Wang Xuebin and Wang Jincheng*

Studies on the preparation and properties of biodegradable polyester from soybean oil

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Abstract: Crude dimer acid (DA) was prepared with soybean oil (SO) used as raw material and organic montmorillonite as a catalyst. Fourier transform infrared (FTIR) spectroscopy, hydrogen nuclear magnetic resonance (^{1}H-NMR) and gel permeation chromatography (GPC) were used to characterize the structure of DA. It was demonstrated that the synthesis of crude DA using SO was feasible. A molecular weight of 995–1304 g/mol was obtained by GPC measurement. Then, a type of polyester was synthesized using the crude DA and polyethylene glycol. The effects of reaction temperatures and different catalysts on the conversion rate were explored. The results showed that the esterification conversion rate was improved to 83.13% when $SnCl_2$ was used as the catalyst, with a reaction temperature of 180°C The FTIR, ^{1}H-NMR, GPC and TGA were used to characterize the structure and performance of this polyester. The polyester had a molecular weight ranging from 8259 to 10892 g/mol. In addition, its biodegradable behavior was analyzed by the soil burial test and was compared with that of terephthalic acid. The results showed that the composites prepared from DA had a pronounced effect on weight loss during biodegradation.

Keywords: biodegradable; performance; polyester; preparation conditions; soybean oil.

1 Introduction

In today's market, the requirements of renewable materials are increasing. First, lower costs for producing renewable fuels are needed compared with those incurred from using petroleum derivatives. Then, other reasons remained, such as the reduction of reserves, high oil prices and the desire for green or biodegradable materials [1]. In addition, social emphasis concerning waste disposal, the depletion of nonrenewable resources and the environment are considered the other main benefits from the application of bio-based products. For these reasons, vegetable oils are often chosen to produce fuels and polymeric materials [2, 3].

Waste vegetable oil can be used to produce biodiesel. Researchers focused on biodiesel production using different types of catalyzed transesterification reactions [4]. The conversion, yield and quality of biodiesel are commonly affected by certain parameters, such as membrane reactor, reactive absorption and ultrasonic irradiation. Guzatto et al. [5, 6] modified the double-step transesterification process, in which ethanol was used as a type of transesterification agent to produce biodiesel from vegetable and waste oils. The obtained biodiesels were analyzed by hydrogen nuclear magnetic resonance (^{1}H-NMR), ^{13}C-NMR and Fourier transform infrared (FTIR) spectroscopy as well as by standard physico-chemical techniques. These results indicated that the biodiesel products had high quality and purity. Istadi et al. [7] prepared a novel type of solid acid catalysts, sulphated zinc oxide, in the transesterification of soybean oil with methanol to produce biodiesel. From the testing results, this catalyst exhibited properties of being a good candidate catalyst for the transesterification of soybean oil to produce biodiesel. Zargar et al. [8] used waste vegetable oil to replace a natural agent for bitumen. The properties of the original, aged and rejuvenated bitumen were all evaluated. The results showed that the physical properties of aged bitumen group 40/50 was almost the same as the properties of the original bitumen (80/100) with the addition of 3–4% of waste vegetable oil.

In addition, because of their biodegradability, nontoxicity and low production cost, vegetable oils have also been used as raw materials for the preparation of novel polymers instead of traditional polymers. Liu and Erhan [9] synthesized biopolymers based on soybean oil (SO) using the cationic polymerization method. This process occurred in the supercritical carbon dioxide solvent and initiated by the boron trifluoride diethyl etherate. The molecular weight of the obtained polymers ranged from 21,842 to 118,300 g/mol. Guo et al. [10] investigated the preparation of the rigid polyurethane foams from polyols derived from soybean oil, and found that these foams possessed good mechanical and thermoinsulating properties together with

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***Corresponding author: Wang Jincheng,** School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 201620, P.R. China, e-mail: wjc406@126.com
Wang Xuebin: School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, P.R. China

better thermal degradation and thermal oxidation properties compared with that of foams synthesized from petrochemical origin. Sahoo Sushanta et al. [11] used the *in situ* method to synthesize a novel type of bioresin and epoxidize SO to blend with epoxy in different ratios. It may act as a kind of reactive diluent, thus improving the processibility and toughened nature of the epoxy. Their results showed that 20 wt% bioresin in the composite improved impact strength compared with the virgin epoxy. However, the above methodology only gave two ways for the utilization of vegetable oils. To date, the preparation and characterization of dimer acid (DA) and polyester using vegetable oils had not been systematically researched.

In the present work, crude DA and a type of biodegradation polyester was prepared using SO. The preparation, structure, morphology, thermal stability and biodegradation behavior of this polymer were investigated.

2 Materials and methods

2.1 Materials

The SO employed in this study was bought from Legou Supermarket (Shanghai, China). The stannous chloride, ammonia acid, phenolphthalein, concentrated sulfuric acid, acetic acid, acetone, acetate, ethanol, potassium hydroxide and terephthalic acid (TA) were chemically pure and obtained from the Shanghai Guoyao Agent Company (Shanghai, China). The polyethylene glycol (PEG) of chemical grade was obtained from Zhenjiang Huaxing New Materials Co., Ltd. (Jiangsu, China). The organic montmorillonite was homemade and of industrial grade [12].

2.2 Preparation of DA and polyester

About 10 g of SO was added into a three-necked flask with 5 ml of acetate buffer. Then, 20 ml of acetone and ethanol with a ratio of 1:1 was added to the flask. By titration with 0.1 N KOH aqueous solution, the total fatty acid generated in the mixture was determined.

Next, 1.2 g of organic montmorillonite was dissolved in 100 g of the fatty acid. The above mixture was then added into a three-necked flask, heated to 200°C and treated at this temperature for 6 h to allow the reaction to proceed completely. Crude DA was thus prepared. Then, 14 g of crude DA was poured into a three-necked flask, to which 25 g of PEG and 0.12 g of catalyst were added. This mixture was cured for 6 h at 190°C. Thus, a type of polyester was obtained.

2.3 Characterization of the DA and polyester

The FTIR was performed on a Nicolet Avatar 370 spectrophotometer. The ranges were between 4000 and 700 cm^{-1} with a resolution of 2 cm^{-1}. The pellets were formed by grinding samples with KBr. The spectra with good signal-to-noise ratios were obtained by 64 scans.

The ^{1}H-NMR was conducted on a Bruker AV600 spectrometer. Deuterated chloroform ($CDCl_3$, 99.8%) was used to prepare the sample solutions for testing. The tetrahydrofuran was used to dissolve the above liquids. An internal standard was referred to tetramethylsilane (TMS).

The molecular weight was measured by gel permeation chromatography (GPC) (PL-GPC50, the relative molecular mass range: 500~19,000, British). Tetrahydrofuran was used as the mobile phase with a flow rate of 1 ml/min.

Thermogravimetric analysis (TGA and DTG) was conducted on a Linseis PT-1000 microbalance. This test was conducted under a nitrogen atmosphere in an increasing rate of temperature, 20°C/min. In addition, 10 mg of the samples was used during the measurement.

The acid values of the polyester were measured according to the Chinese National Standard HG/T 2708-95. The following formula was used in the calculation of the values:

$$A_V = 56.1\frac{(V_1 - V_2)T}{M},$$

where A_V is the acid value of the sample, V_1 is the titration of the sample standard solution of potassium hydroxide (ml), V_2 is the blank test of the titration of the potassium hydroxide standard solution consumed (ml), T is the standard equivalent concentration of potassium hydroxide solution and M is the specimen weight (g).

The soil burial test was conducted to characterize the biodegradable properties. The composites were cut into 60 mm×30 mm×2 mm portions. Their weights were measured, after which they were buried in soil with a depth of 15.24 cm. After a certain number of days, they were taken out from the soil. In addition, the soil was removed from their surface by washing with distilled water. The samples were dried in an oven for 6 h and kept at room temperature for 24 h. Finally, their weight loss was measured, and thus the biodegradability property was obtained.

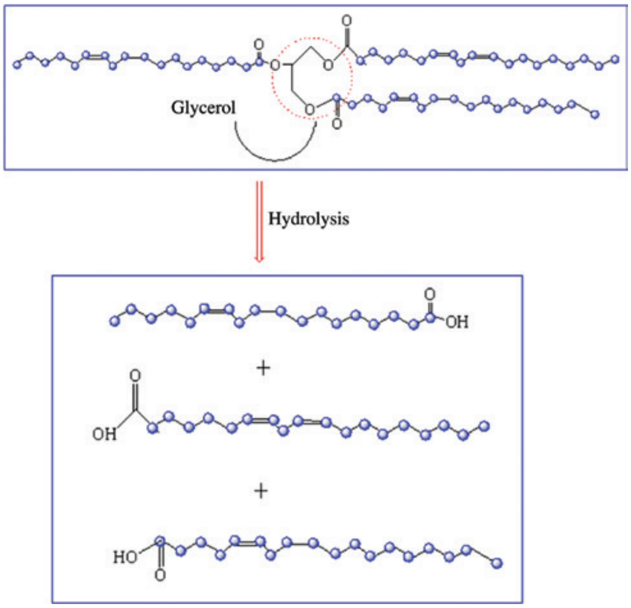
3 Results and discussion

3.1 Preparation of the DA

3.1.1 Preparation mechanism of the DA from SO

The hydrolysis of SO under acid conditions is shown in Scheme 1. The products of this hydrolysis were glycerol and fatty acid. SO is considered a type of semidrying oil due to its lower double-bond density. Among others, it is the second cheapest vegetable oil [13]. The structure of SO consists of the tri-glyceride ester of fatty acids [8, 14]. The unsaturation in the fatty acid makes it an ideal monomer for preparing other polymers. However, its reactivity is rather low due to its multiple chain structure.

The preparation mechanism of DA from the hydrolysis product of SO was via the Diels-Alder reaction. In this reaction, a conjugated diene is produced from the non-conjugated diene. Then, it reacts with a double bond in another unsaturated fatty group. This reaction could be an intramolecular cycloaddition from which cyclic products could be



Scheme 1: Hydrolysis of SO.

formed [15]. Polymers with high molecular weight can be synthesized between dimers and trimers through polymerization and intermolecular Diels-Alder reactions.

3.1.2 Characterization of the DA

Photos of the DA are shown in Figure 1. As can be seen from the photo, SO is a kind of transparent liquid with a pale yellow color, whereas the crude DA is brown, viscous and can be crystallized at low temperatures.

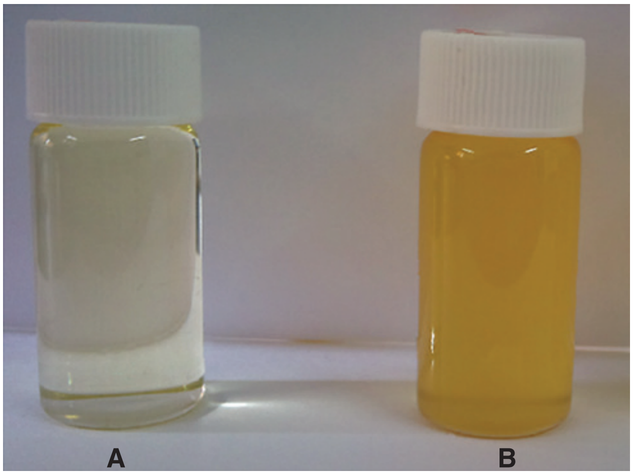


Figure 1: Digital photos of the raw material and the intermediate (A) SO, (B) DA. These photos were conducted at an ambient temperature.

From the FTIR spectrum of SO, Figure 2A, three obvious absorption peaks were observed at 3000, 2800 and 1550 cm^{-1}, respectively. These peaks were related to the stretching and bending vibrations of C-H bonds in the compound. The peaks at 3000–3100 cm^{-1} and 950 cm^{-1} were ascribed to the stretching and bending vibrations of =CH. The very obvious absorption peak at 1750 cm^{-1} resulted from the stretching vibrations of the C=O groups. In addition, the peaks at 1180 cm^{-1} resulted from the C-O bonds, indicating that the -COO groups remained in the structure.

In the spectrum of DA (Figure 2B), strong peaks appeared at 3000–2800 and 1400–1500 cm^{-1}, which resulted from the stretching and bending vibrations of the C-H bonds in the structure. The absorption peaks at 3000–3100 cm^{-1} disappeared, illustrating that the double bond reactions and α-carbon reaction occurred in this olefin [16, 17]. The absorption peak at 1720 cm^{-1} resulted from the stretching vibrations of the C=O bonds, and those at 1180 cm^{-1} were ascribed to C-O. This demonstrated that the -COO groups also existed in this molecule. Wider peaks appeared at 1150–1350 cm^{-1}, which resulted from the bending vibration of =CH caused by the cyclohexene. This proved that the cyclohexene structure existed in the molecular structure of DA [18]. In other words, the DA product had the typical structure of a dimer.

The ^{1}H-NMR spectra of SO and DA are shown in Figure 3. the signals at 5.2–5.4 ppm, shown in Figure 3A, can be ascribed to the olefinic hydrogens, whereas those

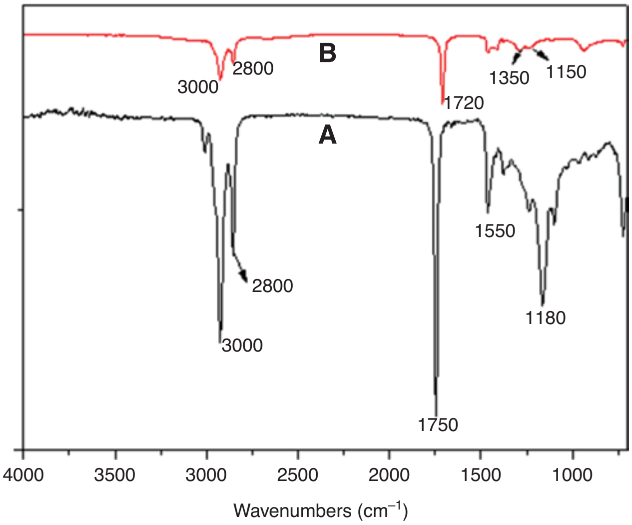


Figure 2: FTIR of the raw material and the intermediate (A) SO, (B) DA. The scanning was performed in a range between 4000 and 700 cm^{-1} with a resolution of 2 cm^{-1}.

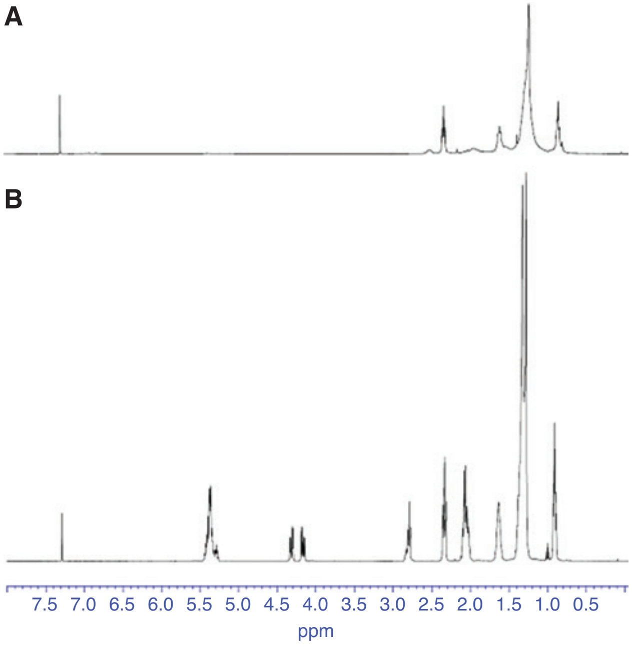


Figure 3: The ^{1}H-NMR spectra of the raw material and the intermediate (A) SO, (B) DA. Deuterated chloroform ($CDCl_3$, 99.8%) was used to prepare the sample solutions for testing.

at 4.1–4.4 ppm were the methylene protons in the $-CH_2$ adjacent to the C=C bond. The signals at 1.1–2.9 ppm also resulted from the methylene protons of $-CH_2-CH_2-CH_2-$ in the glycerin. In Figure 3B, the peaks at 1.2–1.5 and 2.1–2.4 ppm were greatly decreased compared with the proton in SO. The peaks at 5.2–5.4, 4.1–4.5 and 2.8 ppm also disappeared. This observation illustrated the reduced number of C=C bonds and the successful polymerization of DA [9, 15, 19].

The GPC results of the prepared DA are summarized in Table 1. As can be seen, about 87% of the average molecular weights ranged from 995 to 1304 g/mol, which were higher than the theoretical average molecular weight of 560 g/mol. This was due to the complex components in the edible SO, which contained different ratios of palmitic acid, arachidic acid and stearic acid. The unsaturated groups in these components may participate in the conjugation reactions, thus increasing the molecular weight of DA [20].

Table 1: The GPC results of DA.

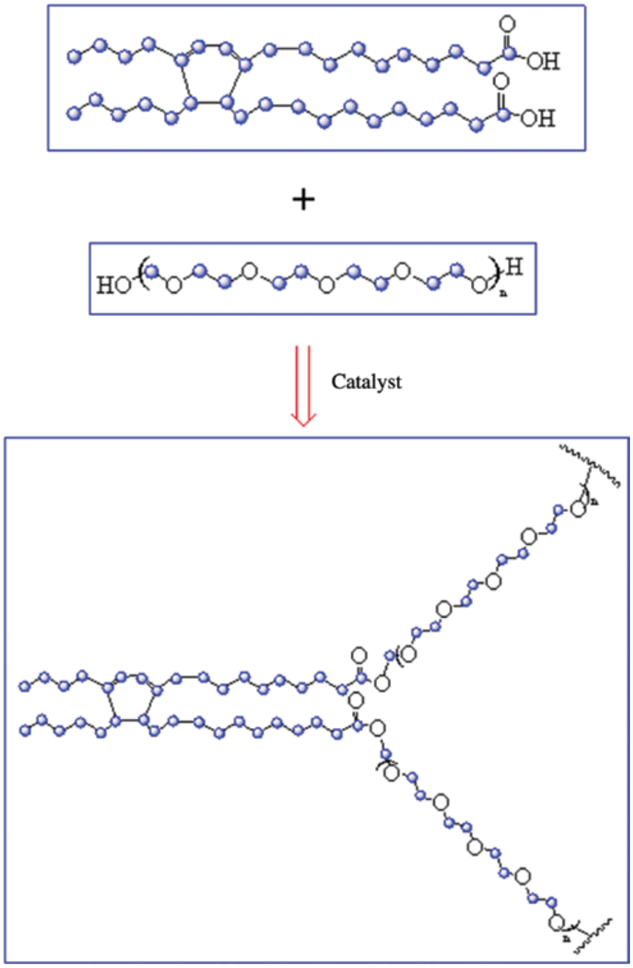
DA	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	Ratio (%)
1	3402	4817	7668	13.05
2	1304	1314	1324	44.89
3	995	1012	1025	42.06

3.2 Preparation of the DA/PEG polyester

3.2.1 Preparation mechanism of the DA/PEG polyester

The preparation process of polyester from DA and PEG is shown in Scheme 2. The main factors that affected the esterification between DA and PEG were dosage, reaction time, reaction temperature and reactant ratios. The experiments were conducted to investigate these factors. Two reaction temperatures, 180°C and 190°C, were selected due to the limited experimental conditions. In this experiment, the ratios of the reactants and the reaction time were fixed, but the catalyst and reaction temperature were changed.

Table 2 shows the results of the acid values and ester conversion rates using different types of catalyst. It can be seen that the conversion rate was the highest when $SnCl_2$ was used as the catalyst. The catalytic mechanism [21–23] of $SnCl_2$ was illustrated as follows. First, $SnCl_2$ had antioxidant abilities; when it was added to the reaction system,



Scheme 2: The preparation process of polyester from DA and PEG.

Table 2: The acid value and ester conversion rate of polyester.

Catalyst	Temperature (°C)	Mass (g)	Consummation of KOH (ml)	Conversion rate (%)
No.	180	2.2118	26.80	60.26
Stannous chloride	180	2.3411	16.45	83.13
Stannous chloride	190	2.1947	17.50	79.76
Concentrated sulfuric acid	180	2.0742	20.70	71.38
Concentrated sulfuric acid	190	2.2293	25.00	64.35
Glacial acetic acid	180	2.2163	24.60	64.98
Glacial acetic acid	190	2.2707	26.30	62.32
Ammonia acid	180	2.1545	25.90	61.16
Ammonia acid	190	2.6653	31.95	58.00

the incidence of side effects was effectively reduced and the esterification rate increased. Second, the catalyst $SnCl_2$ provided a no-electron atomic orbit and combined with the lone pair electrons of the oxygen in the carbonyl. This enhanced the positive electrical charge of the carbon in carbonyl. Due to these reasons, the oxygen in the hydroxyl groups of PEG combined with the carbon atoms in the carbonyl. Thus, the appropriate amount of $SnCl_2$ was suitable to accelerate this reaction.

In Table 2, it was shown that the conversion rate under 180°C was 83.13%, which was higher than that under 190°C. The decarboxylation of the fatty acid can be caused by high temperatures. This increased the pressure in the flask, which resulted in an increase of the monomer content and a decrease of the acid value and viscosity [24]. Therefore, using $SnCl_2$ as catalyst and setting the the reaction temperature to 180°C were the optimal conditions for the preparation of the polyester.

3.2.2 Characterization of the DA/PEG polyester

Figure 4 presents the FTIR spectrum of the DA/PEG polyester. The table shows two obvious absorption peaks at 3300–3700 and 3000–2800 cm^{-1}, respectively. These corresponded to the stretching vibrations of the O-H and C-H bonds in the structure. The obvious peak at 1730 cm^{-1} resulted from the stretching vibration of the C=O group. Those at 1160 cm^{-1} were related to the C-O bond. This showed that the -COO groups existed in the polymer. There were no absorptions at 1800–2700 cm^{-1}, indicating that the sample had a high purity [25]. In conclusion, the polyester was properly synthesized by the DA and PEG.

The ^{1}H-NMR spectrum of the polyester is illustrated in Figure 5. The chemical shifts between 3.5 and 4.1 ppm resulted from the CH_2-O group. The bands appearing between 2.0 and 2.5 ppm resulted from the -$COCH_3$ structure in the remaining monomers. Moreover, the multiple

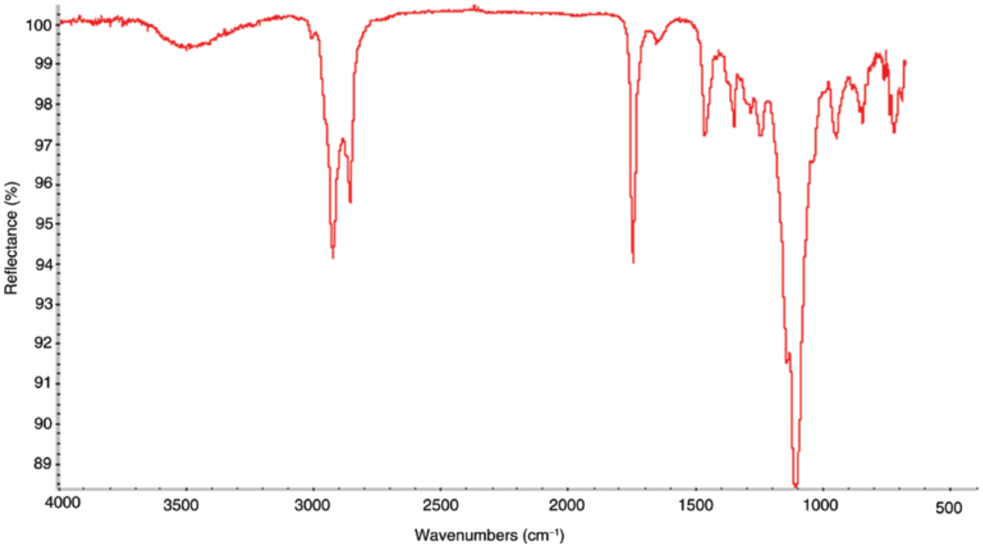


Figure 4: The FTIR of DA/PEG polyester.

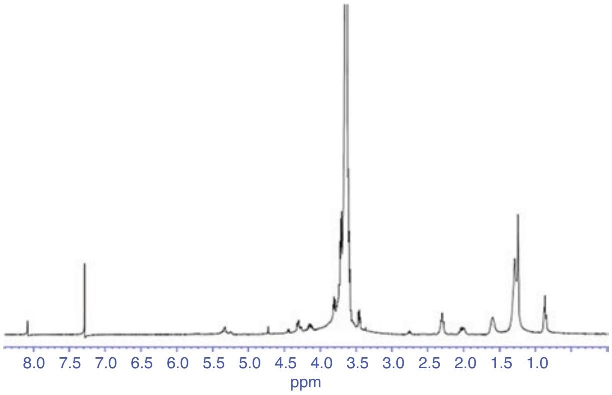


Figure 5: The ^{1}H-NMR spectrum of DA/PEG polyester.

peaks at 0.8–1.7 ppm may be due to the complicated chemical environment of the H protons in the methyl groups among the macromolecular chains [26].

The TGA and DTG curves of the DA/PEG polyester are shown Figure 6. Its degradation under air occurred in three successive steps. Initial weight loss was first shown between 250°C and 320°C. This was due to the degradation of the synthetic monomer, such as DA and PEG, in the resin. The second step was observed between 320°C and 440°C. This was attributed to the degradation of the alkane hydrocarbon groups in the structure. The third step appeared between 440°C and 510°C, and showed the highest degradation rate at about 440°C. This had something to do with the degradation of the resin residue sin. This resin showed a characteristic thermal behavior of polymer resins [27]. In conclusion, the results above demonstrated that this polyester resin was successfully prepared.

Table 3 records the GPC results of the DA/PEG polyester. About 55% of the molecular weight of the polyester was 10,892 g/mol, whereas 45% was 8259 g/mol. This showed that the condensation reaction was not sufficient.

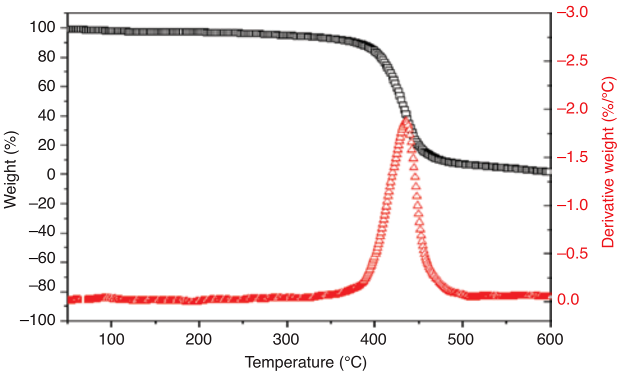


Figure 6: The TGA and DTG curves of DA/PEG polyester.

Table 3: GPC results of DA/PEG polyester.

DA/PEG polyester	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	Ratio (%)
1	10,892	11,548	12,892	55.5
2	8259	9564	10,257	44.5

It can be inferred that the dehydration reaction of the crude DA occurred, and the product with a carboxyl group was reduced. Hence, the carboxyl functional groups were unable to form a double DA, leading to a capped reaction in PEG. This phenomenon was not beneficial for the possible formation of polyesters with high molecular weights. In addition, according to the principle of kinetics, the formation of the polyester may be blocked due to the presence of water [28].

The biodegradability of the polyester was determined by measuring the weight loss of the composite during the soil burial test. Figure 7 describes the percentage weight loss of the biodegraded polymers after 35 days. In order to know its biodegradable property, the polyesters prepared from the crude DA and PEG were compared with those from TA and PEG.

The weight loss showed an approximately linear relation with degradation time for both materials. The weight loss of the polyester prepared from TA was about 25% after biodegradation for 15 days. The average degradation rate was at a relatively lower rate of 1.6%. In comparison, the weight loss of polyester prepared from crude DA was at 60%. The average degradation rate was about 4% per day. These data indicated that the weight loss of the polyester prepared from the DA was relatively higher compared with that prepared from TA. In other words, the presence of DA

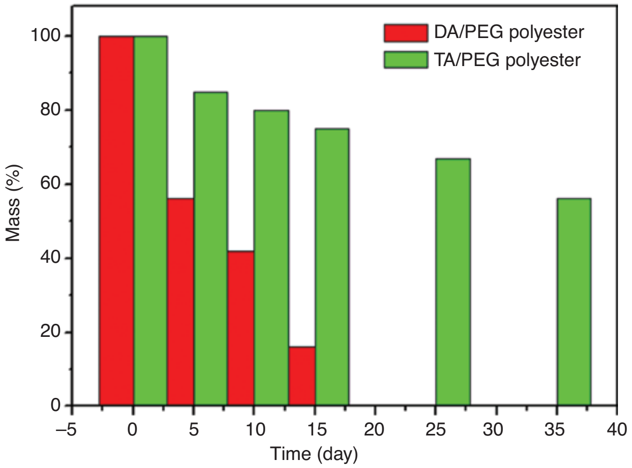


Figure 7: The weight losses of different polyesters under the soil burial test.

prepared from SO had a pronounced effect on the weight loss during biodegradation.

4 Conclusions

The biodegradable polyester was prepared by a novel method using SO. The new method was based on the first preparation of the DA. The proposed method was feasible for the synthesis of crude DA by using SO. The experimental conditions were the combination of the following conditions: temperature of 200°C, organic montmorillonite as a catalyst, and the reaction time of 6 h. The structure and properties of DA were analyzed by FTIR, ^{1}H-NMR and GPC. The DA had an average molecular weight of 995–1304 g/mol.

The optimal experimental conditions for the preparation of the biodegradation polyesters were determined: temperature of 180°C and $SnCl_2$ as the catalyst. The structure and properties of the polyester were analyzed by FTIR, ^{1}H-NMR, GPC and soil burial test. The polyester had a molecular weight of 8259–10,892 g/mol. Meanwhile, the polyester prepared from the crude DA and PEG showed a better biodegradation property than that obtained from TA and PEG.

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