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ORIGINAL PAPER

An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis

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Abstract Traditional method for extraction of lignin from black liquor in chemical pulping processes requires a huge amount of toxic inorganic acids like sulfuric acid which are potentially harmful to our environment and life. Furthermore, the traditional method always contains multiple steps, and thus it is time-consuming process. With a purpose to eliminate all these above disadvantages, in this study, we successfully developed an efficient process for the extraction of lignin from black liquor using a non-toxic aluminum potassium sulfate dodecahydrate ($AlK(SO_4)_2 \cdot 12H_2O$). The developed process is simple, efficient, and short-time, which obviously have more advantages over the traditional extraction method. Furthermore, the lignin extracted in this study was used to synthesize a copolyester through polyesterification between lignin and sebacoyl chloride. The copolymer possesses a molecular weight of 31,800, corresponding to four to five repeating units of lignin macromonomers. Notably, it showed a good thermal stability up to 200 °C in TGA analysis. It was also possible to shape the copolymer using solvent

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casting. We believe that this newly developed method of lignin extraction may exploit new applications for eco-friendly sustainable materials in various fields.

Keywords Black liquor · Chemical pulping · Eco-friendly materials · Lignin · Polyesterification

Introduction

Lignin is an amorphous, polyphenolic material arising from enzymatic dehydrogenative polymerization of three phenylpropanoid monomers coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol. For many years, it has been considered as a waste product in pulping process. Currently, however, extensive research is being carried out to utilize the lignin for industry; for example, to produce concrete admixtures and matrix materials of eco-friendly composite systems [1]. Lignin is one of the most abundant renewable natural polymers, and it is believed to be excellent raw material which is an alternative to petroleum-derived chemicals [2]. Lignin is present in the cell walls of vascular plants and in the stems of hard and soft woods such as wood fibers, vessels, and tracheids, in which the content of lignin is around 20–30 wt% [3]. Lignin is present as soluble form in by-product "black liquor" and is produced in extremely large quantities in chemical pulping processes. The conversion of these abundant by-products to value-added materials is considered as a key issue in developing eco-friendly materials as well as resolving the global warming problems.

The most common pulping process is Kraft pulping, where the Kraft lignin is produced, and another popular process is sulfite pulping, where lignosulfonate is produced [4, 5]. Currently, lignin is mostly used as a fuel for the pulping boilers. However, modern pulp mills cannot spend all the black liquors produced in the pulping processes. Thus, many studies on the lignin have been carried out for its conversion to the value-added products [6]. For example, lignin has been used as an additive in concrete, surfactant agent, adsorbent, fertilizer, and rubbers [7]. It has also been utilized in the polymer blend systems together with various polymers such as polypropylene, polyethylene [8, 9], poly(vinyl alcohol) [10], and polystyrene [11]. Furthermore, lignin has been used as monomers to synthesize a variety of polymers for various applications [12–22]. Most recently, the lignin macromolecules were successfully polymerized under condensation reaction with sebacoyl chloride in the presence of triethylamine as a catalyst. The molecular weight of the obtained thermoplastic was controlled by polymerization temperature and reactant ratio and achieves a value of 39,000, corresponding to four to five repeating units of lignin macromonomers [1].

The lignin extraction process from black liquor is the first step of lignin utilization to recover the valuable organic materials from the waste. Kraft lignins are traditionally extracted from black liquor by precipitation with sulfuric acid through two steps. First, carbon dioxide gas is used to reduce the pH of the liquor from 12 to 9–10 in a slow and controlled manner. Second, the pH of the solution is lowered further to 3 or less with sulfuric acid solution and the purified lignin can be obtained after washing with water several times to eliminate impurities [23]. Obviously, the procedure needs a huge amount of sulfuric acid to reduce pH from 9–10 to 3, which is inevitably toxic and dangerous processing procedure. It also needs a long period of time for the safety and consistent manufacturing. Thus, it is necessary to develop an alternative method that eliminates all mentioned disadvantages.

In this study, we successfully developed a new, facile and safe method for extracting lignin from black liquor using aluminum potassium sulfate dodecahydrate solution (alum). In this approach, aluminum potassium sulfate dodecahydrate, a cheap and non-toxic chemical widely used in water purification, was used instead of sulfuric acid to precipitate lignin in a very fast and controlled manner, which ensures a mass production with a short period of extraction time and a safe and eco-friendly procedure. The obtained lignin shows a molecular weight M_w of 6,000 and a narrow molecular weight distribution (MWD) of 1.6. Besides, the TGA analysis shows an initial decomposition temperature of 155 °C and the maximum decomposition temperature of 337 °C for the extracted lignin, which is comparable with that of the commercialized lignin of Sigma-Aldrich Co. Furthermore, to demonstrate the utilization of the lignin extracted by the developed method, the lignin was successfully utilized as macromonomers in lignin-based copolyester synthesis. The TGA and GPC analysis results show that the thermoplastic copolyester based on lignin-SKKU has comparable properties with that of copolyester synthesized in the same way using a commercialized lignin from Sigma-Aldrich Corporation.

Experimental

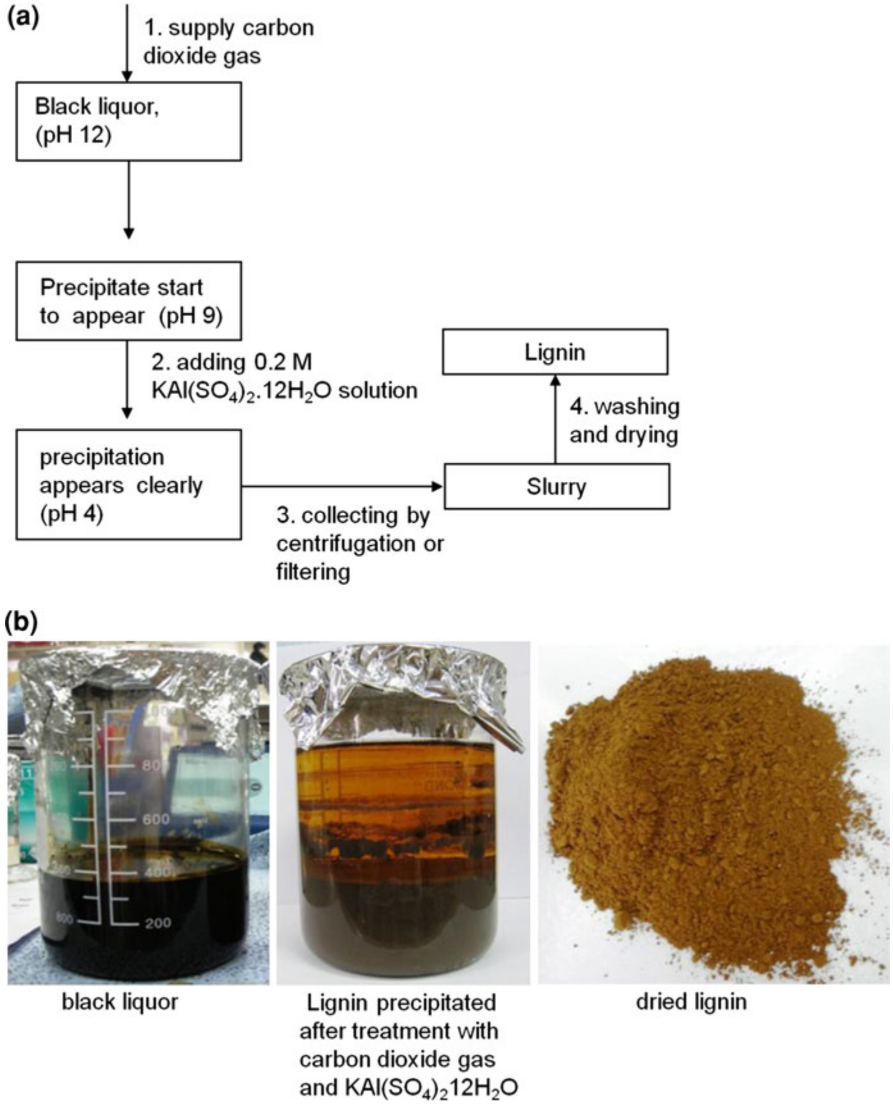
Materials

Black liquor was received from Dong-Hwa Pulp Company. Aluminum potassium sulfate dodecahydrate ($AlK(SO_4)_2 \cdot 12H_2O$), Sebacoyl chloride (SC) ($C_{10}H_{16}O_2Cl_2$) were purchased from Sigma-Aldrich Corporation, USA. *N*,*N*-dimethylacetamide (DMAc) (99%) was supplied by Junsei Co., Japan. Triethylamine (TEA) (99%) was obtained from SamChun Co., South Korea. Lignin obtained from Sigma-Aldrich Corporation was used as the reference with the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of 6,500 and 4,700, respectively; thus, MWD of 1.4. deionized (DI) water was used through the experiment.

Method

Extraction of lignin from black liquor

As demonstrated in the Scheme (Fig. 1), first, 1000 mL pristine black liquor (pH = 12, the solid content was 49.5 wt% as measured after the black liquor was dried in an oven at 100 °C for 24 h) was purged with carbon dioxide gas for around 30 min at 60 °C. After treatment with carbon dioxide gas, the pH of the solution



black liquor

Lignin precipitated after treatment with carbon dioxide gas and $KAl(SO_4)_2 12H_2O$

dried lignin

Fig. 1 Extraction procedure of lignin from black liquor (**a**) and digital camera images of black liquor precipitates and dried lignin-SKKU (**b**)

was reduced to 9, thereby the lignin started to precipitate, and the black color of the black liquor changed to dark yellow (Fig. 1). In the next step, 5000 mL of 0.2 M aluminum potassium sulfate dodecahydrate ($AlK(SO_4)_2 \cdot 12H_2O$) was added quickly to reduce the pH to around 4 with vigorous mechanical stirring at room temperature. The mixture was then left to stand overnight to ensure the precipitation of lignin in the solution. The precipitate was then observed clearly and it can be easily collected by filtering or centrifugation. The slurry was carefully washed with DI water several times to eliminate impurities. The powder was finally vacuum-dried for 48 h.

Synthesis of copolyesters from lignin-SKKU and lignin-Aldrich

Briefly, 20 g lignin was dissolved in 180 mL DMAc at 40 °C for 20 min. SC (53.1 g) ($COCl/OH_{lignin}$ ratio = 2; the COCl/OH was calculated based on the chemical structure and molecular weight of lignin and SC) was dissolved in DMAc (20 wt%), and then added to the lignin solution at room temperature. Subsequently, TEA (6.5 g) (COCl/TEA molar ratio = 4/1) was added slowly to the above mixture. The reaction mixture was heated to 110 °C for 22 h with mechanical stirring. The mixture was then cooled down to room temperature, washed several times with DI water to remove the impurities, and finally freeze-dried to a constant mass [1].

Characterizations

Gel permeation chromatography (GPC) was used to analyze the molecular weight of lignin using a NS 3000-i system (FUTECS Co., Ltd.). The FTIR was studied using a NICOLET IR 200 spectrometer. The weight loss behavior was measured at temperatures ranging from 50 to 700 °C and at a heating rate of 10 °C min^{-1} in N_2 gas using a TGA-2050-TA Instrument Inc. Differential scanning calorimetry (DSC) was performed on a DSC-2910-TA Instrument Inc. at temperature ranging from −100 to 300 °C and at a heating rate of 10 °C min^{-1}.

Results and discussion

The developed method in this study has several advantages compared with the traditional method [23], ensuring a short processing time and making use of nontoxic alum chemicals instead of toxic and corrosive sulfuric acid. Figure 1 shows the extraction procedure of lignin from the pristine black liquor (a), and digital camera images of pristine black liquor, precipitates and dried lignin in our experiment represented as lignin-SKKU (b). The synthesized lignin is dark yellow, which is similar to that of commercialized lignin purchased from Sigma-Aldrich Co. (represented as lignin-Aldrich). The recovery of lignin extracted from the black liquor was estimated to be around 20 wt%, indicating a quite high loading content of lignin in the black liquor. As mentioned in the "Experimental" section, the solid content in the black liquor was estimated to be 49.5 wt%. The remaining 29.5 wt% of solid content in the black liquor can be regarded as such substances as hemicelluloses and the inorganic chemicals often used in the Kraft pulping process.

The GPC results show the M_w, M_n, and MWD of the synthesized lignin are 6000, 3700, and 1.6, respectively. From the GPC data, lignin-SKKU has a lower molecular weight than that of lignin-Sigma, indicating that the lignin-SKKU included in the received black liquor was broken into smaller fragments than those of the lignin-Aldrich. However, as calculated, the MWD of lignin-SKKU is 1.6

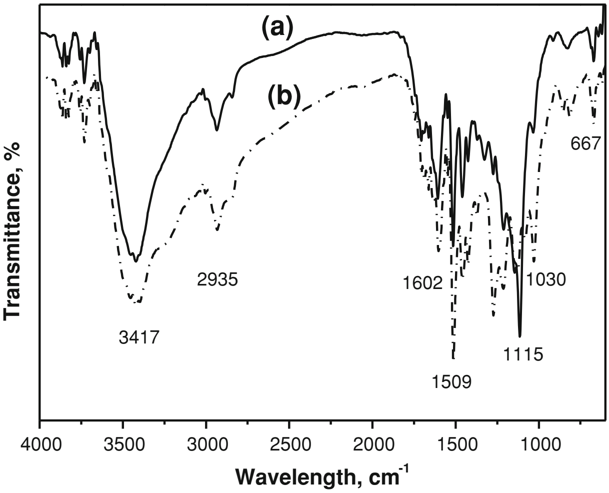


Fig. 2 FT-IR spectra of lignin-SKKU (*a*) and lignin-Aldrich (*b*)

exhibiting a similar uniformity in terms of molecular weight to that of lignin-Aldrich.

Figure 2 compares the IR spectra of the pristine lignin-SKKU (a) and lignin-Aldrich (b). As seen, both IR spectra show characteristic peaks of the Kraft lignin. For example, a peak at 2,935 cm^{-1} is assigned to CH stretching of methyl or methylene groups. Moreover, two bands at 1,509 and 1,602 cm^{-1} are characteristic peaks of benzene rings due to the vibrations. The strong and broad peak at 3,417 cm^{-1} is characteristic peak of OH groups or phenolic compounds. The band at 1,115 cm^{-1} is regarded to the ether stretching. The sharp peak at 667 cm^{-1} is characterized as the CS group, which is formed during the Kraft pulping processes [1, 24].

In Fig. 3, the TGA thermograms (a) and its derivative curves (b) are compared between the lignin-SKKU and lignin-Aldrich products. In order to compare the thermal stability of the two lignins in this study, we defined the initial decomposition temperature (T_{id}) as the temperature where a 2% of weight loss occurred. The T_{id} of the lignin-SKKU is 155 °C, which is similar to that of lignin-Aldrich (148 °C). Moreover, from the derivatives of the spectra in Fig. 3b, the maximum decomposition temperatures (T_{maxd}, where 70% of weight loss occurs) of the lignin-SKKU and lignin-Aldrich are located at 337 and 343 °C, respectively. It is clearly demonstrated that the lignin-SKKU is as thermally stable as lignin-Aldrich.

Furthermore, DSC was used to study the glass transition temperatures (T_{g}) of the lignins and the result was illustrated in Fig. 4. As seen, T_{g} of the lignin-SKKU and lignin-Aldrich are determined from the spectra to be 46 and 48 °C, respectively, which are in a very good agreement. However, the glass transition regions of the two lignins are quite broad seemingly because of the nature of the randomly distributed functional groups and conformational or configurational irregularity of the lignins.

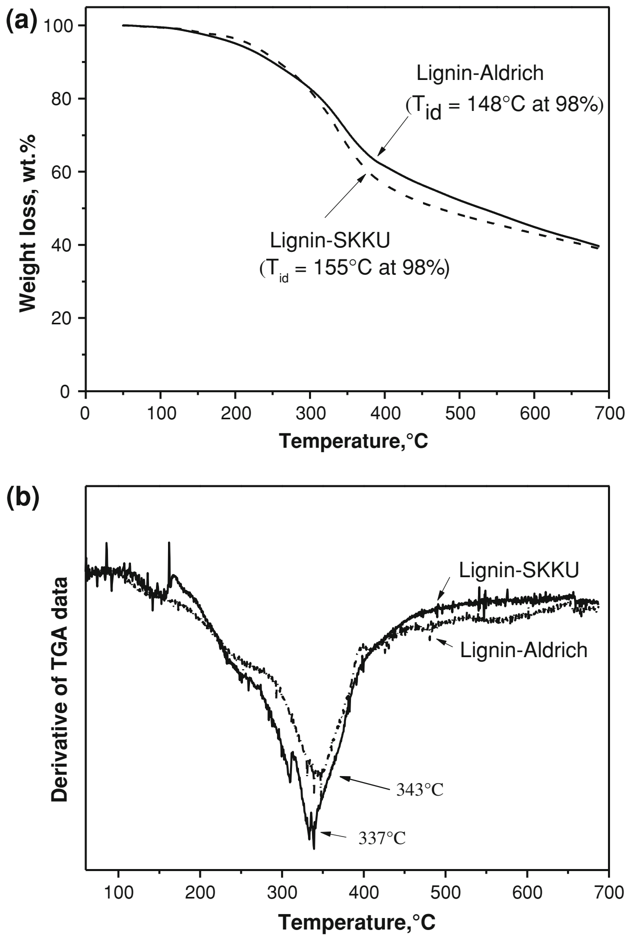


Fig. 3 TGA thermograms of weight loss (**a**) and its derivatives (**b**) of lignin-SKKU and lignin-Aldrich

We synthesized a copolyester using lignin-SKKU (lignin-SKKU-based copolyester) and lignin-Aldrich-based copolyester was also synthesized in the same way as a reference. Figure 5a shows the synthesis pathway of lignin-based copolyester from polyesterification between lignin and sebacoyl chloride catalyzed by TEA. In this polyesterification reaction, OH groups in lignin react with the COCl groups of SC to create new ester bonds, thereby connecting the lignin units together. During the reaction, HCl molecules were generated as byproducts which acted like an inhibitor and were effectively removed by TEA. In Fig. 5b, camera pictures show reaction mixture (a), lignin-based copolymer precipitated in water after washing (b), dried copolyester powder (c), and copolyester film made by spinning coating of a copolyester/DMAc solution (15 wt% of polymer), exhibiting a yellow transparent thin film on a glass substrate.

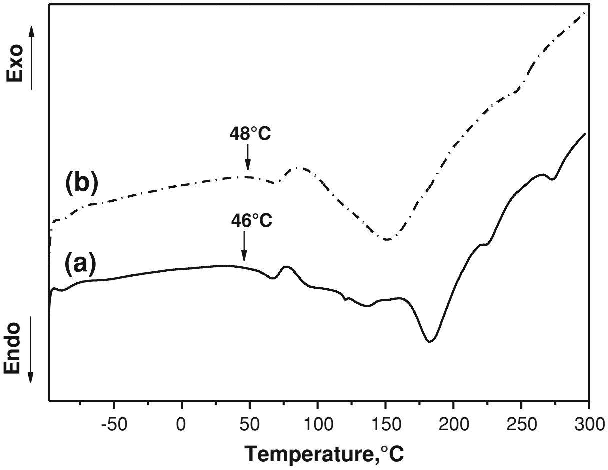


Fig. 4 DSC diagrams of the lignin-SKKU (*a*) and lignin-Aldrich (*b*)

As measured by GPC, M_w, M_n, and MWD values are 31800, 16300, and 1.9 for copolyester based on lignin-SKKU and 39700, 13200, and 3.0 for lignin-Aldrich-based copolyester, respectively. From the molecular weight values, it is estimated that there are four to five lignin macromolecules in one lignin-based copolyester chain.

Figure 6 compares the IR spectra of lignin-SKKU-based copolyester (a) and lignin-Aldrich-based copolyester (b) synthesized at 110 °C for 22 h. As seen clearly, IR spectra show the peaks of C–H at 2,854 and 2,926 cm^{-1}, a benzene ring at 1,510 and 1,610 cm^{-1}, and OH at 3,420 cm^{-1}. Notably, both copolyesters exhibit the characteristic peak of the ester bond at 1,731 cm^{-1}, which confirms that the esterification reaction took place successfully between the OH groups in lignin and COCl groups in sebacoyl chloride [1, 24].

TGA thermograms (Fig. 7a) and their derivatives (Fig. 7b) for two copolymers are presented to quantify the thermal stability of lignin-SKKU-based copolyester in comparison with that of copolyester from commercial lignin-Aldrich. As calculated from the TGA curves, the T_{id} values for lignin-SKKU-based polyester and lignin-Aldrich-based copolyester are 199 and 215 °C, respectively. Furthermore, the T_{maxd} of lignin-SKKU-based polyester and lignin-Aldrich-based copolyester, defined at 30 wt% of char content, is 466 and 521 °C, respectively. The differences between the T_{id} and T_{maxd}, between two polymers, are 16 and 55 °C, respectively, confirming that although the lignin-SKKU-based copolyester is less thermally stable than that of lignin-Aldrich copolyester, good values of T_{id} and T_{maxd} make it good candidate in eco-friendly material development.

Overall, the developed methodology provides a simple, fast, and eco-friendly way to extract lignin from black liquor and its utilization in lignin-based copolyester synthesis. We believe that the developed method could be widely used in eco-friendly material industry because of their advantages over the previously developed method reported by the others.

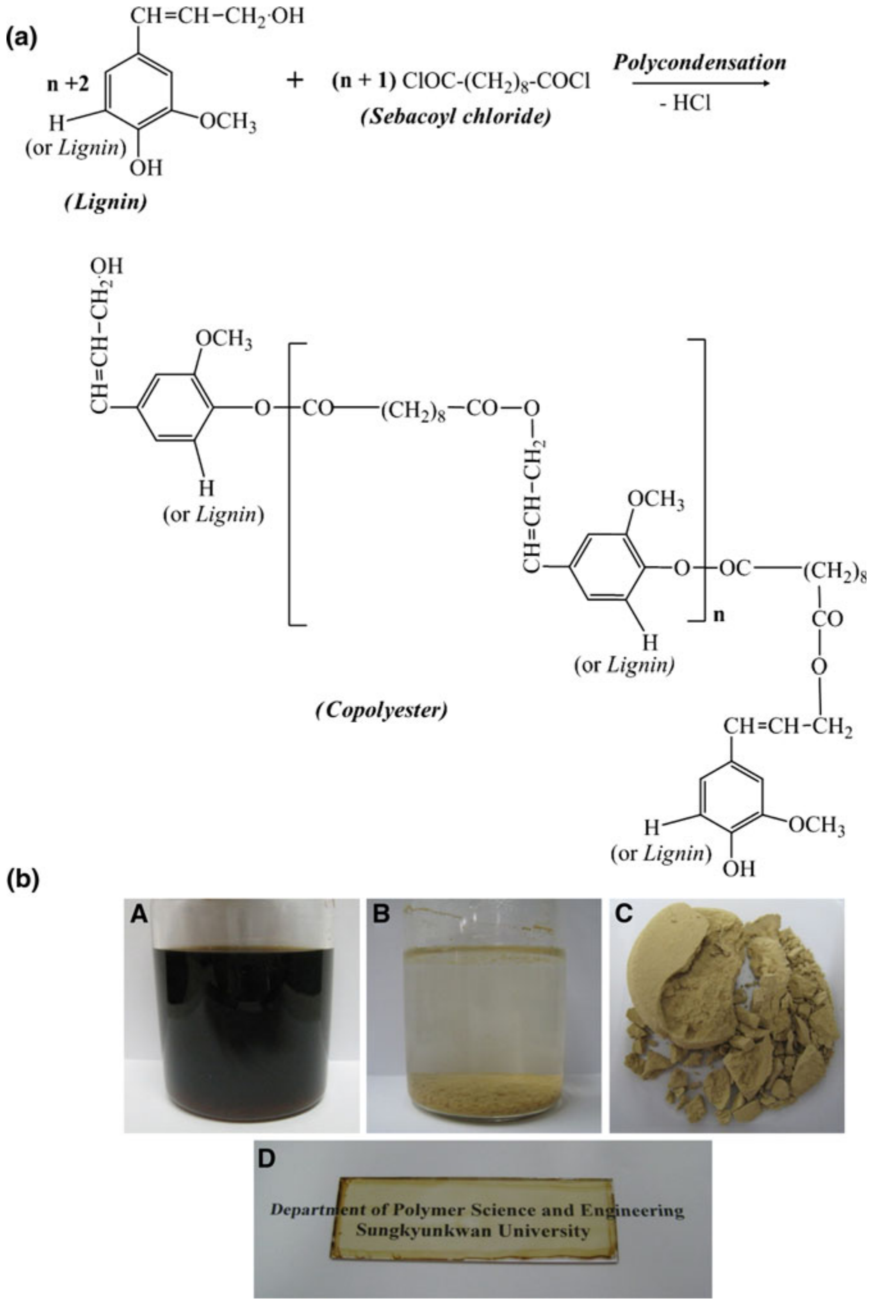


Fig. 5 **a** Synthesis pathway of lignin-based copolyester from polyesterification between lignin and sebacoyl chloride catalyzed by triethyl amine; **b** Camera pictures of reaction mixture (A), lignin-based copolymer precipitated in water after washing (B), dried copolyester powder (C), and copolyester film made by spinning coating of a copolyester/DMAc solution (15 wt% of polymer), showing a yellow transparent thin film on a glass substrate

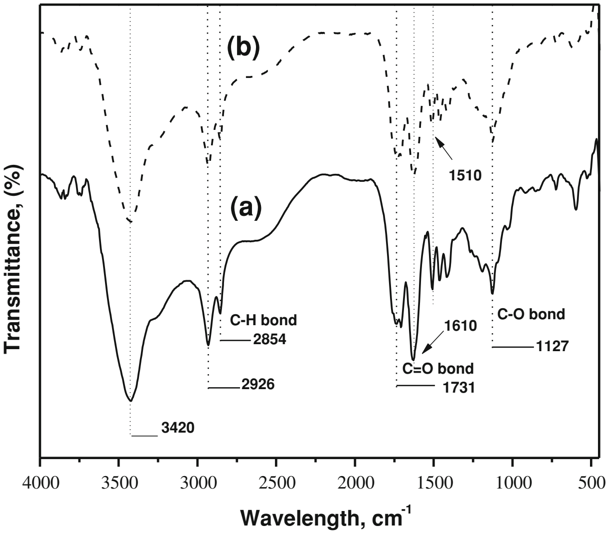


Fig. 6 FT-IR spectra of lignin-SKKU based copolyester (*a*) and lignin-Aldrich based copolyester (*b*)

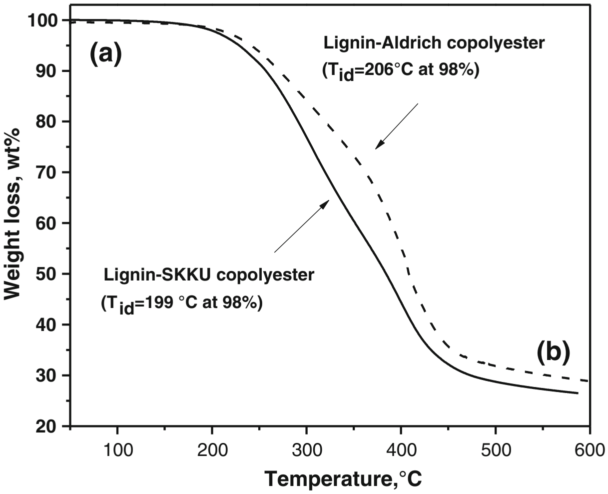


Fig. 7 TGA thermograms of weight loss lignin-SKKU-based copolyester (*a*) and lignin-Aldrich-based copolyester (*b*)

Conclusions

We successfully developed a facile route to extract lignin from black liquor. The developed method was proved to be efficient and simple, which are believed to be attractive for the lignin extraction processes from black liquor in pulping industry. Thermoplastic copolyester based on the extracted lignin was successfully synthesized as an evident for the utilization of lignin for eco-friendly material development.

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