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Contributed Paper

Preparation and Characterization of PET-PLA Copolyester from Waste PET and Lactic Acid (LA)

Achanai Buasri*[a,b], Nattawut Chaiyut [a,b], Tanit Jenjaka [a], Sasirada Weerasunthorn [a] and Sureerat Juengrungchaiwattana [a]

[a] Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand.

[b] Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand.

*Author for correspondence; e-mail: achanai130@gmail.com

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ABSTRACT

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester with excellent tensile and impact strength, chemical resistance, clarity, processability, transparency, and appropriate thermal stability. With the widespread use and increasing consumption of PET, the amount of waste PET is growing rapidly. Although this kind of polyester does not create a direct hazard to the environment, it does not decompose readily in nature. Thus, the effective recycling of PET wastes for the preservation of resources and protection of the environment has received considerable attention. In this study, waste PET was depolymerised using excess ethylene glycol (EG) in the presence of zinc acetate as a transesterification catalyst. The glycolysis reaction was carried out at the boiling point of EG under nitrogen atmosphere up to 8 h. It was found that the glycolysis products consist mainly of bis-2-hydroxy ethylene terephthalate (BHET) monomer which was effectively separated from dimer in quite pure crystalline form. Poly(ethylene terephthalate)-poly(lactic acid) (PET-PLA) copolyesters were synthesized by the melt reaction of BHET with lactic acid monomers (LA) in the presence of catalytic system. The copolymerization was studied by varying reaction temperature, reaction time and amount of catalyst. Results show that reaction temperature is a critical factor in this process. The optimum conditions for the copolymerization of PET-PLA copolyesters were synthesized by the melt polymerization at 200^{o}C of LA and BHET. The most select of reaction time and amount of catalyst for synthesis copolyester were 8 h of and 0.4% catalyst by weight of PET. In addition, the NMR studies confirm the incorporation of lactate units in PET chains after reaction.

Keywords: poly (ethylene terephthalate), poly(lactic acid), biodegradable copolyester, depolymerization, copolymerization.

1. INTRODUCTION

In recent years, recycling of polymers has received a great deal of attention. Chemical recycling, applied to the post-consumer condensation polymers, might be of great interest. Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics which are widely used in the manufacture of high strength fibers, audio and video tapes and various types of packaging, mainly soft drink bottles and jars. The production of such a large amount of waste PET has created an environmental problem of gigantic proportions, since these wastes are not reused by the manufacturers and therefore are left as plastic waste, which do not decompose readily in nature [1, 2]. The effective solution to solve this problem is to recycle these waste PET.

The waste PET can be recycled into new items (mechanical recycling) or into monomers or oligomers (chemical recycling). These oligomers or monomers are generally hydroxy-terminated and can be used for the synthesis of virgin PET or derived polyesters, or as precursors for polyurethane preparation [3].

The biodegradable polymer poly(lactic acid) (PLA) is widely used to construct cell scaffolds for tissue engineering purposes due to its excellent biocompatibility, which can degrade into lactic acid and be eliminated from body by normal metabolic pathway [4]. The synthesis of potentially biodegradable copolyesters of PET has received a growing interest. Copolyesters of PET and aliphatic polyesters, such as PET-poly (lactide), PET-poly (glycolide), PET-poly (ethylene adipate) or PET-poly (ε-caprolactone) have been described as environmentally degradable or hydrolysable. Depending on comonomer ratio and chain microstructure, the resulting materials are suitable for a range of applications. Since bis-2-hydroxy ethylene terephthalate (BHET) is readily available by glycolysis of waste PET, poly (ethylene terephthalate)-poly (lactic acid) (PET-PLA) copolyester was thus synthesized by reacting BHET or glycolyzed PET and lactic acid monomer (LA) [5].

In the present research work the recycling of the waste PET was done by glycolysis and the product was converted into biodegradable copolyesters. Copolymers were synthesized by the melt reaction of BHET with LA. The copolymerization was optimized by varying temperature, amount of catalyst and reaction time.

2. MATERIALS AND METHODS

2.1 Materials

The PET was obtained from Kangwal Polyester Company, Limited, which were cut into short fibers for producing waste PET. The ethylene glycol (EG) was purchased from Sigma-Aldrich, is used for glycolysis and subsequent depolymerization of PET, whereas zinc acetate is used as catalyst. Lactic acid (85 wt% aqueous solution, lab grade) was purchased from Sigma-Aldrich. Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and p-toluene sulfonic acid monohydrate (p-TSA) were purchased from Fluka. All chemicals and reagents were of analytical reagent grade.

2.2 Synthesis of BHET by Glycolysis of Waste PET

The conversion of waste PET in presence of glycol is known as alcoholysis or glycolysis in the presence of a catalyst. A three-necked round bottom flask (reactor) was used for glycolysis experiments. The reactor was equipped with a thermometer and a reflux condenser. A magnetic stirrer was put in the reactor to ensure proper mixing. The quantity of waste PET and EG were 40 g and 70.5 ml, respectively. The glycolysis temperature was set at 180°C and glycolysis time was 5 h. The amount of zinc acetate (catalyst) was 0.2% by weight of waste PET.

2.3 Synthesis of PET-PLA by Copolymerization

BHET 30g and LA 9 ml were reacted in the bulk in the presence of $SnCl_2 \cdot 2H_2O$ (0.1-0.8 wt%) and p-TSA (0.91 mol/mol $SnCl_2$). The reaction mixture was placed in a three-necked round bottom flask (reactor) connected to a vacuum line (0.6 cm Hg) and immersed in an oil bath at 150-210°C for 3-9 h. While the reactants were stirred, glycol and water slowly distilled out. The resulting copolyesters were dissolved in $CHCl_3$, precipitated in methanol, filtered and dried at 70°C.

3. RESULTS AND DISCUSSION

3.1 Effect of Temperature

The Figure 1 shows the relationship between the polymerization temperature and %conversion of PET-PLA. In this study, the polymerization time was fixed at 6 h and catalyst at 0.4% by weight of PET. It was found that the %conversion was almost 0% at temperature below 150°C. The %conversion slowly increased after 150°C and was about 54% at 180°C and was 98% at 200°C.

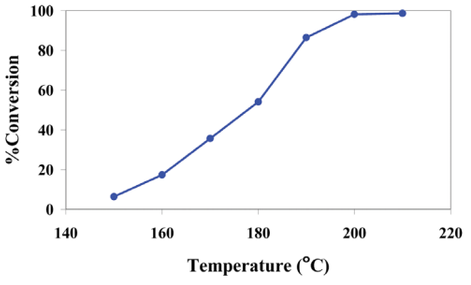

Figure 1. Effect of the temperature on the %conversion of the PET-PLA copolyester.

3.2 Effect of Amount of Catalyst

In the study of polymerization of PET-PLA, temperature was set at 180°C, reaction time was 6 h and the amount of catalyst was varied from 0.1 to 0.8% by weight of PET [5]. It was observed that the %conversion increased with an increase in the amount of catalyst. But after a critical amount of catalyst was reached the %conversion decreased, because of equilibrium among the chemicals in system [6,7]. The %conversion was found maximum when the $SnCl_2$ was 0.4% by weight of PET (Figure 2).

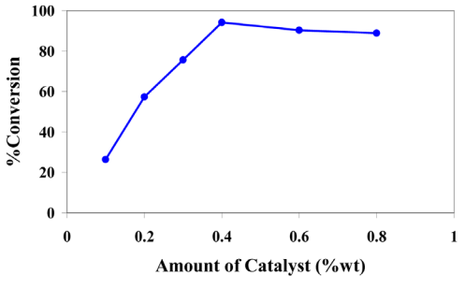

Figure 2. Effect of the amount of catalyst on the %conversion of the PET-PLA copolyester.

3.3 Effect of Reaction Time

The influence of the variation of reaction time on %conversion of PET-PLA was studied by fixing the temperature at 180°C and the amount of catalyst as 0.4% by weight of PET. The polymerization time was varied from 3 to 9 h. It was observed that the %conversion increased with an increase in the polymerization time and approached a steady state at about 8 h, it was 90% at 6 h and about 100% beyond 9 h (Figure 3). As can be seen from the curve even at the verry initial stage polymerization proceed at a high rate. Longer reaction time leads to further but quite moderate increase of yield of PET-PLA. It reaches the highest yield at 8 h of reaction. It seems that equilibrium state is reached at 8-10 h of reaction [7].

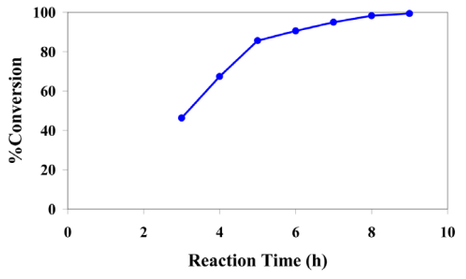

Figure 3. Effect of the reaction time on the %conversion of the PET-PLA copolyester.

3.4 Characterization of Copolyester

The ^{1}H and ^{13}C NMR studies confirm the incorporation of lactate units in PET chains after reaction. Copolyesters containing nearly equimolar terephthalate/lactate ratio are not completely random and present some block-copolymer character, while the microstructure of PET-rich copolyesters is a random one. The typical ^{1}H NMR and ^{13}C NMR spectrum are given in Figure 4 and 5 for the copolyester.

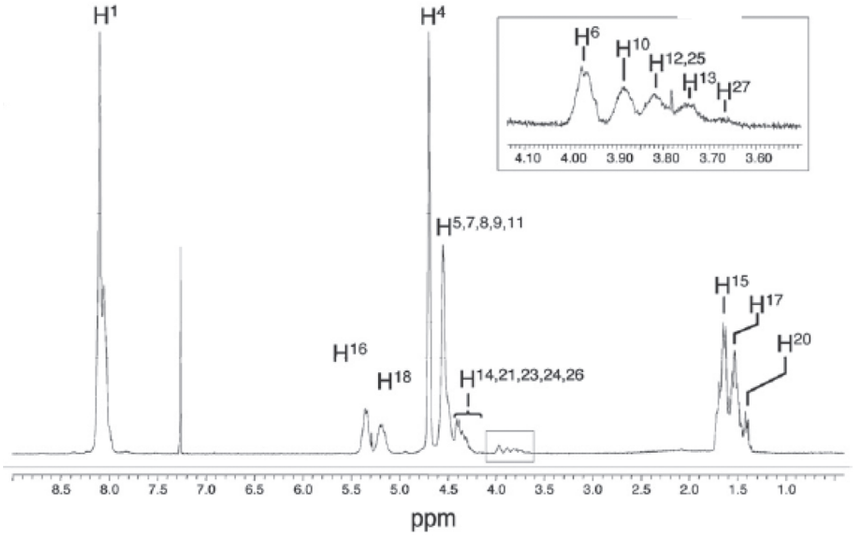

Figure 4. ^{1}H NMR spectrum of copolyester.

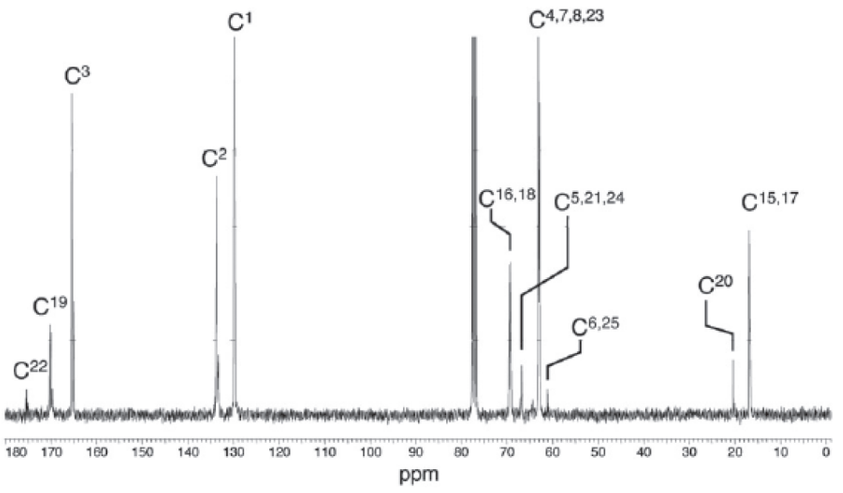

Figure 5. ^{13}C NMR spectrum of copolyester.

Characteristic were observed in the thermal behavior of the copolyesters synthesized. As expected for copolyesters exhibiting a random character, only one glass transition temperature (Tg) was detected, between the Tg of PET and PLA homopolymers. This Tg is close to 60°C for copolyester.

The PET–PLA copolyesters are amorphous when their composition is equimolar, and exhibit a melting point only when the PET block length is close to 9 monomer units. It is well known, including for terephthalate copolyesters [8].

4. CONCLUSIONS

The plastic waste may be used after recycling to produce copolyester by proper glycolysis of PET fiber. The conditions for the glycolysis of waste PET were observed at temperature 180°C, 5 h of glycolysis time and 0.2% catalyst by weight of PET. The optimum conditions for the copolymerization of PET-PLA copolyesters were synthesized by the melt polymerization at 200°C of LA and BHET obtained by glycolysis of post-consumer PET. The optimum of reaction time and amount of catalyst for synthesis copolyester were 8 h of and 0.4% catalyst by weight of PET.

5. ACKNOWLEDGEMENTS

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