

Degradation of Poly(butylene terephthalate) in Different Supercritical Alcohol Solvents

Junhe Yang,¹ Jie Huang,² Minking K. Chyu,³ Qing-Ming Wang,³ Danliu Xiong,² Zibin Zhu²

¹School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

²School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

³Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Received 23 March 2009; accepted 21 October 2009

DOI 10.1002/app.31649

Published online 14 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Reactions were carried out in a batch autoclave reactor. Poly(butylene terephthalate) (PBT) and different alcohol solvents were used in the vessel. The reaction products were analyzed by infrared spectroscopy and gas chromatography/mass spectrometry. Alcoholysis of PBT occurred in supercritical methanol, ethanol, and propanol, and we obtained dimethyl terephthalate (DMT), diethyl terephthalate (DET), and dipropyl terephthalate (DPT), respectively. The conversion of PBT at different temperatures showed similar trends but different degrada-

tion degrees. The reactivity for the alcoholysis of PBT in supercritical methanol was much higher than those in supercritical ethanol and propanol. DMT and 1,4-butanediol obtained from the depolymerization of PBT in supercritical methanol reached 98.5 and 72.3%, respectively, at 583 K for 75 min. The yield of DET reached 76% for 75 min. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2269–2274, 2010

Key words: degradation; monomers; recycling

INTRODUCTION

The recovery of valuable products through the chemical recycling of polymers has been attracted attention in recent years for both environmental and economic reasons. There is a lot of ongoing research to find efficient technologies to degrade waste plastics.¹

The exploration of supercritical fluids as solvents and as reaction media for polymer degradation has attracted particular interest over the past decade.^{2–4} Because of their unique physical and chemical properties, they have many advantages when they are used in polymer degradation, such as reaction in the homogeneous phase and high decomposition rates.^{5,6} Tagaya et al.⁷ investigated the degradation of polycarbonate (PC) in supercritical water with temperatures above 647 K. Chen et al.⁸ observed that high yields of bisphenol A and dimethyl carbonate were obtained with methanol to depolymerize PC. Huang et al.⁹ studied the depolymerization of PC in ethanol. Sako and coworkers^{10,11} studied the characteristics of the depolymerization of poly(ethylene terephthalate) (PET) in supercritical methanol using a high-pressure reactor. PET could convert

into monomer completely at 603 K after 45 min. Kim et al.¹² investigated the mechanism of the alcoholysis of PET. Campanelli et al.¹³ studied the depolymerization of PET in critical water at 523–553 K. Yang et al.¹⁴ studied the methanolytic depolymerization of PET with supercritical methanol. Meng and coworkers^{15,16} studied the alcoholysis kinetics of poly(butylene terephthalate) (PBT) in supercritical methanol and the effect of the reaction temperature and pressure on the decomposition of PBT. Shibata and Masuda¹⁷ reported that the depolymerization of PBT at high temperature was an effective method for the quantitative recovery of dimethyl terephthalate (DMT) and 1,4-butanediol (BG). Huang and coworkers^{18,19} studied the characteristics of the depolymerization of PBT in supercritical methanol.

However, the depolymerization of PBT in different alcohol solvents, such as ethanol and propanol, has not yet been reported. Thus, in this study, we examined the degradation of PBT performed in supercritical methanol, ethanol, and propanol in a batch-type autoclave reactor. The effects of the temperature and reaction time on the degradation degree, molecular weight, and yields of monomers were investigated.

Correspondence to: J. Huang (jie_h_64@hotmail.com).

Contract grant sponsor: National Natural Science Foundation of the People's Republic of China; contract grant number: 50773040.

EXPERIMENTAL

Material and solution

The PBT used in the experiments was a commercial slice with a molar-average molecular weight (M_n) of

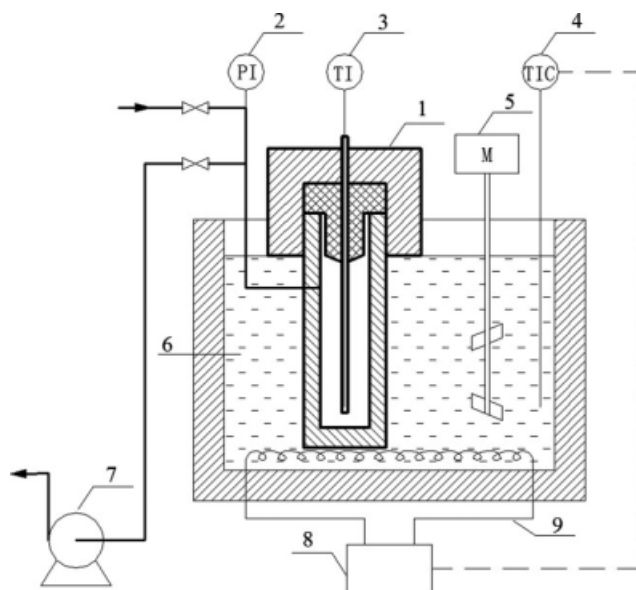


Figure 1 Apparatus for PBT degradation: (1) reactor, (2) pressure pickup, (3) thermocouple, (4) thermocouple, (5) agitator, (6) salt bath, (7) vacuum pump, (8) temperature controller, and (9) heater. PI, pressure indicator; TI, temperature indicator; M, mixer; TIC, temperature controller.

29,700 and produced by the Shanghai Polyester Fiber Factory (Shanghai, China). The solutions used in the experiments were chromatography-grade methanol, ethanol, and propanol.

Degradation of PBT

A batch-type reaction was used for the degradation experiments. The experimental apparatus is shown in Figure 1. The reactor was made of 316 stainless steel, and the inner volume was about 20 cm³. The reactor was heated by molten salts (KNO₃ and NaNO₂). The temperature was maintained by a temperature controller in conjunction with a thermocouple immersed in the melting salts. To prevent the effect of atmosphere on the degradation of PBT, the atmosphere in the reactor was extracted by a vacuum pump after 1.0 g of PBT was added, and then, 12.5 mL of alcohol solvent was input by negative pressure. The reactor was immersed in the melting salts, and the thermocouple and pressure indicator were used to detect the temperature and pressure of the reaction system. When the reaction ended, the reactor was taken out of the melting salt and immersed quickly in cold water. The temperature of the reactor decreased to room temperature in 1 min. The undegraded solid products were cleaned by an alcohol solvent and dried for analysis.

The degree of PBT conversion was defined by eq. (1):

$$\text{Conversion}(\%) = \left(1 - \frac{M_t}{M_0}\right) \times 100 \quad (1)$$

where M_0 is the weight of the feed PBT and M_t is the weight of the solid products after degradation. To study the influence of the different solvents, reaction temperature, and reaction time on the degradation, the experiments were carried out at different temperatures with reaction times of 10–40 min in methanol, ethanol, and propanol.

The effects of different alcohol solvents on the yields of products were investigated in methanol and ethanol at 583 K with reaction times of 5–90 min. The reaction products identified by gas chromatography (GC)/mass spectrometry were mainly composed of DMT and BG in methanol and diethyl terephthalate (DET) and BG in ethanol. The yields of DMT, DET, and BG were represented as the percentage of the DMT, DET, and BG amounts in the products calculated from GC data against that of the theoretical amount if the feed PBT was completely depolymerized. The formula is shown as follows:

$$\text{Yield of X}(\%) = \frac{\text{Weight of monomer X}}{\text{Theoretical weight}} \times 100 \quad (2)$$

where X is DMT, DET, or BG.

Analysis

A certain amount of alcohol solvent was dropped into the reactor. After the filtration of the products, the residue was the PBT not yet decomposed and the liquid, including some reaction products. The solid products were measured on a 25PC Fourier transform infrared (FTIR) spectrograph (Bio-Rad, USA) by the KBr method. The surfaces of the solid products were observed with a scanning electron microscope (JEOL JSM-6360LV, Japan). The liquid products were identified with an Agilent 6890 series gas chromatograph equipped with a mass spectrometer (GC/mass spectrometry) with a CBP20-S25-050 column and quantified with a GBC-930 plus GC/flame ionization detection (GC/FID) system with the same column. The viscosity of the polymer was measured with a rotational viscometer (Shanghai, China) at 300 K with phenol and tetrachloroethane solvents (3 : 2 wt/wt), and the molecular weight was calculated.

RESULTS AND DISCUSSION

Analysis of the products

The IR spectra of the purified PBT and undegraded solid in methanol were measured and are shown in Figure 2(a,b). As shown in Figure 2, the residue was the PBT, which had not decomposed completely. The same results were obtained from analysis of the solids in the ethanol and propanol solvents. The reaction products of PBT in methanol, ethanol, and

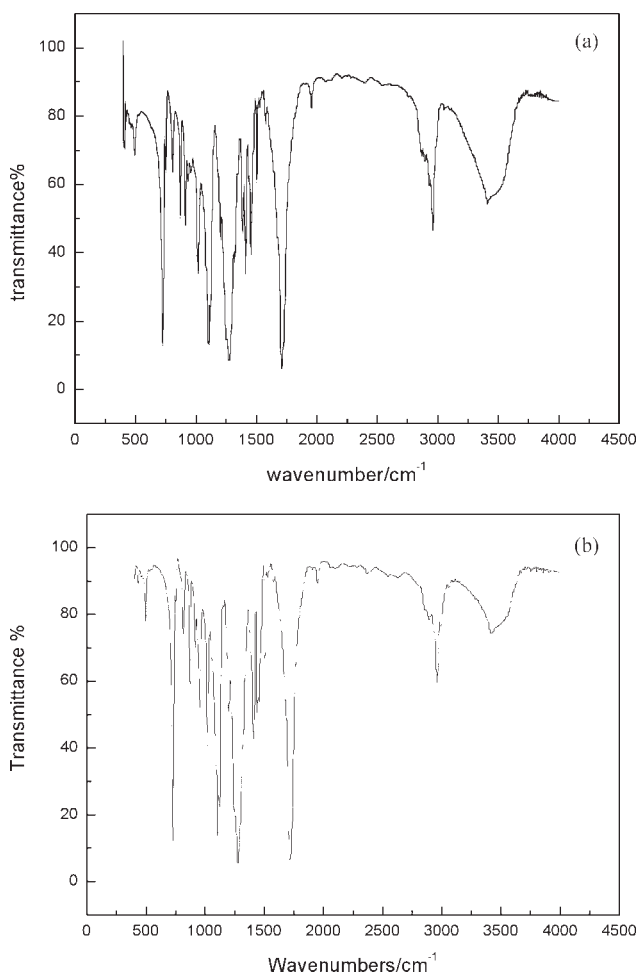


Figure 2 FTIR spectra of (a) PBT and (b) undegraded solid in methanol (483 K, 30 min).

propanol were DMT and BG, DET and BG, and dipropyl terephthalate and BG, respectively.

Effects of the different alcohol solvents on the degradation of PBT

Figure 3 shows the relationship between the reaction time and conversion of PBT in different alcohol solvents. We observed that the degradation of PBT increased with the reaction process in methanol, ethanol, and propanol but to varying degradation degrees. When the temperature was maintained at 503 K for 20 min, the conversions of PBT were 75.2% in methanol, 52.1% in ethanol, and 41.1% in propanol. When the reaction time reached 25 min, the conversions of PBT were 92.3, 62.0, and 52.1% in methanol, ethanol, and propanol, respectively.

Figure 4 shows the conversion of PBT in different alcohol solvents at different temperatures. When the temperature reached 523 K, PBT dissolved in supercritical methanol and decomposed completely in a homogeneous phase for 20 min, whereas the conversions of PBT were about 75 and 57.7% in ethanol

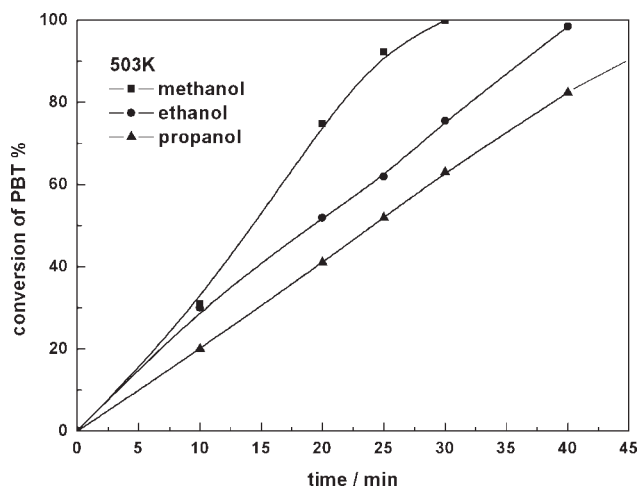


Figure 3 Relationship between the time and conversion of PBT in different solvents.

and propanol, respectively. Methanol was more favorable than ethanol and propanol in this process.

Effects of the different alcohol solvents on the decrease in molecular weight

The molecular weights of PBT degraded in different alcohol solvents was observed at different reaction times. Figure 5 shows the relationship between M_n and the reaction time in methanol, ethanol, and propanol at 483 K. The average molecular weight of PBT decreased with the process of PBT degradation. M_n dropped from 29,700 to 4800, 5700, and 7300 at 483 K within 20 min and to 2600, 3700, and 4500 within 30 min in methanol, ethanol, and propanol, respectively. The average molecular weight of PBT decreased with the conversion of PBT in alcohol solvents, as shown in Figure 6. When the conversion of

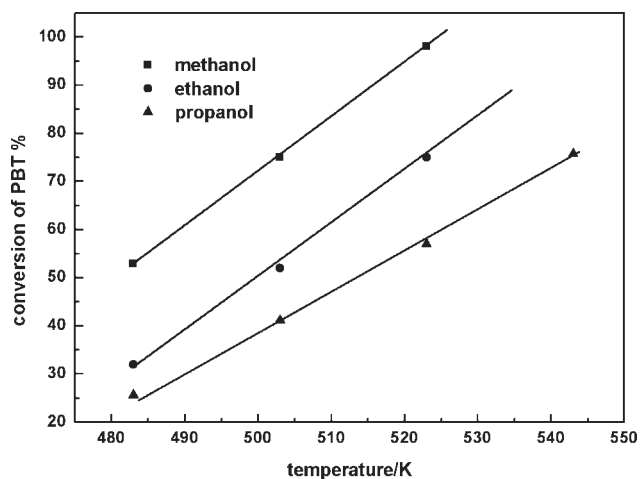


Figure 4 Relationship between the temperature and conversion of PBT in different solvents (reaction time = 20 min).

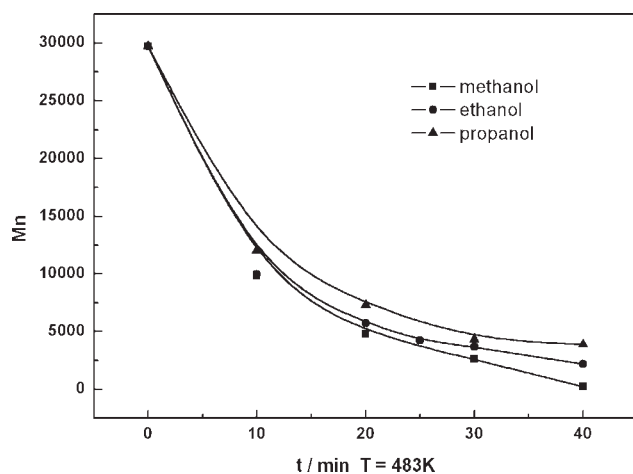


Figure 5 Relationship between the molecular weight and the reaction time (t) in different solvents. T, reaction temperature.

PBT reached 30%, the molecular weight dropped to 6000, 6800, and 7600 in methanol, ethanol, and propanol, respectively, at 483 K. As the molecular weight dropped nearly 1000, the conversion of PBT was about 75% in the alcohol solvents.

The scanning electron microscopy (SEM) micrographs of the surface of the solid products obtained from depolymerization of PBT at different reaction temperatures are presented in Figure 7. The surface of the PBT feed was compact and smooth, as shown in Figure 7(a). As the temperature increased, PBT showed a swelling process. Propanol reacted with the surface of the material, which showed many cavities, as depicted in Figure 7(b). This meant the propanol diffused into the PBT. The conversion of PBT was 25.6% in propanol at 483 K for 20 min. A crystal structure morphology was observed in the PBT depolymerized at 523 K, which is shown in Figure

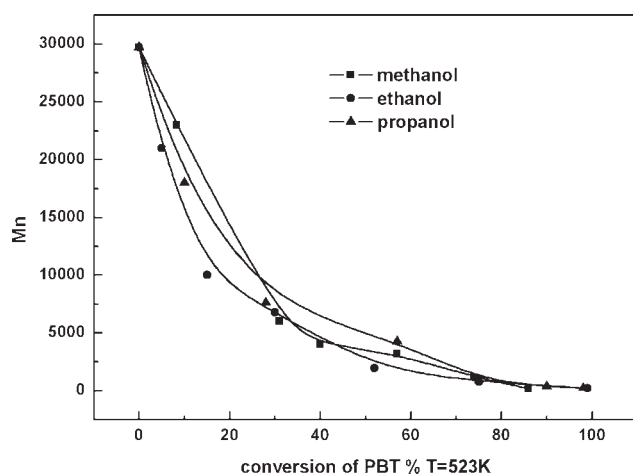
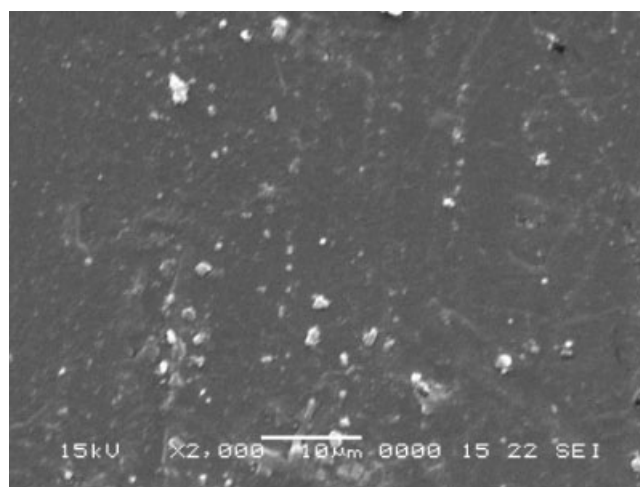
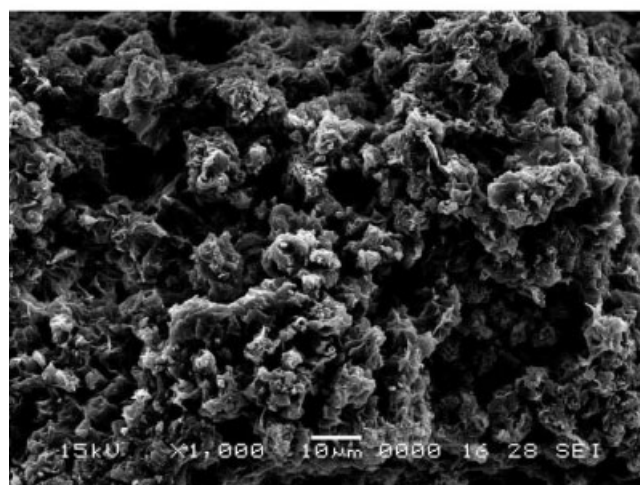


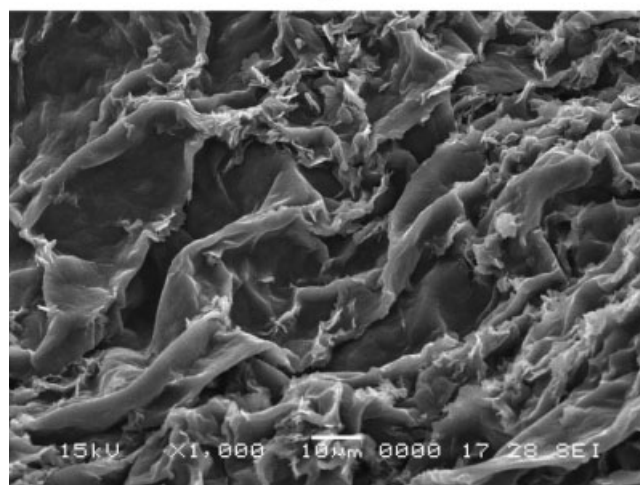
Figure 6 Relationship between the molecular weight and conversion in different solvents.



(a)



(b)



(c)

Figure 7 SEM of PBT in propanol [t (reaction temperature) = 20 min]: (a) raw material, (b) at 483 K with a 25.6% conversion of PBT, and (c) at 523 K with a 57.7% conversion of PBT.

7(c); the conversion of PBT reached 57.7%. The SEM micrographs of the surface of PBT degradation in methanol and ethanol depicted similar conditions.



CONCLUSIONS

The degradation of PBT increased with the reaction process in methanol, ethanol, and propanol. The conversion of PBT in alcohol solvents showed similar trends but different degradation degrees. The products of PBT in methanol, ethanol, and propanol were DMT and BG, DET and BG, and dipropyl terephthalate and BG, respectively. Methanol was more favorable than ethanol and propanol in the degradation process.

References

1. Kiran, N.; Ekinic, E.; Snape, C. E. *Resour Conserv Recycl* 2000, 29, 273.
2. Watanabe, M.; Hirakoso, H.; Sawamoto, S.; Adschiri, T.; Arai, K. *J Supercrit Fluids* 1998, 13, 247.
3. Chen, L.; Wu, Y. Q.; Ni, Y. H.; Zhu, Z. B. *J Chem Eng Chin Univ* 2004, 18, 585.
4. Fang, Z.; Kozinski, J. A. *J Appl Polym Sci* 2001, 81, 3565.
5. Fang, Z.; Smith, R. L.; Inomata, H.; Arai, K. *J Supercrit Fluids* 1999, 15, 229.
6. Werner, H. H. *Chemosphere* 2001, 43, 123.
7. Tagaya, H.; Katoh, K.; Kadokawa, J. I. *Polym Degrad Stab* 1999, 64, 289.
8. Chen, L.; Wu, Y. Q.; Ni, Y. H.; Huang, K.; Zhu, Z. B. *Acta Sci Circumstantiae* 2004, 24, 60.
9. Huang, J.; Huang, K.; Zhou, Q.; Chen, L.; Wu, Y. Q.; Zhu, Z. B. *Polym Degrad Stab* 2006, 91, 2307.
10. Sako, T.; Sugeta, T.; Otake, K.; Nakazawa, N.; Sato, M.; Namiki, K. *J Chem Eng Jpn* 1997, 30, 342.
11. Sako, T.; Okajima, I.; Sugeta, T.; Otake, K.; Yoda, S.; Takebayashi, Y. *Polym J* 2000, 32, 178.
12. Kim, B. K.; Hwang, G. C.; Bae, S. Y.; Yi, S. C.; Kumazawa, H. *J Appl Polym Sci* 2001, 81, 2102.
13. Campanelli, J. R.; Kamal, M. R.; Cooper, D. C. *J Appl Polym Sci* 1993, 48, 443.
14. Yang, Y.; Lu, Y. J.; Xiang, H. W.; Xu, Y. Y.; Li, Y. W. *Polym Degrad Stab* 2002, 75, 185.
15. Meng, L. H.; Zhang, Y.; Huang, Y. D. *J Chem Eng Chin Univ* 2004, 18, 155.
16. Meng, L. H.; Huang, Y. D.; Zhi, H. L.; Shibata, M.; Yosomiya, R. *Mater Sci Technol* 2002, 10, 291.
17. Shibata, M.; Masuda, T. *J Appl Polym Sci* 2000, 77, 3228.
18. Huang, J.; Huang, K.; Qi, W. J.; Zhu, Z. B. *Polym Degrad Stab* 2006, 91, 2527.
19. Huang, J.; Qi, W. J.; Huang, K.; Wu, Y. Q.; Zhu, Z. B. *J Chem Eng Chin Univ* 2007, 21, 48.