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Neopentyl glycol as an alternative solvent for the chemical recycling of complex PET waste†

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The current work reports a novel and effective solvolysis process for the treatment of complex poly(ethylene terephthalate) (PET) waste using neopentyl glycol (NPG) as a depolymerization agent, which to date has not been studied much for chemical recycling. Different complex PET waste samples (multilayers and textiles) were conditioned for glycolysis in the presence of NPG and zinc acetate as a catalyst. The reaction parameters, including temperature and NPG/PET molar ratios, were optimized to maximize the yield of the bis-(hydroxy neopentyl) terephthalate (BHNT) monomer. The reaction progress was gravimetrically determined, and the resulting BHNT monomers were characterized by means of various techniques (FTIR, DSC, and NMR). A novel purification step with active carbon was developed in order to remove dyes and other impurities present in the raw products. The results indicated that an NPG/PET molar ratio of 6:1 and a reaction temperature of 200 °C were optimal for achieving high PET conversion and raw BHNT yield. The purification process successfully enhanced the purity of BHNT, increasing the presence of the monomer in the purified samples from 60% to 95% in mol and reducing the oligomer and by-product content. The obtained products have the potential to replace fossil-based NPG in the synthesis of resins or coatings.

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Introduction

The term plastic refers to a wide range of polymers, typically mixed with additives, fillers or reinforcements that are used in a variety of applications due to their light weight, durability and affordability.¹ Global annual production of plastics has doubled from 234 million tonnes (Mt) in 2000 to 460 Mt in 2019 and is projected to grow to 1231 Mt by 2060.² Consequently, global plastic waste generation, due to the short life span of many of their applications, has more than doubled from 156 Mt in 2000 to 353 Mt in 2019 and, if the current production trend continues, it is expected to almost triple to 1014 Mt by 2060.³ Among all the plastic waste globally produced in 2019, only 9% was ultimately recycled, while 19% was incinerated and almost 50% went to landfills. The remaining 22% was disposed of in uncontrolled landfills or leaked into the environment.⁴ It should also be noted that only about an estimated 9% of the plastics ever produced have been recycled and 12% have been incinerated.⁵ The remaining is either still in use or has

either been disposed of in landfills or released into the environment, including the oceans, in the form of macro- and microplastics.^{6–8} Addressing plastic waste by increasing the circularity of the plastics value chain is therefore urgent.

In recent years, one of the most widely used recyclable polymers has been poly(ethylene terephthalate) (PET) due to its excellent properties such as lightweight, transparency and high mechanical strength.⁹ PET is a long-chain polymer belonging to the polyester family and is widely used in packaging applications, including sheet and bottle production. In 2022, a total of 5 Mt of PET was utilized in packaging (bottles, trays and films) placed on the market in the EU27 + 3 region. Of this, 3 Mt were collected, bringing the collection rate to 60%. The vast majority of the collected PET packaging was bottles, accounting for 2.8 Mt.¹⁰ Nevertheless, the rate of all PET waste sorted for recycling stood at 54% in 2022 across Europe. Of the remainder, most waste ends up in incinerators or landfills and a significant amount ends up in the sea.¹¹ In practice, mechanical recycling is the most commonly used method to recycle waste PET. However, reprocessing PET at high temperatures can deteriorate or alter the properties of the recycled products¹² and the more complex streams (multi-layered, highly coloured and contaminated) cannot be recycled in this way. Several chemical recycling technologies have been studied recently due to their high potential for improving circularity in PET waste recycling.¹³ Different chemical recycling processes can be

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used for PET materials, including depolymerization into monomeric compounds through solvolysis.¹⁴ Solvents such as ethylene glycol (EG), methanol, water, ammonia or amines can be used as degradation agents.¹⁵ For example, PET can be chemically recycled through glycolysis¹⁶ or hydrolysis¹⁷ to produce bis(2-hydroxyethyl) terephthalate (BHET) or terephthalic acid (TPA), respectively.¹⁸ Glycolysis is one of the most researched depolymerization processes for PET waste and has been reported as one of the best options for the chemical recycling of PET streams due to the relatively low volatility of the diol solvent, the feasibility of continuous operation, its adaptability to existing industrial scale polymerization processes and the capacity to handle the most complex PET streams.^{19–21} The PET reacts with the glycol, breaking the ester bonds of the polymer chain and replacing them with hydroxyl groups. This process results in different oligomers and, ultimately, the monomer.²² The rate of glycolysis is dependent on various parameters, such as temperature, pressure, solvent ratio, and the type and amount of catalyst.

The use of ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), polyethylene glycol (PEG) and tetraethylene glycol (TEG) for the glycolysis of PET has been extensively studied.^{23–31} Additionally, the use of triols such as glycerol³² and trimethylolpropane (TMP)³³ has also been reported. It has been shown that zinc (Zn) acetate is the best catalyst for glycolysis, regardless of the glycol used.^{34–37} Zinc based catalysts form strong coordination complexes with carboxyl groups, enhancing nucleophilic attack and promoting degradation more efficiently than other metal cations.³⁸ In addition, recent literature indicates that heterogeneous organocatalysts³⁹ and biobased solvents⁴⁰ have been used to efficiently proceed with glycolysis under mild reaction conditions. However, neopentyl glycol (NPG) remains relatively unexplored as an alternative solvent for the glycolysis of complex PET waste streams.^{41–43} NPG is an organic compound commonly used in the synthesis of polyesters, paints, lubricants, and plasticizers. Its incorporation into polyester production enhances product stability against heat, light, and water, making it a highly valuable component within the chemical industry. Notably, NPG holds significant demand among manufacturers of saturated polyester resins for powder coating applications. Anticipated industry growth is evidenced by ongoing expansions, such as BASF and Khua's recent announcement of a new plant in China.⁴⁴ This expansion is projected to elevate BASF's global NPG capacity from 255 000 to 335 000 metric tons annually. One of the many advantages of NPG is that bis-(hydroxy neopentyl) terephthalate (BHNT) can be obtained as a product after depolymerization of waste PET (Fig. 1), which lacks β -hydrogen and enhances the chemical resistance of the resulting polymer.⁴³

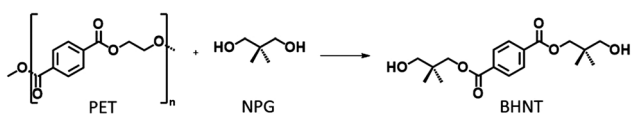


Fig. 1 Reaction scheme of PET glycolysis using NPG.

Previous research has identified glycolysis as one of the most suitable chemical recycling processes for PET recycling. However, applications developed from these findings mainly focus on relatively clean PET materials with a known composition.^{45,46} The present work focuses on studying the feasibility of using NPG, an unexplored solvent for the glycolysis of complex plastic materials that are currently being landfilled or incinerated,⁴⁷ instead of ideal one-component models. Additionally, a purification step has been developed in order to remove dyes and other impurities present in the raw products to ensure that the monomers meet the required specifications to manufacture new value-added products.

Experimental

Materials

All PET waste samples were provided by the company Sacry Environment. The samples received at Gaiker consist of real PET waste that presents different degrees of complexity and therefore are not treated by mechanical recycling methods (Table 1). Among these PET samples, multilayer trays, highly coloured bottles, and polyester textiles from both postconsumer clothing and end-of-life tyres can be found. All samples were characterized and conditioned by means of a blade mill to produce particle sizes smaller than 6 mm in diameter prior to the glycolysis reaction. NPG and Zn acetate were purchased from Sigma Aldrich-Merck. NORIT[®] KB-EV SUPRA activated carbon (AC) was provided by Cabot.

Characterization of PET waste

Since moisture can interfere in the characterization of PET or could also cause hydrolytic degradation during processing resulting in a reduction of the molecular weight,⁴⁸ all samples were conditioned for 12 h at 105 °C in an oven to control the water content before any characterization or treatment. The density and moisture content of PET samples were determined by gravimetric analysis. The chemical structure of the PET samples was measured by means of a Fourier transform infrared (FTIR) spectrometer (Shimadzu IRAffinity-1S) in the transmittance mode in the wavenumber range from 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1} . The inorganic matter content was quantified by calcination of PET samples in a muffle furnace (Nabertherm B180) in air at 625 °C for 4 h, following a heating rate of 10 °C min^{-1} . After calcination, the remaining ashes were weighed and also analyzed using FTIR in order to determine the nature of the inorganic matter present in the samples.

Glycolysis of PET waste using neopentyl glycol

The glycolysis reactions of PET waste were carried out in a 1000 mL three necked glass reactor, equipped with a mechanical stirrer that was set at 250 rpm, a thermometer, and a reflux condenser. NPG was chosen as the glycolysis reagent due to the potential application of the obtained monomers in the synthesis of resins, coatings and PUDs. NPG and Zn acetate as the



Table 1 PET waste sample characteristics

PET	Material description	Complexity
PET-1	Postconsumer monolayer trays	Low polyolefin concentration
PET-2	Postconsumer coloured bottles	Highly coloured plastic
PET-3	Textile from end-of-life (EoL) tyres	Low density and presence of rubber
PET-4	Textile from postconsumer clothing	Low density and presence of other fibres
PET-5	Postconsumer multilayer trays	High polyolefin concentration

catalyst were added and heated to 200 °C. A fixed NPG/PET molar ratio of 6:1 was used, with 1 wt% of Zn acetate as a catalyst. Finally, 100 g of waste PET particles were fed into the reactor. Glycolyzed samples were taken at specific reaction times (1, 2, 3 and 4 h) in order to quantify the degree of progress of the glycolysis reaction by monitoring the generation of the BHNT monomer, dimers and other species. Several runs were carried out for each test in order to determine experimental error. In addition, the influence of the NPG/PET molar ratio (2:1, 4:1, 6:1, 7.6:1) was also studied at a fixed reaction time of 2 h and temperatures of 180–220 °C in order to optimize one of the key variables in the glycolysis processes.

Reactions were also carried out with all the PET waste samples and at different reaction times (1, 2, 3 and 4 h) in order to study the PET conversion and raw BHNT yield (before purification) over time. The final reaction product, also known as the glycolyzed product, was filtered hot (150 °C) and under pressure (2 bar) in order to remove unreacted material. Then, demineralized water at a ratio of 2:1 vol. (Water/NPG) was added to the filtered product, and hot extraction of oligomers was carried out at 90 °C. Finally, the raw BHNT monomer was obtained after the crystallization process at 5 °C and filtration using a 0.7 µm microfiber filter. The overall process of the solvolysis reaction is shown in Fig. 2. The results were evaluated in terms of PET conversion and raw BHNT yield. PET conversion was gravimetrically determined on the basis of the weights of the unreacted PET material using eqn (1).

$$\text{PET}_{\text{conversion}}(\%) = \frac{W_{\text{PET}}^0 - W_{\text{PET}}^t}{W_{\text{PET}}^0} \times 100 \quad (1)$$

where W_{PET}^0 (g) and W_{PET}^t (g) refer to the initial weight of PET fed and PET weight at a specific reaction time, respectively.

The raw BHNT yield was gravimetrically determined based on the unpurified monomer weight after each run using eqn (2).

$$\text{Raw BHNT}_{\text{yield}}(\%) = \frac{W_{\text{BHNT}}^t / \text{MW}_{\text{BHNT}}}{W_{\text{PET}}^0 / \text{MW}_{\text{PET}}} \times 100 \quad (2)$$

where W_{BHNT}^t (g) refers to the weight of raw BHNT at a specific reaction time. MW_{BHNT} and MW_{PET} are the molecular weights of BHNT (338.4 g mol⁻¹) and the PET monomer (192.0 g mol⁻¹), respectively.

Purification of the BHNT monomer

Since the obtained raw products are coloured due to the dyes contained in the PET residue and also other impurities such as metals, an exhaustive purification of the obtained monomer is carried out in order to remove the colour and reduce the metal

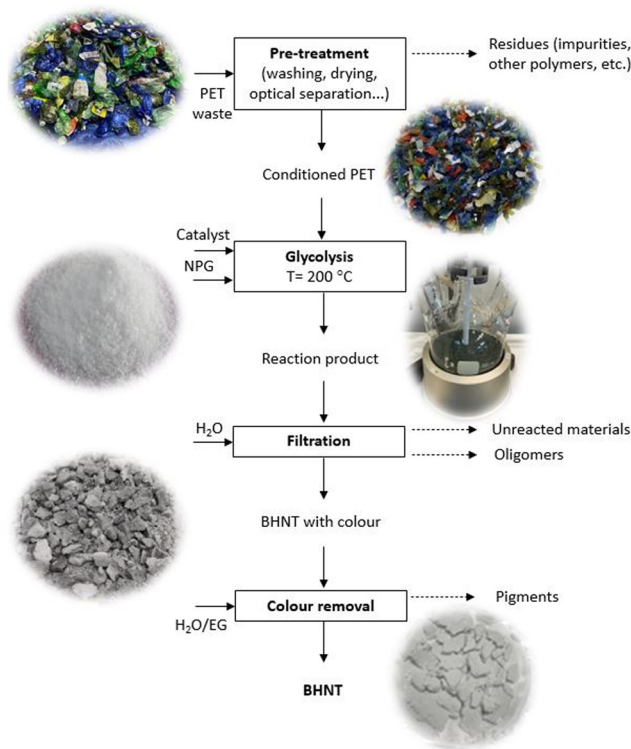


Fig. 2 The PET glycolysis reaction and product purification process.

content. For this purpose, a certain quantity of raw BHNT monomer is dissolved in a 1 to 1 vol. mixture of demineralized water and EG, and AC is added to this dissolution for the colour removal process. After a given time, the AC is filtered out of the solution using a microfiber filter and a colourless BHNT is obtained after crystallization. Finally, monomer rinsing is carried out using demineralized water, in order to reduce the concentration of metals in the BHNT, especially Zn.

BHNT monomer characterization

The chemical structures of the reaction products were measured by means of an FTIR spectrometer (Shimadzu IRAffinity-1S) in the transmittance mode in the wavenumber range from 600 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. DSC (TA Instruments DSC Q100 Model) was used for the thermal analysis of glycolyzed products. Samples were heated from room temperature to 280 °C with a heating rate of 10 °C min⁻¹ under a nitrogen flow of 50 mL min⁻¹. Characterization of the colour of BHNT produced before and after purification was also carried out using a CM-2300d model spectrophotometer with a



wavelength range between 360 nm and 740 nm. The CIE 1976 $L^*a^*b^*$ (CIELAB) colour space was used, which defines the colour of an object through three parameters: L^* (100 = white; 0 = black), a^* (positive = red; negative = green; and 0 = gray) and b^* (positive = yellow; negative = blue; and 0 = gray). Proton nuclear magnetic resonance ($^1\text{H-NMR}$) was also used to characterize the composition of BHNT samples. The proton NMR spectra were acquired using a 400 MHz Bruker apparatus. The sample preparation consisted of dissolving approximately 15 mg of the sample in 2 mL of deuterated chloroform. Under these conditions, all analyzed samples were completely soluble. Spectra were acquired using 16 accumulations for each spectrum. For the treatment of the spectra, the MestReNova program was used and all the spectra were referenced to the residual signal of the solvent, located at 7.26 ppm. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was carried out using an Agilent ICP-OES 720 (Agilent Technologies) in order to determine the Zn content of the obtained BHNT samples.

Results and discussion

Characterization of PET waste

Table 2 summarizes the main properties of as-received PET waste samples prior to the glycolysis reaction using NPG. All PET waste samples show a similar moisture content with the exception of PET-3. The lower value of this sample can be related to the conditioning processes carried out in end-of-life tyre treatment facilities. In addition, the PET-3 sample is the one with the highest inorganic matter content (4.77%) after calcination due to the presence of rubber and other inorganic materials in the textile fibres. A low bulk density value is

observed for the PET-4 sample (0.034 g cm^{-3}), due to its textile nature, while the rest of the samples present typical density values for PET to be fed to a solvolysis process.

Fig. 3a shows the FTIR spectrum of all PET wastes. All samples present the typical bands of PET, namely 1712 cm^{-1} (C=O stretching of the carboxylic acid group), $1410\text{--}1338 \text{ cm}^{-1}$ (stretching of the C–O group, deformation of the O–H group and bending vibrational modes and oscillation of the ethylene glycol segment), 1240 cm^{-1} (terephthalate group, $\text{OOC}_6\text{H}_4\text{COO}$), $1090\text{--}1030 \text{ cm}^{-1}$ (methylene group and vibrations of the C–O ester bond) and 720 cm^{-1} (interaction of polar ester groups and benzene rings).⁴⁹

As previously mentioned, the chemical nature of the inorganic compounds, present after the calcination of PET samples, was also characterized by FTIR. The following characteristic bands were identified (Fig. 3b): silicates, in the $1000\text{--}1100 \text{ cm}^{-1}$ range, which was accompanied by the band at 670 cm^{-1} , showing the existence of silicon oxide compounds or silicates. Furthermore, the bands of calcium carbonate were observed (1400 and 870 cm^{-1}). These bands represent the union of CO_3^{2-} associated with calcite.⁴⁹ The addition of calcium carbonate in PET plastics improves the thermal stability of the matrix.⁵⁰

Glycolysis of PET: optimizing variables and reaction progress evaluation

The evolution of the raw BHNT yield with different NPG/PET molar ratios has been followed, for a fixed time (2 h) and catalyst content (1 wt%). The reaction temperature was also a parameter that varied in the experiments, with the tests being carried out at $180\text{--}220 \text{ }^\circ\text{C}$. The PET-1 sample was used as feedstock for these tests. The NPG concentration range studied is between 2 : 1 and 7.6 : 1 (mol mol^{-1}) (Fig. 4). The raw BHNT yield significantly increases with the ratio until a stable equilibrium value is obtained. For instance, the tests carried out at $200 \text{ }^\circ\text{C}$ reached around 33% for an NPG/PET ratio of 2 : 1 and above 90% for an NPG/PET ratio of 7.6 : 1. The lower yields obtained for reactions with an NPG/PET ratio lower than 6 : 1, regardless of the temperature, can be attributed to solvent quantity limitations since it was observed that the amount of

Table 2 PET waste sample characterization results

PET	Moisture (%)	Ash content (%)	Bulk density (g cm^{-3})
PET-1	2.42	0.10	0.462
PET-2	2.35	0.34	0.220
PET-3	0.76	4.77	0.261
PET-4	2.11	1.08	0.034
PET-5	2.42	0.06	0.394

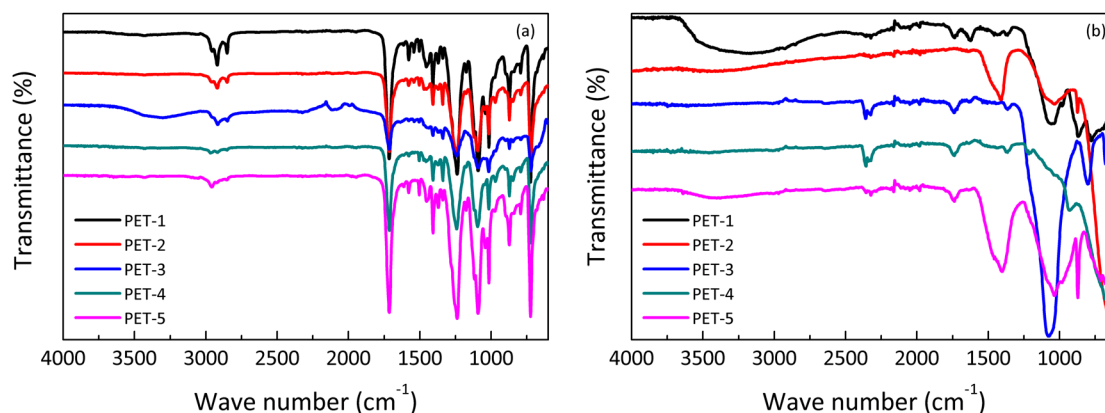


Fig. 3 FTIR spectra of (a) PET waste samples and (b) their ashes.



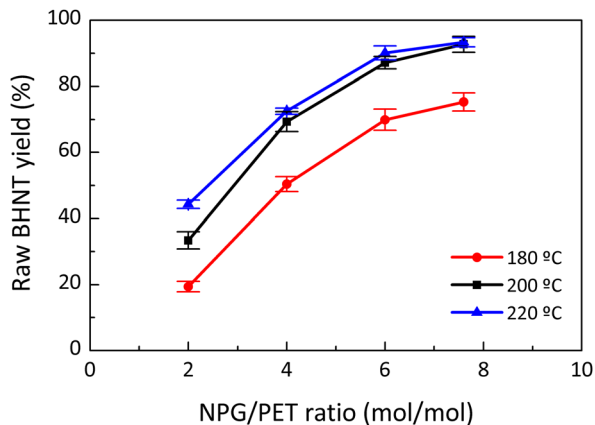


Fig. 4 Evolution of raw BHNT yield versus NPG/PET molar ratio.

NPG added, when melted, was inadequate to properly mix with the PET sample resulting in mixtures of reduced homogeneity.⁴⁷

Regarding the reaction temperature, it can be observed that the raw product yield is lower for the tests carried out at 180 °C, while it is up to 20% higher for 200–220 °C temperature values. Nevertheless, just a slight improvement was observed when increasing the test temperature from 200 °C to 220 °C. For the previous reasons, and although the performance differences of the most highly diluted mixtures (6:1 and 7.6:1) are relatively small, the NPG/PET ratio of 6:1 and a temperature of 200 °C have been selected as optimal for further studies.

Fig. 5 shows the evolution of PET conversion and raw monomer yield over the reaction time for all wastes. As seen in Fig. 5a, it can be concluded that all PET samples reach almost full depolymerization after 2 hours of reaction, maintaining a constant conversion profile from this value onward, with the exception of the PET-3 sample because its high contents of rubber and other textile fibres cause the overall conversion of the sample into monomer decrease to values lower than 6%. The optimum reaction time for obtaining maximum values of both PET conversion and yield can be set at 2 hours, reaching 95.6% PET conversion and 87.4% raw BHNT yield in the case of the PET-2 sample. From Fig. 5b it can be concluded that extending the reaction after equilibrium has been reached causes the reaction to shift backwards (from depolymerization to polymerization), increasing the amount of dimer with a slight loss of the BHNT monomer.^{51–53} Nevertheless, high conversion and yield values have been obtained during glycolysis of PET waste using NPG as a solvent, the best results being for the monolayer materials and somewhat lower for the multilayer and fibre containing samples due to the presence of non-PET materials, including PET-3 which is the most difficult waste stream to treat *via* glycolysis.⁵⁴

BHNT purification and characterization

FTIR spectra (Fig. 6) of the obtained reaction products reveal significant and broad transmission peaks at 1386 cm^{-1} and 1439 cm^{-1} , indicating the presence of *tert*-butyl groups.

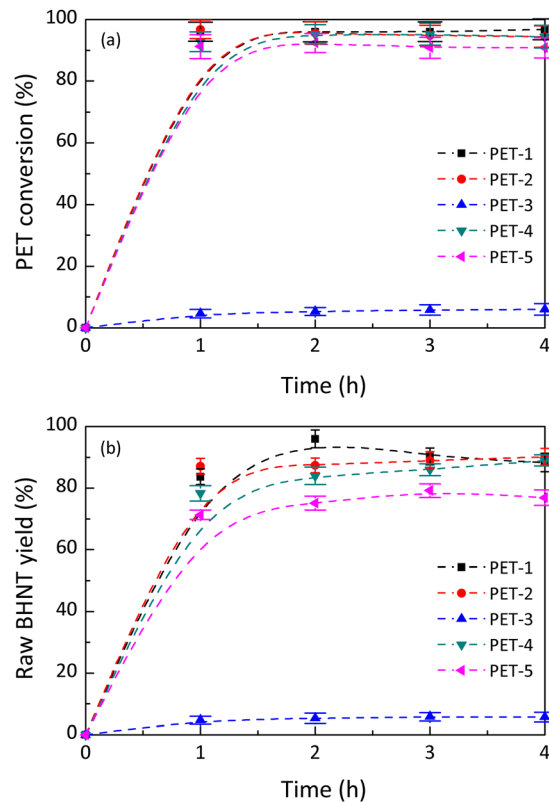


Fig. 5 Effect of the reaction time on (a) PET conversion and (b) raw BHNT yield.

Additionally, a moderate transmission band at around 1503 cm^{-1} indicates stretching vibrations of methyl and methylene groups typically found in branched hydrocarbons, such as the neopentyl group. The strong peak at 1386 cm^{-1} further confirms the existence of methylene linkages within the structure. Another prominent transmission band at 3555 cm^{-1} indicates primary hydroxyls due to O–H bending vibrations, with a distinct peak at 1063 cm^{-1} supporting the presence of these hydroxyl groups. Ester bonds within the structure are identified by robust transmission bands at 1093 cm^{-1} and 1678 cm^{-1} . Additionally, characteristic bands at 2864 cm^{-1} and 2929 cm^{-1} correspond to C–H stretching vibrations commonly observed in saturated hydrocarbons containing methyl groups.⁴³ DSC analysis for the glycolized samples was performed to study thermal properties. The DSC spectra recorded are shown in Fig. S1 (ESI[†]) and resulted in a broad melting region at around 90 °C for most of the samples. Some products showed pronounced peaks at higher temperature regions due to the presence of dimers and oligomers, with PET-2 and PET-3 showing the most prominent peaks.

The raw and purified products were also characterized by NMR analysis as shown in Fig. S2 (ESI[†]). Since the glycol used in the reaction is different from EG (commonly used to generate BHET), new species from those previously described in the literature can be generated. First, the assignments for the proton NMR spectrum of a purified BHNT sample are presented. The broad signal at 1.98 ppm corresponds to the



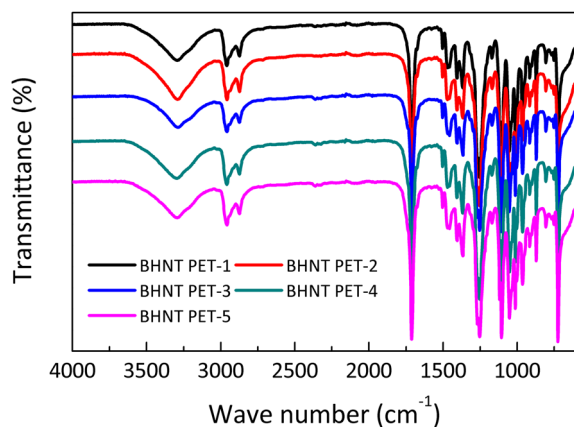


Fig. 6 Characterization of reaction products before purification by means of FTIR.

alcohol (R-OH) groups present in the molecule. Since the position of this peak varies considerably with sample concentration, it was discarded for the compositional analyses of all samples. In the aromatic hydrogen region, at 8.11 ppm the terephthalic ring protons labeled as a are observed. Then, at 4.21 and 3.41 ppm, the protons of the methylene group labeled as b and c are located, respectively. At 1.02 ppm the protons of the methyl groups labeled as d are observed. Finally, the intense signal at 3.73 ppm corresponds to ethylene glycol. This product comes from the degradation of PET, but no BHET monomer was reported.

Fig. 7 shows the NMR assignments for the rest of the compounds present in the samples glycolyzed with NPG. The signals corresponding to the unreacted NPG can be seen at 0.92

and 3.52 ppm. The BHNT dimer and trimer peaks are positioned at 4.28 and 1.18 ppm, corresponding to the b' and d' labeled protons, respectively. The peak at 4.28 ppm is particularly significant as it will be deconvoluted to determine the quantities of the BHNT dimer and trimer (Fig. S3, ESI[†]). Additionally, the pseudo-triplets located at 4.50 and 3.98 ppm are attributed to a product referred to as asymmetric (Asymm.), which arises from the partial glycolysis of PET.⁴³ Unlike BHNT, which contains a neopentyl group at both sides of the aromatic ring attached with an ester group, the asymmetric structure contains one unit of neopentyl and ethylene groups each. This can be considered an intermediate structure between BHNT and BHET monomers. Fig. 8 illustrates the chemical structures of all species present in the analyzed samples.

Once all the signs of the species present in the samples were identified, the chemical composition of the samples was determined. The quantification of the composition was carried out before and after the reaction product purification process in order to determine the performance of this step (Table S1, ESI[†]). For the unpurified samples, with the exception of PET-2, the major product is BHNT. Its content varies greatly in each sample, ranging from 63% to 89% in mol. In the particular case of sample PET-2, a high content of NPG from glycolysis has been detected. In fact, the NPG and BHNT content is around 40% for both species. After that, the BHNT dimer has a variable percentage, although in all cases this value is less than 10% in mol. This product could have originated from the partial glycolysis of the PET chain or a condensation reaction between two molecules of BHNT.⁵⁵ Regarding the asymmetric structure coming from the partial glycolysis of PET, its concentration is between 3 and 8% in mol. For the purified samples, the

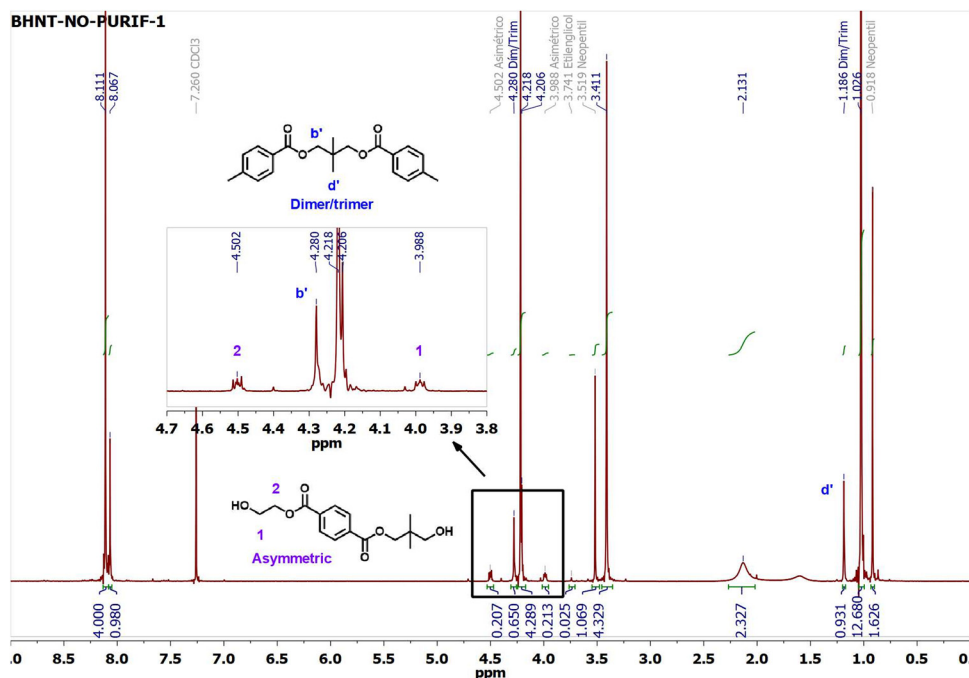


Fig. 7 NMR spectra of the reaction product after glycolysis and before purification.



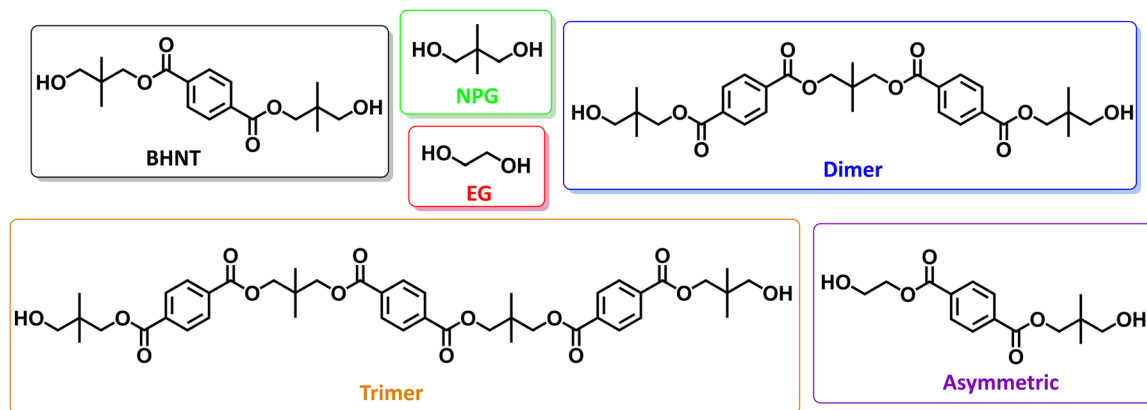


Fig. 8 Chemical structures of the products found in glycolysis of PET with NPG.

proposed purification process has caused a rise in the BHNT content, exceeding 90% in mol for all the samples. In this series, the peak at 4.28 ppm could be deconvoluted with a single peak meaning that there is no trimer in the analyzed products. The highest BHNT content is found in sample PET-3 reaching a content of 95% in mol. Regarding the remaining NPG in the glycolysis product, it has been eliminated for practically all the samples. Finally, the content of dimer and asymmetric species is very similar (2–5% in mol) between the two even though a correlation between the contents of the two species is not expected. The dimer content of the purified samples is lower compared to the unpurified ones and can be set at less than 5%. Furthermore, no signal of EG was found in the analyzed samples so the traces of free ethylene glycol were completely removed. Since the purification step was successful in reducing the concentration of the by-products and increasing the BHNT content, the molecular weight (M_n) values of the monomer samples are very close to that of the theoretical BHNT value (338.4 g mol^{-1}). Fig. 9 illustrates the chemical composition of the samples analyzed by means of NMR, together with the calculated molecular weight.

Table S2 (ESI[†]) shows the measured colour parameters and Zn content of the produced BHNT samples, before and after purification. In PET chemical recycling processes, the colored and metallic impurities have to be removed from the monomers to produce good quality products (rPET granulate, resins

or coatings). Despite the intense colour of the unpurified BHNT samples, after the developed purification process involving active carbon mixing, filtration and washing with demineralized water, the final product loses much of its colour and clean and purified BHNT is obtained. The whiteness (L^*) of all samples greatly increased from around 70 to over 90 ($L^* = 100$ for pure white), together with the improvement in parameters a^* and b^* , approaching the 0 value for both after the purification step, indicating the effectiveness of decolorization. Furthermore, the Zn content of the unpurified samples was significantly reduced under the investigated purification conditions, reaching values lower than 10 mg kg^{-1} , which is indeed a clear advantage for the subsequent polymerization of BHNT to produce colourless plastics or coatings.

Conclusions

The results demonstrate that NPG, a novel glycolysis agent when referring to recycling of complex PET waste streams instead of ideal one-component models, can effectively depolymerize various PET waste materials, including multilayer trays, colored bottles, and textiles from post-consumer clothing and end-of-life tires, to produce the BHNT monomer. Reaction parameters were optimized, with a molar ratio of NPG to PET of 6 : 1 and a reaction temperature of $200 \text{ }^\circ\text{C}$ identified as optimal conditions. Under these parameters, high PET conversion rates (up to 95.6%) and raw monomer yields (up to 87.4%) were achieved within 2 hours of reaction time. However, the presence of non-PET materials such as PE in multilayers, PA or cotton in postconsumer textiles and rubber in EoL tyre textiles caused the raw monomeric product yield to decrease up to 20% in comparison to monomaterial PET waste.

A novel purification step based on solid–liquid contact and filtration was developed in order to remove dyes and other impurities present in the raw products, and therefore high-purity BHNT monomers were obtained. This step significantly increased the BHNT content to over 90% in mol for all samples according to NMR results. The study highlights the potential for utilizing NPG in the industrial-scale chemical recycling of

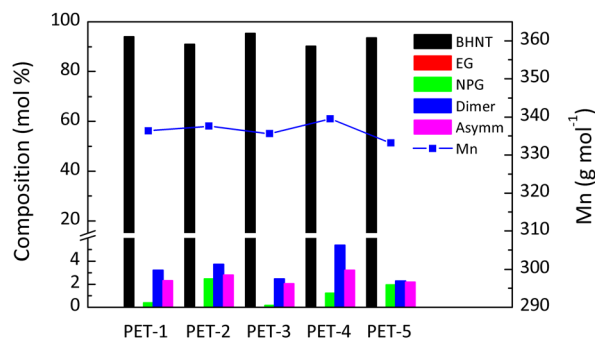


Fig. 9 The molar composition of purified BHNT samples by NMR.



PET, particularly for complex and contaminated waste streams that cannot be mechanically recycled. The production of high-purity BHNT monomers can contribute to the creation of value-added products, enhancing the circularity of PET materials.

In conclusion, the use of NPG for the glycolysis of PET waste represents a promising advancement in chemical recycling technology. This approach not only addresses the recycling of complex PET waste streams but also aligns with the goals of enhancing plastic circularity and reducing environmental impact. Future research should focus on scaling up the process and integrating it into existing industrial operations to fully realize its potential in sustainable waste management and material recovery.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- I. Saputra-Lase, D. Tonini, D. Caro, P. F. Albizzati, J. Cristóbal, M. Roosen, M. Kusenber, K. Ragaert, K. M. Van Geem, J. Dewulf and S. De Meester, *Resour., Conserv. Recycl.*, 2023, **192**, 106916.
- OECD, *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*, ed. S. Agrawala, M. Dubois, P. Börkey and E. Lanzi, OECD Publishing, Paris, 2022.
- S. Shekhar, M. E. Hoque, P. K. Bajpai, H. Islam and B. Sharma, *Environ. Dev. Sustainability*, 2023, **26**, 5629–5664.
- R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, 7.
- European Environment Agency, *Plastics*, <https://www.eea.europa.eu/en/topics/in-depth/plastics>, (accessed June 2024).
- M. W. Ryberg, M. Z. Hauschild, F. Wang, S. Averous-Monnelly and A. Laurent, *Resour., Conserv. Recycl.*, 2019, **151**, 104459.
- Plastic Leak Project*, <https://quantis.com/report/the-plastic-leak-project-guidelines>, (accessed June 2024).
- J. Boucher, G. Billard, E. Simeone and J. Sousa, *The Marine Plastic Footprint*, IUCN, Gland, Switzerland, 2020.
- V. Sinha, M. R. Patel and J. V. Patel, *J. Polym. Environ.*, 2010, **18**, 8–25.
- Plastics Recyclers Europe. PET Market in Europe. State of Play 2022, <https://www.plasticsrecyclers.eu/publications>, (accessed June 2024).
- E. P. Chassignet, X. Xu and O. Zavala-Romero, *Front. Mar. Sci.*, 2021, **8**, 667591.
- L. Bartolome, M. Imran, B. G. Cho, W. A. Al-Masry and D. H. Kim, in *Material Recycling - Trends and Perspectives*, ed. D. S. Achilias, IntechOpen, London, 2012, **2**, 65–68.
- G. Jeya, R. Dhanalakshmi, M. Anbarasu, V. Vinitha and V. Sivamurugan, *J. Indian Chem. Soc.*, 2022, **99**, 100291.
- M. Babaei, M. Jalilian and K. Shahbaz, *J. Environ. Chem. Eng.*, 2024, **12**, 112507.
- B. Geyer, G. Lorenz and A. Kandelbauer, *EXPRESS Polym. Lett.*, 2016, **10**, 559–586.
- E. Mendiburu-Valor, G. Mondragon, N. González, G. Kortaberria, A. Eceiza and C. Peña-Rodríguez, *Polymers*, 2021, **13**, 1461.
- A. Barredo, A. Asueta, I. Amundarain, J. Leivar, R. Miguel-Fernández, S. Arnaiz, E. Epelde, R. López-Fonseca and J. I. Gutiérrez-Ortiz, *J. Environ. Chem. Eng.*, 2023, **11**, 109823.
- A. Aguado, L. Martínez, L. Becerra, M. Arieta-araunabeña, S. Arnaiz, A. Asueta and I. Robertson, *J. Mater. Cycles Waste Manage.*, 2014, **16**, 201–210.
- R. Meys, F. Frick, S. Westhues, A. Sternberg, J. Klankermayer and A. Bardow, *Resour., Conserv. Recycl.*, 2020, **162**, 105010.
- M. Solis and S. Silveira, *Waste Manage.*, 2020, **105**, 128–138.
- A. Asueta, S. Arnaiz, R. Miguel-Fernández, J. Leivar, I. Amundarain, B. Aramburu, J. I. Gutiérrez-Ortiz and R. López-Fonseca, *Polymers*, 2023, **15**, 4196.
- E. Mendiburu-Valor, G. Mondragon, N. González, G. Kortaberria, L. Martin, A. Eceiza and C. Peña-Rodríguez, *Resour., Conserv. Recycl.*, 2022, **184**, 106413.
- N. D. Pingale, V. S. Palekar and S. R. Shukla, *J. Appl. Polym. Sci.*, 2010, **115**, 249–254.
- C. H. Chen, C. Y. Chen, Y. W. Lo, C. F. Mao and W. T. Liao, *J. Appl. Polym. Sci.*, 2001, **80**, 956–962.
- P. K. Roy, R. Mathur, D. Kumar and C. Rajagopal, *J. Environ. Chem. Eng.*, 2013, **1**, 1062–1069.
- G. Colomines, F. Rivas, M. L. Lacoste and J. J. Robin, *Macromol. Mater. Eng.*, 2005, **290**, 710–720.
- E. S. Barboza, D. R. Lopez, S. C. Amico and C. A. Ferreira, *Resour., Conserv. Recycl.*, 2009, **53**, 122–128.
- M. Lu and S. Kim, *J. Appl. Polym. Sci.*, 2001, **80**, 1052–1057.
- A. A. Ovalle-Sánchez, P. Elizondo-Martínez, N. A. Pérez-Rodríguez, E. Hernández-Fernández and M. G. Sánchez-Anguiano, *J. Chil. Chem. Soc.*, 2017, **62**, 4.
- C. Zhu, L. Yang, C. Chen, G. Zeng and W. Jiang, *Phys. Chem. Chem. Phys.*, 2023, **25**, 27936–27941.
- C. Zhu, C. Fan, Z. Hao, W. Jiang, L. Zhang, G. Zeng, P. Sun and Q. Zhang, *Appl. Catal., A*, 2022, **641**, 118681.
- F. Pardal and G. Tersac, *Polym. Degrad. Stab.*, 2006, **91**, 2567–2578.



- 33 A. M. Atta, A. F. El-Kafrawy, M. H. Aly and A. A. Abdel-Azim, *Prog. Org. Coat.*, 2007, **58**, 13–22.
- 34 V. Pimpan, R. Sirisook and S. Chuayjuljit, *J. Appl. Polym. Sci.*, 2003, **88**, 788–792.
- 35 M. Ghaemy and K. Mossaddegh, *Polym. Degrad. Stab.*, 2005, **90**, 570–576.
- 36 A. Carné-Sánchez and S. R. Collinson, *Eur. Polym. J.*, 2011, **47**, 1970–1976.
- 37 I. Duque-Ingunza, R. López-Fonseca, B. de Rivas and J. I. Gutiérrez-Ortiz, *J. Chem. Technol. Biotechnol.*, 2014, **89**, 97–103.
- 38 S. R. Shukla and A. M. Harad, *J. Appl. Polym. Sci.*, 2005, **97**, 513–517.
- 39 I. Olazabal, E. J. Luna-Barrios, S. De Meester, C. Jehanno and H. Sardon, *ACS Appl. Polym. Mater.*, 2024, **6**, 4226–4232.
- 40 I. Amundarain, S. López-Montenegro, L. Fulgencio-Medrano, J. Leivar, A. Iruskietta, A. Asueta, R. Miguel-Fernández, S. Arnaiz and B. Pereda-Ayo, *Polymers*, 2024, **16**, 142.
- 41 X. Zhou, C. Fang, Q. Yu, R. Yang, L. Xie, Y. Cheng and Y. Li, *Int. J. Adhes. Adhes.*, 2017, **74**, 49–56.
- 42 G. Monte, *WIPO*, 2017006217A1, 2017.
- 43 M. Kathalewar, N. Dhopatkar, B. Pacharane, A. Sabnis, P. Raut and V. Bhave, *Prog. Org. Coat.*, 2013, **76**, 147–156.
- 44 BASF to build Neopentyl Glycol plant at Zhanjiang Verbund site in China, <https://www.basf.com/global/en/media/news-releases/2022/10/p-22-374.html>, (accessed June 2024).
- 45 D. Damayanti and H. S. Wu, *Polymers*, 2021, **13**, 1475.
- 46 J. Jiang, K. Shi, X. Zhang, K. Yu, H. Zhang, J. He, Y. Ju and J. Liu, *J. Environ. Chem. Eng.*, 2022, **10**, 106867.
- 47 C. Soares, M. Ek, E. Ostmark, M. Gallstedt and S. Karlsson, *Resour., Conserv. Recycl.*, 2022, **176**, 105905.
- 48 M. Abbasi, M. R. M. Mojtahedi and A. Khosroshahi, *J. Appl. Polym. Sci.*, 2007, **103**, 3972–3975.
- 49 R. Huang, Q. Zhang, H. Yao, X. Lu, Q. Zhou and D. Yan, *ACS Omega*, 2021, **6**, 12351–12360.
- 50 F. Alvarado-Chacon, M. T. Brouwer and E. U. Thoden van Velzen, *Packag. Technol. Sci.*, 2020, **33**, 347–357.
- 51 Y. Geng, T. Dong, P. Fang, Q. Zhou, X. Lu and S. Zhang, *Polym. Degrad. Stab.*, 2015, **117**, 30–36.
- 52 S. Javed, J. Fisse and D. Vogt, *Polymers*, 2023, **15**, 687.
- 53 J. Xin, Q. Zhang, J. Huang, R. Huang, Q. Z. Jaffery, D. Yan, Q. Zhou, J. Xu and X. Lu, *J. Environ. Manage.*, 2021, **296**, 113267.
- 54 K. Kirshanov, R. Toms, P. Melnikov and A. Gervald, *Polymers*, 2022, **14**, 684.
- 55 K. Espinoza-García, R. Navarro, A. Ramírez-Hernández and A. Marcos-Fernández, *Polym. Degrad. Stab.*, 2017, **144**, 195–206.

