



Titanate Nanotubes Modified With Zinc and Its Application in Post-Consumer PET Depolymerization

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The development of nanostructures has received notoriety due to the properties that the nanometric scale provides to the material. Among these properties, the increase in the catalytic activity due to the high specific surface area of nanostructures has been the focus of several studies. Among the nanometric catalysts that have been studied, titanate nanotubes present versatility of applications since they can be modified through the functionalization or ion exchange adding the structure metals that increase the catalytic efficiency. For the depolymerization of post-consumer polyethylene terephthalate (PET) bottles by glycolysis, a chemical recycling method that is in accordance with the principles of sustainable development, which aims to obtain the bis(2-hydroxyethyl) terephthalate (BHET) monomer, sodium titanate nanotubes (NaTNT) and zinc titanate nanotubes (ZnTNT) were used as catalysts. The nanostructures were efficient in the PET depolymerization reaction for 2, 3, and 4 h, converting PET into BHET with yield higher than 65% (w/w).

Without the use of catalysts, the reaction is extremely slow,^[7] taking up to 9 h to reach conversions above 50%.^[4,8] Several catalysts are mentioned in literature, such as manganese, cobalt and zinc oxides, ionic liquids and silicon-doped metal nanoparticles,^[5,9,10] but the most commonly used is zinc acetate, which presents good results of PET conversion and BHET yield.^[4,11] However, these examples may require high energy or high cost for the production of the catalysts. Therefore, the search for the development of catalysts that allow the use of mild conditions for the reaction becomes necessary.^[6]

In previous work, our group showed that sodium titanate nanotubes (NaTNT) were efficient catalysts in the PET glycolysis reaction.^[12,13] In addition, these nanostructures present the possibility of metallic cations doping that can increase the catalytic efficiency of catalyst.^[14] Zinc compounds are interesting catalyst for

the PET depolymerization by glycolysis either by using zinc acetate as the catalyst or by modifying polyoxometalate type compounds in yields of approximately 80% in BHET and 100% conversion of PET.^[2]

In this context, the present work aims to modify titanate nanotubes with zinc (ZnTNT) to evaluate the influence of sodium cation exchange (NaTNT) on zinc (ZnTNT) in post-consumer PET glycolysis.

1. Introduction

Among the many ways to chemically recycle polyethylene terephthalate (PET), currently one of the most important polymers, glycolysis is the most advantageous.^[1,2] This polymer has a high global production and consumption due to its many applications (packaging, fiber, films)^[3] and, in consequence, the inadequate disposal of post-consumer PET waste becomes an environmental and economic concern. Glycolysis method consists in the insertion of excess glycols, most commonly ethylene glycol (EG) to the PET chain for the production of the monomer bis(2-hydroxyethyl) terephthalate (BHET)^[4,5] that can be reinserted in the PET production process. The production of the main monomer BHET is what makes chemical recycling in accordance with the principles of sustainable development.^[6]

2. Experimental Section

The reagents used in the synthesis of titanate nanotubes and BHET were sodium hydroxide (99%, Vetec), titanium dioxide (anatase phase, 98%, JB Chemistry), zinc chloride (ZnCl₂, 97%, NEON), ethylene glycol (99.5%, Dynamics) and post-consumer PET. All reagents were used as received.

2.1. Titanate Nanotubes Synthesis

Titanate nanotubes (NaTNT) were synthesized by the hydrothermal method according to the literature.^[15,16] In a typical synthesis, a mixture of 1.5 g of TiO₂ in 120 mL of NaOH aqueous solution (10 mol L⁻¹) was prepared under magnetic stirring for 30 min at room temperature. After this, the mixture was transferred to autoclave reactor and maintained at 135 °C for 72 h. Finally, the

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DOI: 10.1002/masy.201800008

solid formed was centrifuged, washed with distilled water (until pH = 8) and dried at 80 °C for 6 h. For the Na ion exchange, 1 g of NaTNT was suspended in a ZnCl₂ aqueous solution (0.5 mol L⁻¹), remaining in magnetic stirring for 30 min. After, the formed solid was centrifuged and dried at 80 °C for 6 h.

For the characterization of NaTNT and ZnTNT nanostructures were made analysis of dispersive energy spectroscopy (SEM, FEI Inspect F50), transmission electron microscopy (TEM, FEI Tecnai G2 T20) using copper grids with carbon film (300 mesh) and the measures of TNTs dimensions were obtained by TEM analysis using Image J software (number of measurements = 25). The diffraction patterns of the nanostructures were analyzed by X-ray diffraction (XRD, Shimadzu XRD 7000) using radiation K α of the copper ($\lambda = 1.542 \text{ \AA}$), voltage 40 kV, 30 mA, scanning between 5° and 70° 2 θ and scan speed of 0.02° and counting time of 2.0 s. Nitrogen adsorption-desorption isotherms were measured using a 77 K (-196 °C) volumetric method (Micromeritics Instruments Corporation, TriStar II model 302 V1.03). The isotherms were measured in the absolute N₂ pressure range of 0.010–1.05 atm for 6 h. The specific area was calculated using Brunauer-Emmet-Teller (BET) method.

2.2. PET Glycolysis

For the glycolysis reactions of PET, only the body of transparent post-consumer PET bottles of carbonated beverages, exclusively of soda, was used. They were then milled in a knife mill (Retsch model SM 300) using a 1 and 5 mm aperture mesh. The ground PET was separated in granulometry between 1.00–2.36 mm AAKER screens with 16 and 8 mesh apertures.

The reaction was adapted from literature,^[9] where 15 g of ground PET grains, 60 g of ethylene glycol (EG) and 50 mg of catalyst are added to a 500 mL round bottom flask equipped with heating system and magnetic stirrer, thermometer and reflux condenser. The glycolysis reaction was performed at different times (2, 3, and 4 h) at 196 °C. At the end, 300 mL of boiling water was added to reactional system and after, it was filtered under reduced pressure in Büchner funnel. The filtrate being stored at 6–10 °C for 72 h obtaining so the BHET crystals. BHET crystals

were filtrated on G4 sintered glass funnel and the dried at 60 °C for 24 h. The yield of BHET (Y,%) produced by depolymerization of PET was calculated according to Equation (1):

$$Y = \frac{W_{BHET,f}/MW_{BHET}}{W_{PET,i}/MW_{PET}} \times 100 \quad (1)$$

where Y represents the yield of BHET, $W_{BHET,f}$ represents the final mass of BHET, MW_{BHET} represents the molar mass of BHET (254 g mol⁻¹), $W_{PET,i}$ represents the initial mass of PET used in the reaction, and MW_{PET} represents molar mass of the PET repeating unit (192 g mol⁻¹).^[17]

The turn over frequency (TOF), which is the number of cycles that this catalyst is capable of making per unit time,^[18] of the catalyst was calculated based on Equation (2):

$$TOF = \frac{mmol \text{ of product}}{g \text{ of catalyst} \times time(h)} \quad (2)$$

The efficiency of the PET depolymerization reaction was evaluated by differential scanning calorimetry (DSC, TA Instruments, model Q20) in the range of 45–270 °C, with a heating rate of 10 °C min⁻¹ under N₂ inert atmosphere. In order to confirm the production of BHET, ¹H-NMR were recorded on a Bruker Ascend 400 NMR spectrometer operating at 400 MHz in deuterated DMSO solution.

3. Results and Discussion

The morphological characteristics of the titanate nanotubes nanostructures are shown in **Figure 1a** and **1b**. Both NaTNT and ZnTNT exhibit tubular morphology, as expected. It is possible to observe that the nanotubes are formed by winding at least three titanates multilayer lamellar walls and have an external diameter of 8.3 ± 0.9 nm (NaTNT) and 8.7 ± 0.6 nm (ZnTNT). These results are in agreement with those found by Monteiro et al.^[19]

In order to verify the exchange of the sodium metal by zinc in the TNT, EDS analyzes were also performed (**Figure 2a,b**). The NaTNT nanostructures show signals for sodium (Na), titanium

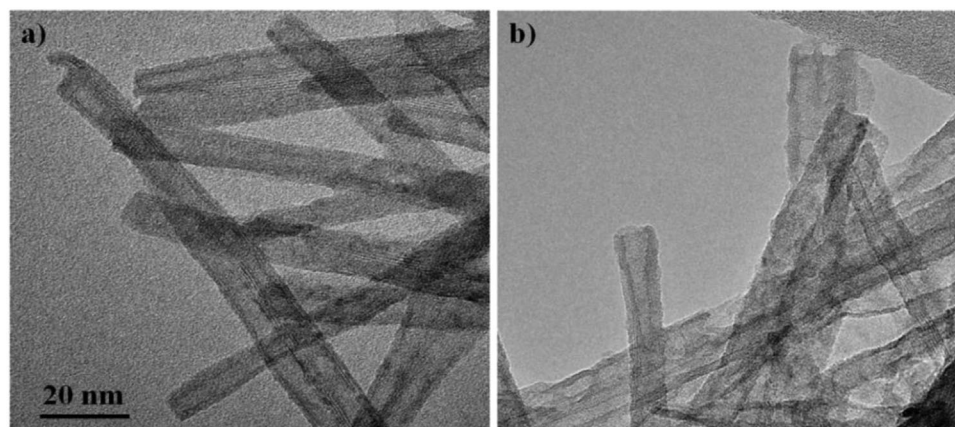


Figure 1. TEM images, 410 k magnification, for the (a) NaTNT and (b) ZnTNT.

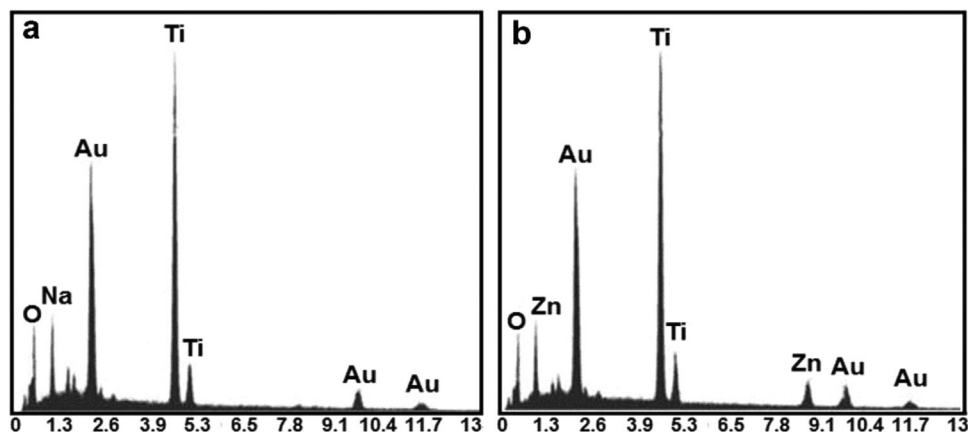


Figure 2. EDS results for the (a) NaTNT and (b) ZnTNT.

(Ti), and oxygen (O) elements, as well as the signal for gold element (Au) used in the metallization of samples. As observed, the ZnTNT nanostructures present signals for the element zinc (Zn) (Figure 2b) and, in addition, does not present the signal for the element Na demonstrating an ion exchange of sodium by zinc atoms.

The results obtained for the characterization of the crystalline structure as well as specific area and pore diameter, corresponding to the agglomerated nanostructures,^[16] are presented in **Figure 3**. NaTNT show characteristic diffraction peaks for a $\text{Na}_2\text{Ti}_3\text{O}_7$ structure similar to that described in the literature^[16,20] corresponding to the angles of $2\theta = 10^\circ, 24^\circ, 28^\circ, 48^\circ,$ and 62° (Figure 3a). The exchange by zinc metal led to a structure with lower crystallinity due to the enlargement of the signal between 17° and 35° characteristic of amorphous region and the decrease of the intensity of the signals located at $2\theta = 10^\circ, 24^\circ, 28^\circ, 48^\circ,$ and 62° . The signal located at 10° refers to interlamellar distance and using the Bragg equation, values of 0.87 nm for NaTNT and

0.88 nm for ZnTNT were found, showing no significant difference between nanostructures.

The adsorption-desorption isotherms of N_2 (Figure 3b) show that the two nanostructures exhibit a type IV isotherm behavior with a hysteresis in the range $P/P_0 = 0.5\text{--}1.0$ indicating both the presence of mesopores (2–50 nm) as well as macropores (>50 nm).^[14,16,21] Specific area for the nanostructures were $155\text{ m}^2\text{ g}^{-1}$ (NaTNT) and $140\text{ m}^2\text{ g}^{-1}$ (ZnTNT). As shown in Figure 3c, the two nanostructures show monomodal pore diameter distribution, corresponding to pores formed by aggregation of the nanostructures, with maximum at 17 nm (NaTNT) and 15 nm (ZnTNT).

The results obtained by DSC for the glycolysis reactions of PET using NaTNT and ZnTNT as catalysts are presented in **Figure 4**. The profiles of the DSC curves for the PET glycolysis product at 2, 3, and 4 h were similar showing an endothermic peak located at 110°C corresponding to the BHET melting temperature.^[22]

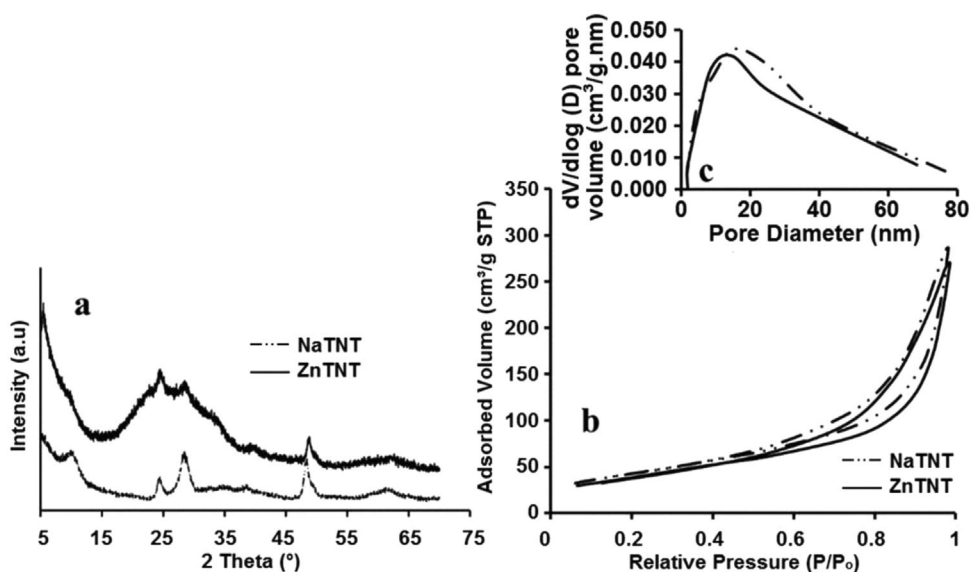


Figure 3. NaTNT and ZnTNT results obtained by (a) XRD, (b) adsorption-desorption isotherms of N_2 , and (c) pore diameter.

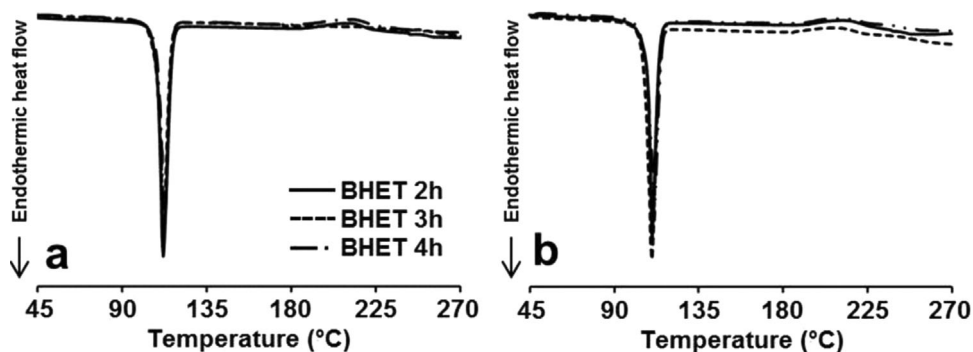


Figure 4. Comparative DSC curves to BHET obtained by the use of (a) NaTNT and (b) ZnTNT as catalysts to the different reaction time of PET glycolysis.

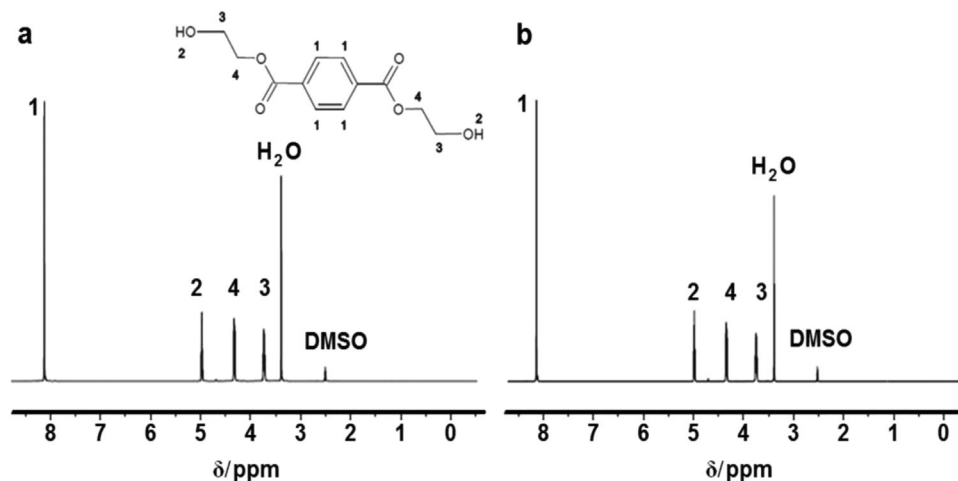


Figure 5. $^1\text{H-NMR}$ spectrum for BHET produced by glycolysis with (a) NaTNT and (b) ZnTNT.

The chemical structure of BHET was analyzed by nuclear magnetic resonance (NMR) spectroscopy. The $^1\text{H-NMR}$ spectrum of BHET is shown in **Figure 5** with chemical structure illustration.

The signs labelled 1, 2, 3, and 4 (**Figure 5**) are assigned the protons of the aromatic ring ($\delta_{\text{H}} = 8.1$ ppm, s, 4H), hydroxyl groups ($\delta_{\text{H}} = 4.95$ ppm, t, 2H), methylenes ($-\text{CH}_2-$) adjacent to the $-\text{OH}$ groups ($\delta_{\text{H}} = 3.73$ ppm, m, 4H), methylenes ($-\text{CH}_2-$) adjacent to the $-\text{COO}$ groups ($\delta_{\text{H}} = 4.33$ ppm, t, 4H), respectively. The sign around 2.5 ppm is DMSO and in 3.3 can be attributed to H_2O .^[23,24] For both catalysts used $^1\text{H-NMR}$ analysis presents the same spectrum. This confirms that de modification of NaTNT with ZnCl_2 to obtain ZnTNT is effective to the production of BHET from PET glycolysis.

The yield values of BHET for the reactions performed are presented in **Table 1**. The yields obtained with both catalysts show maximum values for 3 h reaction time. The decrease on yield value for 4 h reaction time may be an indicative that the glycolysis has reached the reaction equilibrium, since the depolymerization of PET can be considered a reversible reaction.^[17] The ZnTNT nanostructures were more efficient with yields of 82, 87, and 84% for 2, 3, and 4 h, respectively, higher than NaTNT (yields of 67, 80, and 77% for 2, 3, and 4 h, respectively). PET conversion values for all reactions were greater than 99%.

ZnTNT nanostructures present a different behavior from NaTNT since Zn atoms act as Lewis acid by activating the carbonyl of the ester group.^[2] This higher catalytic efficiency is proven by analyzing TOF values (**Table 1**). Values presented for 2, 3, and 4 h were 640, 453, and 328 $\text{mmol g}^{-1} \text{h}^{-1}$ (ZnTNT) and 523, 416, 301 $\text{mmol g}^{-1} \text{h}^{-1}$ (NaTNT) respectively.

4. Conclusions

Through the hydrothermal method, titanate nanotubes with sodium content and high specific area were successfully

Table 1. Yield results of BHET (Y, %) and the turn over frequency (TOF, $\text{mmol g}^{-1} \text{h}^{-1}$) to different catalysts in different reactional times.

Catalyst	Time [h]	Y [%]	TOF [$\text{mmol g}^{-1} \text{h}^{-1}$]
NaTNT	2	67	523
	3	80	416
	4	77	301
ZnTNT	2	82	640
	3	87	453
	4	84	328

synthesized. In addition, by suspending these TNT in solution of $ZnCl_2$ it was possible to carry out the modification with Zn atoms, maintaining the high specific area, but with decrease in crystallinity. The nanostructures were used as catalysts in the depolymerization of PET by glycolysis for times of 2, 3, and 4 h and both were efficient, but ZnTNT resulted in higher BHET yields when compared to NaTNT. DSC and 1H -NMR analysis confirmed BHET production.

Acknowledgements

G.R.L. and W.F.M. contributed equally to this work. The authors thank CNPq and CAPES for the scholarships, LACOR for the use of the knife mill, Laboratório Central de Microscopia e Microanálise (LabCEMM/PUCRS) by morphological analyzes, Profa. Michèle Oberson de Souza (IQ-UFRGS) by the analyzes of nitrogen adsorption-desorption and PUCRS for technical support.

Keywords

catalysis, chemical recycling, glycolysis, ion exchange, PET, titanate nanotubes

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