Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
e-ISSN 1984-6428

| Vol 10 | | No. 3 | | Special Issue May 2018 |

FULL PAPER

Chemical Recycling of Poly(ethylene terephthalate) (PET) by Alkaline Hydrolysis and Catalyzed Glycolysis

Tânia Marina Palhano Zanela*[a], Edvani Curti Muniz[b], and Carlos Alberto Policiano Almeida[a]

[a]Departamento de Química, Universidade Estadual do Centro-Oeste, 85040-080, Guarapuava, PR, Brazil.
[b]Departamento de Química, Universidade Estadual de Maringá, 87020-900, Maringá, PR, Brazil

Article history: Received: 27 October 2017; revised: 09 February 2018; accepted: 12 February 2018. Available online: 20 May 2018. DOI: http://dx.doi.org/10.17807/orbital.v10i3.1104

Abstract:

The poly(ethylene terephthalate) (PET) is a thermoplastic polyester, non-degradable in the environment with high resistance to chemical and physical agents. Due to the substantial amount of waste generated and accumulated in the environment, chemical recycling of post-consumer PET has been considered the most successful method for polymer recycling. This work presents results of chemical recycling of post-consumer PET via alkaline hydrolysis and glycolysis. The alkaline hydrolysis is considered the most suitable to the green chemistry and this method can be carried out using mild reaction conditions. The process results in a good yield (97%) to terephthalic acid (TPA). The catalyzed glycolysis of post-consumer PET was carried out in a short reaction time and relatively low temperature, with bis (2-hydroxyethyl) terephthalate (BHET) yield of 75%. TPA and BHET were characterized by FTIR and ^{1}H NMR techniques. The analyses proved to be successful in obtaining both products. Therefore, this work contributes to the chemical recycling studies of PET waste and encourages further studies along this research area.

Keywords: poly(ethylene terephthalate); chemical recycling; glycolysis; hydrolysis, bis(2-hydroxyethyl) terephthalate; terephthalic acid

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely commercialized. It is applied in the production of many materials such as textile fibers, copolymers, resins, carpet yarn, PET bottles and packaging films [1,2]. The great industrial importance of PET is due to the extensive application and excellent chemical and physical properties [3]. However, its intensive use and difficulty of degradation leads to accumulation in the environment, making the PET waste management an important social issue. Hence, various alternatives have been sought to minimize the environmental impact caused by the undesirable disposing of the waste of conventional polymers, such as the development of biodegradable plastics, energy recovery, reuse and recycling [4].

Chemical recycling of PET represents an example of the most successful polymer recycling [5]. PET presents functional groups able to react with reagents such as: water, acid or base (hydrolysis), alcohols as methanol (methanolysis), amines (ammonolysis) and glycols (glycolysis) [2, 6, 7].

Besides the environmental purpose, the increasing interest in the chemical recycling of post-consumer PET via hydrolysis is associated with the obtaining of terephthalic acid (TPA) and ethylene glycol (EG) as main products of the reaction [8]. For this reason, PET can be synthesized through these precursors obtained from PET waste, which would contribute with the conservation of fossil fuels. Although the hydrolysis of post-consumer PET is commonly

---

*Corresponding author. E-mail: palhano.tania@hotmail.com

associated with a high cost process due to the application of high temperature and pressure [8], currently many studies from the literature report pathways for the complete depolymerization of post-consumer PET under mild experimental conditions [9–11].

Kosmidis et al. [9], for example, studied the depolymerization reaction of PET post-consumer using the trioctylmethylammonium bromide (TOMAB) catalyst, 5 to 15% w/w sodium hydroxide solutions and temperatures of 70 to 95 °C. Among the parameters evaluated (NaOH concentration, temperature and the catalyst proportion), higher concentrations and temperatures (15% w/w, 95 ºC) promote the depolymerization process. The TOMAB catalyst also positively influenced the process, being the TPA yield of 98%. In order to reduce the costs associated with the process, Fonseca et al. [10] studied obtaining TPA pure from the alkaline hydrolysis of PET post-consumer, applying lower temperatures (70 ºC) in the absence of a catalyst. The yield was approximately 92%.

Likewise, the optimization of the reaction conditions to glycolysis process (temperature, time, PET/EG ratio, PET/catalyst ratio) has been the subject of much research [12, 13], in addition to the development of high efficiency catalysts [2, 14]. Glycolysis is the most widely studied process due to the efficiency and the possibility to apply mild reaction conditions. The process occurs from the molecular degradation of PET by glycols, through transesterification catalysts, where ester bonds are broken and replaced by hydroxyl terminals [5]. Bis (2-hydroxyethyl) terephthalate (BHET) is the major product formed in this reaction. The PET monomer, BHET, can be used in several applications, such as the production of polyurethane coatings [4], unsaturated polyester resin [5,12], unsaturated polyester [16], epoxy resin [17], polymer concrete [17], hydrophobic textile dyes [18] and textile auxiliaries [19].

In this context, it is noticed that recycling plastics, especially poly(ethylene terephthalate), has impressive environmental, economic and social impacts. Among the various options of chemical recycling of PET, the hydrolysis is considered one that really contributes to the environment while the glycolysis is de most widely studied process due to the several applications of BHET. Therefore, the purpose of this work was to study the viability and efficiency of the glycolysis and hydrolysis processes using mild conditions.

2. Material and Methods

Flakes of PET fiber from post-consumer bottles were provided by Plaspet Reciclagem Ltd (Maringá-Paraná, Brazil). The particles of PET, of an average size of 1 x 1 mm, were washed in running water and dried at 60 °C for 12 h in an oven. All the reagents were of analytical grade and used without further purification: ethylene glycol (>99.5%, Biotec), zinc acetate (98.0–101.0%, Perquim), sulfuric acid (98%, Synth), sodium hydroxide (98%, Alphatec).

2.1. Glycolysis process

BHET was obtained by catalyzed glycolysis according to the literature [18, 20], however, a lower temperature and shorter time reaction were used. In a glass reactor were added ethylene glycol (60.0 g) and zinc acetate (1.76 g - 10.0% zinc acetate/PET (w/w)) and heated at 190 °C. Simultaneously, PET (15.0 g) was heated in an oven at the same temperature (190°C) and then, transferred to the reactor. After a reaction time of 1.5 h, the heat was turned off, and boiling water (200mL) was slowly added to the system. The unreacted solid PET was separated using a sieve, and the aqueous solution was filtered through a filter paper. The solution was cooled in an ice bath (at *ca.* 4.0 °C) in order to precipitate BHET. The precipitate was filtered and purified by further washing it in cold water (*ca.* 100 mL) and dried at 50°C in an oven to constant weight. The yield of BHET was calculated by the following equation:

$$\text{Yield of BHET (\%)} = \frac{\text{Moles of BHET produced}}{\text{Moles of PET units}} \text{ x } 100 \quad (1)$$

The Figure 1 shows the scheme for catalyzed glycolysis of PET post-consumer according to the literature [13].

2.2. Hydrolysis process

The TPA was obtained by alkaline hydrolysis based on the literature, but with some methodology adaptations [10, 11]. In the flask was introduced: sodium hydroxide (100 mL, 10.82 mol

L^{-1}), then the solution was heated to 90 ºC and PET flakes (2 g) was transferred to the flask. After 9 hours of reaction, the heat was turned off and the solution was cooled in an ice bath (at *ca.* 5.0 °C). Then, concentrated sulfuric acid was added to the solution in order to neutralize the reaction medium and promote the formation of TPA. The precipitate was filtered and purified by further washing it with water in excess and dried at 100 °C in an oven to constant weight. The TPA yield was calculated by the following equation:

$$\text{Yield of TPA (\%)} = \frac{\text{Moles of TPA produced}}{\text{Moles of TPA theoretical}} \text{ x } 100 \qquad (2)$$

Figure 2 shows a scheme for the alkaline hydrolysis of post-consumer PET according to the literature [9].

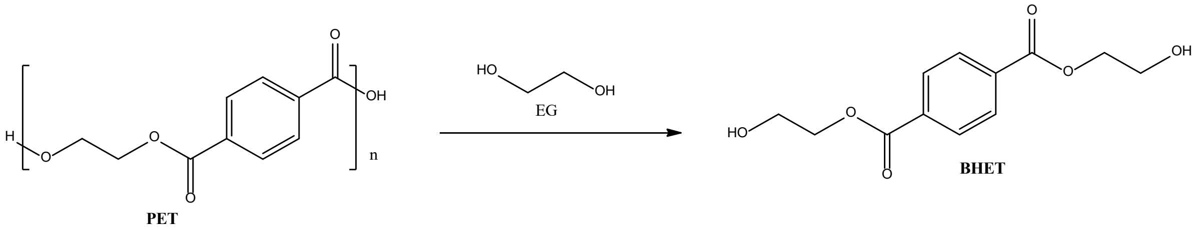

Figure 1. Scheme of catalyzed glycolysis reaction of PET post-consumer**.**

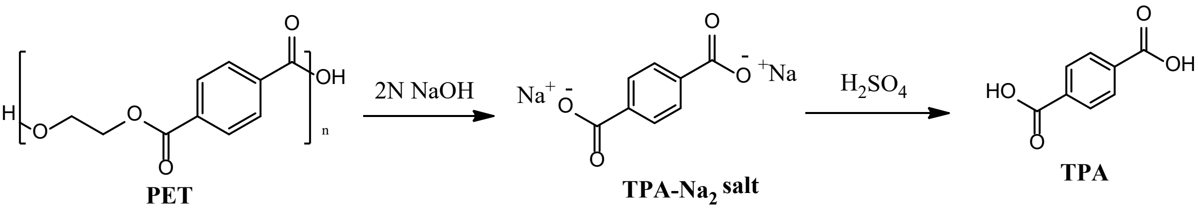

Figure 2. Scheme of alkaline hydrolysis of PET post-consumer.

2.3. Characterizations

The ^{1}H NMR spectra were obtained with a Bruker, model AVANCE III HD, TOPSPIN software 3.2 version, operating at 300 MHz. The samples were obtained using solutions in d$_6$-Ethanol and d$_6$-DMSO (0.015M) and transferred to NMR tubs with 5.0 mm diameter. The FTIR spectra were obtained with a Bruker Vertex 70, with attenuated total reflectance (ATR) operating in transmission mode. Samples were analyzed in the range of 4000 to 400 cm^{-1}, resolution of 4 cm^{-1} and 16 scans. The morphology of the simples were evaluated in a scanning electron microscope, model TM3000, working with a 15kv beam, tungsten filament source, backscattered electron detector with charge reduction vacuum chamber. It was coupled to energy dispersive spectrometer (EDS) (SwiftED3000), with silicon detector type SDD of 30 mm^2 and resolution 161 eV (Cu-Kα) with multichannel analyzer (2048 channels, 10 eV/channel), both of Hitachi brand. The samples were direct placed in an aluminum support

3. Results and Discussion

BHET was obtained by catalytic glycolysis with a yield of 75%. The yield of BHET obtained in this work is high considering the literature. The Table 1 shows a yield comparison among different results found on the literature. Considering the similar catalyst and the mild conditions, this study presents a high yield. The higher yield values are observed to studies, which used high pressure, temperature and/or a novel catalyst. These conditions could increase the BHET yield, but also the process costs.

The FTIR spectrum (Fig. 3) shows characteristic signals of BHET molecule. Bands at 2867 and 2960 cm^{-1} correspond to the absorption peaks of asymmetric and symmetric stretching vibrations of Csp^3-H and Csp^2-H groups, respectively. Bands at 3434 and 3281cm^{-1} are attributed to inter and intrinsically O-H bond vibrations at chain terminations, respectively. The peak at 1132cm^{-1}, related to C-O alcohol bonds, confirms the presence of hydroxyl groups, while the peaks at 1282, 1064 and 1020 cm^{-1} are due to the C-O ester bonds. The peak attributed to carbonyl stretching (C=O) is found at 1721 cm^{-1}. Bands at 1501, 1454 and 720 cm^{-1} correspond to the C=C bonds of the aromatic rings and bands at 1957, 907 and 870 cm^{-1} are related to symmetric p-substitution in the aromatic ring [13].

Table 1. Comparison among BHET yield based on the literature.

Catalyst	Yield (%)	Atmosphere	Temperature (ºC)	Reference
Zinc Acetate	66	Air	196	[20]
Zinc Acetate	85.6	Nitrogen	196	[21]
Zinc Acetate	75	Air	190	This work
Tetragonal $ZnMn_2O_4$ spinel	92.2	Air	260	[22]
(Mg–Zn)–Al LDH	75	Air	190	[7]

In the ^{1}H NMR spectrum, Fig. 4, the singlet at δ 8.16 ppm (s, 4H, H-Ar) (peak d) is attributed to the aromatic hydrogens, suggesting a p-substituted aromatic ring, and the signal at δ 5.31 ppm (peak a) to the protons of hydroxyl groups (s, 2H, H-O). The triplet at δ 4.40 ppm (t, 4H, H-C) (peak c) and the quadruplet at δ 3.86 ppm (m, 4H, H-C) (peak b) are related to the hydrogens of methyl groups closer to the ester, and hydroxyl groups, respectively [22, 23].

TPA obtained by alkaline hydrolysis, presented a yield of 97%. The TPA yield presents in this work was compared with different results found on the literature and it is shown in the Table 2. Considering the similar catalyst and the mild conditions, this study presents a high yield, being that the TPA yield obtained in this work resembles the yield obtained by the Karayannidis et al. [24] study, however the temperature used in this work was more than 2 times lower. The higher yield values are observed to studies, which used high pressure, temperature and/or a novel catalyst. These conditions could increase the TPA yield, but also the process costs.

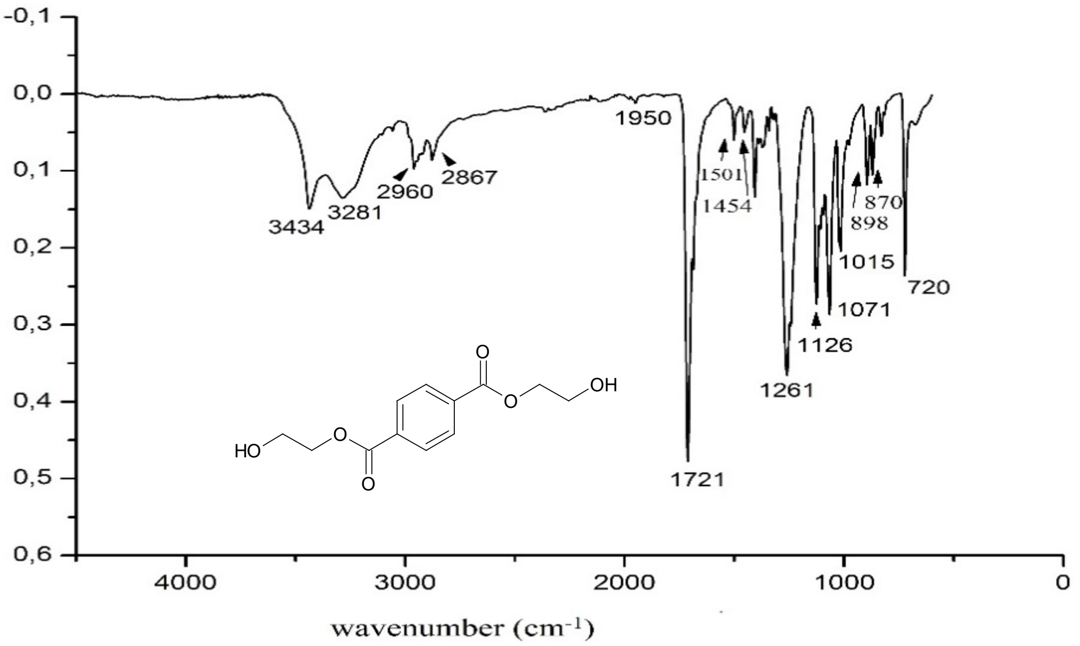

Figure 3. FTIR spectrum of BHET.

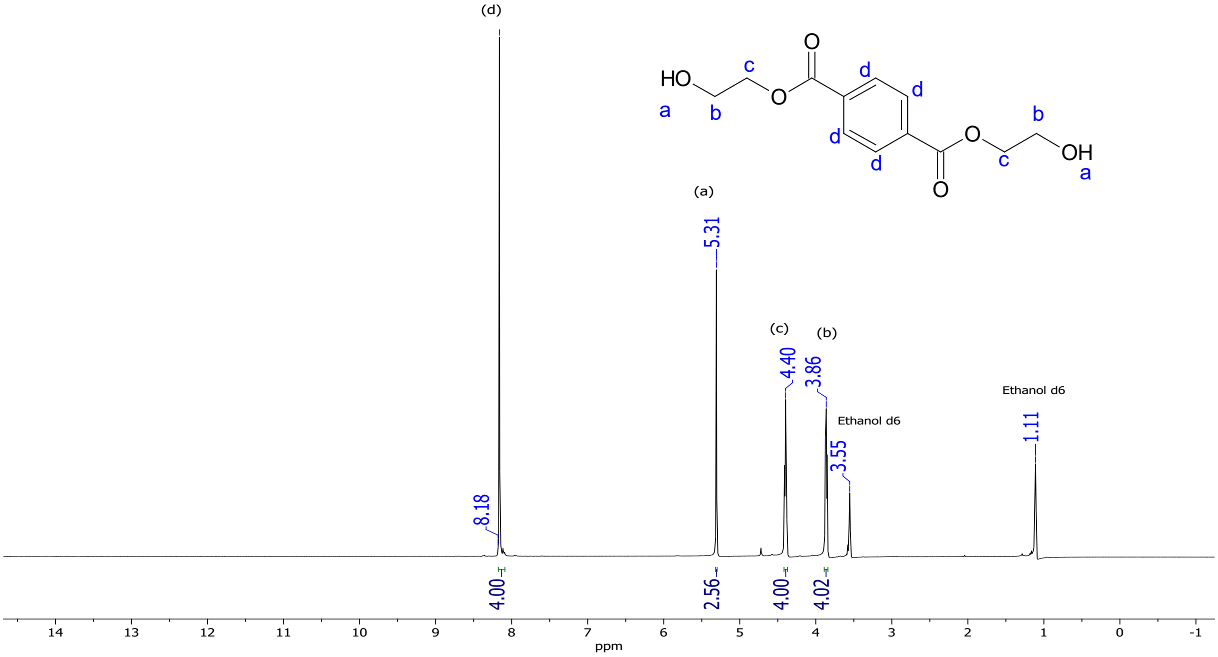

Figure 4. ^{1}H NMR spectrum of BHET.

Table 2. Comparison among BHET yield based on the literature.

Catalyst	Yield (%)	Temperature (ºC)	Time (h)	Reference
No used	97.9	200	1	[24]
No used	92.37	70	9	[10]
No used	97	90	9	This work
Cyclohexylamine	85.12	90	2	[25]
TOMAB	93	80	1	[26]
Ethanol as co-solvent	89	110	0.5	[27]

FTIR (Fig. 5) and ^{1}H NMR (Fig. 6) analyses were used to confirm the TPA. Fig. 5 present bands at 1580, 1430 and 784 cm^{-1} characteristics of C=C bonds of the aromatic rings whereas bands at 1960, 946 and 882 cm^{-1} are related of the deformation vibrations of the 1,4-disubstituted ring. Band at 1690 cm^{-1} characterizes the axial deformation vibrations of the C=O groups, whereas the wide band from 3330 to 2130 cm^{-1} is attributed to vibrations of the carboxylic acid (-COOH group) [10, 28].

The morphology and chemical composition analysis are obtained by SEM and EDS techniques and are shown in the Fig. 7. The morphologic characterization is important criterion, which can determine the material application and it is not a common characterization technic used for PET monomers. The Figure 3 shows SEM images of the PET, BHET and TPA. Fig 7 (a) reveals a PET uniform structure and smooth surface [29]. Fig. 7 (b) reveals a BHET microstructure and its habit layered typical [13], whereas Fig. 7 (c) reveals a TPA amorphous and fibrous structure [29]. The EDS (Fig. 7(b)) shows the organic composition of the simples, being composed by carbon and oxygen. According the EDS data, the simples are composed entirely of carbon and oxygen shows the total consumption of both the catalyst and the solvent and / or reagent used in the chemical recycling process of the PET post-consumer.

The ^{1}H NMR spectrum (Fig. 6) shows characteristic signals of chemical shifts at 8.02 ppm (s, 4H, H-Ar) (peak a) corresponding to hydrogens of the aromatic ring, and 13.24 ppm (s, 2H, -OH) (peak b) corresponds to the hydrogen of the hydroxyl group. [10].

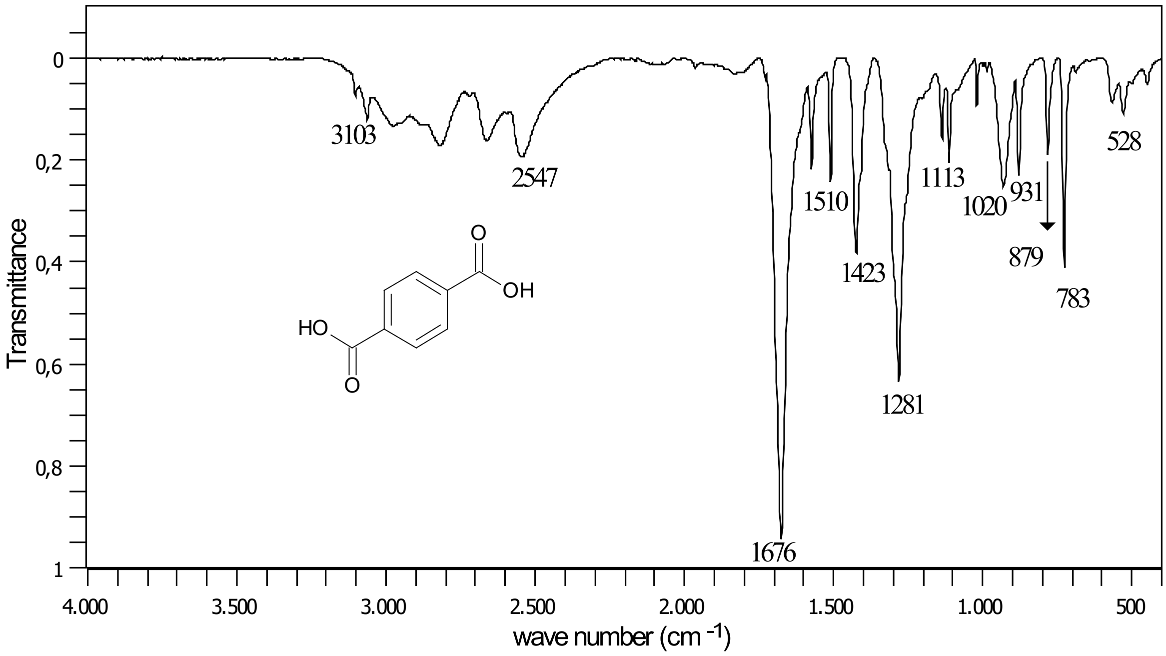

Figure 5. FTIR spectrum of TPA.

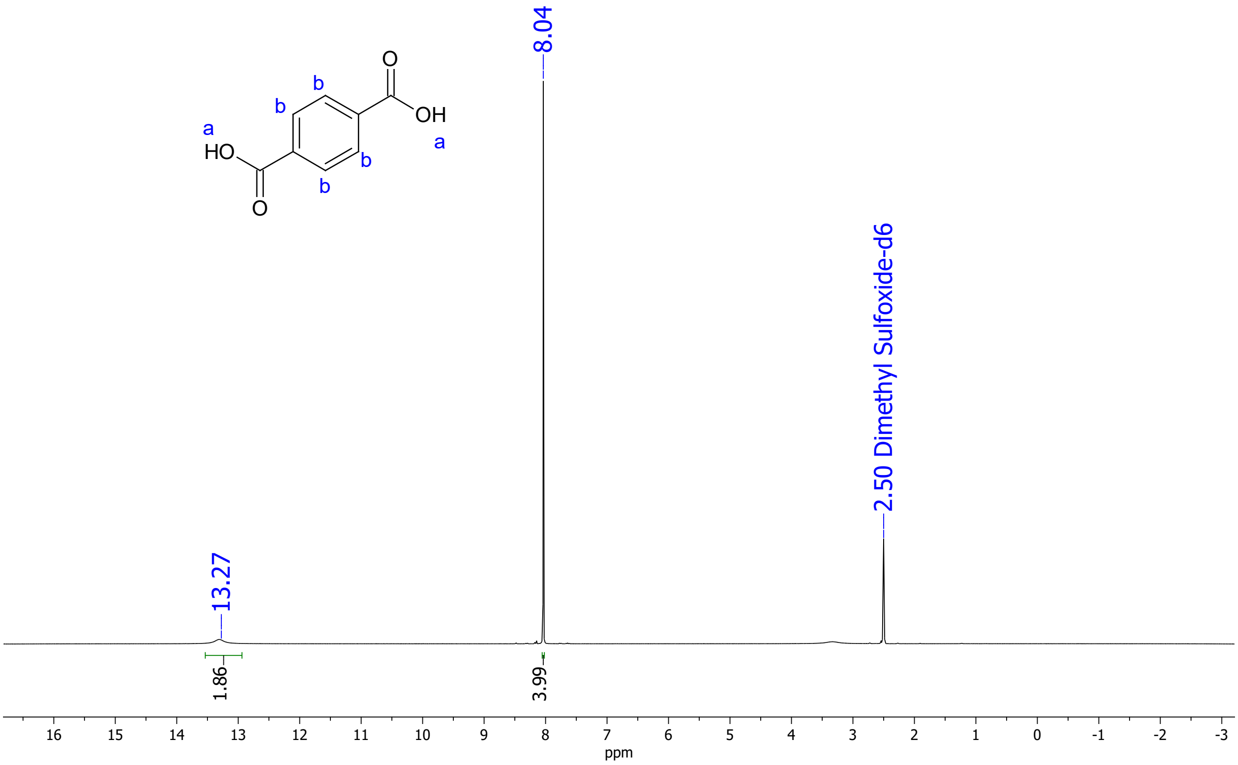

Figure 6. ^{1}H NMR spectrum of TPA.

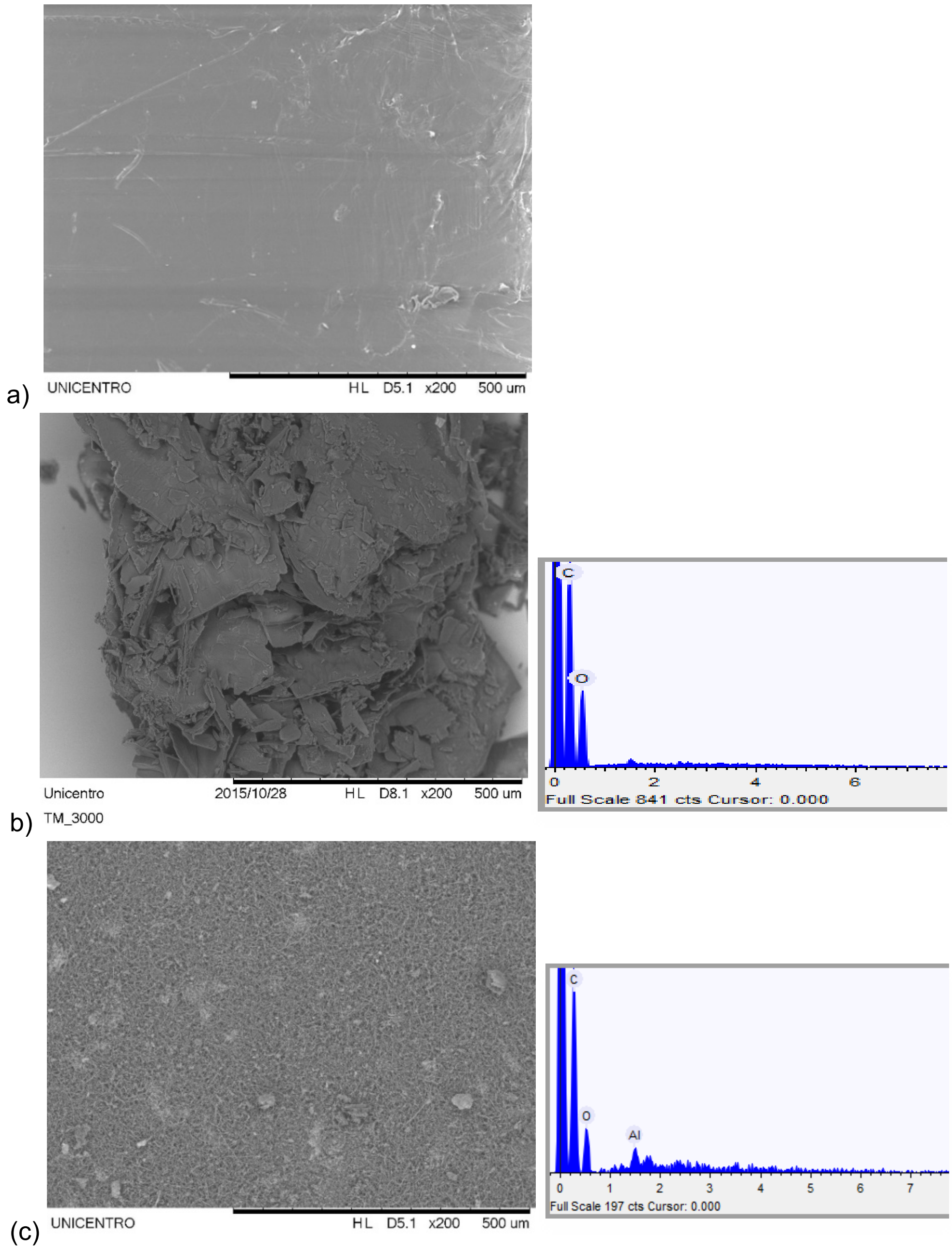

Figure 7. Scanning electron microscopy for PET (a), BHET (b) and TPA (c) at 500 µm.

4. Conclusions

In the present work, alkaline hydrolysis and glycolysis chemical recycling of PET were carried out in order to analyze the viability and efficiency of both processes. Chemical recycling of PET bottle waste was carried out by the catalyzed glycolysis and alkaline hydrolysis to produce BHET and TPA, respectively, as confirmed by FTIR and ^{1}H NMR analyses. Both products presented good yields (70 and 86% to BHET and TPA, respectively) which highlight the viability of the chemical recycling.

The catalyzed glycolysis of post-consumer PET was performed in 1.5 hours and at 190 ºC. Thus, glycolysis was considered efficient for PET bottle waste chemical recycling, since it can be conducted at atmospheric pressure and relatively mild operating conditions when is compared with other methods. Similarly, the alkaline hydrolysis is a process that uses mild reaction conditions, temperature of 90 ºC and aqueous solution to promote the scission of the polymer chain. The TPA presented purity and high yield, being a promising process to obtain PET precursor, which contributes with the environment and the conservation of fossil fuels.

The SEM and DLS results can be used to infer the complete depolymerization, since the PET morphology is crystalline and its monomers present an amorphous morphology. In addition, they are composed by carbon and oxygen, since the monomers are organic compounds. Therefore, this work contributes to the chemical recycling studies and encourages further studies along this research area. In addition, it has demonstrated that both possibilities of recycling of post-consumer PET are viable since they can be carried out in mild conditions.

Acknowledgments

The authors are grateful to Capes for the financial support as well as Rodrigo Pereira, Paulo Souza for the FTIR and ^{1}H NMR analyses.

References and Notes

[1] Singh, N.; Hui, D.; Singh, R.; Ahuja, I. P. S.; Feo, L.; Fraternali, F. *Compos. Part B Eng.* **2017**, 115, 409. [Crossref]

[2] Yue, Q. F.; Wang, C. X.; Zhang, L. N.; Ni, Y.; Jin, Y.X. *Polym. Degrad. Stab.* **2011**, 96, 399. [Crossref]

[3] Bartolome, L.; Imran, M.; Cho, B. G.; Al-Masry, W. A.; Kim, D. H. *Mater. Recycl. - Trends Perspect.* **2012**, 65. [Crossref]

[4] Patel, M. R.; Patel, J. V.; Sinha, V. K. *Polym. Degrad. Stab.* **2005**, *90*, 111. [Crossref]

[5] Karayannidis, G. P.; Achilias, D. S.; Sideridou, I. D.; Bikiaris, D. N. *Eur. Polym. J.* **2005**, *41*, 201. [Crossef]

[6] Wang, S.; Wang, C.; Wang, H.; Chen, X.; Wang, S. *Polym. Degrad. Stab.* **2015**, **114**, *105*. [Crossref]

[7] Eshaq, G.; Elmetwally, A. E. *J. Mol. Liq.* **2016**, *214*, 1. [Crossref]

[8] Al-Sabagh, A. M.; Yehia, F. Z.; Eshaq, G.; Rabie, A. M. A.; ElMetwally, E. *Egypt. J. Pet.* **2016**, *25*, 53. [Crossref]

[9] Kosmidis, V. A.; Achilias, D. S.; Karayannidis, G. P. *Macromol. Mater. Eng.* **2001**, *286*, 640. [Crossref]

[10] Fonseca, T. G.; de Almeida, Y. M. B.; Vinhas, G. M. *Polímeros* **2014**, *24*, 567. [Crossref]

[11] Spaseska, D.; Civkaroskao, M. *J. Univ. Chem. Technol. Metall.* **2010**, *45*, 379.

[12] Duque-Ingunza, I.; López-Fonseca, R.; de Rivas, B.; Gutiérrez-Ortiz, J. I. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 97. [Crossref]

[13] Stoski, A.; Viante, M. F.; Nunes, C. S.; Muniz, E. C.; Felsner, M. L.; Almeida, C. A. P. *Polym. Int.* **2016**, *65*, 1024. [Crossref]

[14] de Castro, A. M.; Carniel, A. *Biochem. Eng. J.* **2017**, *124*, 64. [Crossref]

[15] Auvergne, R.; Saint-Loup, R.; Joly-Duhamel, C.; Robin, J. J.; Boutevin, B. *J. Polym. Sci. Part A Polym. Chem.* **2007**, *45*, 1324. [Crossref]

[16] Tong, S.; Chen, D.; Chen, C.; Chung, L. *Polym. J.* **1983**, *24*, 469. [Crossref]

[17] Abdel-Azim, A. M.; Abdel-Azim A.; Atta. *Polym. J.* **1997**, *29*, 21. [Crossref]

[18] Shukla, S. R.; Harad, A. M.; Jawale, L. S. *Polym. Degrad. Stab.* **2009**, *94*, 604. [Crossref]

[19] Shukla, S. R.; Harad, A. M.; Jawale, L. S. *Waste Manag.* **2008**, *28*, 51. [Crossref]

[20] López-Fonseca, R.; Duque-Ingunza, I.; de Rivas, D.; Arnaiz, S.; Gutiérrez-Ortiz, J. I. *Polym. Degrad. Stab.* **2010**, *95*, 1022. [Crossref]

[21] Xi, G.; Lu, M.; Sun, C. *Polym. Degrad. Stab.* **2005**, *87*, 117. [Crossref]

[22] Imran, M.; Kim, D. H.; Al-Masry, W. A.;Mahmood, A.; Hassan, A.; Haider, S.; Ramay, S. M. *Polym. Degrad. Stab.* **2013**, *98*, 904. [Crossref]

[23] Imran, M.; Kim, B. K.; Han, M.; Cho, B. G.; Kim, D. H. *Polym. Degrad. Stab.* **2010**, *95*, 1685. [Crossref]

[24] Karayannidis, G. P.; Chatziavgoustis, A. P.; Achilias, D. S. *Adv. Polym. Technol.* **2002**, *21*, 250. [Crossref]

[25] Mishra, S.; Goje, A. S. *Polym. React. Eng.* **2003**, *11*, 963. [Crossref]

[26] Polk, M. B.; Leboeuf, L. L.; Shah, M.; Won, C.-Y.; Hu, X.; Ding, W. *Polym. Plast. Technol. Eng.* **1999**, 38, 459. [Crossref]

[27] Yamashita, M.; Mukai, H. *Sci. Eng. Rev. Doshisha Univ.* **2011**, *52*, 51.

[28] Mancini, S. D.; Zanin, M. *Polímeros Ciência e Tecnol.* **2002**, *12*, 34. [Crossref]

[29] Li, X.-K.; Lu, H.; Guo, W. -Z.; Cao, G. -P.; Liu, H. -L.; Shi, Y.-H. *AIChE J.* **2015**, *61*, 2004. [Crossref]