

Depolymerization of Poly(ethylene terephthalate) Wastes Using Ethanol and Ethanol/Water in Supercritical Conditions*

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ABSTRACT: Chemical recycling of poly(ethylene terephthalate) (PET) in supercritical ethanol has been investigated. In the presence of water, under supercritical conditions (temperature and pressure above 516 K and 6,384 kPa, respectively) excess ethanol reacts with PET to form diethyl terephthalate (DET) as the main product. A laboratory-made 0.1 L-batch reactor was used at 528 K under pressures from 7,600 and 11,600 kPa. After the required reaction times, the reaction products were analyzed by reverse phase high pressure liquid chromatography and nuclear magnetic reso-

nance. It was found that PET is completely depolymerized into monomers in about 5 h. The influences of water, pressure, ethanol/PET weight ratio, PET sources, as well as depolymerization time were investigated. Maximum DET recovery yield was 98.5%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2009–2016, 2006

Key words: poly(ethylene terephthalate); supercritical ethanol; diethyl terephthalate; depolymerization; chromatography

INTRODUCTION

Over recent years, environmental concerns have received a great deal of attention and green processing has been the issue of several discussions.^{1–3} As industrial sustainable development programs are under pressure due to globalization and the changes of many traditional markets, the chemical industry plays a key support role in the world economy.⁴

Plastic has an excellent performance over other packing materials like glass, and wood. The growing interest in poly(ethylene terephthalate) (PET) recycling is due to its widespread and increasing use in packaging, mainly since the mid 70s as a consequence of its use in the production of soft drink bottles.⁵ A further increase in this application is predicted.^{6,7} However, plastic waste has been under mounting environmental pressure, and recovery and recycling

seem to be the best alternatives to minimize its hazards.

Postconsumer PET bottles are mainly mechanically recycled into textiles, carpets, and plastic sheets. Nevertheless, mechanical processing results only in low-grade material.⁸ Pyrolysis is another technique commonly used to degrade polymers, yet, it presents some disadvantages such as nonuniform heat transfer, low final product yields, and excessive formation of char and gases.^{9,10} In contrast, as chemical recycling or depolymerization involves treating waste materials and recovering their monomers, it enables monomer repolymerization and the production of virgin polymers from recycled materials.¹¹ An additional advantage over mechanical recycling processes is that chemical processes can be applied to low-grade mechanically recycled materials.¹² Moreover, chemical recycling has also been proposed to mitigate some of the above-mentioned problems associated with pyrolysis.¹¹

Chemical PET recycling was started in the 50s, nearly in parallel to its commercial-scale manufacture.¹¹ Initially, chemical recycling found application as a way to use PET production waste. Nowadays, this technology is spread and targeted on postconsumer PET.

Condensation polymers can be depolymerized by solvolytic chain cleavage reactions. Several techniques have been extensively studied, especially those using

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catalytic reactions. The catalysts most frequently studied are basic, acid,^{13,14} and metal salts.^{15–17} Processes involving the depolymerization of PET in supercritical conditions were first used in Japan in 1997 by Adschiri et al.,¹⁸ who depolymerized PET using supercritical water, and Sako et al.,¹⁹ using supercritical methanol.

Supercritical fluids are very attractive media for conducting chemical transformations,²⁰ mainly because the solvent and transport properties of a single solution can be appreciably and continuously varied with relatively minor changes in either temperature or pressure.²¹ The variation of the supercritical fluid density also influences the chemical potential of solutes, and thus, reaction rate and equilibrium constant.^{22,23}

Although methanolysis has been extensively studied in recent years,^{19,24–26} to the best of our knowledge, this is the first study on the use of ethanolysis as a PET depolymerization method. This study represents a new alternative for the recycling industry, especially for the Brazilian industry, since sugarcane ethanol is abundant and relatively cheap in Brazil. In this work, a series of experiments were conducted to develop and understand PET depolymerization by supercritical ethanol, particularly to determine the effects of water, pressure, ethanol/PET weight ratio, postconsumer PET sources as well as the time required for complete PET depolymerization.

MATERIALS AND METHODS

Different PET sources have been used, green and colorless PET bottles, polyester strings, and mechanically recycled PET fibers. Degradation reaction was carried out in a 0.1-L laboratory-made batch-type reactor made of stainless steel 316® equipped with inlet and outlet valves, a manometer, a thermometer, and fit with a heating collar controlled by a programmable temperature controller used to heat the reactor to the required temperature. The reaction temperature used was 528 K. The precision of the reactor temperature was estimated to be ± 5 K. Temperature was measured by a J-type thermocouple.

For the experiments, specific amounts of PET, anhydrous ethanol abs p.a., CAS ISO Merck, and distilled water were charged into the reactor at room temperature. Then, the vessel and its contents were heated (at about 8 K/min) to a reaction temperature of 528 K. Reactor pressure was attained by varying the initial amount of solution so that pumping pressurized gas was not necessary. Reactions were carried out using initial pressures ranging from 11,400 to 16,500 kPa. After the required reaction time, the heating collar was removed, and the vessel was quenched to room temperature using large amounts of fresh water. It took less than 5 min to cool down the reaction system to room temperature (around 298 K).

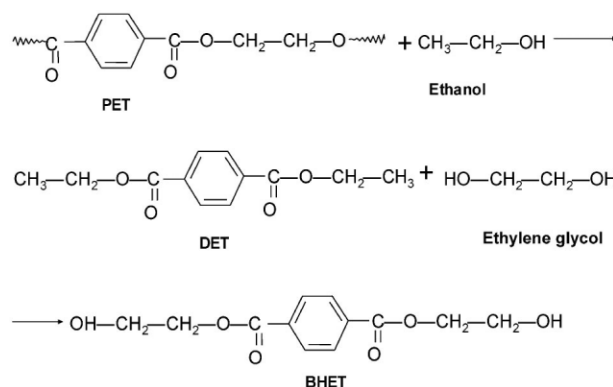


Figure 1 Reaction of depolymerization of PET in supercritical ethanol.

After each run, the reaction products collected from the vessel and their amounts were determined using reverse phase high-performance liquid chromatography (RP-HPLC) and identified by proton nuclear magnetic resonance (¹H NMR). RP-HPLC analysis was performed using a Varian 240 apparatus equipped with a reverse-phase C18-varian column and a Varian 330 ultraviolet detector set at 240 nm. An 80:20 (V/V) methanol/water solution was used as a mobile phase with a flow rate of 1 mL/min and column temperature of (298 K). Diethyl terephthalate (DET) was quantified through external standard method, (DET, purity 98%, Acros Organics, CAS 636–09-9). External standard solutions were prepared within the concentration range of 0.05–1.00 mg/mL. A sample solution with an estimated concentration of 0.05–1.00 mg/mL was prepared for HPLC analysis by diluting the reaction product in methanol (HPLC grade CAS 67–56-1) as a solvent.

Samples were dried and powdered before ¹H NMR analysis. All ¹H NMR spectra were obtained on a Varian spectrometer model Oxford 300 operating at 300 MHz. The angle pulse and the relaxation time used to obtain ¹H NMR spectra were fixed at 45° and 1.36 s, respectively. Sample temperature in ¹H NMR experiments was maintained at 298 K. Tetramethylsilane was used as an internal reference. Chemical shift was given in ppm. The solvent used was acetone-*d*₆.

RESULTS AND DISCUSSION

The products obtained from the depolymerization of PET in supercritical ethanol were mainly DET, and either ethylene glycol (EG) or bis(2-hydroxyethyl) terephthalate (BHET), as shown in Figure 1. In addition, it was also possible to obtain by-products like ethyl-(2-hydroxy-ethyl) terephthalate (EHET), dimers, and oligomers. Following the reaction presented in Figure 1, in which DET is formed as a main product, it can be

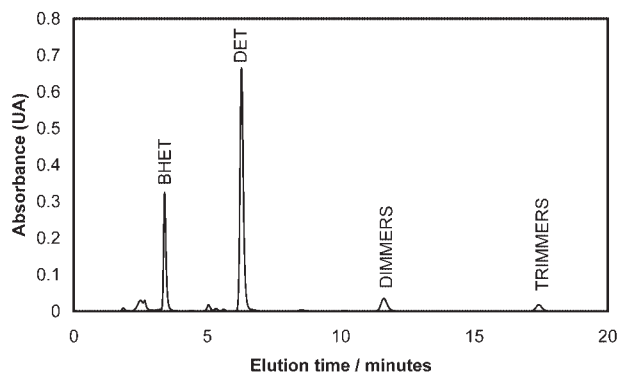


Figure 2 HPLC spectrum of the products of the 5-h reaction at 528 K and 11,600 kPa using 61 mL of anhydrous ethanol and 1 g of PET.

seen that each ester linkage uses one ethanol molecule and creates ethyl end-groups to form DET.

Effect of water on reaction environment

It was investigated whether the presence of water affects the chemical depolymerization environment in

supercritical ethanol. Reactions using anhydrous ethanol or by adding either 1 or 5 mL of water were investigated. The chromatogram in Figure 2, obtained after 5 h of reaction using 61 mL of anhydrous ethanol and 1 g of PET shows the presence of dimers even after the reaction time. The obtained products were also identified through ^1H NMR. After 5 h of reaction, it was possible to identify six different ^1H NMR spectrum signals, which were attributed to the three structures shown in Figure 3. The four aromatic ring hydrogens identified as number 1, showed the signal at δ 8.1 ppm. The hydrogens in the DET ethyl group, numbered 2 and 3, showed the signals at δ 4.3 and δ 1.39 ppm, respectively. The two triplets, numbered 4 and 5, refer to the hydrogens in the BHET ethylene group. Hydrogen signals of DET and BHET aromatic ring were too close to be identified separately. The signal 6 at δ 4.9 ppm was attributed to the $-\text{CH}_2-\text{CH}_2-$ group present in the oligomer structure, and the signal at $\delta = 2.1$ ppm to acetone ($\text{C}_3\text{H}_6\text{O}$) in the $\text{C}_3\text{D}_6\text{O}$ solvent.

Figure 4 shows end-product chromatograms obtained after 5.0, 5.5, and 6.5 h of reaction carried out

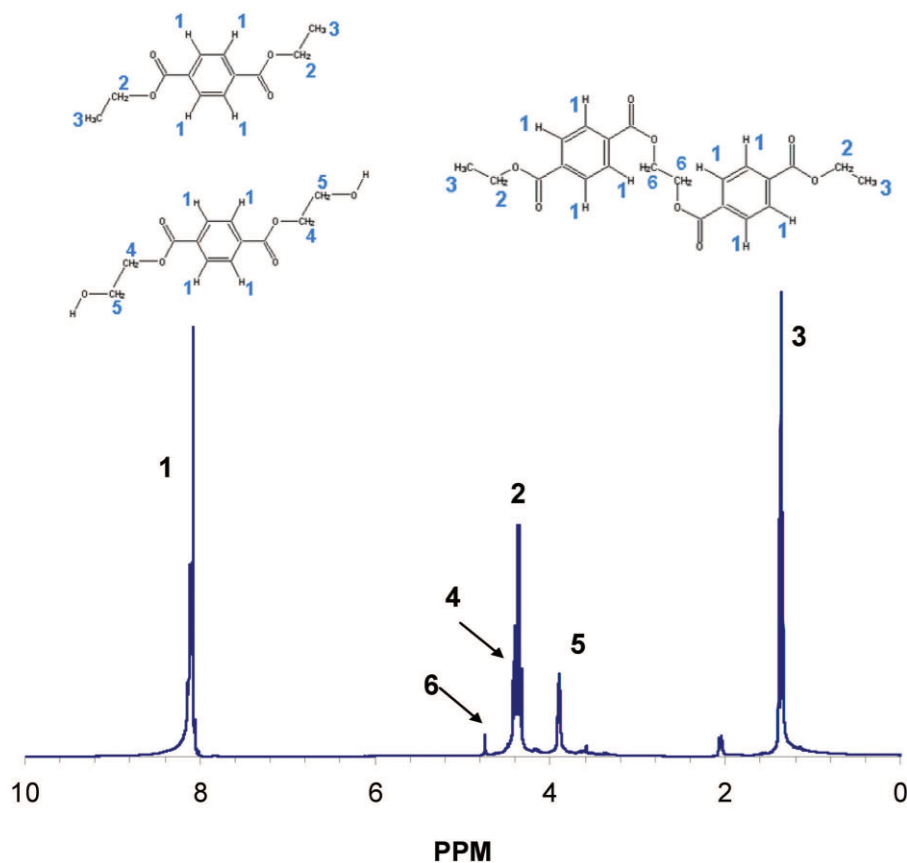


Figure 3 ^1H NMR spectrum run in $\text{C}_3\text{D}_6\text{O}$ of the products of the 5-h reaction at 528 K and 11,600 kPa using 61 mL of anhydrous ethanol and 1 g of PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

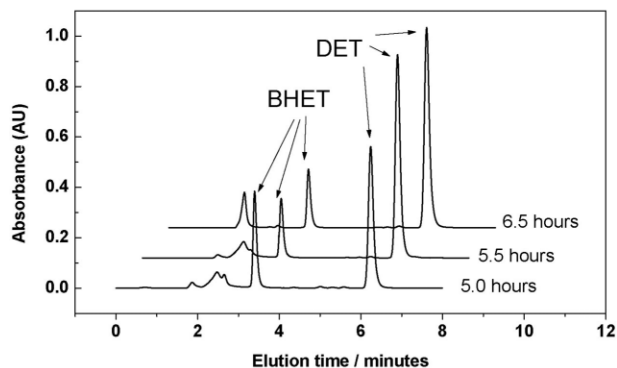


Figure 4 HPLC spectra of the products obtained with different reaction times (5.0, 5.5, and 6.5 h) at 528 K and 11,600 kPa using 60 mL of ethanol, 1 mL of water and 1 g of PET.

using 60 mL of ethanol, 1 mL of water, and 1 g of PET. In Figure 4, only monomers, DET and BHET can be observed after 5 h of reaction. However, after 5.5 h of reaction, the amount of BHET decreased and did not change up to 6.5 h of reaction. In addition, the amount of DET obtained after 5.5 h of reaction was larger than that obtained after 5 h and it did not change up to 6.5 h. On the basis of these results, it can be stated that the reaction practically finishes after 5.5 h, when the equilibrium $\text{DET} + \text{EG} \rightleftharpoons \text{BHET}$ is reached. Also, it can be pointed out that adding small amounts of water affects the reaction environment and accelerates PET depolymerization.

After 5 h of reaction at 528 K and initial pressure of 11,600 kPa using 1 g of PET and 60 mL of ethanol plus 1 mL of water, it was possible to identify five different

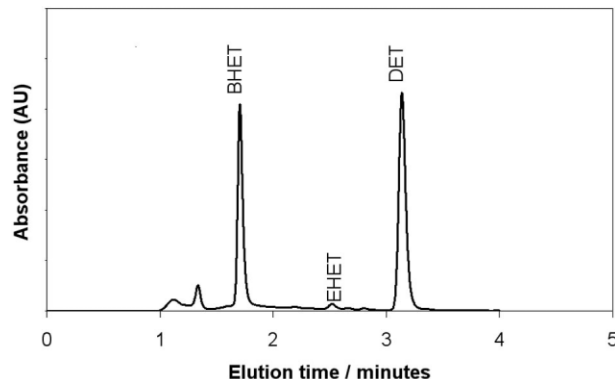


Figure 6 HPLC spectrum of the product of the 5-h reaction at 528 K and 11,600 kPa using 54 mL of ethanol, 5 mL of water, and 1 g of PET.

^1H NMR spectrum signals, which were attributed to the two structures shown in Figure 5. The four aromatic ring hydrogens identified as number 1, showed the signal at δ 8.1 ppm. The hydrogens in the DET ethyl group, numbered 2 and 3, showed the signals at δ 4.3 and δ 1.39 ppm, respectively. Finally, the two triplets in the input in the figure, numbered 4 and 5, refer to the hydrogens in the BHET ethylene group. Hydrogens signals of DET and BHET aromatic ring were too close to be identified separately.

A chromatogram of the product of the 5-h reaction carried out using 5 mL of water, 54 mL of ethanol, and 1 g of PET is shown in Figure 6. For these amounts of water and ethanol, the pressure in the reactor vessel reached 11,600 kPa when heated to 528 K. Figure 6 shows that the product is constituted mostly by BHET

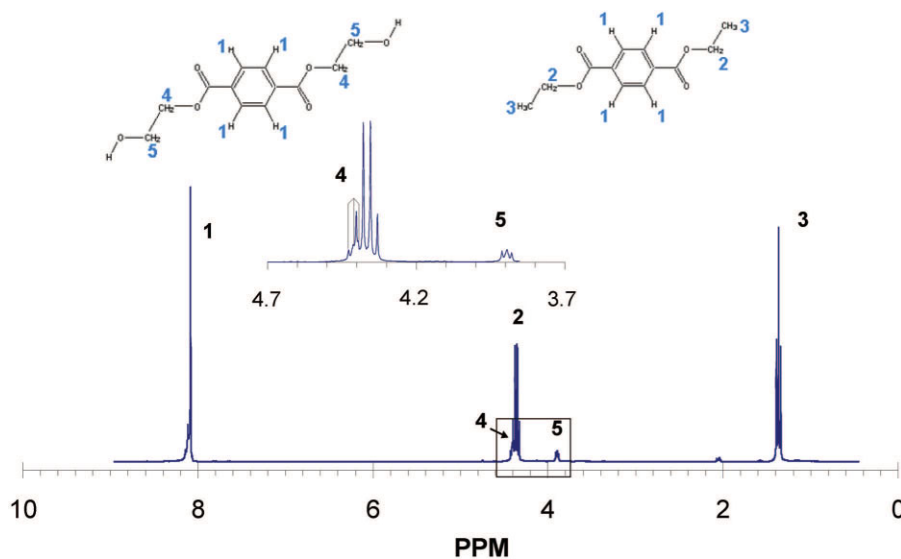


Figure 5 ^1H NMR spectra run in $\text{C}_3\text{D}_6\text{O}$ of the products obtained after 5-h reaction at 528 K and 11,600 kPa using 60 mL of ethanol 1 mL of water and 1 g of PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

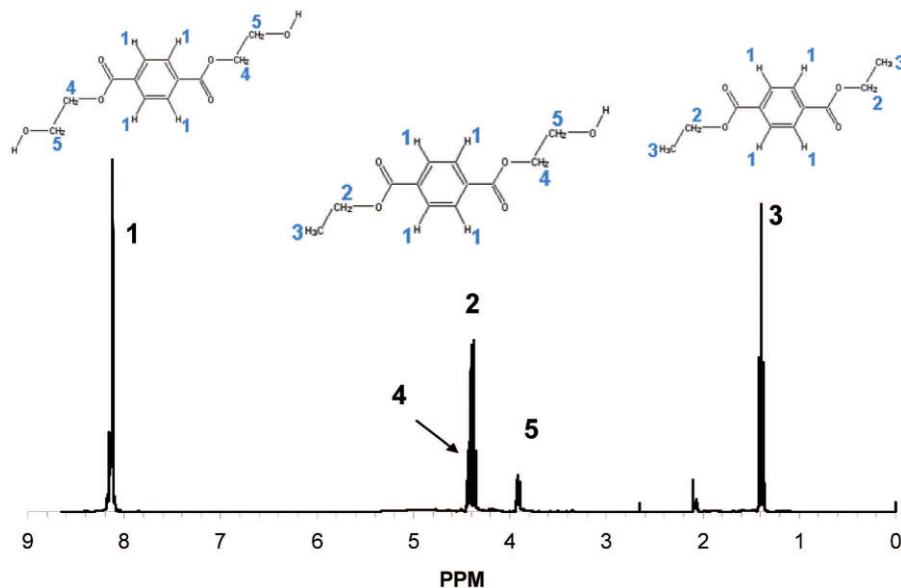


Figure 7 ^1H RMN spectrum run in $\text{C}_3\text{D}_6\text{O}$ of the products of the 5-h reaction at 528 K and 11,600 kPa using 54 mL of anhydrous ethanol, 5 mL of water, and 1 g of PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and DET. However, it was possible to identify a small amount of EHET. The H^1 NMR spectrum of the reaction product presented in Figure 7 confirms the presence of DET, BHET, and EHET. It should be noticed that no signal appears at δ 4.9 ppm, which is indicative of the absence of oligomers after 5 h of reaction. Therefore, it is possible to conclude that small amounts of water change the reaction environment and raises the reaction rate, while large amounts of water tend to produce more hydroxyl-containing products like BHET and EHET.

Akiya and Savage²⁷ asserted that in high-temperature chemical reactions, water can participate in elementary reaction steps as a catalyst. Examples include water as a source of either an acid or a base catalyst, and as a catalyst that modifies and stabilizes transition states. Takahashi et al.²⁸ investigated the catalytic role of water molecules in the oxidation of ethanol and proposed that water modifies the transition states of ethanol molecule, which leads to a decrease in the reaction potential energy barrier, and consequently to an increase in reaction rate constant.

Effect of pressure

To investigate the influence of reaction pressure, experiments were carried out under initial pressures 11,400 and 16,500 kPa (reaching final pressure among 7,600 and 11,600 kPa). The observed pressure was attained by varying the initial amount of solution in the vessel. In this way, heating the vessel filled with 54 mL of ethanol and 0.9 mL of water at 528 K the final

7,600 kPa was achieved, while with 60 mL of ethanol and 1 mL of water, the pressure rose to 9,650 kPa at the same temperature. Figure 8 shows the chromatograms of products obtained under each of these two final pressures. It was observed that the same products were obtained at either 7,600 or 11,600 kPa and 528 K, and that the change in DET yield was not significant. Based on these results, we can conclude that if the pressure is maintained between these two levels at 528 K, no influences on supercritical ethanol PET depolymerization are observable.

Effect of PET/ethanol ratio

The effect of PET/ethanol ratio on depolymerization at 528 K and 11,600 kPa for a 5-h reaction time was

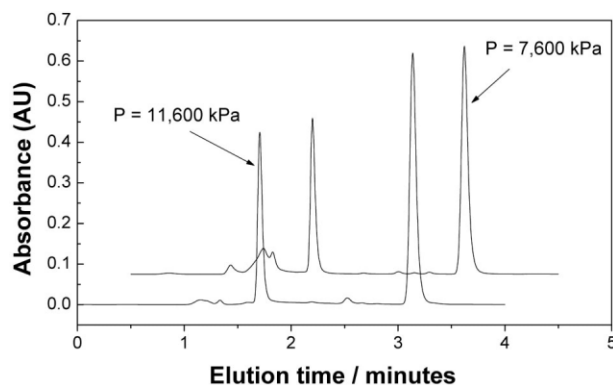


Figure 8 HPLC spectra of the products after 5-h of reaction at 7,600 kPa and 11,600 kPa.

TABLE I
DET Yield for Varying Reaction Conditions and PET Amounts

Ethanol (mL)	Water (mL)	PET (g)	Initial pressure (kPa)	Final pressure (kPa)	Amount of obtained DET (g)	Yield (%)
60	1.0	1	11,600	11,600	0.74	64
54	0.9	5	11,400	9,650	3.53	61
54	0.9	10	11,600	7,600	7.41	64
60	1.0	15	16,500	9,650	11.44	66

investigated. Table I summarizes the results. Since ethanol is the solvent responsible for the increase in the pressure inside the vessel and considering that ethanol is consumed during reaction to form DET, the pressure inside the vessel decreases during reaction. Table I shows the initial and final pressure in the vessel for varying ethanol/PET ratios. It is worth recalling that, as previously mentioned, pressure does not affect either BHET or DET yields. Table I also shows the amount of DET produced (values obtained through HPLC). Yields were calculated considering the theoretical reaction values that would result in 100% DET under stoichiometric molar mass balance. DET yield was not significantly influenced by the PET/ethanol ratio. In addition, Figure 9 shows that oligomers were not found among the reaction products. These results indicate that even though the ethanol/PET ratio affects pressure, it does not influence the reaction products obtained.

The effect of different kinds of PET

We have also investigated depolymerization of different PET sources, namely, polyester strings, green and colorless PET bottles, and fibers obtained from me-

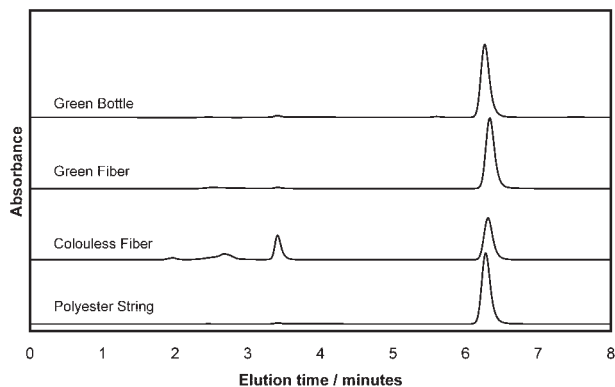


Figure 9 HPLC spectra of the products of the 5-h reaction at 528 K and 11,600 kPa using 60 mL of ethanol, 1 mL of water, and 1 g of different kinds of PET obtained from (A) green bottles, (B) mechanically recycled green bottles, (C) mechanically recycled colorless bottles, and (D) polyester string.

chanically recycled PET soft drink bottles. Recycled PET fibers are used by industry as pillow, mattress, and teddy-bear stuffing, while polyester strings are used in the textile industry. Table II and Figure 9 summarize depolymerization results. Depolymerization was performed using 1 g of polymer under initial pressure of 11,600 kPa at 528 K. Figure 9(A) shows the chromatogram of depolymerized green bottle PET. Comparing the chromatograms of colorless [Fig. 9(C)] and green bottle PET, it can be seen that green bottle PET depolymerization produces more DET than BHET. Moreover, Table II shows that green bottle PET yields about DET 94.2%. This value is much higher than that of colorless bottle PET, 64%, Table I. By comparing Figures 9(B) and 9(C), it can be seen that much more DET is produced using green fibers than colorless ones. These results indicate that the green dye incorporated into PET favors DET formation under supercritical ethanol depolymerization.

In an attempt to explain the influence of the dye on the depolymerization reaction, experiments were performed using half as green PET and half as colorless PET. In this way, it was expected that after the depolymerization of green PET, the dye could help the reaction of BHET formed from colorless PET with excess ethanol to form DET. However, this result was not attained. Figure 10 shows chromatograms of the products for the three reactions carried out using: (i) 1 g of green PET; (ii) 1 g of colorless PET, and (iii) a mixture containing 0.5 g of green PET and 0.5 g of colorless PET. By the analysis of Figure 10, it can be seen that green and colorless PET reacted indepen-

TABLE II
DET Yield for Reactions with PET from Different Sources

Polymer source	DET (g)	Yield ^a (%)
(C) Green bottle PET	1.09	94.2
(B) Mechanically recycled colorless fiber	0.74	64.5
(A) Mechanically recycled green fiber	1.09	94.3
(D) Polyester string	1.14	98.5

^a Yield based on the maximum amount of DET obtained per gram of PET (1.00 g of PET yields a maximum of 1.56 g of DET).

dently from each other in the mixture. Thus, it can be inferred that the green dye influences depolymerization only when it was previously incorporated into the polymer matrix (in the bulk). The possible presence of hydroxide and wetting agents remaining from the dyeing process also explains the increase in DET yield. According to Roh and Bae,²⁹ terephthalic acid can be produced from PET waste using alkaline hydrolysis of wastewater containing alkaline hydroxide and wetting agents from the polyester fiber chromatic treatment process.

It also can be seen that the reaction using PET from the textile industry produces more DET than BHET in comparison to the colorless one. It is well known that PET strings contain color-changing carriers.³⁰ In our laboratory, the PET string carrier was identified as TiO₂ through atomic absorption spectrophotometry. The influence of TiO₂ on supercritical ethanol PET depolymerization was also investigated. Figure 11 shows a chromatogram of a 5-h reaction of colorless bottle PET, 60 mL of ethanol, 1 mL of water, and 0.1 g of TiO₂ (purchased from Aldrich, P25 CAS 13,463–67-7). It can be seen that TiO₂ influences the final reaction step and BHET \rightleftharpoons DET + EG equilibrium. As a result, the reaction product is richer in DET than in BHET, which is consistent with literature works describing TiO₂ as a catalyst in supercritical fluid.³¹

No differences were observed between the results of mechanically recycled postconsumer PET bottles and fibers. In the depolymerization reaction, green and colorless polymers presented similar behaviors before and after mechanical processing.

CONCLUSIONS

Depolymerization of waste PET was carried out in a laboratory-made batch reactor using anhydrous ethanol in supercritical conditions (528 K and pressures

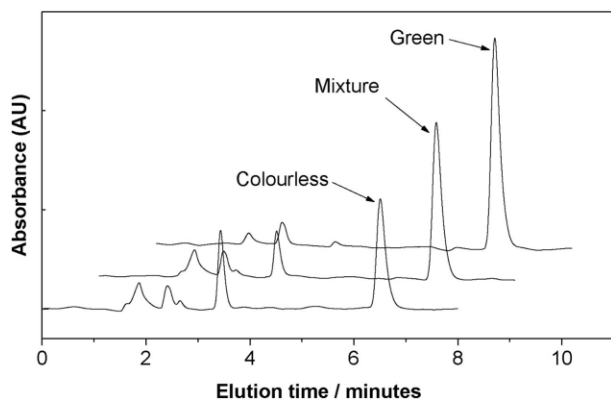


Figure 10 HPLC spectra of the products of the 5-h reaction at 528 K and 11,600 kPa using 60 mL of ethanol, 1 mL of water, and (A) 1 g of colorless PET, (B) 1 g of green PET, and (C) a mixture of 0.5 g of colorless and 0.5 g green PET.

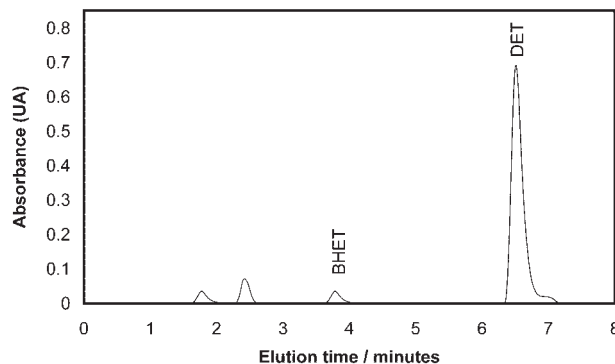


Figure 11 HPLC spectrum of the product of the 5-h reaction at 528 K and 11,600 kPa using 60 mL of ethanol 1 mL of water, 1 g of colorless PET, and 0.1 g of TiO₂.

from 7,600 to 11,600 kPa) in the presence of water. According to our results, PET can be completely depolymerized to monomers in supercritical ethanol in about 5 h. This reaction is strongly influenced by the amount of water, the green PET dye, and TiO₂. In addition, the PET/ethanol weight ratios and the pressures lie in the range investigated in this work did not influence significantly the final product yield. The data revealed a maximum DET recovery yield of 98.5%.

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References

- Awaja, F.; Pavel, D. *Eur Polym Mater* 2005, 41, 1453.
- DeSimone, J. M. *Science* 2002, 297, 799.
- Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* 1999, 399, 28.
- Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T. *Science* 2002, 297, 807.
- Ward, S.; Jones, K. M.; Marbrow, R. A. In *Chemical Aspects of Plastics Recycling*; Hoyle, W., Karsa, D. R., Eds; The Royal Society of Chemistry: Cambridge, UK, 1997; p 79.
- PetCor PET Container Recycling Europe Information on Plastics Additives & Compounding, May 2001.
- ABIPET. ASSOCIAÇÃO BRASILEIRA DOS FABRICANTES DE EMBALAGENS PET. Available at www.abipet.org.br. Accessed in November 18, 2005.
- KenPlas inform, available at <http://www.kenplas.com>. Accessed in November 18, 2005.
- Li, Y.; White, D. J.; Peyton, R. L. *Resour Conservat Recycl* 1998, 24, 87.
- Guddeti, R. R.; Knight, R.; Grossmann, E. D. *Ind Eng Chem Res* 2000, 20, 37.
- Paszun, D.; Spychaj, T. *Ind Eng Chem Res* 1997, 36, 1373.
- Macini, S. D.; Zanin, M. *J Appl Polym Sci* 2000, 76, 266.
- Yoshioka, T.; Sato, T.; Okuwaki, A. *J Appl Polym Sci* 1994, 52, 985.
- Macini, S. D.; Zanin, M. *Polim Cienc Tecnol* 2002, 12, 34.
- Campanelli, J. R.; Cooper, D. G.; Kamal, M. R. *J. Appl Polym Sci* 1994, 53, 985.

16. Kao, C. Y.; Cheng, W. H.; Wan, B. Z. *Thermochim Acta* 1997, 292, 95.
17. Kurokawa, H.; Ohshima, M.; Sugiyama, K.; Miura, H. *Polym Degrad Stab* 2003, 79, 529.
18. Adschiri, T.; Sato, O.; Machide, K.; Saito, N.; Arai, K. *Kagaku Kogaku Ronbunshu* 1997, 23, 505.
19. Sako, T.; Sugeta, T.; Otaki, K.; Nakazawa, N. *J. Chem Eng Jpn* 1997, 30, 342.
20. Hutchenson, K.W. In *Supercritical Fluid Technology in Material Science and Engineering*; Sung, Y. P., Eds; Marcel Dekker: New York, 2002; p 87.
21. Eckert, C. A.; Chandler, K. J. *Supercrit Fluid* 1998, 13, 187.
22. Sivalingam, G.; Madras, G. *Ind Eng Chem Res* 2002, 41, 5337.
23. Koningsveld, R.; Stockmayer, W. H.; Nies, E. *Polymer Phase Diagrams*; Oxford University Press: New York, 2001.
24. Sako, T.; Okajima, I.; Sugeta, T.; Otake, K.; Yoda, S.; Takebayashi, Y.; Kamizawa, C. *Polym J* 2000, 32, 178.
25. Yang, Y.; Lu, Y.; Xiang, H.; Xu, Y.; Li, Y. *Polym Degrad Stab* 2002, 75, 185.
26. Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T. *AIChE J* 2002, 48, 136.
27. Akiya, N.; Savage, P. E. *Chem Rev* 2002, 102, 2725.
28. Takahashi, H.; Hisaoka, S.; Nitta, T. *Chem Phys Lett* 2002, 363, 80.
29. Roh, H. D.; Bae, D. U.S. Pat. 6,031,128 (1998).
30. Shaoula, L.; Xiang, Z.; Tianmin, T.; Zhiqi, X.; Qihong, L. *Colorat Technol* 2003, 119, 19.
31. Yu, J. L.; Savage, P. E. *Environ Sci Technol* 2000, 34, 3191.