



Structure and thermal properties of various alcoholysis products from waste poly(ethylene terephthalate)

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ABSTRACT

Waste polyethylene terephthalate (PET) has been a core member in plastic polluters due to the great amount consumption in food packaging, soft-drink bottles, fibers and films. It is essential to recycle waste PET and alcoholysis is a significant way to accomplish chemical recycling. In this work, three kinds of dihydric alcohols, including neopentyl glycol (NPG), dipropylene glycol (DPG) and poly(propylene glycol) (PPG), were employed to decompose waste PET with different temperatures, catalysts, and PET. A series of alcoholysis products with different appearance were obtained. The bulk structure and thermal properties of alcoholysis products were investigated by FTIR, ¹H NMR, MALDI-TOF, DSC and TG experiments. It is found that poly(propylene glycol) may react with waste PET to generate copolymer instead of oligomer products, dimers or trimers, etc. This product possesses excellent shelf stability and present transparent appearance, which may hold a great potential application in chemical industry. Moreover, the alcoholysis activity of DPG is the lowest comparing with NPG and EG in degradation of waste PET.

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1. Introduction

As one of the most abundantly produced and used synthetic polymers with good performance including mechanical properties, dimensional stability, electrical insulation, optical clarity, non-toxic and odorless characteristics, polyethylene terephthalate (PET) has been used so widely in daily life as well as industries, such as single-use beverage bottles, clothing, packaging, textiles, and electrical insulating materials, etc (Austin et al., 2018; Yoshida et al., 2016; Zhou et al., 2017a,b; Fang et al., 2015). The large amount of post-consumer PET produces equal amount waste PET with an alarming resistance to biodegradation because of their good properties, especially the excellent stability and high thermal resistance (Al-Salem et al., 2009). Since waste PET is chemically inert, natural degradation via air or micro-organisms is difficult (Zhou et al., 2017a,b). Thus, a certain degree of environmental contamination and waste of resources has been caused by the large consume amount of waste PET, and it is necessary and significant to explore how to recycle and reuse waste PET.

Besides the recent novel biological method (Austin et al., 2018; Yoshida et al., 2016), two main ways were developed to recycle

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waste PET plastics, such as physical and chemical methods. The physical approach is to handle the waste PET via simple physical treatments, including directly blending, mixing, melting, granulation, etc. The chemical approach is success due to the production of profitable and sustainable fuel from waste plastic, providing a high product yield and minimum waste (Al-Salem et al., 2009). This chemical process is to handle the waste PET via chemical degradation methods, whereby degradation and broken of PET polymer chains via chemical reagents and heating via processes including hydrolysis, glycolysis, alcoholysis, ammonolysis and aminolysis for fabricating products with low molecular weight, such as dimethyl terephthalate (DMT) (Hermanová et al., 2015), terephthalic acid (TPA) (Deleu et al., 2016), ethylene glycol (EG) (Jamdar et al., 2017), bis hydroxy ethyl terephthalate (BHET) (Bui et al., 2018) and other chemical products (Cakić et al., 2017). All of these can be reused as raw materials in chemical and materials engineering to complete recycle of waste PET. Among these chemical processes, one of the most attractive strategies is alcoholysis by using alcohols as solvents for degradation of waste PET. It has been developed more than 40 years and currently the most used commercial PET recycling method. It has been practiced by the renowned chemical companies including DuPont Goodyear, Shell Polyester, Zimmer, Eastman Kodak, etc. (George and Kurian, 2014). The alcoholysis process has been regarded as one of the most promising way to recycle transparent waste PET scrap without

colorants or dyes nowadays (Welle, 2011; Bedell et al., 2018). It can result in reformation of terephthalate esters followed by decoration of desired organic groups on PET chains (Zhang et al., 2016a,b). Pardal and Tersac (2007) investigated the impact of degradation temperature, catalyst and polymer morphology on the kinetics of waste PET glycolysis for understanding the mechanism of the complex diethylene glycol (DEG) glycolysis reactions in degrading process. They suggested that the degradation time is shorter when the waste PET and DEG were heated at 220 °C before mixing than that after mixing. Amaro et al. (2015) also employed DEG as glycolysis agent to degrade waste PET to obtain the liquid phase. Thereafter, the degradation products were used as secondary plasticizer with di(2-ethylhexyl) phthalate (DEHP) to produce flexible PVC compounds. It is found that the PET degradation products can improve both the processing characteristics and the thermal stability of PVC compounds. Meanwhile, the hardness within the top values of the Shore A scale can be maintained and the plasticizers migration can be reduced by 23%, which may hold a great potential application in plastic industry. In addition, the alcoholysis products of waste PET are able to be employed directly as raw materials for preparation waterborne polyurethane (WPU) according to our previous work (Zhou et al., 2017a,b; Fang et al., 2015). It is proved that the alcoholysis products of waste PET can improve the thermal resistance, particle size, stability of viscosity of WPU. The formulations containing glycolized oligoesters within the hard segment sections of the polyurethanes provide the best performance of WPU. However, owing to the unstable and confused components, the non-purification alcoholysis products should be used matching with fresh chemical agent (for example poly(propylene glycol), poly(ethylene glycol), poly(neopentyl glycol adipate), etc.) in preparing polyurethane to avoid separation (Fang et al., 2015). Therefore, it is essential to analyze the main components of alcoholysis products from waste PET for wide application.

Here we present a facile alcoholysis process to degrade waste PET in a one-pot strategy, and then evaluate the structure and thermal properties of the alcoholysis products. A series of waste PET alcoholysis products were prepared to study the degradation parameters including the waste PET species, degradation temperatures, alcoholysis agents, catalysts. The oligomer (PPG, Mn = 2000) was employed as alcoholysis agent to decompose different waste PET for the first time, which may result in particularly interesting results. For all we know, little research has been devoted to the oligomer alcoholysis process for waste PET. It is noted that when oligomer is employed, the products may hold a great potential application in waterborne polyurethane synthesis due to the necessary of oligomer as soft segment (Zhou et al., 2017a,b). Meanwhile, waste PET with green colorant was used as raw material firstly to investigate the degradation behavior. The prepared alcoholysis products can be directly used in preparation of waterborne polyurethane according to our previous work (Zhou et al., 2017a,b; Fang et al., 2015).

2. Experiments

2.1. Materials

Post-consumer PET bottles with an average molecular weight from 2.5 to 3.0×10^4 g/mol were collected. Neopentyl glycol (NPG) and dipropylene glycol (DPG) were received from Sino-pharm Chemical reagent Co., Shanghai, China. N-Butyl titanate, supplied by Kelong Chemical, Chengdu, China, was used as the trans-esterification catalyst for the depolymerization of PET.

2.2. Mechanical clean process of post consumed PET

The post-consumer PET was collected from the waste Nongfu Spring and other soft drinks bottles. The labels, cap and bottom

of the bottles were abandoned, and then, the bottles were chopped into flakes with average size ca. 5 mm × 5 mm. The PET flakes were washed with deionized water, diluted hydrochloric acid (HCl, 2 mol/L), and potassium hydroxide (KOH, 2 mol/L) respectively to remove the contaminants on the surface of bottles. The washed PET flakes were dried under room temperature for 48 h and then moved in a vacuum drying oven at 50 °C for 8 h.

2.3. Alcoholysis process of post-consumer PET and pure PET sheet

The PET flakes were glycolized by NPG, DPG, PPG and their mixture with proper molar ratio of PET repeating unit to glycol according to the previous [3,8]. These mixtures and 0.5 wt% n-Butyl titanate catalyst were charged in a four necked glass reactor equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic oil bath. The alcoholysis reaction was carried out at 190 °C for 1 h to obtain glycolysis product (GOP) pre-depolymerized products; subsequently the temperature was raised to 210 °C under reflux in nitrogen atmosphere for about 5 h until all the solids disappeared. The obtained glycolized oligoesters were filtrated by a 60 mesh screen to obtain the liquid products, and then dried in a vacuum drying oven at 45 °C and 0.05 MPa for 8 h.

GOP1: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 639 (7), 626(14), 613(10), 595(15), 582(30), 569(19), 538(44), 525 (74), 507(19), 493(53), 480(60), 454(79), 436(97), 411(99), 399 (10), 392(19), 380(31), 366 (100), 354 (16), 339 (32), 326 (28), 322(99), 304(97), 282 (13), 274(35), 266(48), 250 (34), 216 (97), 190 (98).

GOP2: ^1H NMR (400 MHz, DMSO) δ 8.27–7.75 (m, 123H), 5.38–5.00 (m, 15H), 4.95 (s, 9H), 4.82–4.50 (m, 56H), 4.50–4.09 (m, 105H), 4.09–3.93 (m, 27H), 3.83–2.79 (m, 341H), 3.86–2.30 (m, 409H), 3.93–2.30 (m, 416H), 3.10–2.79 (m, 5H), 2.51 (s, 59H), 1.28 (t, J = 9.9 Hz, 37H), 2.07–0.72 (m, 367H), 1.24–1.01 (m, 166H), 1.89–0.72 (m, 363H), 1.00 (d, J = 6.6 Hz, 46H), 0.89 (d, J = 36.4 Hz, 77H), 0.85–0.80 (m, 7H), 0.75 (s, 24H). MALDI-TOF: m/z = 538(2), 525(8), 493(4), 480(7), 454(2), 436(24), 414(5), 410 (17), 392(0.7), 380(0.3), 366(100), 322(72), 309(0.2), 304(21), 290 (0.6), 275(0.2), 216(62), 190(12).

GOP3: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 930 (1.1), 915(3), 898(3), 880(3), 864(2), 507(11), 493(27), 480(46), 454 (31), 436 (83), 410 (89), 397(5), 366(100), 356(23), 340(25), 338(18), 327(14), 322(98), 250(14), 216(91), 190(85).

GOP4: ^1H NMR (400 MHz, CDCl_3) δ 8.43–7.80 (m, 89H), 7.28 (s, 4H), 5.32 (dt, J = 89.3, 41.5 Hz, 4H), 4.71 (s, 5H), 4.54–4.19 (m, 72H), 4.19–4.02 (m, 7H), 4.02–3.14 (m, 329H), 2.81 (s, 175H), 1.59–1.00 (m, 322H), 0.92 (d, J = 17.8 Hz, 96H), 0.77–0.18 (m, 7H). MALDI-TOF: m/z = 914 (0.6), 898(1), 879(3), 863(2), 508 (5), 493(22), 480(44), 436(81), 410(85), 402(13), 397(3), 392(10), 366 (100), 354(5), 338(9), 326(7), 322 (85), 304(63), 290(15), 282(3), 250(23), 216(79), 190(35).

GOP5: ^1H NMR (400 MHz, DMSO) δ 8.24–7.92 (m, 12H), 5.41–5.05 (m, 1H), 4.96 (d, J = 5.3 Hz, 1H), 4.78–4.60 (m, 3H), 4.60–4.34 (m, 11H), 4.34–4.16 (m, 9H), 4.08 (s, 4H), 3.88–3.11 (m, 50H), 3.00–2.51 (m, 1H), 2.51 (s, 1H), 2.55–2.46 (m, 4H), 1.36–1.20 (m, 3H), 1.20–0.65 (m, 54H), 1.20–0.78 (m, 43H). MALDI-TOF: m/z = 538(0.7), 493(1), 480(0.5), 436(9), 410(19), 366(100), 322(51), 304(9), 216(44), 190(0.8).

GOP6: ^1H NMR (400 MHz, DMSO) δ 8.25–7.96 (m, 79H), 5.40–4.97 (m, 6H), 4.96 (d, J = 5.4 Hz, 7H), 4.71 (t, J = 5.5 Hz, 19H),

4.67–4.38 (m, 100H), 4.38–4.16 (m, 75H), 4.08 (s, 32H), 3.85–3.10 (m, 443H), 2.55–2.46 (m, 32H), 1.35–0.80 (m, 379H), 0.75 (s, 108H). MALDI-TOF: m/z = 683(4), 626(9), 582(22), 538(34), 525(59), 507(10), 493(42), 480(48), 436(92), 410(95), 399(5), 366(100), 354(7), 338(15), 326(11), 322(99), 304(93), 282(5), 275(24), 250(12), 216(95), 190(72).

GOP7: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 507(7), 481(7), 448(6), 436(17), 410(26), 366(100), 319(2), 275(5), 230(6), 212(4), 190(24).

GOP8: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 582(0.5), 537(2), 525(6), 480(7), 452(2), 436(20), 410(19), 366(100), 322(35), 304(9), 216(34), 190(3).

GOP9: ^1H NMR (400 MHz, DMSO) δ 8.25–8.00 (m, 60H), 8.00–7.52 (m, 15H), 5.39–5.04 (m, 10H), 4.96 (t, J = 5.4 Hz, 8H), 4.76–4.57 (m, 16H), 4.57–4.36 (m, 104H), 4.36–4.16 (m, 48H), 3.89–2.99 (m, 398H), 4.16–1.83 (m, 421H), 3.89–1.83 (m, 413H), 2.55–2.46 (m, 14H), 1.52–1.06 (m, 96H), 1.23–1.06 (m, 61H), 1.23–1.00 (m, 311H), 1.00–0.33 (m, 38H). MALDI-TOF: m/z = 595(2), 582(4), 537(6), 525(14), 507(2), 480(15), 452(7), 436(31), 410(25), 392(2), 386(4), 366(100), 356(2), 348(2), 340(2), 322(35), 304(14), 250(6), 216(36), 190(7).

GOP10: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 582(1), 538(3), 525(5), 493(2), 480(7), 452(3), 436(22), 410(22), 366(100), 356(0.1), 322(17), 304(8), 250(4), 216(40), 190(2).

GOP11: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 1786(0.2), 1728(0.7), 1670(1), 1612(2), 1554(2), 1495(2), 1437(1), 1379(0.4), 1320(0.1), 582(4), 537(5), 524(4), 506(1), 480(14), 452(7), 436(29), 410(26), 366(100), 264(1), 216(4), 190(0.9).

GOP12: ^1H NMR (400 MHz, DMSO) δ 8.29–7.99 (m, 66H), 4.95 (dd, J = 5.5, 3.4 Hz, 8H), 4.77–4.13 (m, 155H), 4.08 (s, 23H), 3.97–3.12 (m, 343H), 2.51 (dt, J = 3.5, 1.7 Hz, 19H), 1.34–1.23 (m, 10H), 1.23–0.73 (m, 364H), 0.69–0.23 (m, 6H). MALDI-TOF: m/z = 577(2), 565(3), 519(8), 507(21), 464(9), 448(38), 436(10), 410(14), 390(27), 366(100), 322(2), 275(2), 216(0.1), 190(7).

2.4. Characterization of waste PET alcoholysis products

The molecular weights of the prepared GOP samples were investigated by matrix-assisted-laser-desorption-ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) analysis using an UltrafleXtreme Bruker mass spectrometer Smartbeam-II laser. The MALDI-TOF-MS spectra were acquired in the negative and positive ion mode over a mass-to-charge ratio (m/z) range of 100–2000 Da. The prepared GOP samples were dissolved in tetrahydrofuran (THF) in a v/v ratio of 1:5. The matrix solution of alpha-cyano-4-hydroxycinnamic acid (CCA, M_n = 189.17) was employed as the matrix solution. The dissolved samples were mixed with the matrix solution in a v/v ratio of 1:100. ^1H NMR spectra were obtained on a Bruker-400 MHz spectrometer, using sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard, with DMSO as solvent. Fourier transform infrared spectroscopy (FT-IR) was used to identify the structure of the alcoholysis products. The infrared spectra of the liquids were obtained using a Fourier transform IR spectrophotometer (SHIMADZU

FTIR-8400S (CE)) and recorded in the transmission mode at room temperature by averaging 20 scans at a resolution of 16.0 cm^{-1} . The spectra were analyzed in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. Differential scanning calorimetry (DSC) experiments were carried out in NETZSCH DSC 200 F3 Maia[®] instrument with a temperature range from -100 to $300\text{ }^\circ\text{C}$ at a heating rate $10\text{ }^\circ\text{C/min}$ under an nitrogen atmosphere (flow rate: 50 mL/min). To remove the thermal history, three consecutive runs were carried out: (1) Heating from room temperature to $100\text{ }^\circ\text{C}$. (2) Cooling from 100 to $-100\text{ }^\circ\text{C}$ ($20\text{ }^\circ\text{C/min}$). (3) Heating from -100 to $300\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C/min}$). Thermogravimetric (TG) experiment was performed under nitrogen atmosphere with NETZSCH TG209F3. The samples weighing between 4 and 10 mg were placed in an alumina ceramic crucible and heated from 30 to $600\text{ }^\circ\text{C}$ with an air flow of 30 mL/min and heating rates of $10\text{ }^\circ\text{C/min}$. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The high performance liquid chromatography (HPLC) (Shimadzu LabSolutions) experiments were run using isopropyl alcohol/n-hexane of ratio $50/50$ (v/v) as the mobile phase by using thermostatic columns ($40\text{ }^\circ\text{C}$) at a flow rate of 1 mL/min under pumping pressure in the range of $3.5\text{--}7.0\text{ MPa}$. The detection of HPLC was continued for 30 min . The yield of each component was calculated by Eq. (1) (López-Fonseca et al., 2011):

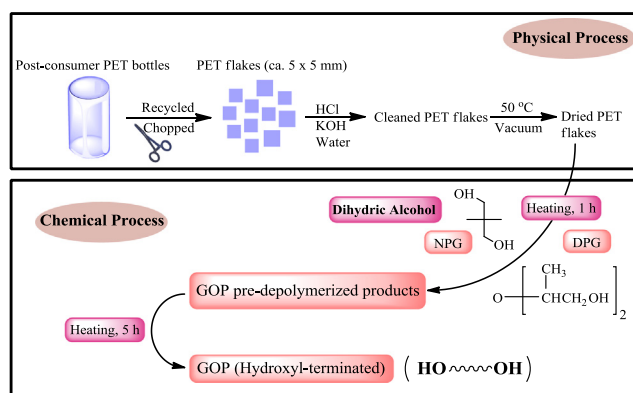
$$X(\%) = \frac{W_{\text{component},t}/Mw_{\text{component}}}{W_{\text{PET},0}/Mw_{\text{PET}}} \times 100 \quad (1)$$

where $W_{\text{PET},0}$ and $W_{\text{component},t}$ refer to the initial weight of PET and the weight of each component in degradation products at a specific reaction time, respectively. Mw_{PET} and $Mw_{\text{component}}$ are the molecular weight of the PET repeating unit (192 g/mol) and each component in the degradation products (relying on the component), respectively. When the degradation component is BHET, the $Mw_{\text{component}}$ should be 254 g/mol . In this work, 16 g waste PET was employed in each degradation experiment.

3. Results and discussion

3.1. Effect of reaction conditions on structure of waste PET alcoholysis products

The cleaning and alcoholysis processes of PET waste with dihydric alcohol proceeds are carried out according to Scheme 1. The possible degradation reactions are illustrated in Fig. 1. The waste PET was chopped and cleaned through the physical process and then degraded via the chemical process under the function of heating and dihydric alcohol. The products, abbreviating of GOP series samples (GOP1, GOP2, GOP3, ..., GOP12), are obtained with the



Scheme 1. The cartoon for alcoholysis of waste PET via the physical and chemical processes.

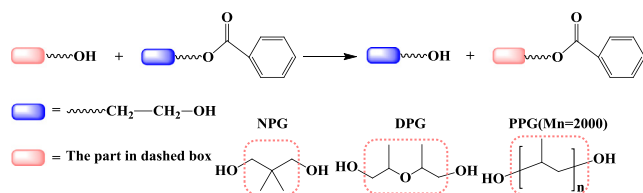


Fig. 1. Mechanism of waste PET alcoholysis using dihydric alcohol.

operation conditions of the alcoholysis listed in Table 1. Alcoholysis agent, temperature, catalyst and type of PET, which are the variable conditions, are investigated and analyzed to study their impact on the GOP components and bulk structure.

As shown in Fig. 2, various liquid degradation products can be obtained by the degradation of waste PET flakes (Fig. 2b) with different alcoholysis agents. The colorless transparent waste PET was the main raw material in this work. As comparison, pure PET (Fig. 2a) and green waste PET (Fig. 2c) were employed to study the effectiveness of the proposed recycling method. A series of alcoholysis products were presented in Fig. 2d, showing a common feature of viscous fluid with different colors. Some samples, such as GOP7 and GOP8, even present obvious stratification phenomenon after degradation, indicating that the combination of NPG and PPG is less effective in degrading waste PET for the preparation of stable chemical agent.

The organic groups and bulk structures of waste PET alcoholysis products were analyzed by FT-IR methods. Fig. 3 shows the FT-IR spectra of glycolized waste PET oligoesters obtained from alcoholysis with a waste PET/glycol agents molar ratio of 1:3. It is obvious that all the alcoholysis products present almost the same FTIR curve in Fig. 3. The band observed in the region of 3479 cm^{-1} is attributed to free hydroxyl groups present in the waste PET oligoesters alcoholysis product. The broad peaks appearing at $3000\text{--}2800\text{ cm}^{-1}$ relate to alkyl and C–H which originate from glycolized oligoesters formed during the alcoholysis reaction. The peak at 1724 cm^{-1} can be attributed to C=O stretching which is a key band and confirms ester bond formation during the alcoholysis of waste PET using glycol. This can be compared with the FT-IR spectra of currently used glycols which do not contain bands around 1750 cm^{-1} (Cakić et al., 2015). Band at 1578 cm^{-1} is mainly referred to C=C stretching vibration and at 1454 cm^{-1} originates from aromatic C–H in the aromatic ring in waste PET degradation products. The peak at 1276 cm^{-1} can be ascribed to the asymmetric bending vibrations of C–O–C from ester groups, and the peak at about 729 cm^{-1} can be ascribed to =CH of the aromatic ring. These transmittance peaks are clear evidence that the organic groups of the final alcoholysis products from all of the operation conditions are similar, which are compounds having hydroxyl and ester groups (Tawfik and Eskander, 2010).

The solvent peak is at ca. 2.5 ppm for DMSO and ca. 7.26 ppm for CDCl_3 . According to the degradation mechanism depicted in Fig. 1, the possible alcoholysis products in GOP sample may be various. To confirm the components in the waste PET alcoholysis products, ^1H NMR and Maldi-TOF experiments were carried out. The ^1H NMR signal appeared at ca. δ 8.1 ppm suggests the presence of the four aromatic protons of the benzene ring in the structure. This signal demonstrates that the waste PET has been degraded by the alcoholysis process. It can also be attested by the Maldi-TOF spectra in Fig. 5(a), showing a series gradient degradation m/e peaks in the regions of 1088–507. The differential value of the labeled peaks in Fig. 5(a) is 58 with four ticks in these regions, which may be related to the monomer of PPG (Fig. 4). It suggests that PPG has reacted with waste PET to generate degradation products. The Maldi-TOF spectra show a common peak at m/e 366 for all the prepared GOP products (GOP1–GOP12), indicating that the monomer is irrelevant to the alcoholysis agent, degradation temperature, catalyst. Thus, it is reasonable that this peak is attributed to the fragment belonging to PET, which may be the two repeating units of PET, namely $-(\text{CH}_2)_2\text{OOC}_6\text{H}_4\text{COO}(\text{CH}_2)_2\text{OOC}_6\text{H}_4\text{CO}-$ (Ghaemy and Mossaddegh, 2005). The high intensity of peak at m/e 366 also suggests that this fragment is stable in waste PET alcoholysis degradation process. Meanwhile, another common peak at m/e 190 may be attributed to the matrix solution of alpha-cyano-4-hydroxycinnamic acid (CCA). Owing to the existence of CCA, the peaks shifts that are lower than m/e 190 may be meaningless for the GOP products structure. It is clear from the Maldi-TOF information that the peaks up to m/e 250 and 216 are related to the monomer bis(hydroxyethyl)terephthalate (BHET), which is produced by PET and intermediate ethylene glycol (GOPP8 in Fig. 4). As depicted in Fig. 1, the ethylene glycol (EG, GOPP9 in Fig. 4, $n = 1$) may be the minimum monomer in degrading PET. It may react with the degraded PET via concerted reaction with the added dihydric alcohol (NPG, DPG or PPG) to produce BHET. The existence of BHET can also be demonstrated by the ^1H NMR data. The signals containing δ 4.4 and 3.9 ppm can be found for all GOP products, which are attributed to the methylene protons COO-CH_2 and $\text{CH}_2\text{-OH}$ of ethylene glycol (EG) from BHET. The signal at δ 4.08 can be attributed to the protons of the hydroxyl group (Bui et al., 2018). The doublet at δ 2.51 should be ascribed to the methylene protons of $-\text{O-CH}_2-$ from PET monomeric unit. All the common peaks and signals for GOP samples indicate that the different kinds of PET can be significantly degraded with the parameters in Table 1.

To investigate the main alcoholysis products of the waste PET, the pure PET sheet was employed as the raw material for comparison, corresponding to sample GOP1 in Table 1. According to the Maldi-TOF and ^1H NMR data of GOP1 (Figs. S1 and S2), the intense peaks at m/e 507, 399, 354, 339, 326 and 282 may be related to GOPP1, GOPP2, GOPP3, GOPP4, GOPP5 and GOPP6, respectively.

Table 1
Operation conditions for the alcoholysis of PET.

Sample	Alcoholysis agent	Temperature (°C)	Catalyst	Types of PET	Molar ratio	Components of glycolysis products
GOP1	NPG:DPG	165/185	Butyl titanate	Pure PET	1:3	GOPP1-6, BHET
GOP2	NPG:DPG	190/210	Butyl titanate	Green waste PET	1:3	GOPP1, GOPP4, BHET
GOP3	NPG:DPG	165/185	Butyl titanate	Waste PET	1:3	GOPP1-5, BHET
GOP4	NPG:DPG	190/210	Butyl titanate	Waste PET	1:3	GOPP1-6, BHET
GOP5	NPG:DPG	165/185	Zinc acetate	Waste PET	1:3	GOPP1-6, BHET
GOP6	NPG:DPG	190/210	Zinc acetate	Waste PET	1:3	GOPP1, GOPP4, BHET
GOP7	NPG:PPG	165/185	Butyl titanate	Waste PET	1:3	GOPP4, GOPP6, GOPP7, BHET, GOPP9
GOP8	NPG:PPG	190/210	Butyl titanate	Waste PET	1:3	GOPP4, GOPP6, GOPP7, BHET, GOPP9
GOP9	DPG	165/185	Butyl titanate	Waste PET	/	GOPP2, GOPP3, BHET
GOP10	DPG	190/210	Butyl titanate	Waste PET	/	GOPP2, GOPP3, BHET
GOP11	PPG	165/185	Butyl titanate	Waste PET	/	BHET, PPG-PET copolymer
GOP12	PPG	190/210	Butyl titanate	Waste PET	/	BHET, PPG-PET copolymer

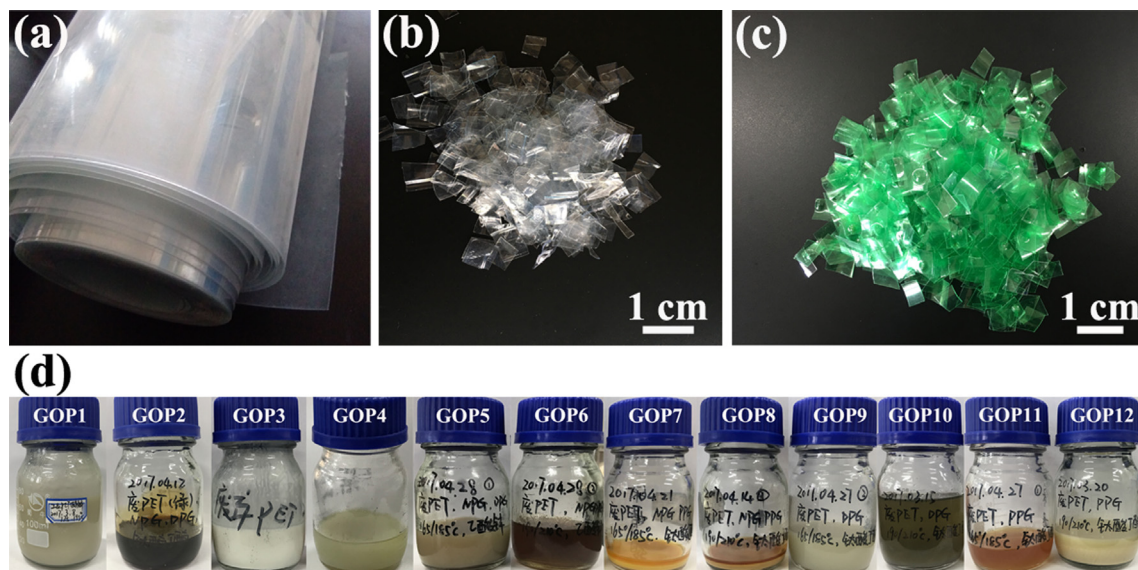


Fig. 2. The digital photos of waste PET flakes and alcoholysis products. (a) Pure PET sheet (b) Transparent waste PET; (c) Green waste PET; (d) Alcoholysis products of the waste PET under different operation conditions.

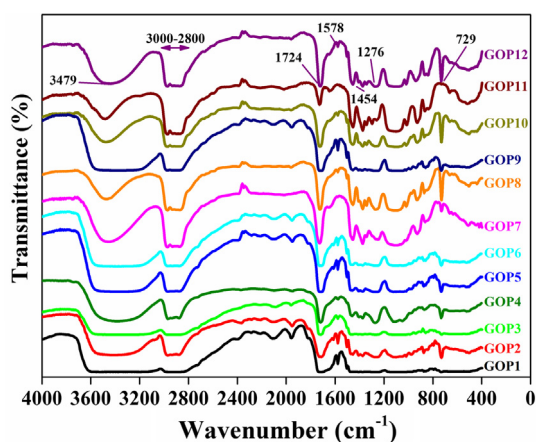


Fig. 3. FTIR spectra of waste PET alcoholysis products (from sample GOP1 to GOP12).

In addition, the peaks at m/e 250 and 216 are related to the monomer BHET (GOPP8), mol. wt. 254 g/mol. The peak at m/e 639 should be attributed to the trimer of PET chain unit (Ghaemy and Mossaddegh, 2005). Thus, the alcoholysis products of pure PET may be various and complex consisting of GOPP1–6 and BHET (GOPP8) in Fig. 4 with the alcoholysis agents of NPG and DPG. Comparing with GOP3, the main m/z peaks and ^1H NMR singlets are similar. Apart from the m/e 282, the intense peaks at m/e 507, 397, 356, 338, 327 and 250 related to GOPP1, GOPP2, GOPP3, GOPP4, GOPP5 and GOPP8 respectively in Fig. 4 can be found in MALDI-TOF analysis. The absence of m/e 282 for GOP3 (Fig. S3) indicates that there is no GOPP6, which may arise from the relatively low glycols reactivity of NPG and EG group. The intense peaks at m/e 930, 915, 898, 880, and 864 are related to the small amount of fragments of $\text{CH}_2\text{OOC}[\text{C}_6\text{H}_4\text{COO}(\text{CH}_2)_2\text{OOC}]_4\text{C}_6\text{H}_4\text{COO}(\text{CH}_2)_2$. Comparing sample GOP4 and GOP3 with different degradation temperature, besides the similar typical peaks with GOP3, the MALDI-TOF data of sample GOP4 (Fig. S4) shows the presence of m/e 282 for GOPP6 with alcoholysis agents of NPG and DPG. It suggests that the higher temperature may assist alcoholysis agents in improving the glycols reactivity to produce GOPP6. In addition, the

absence of m/e 930 in GOP4 indicates that waste PET with higher temperature can degrade deeply. When the green waste PET was employed, the degradation products are slightly different according to the ^1H NMR and MALDI-TOF data. The intense peaks at m/e 493, 322 and 304, 309, 216 may be ascribed to the monomer of GOPP1, GOPP4, GOPP5 and GOPP8 (BHET) respectively, indicating that the degradation behavior of green waste PET (Fig. 2c) is a little different from that of pure PET and transparent waste PET. Moreover, the MALDI-TOF spectrum (Fig. S5) illustrates far more lean peaks distribution than that of GOP1, GOP3 and GOP4, suggesting fewer kinds of monomers in degradation products. Zinc acetate was employed as catalyst instead of butyl titanate to degrade waste PET for preparation of sample GOP5 (Fig. S6) and GOP6 (Fig. S7) under different temperatures. It is obvious that there are GOPP1–GOPP6 and GOPP8 products in GOP6 sample from ^1H NMR and MALDI-TOF data, while there are only GOPP4 at m/e 322 and 304, GOPP8 at m/e 216, and little GOPP1 at m/e 493 in GOP5. We assume that waste PET degrades slightly under the combined temperature of 165/185 with zinc acetate. In addition, comparing with sample GOP3, the components in GOP5 are less, indicating that the catalyst activity of butyl titanate is higher than zinc acetate in degrading waste PET. The presence of GOPP4 and GOPP8, and the absence of DPG alcoholysis products (eg. GOPP2, GOPP3, GOPP5) also imply that the alcoholysis activity of NPG and EG is higher than DPG. DPG possesses the lowest alcoholysis activity in degrading PET. Moreover, the higher degradation temperature of GOP6 endows more ingredients than that of GOP5, which may further attest that high temperature contributes to the glycols reactivity to produce degrading monomer. The MALDI-TOF spectrum of GOP2 is similar with that of GOP5, which may indicate that the components in GOP2 are mainly GOPP1, GOPP4 and GOPP8.

As shown in Fig. 5, the addition of oligomer polyols (PPG, $M_n = 2000$) causes different degradation behavior. A series of regular degradation MALDI-TOF mass peaks can be observed, which may be ascribed to the degradation of both waste PET and PPG. As demonstrated above, in degrading process, GOPP9 with different n values may be produced, which may further act as alcoholysis agents to degrade waste PET to produce a main product of BHET. In this way, PPG may be degraded under the function of GOPP9 as well. As depicted in Fig. 5c, the m/e peaks in 2 blue dashed box area

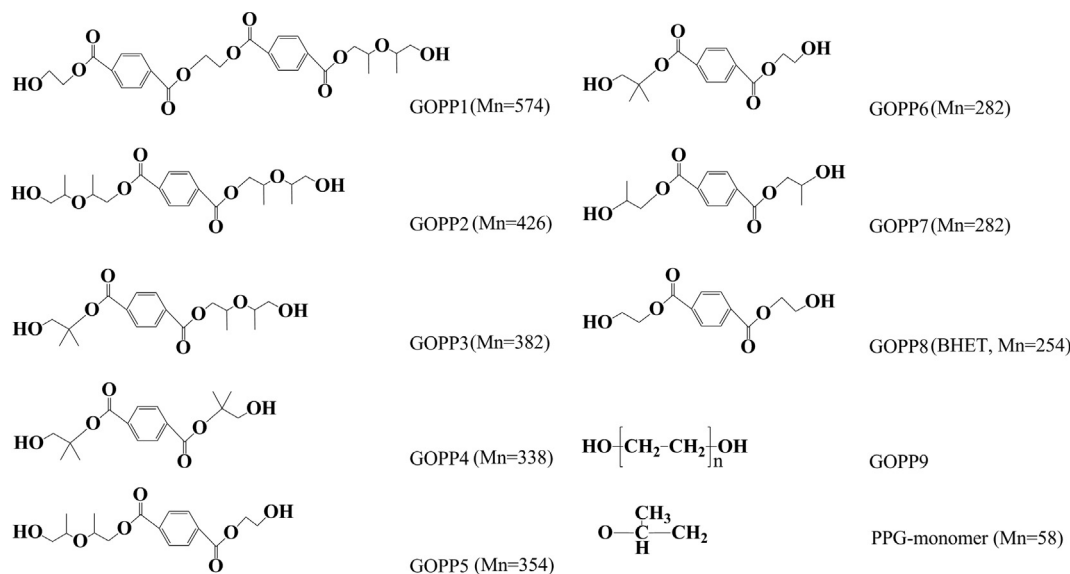


Fig. 4. The main monomer and dihydric alcohol fragments structures of the components in GOP samples.

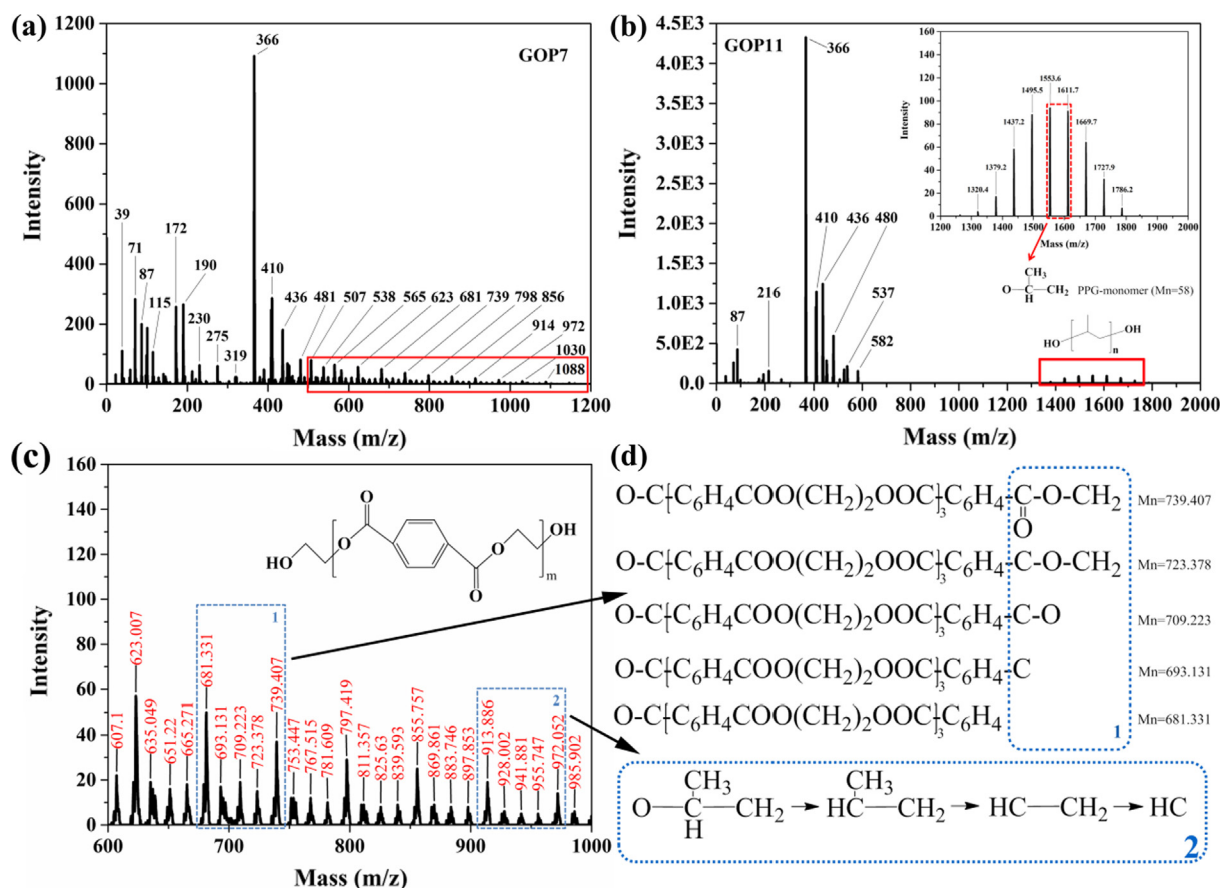


Fig. 5. MALDI-TOF spectra of the alcoholysis products (a) GOP7; (b) GOP11, the inset diagram illustrates the red box area mass spectrum, which ascribed to the degradation of PPG; (c) The partial MALDI-TOF mass spectrum in (a), which ascribed to the degradation of waste PET; (d) The degradation procedure (1) of ester and methylene groups, and the degradation procedure (2) of PPG monomer according to the regular m/e peaks.

(Fig. 5d) may be ascribed to the degradation of PPG, while the m/e peaks in 1 blue dashed box area (Fig. 5d) may be ascribed to the degradation of waste PET. Thus, we believe the reason for such degradation behavior in GOP7 may be attributed to the complex PET-PPG copolymer (uncertain degree of polymerization). In

degradation, PPG plays the role of alcoholysis agent to degrade waste PET, and the PET-PPG copolymer is produced to form feature structure of $-\text{COO}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$ according to the MALDI-TOF mass spectrum (Fig. 5c and d). This can be demonstrated by the ^1H NMR spectrum (Fig. S8), the signals containing δ 3.25, 3.55, and

3.67 ppm should attributed to the protons of the $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ in $-\text{COO}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$, respectively. Thus, the addition of PPG can produce some kind of PET-PPG copolymers by alcoholysis process. To further confirm this result, PPG was used as alcoholysis agent solely to degrade waste PET under different temperature, namely sample GOP11 and GOP12 in Table 1. As illustrated in Fig. 5b, the series m/e peaks in red box area should be ascribed to the degradation of PPG with monomer molecule weight of 58, while these peaks are absent in GOP12 (Fig. S9). It suggests that PPG has reacted with waste PET to generate copolymer. Meanwhile, with the increasing degradation temperature, PPG has degraded totally, indicating that high temperature can improve the glycols reactivity, corresponding to the previous analysis. In addition, the presence of BHET can be confirmed according to the MALDI-TOF data.

It is surprised that none of monomers listed in Fig. 4 can be found except for little BHET, indicating that the alcoholysis process between PPG and PET may be different from NPG and DPG. This also attests indirectly that PPG may react with waste PET to generate other products. Comparing GOP8 with GOP7, it is obvious that the m/z peaks with higher mass are absent (Fig. S10), indicating that the increasing temperature can enhance the degradation degree to generate more monomer, such as BHET. Meanwhile, the peak strength of m/z 250 and 216 referring to BHET for GOP7, GOP8, GOP11, GOP12 are different obviously, and most of them are absent, except for GOP8. It suggests that the presence of PPG dose not benefit production of BHET, indicating further that the generated amount of GOPP9 is little in degrading waste PET by PPG. ^1H NMR spectra may further confirm the main components of the alcoholysis products generated by PPG, as depicted in Figs. 6 and S2. The signal at ca. δ 8.1 ppm indicates the presence of the four aromatic protons of the benzene ring for GOP7, GOP8, GOP11 and GOP12. However, this signal is relatively weak for sam-

ple GOP11 and GOP12, especially for GOP11, which has disappeared on the curve. As depicted in Fig. 6, the other samples present multiple signals around δ 8.1 ppm, except for GOP11. It is obvious that the single difference among GOP11, GOP12, GOP7, GOP8 and GOP 3 is caused by the PPG. When PPG was employed as alcoholysis agent, the signals for the aromatic protons region shifted. For sample GOP7, GOP8 and GOP12, the multiple peaks at ca. δ 8.1 ppm are normal, while that for GOP11 shift to δ 8.24 ppm, 8.21 ppm and 8.076 ppm. These peaks are indeed weak comparing with the others, indicating that there may be an intermediate with novel structure in the alcoholysis products under the function of PPG. The signal at ca. 8.24 ppm may be the characteristic peak for the intermediate due to the relatively strong abundance compared with the aromatic protons of the benzene ring at ca. 8.1 ppm under low degradation temperature (165/185 °C). When the degradation temperature increases, the signal at ca. 8.24 ppm becomes weak compared with the signal at ca. 8.1 ppm for sample GOP8 and GOP12. We assumed that an indistinct intermediate possessing two benzene ring may be produced by the reaction between PPG and PET, as shown in the chemical structure in Fig. 6. The structure of GOP products and mechanism of the PPG alcoholysis waste PET are still unclear. The alcoholysis process and reaction between oligomer polyols and waste PET will be further studied in our future work, as well as the kinetics of the waste PET degradation by oligomers.

DPG was used as alcoholysis agent solely to investigate the function of NPG + DPG and DPG in degrading waste PET. The peak m/e at 392 (Fig. S11) can be attributed to the monomer of $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_2\text{OOCCH}_6\text{H}_4\text{COOCH}_2(\text{CH}_3)\text{CHO}(\text{CH}_3)\text{CHCH}_2-$, belonging to the GOPP2, and the peak m/e at 356 can be attributed to the monomer of GOPP5. The presence of BHET can also be confirmed. As our expected, the monomers are mainly GOPP2, GOPP3 and BHET in GOP9 and GOP10 with DPG as the alcoholysis agent.

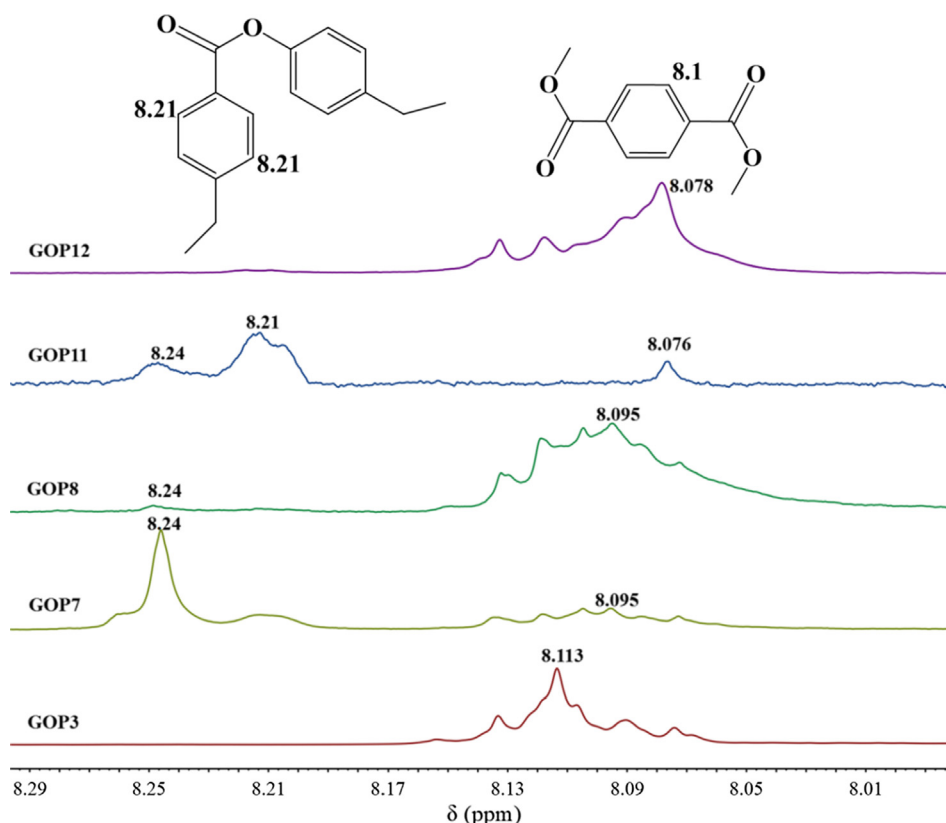


Fig. 6. ^1H NMR spectra for the prepared alcoholysis products by using PPG with δ indicating the aromatic protons.

To further investigate quantitatively the alcoholysis products, HPLC chromatogram of GOP samples was obtained. The solution was prepared by dissolving about 2 μL GOP sample in 2 mL of isopropyl alcohol/n-hexane of ratio 50/50 (v/v) mixture. The typical HPLC chromatogram of GOP7 and GOP11 is shown in Fig. 7. According to the previous (Ghaemy and Mossaddegh, 2005), a dominant peak at the retention time of about 3.75 min can be observed normally, which is attributed to the monomer BHET. For sample GOP7, the two week but continuous peaks at the retention time of 3.537 min and 3.742 min respectively may ascribed to the monomer of BHET, indicating that there is small amount of BHET in GOP7. The peak at retention time of about 4.501 min may be related to the presence of diethylene glycol end groups, corresponding to the MALDI-TOF spectra result. This typical peak of BHET disappeared on the GOP11 chromatogram depicted in Fig. 7(b), suggesting that no BHET exists. This result further confirms that the degradation process of waste PET by PPG is different with that of NPG or DPG. The small peaks at retention time in the range of 4–6 min may be assigned to the presence of dimer or trimer, and the peaks at retention time higher than 7 min may be related to the presence of higher oligomers from the GOP11 chromatogram (Fig. S14) (Ghaemy and Mossaddegh, 2005). For sample GOP2, the peak attributing to BHET appears at retention time of about 3.537 min. A strong peak at the retention time of about 7.242 min can be observed (Fig. S13), indicating the presence of large amount of higher oligomer in green waste PET degradation product. The yield and weight of each monomer calculated by the Eq (1) and peak area of GOP2, GOP7 and GOP11 are listed in Table 2. According to the data in Table 2, the GOP2 alcoholysis product is mainly oligomers from waste PET, indicating that most of the waste PET has degraded into liquid oligomers. This result suggests that the alcoholysis of green waste PET is harder than that of transparent waste PET, corresponding to the previous result

(Welle, 2011; Bedell et al., 2018). Furthermore, there are mainly oligomers in GOP11, which has also been detected by the MALDI-TOF in Fig. 5(b). These oligomers may arise from the possible copolymers generated by PPG and waste PET reaction, or probable residual PPG. This further confirms that the obtained product holds potential application in polyurethane preparation.

3.2. Thermal stability and properties

The thermal resistance of the prepared GOP samples was detected by TG experiments. The decomposition stages and DTG curves were shown in Fig. 8. The temperatures were obtained by the derivative curves of the GOP samples, of which inflection point gave the information of degradation temperatures at a maximum rate of weight loss (Zhou et al., 2017a,b). According to the DTG curves (Fig. 8b), there are one, two or three steps of degradation temperatures as depicted in Table 3 for different GOP samples. For sample GOP1, GOP2, GOP3, GOP4, GOP5, GOP6, GOP9 and GOP10, a first weight loss inflection point around 150–176 $^{\circ}\text{C}$ is presented. This weight loss in the range of 10–60 wt% may be attributed to the thermal decomposition of the BHET fraction formed during the glycolysis reaction (Zhou et al., 2017a,b; Rajasekaran and Maji, 2018). However, this decomposition is absent for the prepared GOP7, GOP8, GOP11 and GOP12 samples, indicating that there is no or just a little BHET when PPG is employed as alcoholysis agent, corresponding to the results in MALDI-TOF and ^1H NMR analysis. The weight loss of BHET in GOP3 is the highest (56 wt%), implying that the content of BHET is highest. It suggests that the content of produced dihydric alcohol (namely GOP9) in GOP3 is the largest, which can possess higher alcoholysis activity (when the $n = 1$, the product is EG) in degrading waste PET comparing with the other three alcoholysis agents. Thus, BHET can be obtained with relatively low degradation temperature in degrading waste PET, reducing the cost for recycling waste PET. The second weight loss inflection point in the range of 205–245 $^{\circ}\text{C}$ with the weight loss of about 10–40 wt% may be due to the thermal decomposition of the dimer or trimer from waste PET for sample GOP1, GOP2, GOP4, GOP5, GOP6 and GOP10. Interestingly, the second thermal decomposition stage is absent for GOP3, indicating that there is no residual dimer or trimer from waste PET and all the waste PET has been transformed into alcoholysis products. This may be caused by the highest alcoholysis activity to produce the largest amount of BHET for GOP3, corresponding to the first decomposition result. Comparing GOP9 and GOP10, waste PET can be degraded into oligomers without residual dimer or trimer when DPG is used solely as alcoholysis agent. Moreover, it is obvious that there is some dimer or trimer form waste PET in GOP12, while no such product can be found in GOP11 with relatively low degradation temperature. These further confirm that waste PET can be degraded to produce BHET with low temperature. For GOP7, GOP8, and GOP11, only one decomposition stage is presented, attributing to the thermal decomposition of oligomers. The last decomposition weight loss in the range of 25–51 wt% with the temperature around 380–442 $^{\circ}\text{C}$ may be also due to the thermal decomposition of the PET produced by the thermal polymerization of oligomers during the thermogravimetric analysis process according to the previous (Rajasekaran and Maji, 2018). As a conclusion, it is suggests that the thermal resistance of the PET produced by the thermal polymerization of oligomers is highest, and then the thermal polymerization of dimer or trimer, and the last is BHET. In addition, in degrading waste PET, relatively low temperature may be benefit to the yield of thermal polymerization of oligomers.

The thermal characteristic of the GOP products were studied by using DSC and the curves and thermal behavior data were shown in Fig. 9 and Table 4. From the heating scan, an apparent glass tran-

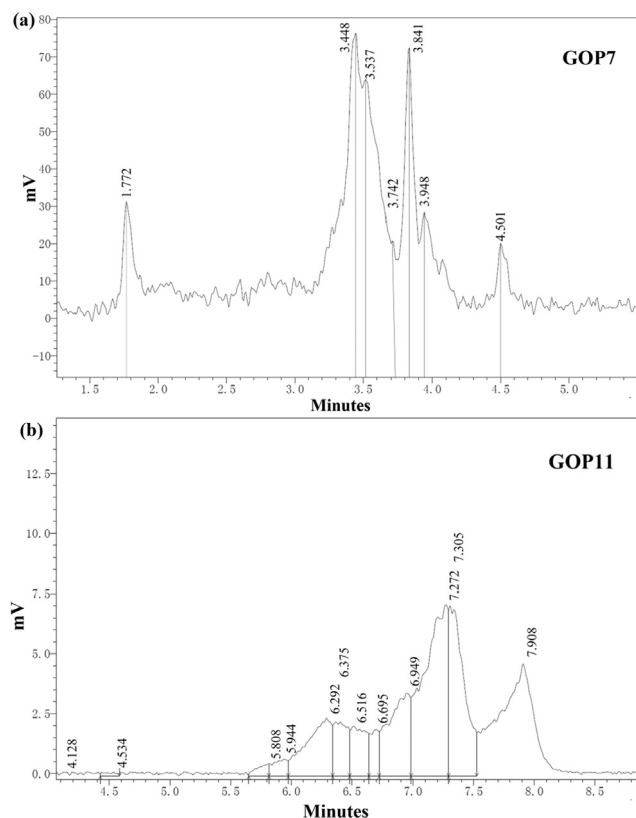
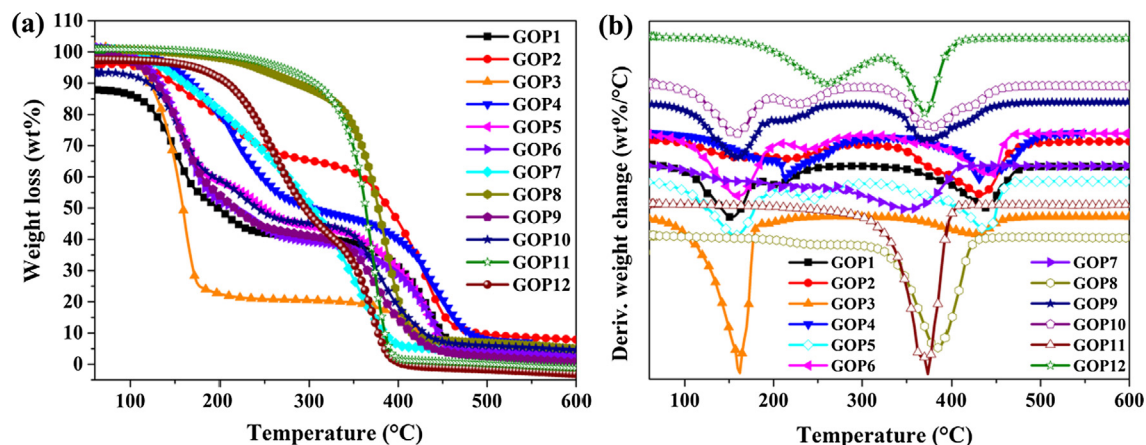


Fig. 7. HPLC chromatogram of the GOP7 and GOP11 (a) GOP7; (b) GOP11.

Table 2

Characterization of component, yield and weight of the alcoholysis product.

Sample	BHET		Dimer or trimer ^a		Oligomers ^b	
	Yield	Weight	Yield	Weight	Yield	Weight
GOP2	5.6%	1.2 g	10.5%	3.36 g	83.6%	37.4 g
GOP7	22.3%	4.72 g	10.4%	3.33 g	/	/
GOP11	/	/	14.9%	4.77 g	63.3%	30.7 g

^a The molecule weight of dimer was assumed as two repeated PET monomer units.^b The molecule weight of dimer was regarded as the highest *m/e* value from the MALDI-TOF data.**Fig. 8.** Thermal stability of all the prepared alcoholysis products (a) TG curves; (b) DTG curves.**Table 3**

Main decomposition of the prepared GOP samples from waste PET.

Samples	First decomposition		Second decomposition		Third decomposition	
	T_a (°C)	Weight loss (wt%)	T_b (°C)	Weight loss (wt%)	T_c (°C)	Weight loss (wt%)
GOP1	150.6	19.6	205.6	40.1	438.1	32.5
GOP2	163.7	13.3	219	11.6	434.3	49.5
GOP3	162.1	56	/	/	427.1	35.2
GOP4	175.6	12	213.3	14	430.8	44.6
GOP5	156.3	27	243.8	25	436.3	36.6
GOP6	161.6	29.2	239.1	25	441.6	33.8
GOP7	/	/	/	/	349.3	72.3
GOP8	/	/	/	/	385.3	60.7
GOP9	157.9	26.2	/	/	380.4	51
GOP10	159.5	20.4	230.5	20.4	381.5	25.3
GOP11	/	/	/	/	373.9	70.5
GOP12	257	27.7	/	/	370.3	52.7

 T_a , T_b , and T_c are the temperatures of inflection point in DTG curves for the first, second, and third decomposition.

sition temperature (T_g) (the points of the arrows in Fig. 9) was observed, of which temperature range has been labeled T_1 , T_2 , T_3 , T_4 in Table 4. Another two peaks belonging to melting temperature (T_m), of which values are listed in Table 4, can be observed on the curves of the most GOP samples (except for GOP11 and GOP12). It is obvious that the T_g of GOP3 (–75.3 to –67.5 °C) is the lowest among all the GOP samples, which may be caused by the large amount of BHET. It is reported that the T_g of degradation products decreased with increasing concentration of BHET (Parab et al., 2014). Thus, the lowest T_g of GOP3 suggests that the amount of BHET may be the highest comparing with other GOP samples, corresponding to the TG results. In verse, the T_g of GOP12 is the highest in degrading transparent waste PET (except for GOP2 with green waste PET), indicating that the amount of BHET is the smallest. It attests that the addition of PPG hinders the depolymerization of BHET from the reaction between waste PET and EG. This assumption is an auxiliary proof for the different

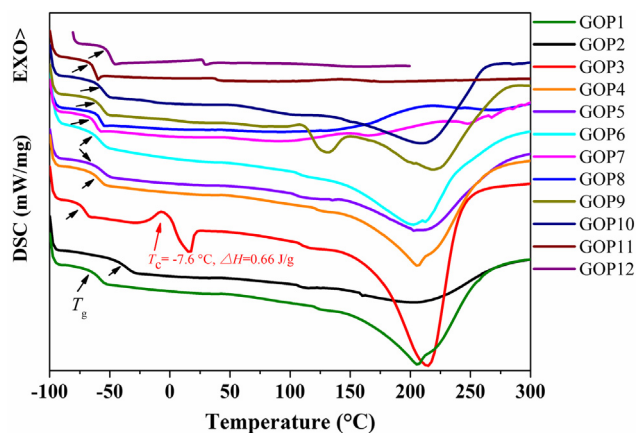
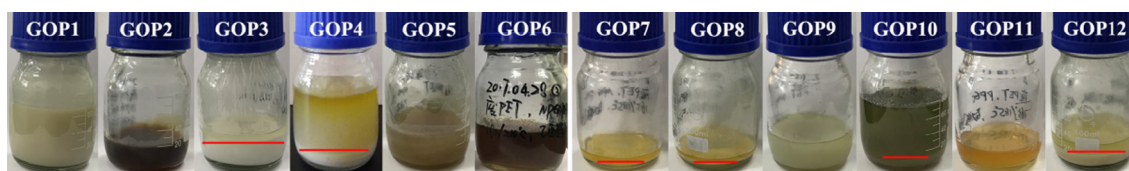
**Fig. 9.** DSC thermogram of all the prepared alcoholysis products.

Table 4

Summary of DSC heating curves of the prepared GOP samples from waste PET.

Samples	Heating process					T_{m1} (°C)	ΔH^{b}_{1} (J/g)	T_{m2} (°C)	ΔH^{b}_{2} (J/g)
	T_g (°C) ^a								
	T_1	T_2	T_3	T_4	ΔC_p (J·g ⁻¹ ·K ⁻¹)				
GOP1	−64.8	−59	−58.6	−54	0.563	125.7	0.4082	206.5	218.3
GOP2	−44.3	−36	−36.8	−29.5	0.532	110.4	0.3114	210.2	110.2
GOP3	−75.3	−71.2	−70.6	−67.5	0.629	115.3	0.6706	214.9	351.7
GOP4	−61.4	−54.5	−52.7	−49.3	0.401	163.1	72.09	244.3	179.8
GOP5	−64.9	−57.1	−54.5	−50	0.62	113	2.011	214.6	178.6
GOP6	−65.5	−58.7	−57.1	−52.8	0.64	111.6	0.1486	213.2	218.7
GOP7	−65.4	−62.1	−61.5	−59	0.681	166.5	0.5866	248.6	14.55
GOP8	−60.8	−58	−57.4	−55.5	0.65	130	0.0845	210.9	36.15
GOP9	−61.4	−56.1	−55.9	−51.3	0.722	132.4	3.885	215.3	142.8
GOP10	−61.5	−56.4	−55.3	−52.1	0.691	127.2	5.127	219.3	172.9
GOP11	−64.8	−62.4	−61.8	−60.6	0.971	37.3	0.021	/	/
GOP12	−53.5	−49.9	−49.2	−46.6	0.893	29.7	1.807	/	/

^a T_g is the glass transition temperature of the samples, and $T_1 - T_4$ are the Onset, Midpoint, Inflect. Pt. and Endset temperature of T_g .^b ΔH is the enthalpy changes of the melting point and calculated by the area of melting peaks.**Fig. 10.** Alcoholysis products of the waste PET under different operation conditions after 12 months.

degradation process of PPG with waste PET comparing with other alcoholysis agents, corresponding to the results of MALDI-TOF and ¹H NMR.

Notably, a crystalline peak at about -7.6 °C with the enthalpy changes (ΔH) of ca. 0.66 J/g can be observed, as shown in Fig. 9. We assume that this crystalline peak can be ascribed to the large amount of BHET in GOP3 due to the first melting point (T_{m1}) of GOP3 belonging to BHET with the ΔH value of ca. 0.6706 J/g, which is approximately the enthalpy changes value of crystalline peak. As known, the melting temperature of BHET monomer is ca. 110 °C. A first melting point (T_{m1}) can be observed in the range of 110 – 167 °C for GOP1–GOP10, which may be attributed to the BHET monomer. The relatively great deviation temperature for some samples, such as GOP4 and GOP7, may be caused by the other components in alcoholysis products. Notably, the T_{m1} for GOP11 and GOP12, which are prepared by using PPG as the sole alcoholysis agent, are really low comparing with that of BHET. It implies that there may be no or infinitesimal BHET in GOP11 and GOP12 since the reaction between PPG and waste PET is totally different. The second melting point (T_{m2}) in the range of 206 – 249 °C may be attributed to the presence of dimers and trimers (Viana et al., 2011). The ΔH_2 of GOP7 and GOP8 is relatively low comparing with other GOP samples, indicating that the dimers and trimers content is low. Furthermore, no obvious T_{m2} peak and ΔH_2 value of GOP11 and GOP12 can be observed, as shown in Fig. 9 and Table 4, indicating that there may be little dimers or trimers. It may be caused by PPG. The existence of dimers and trimers in GOP7 and GOP8 may be due to the reaction between DPG and waste PET. Thus, the addition of PPG may produce some kinds of PET-PPG copolymers instead of decomposing products in alcoholysis process. This can also be demonstrated by the heat capacity change (ΔC_p), which is a function of both the relative amount of the participating amorphous phase and the difference of conformational entropy between the glassy and rubbery state. It is proportional to the quantity of amorphous in samples (Zhou et al., 2017a,b). ΔC_p values of GOP1–GOP10 are lower than that of GOP11 and GOP12, indicating

that the quantity of amorphous are larger in GOP11 and GOP12. The amorphous may be caused by the absence of BHET in these two samples.

The shelf stability was measured by visual observation after 12 months, as shown in Fig. 10. It is obvious that GOP3, GOP4, GOP7, GOP8, GOP10 and GOP12 have appeared stratification phenomenon, as labeled in Fig. 10 by red line. Notably, the decompose products in GOP11 is still yellow transparent, showing excellent shelf stability and appearance. From this aspect, the preparation parameters of GOP11 are the best when PPG is employed. We assume that GOP11 may be a promising raw material in preparation of novel polymer, such as polyurethane, polyacrylate, etc (Zhang et al., 2017a,b, 2016a,b). As for preparation of BHET from waste PET, considering the stability, the products from zinc acetate (GOP5 and GOP6) is better than butyl titanate, the products from green waste PET (GOP2) is better than transparent waste PET, and the products from only one alcoholysis agent (GOP9) with relative low temperatures is better than mixture alcoholysis agents with relative high temperatures.

4. Conclusion

Alcoholysis is a significant way to chemical recycling waste PET. A series alcoholysis products with different alcoholysis agents, degrading temperatures, catalysts and PET types were prepared to investigate the degradation of PET. The main monomers in alcoholysis products are analyzed. When the alcohols with small molecule are used, waste PET can be transformed into oligomers, dimers or trimers, holding a great potential application in polyurethane industry according to our previous work. When oligomer (such as PPG with $M_n = 2000$) is employed, it may react with waste PET to produce copolymers without BHET. In addition, the higher temperature may assist alcoholysis agents in improving the glycols reactivity, and the high alcoholysis activity is good for producing BHET. In degradation of waste PET, the alcoholysis activity of

DPG is the lowest. GOP11 is still yellow transparent after 12 months, showing excellent shelf stability and appearance. The degradation products in this work are mainly dihydric alcohol with good stability, which can be regarded as eco-friendly materials from waste PET and is suitable for long-term application in chemical industry, especially in waterborne polyurethane synthesis.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2018.12.032>.

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