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Simplified, fast, and efficient microwave assisted chemical recycling of poly (ethylene terephthalate) waste

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ABSTRACT

The widespread adoption of chemical recycling of poly (ethylene terephthalate) (PET) is hampered by long reaction times, high energy consumption and the use of metal catalysts that are either toxic or cost prohibitive for industrial use. Herein, we report a simple PET glycolytic process that combines an environmentally friendly and cheap heterogenous catalyst, calcium oxide (CaO) with microwave irradiation to obtain the monomer bis(2-hydroxyethyl) terephthalate (BHET), which can be easily separated by crystallisation. After the process optimisation, depolymerisation of PET waste was achieved in 3.5 min under atmospheric pressure, to obtain highly crystalline BHET with a yield of 75%. To our knowledge, this is the fastest heterogeneous glycolytic process reported in the literature to-date, using a cheap and eco- friendly catalyst. Moreover, by using a heterogenous catalyst and avoiding the need for product precipitation by water addition, CaO and ethylene glycol materials were separated and reused, thus validating this protocol as a potential green and scalable route for PET recycling.

1. Introduction

Plastics play a significant role in almost every aspect of our daily lives. They are used in food and drink containers, clothing and furniture [1]. Among all plastics, poly (ethylene terephthalate) (PET) is the most popular polyester, with an estimated consumption of ~100 million tons per year [2]. Due to its mechanical and chemical properties, PET has very high resistance to degradative assimilation into the environment [3], and consequently, generates leakage to the environment in the form of fibres and macro and microplastics. Among the current recycling options for PET, mechanical recycling is the most commonly employed option, albeit only being a temporary solution, as for each cycle the economic value of PET is reduced (downcycling) due to the loss of mechanical properties. Other options include enzymatic recycling for PET-to-PET conversion, while maintaining the original properties of the polymer. However, enzymatic recycling is far from being optimised and still presents several challenges i.e., long reaction times, expensive enzymes, energy intensive separation and purification steps. Chemical depolymerisation of PET is currently considered a very promising route and could, in principle, solve the problem of downcycling [4]. There are several chemical recycling methods developed for PET

depolymerisation, including glycolysis, hydrolysis and methanolysis. In glycolysis, the main product formed is bis(2-hydroxyethyl terephthalate) (BHET), [5] that can be easily repolymerised to virgin PET, or converted to other products like softeners for the textile industry and unsaturated polyester resins. Glycolysis is also the most common recycling route used at pilot and industrial scale due to the use of non-volatile solvents and ease of scale-up. However, despite recent progress, glycolysis continues to be an energy demanding route that requires high temperatures, prolonged reaction times and sometimes the use of toxic catalysts. Herein, we report a simple, fast, and efficient PET glycolytic process combining CaO and microwave irradiation. We used microwave heating for glycolysis due to its numerous advantages over conventional thermal heating, such as the combination of lower activation energy for transesterification reactions [6] and the high energy absorption of ethylene glycol, thus increasing energy efficiency [7,8]. In order to avoid commonly used catalysts in PET glycolysis that rely on heavy metal cations and are expensive or toxic [9–17], we chose CaO and CaO/Activated Carbon due to its low toxicity, low cost, thermal stability and high transesterification activity [18–28]. The product monomer, BHET, was also separated directly by crystallisation. Both, the catalyst and ethylene glycol, were reused after product crystallisation

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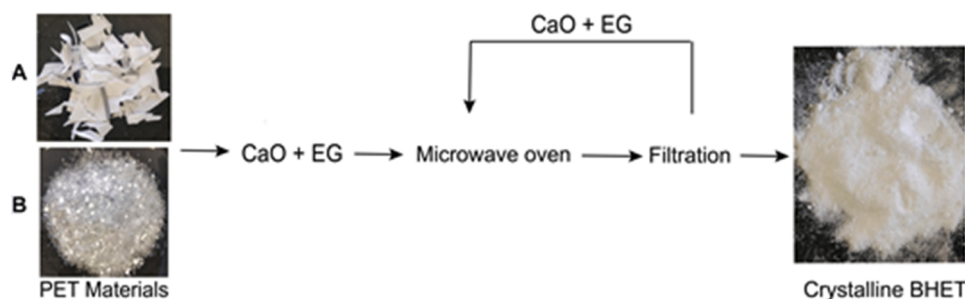


Fig. 1. PET glycolysis using microwave irradiation and CaO as catalyst and 2 different PET sources. A: post-industrial textiles and B: post-consumer water bottles. The BHET product is separated by crystallisation and, CaO and Ethylene glycol, recovered by filtration and reused.

and filtration. To our knowledge, this is the fastest heterogeneous glycolytic process reported to-date, that uses a cheap and eco-friendly catalyst and simplifies the product separation.

2. Experimental section

2.1. Materials and methods

2.1.1. Materials

Post-industrial textile was kindly supplied by O'Neills Ltd (Northern Ireland). Bottles of waste plastic drinking water were collected from post-consumer PET, used after removal of the polyethylene caps and the polypropylene label. The plastic samples were washed with distilled water, dried and then shredded into small pieces ($5 \times 5 \text{ mm}^2$).

2.1.2. Chemicals

Ethylene glycol, calcium oxide (CaO, 99%), $\text{Ca}(\text{NO}_3)_2 \cdot 0.4 \text{ H}_2\text{O}$, activated carbon support (100 mesh particle size), standard BHET and dimethylsulfoxide (DMSO-d_6) were purchased from Aldrich (Steinheim, Germany) and used without further purification.

2.1.3. Characterisation techniques

The FT-IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, the USA) equipped with a diamond ATR attachment, the FT-IR spectra were recorded between 4000 and 400 cm^{-1} . Analysis of thermal stability of BHET was obtained by TGA 4000 (Perkin Elmer, Waltham, MA, United States) under a nitrogen atmosphere. Sample of 10 mg were heated from 30 to 995°C at a heating rate of 10.00°C/min . Differential scanning calorimetry (DSC) were carried out from 20 to 150°C at a rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. High-Performance Liquid Chromatography (HPLC) analysis was performed on an Agilent 1200 HPLC System, $4.6 \times 250 \text{ mm}^2$ analytical column and UV detector measuring at 254 nm. A mixture of methanol/water at a volume fraction of 70/30 was used as the mobile phase at a flow rate of 1 mL/min . ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz on a Bruker Avance III spectrometer in deuterated dimethyl sulfoxide (DMSO-d_6). Gas chromatography (GC-MS) was carried out in a GC Agilent 6890 N, in a HP5-MS column, scan mode, with a MS Agilent 5793 N. The ORIGIN (v.9.0 PRO, OriginLab Corporation, USA) was used to process the recorded spectra.

2.1.4. PET depolymerisation

Supported CaO catalysts were prepared by impregnation of aqueous solutions of the $\text{Ca}(\text{NO}_3)_2 \cdot 0.4 \text{ H}_2\text{O}$ on an activated carbon support (100 mesh particle size, Darco). Calcium nitrate was fully dissolved in deionised H_2O at room temperature with a metal loading of 20 mmol metal/g of support. The support was then added into the solution followed by mixing for 4 h, the paste was dried overnight in an oven at 120°C . Finally, the solid was calcined for 4 h at 450°C [29]. PET waste was treated with ethylene glycol using different PET:EG molar ratios (1:4, 1:6, 1:10 and 1:20) using the microwave oven for time periods up to

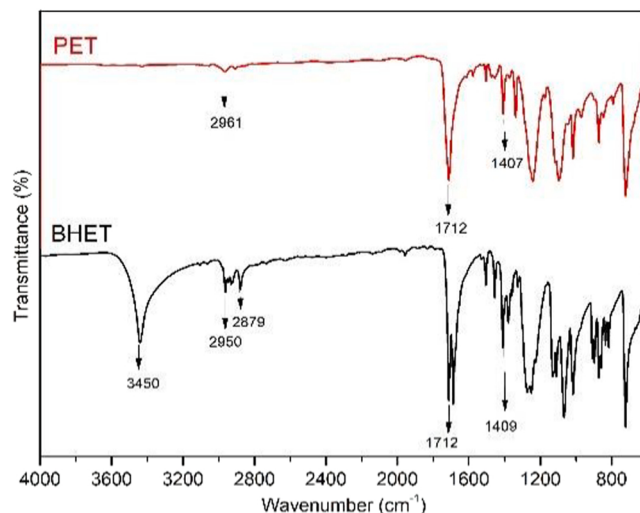


Fig. 2. FTIR spectra of (a) PET and (b) recrystallised BHET generated after glycolysis from post-industrial PET fibres.

maximum 5 min. The catalyst used was calcium oxide (CaO) with different concentrations of 3%, 5% and 10% (w/w) in the reaction mixture, and we further optimised the reaction conditions using supported calcium oxide on activated carbon catalysts CaO/AC. All the reactions were performed at EG boiling temperature of 197°C . PET (1 g) and a certain amount of EG and catalyst were added in a 250 mL round-bottom flask with a magnetic stirring bar and reflux condenser and subject to microwave radiation (800 W). The reaction was considered completed when no visual decrease in the mass of the PET could be detected, which matched with complete dissolution and/or glycolysis of more than 95% of the initial PET (Fig. S11). At the end of the reaction the catalyst was separated by filtration. The solution was cooled down and the crystals obtained were filtered to separate BHET from EG. The BHET product was further purified by recrystallisation in water, dried in an oven at 85°C for 12 h, and then weighed for calculating the yield. Fig. 1.

For the catalyst recycling studies, in each step, the catalyst was filtered, washed with methanol and then dried in an oven at 85°C for 6 h. The calculation of the BHET yield was determined using the following equation:

$$\text{BHET yield}(\%) = \frac{\text{MBHET}}{\text{MWBHET}} \div \frac{\text{MPET}}{\text{MWPET}} \times 100 \quad (1)$$

where, M_{BHET} and M_{PET} refer to the mass of BHET and PET; MW_{BHET} , MW_{PET} refer to the molecular mass of BHET (254 g mol^{-1}) and the PET repeating unit (192 g mol^{-1}) respectively.

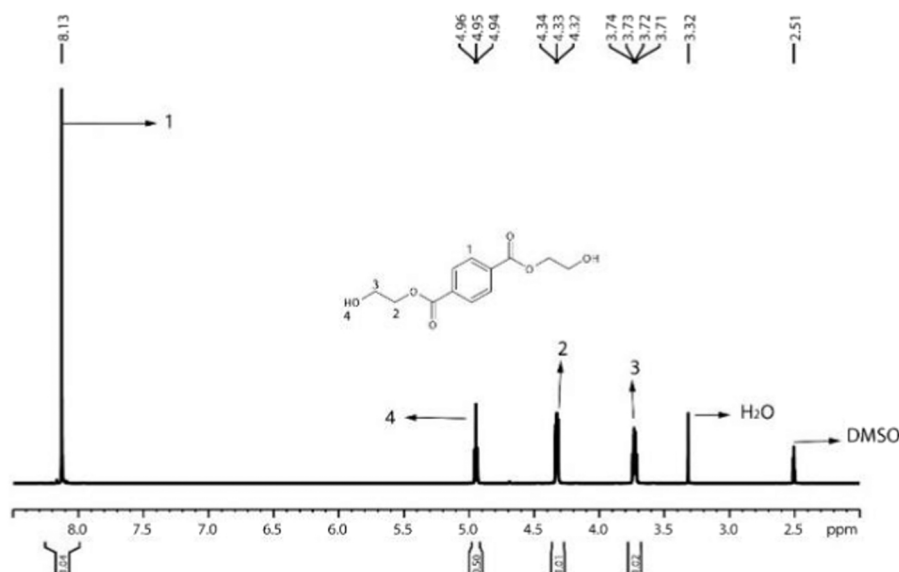


Fig. 3. ^1H NMR spectrum of recrystallised BHET generated from post- industrial PET fibres.

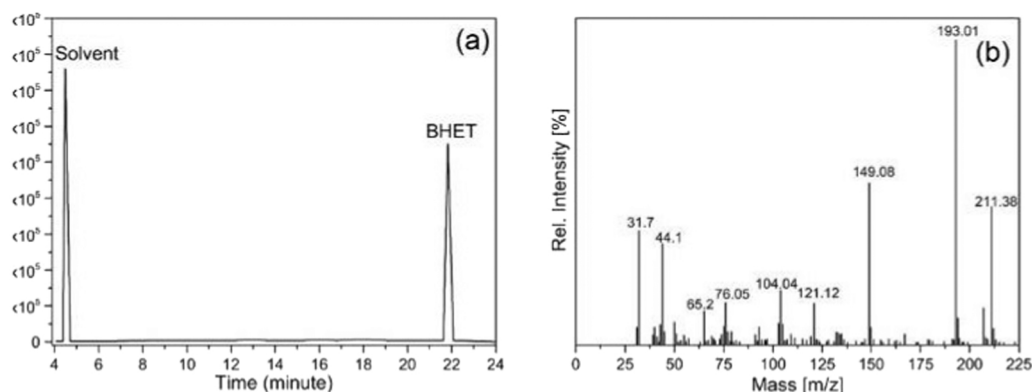


Fig. 4. GC-MS spectrum of recrystallised BHET generated from post- industrial off-cut fibres: (a) GC spectrum; (b) MS spectrum.

3. Results and discussion

The initial PET source was post-industrial PET fibres and post-consumers PET bottles, the product obtained after the glycolysis, BHET, was separated by recrystallisation and characterised by FTIR NMR, GCMS, TGA-DSC and HPLC. FT-IR spectra of the original PET and the BHET obtained are compared in Fig. 2 and Fig. S1. The strong IR band at

3450 cm^{-1} is characteristic of BHET ($-\text{OH}$ stretching vibration), which is absent in PET. There are common bands for PET and the crystallised monomer such as the vibration of alkyl C-H groups at 2950 cm^{-1} and 2879 cm^{-1} , a $\text{C}=\text{O}$ stretching vibration at around 1712 cm^{-1} , and a para-substitute group on a benzene ring at about 1400 cm^{-1} [30,31]. ^1H - and ^{13}C NMR spectra also confirmed BHET as the main product after crystallisation, as shown in Fig. 3, S2, S3 and S4. The structure of BHET

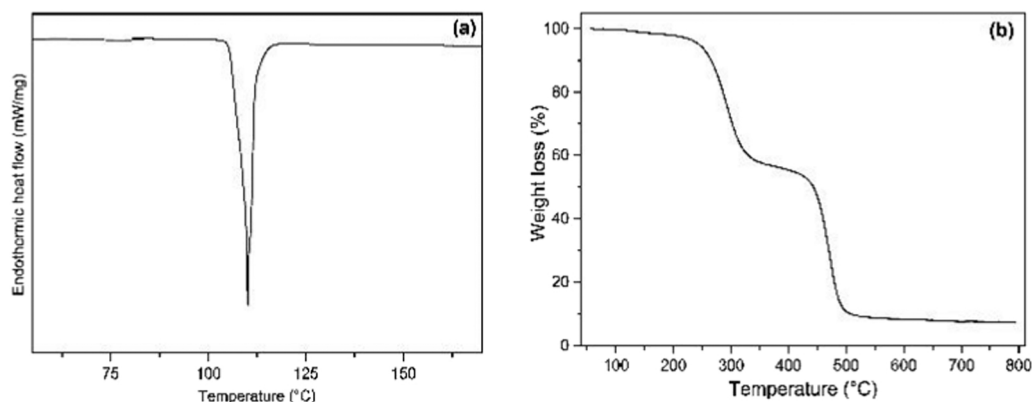


Fig. 5. (a) DSC and (b) TGA curves of recrystallised BHET generated from post-industrial off-cut fibres.

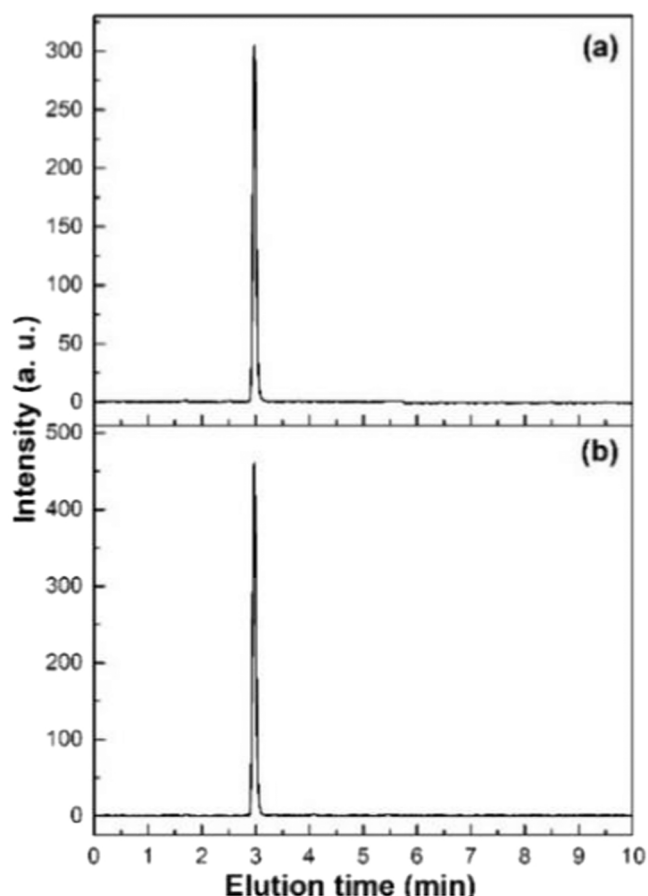


Fig. 6. HPLC data of (a) commercially available BHET, (b) recrystallised BHET generated from post-industrial PET fibers.

monomer has symmetry around the aromatic benzene ring, therefore the protons of a certain group present on either side of the benzene ring resonate at the same frequency. The signal at δ 3.7 ppm (peak 3) represents the protons of the methylene group ($-\text{CH}_2-$) adjacent to the hydroxyl group ($-\text{OH}$). Signals at δ 4.3 (Peak 2) and 4.9 ppm (peak 4) indicates that the protons of the methylene group near COO group and the hydroxyl group, respectively. The signal at δ 8.13 ppm (Peak 1)

indicates the presence of the four aromatic protons on the aromatic benzene ring. The ^1H - and ^{13}C NMR spectra of the BHET match with the reported literature values for pure BHET [32,33].

The GC-MS spectra of the main product from the glycolysis of PET also confirms the presence of only a single compound, which gives a peak at 21.85 min Fig. 4a, attributable to the main product BHET. The peak at 4.47 min corresponds to the solvent (methanol). The intense peaks at m/z 211, 193, 149, 121, 104, 85, 44 and 31 relate to fragments of BHET ($\text{MW} = 254 \text{ g mol}^{-1}$) Fig. 4b. These data demonstrate the high purity of BHET obtained during the crystallisation process. The recrystallised BHET products from all samples were analysed by DSC and TGA. The DSC curve in Fig. 5a shows a sharp endothermic peak at 110°C , which is consistent with the reported melting point of BHET. [34,35]. The melting onset temperature and peak temperature of BHET are 110.9°C and 110°C , respectively.

The TGA curve Fig. 5b shows the first onset of weight loss for the glycolysis sample between 250°C and 318°C in which 39% of the material was lost and can be attributed to the thermal decomposition of the monomer. The 56% loss in weight between 375 and 488°C , can be attributed to thermal polymerisation of BHET during the TGA in accordance with previous reports for commercial BHET [36,37].

Analysis of the crude product obtained from direct crystallization from the reaction by HPLC (Fig. S5) shows a BHET as main product accounting for 82.6%, with dimers and oligomers accounting for 7.7% and 9.7%, respectively. Analysis of the recrystallized BHET product by HPLC, using a reversed-phase column, revealed the presence of a single peak, at a retention times of 3.1 min, assigned to the BHET monomer, similar to the BHET purchased commercially as reference, and consistent with previous reports [38]. This highlights that the monomer fraction consists of pure BHET Fig. 6, S5–S8.

4. Optimal parameters on PET glycolysis

The effect of reaction parameters on the depolymerisation of PET and the yield of crystallised BHET were investigated and optimised Fig. 7.

The yield of BHET was significantly increased when the ratio of EG: PET (w/w) was increased from 4:1–10:1. According to previous studies, an equilibrium between BHET monomer, dimer and other oligomers exists in glycolysis, therefore, an excess amount of solvent is required to decrease the formation of products other than BHET monomers [39,40]. Although the reaction progressed efficiently at lower ratios, the final yield of BHET was lower (65%) when compared with the use of higher EG to PET ratios i.e. 10:1 (75%). Larger EG to PET (w/w) ratios, i.e. 20:1,

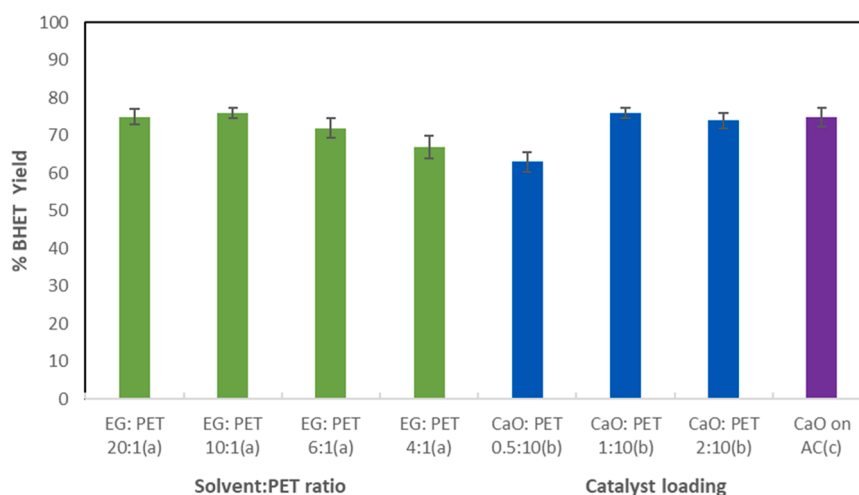


Fig. 7. Results obtained during the optimisation conditions for solvent use (EG: PET ratio (w/w)) and catalyst loading (catalyst: PET ratio (w/w)) and its comparison with the introduction of activated carbon as microwave absorbing material. Conditions: (a) 10 wt% catalyst CaO, 4 min microwave reaction; (b) 10 wt% catalyst CaO, 10 mL of ethylene glycol, 4 min microwave reaction and (c) 15 wt% catalyst, 10 mL of ethylene glycol, 3.5 min microwave reaction.

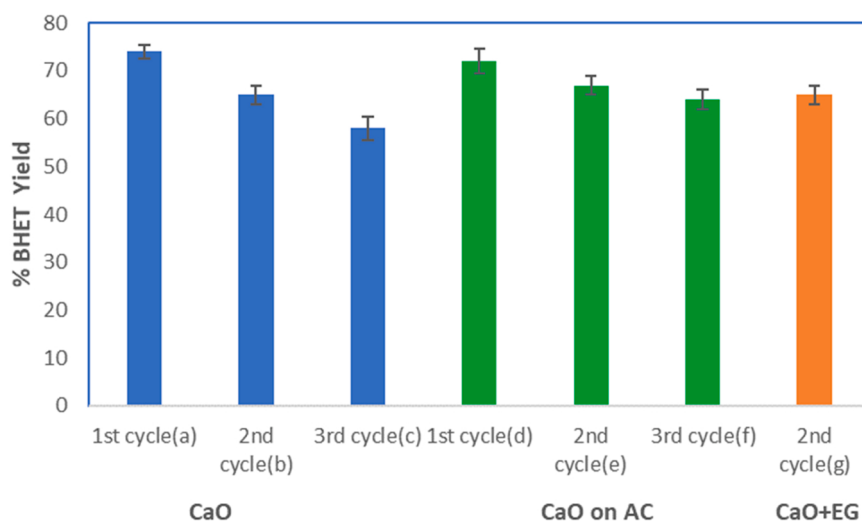


Fig. 8. Reusability of CaO and CaO on AC catalyst represented in terms of yield. (a) 4 min, 10% CaO, (b) 7 min, 10% CaO, (c) 16 min, 10% CaO, (d) 3.5 min, 15% CaO on AC, (e) 6 min, 15% CaO on AC and (f) 16 min, 15% CaO on AC, (g) CaO+ EG reused, 11 min.

did not deliver any significant improvement in yield terms, relative to 10:1. The effect of the % catalyst used on the depolymerisation of PET and the yield of BHET is also shown in Fig. 7. When the mass ratio of the catalyst to PET was increased from 5 to 10 wt%, the total BHET yield increased by approximately 15%, reaching its highest level of 75%. Increasing the catalyst loading above 10 wt% did not result in any substantial improvement in the yield of BHET. The use of activated carbon as a support for the CaO catalyst was also investigated. Activated carbon has previously been shown to be an effective catalyst support in liquid and vapour phase reactions such as heterogeneous transesterification reactions, due to its inert nature and its ability to absorb microwave irradiation [41]. Adding 50 mg (5 wt%) of activated carbon reduced the glycolysis reaction time by 16%, from 4 to 3.5 min, while having a minimal effect on the BHET yield (75% for 4 min vs 72% for 3.5 min).

The optimised parameters were used to evaluate the 'green chemistry metrics' for the microwave glycolysis process. These parameters have recently been proposed to evaluate the efficiency and environmental performance of a chemical process [42], while allowing comparison between chemical processes in terms of fundamental parameters such as temperature, reaction time and the amount of catalyst used. Three main metrics were calculated, (i) the energy efficiency coefficient ϵ , (ii) the environmental factor or E factor, and (iii) the environmental energy impact ξ (Fig. S12). An efficient process is represented by high values of ϵ , and low values of E and ξ . The values obtained for the microwave glycolysis reaction were $\epsilon = 0.00084$, $E = 1.44$ and $\xi = 1740$ for the optimised parameters using CaO as catalyst and $\epsilon = 0.00101$, $E = 1.48$ and $\xi = 1480$ for CaO on activated carbon Fig. S9, where both represent the highest ϵ values reported for any glycolytic process of PET [43]. Both the low E and ξ values obtained for the unsupported and supported catalysts reaction indicates the great potential of our process in terms of energy efficiency and environmental impact compared to the values found in the literature [41]. Another important factor to consider when evaluating the potential of the chemical process is the cost of catalyst used, which is cheap for CaO [44].

4.1. Reusability of the catalyst

Although CaO is considered a low-cost catalyst that can be obtained from waste sources [43–45], the ability to recycle the catalyst is important from a commercial perspective. The reusability of the CaO catalyst in the microwave glycolysis of PET was studied for three cycles Fig. 8, Table S1–S2, Fig. S10. The total catalyst selectivity towards BHET

Table 1

Optimisation parameters for 2 different PET waste sources: a) EG:PET ratio; b) CaO:PET ratio; c) CaO on AC:PET ratio and d) CaO +added AC:PET. i) post-industrial textiles: ii) post-consumer bottles.

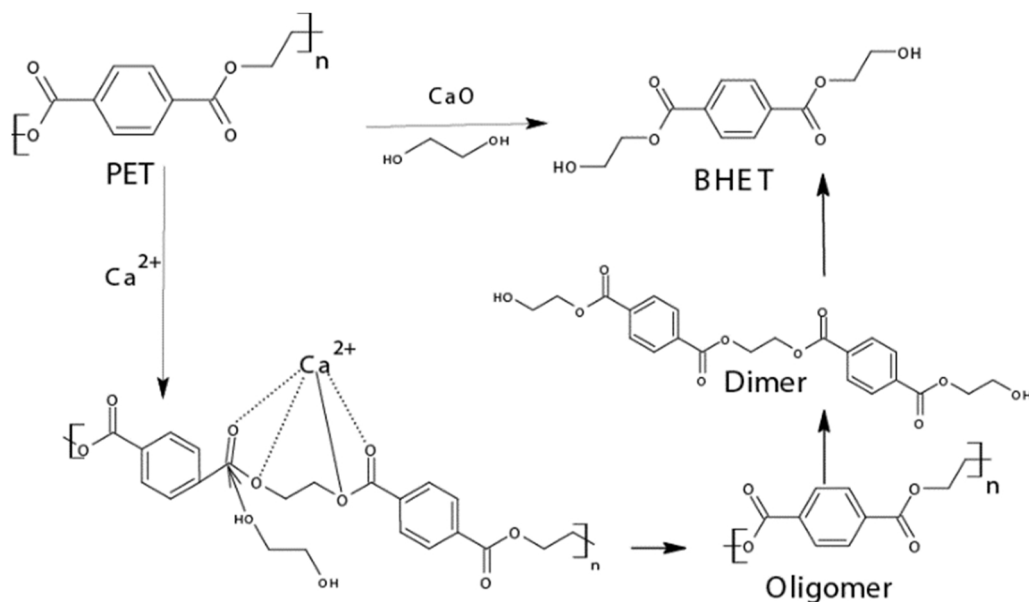
a)	EG:PET (w/w)	ⁱ BHET Yield (%)	ⁱⁱ BHET Yield (%)
	20: 1	75	71
	10: 1	75	73
	6: 1	72	68
	4: 1	67	63
b)	CaO:PET (w/w)	ⁱ BHET Yield (%)	ⁱⁱ BHET Yield (%)
	0.5: 10	63	59
	1: 10	75	73
	2: 10	74	70
c)	CaO on AC:PET (w/w)	ⁱ BHET Yield (%)	ⁱⁱ BHET Yield (%)
	15	75	72

production decreased slightly after three cycles, by approximately 16%, and an increase in the reaction time (6 min vs 16 min). This increase in reaction time and decrease in the yield within each repeated cycle might be attributed to the leaching of the catalyst's active sites in the reaction, the filtration procedure and the initial presence of residual water in the ethylene glycol [46].

Moreover, the recyclability of the CaO/Activated Carbon support was also investigated (Fig. 7d–f). The support was found to improve the catalytic stability of the CaO and decreased leaching [47]. However, the catalyst activity to BHET production was reduced after the third cycle by about 10%. This decay in catalytic activity could be due to the leaching of active sites to the reaction media and the presence of water in the solvent. Overall, the use of CaO/Activated Carbon has a positive effect on the reusability of the catalyst, which is consistent with previous studies [48]. The reuse of both, CaO and EG was also tested in a 2nd cycle Fig. 7g, showing a 65% yield, similar to the yield obtained for 2nd cycle recycling CaO only. This result is promising and shows the great potential of this process for scale-up.

4.2. PET feedstock

To evaluate the versatility of the process, post-consumable PET bottles were also recycled and compared with the polyester fabrics. As shown in Table 1, the microwave process was able generate crystalline BHET, with a 73% yield, from the PET bottles after 6 min in the microwave reactor. These data indicate that our glycolysis process is a versatile route for recycling different PET sources/types, with only small



Scheme 1. Depolymerization of PET into bis (2-hydroxyethyl)terephthalate (BHET) through glycolytic cleavage by CaO catalyst.

variability in BHET yield, suggesting promising possibilities in further practical applications.

5. Glycolysis mechanism

The proposed mechanism for the glycolysis of PET catalysed by CaO is displayed in [Scheme 1](#). To enhance the electrophilicity of the carbon from the C=O group, the coordination between PET and Ca²⁺ cation occurs as the first step, which favours the subsequent nucleophilic attack of ethylene glycol to produce a hydroxyethyl terminal. Apart from the BHET monomer, the repeating cycle could produce oligomers and dimers as by-products. By increasing the catalyst loading, the basicity of the reaction is increased, which leads to a higher concentration of hydroxide ions and promoting the hydrolysis of PET for conversion terephthalic acid and ethylene glycol, thus reducing the BHET yield because by-products.

6. Conclusion

We have demonstrated a simplified and efficient methodology to recycle post-consumer and post-industrial PET by combining an efficient microwave depolymerisation process with CaO and CaO on AC as a non-toxic and reusable heterogeneous catalyst. Crystalline BHET was then separated by filtration, so ethylene glycol could be reused directly. The optimised conditions allowed to obtain crystalline BHET in 3.5 min and 75% yield, which is the fastest reported glycolytic process to date. Overall, this process represents a powerful alternative to the current chemical processes which combines reduced times and a green catalyst and demonstrates the potential of microwave technology in chemical depolymerisation. The green parameters obtained for this process, the energy efficiency coefficient ϵ , the environmental factor or E factor, and the environmental energy impact ξ also indicated the great potential for this process. Ongoing work is focused towards the scale-up of the chemical process and its techno-economic analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.mtcomm.2022.104588](https://doi.org/10.1016/j.mtcomm.2022.104588).

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