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ORIGINAL ARTICLE

Transesterification of Bis 2-Hydroxyethyl Terephthalate for Production of Bis 4-Hydroxybutyl Terephthalate over Homogenous Catalysts

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Abstract

The vast amount of PET waste has made an enormous concern owing to its environmental pollution and human health effects. As an eco-friendly alternative option to treat plastic waste, this study investigated the transesterification of bis 2-hydroxyethyl terephthalate (BHET) into bis 4-hydroxybutyl terephthalate (BHBT) using 1, 4-butanediol (BDO) as a solvent in a typical batch reactor at various temperatures. Zinc acetate (Zn-A), antimony (III) oxide, tin (II) chloride, and titanium isopropoxide (Ti-IP) were utilized as catalysts. The effects of the experimental parameters, including the catalyst type, temperature, and catalyst loading, on the transesterification of BHET into BHBT were evaluated. Ti-IP and Zn-A showed higher catalytic activities than the other catalysts. Furthermore, Zn-A demonstrated to be a promising catalyst at lower temperatures, whereas Ti-IP exhibited higher activity at higher temperatures. An increase in temperature improved the yield of BHBT up to (0.99 mol/L) and showed the highest BHET conversion (98.93%) when Ti-IP was used as a catalyst at 210 °C. BHET conversion and the yield of BHBT were raised greatly when the catalyst amount was increased from 0.1 to 0.3 wt%. This study presents the transesterification of BHET using a Ti-IP catalyst as a novel technology for producing valuable BHBT for industrial applications.

Keywords Transesterification · BHET · BHBT · BDO · Titanium isopropoxide

Abbreviations

BHET	Bis 2-hydroxyethyl terephthalate
BHBT	Bis 4-hydroxybutyl terephthalate BDO
Zn-A	Zinc acetate
An-O	Antimony (III) oxide
Tn-Cl	Tin (II) chloride
Ti-IP	Titanium isopropoxide
PET	Polyethylene terephthalate
r-PET	Recycled PET
MHET	Mono-2-hydroxyethyl terephthalate
EG	Ethylene glycol
PBT	Polybutylene terephthalate
DMF	Dimethylformamide
GC/MS	Gas chromatography–mass spectrometry
THF	Tetrahydrofuran
HPLC	High-performance liquid chromatography
HHT	4-Hydroxybuthyl 2-hydroxyethyl terephthalate

Introduction

Plastic generation grew from 0.5 million tons in 1950 to over 400 million tons in 2018 [1], which resulted in the rapid reduction of oil resources, thus affecting the natural equilibrium of the environment. Plastic waste contains several polymeric compounds, such as polyethylene terephthalate (PET), which is one of the most typically consumed plastic groups,

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particularly for packaging materials, with a high generation amount exceeding 50 million tons annually [2, 3]. Although PET is considered a stable and safe material, its synthesized precursors and degradation byproducts are biotoxic [4, 5]. Physical, chemical, mechanical, and biological methods are conventional solutions for recycling plastic waste [6, 7].

Although the physical recycling of colorless PET bottles into recycled PET (rPET) has been commonly utilized in the PET recycling industry, physical recycling cannot conveniently process colored PET bottles and textiles. Temperature-sensitive plastics are mainly landfilled or incinerated because of difficulties in mechanical handling [6, 8, 9]. In addition, hydrolytic organisms and enzymes are restricted by aerobic organisms and slow reaction rate [10] for degrading PET into monomers such as bis 2-hydroxyethyl terephthalate (BHET) and mono-2-hydroxyethyl terephthalate (MHET) [6, 11–13].

Chemical recycling is promising for obtaining the closed-loop recycling of PET to depolymerize post-consumer PET into BHET via glycolysis. Furthermore, BHET can be polymerized to generate rPET. However, rPET demands are severely restricted owing to considerable limitations caused by colored impurities [14]. The chemical recycling of PET via the hydrolysis of BHET and the esterification of the resulting products, i.e., MHET and terephthalic acid, using dimethyl carbonate has been investigated recently [15–17]. PET glycolysis using ethylene glycol (EG), which generates BHET monomers via transesterification, has been shown to offer a more industrially reliable performance [18].

BHET can be utilized to synthesize new monomers such as bis 4-hydroxybutyl terephthalate (BHBT), which can be used to produce polybutylene terephthalate (PBT). PBT is a semi-crystalline polymer with outstanding solvent persistence and machinability [19], and industrial polyesters are typically employed as commercial fiber and engineering plastic [20]. Engineering plastics, including PBT, possess distinct properties that are highly demanded in the automobile, electronics, and electrical appliance industries [21]. More importantly, the reversible nature of transesterification reactions requires a suitable catalyst to adjust the activation energy of the reaction.

Hence, homogeneous and heterogeneous catalysts for transesterification have been proposed [22–24], including metal acetates, metal oxides, metal chlorides, solid super acids [25], titanium phosphate, and ionic liquids [22, 26, 27]. Although heterogeneous catalysts enhance the chromaticity of the product, they are limited by their low catalytic output, which is caused by their fewer active sites than in the case of homogeneous catalysts [28]. Transesterification in the presence of catalysts containing Lewis acid sites such as zinc acetate (Zn-A), titanium isopropoxide (Ti-IP), and tin (II) chloride (Tn-Cl) is facilitated by the enhancement in the electrophilicity of the adjoining carbon atom [29, 30]. Meanwhile, the Lewis sites increase the electrophilicity of the adjoining carbon atom, thus causing the reactant to be more susceptible to nucleophilic attack [31]. Similarly, Zn-A has been proven to be an effective catalyst for the production of molecules with an ester structure. Ghaemy and Mossaddegh [26] and Xi et al. [32] reported that PET glycolysis using Zn-A resulted in significant activity and a 94.85% yield of BHET with only a few dimers. Zn (II) catalysts are preferred in transesterification reactions because of their high availability, low toxicity, and high efficiency [33]. The mechanism of zinc (II) catalysts involves the ring-opening polymerization of cyclic esters and presents the progression of the reaction through a nucleophilic attack of the alcohol toward the ester carbonyl coordinated on zinc [34]. Titanium-based catalysts exhibit significant transesterification capacity. Ti-catalyzed processes decrease the amount of solvent to three times less than that of other methods, which is one of the important aspects of green chemistry [35]. Accordingly, owing to their cost reduction, effectiveness, and industrial usage, titanium-based catalysts are typically utilized [36, 37]. Casas et al. [29] reported that Tn-Cl undergoes considerable transesterification and esterification at 150 °C. Chiao et al. [8] reported an optimal PET conversion and a BHET yield of 89.7% and 77.7%, respectively, at a temperature of 190 °C within 5 h process.

Furthermore, PET production via BHET transesterification as well as EG and dimethylene terephthalate transesterification in the presence of a suitable catalyst has recently been reported [38, 39]. Antimony-based catalysts have recently been applied to PET production using the polycondensation method [40, 41]. Mohammadi and Enayati [42] reported a BHET yield of 97.5%, which was achieved via the glycolysis of PET using 0.5 wt% An-O as a catalyst under 200 °C for 1 h, however, when the reaction time prolonged to 1.5 h, the BHET yield reduced slightly to 90%.

1,4-Butanediol (BDO) is a biomass-derived chemical with a high boiling point, which reduces the pressure required for the reaction and can be employed as a basic compound for the synthesis of various chemicals, including solvents and polymers [43, 44]. Mullen et al. [43] reported that the use of BDO in pyrolysis favorably restricted polymerization reactions. Accordingly, BDO is industrially produced from renewable resources and is environmentally benign, which may quench acid or radical intermediates during reactions [45–47].

This study was aimed at developing a novel BHBT method via the transesterification of BHET and BDO using a batch reactor. The effects of various parameters such as the catalyst type and reaction temperature on the BHET conversion and reaction yields were investigated to optimize the best condition for BHBT generation.

Experimental

Raw Materials

BHET (Sigma–Aldrich) and BDO (Sigma–Aldrich) were provided and used as precursors while Zn-A (Sigma–Aldrich), Ti-Cl (Sigma–Aldrich), An-O (Sigma–Aldrich), and Ti-IP (Sigma–Aldrich) were applied as catalysts.

Sample analysis was performed using gas chromatography-mass spectrometry (GC/MS, USA) and high-performance liquid chromatography (HPLC, USA) with 1,4-dioxane (Sigma–Aldrich) and bisphenol A (Sigma–Aldrich) as standard materials. In addition, dimethylformamide (DMF) (Samchun Pure Chemical. Co., Ltd.) and THF (Sigma–Aldrich) were used as solvents to dissolve the reactants and products for GC/MS analysis.

Experimental Method

The transesterification experiments were conducted in a batch reactor as can be seen in Fig. 1. In the experiment, 10 g of BHET and 30 g of BDO were mixed in the presence of a known amount of catalyst (0.3 wt% of BHET). Subsequently, the mixture was placed in the batch reactor and stirred (500 rpm) for 15 min. When the predetermined reaction time was reached, the reaction was terminated by placing the reactor in cooling water for 50 min. Moreover, the temperature was set in the range of 130–210 °C to investigate the effect of reaction temperature on BHET conversion and BHBT yield.

Fig. 1 Batch system reactor

Data Analysis

The reactants and products were measured using GC/MS and HPLC. GC analysis was performed by dissolving the samples in DMF to measure the final quantities of EG and BDO, whereas HPLC analysis was performed by dissolving the samples in THF to measure BHET consumption. Helium (99%) was used as a carrier gas in GC/MS (DS 6200, DS Science Inc.), and an Agilent UA-CW column was installed and coupled with a flame ionization detector. The HPLC (1100 series, Agilent) was equipped with a C8 (4.6 × 250 5-Micron) column and a variable wavelength detector. At a column temperature of 40 °C, a buffer solution containing acetonitrile and distilled water (10:90) was used and the flow rate was adjusted to 0.4 mL/min. The BHET conversion, 4-hydroxybuthyl 2-hydroxyethyl terephthalate (HHT), and BHBT yield were calculated as follows:

$$\text{Conversion of BHET (\%)} = \frac{\text{BHET initial mol} - \text{BHET final mol}}{\text{BHET initial mol}} \tag{1}$$

$$\text{BHBT final yield (mol)} = \frac{\text{Production of BHBT(g)}}{\text{BHBT molecular weight}} \tag{2}$$

$$\text{BDO final mol} = \frac{\text{BDO final weight(g)}}{\text{BDO molecular weight}} \tag{3}$$

$$\text{EG final mol} = \frac{\text{Production of EG(g)}}{\text{EG molecular weight}}. \tag{4}$$

$$\begin{aligned}\text{HHT mol} = {} & \text{converted mol of BHET} \\ & - ((\text{BHBT mol}) + (2x \text{ dimer mol}) + (3x \text{ trimer mol}))\end{aligned} \tag{5}$$

$$\text{Molar Concentration}\left(\frac{\text{mol}}{\text{l}}\right) = \frac{\text{Mole of solute}}{\text{Liter of solution}}. \tag{6}$$

Results and Discussion

Brunauer–Emmett–Teller (BET) Analysis

The physical properties of the catalysts were determined via BET analysis, and the results are summarized in Table 1. The specific surface areas (S_{BET}) of the catalysts decreased in the following order: Tn-Cl > Zn-A > An-O. Tn-Cl possesses a higher surface area and pore size than Zn-A; however, the low reactivity of Tn-Cl can be attributed to its partial

Table 1 Physical characteristics of catalysts

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
Zn-A	14.5	0.003	66.3
Tn-Cl	50.2	0.002	98.3
An-O	4.8	0.02	–

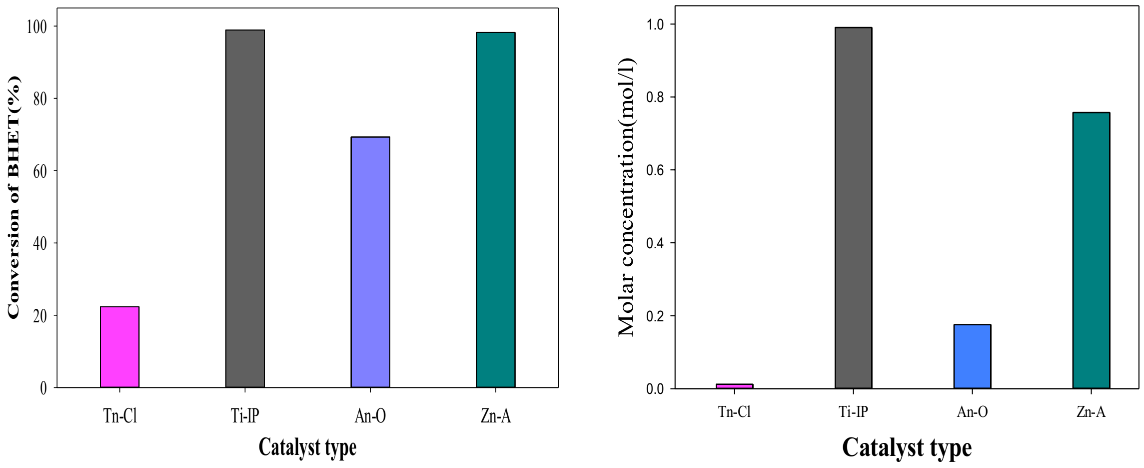
destruction in reactions involving alcohols [48]. Meanwhile, Zn-A has a larger surface area and pore size compared with An-O, resulting in considerable catalytic activity. Ti-IP was not subjected to BET analysis since it is a liquid catalyst.

Effects of Various Catalysts

To compare the effects of different catalysts, 0.3 wt% BHET as a catalyst was applied to a mixture containing BHET and BDO with a weight ratio of 1:3 at 210 °C for 15 min. As shown in Fig. 2a, among all catalysts, Ti-IP and Zn-A showed significant effects on the reaction. The highest BHET conversion rate was indicated by Ti-IP (98.93%), followed by Zn-A (98.23%), An-O (69.32%), and Tn-Cl (22.34%). Furthermore, the highest BHBT production was achieved, using Ti-IP (0.99 mol/L), followed by Zn-A (0.75 mol/L), An-O (0.17 mol/L), and Tn-Cl (0.01 mol/L) (see Fig. 2b). Hence, TI-IP and Zn-A show superior performance compared with other catalysts. The Zn-A operates via activating the carbon and the hydrogen atoms, present in the carbonyl and hydroxyl groups of BHET and BDO respectively [34]. Particularly Zn-A, as a Lewis acid that interacts with the oxygen atoms in the carbonyl groups of BHET [49].This causes it to be more susceptible to nucleophilic attack, thus accelerating the breaking of the molecular chain [19]. The EG group of BHET was replaced with a BDO molecule to form HHT as an intermediate. In addition, the carbon of the carbonyl group in BHET was the largest positive center and attack site for BDO. The two ends of BDO involved in the reaction were most likely to possess positive charges, whereas O exhibited a strong negative charge, which serves as a good attack site for the oxygen atoms in the carboxyl group of BHET [49].

However, An-O showed relatively less activity than Ti-IP and Zn-A, which was attributable to its requirement for high pressure, high temperature, long reaction time, and high quantity [42]. Meanwhile, Tn-Cl did not reach BHET because of the complete solubility of Tn-Cl in BDO, which was attributable to the high pressure (10 MPa) requirement of the reactants owing to their high immiscibility [29, 50]. Hence, Ti-Cl reacted with only one of the diol hydroxyl groups, whereas the second chloride was dislocated by the nucleophilic attack of the second hydroxyl group; consequently, hydrogen chloride was released [48].

The water molecules in the raw materials can degrade some catalysts, particularly during transesterification reactions. This is because of the hydrophilic nature of BDO arising from the presence of two hydroxyl groups in its structure, which form strong hydrogen bonds with water [51]. However, Ti-IP was shown superior to other catalysts because of its feasible reaction with homopolyesters of higher molar masses at higher temperatures [35, 52]. Consequently, Ti-IP and Zn-A were selected as the preferred catalysts in this study.



(a) (b)

Fig. 2 Comparison of **a** the conversion of BHET, **b** the yield of BHBT over the different catalysts at 210 °C (catalyst/BHET = 3/1000)

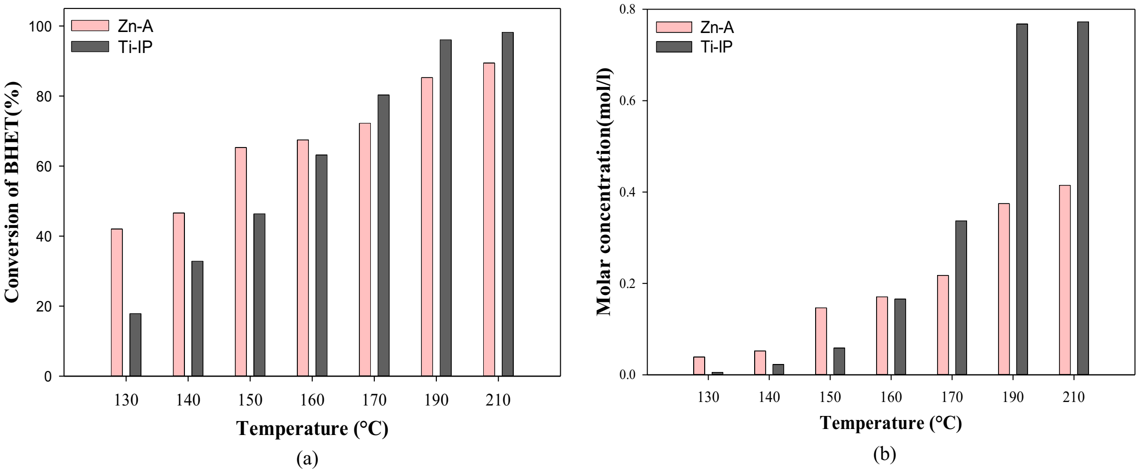


Fig. 3 Effect of temperature on **a** the conversion of BHET, and **b** the yield of BHBT over the different catalysts (catalyst/BHET = 1/1000)

Effects of Different Catalyst Loadings

Figure 3a, b illustrates a comparison between Ti-IP and Zn-A in low catalyst amounts (0.1 wt% and 0.3 wt%) as proposed catalysts. Both catalysts exhibited increased BHET conversion. However, Zn-A could not completely convert the intermediate HHT to BHBT, indicating that the reaction in the second step did not proceed completely, as shown in Fig. 4 which was adapted from [53].

Although Zn-A exhibited greater catalytic activity at lower temperatures compared with Ti-IP, the lower efficiency of Zn-A at higher temperatures compared with the case of Ti-IP was attributed to the performance of Zn-A in reactions performed above the melting points of the materials. Similarly, the formation of layered Zn-A by the interconnection of Zn tetrahedra and a portion of the carboxylate bridges was destroyed, which resulted in the exposure of the Zn acid Lewis sites [51]. The bond dissociation energy between the metal and oxygen atoms of the initial group is important that preserving the catalyst from decomposition during the reaction. Meanwhile, Ti-IP required a bond dissociation energy (662 kJ mol) that was considerably higher than that of Zn-A (284.1 kJ mol), which supported the superior Ti-IP activity and stability at higher temperatures compared with the case of Zn-A [54]. This is well matched with the performance of utilized catalysts in the current study (Figs. 3 and 5) as well as previous studies [35].

The detailed contents of the products were calculated using Eqs. (5)–(7) to investigate the formation of BHET and BHBT oligomers. Table 2 shows that EG improved as the temperature increased from 130 to 210 °C, which can be attributed to its generation via a two-step reaction (R1, R2), thus confirming the production of BHBT. The formation of BHET and BHBT dimers decreased and increased slightly, respectively, as the temperature increased. According to Table 3, EG production showed a linear correlation with the BHBT yield. However, the formation of BHET oligomers decreased at temperatures from 130 to 170 °C, although its

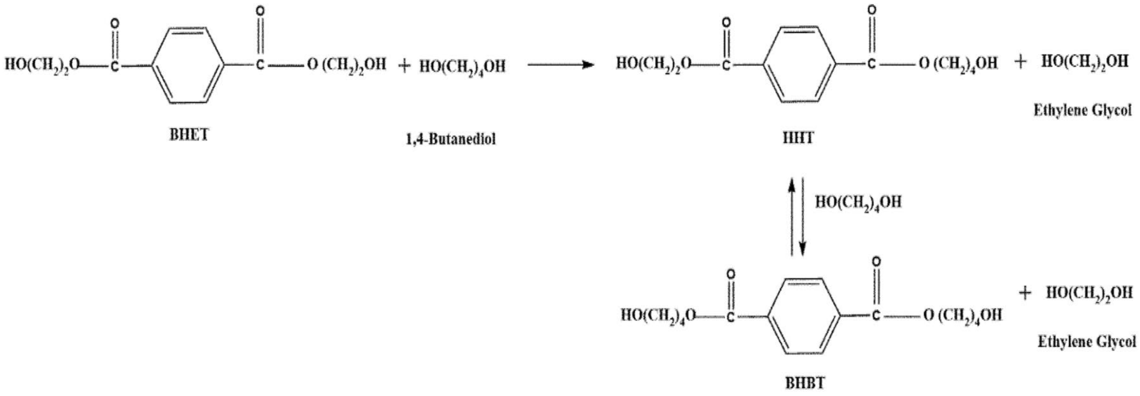


Fig. 4 Suggested reaction pathways

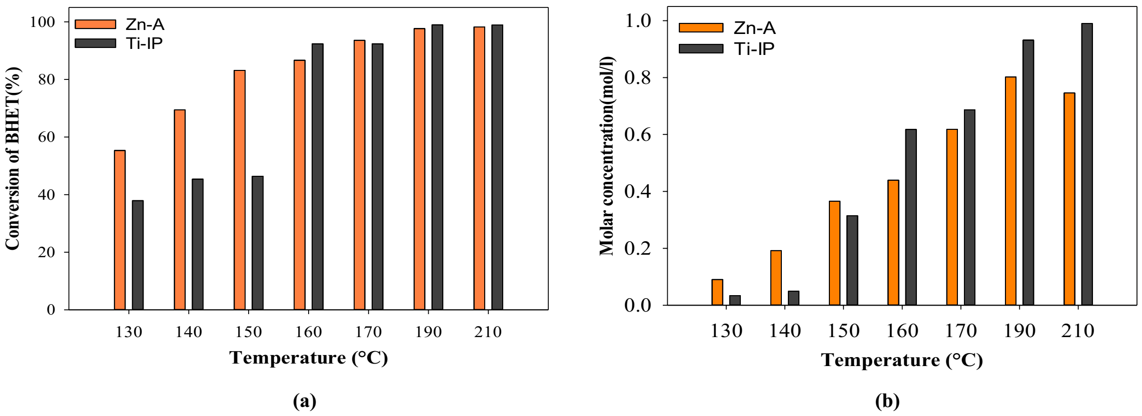


Fig. 5 Effect of temperature on **a** the conversion of BHET, and **b** the yield of BHBT over the different catalysts (catalyst/BHET = 3/1000)

content increased when the temperature increased to 210 °C. This phenomenon was attributable to the superior performance of Ti-IP at higher temperatures, which serves as a catalyst in the oligomerization of BHET and BHBT. During the transesterification reaction, the EG group of BHET was replaced with a BDO group, and a new EG group was generated (R1, R2).

$$\text{BHET} + \text{BDO} \rightarrow \text{HHT} + \text{EG} \quad (\text{R1})$$

$$\text{HHT} + \text{BDO} \leftrightharpoons \text{BHBT} + \text{EG} \quad (\text{R2})$$

As shown in Fig. 5a, b, increasing the catalyst amount to 0.3 wt% gradually increased the BHET conversion and BHBT yield compared with the case when the amount of 0.1 wt%. However, similar catalytic activity was observed, which proved the superiority of Zn-A over Ti-IP at lower temperatures, whereas Ti-IP continuously showed higher activity at higher temperatures. As the temperature increased from 190 to 210 °C, the activity in Zn-A decreased, which was attributable to the reverse reaction in the second step of the reaction (R2). This implies that the same catalyst that catalyzes the transesterification reaction can potentially enhance the reverse reaction [35, 42]. Table 4 presents a comparison of the catalysts performance in the current study with various catalysts applied in previous studies. Previous studies mostly reported the amount of product as a percentage (%) which was calculated based on the obtained and the expected mole of product. To become comparable with the results of previous studies, the results of this study were also converted to percentages (%).

Conclusion

In this study, the transesterification of BHET to BHBT using BDO was investigated. This reaction revealed that the transesterification of BHET proceeded in two stages, from BHET to HHT and BHBT, followed by the replacement of the hydroxyethyl ester end group with the hydroxybutyl ester group. The conversion of BHET over all catalysts intensified gradually as the temperature increased from 130 to 210 °C, although Ti-IP indicated higher activity at higher temperatures in the temperature range from 170 to 210 °C. Moreover, Zn-A showed significant activity at lower temperatures than Ti-IP. In addition, increasing the temperature enhanced the yield of BHET (mol/L), particularly in the case of Ti-IP catalysts. Hence, Ti-IP offers many advantages, including a high transesterification rate at low catalyst concentration. Similarly, Ti-IP, owing to its low price and superior performance compared with other catalysts, is a promising option for transesterification reactions. Hence, the transesterification of BHET to BHBT using BDO in the presence of Ti-IP as a catalyst is an emerging approach for providing valuable products (BHBT) for industrial applications.

Table 2 The yield of compounds involved before and after the reaction over the Zn-A catalyst at different temperatures (catalyst/BHET = 1/1000)

Entry	Temperature (°C)	Initial mole BHET (mol/L)	Initial mole BDO (mol/L)	Final mole BHET (mol/L)	BHET Dimer (mol/L)	Final mole BDO (mol/L)	BHBT final (mol/L)	BHBT dimer (mol/L)	HHT (mol/L)	EG (mol/L)	Conversion (%)
1	130	1.058	8.948	0.613	0.048	8.447	0.038	0	0.399	0.447	42.04
2	140			0.565	0.039	8.382	0.052	0	0.440	0.546	46.60
3	150			0.367	0.022	8.293	0.146	0.002	0.539	0.788	65.29
4	160			0.344	0.020	8.157	0.170	0.002	0.537	0.759	67.47
5	170			0.293	0.016	7.928	0.217	0.005	0.536	0.834	72.23
6	190			0.155	0.007	7.672	0.374	0.013	0.500	1.023	85.27
7	210			0.111	0.005	7.440	0.414	0.019	0.493	1.089	89.43

Table 3 The yield of compounds involved before and after the reaction over the Ti-IP catalyst at different temperatures (catalyst/BHET = 1/1000)

Entry	Temperature (°C)	Initial mole BHET (mol/L)	Initial mole BDO (mol/L)	Final mole BHET (mol/L)	BHET dimer (mol/L)	Final mole BDO (mol/L)	BHBT final (mol/L)	BHBT dimer (mol/L)	HHT (mol/L)	EG (mol/L)	Conversion (%)
1	130	1.058	8.948	0.869	0.060	8.798	0.005	0	0.183	0.465	17.85
2	140			0.710	0.045	8.766	0.022	0	0.324	0.691	32.84
3	150			0.567	0.033	8.458	0.058	0	0.432	0.879	46.38
4	160			0.389	0.020	8.274	0.165	0.003	0.495	1.097	63.18
5	170			0.208	0.007	7.964	0.337	0.010	0.492	1.353	80.31
6	190			0.041	0.043	7.412	0.767	0.054	0.140	1.654	96.06
7	210			0.019	0.039	7.117	0.772	0.058	0.148	1.558	98.19

Table 4 Comparison of the catalysts performance in the current study with various catalysts applied in other studies

Feedstock	Catalyst	Catalyst amount	Condition	Main product	Ref.
BHET	Zinc acetate Titanium(IV) isopropoxide	0.3 wt%	T = 210 °C Time = 15 min	BHBT (70.49%) BHBT (93.56%)	This study This study
PET	Zinc acetate Titanium butoxide	0.01 molar ratio	T = 190 °C Time: 3 h	BHET (69.3%) BHET (63.5%)	[55]
PET	Zinc acetate	0.3 wt%	T = 280 °C Time = 50 min	BHET (87.8%)	[28]
PET	Zinc plates	1:2.5	T = 190 °C Time = 5 h	BHET (77.7%)	[8]
PET	Zinc acetate	0.5 wt%	T = 200 °C Time = 60 min Pressure: 0.7 bar	BHET (93.3%)	[42]
PET	Antimony trioxide	0.5 wt%	T = 200 °C Time = 60 min Pressure: 1.3 bar	BHET (64%)	
Vegetable oils	Tin(II) chloride	0.15:1 molar ratio	T = 150 °C Time = 60 min	Methyl ester (78.1%)	[29]
PHB/PBA	Titanium(IV) isopropoxide	1 mol%	T = 175 °C Time = 20 h Pressure: 3 bar	Copolyesters (79%)	[35]

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