal (μg/g)	Samples		
	Standard TPA	Precipitated TPA	crystallized TPA
Aluminium	1.3	3.0	1.6
Titanium	<0.5	<0.5	<0.5
Chromium	<0.5	<0.5	<0.5
Manganese	<0.5	<0.5	<0.5
Cobalt	<0.5	<0.5	<0.5
Molybdenum	<0.5	<0.5	<0.5
Antimony	<0.5	1.1	0.8
Iron	1.1	1.7	1.3

5.5 Conclusion

In the current study, a green, straight-forward 2 step 100% PET depolymerisation process with high yields of purified TPA monomer utilising low energy, MW technology and green solvents is presented. The proposed depolymerisation methodology completely depolymerised PET into its valuable monomers within a total of 6 min under environmentally friendly and mild operating conditions. PET was initially pre-treated via a green MW method using glycerol as a treating solvent to render PET more amenable for complete degradation. The pre-treated PET residue was further depolymerised via a mild hydrolytic MW assisted process using $NaHCO_3$ in EG. A precipitated TPA yield of 79% was confirmed using HPLC analysis. Furthermore, taking into the consideration the importance of TPA purity for repolymerisation into industrially acceptable PET, a purification process for the precipitated TPA was applied using a dissolution/recrystallisation approach. A TPA purity of 95%(70% isolated yeild), 82.4 APHA colour value, 645.3 mgKOH/g acid number and acceptable heavy metal content was achieved, making the obtained TPA comparable with commercial standard equivalent.

Chapter 6. Conclusions, Implications, and Future Considerations

6.1 Conclusions and Implications

A number of techniques have been developed to contribute in overcoming the challenges associated with managing stockpiles of plastic waste, particularly focusing on PET. The utilization of primary recycling techniques does not provide satisfactory solutions as it produces post-recycling diminished value products and does not address end of use difficulties of materials. Current plastic recycling methods are inefficient and are limited by processing difficulties and diminished value. In contrast, higher recovery of building block monomers or other value-added products can be attained through chemical recycling. With specific reaction conditions and the selection of suitable solvents, desired depolymerised monomers (TPA, MHET, BHET) could be produced. These monomers can be used in repolymerisation of virgin PET plastic to close the loop of plastic circularity and reserve natural petroleum-based resources. Importantly, these monomers can also be used to produce biodegradable biopolymers(Sohn et al., 2020).

This thesis presents combined ultra-green chemical and biocatalytic depolymerisation of polyethylene terephthalate using biodegradable and unique biologically compatible solvent-based low-energy microwave treatments. This research was carried out to evaluate the PET depolymerisation capabilities of different DESs and green reagents in combination with microwave technology. MW-based PET glycolysis, hydrolysis, and enzymatic treatments were performed separately and simultaneously and their efficiencies were compared.

The overall summary of the findings of this research work and its implications towards the plastic recycling field are:

- Paper I comprises green DES of ternary composition of choline chloride, glycerol, and urea served as efficient PET treatment in the presence of MW irradiation. FTIR, TGA, and DSC spectra of the residual PET obtained after treatment with the MW-assisted DES technique showed a significant increase in residual PET carbonyl index and percentage weight loss at T_0 of degradation and maintenance of PET crystallinity percentage. Furthermore, the enzymatic hydrolysis using a variant of LCC cutinase of treated PET demonstrated 1.8% weight loss and 0.55 mM monomers released after enzymatic hydrolysis, while 1.5% weight loss and 0.82 mM monomers were recorded for virgin PET.

- Paper I presents the all green and bio-based depolymerisation of PET. Green-DES based MW treatment of PET plastic followed by enzymatic degradation is a novel, unique and environmentally friendly approach; however, enzymatic treatment requires further research to fasten the reaction times. Therefore, hybrid glycolysis-hydrolysis of PET containing different DES systems with higher MW absorption characteristics under MW irradiation were employed to shorten reaction times.
- In Paper II, A hybrid depolymerization (simultaneous application of glycolysis-hydrolysis) process for PET comprising a fast, low energy MW assisted glycolysis-hydrolysis was investigated. Two DESs, ChCl:urea/ChCl:thiourea and Na_2CO_3 were selected for hybrid glycolysis and hydrolysis of PET under MW irradiation. The proposed DESs proved themselves as efficient MW absorbers and PET depolymerization reaction catalysts owing to their unique properties because the reaction time required for complete depolymerization of PET was only 3.5 min which is considerably short when compared to other studies presenting green approaches for PET degradation. Furthermore, the significant PET conversion (99%) and monomer yield reaching up to 80.66% can render the proposed technique ideal for PET depolymerisation and probably other polyesters from an industrial prospect.
- Paper II presents a novel combination of glycolysis-hydrolysis of PET under MW irradiation coupled with biologically compatible DES solvents. The remarkable 99% depolymerisation of PET was successfully achieved within 3.5 min. The target to get ultrafast depolymerisation of PET with a higher monomer yield was achieved, however, to make this process more benign and environmentally friendly, further research was carried out to evaluate alternative nontoxic, cost-effective, and readily accessible solvents.
- Paper III illustrates a green, straight-forward 2 step 100% PET depolymerisation process produced most efficient results by completely depolymerising PET into high yields of purified TPA. Fast and all-green sequential PET depolymerisation technique comprising MW assisted pre-treatment followed by hydrolysis reaction was employed utilising low energy, MW technology and green solvents. The MW assisted pre-treatment was conducted in the presence of glycerol, and the process was optimised using Box-Behnken design. In the hydrolysis reaction, the pre-treated PET was exposed to MW treatment while using $NaHCO_3$ in EG to completely depolymerise PET into its value-added monomers. A precipitated TPA yield of 79% was confirmed using HPLC

analysis. Furthermore, taking into the consideration the importance of TPA purity for repolymerisation into industrially acceptable PET, a purification process for the precipitated TPA was applied using a dissolution/recrystallisation approach. A TPA purity of 95%, 82.4 APHA colour value, 645.3 mgKOH/g acid number and acceptable heavy metal content was achieved, making the obtained TPA comparable with commercial standard equivalent.

- Building on the conclusion of the last two papers, the final research work presents a completely fast, highly efficient, and ultra-green PET depolymerization via microwave assisted 2 step treatment. The proposed recycling technique allows complete PET depolymerization within 6 min using green solvents, providing a good yield of purified value-added monomer(TPA), which can be used for repolymerization. This work aligns with the UN sustainable development goals number 9, 12 and13.

6.2 Limitations

- The determination of the potential applications of this research as well as its limitations are equally important. The first limitation of this thesis is of the research is its scalability. No large-scale trials have been conducted to evaluate industrial-scale applications. However, Larger MW irradiation systems can be employed to establish this research work on an industrial scale. Indeed, MW depolymerisation systems operating on the industrial scale are emerging such as Gr3n who are producing and commercializing MW de-polymerization plants. Similar systems can reproduce the work on a larger scale. Because such systems require significant investment in research, development, and infrastructure, it is difficult to determine the economic viability of this research at the industrial level. Furthermore, this research work can be reproduced via reactive extrusion to compare both scale-up options to resolve scalability issues.
- A second limitation is the efficient recovery of solvents after MW treatments, which requires purification processes which need to be improved to operate under low energy and low carbon footprint methodologies. To achieve this, energy-efficient separation techniques such as pressure swing distillation, azeotropic distillation, dividing-wall columns, reverse osmosis, ultrafiltration, and nanofiltration can be explored to determine which technique is best suited for selected solvent systems.
- The third limitation is the difficulty in separating the produced monomers which can involve high temperatures, pressurised processes, harsh solvents, and vaporisation and precipitation reactions. Optimizing the depolymerization process parameters can be one of the solutions to address this issue; it can minimize the formation of by-products that can contribute to the ease of monomer separation.
- In order to generate TPA monomer equivalent to the standard TPA from PET waste, contamination could be another challenge to consider.
- Moreover, there should be a consideration regarding the holistic environmental impact of the process which involves considering the selection of plant location in accordance with the best available energy source, such as wind turbines, solar panels, or any other renewable source, to minimise the environmental impact comprehensively.

6.3 Future Considerations

The proposed technology has a high potential for carbon efficient eco-friendly plastic production and is a pertinent technology for a sustainable future. Within this thesis, a number of research questions have been addressed. Following is a list of future considerations that could advance this research.

- In the future, it would be interesting to scale up the green solvent-based microwave depolymerization technology. A deep understating of the constraints (such as mixed incomplete depolymerisation products) in large scale PET waste depolymerisation should be carefully monitored and explored further. Other MW parameters, such as a continuous temperature profile investigation during the reaction, could be considered as an important indication of solvent's behaviour under MW irradiation.
- The feasibility study of the large scale production of TPA monomer from PET waste should be evaluated and compared with monomer yield of the reactive extrusion using same sample size.
- TPA monomer yield should be optimised using different grades of PET waste under MW irradiation. Additionally, effect of PET particle size could be an important aspect to consider in the future research.
- The findings of glycerol /PET-based MW treatment will be an important point to consider for future development. It would be interesting to study the effect of temperature on mild glycolysis of PET using glycerol.
- The utilisation of the produced monomers (TPA) in the repolymerisation of virgin PET as well as in the synthesis of other biopolymers should be assessed. Moreover, Life cycle assessment to evaluate the carbon efficiency of the chemical recycling process for plastic production is an important aspect to consider in future.
- The development of chemical depolymerisation of PET could have great potential in generating circularity for plastics by recycling plastics and conserving resources by generating monomers that can be reused in PET synthesis, thereby decreasing the need to use petroleum based feedstocks.

References

Abbott, A. P., Capper, G., Davies, D. L., McKenzie, K. J., & Obi, S. U. (2006). Solubility of metal oxides in deep eutectic solvents based on choline chloride. *Journal of Chemical and Engineering Data, 51*(4), 1280–1282. https://doi.org/10.1021/je060038c

Abbott, A. P., Capper, G., Davies, D. L., Munro, H. L., Rasheed, R. K., & Tambyrajah, V. (2001). Preparation of novel, moisture-stable, lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. *Chemical Communications, 1*(19), 2010–2011. https://doi.org/10.1039/b106357j

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications, 1*, 70–71. https://doi.org/10.1039/b210714g

Achilias, D. S., & Karayannidis, G. P. (2004). The chemical recycling of PET in the framework of sustainable development. *Water, Air, and Soil Pollution: Focus*, *4*(4–5), 385–396. https://doi.org/10.1023/B:WAFO.0000044812.47185.0f

Ali, S. S., Elsamahy, T., Koutra, E., Kornaros, M., El-Sheekh, M., Abdelkarim, E. A., Zhu, D., & Sun, J. (2021). Degradation of conventional plastic wastes in the environment: A review on current status of knowledge and future perspectives of disposal. *Science of the Total Environment*, *771*, 144719. https://doi.org/10.1016/j.scitotenv.2020.144719

Alnaqbi, M. A., Mohsin, M. A., Busheer, R. M., & Haik, Y. (2015). Microwave assisted glycolysis of poly(ethylene terephthalate) catalyzed by 1-butyl-3-methylimidazolium bromide ionic liquid. *Journal of Applied Polymer Science*, *132*(12), 1–7. https://doi.org/10.1002/app.41666

Alomar, M. K., Hayyan, M., Alsaadi, M. A., Akib, S., Hayyan, A., & Hashim, M. A. (2016). Glycerol-based deep eutectic solvents: Physical properties. *Journal of Molecular Liquids*, *215*, 98–103. https://doi.org/10.1016/j.molliq.2015.11.032

Al-Sabagh, A. M., Yehia, F. Z., Eshaq, G., Rabie, A. M., & ElMetwally, A. E. (2016). Greener routes for recycling of polyethylene terephthalate. *Egyptian Journal of Petroleum*, *25*(1), 53–64. https://doi.org/10.1016/j.ejpe.2015.03.001

Al-Salem, S. M., Lettieri, P., & Baeyens, J. (2009). Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Management*, *29*(10), 2625–2643. https://doi.org/10.1016/j.wasman.2009.06.004

Al-Salem, S. M., Lettieri, P., & Baeyens, J. (2010). The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. *Progress* *in Energy and Combustion Science*, *36*(1), 103–129. https://doi.org/10.1016/j.pecs.2009.09.001

Appu, S. P., De, S. K., Khan, M. J., & Al-Harthi, M. A. (2013). Natural weather ageing of starch/polyvinyl alcohol blend: Effect of glycerol content. *Journal of Polymer Engineering*, *33*(3), 257–263. https://doi.org/10.1515/polyeng-2012-0048

Araújo, R., Silva, C., O'Neill, A., Micaelo, N., Guebitz, G., Soares, C. M., Casal, M., & Cavaco-Paulo, A. (2007). Tailoring cutinase activity towards polyethylene terephthalate and polyamide 6,6 fibers. *Journal of Biotechnology*, *128*(4), 849–857. https://doi.org/10.1016/j.jbiotec.2006.12.028

Attallah, O. A., Azeem, M., Nikolaivits, E., Topakas, E., & Fournet, M. B. (2022). Progressing ultragreen, energy-efficient biobased depolymerization of poly(Ethylene terephthalate) via microwave-assisted green deep eutectic solvent and enzymatic treatment. In *Polymers* (Vol. 14, Issue 1). https://doi.org/10.3390/polym14010109

Attallah, O. A., Janssens, A., Azeem, M., & Fournet, M. B. (2021). Fast, High Monomer Yield from Post-consumer Polyethylene Terephthalate via Combined Microwave and Deep Eutectic Solvent Hydrolytic Depolymerization. *ACS Sustainable Chemistry & Engineering*. https://doi.org/10.1021/acssuschemeng.1c07159

Attallah, O. A., Mojicevic, M., Garcia, E. L., Azeem, M., Chen, Y., Asmawi, S., & Brenan Fournet, M. (2021). Macro and Micro Routes to High Performance Bioplastics: Bioplastic Biodegradability and Mechanical and Barrier Properties. In *Polymers* (Vol. 13, Issue 13). https://doi.org/https://doi.org/10.3390/polym13132155

Austin, H. P., Allen, M. D., Donohoe, B. S., Rorrer, N. A., Kearns, F. L., Silveira, R. L., Pollard, B. C., Dominick, G., Duman, R., Omari, K. El, Mykhaylyk, V., Wagner, A., Michener, W. E., Amore, A., Skaf, M. S., Crowley, M. F., Thorne, A. W., Johnson, C. W., Lee Woodcock, H., … Beckham, G. T. (2018). Characterization and engineering of a plastic-degrading aromatic polyesterase. *Proceedings of the National Academy of Sciences of the United States of America*, *115*(19), E4350–E4357. https://doi.org/10.1073/pnas.1718804115

Azeem, M., Fournet, M. B., & Attallah, O. A. (2022a). Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation. *Arabian Journal of Chemistry*, *15*(7), 103903. https://doi.org/10.1016/j.arabjc.2022.103903

Azeem, M., Fournet, M. B., & Attallah, O. A. (2022b). Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation. *Arabian Journal of Chemistry*, *15*(7), 103903. https://doi.org/10.1016/j.arabjc.2022.103903

Aznar, M. P., Caballero, M. A., Sancho, J. A., & Francés, E. (2006). Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. *Fuel Processing Technology*, *87*(5), 409–420. https://doi.org/10.1016/j.fuproc.2005.09.006

Barnard, E., Rubio Arias, J. J., & Thielemans, W. (2021). Chemolytic depolymerisation of PET: a review. *Green Chemistry*, *23*(11), 3765–3789. https://doi.org/10.1039/D1GC00887K

Barth, M., Oeser, T., Wei, R., Then, J., Schmidt, J., & Zimmermann, W. (2015). Effect of hydrolysis products on the enzymatic degradation of polyethylene terephthalate nanoparticles by a polyester hydrolase from *Thermobifida fusca*. *Biochemical Engineering Journal*, *93*, 222–228. https://doi.org/10.1016/J.BEJ.2014.10.012

Bartolome, L., Imran, M., Cho, B. G., Al-Masry, W. A., & Kim, D. H. (2012). Recent developments in the chemical recycling of PET. *Material Recycling-Trends and Perspectives*, *406*, 576–596.

Bartolome, L., Imran, M., Lee, K. G., Sangalang, A., Ahn, J. K., & Kim, D. H. (2014). Superparamagnetic γ-Fe2O3 nanoparticles as an easily recoverable catalyst for the chemical recycling of PET. *Green Chemistry*, *16*(1), 279–286. https://doi.org/10.1039/c3gc41834k

Beltrán-Sanahuja, A., Casado-Coy, N., Simó-Cabrera, L., & Sanz-Lázaro, C. (2020). Monitoring polymer degradation under different conditions in the marine environment. *Environmental Pollution*, *259*. https://doi.org/10.1016/j.envpol.2019.113836

Benyathiar, P., Kumar, P., Carpenter, G., Brace, J., & Mishra, D. K. (2022). Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: A Review. *Polymers*, *14*(12). https://doi.org/10.3390/polym14122366

Blackshaw, T. (2012). ‘Into’, The. *The SAGE Dictionary of Leisure Studies*. https://doi.org/10.4135/9781446213278.n124

Boghosian, H. H., & Howson, M. A. (1990). Temperature dependence of the electrical conductivity of amorphous VxSi1-x. *Physical Review B*, *41*(11), 7397–7401. https://doi.org/10.1103/PhysRevB.41.7397

Çabuk, H., Yılmaz, Y., & Yıldız, E. (2019). A vortex-assisted deep eutectic solvent-based liquid-liquid microextraction for the analysis of alkyl gallates in vegetable oils. *Acta Chimica Slovenica*, *66*(2), 385–394. https://doi.org/10.17344/acsi.2018.4877

Carta, D., Cao, G., & D'Angeli, C. (2003). Chemical Recycling of Poly(ethylene terephthalate) (PET) by Hydrolysis and Glycolysis. *Environmental Science and Pollution Research*, *10*(6), 390–394. https://doi.org/10.1065/espr2001.12.104.8

Chan, K., & Zinchenko, A. (2021). Conversion of waste bottles' PET to a hydrogel adsorbent via PET aminolysis. *Journal of Environmental Chemical Engineering*, *9*(5). https://doi.org/10.1016/j.jece.2021.106129

Chelliah, A., Subramaniam, M., Gupta, R., & Gupta, A. (2017a). Evaluation on the Thermo-Oxidative Degradation of PET using Prodegradant Additives. *Indian Journal of Science and Technology*, *10*(6), 1–5. https://doi.org/10.17485/ijst/2017/v10i6/111212

Chelliah, A., Subramaniam, M., Gupta, R., & Gupta, A. (2017b). Evaluation on the Thermo-Oxidative Degradation of PET using Prodegradant Additives. *Indian Journal of Science and Technology*, *10*(6), 1–5. https://doi.org/10.17485/ijst/2017/v10i6/111212

Chen, C., Chen, C., Lo, Y., Mao, C., & Liao, W. (2001). Studies of glycolysis of poly (ethylene terephthalate) recycled from postconsumer soft-drink bottles. I. Influences of glycolysis conditions. *Journal of Applied Polymer Science*, *80*(7), 943–948.

Chen, C. H. (2003). Study of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. III. Further investigation. *Journal of Applied Polymer Science*, *87*(12), 2004–2010. https://doi.org/10.1002/app.11694

CHEN, C.-H., & C.-Y CHEN, YU-WEN LO, CHING-FENG MAO, W.-T. L. (2001). Studies of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. I. Influences of glycolysis conditions. *Journal of Applied Polymer Science*, *80*(7), 943–948. https://doi.org/10.1002/app.1174

Chen, F., Wang, G., Shi, C., Zhang, Y., Zhang, L., Li, W., & Yang, F. (2013). Kinetics of glycolysis of poly(ethylene terephthalate) under microwave irradiation. *Journal of Applied Polymer Science*, *127*(4), 2809–2815. https://doi.org/10.1002/app.37608

Chen, J., & Chen, L. (1999). *The Glycolysis of Poly (ethylene terephthalate)*. *73*(June 1998), 35–40.

Chen, W., Yang, Y., Lan, X., Zhang, B., Zhang, X., & Mu, T. (2021). Biomass-derived γ-valerolactone: efficient dissolution and accelerated alkaline hydrolysis of polyethylene terephthalate. *Green Chemistry*, *23*(11), 4065–4073. https://doi.org/10.1039/D1GC00665G

Cho, J. Y., Choi, H. M., & Oh, K. W. (2016). Rapid hydrophilic modification of poly(ethylene terephthalate) surface by using deep eutectic solvent and microwave irradiation. *Textile Research Journal*, *86*(12), 1318–1327. https://doi.org/10.1177/0040517515612362

Cho, J. Y., Hong, C. J., & Choi, H. M. (2013). Microwave-assisted glycolysis for PET with highly hydrophilic surface. *Industrial and Engineering Chemistry Research*, *52*(6), 2309–2315. https://doi.org/10.1021/ie302732g

Choi, H. M., & Cho, J. Y. (2016). Microwave-mediated rapid tailoring of PET fabric surface by using environmentally-benign, biodegradable Urea-Choline chloride Deep eutectic solvent. *Fibers and Polymers*, *17*(6), 847–856. https://doi.org/10.1007/s12221-016-5334-1

Choi, S., & Choi, H. M. (2019). Eco-friendly, Expeditious Depolymerization of PET in the Blend Fabrics by Using a Bio-based Deep Eutectic Solvent under Microwave Irradiation for Composition Identification. *Fibers and Polymers*, *20*(4), 752–759. https://doi.org/10.1007/s12221-019-8931-y

Choi, S., & Choi, H. M. (2021). Choline-based deep eutectic solvent and microwave irradiation as tools for pet identification in blend fabric. *AATCC Journal of Research*, *8*(1), 40–50. https://doi.org/10.14504/ajr.8.1.6

Choudhary, K., Sangwan, K. S., & Goyal, D. (2019). Environment and economic impacts assessment of PET waste recycling with conventional and renewable sources of energy. *Procedia CIRP*, *80*(March), 422–427. https://doi.org/10.1016/j.procir.2019.01.096

Clark, J. H., Alonso, J. A., Villalba, J. A., Aguado, J., Serrano, D. P., & Serrano, D. A. (1999). *Feedstock recycling of plastic wastes* (Vol. 1). Royal society of chemistry.

Cot, S., Leu, M. K., Kalamiotis, A., Dimitrakis, G., Sans, V., de Pedro, I., & Cano, I. (2019). An Oxalate-Bridged Binuclear Iron(III) Ionic Liquid for the Highly Efficient Glycolysis of Polyethylene Terephthalate under Microwave Irradiation. *ChemPlusChem*, *84*(7), 786–793. https://doi.org/10.1002/cplu.201900075

Cui, Y., Chen, Y., Liu, X., Dong, S., Tian, Y., Qiao, Y., Mitra, R., Han, J., Li, C., Han, X., Liu, W., Chen, Q., Wei, W., Wang, X., Du, W., Tang, S., Xiang, H., Liu, H., Liang, Y., … Wu, B. (2021). Computational Redesign of a PETase for Plastic Biodegradation under Ambient Condition by the GRAPE Strategy. *ACS Catalysis*, *11*(3), 1340–1350. https://doi.org/10.1021/acscatal.0c05126

Danso, D., Chow, J., Zimmermann, W., & Wei, R. (2018). *crossm New Insights into the Function and Global Distribution of*. *84*(February), 1–13.

Didaskalou, C., Kupai, J., Cseri, L., Barabas, J., Vass, E., Holtzl, T., & Szekely, G. (2018). Membrane-Grafted Asymmetric Organocatalyst for an Integrated Synthesis-Separation Platform. *ACS Catalysis*, *8*(8), 7430–7438. https://doi.org/10.1021/acscatal.8b01706

Djapovic, M., Milivojevic, D., Ilic-Tomic, T., Lješević, M., Nikolaivits, E., Topakas, E., Maslak, V., & Nikodinovic-Runic, J. (2021). Synthesis and characterization of polyethylene terephthalate (PET) precursors and potential degradation products: Toxicity study and application in discovery of novel PETases. *Chemosphere*, *275*, 130005. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.130005

Doerr, M. L. (1986). *Depolymerization of Condensation Polymers Involving a Pre-Molecular Weight Reduction Step*. *19*.

Donelli, I., Taddei, P., Smet, P. F., Poelman, D., Nierstrasz, V. A., & Freddi, G. (2009). Enzymatic surface modification and functionalization of PET: A water contact angle, FTIR, and fluorescence spectroscopy study. *Biotechnology and Bioengineering*, *103*(5), 845–856. https://doi.org/10.1002/bit.22316

Du, J. T., Sun, Q., Zeng, X. F., Wang, D., Wang, J. X., & Chen, J. F. (2020a). ZnO nanodispersion as pseudohomogeneous catalyst for alcoholysis of polyethylene terephthalate. *Chemical Engineering Science*, *220*, 115642. https://doi.org/10.1016/j.ces.2020.115642

Du, J. T., Sun, Q., Zeng, X. F., Wang, D., Wang, J. X., & Chen, J. F. (2020b). ZnO nanodispersion as pseudohomogeneous catalyst for alcoholysis of polyethylene terephthalate. *Chemical Engineering Science*, *220*, 115642. https://doi.org/10.1016/j.ces.2020.115642

Dzhabarov, G., Sapunov, V., Kozlovskiy, R., Makarova, E., Kha, P. D., Voronov, M., Shadrina, V., Nhi, T. D., & Kurneshova, T. (2020). A method of polyethylene terephthalate depolymerization by biodiesel wastes. *Petroleum and Coal*, *62*(1), 19–26.

El Mejjatti, A., Harit, T., Riahi, A., Khiari, R., Bouabdallah, I., & Malek, F. (2014). Chemical recycling of poly(ethylene terephthalate). application to the synthesis of multiblock copolyesters. *Express Polymer Letters*, *8*(8), 544–553. https://doi.org/10.3144/expresspolymlett.2014.58

Ellis, L. D., Rorrer, N. A., Sullivan, K. P., Otto, M., McGeehan, J. E., Román-Leshkov, Y., Wierckx, N., & Beckham, G. T. (2021). Chemical and biological catalysis for plastics recycling and upcycling. *Nature Catalysis*, *4*(7), 539–556. https://doi.org/10.1038/s41929-021-00648-4

Ezeanu, D. S., & Matei, D. (2021). Natural depolymerization of waste poly (ethylene terephthalate) by neutral hydrolysis in marine water. *Scientific Reports*, 1–7. https://doi.org/10.1038/s41598-021-83659-2

Falah, W., Chen, F. J., Zeb, B. S., Hayat, M. T., Mahmood, Q., Ebadi, A., Toughani, M., & Li, E. Z. (2020). Polyethylene terephthalate degradation by Microalga Chlorella vulgaris along with pretreatment. *Materiale Plastice*, *57*(3), 260–270. https://doi.org/10.37358/MP.20.3.5398

Falkenstein, P., Gräsing, D., Bielytskyi, P., Zimmermann, W., Matysik, J., Wei, R., & Song, C. (2020). UV Pretreatment Impairs the Enzymatic Degradation of Polyethylene Terephthalate. *Frontiers in Microbiology*, *11*(April), 1–10. https://doi.org/10.3389/fmicb.2020.00689

Filella, M. (2020). Antimony and PET bottles: Checking facts. *Chemosphere*, *261*, 127732. https://doi.org/10.1016/j.chemosphere.2020.127732

Fiore, V., Scalici, T., Nicoletti, F., Vitale, G., Prestipino, M., & Valenza, A. (2016). A new eco-friendly chemical treatment of natural fibres : Effect of sodium bicarbonate on properties of sisal fibre and its epoxy composites. *Composites Part B*, *85*, 150–160. https://doi.org/10.1016/j.compositesb.2015.09.028

Formela, K., Hejna, A., Zedler, Colom, X., & Cañavate, J. (2019). Microwave treatment in waste rubber recycling – Recent advances and limitations. *Express Polymer Letters*, *13*(6), 565–588. https://doi.org/10.3144/expresspolymlett.2019.48

Fosse, C., Bourdet, A., Ernault, E., Esposito, A., Delpouve, N., Delbreilh, L., Thiyagarajan, S., Knoop, R. J. I., & Dargent, E. (2019a). Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry. *Thermochimica Acta*, *677*, 67–78. https://doi.org/10.1016/j.tca.2019.03.035

Fosse, C., Bourdet, A., Ernault, E., Esposito, A., Delpouve, N., Delbreilh, L., Thiyagarajan, S., Knoop, R. J. I., & Dargent, E. (2019b). Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry. *Thermochimica Acta*, *677*, 67–78. https://doi.org/10.1016/j.tca.2019.03.035

Frisa-Rubio, A., González-Niño, C., Royo, P., García-Polanco, N., Martínez-Hernández, D., Royo-Pascual, L., Fiesser, S., Žagar, E., & García-Armingol, T. (2021). Chemical recycling of plastics assisted by microwave multi-frequency heating. *Cleaner Engineering and Technology*, *5*. https://doi.org/10.1016/j.clet.2021.100297

Furukawa, M., Kawakami, N., Oda, K., & Miyamoto, K. (2018). Acceleration of Enzymatic Degradation of Poly(ethylene terephthalate) by Surface Coating with Anionic Surfactants. *ChemSusChem*, *11*(23), 4018–4025. https://doi.org/10.1002/cssc.201802096

Genta, M., Goto, M., & Sasaki, M. (2010). Heterogeneous continuous kinetics modeling of PET depolymerization in supercritical methanol. *Journal of Supercritical Fluids*, *52*(3), 266–275. https://doi.org/10.1016/j.supflu.2010.01.007

George, N., & Kurian, T. (2014). Recent developments in the chemical recycling of postconsumer poly(ethylene terephthalate) Waste. *Industrial and Engineering Chemistry Research*, *53*(37), 14185–14198. https://doi.org/10.1021/ie501995m

Gómez, A. V., Biswas, A., Tadini, C. C., Furtado, R. F., Alves, C. R., & Cheng, H. N. (2019). Use of natural deep eutectic solvents for polymerization and polymer reactions. *Journal of the Brazilian Chemical Society*, *30*(4), 717–726. https://doi.org/10.21577/0103-5053.20190001

Gong, J., Kong, T., Li, Y., Li, Q., Li, Z., & Zhang, J. (2018). Biodegradation of microplastic derived from poly(ethylene terephthalate) with bacterial whole-cell biocatalysts. *Polymers*, *10*(12). https://doi.org/10.3390/polym10121326

González-Rivera, J., Husanu, E., Mero, A., Ferrari, C., Duce, C., Tinè, M. R., D'Andrea, F., Pomelli, C. S., & Guazzelli, L. (2020). Insights into microwave heating response and thermal decomposition behavior of deep eutectic solvents. *Journal of Molecular Liquids*, *300*. https://doi.org/10.1016/j.molliq.2019.112357

González-Rivera, J., Mero, A., Husanu, E., Mezzetta, A., Ferrari, C., D'Andrea, F., Bramanti, E., Pomelli, C. S., & Guazzelli, L. (2021). Combining acid-based deep eutectic solvents and microwave irradiation for improved chestnut shell waste valorization. *Green Chemistry*, *23*(24), 10101–10115. https://doi.org/10.1039/d1gc03450b

Güçlü, G., Yalçinyuva, T., Özgümüş, S., & Orbay, M. (2003). Simultaneous glycolysis and hydrolysis of polyethylene terephthalate and characterization of products by differential scanning calorimetry. *Polymer*, *44*(25), 7609–7616. https://doi.org/10.1016/j.polymer.2003.09.062

Gumargalieva, K. Z., Moiseev, Y. V., Daurova, T. T., & Voronkova, O. S. (1982). Effect of infections on the degradation of polyethylene terephthalate implants. *Biomaterials*, *3*(3), 177–180. https://doi.org/10.1016/0142-9612(82)90008-4

Haith, M. S. (2005). Steric Effects in the Basic Hydrolysis. *Journal of Applied Polymer Science*, *12*(1968), 1999–2005.

Hoppe, J., Drozd, R., Byzia, E., & Smiglak, M. (2019). Deep eutectic solvents based on choline cation - Physicochemical properties and influence on enzymatic reaction with β-galactosidase. *International Journal of Biological Macromolecules*, *136*, 296–304. https://doi.org/10.1016/j.ijbiomac.2019.06.027

Hu, L. C., Oku, A., Yamada, E., & Tomari, K. (1997). Alkali-decomposition of poly(ethylene terephthalate) in mixed media of nonaqueous alcohol and ether. Study on recycling of poly(ethylene terephthalate). *Polymer Journal*, *29*(9), 708–712. https://doi.org/10.1295/polymj.29.708

Ikenaga, K., Inoue, T., & Kusakabe, K. (2016). Hydrolysis of PET by Combining Direct Microwave Heating with High Pressure. *Procedia Engineering*, *148*, 314–318. https://doi.org/10.1016/j.proeng.2016.06.442

Imran, M., Kim, B. K., Han, M., Cho, B. G., & Kim, D. H. (2010). Sub-and supercritical glycolysis of polyethylene terephthalate (PET) into the monomer bis(2-hydroxyethyl) terephthalate (BHET). *Polymer Degradation and Stability*, *95*(9), 1686–1693. https://doi.org/10.1016/j.polymdegradstab.2010.05.026

Is¸ılAcar, M. (2011a). Aminoglycolysis of Waste Poly(ethylene terephthalate) With Diethanolamine and Evaluation of the Products as Polyurethane Surface Coating Materials. *Polymer Engineering and Science*, 746–754. https://doi.org/10.1002/pen

Is¸ılAcar, M. (2011b). Aminoglycolysis of Waste Poly(ethylene terephthalate) With Diethanolamine and Evaluation of the Products as Polyurethane Surface Coating Materials. *Polymer Engineering and Science*, 746–754. https://doi.org/10.1002/pen

Kadhom, M. A., Abdullah, G. H., & Al-Bayati, N. (2017). Studying Two Series of Ternary Deep Eutectic Solvents (Choline Chloride–Urea–Glycerol) and (Choline Chloride–Malic Acid–Glycerol), Synthesis and Characterizations. *Arabian Journal for Science and Engineering*, *42*(4), 1579–1589. https://doi.org/10.1007/s13369-017-2431-4

Kanelli, M., Vasilakos, S., Nikolaivits, E., Ladas, S., Christakopoulos, P., & Topakas, E. (2015). Surface modification of poly(ethylene terephthalate) (PET) fibers by a cutinase from Fusarium oxysporum. *Process Biochemistry*, *50*(11), 1885–1892. https://doi.org/10.1016/j.procbio.2015.08.013

Karayannidis, G. P., Chatziavgoustis, A. P., & Achilias, D. S. (2002). Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid by alkaline hydrolysis. *Advances in Polymer Technology*, *21*(4), 250–259. https://doi.org/10.1002/adv.10029

Kawai, F. (2021). The current state of research on PET hydrolyzing enzymes available for biorecycling. *Catalysts*, *11*(2), 1–10. https://doi.org/10.3390/catal11020206

Kawai, F., Kawabata, T., & Oda, M. (2019). Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields. *Applied Microbiology and Biotechnology*, *103*, 4253–4268.

Kawai, F., Oda, M., Tamashiro, T., Waku, T., Tanaka, N., Yamamoto, M., Mizushima, H., Miyakawa, T., & Tanokura, M. (2014). A novel Ca2+-activated, thermostabilized polyesterase capable of hydrolyzing polyethylene terephthalate from Saccharomonospora viridis AHK190. *Applied Microbiology and Biotechnology*, *98*(24), 10053–10064. https://doi.org/10.1007/s00253-014-5860-y

Kazarian, S. G., & Martirosyan, G. G. (2002). ATR-IR spectroscopy of superheated water and in situ study of the hydrothermal decomposition of poly(ethylene terephthalate). *Physical Chemistry Chemical Physics*, *4*(15), 3759–3763. https://doi.org/10.1039/b202119f

Khoonkari, M., Haghighi, A. H., Sefidbakht, Y., Shekoohi, K., & Ghaderian, A. (2015). Chemical Recycling of PET Wastes with Different Catalysts. *International Journal of Polymer Science*, *2015*. https://doi.org/10.1155/2015/124524

Kirshanov, K., Toms, R., Aliev, G., Naumova, A., Melnikov, P., & Gervald, A. (2022). Recent Developments and Perspectives of Recycled Poly(ethylene terephthalate)-Based Membranes: A Review. *Membranes*, *12*(11). https://doi.org/10.3390/membranes12111105

Kosloski-Oh, S. C., Wood, Z. A., Manjarrez, Y., De Los Rios, J. P., & Fieser, M. E. (2021). Catalytic methods for chemical recycling or upcycling of commercial polymers. *Materials Horizons*, *8*(4), 1084–1129. https://doi.org/10.1039/d0mh01286f

Kot, P., Shaw, A., Jones, K. O., Cullen, J. D., Kot, P., Shaw, A., Jones, K. O., Mason, A., & Al-Shamma', A. I. (2014). *The feasibility of using electromagnetic waves in determining the moisture content of building fabrics and the cause of the water ingress Electromagnetic Cavity Applications View project The feasibility of using electromagnetic waves in determining the moisture content of building fabrics and the cause of the water ingress*. https://www.researchgate.net/publication/303751697

Kulkarni, N. G., Avadhani, C. V., & Sivaram, S. (2004). Efficient method for recycling poly(ethylene terephthalate) to poly(butylene terephthalate) using transesterification reaction. *Journal of Applied Polymer Science*, *91*(6), 3720–3729. https://doi.org/10.1002/app.13453

Lamberti, F. M., Román-Ramírez, L. A., & Wood, J. (2020). Recycling of Bioplastics: Routes and Benefits. *Journal of Polymers and the Environment*, *28*(10), 2551–2571. https://doi.org/10.1007/s10924-020-01795-8

Li, W., Zhang, C., Chi, H., Li, L., Lan, T., Han, P., Chen, H., & Qin, Y. (2017a). Development of antimicrobial packaging film made from poly(lactic acid) incorporating titanium dioxide and silver nanoparticles. *Molecules*, *22*(7). https://doi.org/10.3390/molecules22071170

Li, W., Zhang, C., Chi, H., Li, L., Lan, T., Han, P., Chen, H., & Qin, Y. (2017b). Development of antimicrobial packaging film made from poly(lactic acid) incorporating titanium dioxide and silver nanoparticles. *Molecules*, *22*(7). https://doi.org/10.3390/molecules22071170

Lima, G. R., Monteiro, W. F., Ligabue, R., & Santana, R. M. C. (2017). Titanate nanotubes as new nanostrutured catalyst for depolymerization of PET by glycolysis reaction. *Materials Research*, *20*, 596–602. https://doi.org/10.1590/1980-5373-mr-2017-0645

Lima, G. R., Monteiro, W. F., Toledo, B. O., Ligabue, R. A., & Santana, R. M. C. (2019). Titanate Nanotubes Modified With Zinc and Its Application in Post-Consumer PET Depolymerization. *Macromolecular Symposia*, *383*(1), 1–5. https://doi.org/10.1002/masy.201800008

Liu, B., Fu, W., Lu, X., Zhou, Q., & Zhang, S. (2019a). Lewis Acid-Base Synergistic Catalysis for Polyethylene Terephthalate Degradation by 1,3-Dimethylurea/Zn(OAc)2 Deep Eutectic Solvent [Research-article]. *ACS Sustainable Chemistry and Engineering*, *7*(3), 3292–3300. https://doi.org/10.1021/acssuschemeng.8b05324

Liu, B., Fu, W., Lu, X., Zhou, Q., & Zhang, S. (2019b). Lewis Acid-Base Synergistic Catalysis for Polyethylene Terephthalate Degradation by 1,3-Dimethylurea/Zn(OAc)2 Deep Eutectic Solvent. *ACS Sustainable Chemistry and Engineering*, *7*(3), 3292–3300. https://doi.org/10.1021/acssuschemeng.8b05324

Liu, L., Zhang, D., An, L., Zhang, H., & Tian, Y. (2005). Hydrolytic depolymerization of poly(ethylene terephthalate) under microwave irradiation. *Journal of Applied Polymer Science*, *95*(3), 719–723. https://doi.org/10.1002/app.21231

Liu, Y., Wang, M., & Pan, Z. (2012). Catalytic depolymerization of polyethylene terephthalate in hot compressed water. *Journal of Supercritical Fluids*, *62*, 226–231. https://doi.org/10.1016/j.supflu.2011.11.001

López-Fonseca, R., Duque-Ingunza, I., de Rivas, B., Arnaiz, S., & Gutiérrez-Ortiz, J. I. (2010a). Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts. *Polymer Degradation and Stability*, *95*(6), 1022–1028. https://doi.org/10.1016/j.polymdegradstab.2010.03.007

López-Fonseca, R., Duque-Ingunza, I., de Rivas, B., Arnaiz, S., & Gutiérrez-Ortiz, J. I. (2010b). Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts. *Polymer Degradation and Stability*, *95*(6), 1022–1028. https://doi.org/10.1016/j.polymdegradstab.2010.03.007

López-Fonseca, R., Duque-Ingunza, I., de Rivas, B., Flores-Giraldo, L., & Gutiérrez-Ortiz, J. I. (2011). Kinetics of catalytic glycolysis of PET wastes with sodium carbonate. *Chemical Engineering Journal*, *168*(1), 312–320. https://doi.org/10.1016/j.cej.2011.01.031

Marichamy, S., Stalin, B., Ravichandran, M., & Sudha, G. T. (2020). Optimization of machining parameters of EDM for α-β Brass using response surface methodology. *Materials Today: Proceedings*, *24*, 1400–1409. https://doi.org/10.1016/j.matpr.2020.04.458

Martins, M. A. R., Pinho, S. P., & Coutinho, J. A. P. (2019). Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *Journal of Solution Chemistry*, *48*(7), 962–982. https://doi.org/10.1007/s10953-018-0793-1

Marullo, S., Rizzo, C., Dintcheva, N. T., & D’Anna, F. (2021). Amino Acid-Based Cholinium Ionic Liquids as Sustainable Catalysts for PET Depolymerization. *ACS Sustainable Chemistry and Engineering*, *9*(45), 15157–15165. https://doi.org/10.1021/acssuschemeng.1c04060

Mastellone, M. L. (1999). Thermal treatments of plastic wastes by means of fluidized bed reactors. *Second University of Naples: Italy*.

Meng, X., Yang, L., Liu, H., Li, Q., Xu, G., Zhang, Y., Guan, F., Zhang, Y., Zhang, W., Wu, N., & Tian, J. (2021). Protein engineering of stable IsPETase for PET plastic degradation by Premuse. *International Journal of Biological Macromolecules*, *180*, 667–676. https://doi.org/10.1016/j.ijbiomac.2021.03.058

Musale, R. M., & Shukla, S. R. (2016). Deep eutectic solvent as effective catalyst for aminolysis of polyethylene terephthalate (PET) waste. *International Journal of Plastics Technology*, *20*(1), 106–120. https://doi.org/10.1007/s12588-016-9134-7

Nikje, M. M. A., & Ghamary, E. (2015). Organic / inorganic nanosilica support role in the recovery of terephthalic acid from poly(ethylene terephthalate) wastes. *Progress in Rubber, Plastics and Recycling Technology*, *31*(4), 297–305. https://doi.org/10.1177/147776061503100404

Nikolaivits, E., Kanelli, M., Dimarogona, M., & Topakas, E. (2018). A middle-aged enzyme still in its prime: Recent advances in the field of cutinases. *Catalysts*, *8*(12). https://doi.org/10.3390/catal8120612

Nikolaivits, E., Pantelic, B., Azeem, M., Taxeidis, G., Babu, R., Topakas, E., Brennan Fournet, M., & Nikodinovic-Runic, J. (2021). Progressing Plastics Circularity: A Review of

Mechano-Biocatalytic Approaches for Waste Plastic (Re)valorization. *Frontiers in Bioengineering and Biotechnology*, *9*(June), 1–31. https://doi.org/10.3389/fbioe.2021.696040

Ohno A. (1977) Thiones. In: Oae S. (eds) Organic Chemistry of Sulfur. Springer, Boston, MA. https://doi.org/10.1007/978-1-4684-2049-4_5. (n.d.).

Oku, A., Hu, L. C., & Yamada, E. (1997). Alkali decomposition of poly(ethylene terephthalate) with sodium hydroxide in nonaqueous ethylene glycol: A study on recycling of terephthalic acid and ethylene glycol. *Journal of Applied Polymer Science*, *63*(5), 595–601. https://doi.org/10.1002/(SICI)1097-4628(19970131)63:5<595::AID-APP7>3.0.CO;2-P

Organic Chemical Process Industry 6.11-1. (2000). *83*, 1–5.

Öztürk, Y., & Güçlü, G. (2004). Unsaturated polyester resins obtained from glycolysis products of waste PET. *Polymer - Plastics Technology and Engineering*, *43*(5), 1539–1552. https://doi.org/10.1081/PPT-200030272

Padhan, R. K., & Sreeram, A. (2019a). Chemical Depolymerization of PET Bottles via Combined Chemolysis Methods. In *Recycling of Polyethylene Terephthalate Bottles*. Elsevier Inc. https://doi.org/10.1016/b978-0-12-811361-5.00007-9

Padhan, R. K., & Sreeram, A. (2019b). Chemical depolymerization of PET bottles via combined chemolysis methods. In *Recycling of Polyethylene Terephthalate Bottles* (pp. 135–147). Elsevier.

Pagliaro, M., Ciriminna, R., Kimura, H., Rossi, M., & Della Pina, C. (2007). From glycerol to value-added products. *Angewandte Chemie - International Edition*, *46*(24), 4434–4440. https://doi.org/10.1002/anie.200604694

Park, S. H., Alammar, A., Fulop, Z., Pulido, B. A., Nunes, S. P., & Szekely, G. (2021). Hydrophobic thin film composite nanofiltration membranes derived solely from sustainable sources. *Green Chemistry*, *23*(3), 1175–1184. https://doi.org/10.1039/d0gc03226c

Pasula, R. R., Lim, S., Ghadessy, F. J., & Sana, B. (2022). The influences of substrates' physical properties on enzymatic PET hydrolysis: Implications for PET hydrolase engineering. *Engineering Biology*, *6*(1), 17–22. https://doi.org/10.1049/enb2.12018

Paszun, D., & Spychaj, T. (1997). Chemical Recycling of Poly(ethylene terephthalate). *Industrial and Engineering Chemistry Research*, *36*(4), 1373–1383. https://doi.org/10.1021/ie960563c

Patterson, J. D., Balik, C. M., Hinestroza, J., Roberts, G., & Khan, S. (2007). *Continuous Depolymerization of Poly(Ethylene Terephthalate) Via Reactive Extrusion*. *13*.

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

Payne, J., & Jones, M. D. (2021). The Chemical Recycling of Polyesters for a Circular Plastics Economy: Challenges and Emerging Opportunities. *ChemSusChem*, *14*(19), 4041–4070. https://doi.org/10.1002/cssc.202100400

Pestana, S. C., Machado, J. N., Pinto, R. D., Ribeiro, B. D., & Marrucho, I. M. (2021). Natural eutectic solvents for sustainable recycling of poly(ethyleneterephthalate): closing the circle. *Green Chemistry*, *23*(23), 9460–9464. https://doi.org/10.1039/D1GC02403E

Pingale, N. D., & Shukla, S. R. (2008). Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste. *European Polymer Journal*, *44*(12), 4151–4156. https://doi.org/10.1016/j.eurpolymj.2008.09.019

Pudack, C., Stepanski, M., & Fässler, P. (2020). PET Recycling – Contributions of Crystallization to Sustainability. *Chemie-Ingenieur-Technik*, *92*(4), 452–458. https://doi.org/10.1002/cite.201900085

Quartinello, F., Vajnhandl, S., Volmajer Valh, J., Farmer, T. J., Vončina, B., Lobnik, A., Herrero Acero, E., Pellis, A., & Guebitz, G. M. (2017). Synergistic chemo-enzymatic hydrolysis of poly(ethylene terephthalate) from textile waste. *Microbial Biotechnology*, *10*(6), 1376–1383. https://doi.org/10.1111/1751-7915.12734

Rabnawaz, M., Wyman, I., Auras, R., & Cheng, S. (2017). A roadmap towards green packaging: The current status and future outlook for polyesters in the packaging industry. *Green Chemistry*, *19*(20), 4737–4753. https://doi.org/10.1039/c7gc02521a

Ronkvist, Å. M., Xie, W., Lu, W., & Gross, R. A. (2009). Cutinase-Catalyzed hydrolysis of poly(ethylene terephthalate). *Macromolecules*, *42*(14), 5128–5138. https://doi.org/10.1021/ma9005318

Rorrer, N. A., Nicholson, S., Carpenter, A., Biddy, M. J., Grundl, N. J., & Beckham, G. T. (2019). Combining Reclaimed PET with Bio-based Monomers Enables Plastics Upcycling. *Joule*, *3*(4), 1006–1027. https://doi.org/10.1016/j.joule.2019.01.018

Rouillon, C., Bussiere, P. O., Desnoux, E., Collin, S., Vial, C., Therias, S., & Gardette, J. L. (2016). Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? *Polymer Degradation and Stability*, *128*, 200–208. https://doi.org/10.1016/j.polymdegradstab.2015.12.011

Rubio Arias, J. J., & Thielemans, W. (2021). Instantaneous hydrolysis of PET bottles: an efficient pathway for the chemical recycling of condensation polymers. *Green Chemistry*. https://doi.org/10.1039/D1GC02896K

Sachin Kumar Achyut K. Panda, R. K. S. (2011). A review on tertiary recycling of high-density polyethylene to fuel. *Resources, Conservation and Recycling*, *55*(11), 893–910. https://doi.org/10.1016/j.resconrec.2011.05.005

Sadat-Shojai, M., & Bakhshandeh, G. R. (2011). Recycling of PVC wastes. *Polymer Degradation and Stability*, *96*(4), 404–415. https://doi.org/10.1016/j.polymdegradstab.2010.12.001

Sadeghi, B., Marfavi, Y., AliAkbari, R., Kowsari, E., Borbor Ajdari, F., & Ramakrishna, S. (2021). Recent Studies on Recycled PET Fibers: Production and Applications: a Review. *Materials Circular Economy*, *3*(1). https://doi.org/10.1007/s42824-020-00014-y

Sert, E., Yılmaz, E., & Atalay, F. (2019a). Chemical Recycling of Polyethlylene Terephthalate by Glycolysis Using Deep Eutectic Solvents. *Journal of Polymers and the Environment*, *27*, 1–7. https://doi.org/10.1007/s10924-019-01578-w

Sert, E., Yılmaz, E., & Atalay, F. S. (2019b). Chemical Recycling of Polyethlylene Terephthalate by Glycolysis Using Deep Eutectic Solvents. *Journal of Polymers and the Environment*, *27*(12), 2956–2962. https://doi.org/10.1007/s10924-019-01578-w

Sheel, A., & Pant, D. (2019). Chemical Depolymerization of PET Bottles via Glycolysis. In *Recycling of Polyethylene Terephthalate Bottles* (pp. 61–84). Elsevier Inc. https://doi.org/10.1016/b978-0-12-811361-5.00004-3

Shirke, A. N., White, C., Englaender, J. A., Zwarycz, A., Butterfoss, G. L., Linhardt, R. J., & Gross, R. A. (2018a). Stabilizing Leaf and Branch Compost Cutinase (LCC) with Glycosylation: Mechanism and Effect on PET Hydrolysis. *Biochemistry*, *57*(7), 1190–1200. https://doi.org/10.1021/acs.biochem.7b01189

Shirke, A. N., White, C., Englaender, J. A., Zwarycz, A., Butterfoss, G. L., Linhardt, R. J., & Gross, R. A. (2018b). Stabilizing Leaf and Branch Compost Cutinase (LCC) with Glycosylation: Mechanism and Effect on PET Hydrolysis. *Biochemistry*, *57*(7), 1190–1200. https://doi.org/10.1021/acs.biochem.7b01189

Shukla, S. R., & Harad, A. M. (2005). Glycolysis of polyethylene terephthalate waste fibers. *Journal of Applied Polymer Science*, *97*(2), 513–517. https://doi.org/10.1002/app.21769

Shukla, S. R., & Kulkarni, K. S. (2002). Depolymerization of poly(ethylene terephthalate) waste. *Journal of Applied Polymer Science*, *85*(8), 1765–1770. https://doi.org/10.1002/app.10714

Shukla, S. R., & Mathur, M. R. (2000). Action of alkali on polybutylene terephthalate and polyethylene terephthalate polyesters. *Journal of Applied Polymer Science*, *75*(9), 1097–1102. https://doi.org/10.1002/(SICI)1097-4628(20000228)75:9<1097::AID-APP2>3.0.CO;2-7

Shukla, S. R., Palekar, V., & Pingale, N. (2008). Zeolite catalyzed glycolysis of poly (ethylene terephthalate) bottle waste. *Journal of Applied Polymer Science*, *110*(1), 501–506.

Siddiqui, M. N., Achilias, D. S., Redhwi, H. H., Bikiaris, D. N., Katsogiannis, K. A. G., & Karayannidis, G. P. (2010). Hydrolytic depolymerization of PET in a microwave reactor. *Macromolecular Materials and Engineering*, *295*(6), 575–584. https://doi.org/10.1002/mame.201000050

Singh, N., Hui, D., Singh, R., Ahuja, I. P. S., Feo, L., & Fraternali, F. (2017a). Recycling of plastic solid waste: A state of art review and future applications. *Composites Part B: Engineering*, *115*, 409–422. https://doi.org/10.1016/j.compositesb.2016.09.013

Singh, N., Hui, D., Singh, R., Ahuja, I. P. S., Feo, L., & Fraternali, F. (2017b). Recycling of plastic solid waste: A state of art review and future applications. *Composites Part B: Engineering*, *115*, 409–422. https://doi.org/10.1016/j.compositesb.2016.09.013

Sinha, V., Patel, M. R., & Patel, J. V. (2010). Pet waste management by chemical recycling: A review. *Journal of Polymers and the Environment*, *18*(1), 8–25. https://doi.org/10.1007/s10924-008-0106-7

Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep Eutectic Solvents (DESs) and Their Applications. *Chemical Reviews*, *114*(21), 11060–11082. https://doi.org/10.1021/cr300162p

Sohn, Y. J., Kim, H. T., Baritugo, K. A., Jo, S. Y., Song, H. M., Park, S. Y., Park, S. K., Pyo, J., Cha, H. G., Kim, H., Na, J. G., Park, C., Choi, J. Il, Joo, J. C., & Park, S. J. (2020). Recent Advances in Sustainable Plastic Upcycling and Biopolymers. In *Biotechnology Journal* (Vol. 15, Issue 6). Wiley-VCH Verlag. https://doi.org/10.1002/biot.201900489

Spychaj, T., Fabrycy, E., & Spychaj, S. (2001). Aminolysis and aminoglycolysis of waste poly (ethylene terephthalate). *J Marter Cycles Waste Manag*, 24–31.

Subramanian, P. M. (2000). Plastics recycling and waste management in the US. *Resources, Conservation and Recycling*, *28*(3–4), 253–263. https://doi.org/10.1016/S0921-3449(99)00049-X

Sulaiman, S., Yamato, S., Kanaya, E., Kim, J. J., Koga, Y., Takano, K., & Kanaya, S. (2012). Isolation of a novel cutinase homolog with polyethylene terephthalate-degrading activity from leaf-branch compost by using a metagenomic approach. *Applied and Environmental Microbiology*, *78*(5), 1556–1562. https://doi.org/10.1128/AEM.06725-11

Sun, C. hao, Chen, X. ping, Zhuo, Q., & Zhou, T. (2018). Recycling and depolymerization of waste polyethylene terephthalate bottles by alcohol alkali hydrolysis. *Journal of Central South University*, *25*(3), 543–549. https://doi.org/10.1007/s11771-018-3759-y

Sun, J., Liu, D., Young, R. P., Cruz, A. G., Isern, N. G., Schuerg, T., Cort, J. R., Simmons, B. A., & Singh, S. (2018). High loading solubilization and upgrading of poly (ethylene terephthalate) in low cost bifunctional ionic liquid. *ChemSusChem*, *11*(4), 781–792.

Sun, J., Wang, W., & Yue, Q. (2016). Review on microwave-matter interaction fundamentals and efficient microwave-associated heating strategies. In *Materials* (Vol. 9, Issue 4). MDPI AG. https://doi.org/10.3390/ma9040231

Taheri, M., Jahanfar, M., & Ogino, K. (2019). Synthesis of acrylic resins for high-solids traffic marking paint by solution polymerization. *Designed Monomers and Polymers*, *22*(1), 213–225. https://doi.org/10.1080/15685551.2019.1699349

Tan, Y. T., Ngoh, G. C., & Chua, A. S. M. (2018). Evaluation of fractionation and delignification efficiencies of deep eutectic solvents on oil palm empty fruit bunch. *Industrial Crops and Products*, *123*(June), 271–277. https://doi.org/10.1016/j.indcrop.2018.06.091

Tang, X., & Chen, E. Y. X. (2019). Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters. *Chem*, *5*(2), 284–312. https://doi.org/10.1016/j.chempr.2018.10.011

Then, J., Wei, R., Oeser, T., Barth, M., Belisário-Ferrari, M. R., Schmidt, J., & Zimmermann, W. (2015). Ca2+ and Mg2+ binding site engineering increases the degradation of polyethylene terephthalate films by polyester hydrolases from Thermobifida fusca. *Biotechnology Journal*, *10*(4), 592–598. https://doi.org/10.1002/biot.201400620

Then, J., Wei, R., Oeser, T., Gerdts, A., Schmidt, J., Barth, M., & Zimmermann, W. (2016). A disulfide bridge in the calcium binding site of a polyester hydrolase increases its thermal stability and activity against polyethylene terephthalate. *FEBS Open Bio*, *6*(5), 425–432. https://doi.org/10.1002/2211-5463.12053

Thiyagarajan, S., Maaskant-Reilink, E., Ewing, T. A., Julsing, M. K., & Van Haveren, J. (2022). Back-to-monomer recycling of polycondensation polymers: Opportunities for chemicals and enzymes. *RSC Advances*, *12*(2), 947–970. https://doi.org/10.1039/d1ra08217e

Tournier, V., Topham, C. M., Gilles, A., David, B., Folgoas, C., Moya-Leclair, E., Kamionka, E., Desrousseaux, M.-L., Texier, H., Gavalda, S., Cot, M., Guémard, E., Dalibey, M., Nomme, J., Cioci, G., Barbe, S., Chateau, M., André, I., Duquesne, S., & Marty, A. (2020). An engineered PET depolymerase to break down and recycle plastic bottles. *Nature*, *580*(7802), 216–219. https://doi.org/10.1038/s41586-020-2149-4

Vaidya, U. R., & Nadkarni, V. M. (1988). Polyester polyols for polyurethanes from pet waste: Kinetics of polycondensation. *Journal of Applied Polymer Science*, *35*(3), 775–785. https://doi.org/10.1002/app.1988.070350317

Wang, Q., Yao, X., Geng, Y., Zhou, Q., Lu, X., & Zhang, S. (2015). Deep eutectic solvents as highly active catalysts for the fast and mild glycolysis of poly(ethylene terephthalate)(PET). *Green Chemistry*, *17*(4), 2473–2479. https://doi.org/10.1039/c4gc02401j

Wang, Q., Yao, X., Tang, S., Lu, X., Zhang, X., & Zhang, S. (2012a). Urea as an efficient and reusable catalyst for the glycolysis of poly(ethylene terephthalate) wastes and the role of hydrogen bond in this process. *Green Chemistry*, *14*(9), 2559–2566. https://doi.org/10.1039/c2gc35696a

Wang, Q., Yao, X., Tang, S., Lu, X., Zhang, X., & Zhang, S. (2012b). Urea as an efficient and reusable catalyst for the glycolysis of poly(ethylene terephthalate) wastes and the role of hydrogen bond in this process. *Green Chemistry*, *14*(9), 2559–2566. https://doi.org/10.1039/c2gc35696a

Wang, Y., Zhang, Y., Song, H., Wang, Y., Deng, T., & Hou, X. (2019). Zinc-catalyzed ester bond cleavage: Chemical degradation of polyethylene terephthalate. *Journal of Cleaner Production*, *208*, 1469–1475. https://doi.org/10.1016/j.jclepro.2018.10.117

Weerasooriya, P. R. D., Karunanayake, U. P. A. B. P., Udayakumara, S. V, & Gunapala, O. (2011). *Use of soda ash as a recycling agent to reduce Non-degradable PET Waste in Sri Lanka*.

Wei, R., Breite, D., Song, C., Gräsing, D., Ploss, T., Hille, P., Schwerdtfeger, R., Matysik, J., Schulze, A., & Zimmermann, W. (2019a). Biocatalytic Degradation Efficiency of Postconsumer Polyethylene Terephthalate Packaging Determined by Their Polymer Microstructures. *Advanced Science*, *6*(14), 1900491. https://doi.org/10.1002/advs.201900491

Wei, R., Breite, D., Song, C., Gräsing, D., Ploss, T., Hille, P., Schwerdtfeger, R., Matysik, J., Schulze, A., & Zimmermann, W. (2019b). Biocatalytic Degradation Efficiency of Postconsumer Polyethylene Terephthalate Packaging Determined by Their Polymer

Microstructures. *Advanced Science*, *6*(14), 1900491. https://doi.org/10.1002/advs.201900491

Wei, R., & Zimmermann, W. (2017). Biocatalysis as a green route for recycling the recalcitrant plastic polyethylene terephthalate. *Microbial Biotechnology*, *10*(6), 1302–1307. https://doi.org/10.1111/1751-7915.12714

Wernke, M. J. (2014). Glycerol. *Encyclopedia of Toxicology: Third Edition*, 754–756. https://doi.org/10.1016/B978-0-12-386454-3.00510-8

West, Simon, M. (1993). Improved Polyethlene terephthalate Decontamination. In *world intellectual property organization*. https://doi.org/93/23465

Winter, R. (2013). Method and apparatus for recycling of organic waste preferably used tires using microwave technique. *European Patent Application*, *1*(19), 1–23.

Worch, J. C., & Dove, A. P. (2020). 100th Anniversary of Macromolecular Science Viewpoint: Toward Catalytic Chemical Recycling of Waste (and Future) Plastics. *ACS Macro Letters*, *9*(11), 1494–1506. https://doi.org/10.1021/acsmacrolett.0c00582

Wu, S. C., Cheng, Z. M., Wang, S. D., & Shan, X. L. (2011a). Recovery of Terephthalic Acid from Alkali Reduction Wastewater by Cooling Crystallization. *Chemical Engineering and Technology*, *34*(10), 1614–1618. https://doi.org/10.1002/ceat.201100096

Wu, S. C., Cheng, Z. M., Wang, S. D., & Shan, X. L. (2011b). Recovery of Terephthalic Acid from Alkali Reduction Wastewater by Cooling Crystallization. *Chemical Engineering and Technology*, *34*(10), 1614–1618. https://doi.org/10.1002/ceat.201100096

Xi, G., Lu, M., & Sun, C. (2005). Study on depolymerization of waste polyethylene terephthalate into monomer of bis(2-hydroxyethyl terephthalate). *Polymer Degradation and Stability*, *87*(1), 117–120. https://doi.org/10.1016/j.polymdegradstab.2004.07.017

Yang, Z., Peng, H., Wang, W., & Liu, T. (2010). Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites. *Journal of Applied Polymer Science*, *116*(5), 2658–2667. https://doi.org/10.1002/app

Yassin, L., Lettieri, P., Simons, S., & Germanà, A. (2005). Energy recovery from thermal processing of waste: A review. *Proceedings of the Institution of Civil Engineers: Engineering Sustainability*, *158*(2), 97–103. https://doi.org/10.1680/ensu.2005.158.2.97

Yoon, K. H., Kwon, M. H., Jeon, M. H., & Park, O. O. (1993). Diffusion of ethylene glycol in solid state poly(ethylene terephthalate). *Polymer Journal*, *25*(3), 227–236. https://doi.org/10.1295/polymj.25.219

Yoshida, S. (2016). et all., A bacterium that degrades and assimilates poly (ethylene terephthalate). *Science*, *351*.

Yoshioka, T., Ota, M., & Okuwaki, A. (2003). Conversion of a used poly (ethylene terephthalate) bottle into oxalic acid and terephthalic acid by oxygen oxidation in alkaline solutions at elevated temperatures. *Industrial & Engineering Chemistry Research*, *42*(4), 675–679.

Yue, Q. F., Xiao, L. F., Zhang, M. L., & Bai, X. F. (2013). The glycolysis of poly(ethylene terephthalate) waste: Lewis acidic ionic liquids as high efficient catalysts. *Polymers*, *5*(4), 1258–1271. https://doi.org/10.3390/polym5041258

Yunita, I., Putisompon, S., Chumkaeo, P., Poonsawat, T., & Somsook, E. (2019). Effective catalysts derived from waste ostrich eggshells for glycolysis of post-consumer PET bottles. *Chemical Papers*, *73*(6), 1547–1560. https://doi.org/10.1007/s11696-019-00710-3

Zanela, T. M. P., Muniz, E. C., & Almeida, C. A. P. (2018). Chemical recycling of poly(Ethylene terephthalate) (PET) by alkaline hydrolysis and catalyzed glycolysis. *Orbital*, *10*(3), 226–233. https://doi.org/10.17807/orbital.v10i3.1104

Zhang, J., Wang, X., Gong, J., & Gu, Z. (2004). A study on the biodegradability of polyethylene terephthalate fiber and diethylene glycol terephthalate. *Journal of Applied Polymer Science*, *93*(3), 1089–1096. https://doi.org/10.1002/app.20556

Zhang, L., Gao, J., Zou, J., & Yi, F. (2013). Hydrolysis of poly(ethylene terephthalate) waste bottles in the presence of dual functional phase transfer catalysts. *Journal of Applied Polymer Science*, *130*(4), 2790–2795. https://doi.org/10.1002/app.39497

Zhang, S., Xu, W., Du, R., Zhou, X., Liu, X., Xu, S., & Wang, Y. Z. (2022). Cosolvent-promoted selective non-aqueous hydrolysis of PET wastes and facile product separation. *Green Chemistry*, 3284–3292. https://doi.org/10.1039/d2gc00328g

Zimmermann, W., & Billig, S. (2011). Enzymes for the Biofunctionalization of Poly(Ethylene Terephthalate). In G. S. Nyanhongo, W. Steiner, & G. Gübitz (Eds.), *Advances in Biochemical Engineering/Biotechnology* (Vol. 125, pp. 97–120). Springer Berlin Heidelberg. https://doi.org/10.1007/10_2010_87

Appendices

Appendix A Journal Publications

polymers

MDPI

Article

Progressing Ultragreen, Energy-Efficient Biobased Depolymerization of Poly(ethylene terephthalate) via Microwave-Assisted Green Deep Eutectic Solvent and Enzymatic Treatment

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Abstract: Effective interfacing of energy-efficient and biobased technologies presents an all-green route to achieving continuous circular production, utilization, and reproduction of plastics. Here, we show combined ultragreen chemical and biocatalytic depolymerization of polyethylene terephthalate (PET) using deep eutectic solvent (DES)-based low-energy microwave (MW) treatment followed by enzymatic hydrolysis. DESs are emerging as attractive sustainable catalysts due to their low toxicity, biodegradability, and unique biological compatibility. A green DES with triplet composition of choline chloride, glycerol, and urea was selected for PET depolymerization under MW irradiation without the use of additional depolymerization agents. Treatment conditions were studied using Box-Behnken design (BBD) with respect to MW irradiation time, MW power, and volume of DES. Under the optimized conditions of 20 mL DES volume, 260 W MW power, and 3 min MW time, a significant increase in the carbonyl index and PET percentage weight loss was observed. The combined MW-assisted DES depolymerization and enzymatic hydrolysis of the treated PET residue using LCC variant ICCG resulted in a total monomer conversion of ≈16% (*w/w*) in the form of terephthalic acid, mono-(2-hydroxyethyl) terephthalate, and bis-(2-hydroxyethyl) terephthalate. Such high monomer conversion in comparison to enzymatically hydrolyzed virgin PET (1.56% (*w/w*)) could be attributed to the recognized depolymerization effect of the selected DES MW treatment process. Hence, MW-assisted DES technology proved itself as an efficient process for boosting the biodepolymerization of PET in an ultrafast and eco-friendly manner.

Keywords: enzymatic hydrolysis; deep eutectic solvents; polyethylene terephthalate; Box-Behnken design; microwave depolymerization

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1. Introduction

All-green routes to continuous circular material and commodity production, unmaking and remaking in a manner analogous to nature's many resource cycles, remain largely elusive for plastics [1]. Polyethylene terephthalate (PET) plastic value chain is a pertinent example of many current linear mine, use, and dispose economic processes. PET is highly recalcitrant and widely used in the manufacturing of packaging materials, beverage bottles, and synthetic fibers due to its high mechanical and thermal properties, nontoxicity, and excellent transparency [2]. The unabated increase in the demand for PET production is a

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ORIGINAL ARTICLE

Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation

Muhammad Azeem [a], **Margaret Brennan Fournet** [a], **Olivia A. Attallah** [a,b,*]

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KEYWORDS

Depolymerization;
Microwave;
Deep eutectic solvent;
Polyethylene terephthalate;
Monomers;
Recycling

Abstract Effective and efficient hybrid depolymerisation technologies are emerging as high potential sustainable routes with considerable benefits over conventional recycling methods for the achievement of circular economies for plastics. Herein, combined green and fast glycolysis-hydrolysis depolymerization of polyethylene terephthalate (PET) was carried out under microwave irradiation (MW) with excellent efficiencies. In MW assisted glycolysis of PET, the catalytic activity of two deep eutectic solvents (DES) based on (choline chloride-urea (DES 1)) and (choline chloride-thiourea (DES 2)) was evaluated and compared. Optimised glycolysis conditions were determined using Box Behnken Design (BBD) to attain maximum weight loss of PET, low crystallinity and increased carbonyl index of residual PET. DES volume of 4 mL, 5.5–6 mL of ethylene glycol, and 0.5 min MW irradiation time resulted in a prominent rise in PET weight loss and carbonyl index of residual PET. DES 2 showed an improved catalytic activity than that of DES 1 which is associated to its stronger interaction with EG and PET polymer chains during the course of the reaction. Residual PET obtained post glycolysis reaction was further depolymerized using MW assisted hydrolysis in the presence of weakly basic Na_2CO_3 and EG. Within 3-minute, the proposed sequential depolymerization technologies facilitated ≈99% conversion of PET to terephthalic acid (TPA), monohydroxyethyl terephthalate (MHET), and bis (2-hydroxyethyl) terephthalate (BHET) monomers produced at a yield of 62.79–80.66%, 17.22–34.79% and 0.54–0.59% respec-

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ORIGINAL PAPER

All Green Microwave Assisted 99% Depolymerisation of Polyethylene Terephthalate into Value Added Products via Glycerol Pre-treatment and Hydrolysis Reaction

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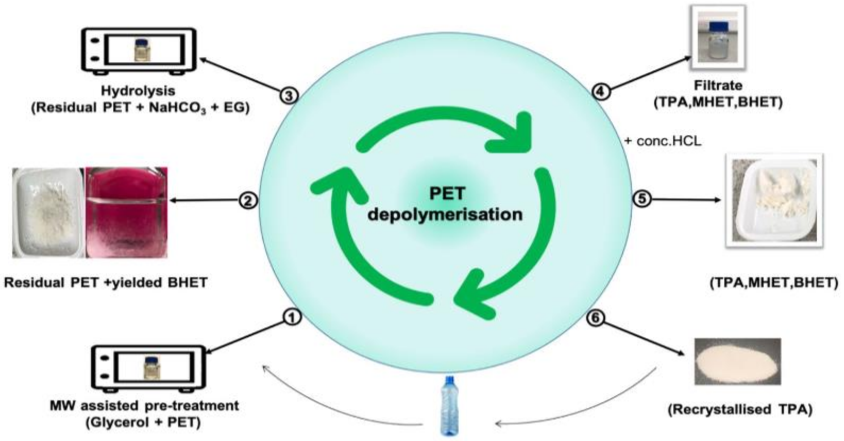
Abstract

Energy-efficient and fast depolymerisation technologies present as new sustainable and green recycling routes for achieving a circular economy for plastics. Herein, we present a highly efficient 2-step microwave-based (MW) degradation of polyethylene terephthalate (PET). Initially, a MW-assisted pre-treatment was evaluated using glycerol as a non-toxic reagent for the conversion of PET into a modified form that makes it easily depolymerised. Box Behnken Design was employed to determine the optimised pre-treatment conditions attaining maximum PET weight loss and favourable crystallinity and carbonyl indices for the pre-treated PET. Glycerol of 12 mL volume and 3 min of 182W MW irradiation resulted in 11% PET weight loss at onset temperature of degradation and gave rise to carbonyl index up to 4.22 and 33% crystallinity of pre-treated PET. MW assisted hydrolysis of the pre-treated PET was then performed in the presence of sodium bicarbonate and ethylene glycol as depolymerizing agents. Within 3 min, the proposed depolymerisation methodology provided 99.9% conversion of PET into 79.1% terephthalic acid (TPA), 17.6% monohydroxyethyl terephthalate (MHET), and 1.8% bis (2-hydroxyethyl) terephthalate (BHET). The obtained TPA was separated from the monomers mixtures and its purification was evaluated via different characterization techniques against a standard TPA. A purity of 95%, 82.4 APHA colour value, 645.3 mgKOH/g acid number and acceptable heavy metal content indicated that the purified TPA can be repolymerised as virgin PET.

Graphical Abstract



Keywords Depolymerisation · Polyethylene terephthalate · Microwave · Recycling · Monomers · Glycerol pre-treatment · Hydrolysis

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Extended author information available on the last page of the article

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Research Article

Color Stability Enhancement of Curcumin Bioplastic Films Using Natural Hybrid Fillers of Montmorillonite and Revalorized Cellulose

Jeovan A. Araujo,* Muhammad Azeem, Chaitra Venkatesh, Marija Mojicevic, Margaret Brennan Fournet, and Olivia A. Attallah*

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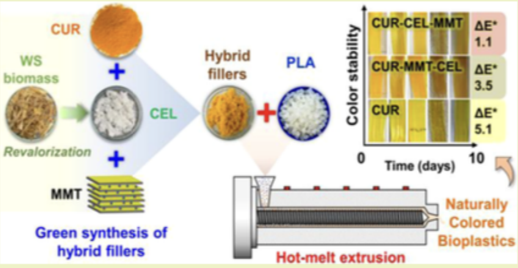

ABSTRACT: Naturally colored packaging systems with improved color stability are essential as alternatives to mainstay synthetic colored conventional plastics, which typically present high toxicity and environmental pollution challenges. Herein, we report a versatile all green fabrication process for colored bioplastic films. Curcumin (CUR), a model plant-based colorant, was incorporated with newly developed natural hybrid fillers of montmorillonite (MMT) and biomass waste-recovered cellulose (CEL) for improved color stability performance. The CUR-based hybrid fillers were compounded with polylactic acid (PLA) to fabricate sustainable, colored composite films via hot-melt extrusion. Fourier transform infrared (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) results indicated good compatibility between the filler counterparts. Macro- and microstructure analysis of the colored films confirmed the good dispersion of the natural hybrid fillers within the PLA matrix. No change was observed in the thermal properties of the colored films, while dynamic mechanical analysis (DMA) results demonstrated a moderate increase in the films' elastic modulus, from 870 to 970 MPa. The color entrapment efficiency of the hybrid filler-based films was evaluated through a study of CUR release in ethanol. A sustained CUR release profile reaching around 50% after 48 h was observed in the hybrid filler-based films in contrast to 80% in the PLA−CUR film. This was correlated with the significantly improved color stability of the PLA films containing the hybrid fillers under weathering conditions of UV irradiation, high temperature, and humidity. Over a period of 10 days, the CUR-CEL-MMT-based films had relatively consistent color stability, showing a color shift value (Δ*E**) of only 1.1 in comparison to 5.1 for the PLA film containing only CUR.

KEYWORDS: *natural colorants, biomass valorization, clay mineral, natural composites, renewable polymers, color stability*

INTRODUCTION

The development of active packaging materials for maintaining the quality and shelf life of food products has attracted considerable attention in the modern food industry. A number of studies have shown great potential in utilizing synthetic compounds to decelerate the oxidation of food, resulting in a longer shelf life of packaging products; however, color can migrate to food products and make packaging end applications questionable.[1] Instability of synthetic coloring additives in food packaging also restricts their large-scale application before reaching customers.[2] Thus, color stability is considered a major processing requirement for any acceptable packaging system.

In recent years, green, natural dyes have shown good potential as colorants for food packaging applications. This is due to their minimal color migration and efficient water vapor barrier characteristics.[3] Curcumin (CUR), a naturally occurring yellow-orange polyphenol derived from the turmeric plant (*Curcuma longa*), has been widely investigated for a range of biotechnological applications, including its use as a natural dye in the packaging industry.[4−7] However, CUR is sensitive to moisture, heat, and changes in pH. The main coloring components of CUR are relatively stable at acidic pH, but they rapidly degrade under neutral or basic pH conditions and have significant light instability in solutions.[8]

Some natural dyes show a deficiency of color stability which is greatly impacted by exposure conditions such as light, temperature, and humidity. Several studies have been performed to overcome the problems of the light instability of natural pigments. In a previous report, Park et al.[9] attempted to combine chitosan biopolymer and a low-temperature plasma pretreatment to improve the color stability of poly(ethylene terephthalate) fabric dyed with a natural colorant extract from *Caesalpinia sappan* L., a species of flowering tree in the legume

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Research Article

Fast, High Monomer Yield from Post-consumer Polyethylene Terephthalate via Combined Microwave and Deep Eutectic Solvent Hydrolytic Depolymerization

Olivia A. Attallah,* Arno Janssens, Muhammad Azeem, and Margaret Brennan Fournet

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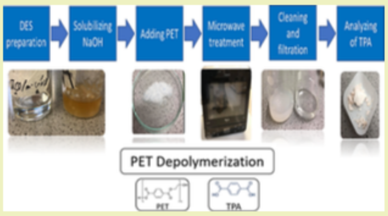

ABSTRACT: Efficient low carbon foot print methods are critical to achieving circularity for the dominant post-consumer plastic polyethylene terephthalate (PET). In a strong sustainability advancement over previous technologies, depolymerization of waste PET bottles was performed using a dissolution/degradation approach optimized in accordance with polymer mechanical parameter inter-relationships. A dual functioning deep eutectic solvent (DES), comprising *m*-cresol and choline chloride, served as both the solubilizing and catalyzing agent for alkaline hydrolysis of PET using high energy efficiency microwave (MW) irradiation. The PET depolymerization process was optimized using Box−Behnken design while tailoring the DES volume, concentration of the depolymerizing agent (sodium hydroxide), and MW irradiation time as independent variables. The percentage PET weight loss as high as 84% was obtained using 15 mL of DES containing 10% (w/v) NaOH under 90 s MW irradiation. Simple, cost-effective purification steps were afforded by the DES's advantageous physicochemical nature and were implemented to provide the terephthalic acid (TPA) monomer with acceptable yield. Validation of the PET depolymerization and identification of obtained monomers were carried out by a range of characterization techniques including FTIR, NMR, DSC, and HPLC. Post-consumer PET bottle depolymerization was evaluated, and a 91.55% TPA monomer yield ready for repolymerization as virgin PET demonstrates the high potential market application of this low energy, low carbon solvent virgin to virgin approach to PET circularity.

KEYWORDS: *polyethylene terephthalate, deep eutectic solvent, hydrolysis, dissolution, microwave irradiation, recycling*

■ INTRODUCTION

New sustainable scientific techniques using selected combination processes have the potential to provide viable solutions to the pressing global plastic challenge. The ubiquitous thermoplastic polymer polyethylene terephthalate (PET) has considerable chemical resistance, translucency, and impermeability to water and gases such as CO_2. Such properties render PET as one of the most widely utilized polymers nowadays in an extensive range of products, from beverage bottles to textiles.[1] In 2019, the overall world production of polyethylene terephthalate was about 30.47 million tons and is rising.[2]

Chemical resistance and durability of plastics in general, although highly advantageous for market applications, render PET and the majority of its petroleum counterparts largely impervious to nature's biodegradation processes. While slowly disintegrating, harmful microplastics and chemicals, which are hazardous to plants, animals, and the surrounding environment, are produced.[3] Aiming to minimize the pollution problems caused by the overproduction and incineration of plastics, plastic recycling, primarily using chemical and mechanical processes, is the current mainstay adopted approach. In mechanical recycling, the plastic is cleaned and shredded into pellets to be reprocessed, either in combination with virgin PET or downcycled into lower-grade products. In chemical recycling, the plastic is chemically disassembled into its monomers typically using harsh conditions such as solvents and prolonged high temperature reactions.[4] PET being a polyester has ester groups that can be cleaved by various techniques including hydrolysis,[5−7] glycolysis,[8,9] methanolysis,[10,11] and aminolysis.[12,13] Nevertheless, despite the ability of these reactions to produce monomers from which PET is produced, they suffer from slow reaction rates, high solvent volume requirements, catalyst deactivation, product purification complexities, and high energy and large infrastructure demands, making them expensive and strongly impeding industrial implementation.[4,14] The development of new sustainable and cost-effective methods for chemical recycling of PET that allow fast, highly efficient PET depolymerization with low energy consumption and simple purification steps is

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ORIGINAL PAPER

Rendering Bio-inert Low-Density Polyethylene Amenable for Biodegradation via Fast High Throughput Reactive Extrusion Assisted Oxidation

Pablo Ferrero[1] · Olivia A. Attallah[2,3] · Miguel Ángel Valera[1] · Ivana Aleksic[4] · Muhammad Azeem[2] · Jasmina Nikodinovic-Runic[4] · Margaret Brennan Fournet[2]

Accepted: 3 February 2022

Abstract

An energy-efficient high throughput pre-treatment of low-density polyethylene (LDPE) using a fast, reactive extrusion (REX) assisted oxidation technique followed by bacterial attachment as an indicator for bio-amenability was studied. Silicon dioxide (SiO_2) was selected as a model oxidizing and catalytic reagent with the REX process demonstrated to be effective both in the presence and absence of the catalyst. Optimized 5-min duration pre-treatment conditions were determined using Box–Behnken design (BBD) with respect to screws speed, operating temperature, and concentration of SiO_2. The crystallinity index, carbonyl index and weight loss (%) of LDPE were used as the studied responses for BDD. FTIR and DSC spectra of the residual LDPE obtained after pre-treatment with the REX assisted oxidation technique showed a significant increase in residual LDPE carbonyl index from 0 to 1.04 and a decrease of LDPE crystallinity index from 29 to 18%. Up to fivefold molecular weight reductions were also demonstrated using gel permeation chromatography. Optimum LDPE pre-treatment with a duration of 5 min was obtained at low screw speed (50 rpm), operating temperature of 380–390 °C and variable concentration of SiO_2 (0 and 2% (w/w)) indicating that effective pre-treatment can occur under noncatalytic and catalysed conditions. Biofilms were successfully formed on pre-treated LDPE samples after 14 days of incubation. Furthermore, the technique proposed in this study is expected to provide a high throughput approach for pre-treatment of pervasive recalcitrant PE-based plastics to reduce their bio inertness.

Keywords Low-density polyethylene · Reactive extrusion · High throughput · Bio-adhesion · Biofilm · Box–Behnken design

Introduction

Plastics production has been in continuous growth since their discovery. To date, global plastic production has reached 368 million tons giving direct employment to more than 1.56 million people in Europe [1]. Their remarkable properties and high performances at low market prices mean that plastic materials are now commonplace across the globe. The pervading use of plastics and the absence of suitable treatments at the end of their life cycle continues to lead to damaging pollution of the natural environment. An important example of such consumption is plastic bags which are estimated to be in the range of 500 billion to 1 trillion plastic bags each year worldwide [2]. Most of these plastic bags are made from low-density polyethylene (LDPE); a polymer widely used in food packaging and agriculture applications. One of the main characteristics of LDPE is its inertness,

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Pablo Ferrero and Olivia A. Attallah have contributed equally to this work.

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polymers

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Review

Macro and Micro Routes to High Performance Bioplastics: Bioplastic Biodegradability and Mechanical and Barrier Properties

Olivia A. Attallah [1], Marija Mojicevic [1,*], Eduardo Lanzagorta Garcia [1], Muhammad Azeem [1], Yuanyuan Chen [1], Shumayl Asmawi [2] and Margaret Brenan Fournet [1]

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Abstract: On a score sheet for plastics, bioplastics have a medium score for combined mechanical performance and a high score for biodegradability with respect to counterpart petroleum-based plastics. Analysis quickly confirms that endeavours to increase the mechanical performance score for bioplastics would be far more achievable than delivering adequate biodegradability for the recalcitrant plastics, while preserving their impressive mechanical performances. Key architectural features of both bioplastics and petroleum-based plastics, namely, molecular weight (M_w) and crystallinity, which underpin mechanical performance, typically have an inversely dependent relationship with biodegradability. In the case of bioplastics, both macro and micro strategies with dual positive correlation on mechanical and biodegradability performance, are available to address this dilemma. Regarding the macro approach, processing using selected fillers, plasticisers and compatibilisers have been shown to enhance both targeted mechanical properties and biodegradability within bioplastics. Whereas, regarding the micro approach, a whole host of bio and chemical synthetic routes are uniquely available, to produce improved bioplastics. In this review, the main characteristics of bioplastics in terms of mechanical and barrier performances, as well as biodegradability, have been assessed—identifying both macro and micro routes promoting favourable bioplastics' production, processability and performance.

Keywords: biomaterials; biodegradation; bioplastics; mechanical performance; barrier performance; processability

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1. Introduction

Pervasive plastics are leaving an indelible imprint on our planet. As high performance and energy-saving materials, plastics are ubiquitous and central to socio-economic advancement. Current mainstay plastics are processed from fossil fuel resources, with production requirements expected to double over the next 20 years. After use, these recalcitrant plastics are contributing to waste stockpiles and alarming pollution. Recycling technologies, which primarily include mechanical and thermochemical approaches, does not meet the efficiency levels required to safeguard the planet and adequately revalorise plastics as new products. The current linear economic model of resource mining, use and discarding, is now widely recognised as unsustainable. A circular approach, where resources are repurposed cyclically, akin to biological lifecycles, is essential in achieving a sustainable socio-economic ecosystem.

Nature readily operates elegant and efficient regenerative cycles for natural polymers and end of life bio-based materials. Such biodegradation and bio-regeneration processes

frontiers
in Bioengineering and Biotechnology

REVIEW
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Progressing Plastics Circularity: A Review of Mechano-Biocatalytic Approaches for Waste Plastic (Re)valorization

Efstratios Nikolaivits[1], Brana Pantelic[2], Muhammad Azeem[3], George Taxeidis[1], Ramesh Babu[4], Evangelos Topakas[1], Margaret Brennan Fournet[3]* and Jasmina Nikodinovic-Runic[2]*

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Inspirational concepts, and the transfer of analogs from natural biology to science and engineering, has produced many excellent technologies to date, spanning vaccines to modern architectural feats. This review highlights that answers to the pressing global petroleum-based plastic waste challenges, can be found within the mechanics and mechanisms natural ecosystems. Here, a suite of technological and engineering approaches, which can be implemented to operate in tandem with nature's prescription for regenerative material circularity, is presented as a route to plastics sustainability. A number of mechanical/green chemical (pre)treatment methodologies, which simulate natural weathering and arthropodal dismantling activities are reviewed, including: mechanical milling, reactive extrusion, ultrasonic-, UV- and degradation using supercritical CO_2. Akin to natural mechanical degradation, the purpose of the pretreatments is to render the plastic materials more amenable to microbial and biocatalytic activities, to yield effective depolymerization and (re)valorization. While biotechnological based degradation and depolymerization of both recalcitrant and bioplastics are at a relatively early stage of development, the potential for acceleration and expedition of valuable output monomers and oligomers yields is considerable. To date a limited number of independent mechano-green chemical approaches and a considerable and growing number of standalone enzymatic and microbial degradation studies have been reported. A convergent strategy, one which forges mechano-green chemical treatments together with the enzymatic and microbial actions, is largely lacking at this time. An overview of the reported microbial and enzymatic degradations of petroleum-based synthetic polymer plastics, specifically: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), polyethylene terephthalate (PET), polyurethanes (PU) and polycaprolactone (PCL) and selected prevalent bio-based or bio-polymers [polylactic acid (PLA), polyhydroxyalkanoates (PHAs) and polybutylene succinate (PBS)], is detailed. The harvesting of depolymerization products to produce

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An assessment of the transparency of contemporary technology education research employing interview-based methodologies

Jeffrey Buckley[1,2] · **Latif Adams**[3] · **Ifeoluwapo Aribilola**[1] · **Iram Arshad**[1] · **Muhammad Azeem**[1] · **Lauryn Bracken**[3] · **Colette Breheny**[1] · **Ciara Buckley**[1] · **Ismael Chimello**[4] · **Alison Fagan**[3] · **Daniel P. Fitzpatrick**[3] · **Diana Garza Herrera**[1] · **Guilherme Daniel Gomes**[1] · **Shaun Grassick**[3] · **Elaine Halligan**[1] · **Amit Hirway**[1] · **Tomás Hyland**[1] · **Muhammad Babar Imtiaz**[1] · **Muhammad Bilal Khan**[1] · **Eduardo Lanzagorta Garcia**[1] · **Paul Lennon**[1,5] · **Eyman Manaf**[1] · **Jing Meng**[4] · **Mohd Sufino Zuhaily Mohd Sufian**[4,6] · **Adrielle Moraes**[1] · **Katja Magdalena Osterwald**[3] · **Anastasia Platonava**[4] · **Clodagh Reid**[1] · **Michèle Renard**[3] · **Laura G. Rodriguez-Barroso**[1] · **Bianca Simonassi-Paiva**[3] · **Maulshree Singh**[1] · **Tomasz Szank**[3] · **Mehwish Tahir**[1] · **Sowmya Vijayakumar**[1] · **Cormac Ward**[3] · **Xinyu Yan**[1,7] · **Ismin Zainol**[1] · **Lin Zhang**[1]

Accepted: 10 August 2021

Abstract
A high level of transparency in reported research is critical for several reasons, such as ensuring an acceptable level of trustworthiness and enabling replication. Transparency in qualitative research permits the identification of specific circumstances which are associated with findings and observations. Thus, transparency is important for the repeatability of original studies and for explorations of the transferability of original findings. There has been no investigation into levels of transparency in reported technology education research to date. With a position that increasing transparency would be beneficial, this article presents an analysis of levels of transparency in contemporary technology education research studies which employed interviews within their methodologies, and which were published within the *International Journal of Technology and Design Education* and *Design and Technology Education: An International Journal* ($n=38$). The results indicate room for improvement, especially in terms of documenting researcher positionality, determinations of data saturation, and how power imbalances were managed. A discussion is presented on why it is important to improve levels of transparency in reported studies, and a guide on areas to make transparent is presented for qualitative and quantitative research.

Keywords Replicability · Transparency · Trustworthiness · Repeatability · Reporting practices · Qualitative research · Technology education research

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Extended author information available on the last page of the article

Springer

Appendix B Conference Proceedings

chemistry proceedings

MDPI

Abstract

Enhanced Biodegradation of Polyethylene Terephthalate (PET) via Microwave-Assisted Green Bio-Based Deep Eutectic Solvent Pre-Treatment Technique †

Muhammad Azeem *, Olivia Adly Attallah and Margaret Brennan Fournet

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† Presented at the 2nd International Electronic Conference on Catalysis Sciences—A Celebration of Catalysts 10th Anniversary, 15–30 October 2021; Available online: https://eccs2021.sciforum.net/ (accessed on 21 June 2021).

Abstract: Most plastic degradation methods are currently inefficient and are limited by processing difficulties, quality loss, and diminished value. This research focuses on the development of novel mechano-chemical disintegration processes for the breakdown of waste plastics. The outputs will be biocatalyzed and used as building blocks for new polymers or other bioproducts. For the purpose of this research, microwave pre-treatment technology was used. Microwave technology is an ideal pre-treatment process for the degradation of plastics due to its lower treatment times under lower energy inputs. In the previous work, extensive research has been carried out utilizing different solvents and catalysts to develop efficient degradation mechanisms under microwave irradiations. A new class of ionic liquids (deep eutectic solvents) were used as catalysts to make a suspension with poly(ethylene terephthalate) (PET) and develop an alcoholysis reaction. Certain degradation parameters like crystallinity index, weight loss, and carbonyl index were depicted using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR) characterization techniques. Furthermore, enhanced enzymatic degradation using LCC variant ICCG proved that microwave technology is an efficient process for the alcoholysis reaction and degradation of PET under mild conditions into its monomers.

Keywords: poly(ethylene terephthalate); chemical recycling; enzymatic degradation; alcoholysis; deep eutectic solvents; sustainability

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Citation: Azeem, M.; Attallah, O.A.; Fournet, M.B. Enhanced Biodegradation of Polyethylene Terephthalate (PET) via Microwave-Assisted Green Bio-Based Deep Eutectic Solvent Pre-Treatment Technique. *Chem. Proc.* **2022**, *6*, 9. https://doi.org/10.3390/ECCS2021-11181

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chemistry proceedings

MDPI

Abstract

Ultrafast, Optimized Hydrolytic Depolymerization of Polyethylene Terephthalate Using a Dissolution/Degradation Approach †

Olivia A. Attallah [1,2,*], Arno Janssens [3], Muhammad Azeem [1] and Margaret Brennan Fournet [1]

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† Presented at the 2nd International Electronic Conference on Catalysis Sciences—A Celebration of Catalysts 10th Anniversary, 15–30 October 2021; Available online: https://sciforum.net/event/ECCS2021.

Abstract: Directed thermo-mechano-chemical-irradiative methodologies that can permeate significant plastic chemical resistance are central to achieving circularity in the life cycles of plastics. Here, a novel combined deep eutectic solvent (DES) microwave irradiation technique for fast, high-efficiency, high-yield polyethylene terephthalate (PET) hydrolytic depolymerization with high amenability for sustainable industrial scalability is presented. In this work, depolymerization of PET was performed using a dissolution/degradation approach. A dual-functioning DES served as the solubilizing and catalyzing agent for PET alkaline hydrolysis. Microwave (MW) irradiation was utilized for facilitating the depolymerization process with high energy efficiency. The PET depolymerization process was optimized using Box–Behnken design while studying the volume of DES, concentration of depolymerizing agent and MW irradiation time as independent variables. A percentage weight loss of PET reaching 84% was obtained in 90 s of MW irradiation. Various characterization techniques such as FTIR, DSC and HPLC validated the depolymerization of PET and obtained monomers (mainly terephthalic acid (TPA)). Finally, a postconsumer PET sample was also evaluated to prove that the developed dissolution/degradation approach could have practical application in market. Post analysis, the insoluble matter content was calculated to be 3.70% and the yield of pure TPA was 91.54%.

Keywords: polyethylene terephthalate; deep eutectic solvent; hydrolysis; dissolution; microwave irradiation; recycling

check for updates

Citation: Attallah, O.A.; Janssens, A.; Azeem, M.; Fournet, M.B. Ultrafast, Optimized Hydrolytic Depolymerization of Polyethylene Terephthalate Using a Dissolution/Degradation Approach. *Chem. Proc.* **2022**, *6*, 7. https://doi.org/10.3390/ECCS2021-11111

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Author Contributions: O.A.A. Conceptualization, Data curation, Investigation, Writing and reviewing original draft; A.J. practical experimenting; Writing original draft; M.A. Analysis, Data curation; M.B.F. Supervision, Validation, Writing original draft. All authors have read and agreed to the published version of the manuscript.

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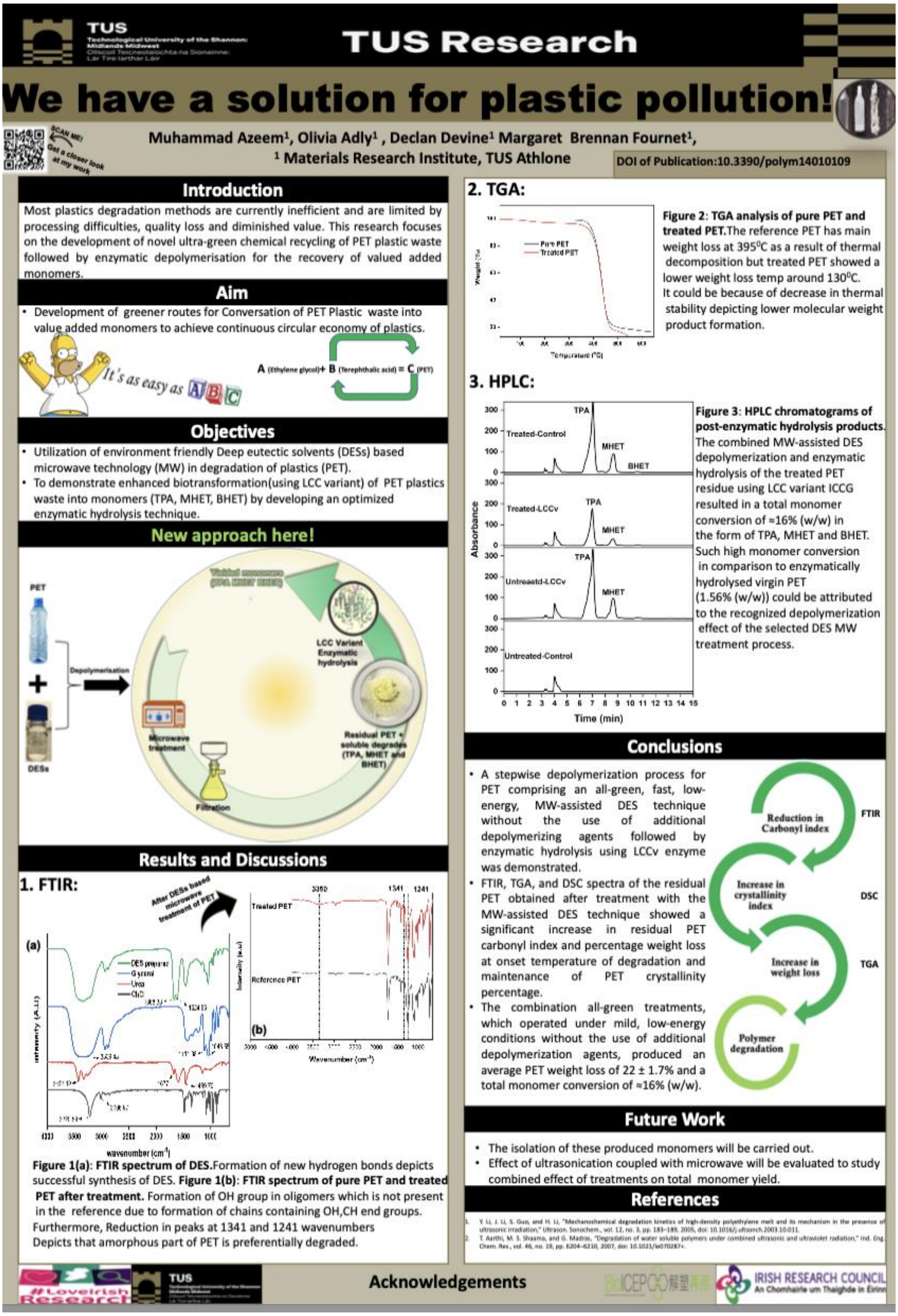
Appendix C Conference Posters



TUS Research

We have a solution for plastic pollution!

Muhammad Azeem[1], Olivia Adly[1] , Declan Devine[1] Margaret Brennan Fournet[1],
[1] Materials Research Institute, TUS Athlone

DOI of Publication:10.3390/polym14010109

Introduction

Most plastics degradation methods are currently inefficient and are limited by processing difficulties, quality loss and diminished value. This research focuses on the development of novel ultra-green chemical recycling of PET plastic waste followed by enzymatic depolymerisation for the recovery of valued added monomers.

Aim

- Development of greener routes for Conversation of PET Plastic waste into value added monomers to achieve continuous circular economy of plastics.

Objectives

- Utilization of environment friendly Deep eutectic solvents (DESs) based microwave technology (MW) in degradation of plastics (PET).
- To demonstrate enhanced biotransformation(using LCC variant) of PET plastics waste into monomers (TPA, MHET, BHET) by developing an optimized enzymatic hydrolysis technique.

New approach here!

Results and Discussions

1. FTIR:

Figure 1(a): FTIR spectrum of DES. Formation of new hydrogen bonds depicts successful synthesis of DES. **Figure 1(b): FTIR spectrum of pure PET and treated PET after treatment.** Formation of OH group in oligomers which is not present in the reference due to formation of chains containing OH,CH end groups. Furthermore, Reduction in peaks at 1341 and 1241 wavenumbers Depicts that amorphous part of PET is preferentially degraded.

2. TGA:

Figure 2: TGA analysis of pure PET and treated PET. The reference PET has main weight loss at 395^{0}C as a result of thermal decomposition but treated PET showed a lower weight loss temp around 130^{0}C. It could be because of decrease in thermal stability depicting lower molecular weight product formation.

3. HPLC:

Figure 3: HPLC chromatograms of post-enzymatic hydrolysis products. The combined MW-assisted DES depolymerization and enzymatic hydrolysis of the treated PET residue using LCC variant ICCG resulted in a total monomer conversion of ≈16% (w/w) in the form of TPA, MHET and BHET. Such high monomer conversion in comparison to enzymatically hydrolysed virgin PET (1.56% (w/w)) could be attributed to the recognized depolymerization effect of the selected DES MW treatment process.

Conclusions

- A stepwise depolymerization process for PET comprising an all-green, fast, low-energy, MW-assisted DES technique without the use of additional depolymerizing agents followed by enzymatic hydrolysis using LCCv enzyme was demonstrated.
- FTIR, TGA, and DSC spectra of the residual PET obtained after treatment with the MW-assisted DES technique showed a significant increase in residual PET carbonyl index and percentage weight loss at onset temperature of degradation and maintenance of PET crystallinity percentage.
- The combination all-green treatments, which operated under mild, low-energy conditions without the use of additional depolymerization agents, produced an average PET weight loss of 22 ± 1.7% and a total monomer conversion of ≈16% (w/w).

Future Work

- The isolation of these produced monomers will be carried out.
- Effect of ultrasonication coupled with microwave will be evaluated to study combined effect of treatments on total monomer yield.

References

1. Y. Li, J. Li, S. Guo, and H. Li, "Mechanochemical degradation kinetics of high-density polyethylene melt and its mechanism in the presence of ultrasonic irradiation," Ultrason. Sonochem., vol. 12, no. 3, pp. 183–189, 2005, doi: 10.1016/j.ultsonch.2003.10.011.
2. T. Aarthi, M. S. Shaama, and G. Madras, "Degradation of water soluble polymers under combined ultrasonic and ultraviolet radiation," Ind. Eng. Chem. Res., vol. 46, no. 19, pp. 6204–6210, 2007, doi: 10.1021/ie070287+.

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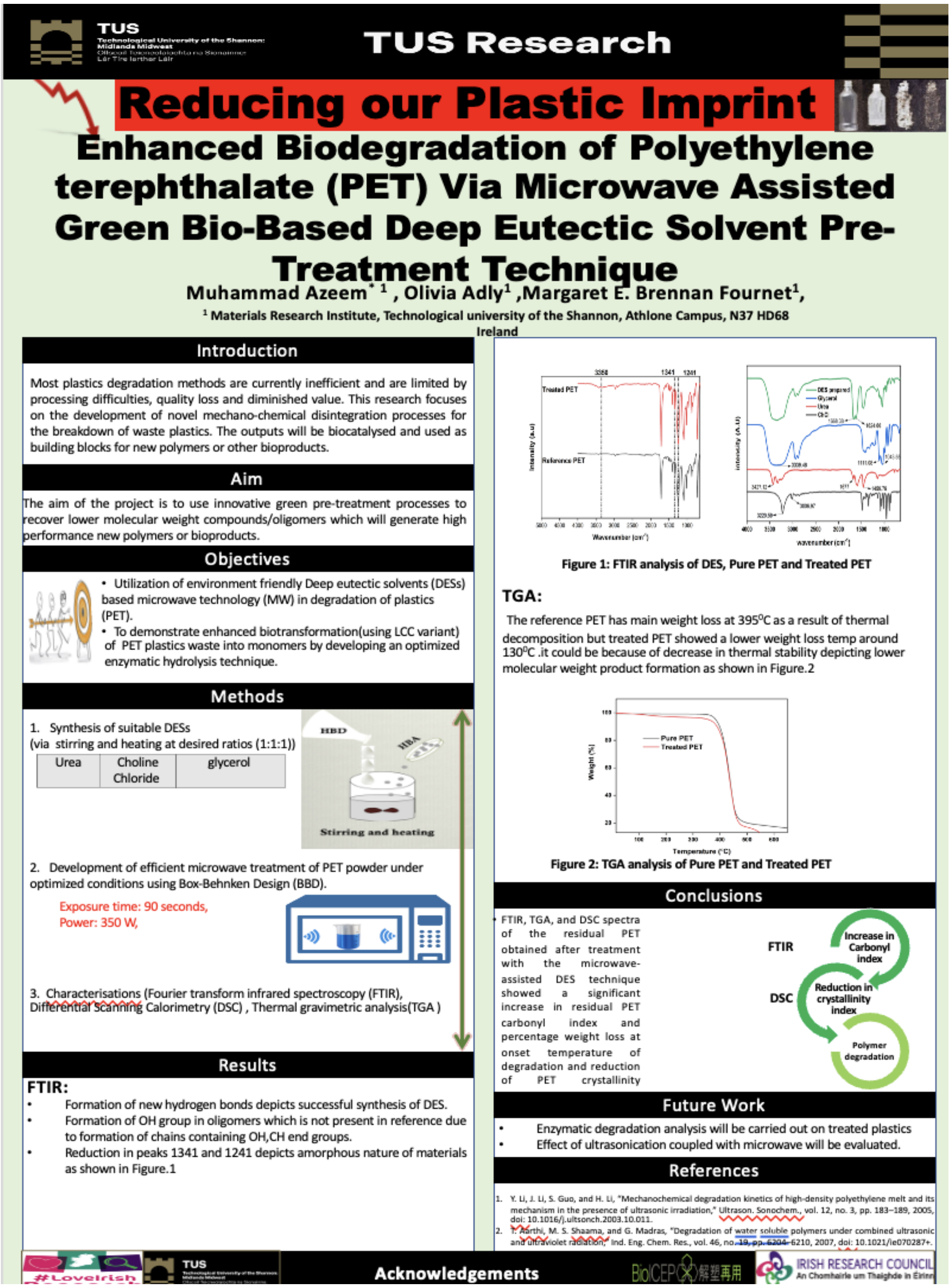

TUS Research

Reducing our Plastic Imprint

Enhanced Biodegradation of Polyethylene terephthalate (PET) Via Microwave Assisted Green Bio-Based Deep Eutectic Solvent Pre-Treatment Technique

Muhammad Azeem*[1], Olivia Adly[1], Margaret E. Brennan Fournet[1],

[1] Materials Research Institute, Technological university of the Shannon, Athlone Campus, N37 HD68 Ireland

Introduction

Most plastics degradation methods are currently inefficient and are limited by processing difficulties, quality loss and diminished value. This research focuses on the development of novel mechano-chemical disintegration processes for the breakdown of waste plastics. The outputs will be biocatalysed and used as building blocks for new polymers or other bioproducts.

Aim

The aim of the project is to use innovative green pre-treatment processes to recover lower molecular weight compounds/oligomers which will generate high performance new polymers or bioproducts.

Objectives

- Utilization of environment friendly Deep eutectic solvents (DESs) based microwave technology (MW) in degradation of plastics (PET).
- To demonstrate enhanced biotransformation(using LCC variant) of PET plastics waste into monomers by developing an optimized enzymatic hydrolysis technique.

Methods

1. Synthesis of suitable DESs (via stirring and heating at desired ratios (1:1:1))

Urea	Choline Chloride	glycerol

2. Development of efficient microwave treatment of PET powder under optimized conditions using Box-Behnken Design (BBD).

Exposure time: 90 seconds,
Power: 350 W,

3. Characterisations (Fourier transform infrared spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) , Thermal gravimetric analysis(TGA)

Results

FTIR:

- Formation of new hydrogen bonds depicts successful synthesis of DES.
- Formation of OH group in oligomers which is not present in reference due to formation of chains containing OH,CH end groups.
- Reduction in peaks 1341 and 1241 depicts amorphous nature of materials as shown in Figure.1

Figure 1: FTIR analysis of DES, Pure PET and Treated PET

TGA:

The reference PET has main weight loss at 395⁰C as a result of thermal decomposition but treated PET showed a lower weight loss temp around 130⁰C .it could be because of decrease in thermal stability depicting lower molecular weight product formation as shown in Figure.2

Figure 2: TGA analysis of Pure PET and Treated PET

Conclusions

- FTIR, TGA, and DSC spectra of the residual PET obtained after treatment with the microwave-assisted DES technique showed a significant increase in residual PET carbonyl index and percentage weight loss at onset temperature of degradation and reduction of PET crystallinity

FTIR
Increase in Carbonyl index
DSC
Reduction in crystallinity index
Polymer degradation

Future Work

- Enzymatic degradation analysis will be carried out on treated plastics
- Effect of ultrasonication coupled with microwave will be evaluated.

References

1. Y. Li, J. Li, S. Guo, and H. Li, "Mechanochemical degradation kinetics of high-density polyethylene melt and its mechanism in the presence of ultrasonic irradiation," Ultrason. Sonochem., vol. 12, no. 3, pp. 183–189, 2005, doi: 10.1016/j.ultsonch.2003.10.011.
2. T. Aarthi, M. S. Shaama, and G. Madras, "Degradation of water soluble polymers under combined ultrasonic and ultraviolet radiation," Ind. Eng. Chem. Res., vol. 46, no. 19, pp. 6204–6210, 2007, doi: 10.1021/ie070287+.

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AIT Research

Reducing our Plastic Imprint

Pre-Treatment Processes Promoting waste plastic bio-degradation and Upcycling

Supervisor: Dr. Margaret Brennan Fournet **Co-Supervisor**: Dr. Patrick Murray (LIT)

Most plastics degradation methods are currently inefficient and are limited by processing difficulties, quality loss and diminished value. This research focuses on the development of novel mechano-chemical disintegration processes for the breakdown of waste plastics. The outputs will be biocatalysed and used as building blocks for new polymers or other bioproducts.

Approach

For the purpose of this research, sonic green chemical technology will be used. Polymers undergo degradation when they are subjected to ultrasound irradiation of high intensity due to cavitation phenomenona.

Expected Results

Ultrasonic wave shearing forces of sufficient magnitude can cause polymer bond ruptures. This can lead to carbonyl and vinyl group formation supporting enzymatic digestion and facilitating fermentation processes in next stages of degradation and revalorisation.

Research Methodology

Synthesis of suitable DETSs
- Via stirring and heating at desired ratios

Depolymerisation
- Via Ultrasonication, UV exposure, Magnetic field,ScCO$_2$

Characterisations
- (DSC, Raman, FTIR, Tensile testing, TGA, Rheology)

References

1. Y. Li, J. Li, S. Guo, and H. Li, "Mechanochemical degradation kinetics of high-density polyethylene melt and its mechanism in the presence of ultrasonic irradiation," Ultrason. Sonochem., vol. 12, no. 3, pp. 183–189, 2005, doi: 10.1016/j.ultsonch.2003.10.011.
2. T. Aarthi, M. S. Shaama, and G. Madras, "Degradation of water soluble polymers under combined ultrasonic and ultraviolet radiation," Ind. Eng. Chem. Res., vol. 46, no. 19, pp. 6204–6210, 2007, doi: 10.1021/ie070287+.
3. W. Y. Guo and B. Peng, "Ultrasonic degradation studies and its effect on thermal properties of polypropylene," Polym. - Plast. Technol. Eng., vol. 46, no. 9, pp. 879–884, 2007, doi: 10.1080/03602550701280224.

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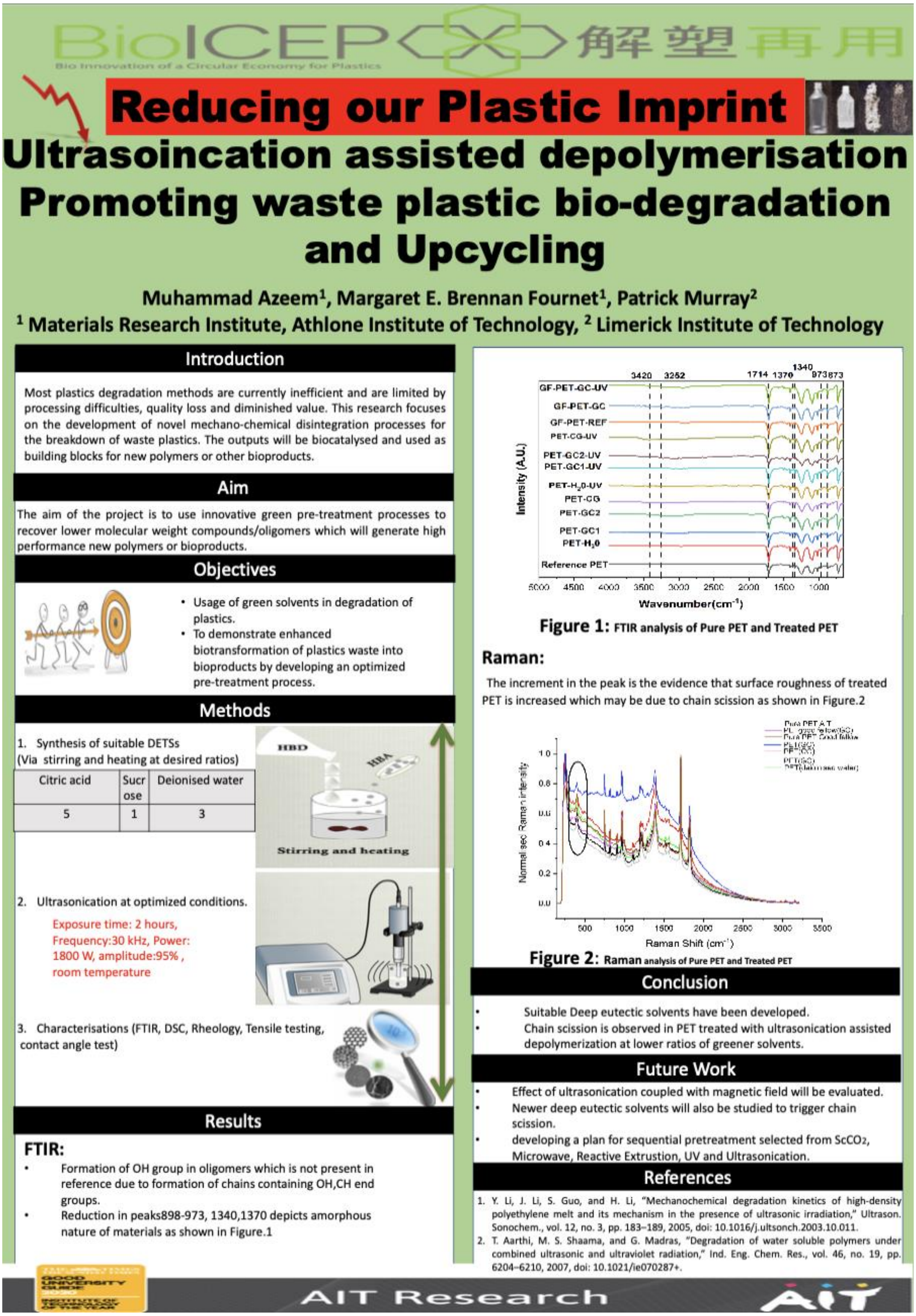

BioICEP 解塑再用
Bio Innovation of a Circular Economy for Plastics

Reducing our Plastic Imprint

Ultrasoincation assisted depolymerisation Promoting waste plastic bio-degradation and Upcycling

Muhammad Azeem[1], Margaret E. Brennan Fournet[1], Patrick Murray[2]
[1] Materials Research Institute, Athlone Institute of Technology, [2] Limerick Institute of Technology

Introduction

Most plastics degradation methods are currently inefficient and are limited by processing difficulties, quality loss and diminished value. This research focuses on the development of novel mechano-chemical disintegration processes for the breakdown of waste plastics. The outputs will be biocatalysed and used as building blocks for new polymers or other bioproducts.

Aim

The aim of the project is to use innovative green pre-treatment processes to recover lower molecular weight compounds/oligomers which will generate high performance new polymers or bioproducts.

Objectives

- Usage of green solvents in degradation of plastics.
- To demonstrate enhanced biotransformation of plastics waste into bioproducts by developing an optimized pre-treatment process.

Methods

1. Synthesis of suitable DETSs
(Via stirring and heating at desired ratios)

Citric acid	Sucrose	Deionised water
5	1	3

2. Ultrasonication at optimized conditions.

Exposure time: 2 hours,
Frequency:30 kHz, Power:
1800 W, amplitude:95% ,
room temperature

3. Characterisations (FTIR, DSC, Rheology, Tensile testing, contact angle test)

Results

FTIR:

- Formation of OH group in oligomers which is not present in reference due to formation of chains containing OH,CH end groups.
- Reduction in peaks898-973, 1340,1370 depicts amorphous nature of materials as shown in Figure.1

Figure 1: FTIR analysis of Pure PET and Treated PET

Raman:

The increment in the peak is the evidence that surface roughness of treated PET is increased which may be due to chain scission as shown in Figure.2

Figure 2: Raman analysis of Pure PET and Treated PET

Conclusion

- Suitable Deep eutectic solvents have been developed.
- Chain scission is observed in PET treated with ultrasonication assisted depolymerization at lower ratios of greener solvents.

Future Work

- Effect of ultrasonication coupled with magnetic field will be evaluated.
- Newer deep eutectic solvents will also be studied to trigger chain scission.
- developing a plan for sequential pretreatment selected from $ScCO_2$, Microwave, Reactive Extrustion, UV and Ultrasonication.

References

1. Y. Li, J. Li, S. Guo, and H. Li, "Mechanochemical degradation kinetics of high-density polyethylene melt and its mechanism in the presence of ultrasonic irradiation," Ultrason. Sonochem., vol. 12, no. 3, pp. 183–189, 2005, doi: 10.1016/j.ultsonch.2003.10.011.
2. T. Aarthi, M. S. Shaama, and G. Madras, "Degradation of water soluble polymers under combined ultrasonic and ultraviolet radiation," Ind. Eng. Chem. Res., vol. 46, no. 19, pp. 6204–6210, 2007, doi: 10.1021/ie070287+.

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In a sustainable way, we can cut the plastic away!

SCAN ME!
Get a closer look at my work

Muhammad Azeem[1], Olivia Adly[1] , Declan Devine[1] Margaret Brennan Fournet[1],
[1] PRISM Research Institute, TUS Athlone

DOI of Publication:10.1016/j.arabjc.2022.103903

❶ Introduction

The production of PET is doubled resulting in a growth rate of 8% per annum and the elevation of plastic waste up to 8 million tons every year. Therefore it is imperative to develop sustainable and scalable plastics recycling methodologies to reduce plastic accumulations. This research focuses on the development of novel ultra-green chemical recycling of PET plastic waste for the recovery of valued added monomers that can be used again to repolymerise virgin PET.

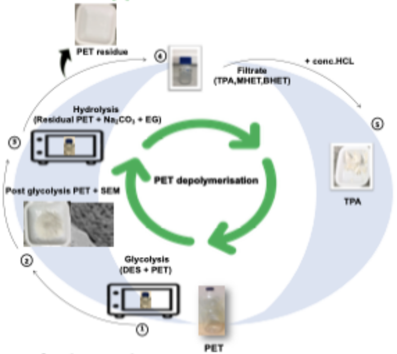
❷ Aim

Development of greener routes for Conversation of PET Plastic waste into value added monomers to achieve continuous circular economy of plastics.

❸ Objectives

- Utilisation of environment friendly Deep eutectic solvents (DESs) based microwave technology (MW) in sequential glycolysis hydrolysis depolyemrisation of plastics (PET).
- To demonstrate enhanced catalytic activities of PET plastics waste into monomers (TPA, MHET, BHET) by developing an optimised ultra green and sustainable glycolysis-hydrolysis technique.

❹ Here is the New approach!



❺ Results and Discussions

➢ FTIR Spectra:

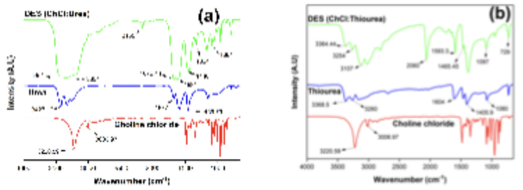


Figure 1(a): **FTIR spectrum of DES 1** (Choline chloride: urea). **Figure 1(b)**: **FTIR spectrum of DES 2** (Choline chloride: thiourea). The FTIR analysis of the prepared DESs confirmed the presence of the expected functional groups together with some shifting in the peaks' frequency which indicated the new characteristics of the formed DESs.

➢ Optimised Glycolysis Reaction:

Box Behnken Design was used to get optimum MW assisted glycolysis reaction conditions(4ml DES volume, 5.5-6ml EG, and 0.5 min MW irradiation time) at a prominent rise in weight loss and carbonyl index (Figure 2).

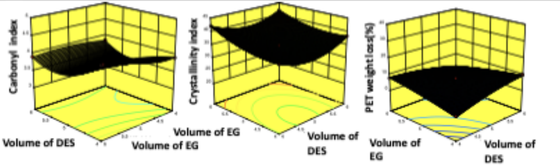


Figure 2: **3D plots** of the effect of the interaction of DES volume (ml) and EG volume (ml) on carbonyl index, crystallinity index, and weight loss of PET (%) for MW assisted glycolysis of PET using DES 2.

➢ Hydrolytic depolymerisation of post glycolysis PET:

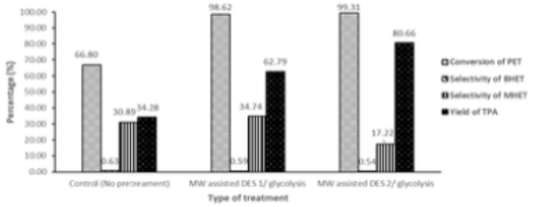
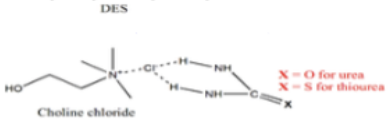


Figure 3: **The effect of type of treatment** on the conversion of PET and the selectivity of BHET, MHET and the yield of TPA . DES 2 showed better results as compared to DES 1 which could be related to thiourea providing better interactions with PET polymer chains.

➢ Glycolysis-hydrolysis Reaction Mechanism:



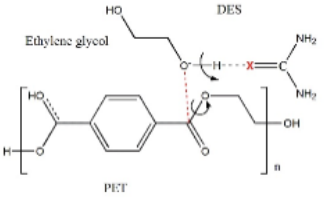


Figure 4: Schematic diagram for the interactions of DESs with EG and PET. The H-bond action between EG and the urea (C=O) and thiourea (C=S) of DES 1 and 2 catalysts is expected to change the charge density of the hydroxyl (OH) group in EG.

❻ Conclusions

- A hybrid depolymerization process for PET comprising a fast, green, low energy MW assisted glycolysis-hydrolysis was presented.
- The proposed hybrid technique achieved improved PET depolymerization with a total of ≈99% PET conversion under green, environmentally friendly operating conditions in only 3.5 min .Thus, the proposed technology seems advantageous over conventional techniques and have the potential for industrial scale up.

❼ Future Work

- Upscaling the process and purity of produced monomers.
- utilisation of produced TPA in repolymerisation with virgin PET.

❽ References

- Attallah OA, Azeem M, Nikolaivits E, Topakas E, Fournet MB. Progressing Ultragreen, Energy-Efficient Biobased Depolymerization of Poly(ethylene terephthalate) via Microwave-Assisted Green Deep Eutectic Solvent and Enzymatic Treatment. Polymers. 2022; 14(1):109. https://doi.org/10.3390/polym14010109

Acknowledgements

IRISH RESEARCH COUNCIL
An Chomhairle um Thaighde in Éirinn

Appendix D Certificates

Maynooth University
National University of Ireland Maynooth

Certificate of Competence

Muhammad Azeem

Has completed **GST10 - Innovation and Research Commercialisation**

Has gained competency in
Intellectual Property
Product Development and Marketing
Basic Legal Contracts and
Business Model Canvas Development

Dr Karen Griffin *Dr Paul Tyndall* *Mr Peter Conlon*

Maynooth University MaynoothWorks (December 2020)

SHORT
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CERTIFICATE OF PARTICIPATION

This is to certify that **Muhammad Azeem** has successfully completed the **Short Advanced Programme (SAP)** **Circular Design with Plastics**, from 28 November 2022 to 16 December 2022 jointly organised by the Polytechnic Institute of Cavado and Ave, Portugal, NHL Stenden University of Applied Sciences, the Netherlands, and Technological University of the Shannon, Ireland, within the scope of the **Regional University Network – European University,** having been awarded 2 ECTS credits.

11 January 2023

On behalf of all rectors/presidents of the alliance,

Assinado por : **RICARDO JOÃO FERREIRA SIMÕES**
Num. de Identificação: 10852572
Data: 2023.01.11 23:29:37+00'00'

Ricardo J. F. Simões, IPCA

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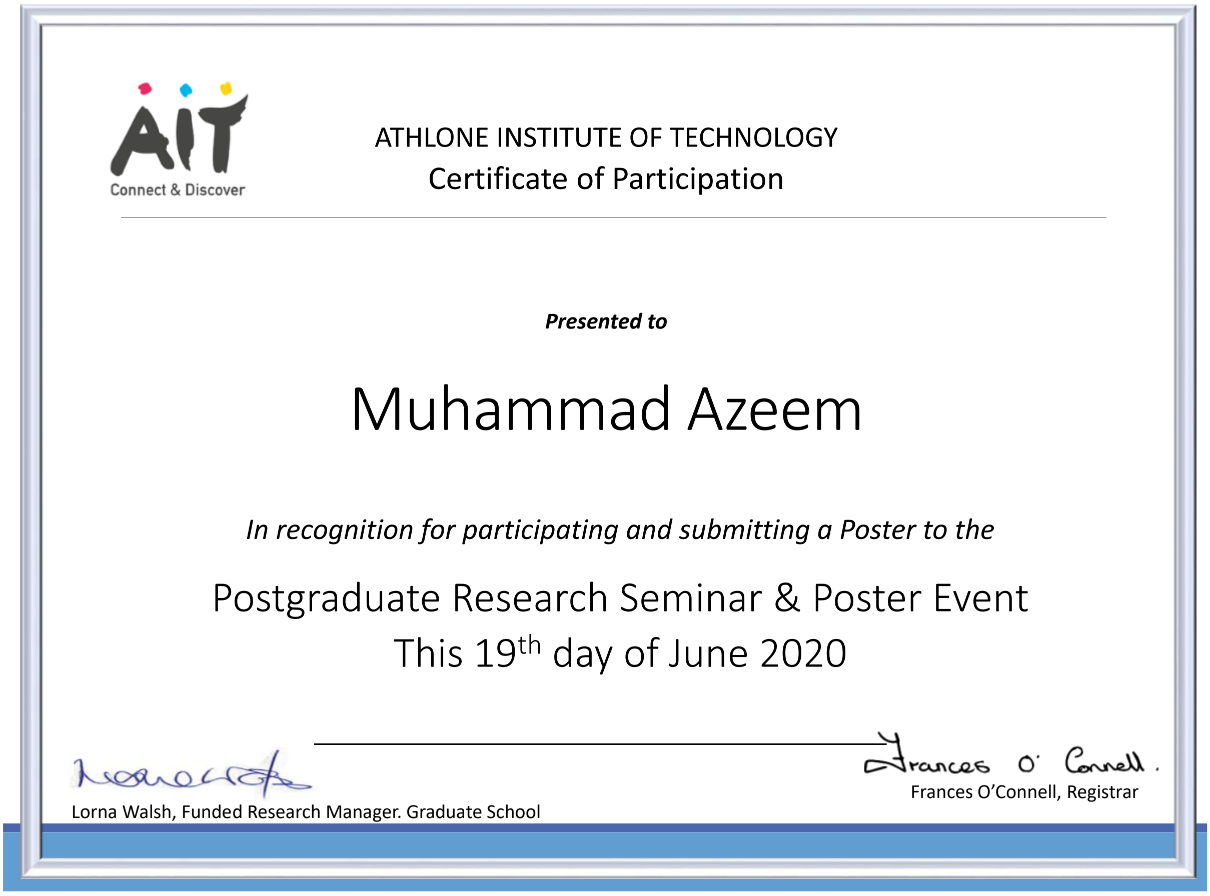

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Muhammad Azeem

In recognition for participating and submitting a Poster to the

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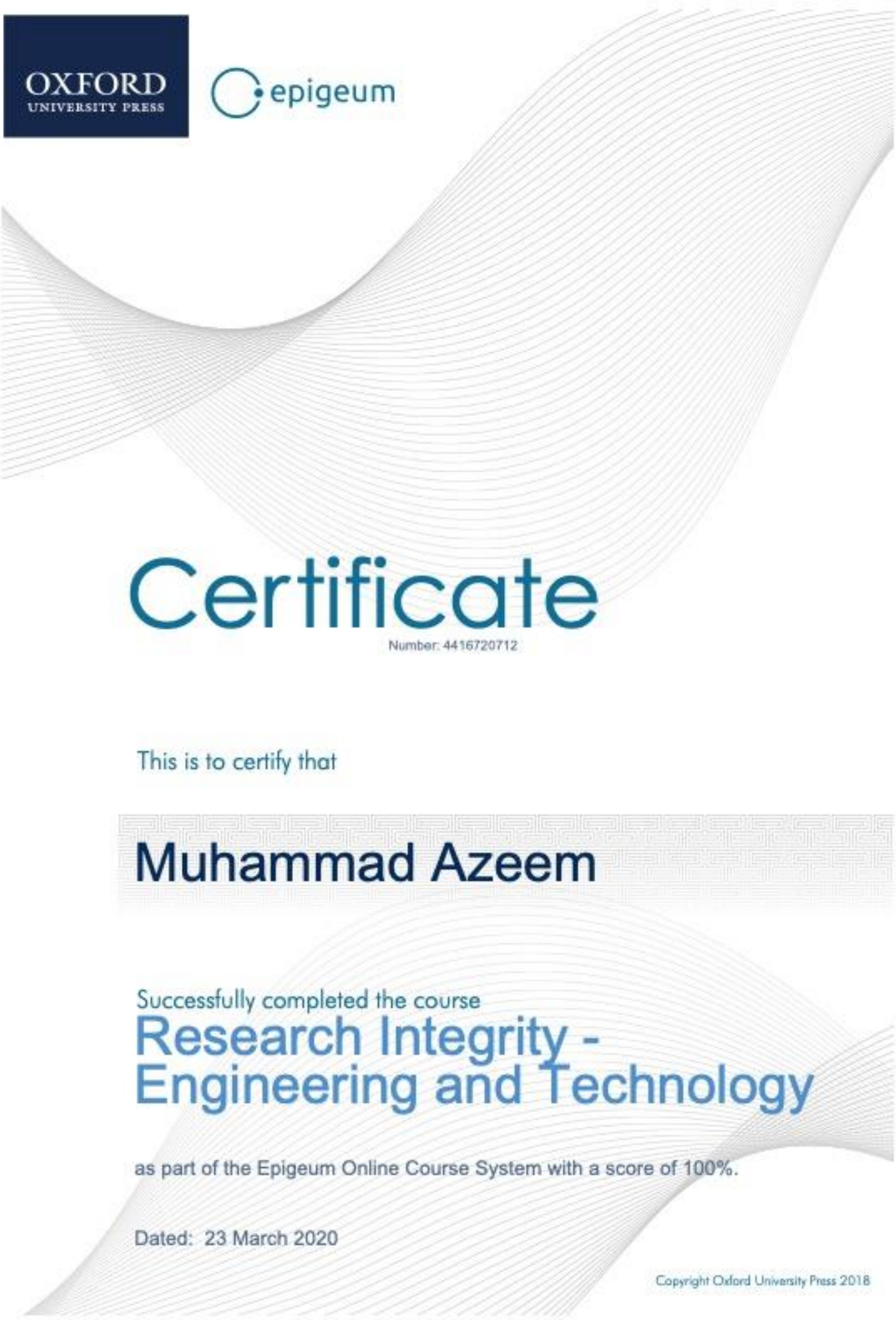
This 19th day of June 2020

Lorna Walsh, Funded Research Manager. Graduate School

Frances O' Connell.
Frances O'Connell, Registrar



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Research Integrity - Engineering and Technology

as part of the Epigeum Online Course System with a score of 100%.

Dated: 23 March 2020

chemistry proceedings

an Open Access Journal by MDPI

CERTIFICATE OF ACCEPTANCE

Certificate of acceptance for the manuscript (**chemproc-1610749**) titled:

Ultrafast, optimized hydrolytic depolymerization of polyethylene terephthalate using a dissolution/degradation approach

Authored by:

Olivia A. Attallah; Arno Janssens; Muhammad Azeem; Margaret Brennan Fournet

has been accepted in *Chem. Proc.* (ISSN 2673-4583) on 29 April 2022

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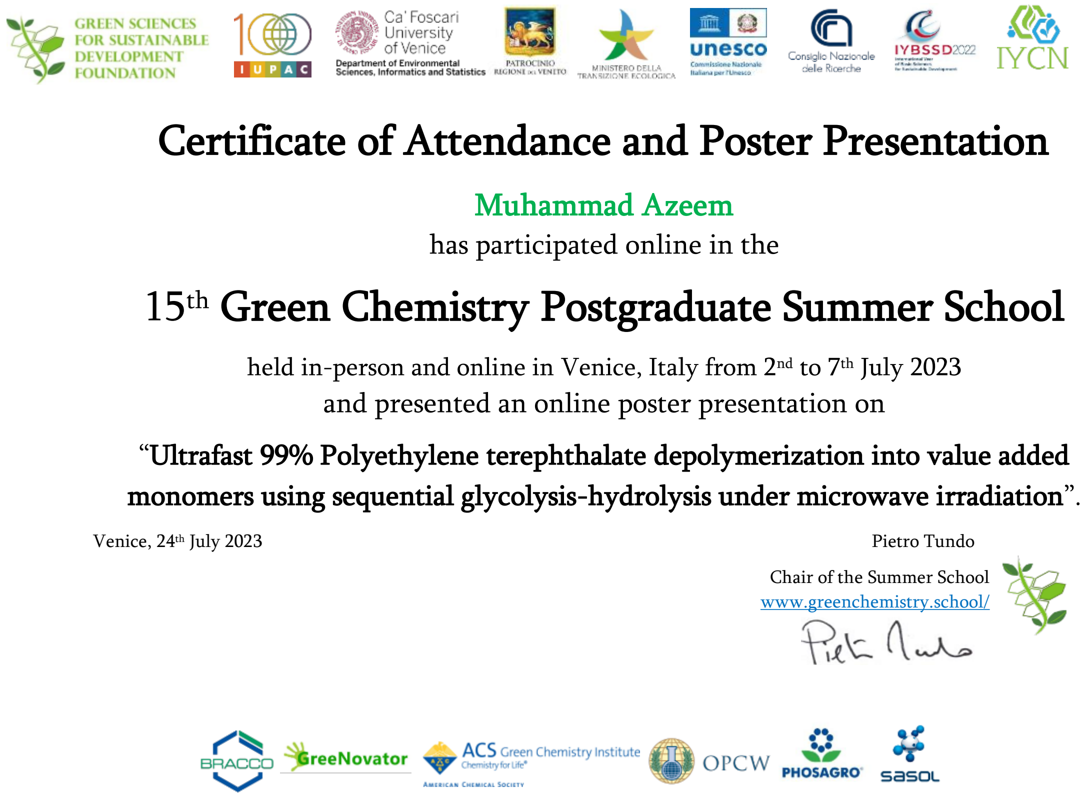
Basel, April 2022



Certificate of Attendance and Poster Presentation

Muhammad Azeem

has participated online in the

15th Green Chemistry Postgraduate Summer School

held in-person and online in Venice, Italy from 2nd to 7th July 2023
and presented an online poster presentation on

"**Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation**".

Venice, 24th July 2023

Pietro Tundo
Chair of the Summer School
www.greenchemistry.school/

FAM
FONDAZIONE ALMA MATER

CERTIFICATE OF TRAINING SCHOOL ATTENDANCE

It is hereby certified that:

Mr Muhammad Azeem,

from Technological University of the Shannon Athlone campus Ireland, has attended the COST Action CA18112 MechSustInd Training School “SCALE UP OF MECHANOCHEMICAL REACTIONS”, held at the Max-Planck-Institut für Kohlenforschung (Mülheim an der Ruhr, Germany) from March 27th to March 30th 2023.
This aim of the course was to enable participants to gain basic training in carrying out and to scale up (to kg-amounts) solid state reactions in general using different types of ball mills

The certificate is issued upon request of the student and for the uses permitted by law.

I remain at your disposal for any further information and send you my warmest regards..

Bologna, 09/08/2023

Bruno Cortesi
GH Manager of the COST Action 18112

Fondazione Alma Mater – Università di Bologna

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