

Enzyme-catalyzed Synthesis of Novel Solid–liquid Phase Change Energy Storage Materials Based on Levulinic Acid and 1,4 butanediol

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Research

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Abstract

With the rapid development of society, all kinds of non-renewable energy resources are constantly developed and utilized, energy storage is one of the best ways to solve the energy shortage. In this study, levulinic acid (LA) and 1,4 butanediol (BDO) were used to synthesize a novel polyol ester (LABDO) by biological and chemical methods. The biological method exhibited excellent performance in the synthesis process, where 87.5% of LABDO yield under optimal conditions, while the chemical method had more byproducts and higher energy consumption. Finally, the thermal properties of the obtained phase change materials (PCMs) were evaluated. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed that the melting temperature of LABDO was 50.51 °C, the latent heat of melting was 156.1 J/g, and the pyrolysis temperature was 150-160 °C. Compared with traditional paraffin wax, the prepared PCMs have suitable phase transition temperature, higher latent heat of melting and better thermal stability. The thermal conductivity can be increased to $0.34 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ by adding expanded graphite. In summary, LABDO can be used as low temperature phase change energy storage materials.

1. Introduction

Energy is the key factor restricting economic development and social progress. With the rapid development of society, all kinds of non-renewable energy resources are constantly developed and utilized, energy storage is one of the best ways to solve the energy shortage (Weiyi Zhang et al., 2018). In the process of energy transition, the use of renewable energy is attracting more and more attention from industrial and building sectors (Stamatiou et al., 2017). To account for fluctuations in renewable energy supply, storage systems will be an important part of future energy supply systems (Kant et al., 2016). As a typical latent kind of high efficiency energy storage material, Phase change materials (PCMs) could absorb or release a lot of latent heat at their melting point as the surrounding temperature increases and decreases (Yuang Zhang et al., 2016; Rui Wang et al., 2018), has received much attention from researchers in recent years (Weiyi Zhang et al., 2018; Kant et al., 2016). Organic PCMs include paraffin and non-paraffin compounds (Ghadim et al., 2019). The role of paraffin is obvious in the application of thermal energy storage (TES). It can be used at low to medium temperature, and has good latent heat of phase change, no supercooled precipitation phenomenon, stable performance, non-toxic, cheap and other advantages, which often used as the basic raw material of composite phase change materials. However, its low thermal conductivity, poor flammability and non-renewability further limit its application (Ahmet Sari, 2012; Sari and Karaipekli, 2012; Stamatiou et al., 2017; Ravotti et al., 2020).

Compared with paraffin wax, non-paraffin PCMs are non-flammable, has good latent heat properties of phase transition, and is easily biodegradable. Fatty acids and their derivatives belong to non-paraffin PCMs, and their melting point and melting enthalpy are in the range of 0-60 °C and 150-200 J/g, respectively, which is similar to paraffin wax (Mazman et al., 2008; Sari et al., 2010; A. Sari et al., 2011; Liston et al., 2016). And fatty acids can be made from biological sources such as vegetable oils and animal fats (such as lard, butter, palm, coconut, and soy) (Hamid et al., 2012). But some of these oils are edible, and their use in the production of cryogenic phase change energy storage materials indirectly

increases food demand(Ji et al., 2015) .Therefore, more and more attention has been paid to the preparation of non-edible oil polyols. Levulinic acid, with carboxyl and carbonyl functional groups of carbon atoms, and can be easily produced from glucose, fructose, starch and lignocellulosic residues. It has been identified as a top platform chemical by the U.S. Department of Energy and is considered one of the twelve most promising molecules derive from biomass, because it can be converted to a variety of other important compounds in the chemical industry(Oliveira and Teixeira da Silva, 2014; Jeong et al., 2017). The levulinate esters obtained by esterification of LA with alcohols have various of potential applications in the diesel fuel additive, plasticizer and flavoring industries.(Jones et al., 2016; Dutta et al., 2019; T. Adeleye et al., 2019).

Up to now, chemical method is still the main method for the production of levulinic polyol ester. Acid catalysts including homogeneous acid catalysts and heterogeneous acid catalysts are commonly used in the synthesis of polyol esters(Chang et al., 2012).Homogeneous acid catalyst (such as sulfuric acid, p-toluenesulfonic acid) has low cost and high efficiency, but it is difficult to separate and corrosion equipment(Zhou et al., 2018). Considering these disadvantages of homogeneous acid catalysts, heterogeneous acid catalysts, including immobilized heteropoly acids and acidic ionic liquids, are also used in esterification reactions(Trombettoni et al., 2017). However, esterification usually requires a high reaction temperature, which is easy to cause side reactions(Zheng et al., 2012; Liu et al., 2021). In recent years, enzymatic synthesis of polyol esters has attracted more and more attention due to its mild reaction conditions, environmental friendliness and fewer by-products(Mukherjee et al., 2015; Jaiswal and Rathod, 2021). The application of lipase in enzymatic esterification reaction has been developed significantly, and the immobilized lipase has significantly improved the catalytic activity and stability of the enzyme(Moon et al., 2021; Song et al., 2021).The addition of organic solvents provides many benefits for enzyme-catalyzed reactions(Zhu et al., 2020). However, using organic solvents requires expensive reactors and tools, leading to their limited use in industry. Esterification in solvent-free systems helps to overcome these shortcomings(Liu et al., 2021). In addition, high selectivity and simple purification steps are important advantages of the solvent-free system. In solvent-free system, the synthesis of levulinic acid polyol ester by biological esterification with lipase as catalyst is rarely studied(Jaiswal and Rathod, 2021).

In this study, we used immobilized *Candida antarctica* lipase B (Novozym 435) as a catalyst to synthesize LABDO from LA and BDO, and investigated the effects of reaction parameters such as reaction temperature, enzyme dosage, substrate molar ratio on the synthesis of LABDO and the reusability of the biocatalyst. The LABDO was purified by a rotary membrane molecular distillation system. Otherwise, the levulinate esters as phase change material is rarely reported. The latent heat properties, thermal stability, and thermal conductivity of the prepared polyol esters were analyzed. The potential of the synthesized esters as base stocks for solid–liquid phase change energy storage materials were also evaluated.

2. Materials And Methods

2.1. Materials

Levulinic acid with a purity of 99% was purchased from Adamas Reagent Co., Ltd. (Shanghai, China); 1,4-butanediol from Maclean Biochemical Technology Co., Ltd. (Shanghai, China); Immobilized *Candida antarctica* lipase B (Novozym 435) with an initial activity of 10,000 U/g as provided by Beijing Ruisen Co., Ltd. (Beijing, China); Amberlyst-15 from Aladdin Reagent Co., Ltd. (Shanghai); H₂SO₄ from Beijing Chemical Factory (Beijing, China).

2.2 Preparation of LABDO

The reaction was carried out in a heated magnetic stirring reactor with controlled stirring rate and temperature. LA and BDO were evenly mixed in the reactor at a certain mole ratio (1:1.8-2.6), and a certain amount of lipase (1%-5%) was added into the reactor. The reaction speed was kept at 200rpm/min, and the reaction time and temperature were set at 0-8h, 40-60°C. The crude product was synthesized by BDO and LA under the catalysis of enzyme. The ester content was monitored by gas chromatography during the reaction process.

The crude product of LABDO was separated from the product by centrifugation at 10000rpm for 10min, and the recovered lipase was washed for recycling and utilization. The crude product was distilled by Rotary Film Molecular Distillation (VTA GMBH & Co. KG, Germany) inlet temperature, 60°C; scraper evaporator temperature, 140°C; central cooling tube temperature, 20°C; heavy-phase outlet temperature, 30°C and 1 mbar to remove sulfuric acid and excess LA. After that, the obtained product from the first distillation was distilled once again at scraper evaporator temperature 200°C and 0.3 mbar to get the final LABDO product.

2.3 Analytical procedure

For GC analysis of LABDO, the samples were first diluted with ethyl acetate to 1×10^4 ppm. The GC analysis of the PE was performed using the Shimadzu GC2030-FID equipped with a DB-1Ht column (30 m \times 0.25 mm \times 0.1 μ m, Agilent, USA) with nitrogen as the carrier gas, a total flow rate of 53.4 mL/min, and pressure of 138.9 kPa. The split ratio, injection temperature, and FID detector temperature were 30, 300°C, and 360°C, respectively. The column temperature was held at 110°C, then heated to 132°C at 12°C/min, and to 180°C at 30°C/min and finally to 300°C at 20°C/min and then maintained for 5 min. The temperatures of the injector and detector were both set at 300°C.

NMR analyses were used for structural characterization. First, 0.25 μ L of the sample was diluted with 0.5 mL of CDCl₃ solvent, mixed well, and transferred to the NMR tube. ¹H NMR and ¹³C NMR spectra were recorded using the AV400 NMR spectrometer (Bruker Co., Ltd., GER).

2.4 LABDO thermal performance analysis

The phase change materials were characterized by Mettler-Toledo DSC differential scanning calorimeter. Place the sample in an aluminum standard dish for each measurement. The measurements were

performed by varying the temperature from -40°C to 80°C with a heating rate of 5°C/min. The differential scanning calorimetry measurements are performed under nitrogen environment with a volume flow rate of 100 mL/min. Each sample was analysed three times and the average was taken. After the first measurement, the second temperature characteristic curve was tested at the same initial temperature, termination temperature and heating rate, and the cycle was 30 times to measure the cyclic stability of PCMs.

Thermal conductivity of the synthesized PCMs was measured by using LFA467 thermal conductivity measuring apparatus at room temperature. Thermogravimetric analysis is a measure to evaluate the thermal stability of materials. A higher TGA onset temperature represents a higher thermal stability of a material. Thermal behavior of the LA-based polyol ester was studied using a METTLER thermogravimetric differential thermal analyzer under a flow of nitrogen (flow rate of 40 mL/min) at a constant heating rate of 10°C /min.

3. Results And Discussion

3.1 Comparison of chemical and biological methods

Esterification methods mainly include biological and chemical methods. This study compares these two methods. It can be seen from Table 1, the chemical method using sulfuric acid as homogeneous catalyst, although it takes less time, it must be under the high temperature reaction. In addition, sulfuric acid will cause the partial oxidation of raw materials and corrosion of equipment because of its strong oxidizing and acidity. Otherwise, as a homogeneous catalyst, the sulfuric acid and the products are not easy to separate. While using heterogeneous catalyst of Amberlyst-15 overcome the difficulty of separation, it still need to be catalyzed at high temperature, and its catalytic efficiency is low, where the diester content is only 47.07% (Robles-Medina et al., 2009). In biological method, Novozym 435 was used as catalyst. Compared with chemical method, the diester conversion rate was the highest, reaching 85.81%. And less byproducts, mild reaction conditions, catalyst recycling, low pollution emissions, low energy consumption advantages. Novozym 435 is a stable and versatile biocatalyst for the synthesis of chiral alcohols, amines and acids (Qin et al., 2016). Therefore, Novozym 435 was used as catalyst in this study to further optimize the reaction.

Table 1
Esterification of BDO and LA Catalyzed by Various catalysts

Entry	Catalyst	Monoester conversation (%)	Diester conversation (%)
1	H ₂ SO ₄	7.26±1.23	73.33±0.96
2	Amberlyst-15	3.26±0.95	47.07±1.21
3	Novozym 435	6.92±0.82	85.81±0.81

Reaction conditions:1: 0.22mol LA, 0.1mol BDO,1% H₂SO₄,90°C,3 h,200rpm/min. 2: 0.22mol LA, 0.1mol BDO,5% Amberlyst-15,90°C,7 h,200rpm/min. 3. 0.22mol LA, 0.1mol BDO,5% Novozym 435,50°C,7 h,200rpm/min.

3.2 Reaction condition optimization

In order to get better esterification performance, esterification reaction enzyme-catalyzed by LA and BDO was carried out under different experimental conditions. Firstly, under the conditions of 50°C, 5% enzyme load, acid alcohol ratio 1:2.2, the effect of time 0-12 h on LABDO synthesis was analyzed. As can be seen from Figure 2(A), The conversion rate of enzymatic reaction increased obviously within 0-1 h, which was due to the high concentration of LA and BDO at the beginning of the reaction and the low concentration of the product. When the time was 1 h, the contents of mono-ester and diester were 28.9% and 35.4%, respectively. During the reaction time of 1-6 h, as the content of diester gradually increased, the monoester content gradually decreased. When the reaction time was 7 h, the reaction system gradually tended to equilibrium due to the reduction of the concentration of reactants, and the yields of diester reached 86.2%. Further prolonging the reaction time, the conversion rate barely changed. Therefore, when Novozym 435 catalyzes LA esterification to reach thermodynamic equilibrium, the reaction time is 7 h.

In non-aqueous phase enzymatic reactions, temperature affects the enzymatic reaction mainly by affecting enzyme stability, enzyme activity, substrate solubility and mass transfer resistance. The influence of temperature 40-60°C on the synthesis of LABDO was analyzed under the conditions of 5% enzyme load, acid to alcohol ratio 1:2.2 and reaction for 12h. As can be seen from the figure 2(B), the diester content increases from 72.3–87.9% as the temperature rises from 40 to 50°C. The reason is that with the increase of temperature, the interfacial mass transfer and the conformational flexibility of the enzyme are improved, and the release rate of water in the system is also increased, resulting in a faster reaction rate. However, continue to raise the temperature to 60°C, the diester content decreased from 87.9–43.01%, because too high temperature would affect the three-dimensional conformation and intermolecular force of the enzyme, thus affecting the formation of intermediate complexes, resulting in reduced reaction rate and enzyme activity. Therefore, 50°C is the best reaction temperature for esterification reaction.

The amount of enzyme has a great influence on diester conversion. Under the conditions of 50°C, acid to alcohol ratio 1:2.2 and reaction time 12h, the influence of enzyme content 1-6% on the synthesis of LABDO was analyzed. As can be seen from Figure 1(B), the maximum diester conversion rate is 3.18% when the enzyme content is 1%. The reason is that when the amount of enzyme added is low, due to the saturation of enzyme active center and substrate, competitive inhibition occurs. With the increase of enzyme dosage, competitive inhibition was relieved, and the reaction rate increased from zero-order reaction to first-order reaction. Therefore, when the enzyme dosage increased from 1–4%, the content of diester increased significantly. However, when the reaction equilibrium is reached, the conversion rate tends to be constant, so when the enzyme content increases from 5–6%, the conversion rate does not increase significantly. Therefore, the optimal reaction enzyme dosage is 5%.

The influence of the molar ratio of BDO to LA on the reaction is shown in Figure 2(D). The effect of substrate initial molar ratio of 1:1.8-1:2.6 on the synthesis of LABDO was analyzed at 50°C with 5% enzymatic load for 7h. The high molar ratio significantly increases the reaction rate. With the increase of the molar ratio of BDO to LA, the conversion rate of diesters increased from 78.91–87.87%. It was found that the ratio of BDO to LA mainly affected the relative concentration monoester and diester, which was similar to the results of previous studies (Åkerman et al., 2011). For a certain amount of BDO, the increase of LA content will lead to the increase of LABDO yield. When the molar ratio of BDO to LA was 1:2.4, the content of the target product reached 87.33%. Adding more LA would not further increase the proportion of LABDO, nor would it be conducive to the separation of subsequent products. Therefore, 1:2.4 is the best alcohol-acid ratio.

3.3 Recycling of catalysts

Compared with traditional chemical catalysts, biocatalysts have the advantages of high selectivity and environmental friendliness. However, relatively high prices generally limit their industrial applications. Recyclable immobilized biocatalysts can significantly reduce catalytic costs. Fig. 3 shows the reusability of biocatalysts during LABDO synthesis. The experiment was repeated for 5 times, and the yield of LABDO still reached 84.2%. After 8 times, LABDO still achieved a yield of 75.2%. In the experiment, partial damage of the immobilized enzyme particles was observed after 8 uses, resulting in a slight decrease in LABDO production. Further development of enzymes with better cyclic stability is needed.

3.4 Structural characterization of LABDO

The target product LABDO was present in the heavy phase, and the diester concentration determined by GC analysis was higher than 95% after molecular distillation.

The results of the NMR spectral analysis of LABDO are shown in Fig. 4(A), and the main chemical shifts are given below: ^1H NMR (CDCl_3 , ppm): 1.72 [m, 4H, (-CH₂-)], 2.21 [s, 6H, (-CH₃)], 2.59 [t, Hz, 6H, (-C=O-CH₂-)], 2.77 [q, 4H, (-CH₂-C=O-)], 4.12 [t, 4H, (-C=O-O-CH₂-)]

NMR analysis showed that LABDO had C and H structures, which were consistent with the expected structure.

Figure 4. ^1H NMR and ^{13}C NMR spectra of LABDO (A:a; b; c; d; e for different hydrogen labeling and chemical structure corresponding to the position. B:a;b;c;d;e;f;g for different carbon labeling and chemical structure corresponding to the position).

3.5 Thermal properties of the prepared PCMs

In order to evaluate the performance of LABDO as PCMs, the melting temperature, thermal melting, thermal conductivity and thermal stability of LABDO paraffins were compared with traditional paraffins.

The heat storage performance of the synthesized PCMs was determined by DSC. Paraffin contains two endothermic peaks of varying sizes, while 1, 4-butanediol levulinate has only one. The enthalpy of

paraffin melting is 161.6 J/g and the melting temperature is 55.99°C. The melting enthalpy of LABDO is 156.1 J/g and the melting temperature is 50.51°C. The results show that the melting temperature and enthalpy of LABDO are similar to paraffin wax, which indicates that LABDO is a promising alternative to paraffin wax, and the transformation temperature of LABDO makes it suitable for low temperature thermal energy storage in solar heating applications (Zanshe Wang et al., 2020). Thermal cycling tests on LABDO were carried out on DSC. After 30 cycles, the phase transition temperature and latent heat value of phase transition do not change much. Any degradation does not result in a change in the chemical structure of the ester. This means that the synthesized PCMs have good thermal stability over a long service life.

Thermal stability of phase change materials is one of the most important parameters in thermal energy storage applications, because thermal decomposition, degradation and sublimation limit their availability. The thermal stability of paraffin and LABDO was studied by thermogravimetric analysis. Compared with paraffin wax, which is widely used as low temperature energy storage material, the decomposition temperatures of the two are similar, which are 150-160°C, far higher than the melting temperature of LABDO. At temperatures below 100°C, neither phase change material degrades or has almost no weight loss, indicating that it has good thermal durability in its operating temperature range. Both paraffin and LABDO decompose rapidly at 250-300°C. When the temperature exceeds 300°C, LABDO is almost completely decomposed without residual residue. Based on the TGA results, it can be concluded that the prepared LABDO have high thermal durability for thermal energy storage applications.

Thermal conductivity of PCMs is also important parameter in energy storage applications, as well as their phase change temperature and latent heat values. Low thermal conductivity is the main shortcoming of phase change materials in heat storage and heat release process. Therefore, low thermal conductivity limits the range of PCMs applications. Adding graphite or expanded graphite (EG) to PCMs are one of the most effective because of its high thermal conductivity porous structure, compatibility with organic materials, light weight, chemical inertia and ease of use (Mazman et al., 2008). The measured thermal conductivity of LABDO esters and paraffin were 0.22 and 0.27 W·m⁻¹·K⁻¹ at the room temperature, respectively. Expanded graphite with high thermal conductivity was added to the prepared PCMs at a mass fraction of 5%, and the thermal conductivity was measured to be 0.34 and 0.31 W·m⁻¹·K⁻¹. The results show that after adding EG, the thermal conductivity of LABDO and paraffin wax are increased by 54.5% and 14.8%, respectively, and the thermal conductivity of LABDO is better than that of traditional paraffin wax.

4. Conclusions

Thermal energy storage has gradually attracted attention due to its high energy density and isothermal charge-discharge potential. Therefore, it is of great interest to develop reliable, cost-effective and sustainable phase change materials. In this paper, A novel polyol ester was synthesized from LA and BDO. Biological and chemical methods were used in the synthesis process. Enzymatic catalytic method showed excellent performance in the synthesis process, and the optimal conditions were as follows:

temperature 50°C, acid-alcohol ratio 2.4:1, enzyme dosage 5%, reaction time 7 h. Under these conditions, the total conversion rate of enzymatic method is 92.7%, LABDO yield is 87.5%, while chemical method has more byproducts and higher energy consumption. And the thermal properties of the phase change materials were evaluated. The melting temperature of LABDO is 50.51°C, and the latent heat of melting is 156.1J/g. Compared with traditional paraffin wax, the prepared PCMs have similar transformation temperature and higher melting enthalpy, which has a wide application prospect. All samples decompose above 150-160°C and have good thermal stability at low temperature. At room temperature, the thermal conductivity of the paraffin and the prepared PCMs are 0.22 and 0.27W·m⁻¹·k⁻¹, respectively. With the addition of expanded graphite, the thermal conductivity of LABDO is higher than that of paraffin wax, reaching 0.34 W·m⁻¹·K⁻¹. Unlike inorganic PCMs, LABDO has no significant supercooling effect, no phase separation, and no corrosion. In addition, they have completely consistent phase transition behavior and have great cyclic stability. The raw materials are biologically based and the synthetic process conditions are mild, making them a more sustainable option than other types of PCMs.

Abbreviations

BDO: 1,4 butanediol

LA: levulinic acid

LABDO: levulinic acid 1,4 butanediol easter

PCMs: phase change materials

DSC: differential scanning calorimetry

TGA: thermogravimetric analysis

TES: thermal energy storage

Novozym 435: Immobilized *Candida antarctica* lipase B

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data are fully available without restriction.

Competing interests

The authors declare no competing interests.

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Authors' contributions

Siyu Zhai: carried out the experiments, analyzed the results and drafted the manuscript. Lihe Zhang and Xi Zhao: review & editing. Qian Wang, Yin Yan and Cui Li: Formal analysis. Xu Zhang: Supervision, Investigation. All authors read and approved the final manuscript. All authors commented on the manuscript. All authors read and approved the final manuscript.

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Figures

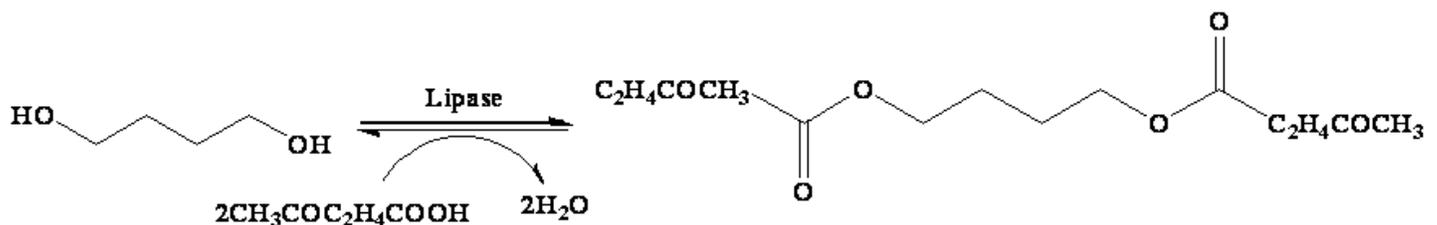


Figure 1

Schematic representation of the esterification reaction between LA and BDO.

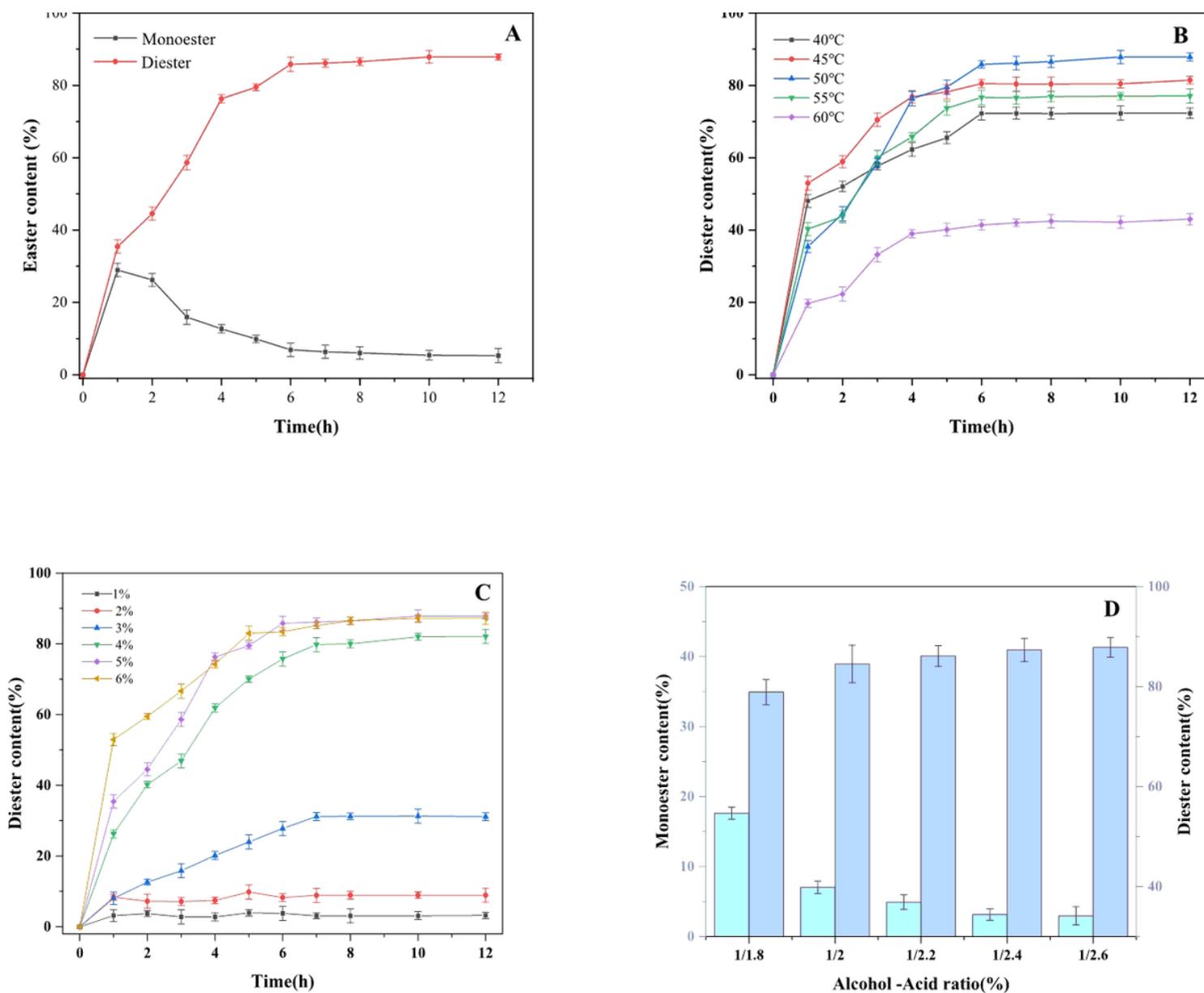


Figure 2

Optimization of reaction conditions for the enzyme-catalyzed synthesis of PCMs. ((A), under certain conditions, LABDO content changes with reaction time;((B), the change of LABDO content with reaction time at different temperatures;(C), the change of LABDO content with reaction time at different ratios of enzyme addition ;(D), the relative percentages of LABDO content in the product at different acid-alcohol ratios).

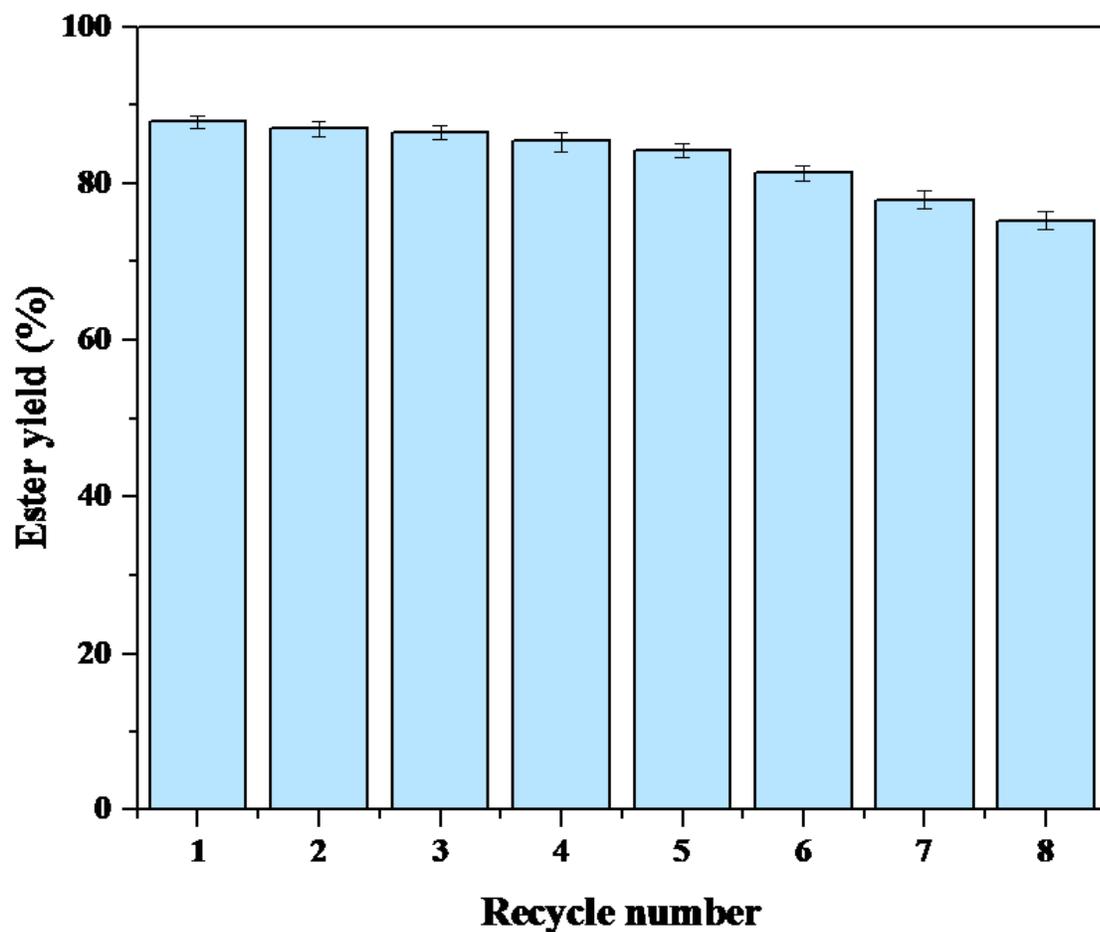


Figure 3

Effects of repeated use of Nov435 on LABDO yield

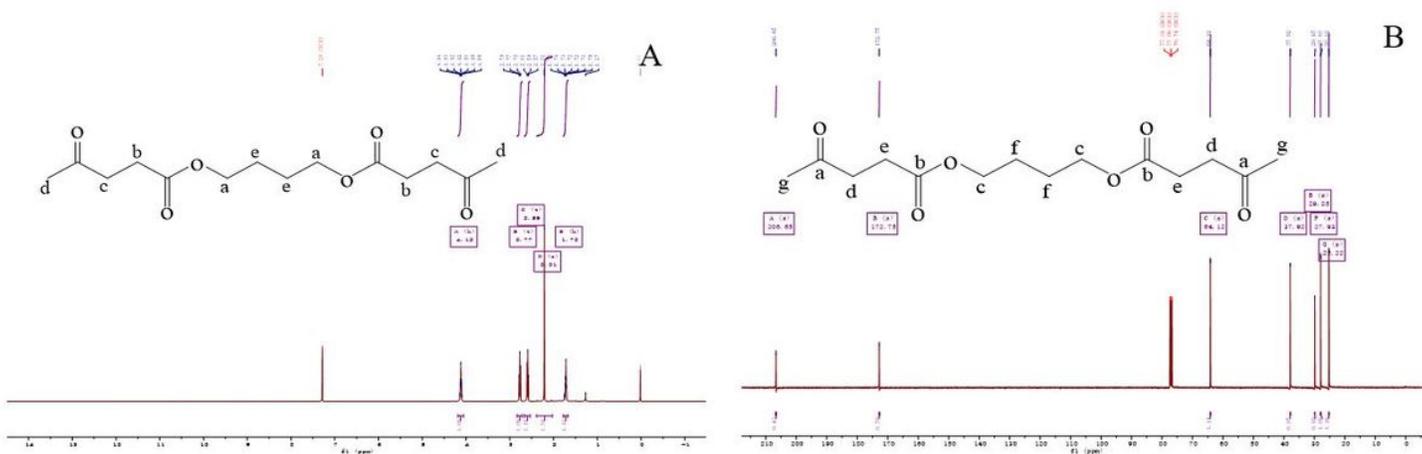


Figure 4

¹H NMR and ¹³C NMR spectra of LABDO (A:a; b; c; d; e for different hydrogen labeling and chemical structure corresponding to the position.B:a;b;c;d;e;f;g for different carbon labeling and chemical structure corresponding to the position).

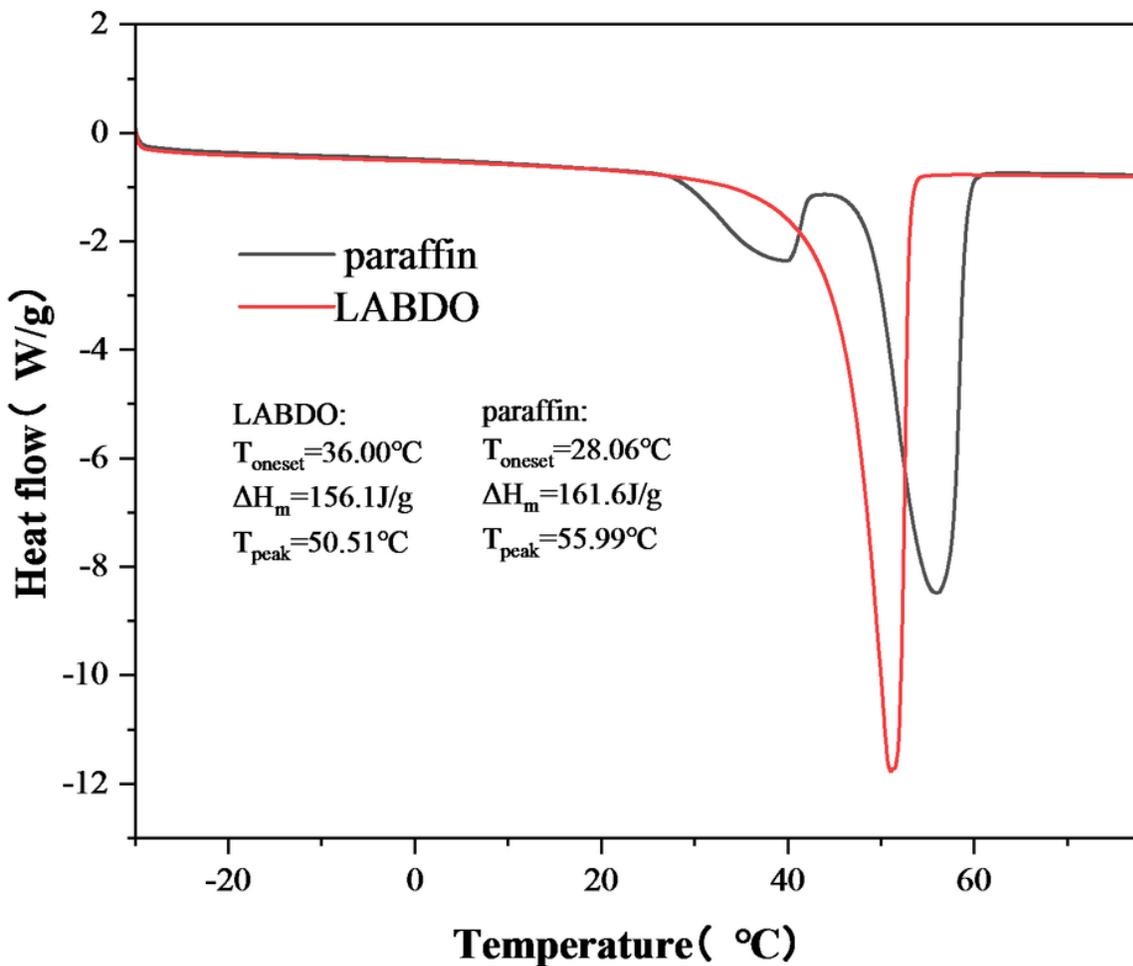


Figure 5

Differential scanning calorimetry (DSC) melting curves for LABDO and paraffin

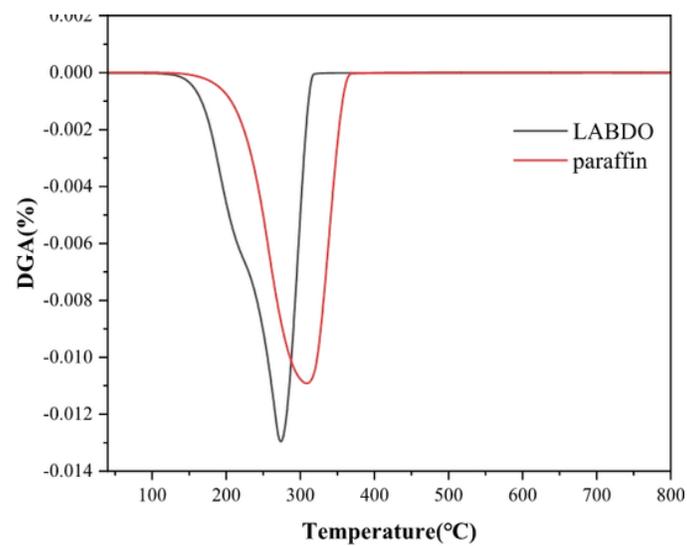
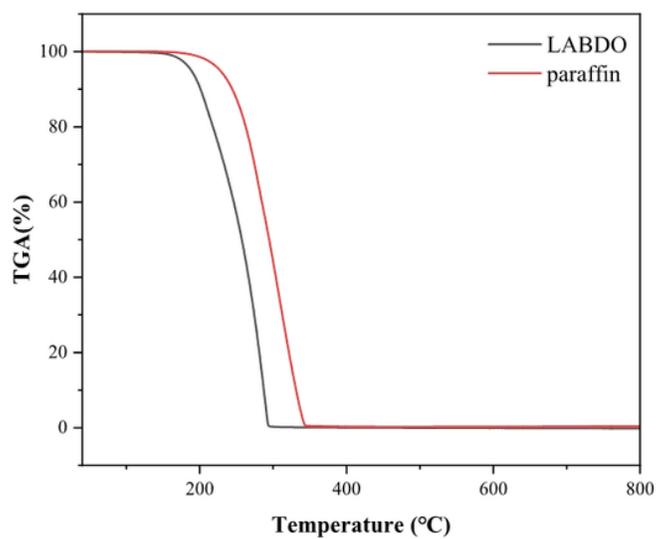


Figure 6

The TGA curves of the LABDO and paraffin

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