Investigation of the potential for utilization of sugarcane bagasse lignin for carbon fiber production: Thailand case study

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Abstract

Lignin is an attractive biomaterial to replace petroleum aromatics due to its intrinsic aromatic structure and availability. In Thailand, the sugar industry has potential as a source of around 7.5 million tons of lignin per annum. Sugarcane bagasse lignin was developed as a low-cost precursor in carbon fiber production to replace polyacrylonitrile, a petroleum-derived polymer using the electrospinning technique. A technical study and financial assessment of carbon fiber production feasibility from bagasse lignin at the laboratory scale were performed in parallel, and the Thai carbon fiber market was surveyed. Results showed that electrospun carbon nanofiber could be produced from a mixture of 25% lignin and 75% polyacrylonitrile with diameter of 171 nm. The surface area of carbon nanofiber produced from lignin-polyacrylonitrile mixture was higher than that of pure polyacrylonitrile. However, increasing lignin content in the mixture resulted in lower conductivity. Lignin-polyacrylonitrile carbon nanofiber obtained was appropriate for those where higher surface area was required rather than structural application. A market survey indicated increasing exploitation of carbon fiber in Thailand during the last 5 years even though there was no industrial production of carbon fiber due to technical and financial constraints. Both carbon nanofiber and lignin production costs at laboratory scale (12.4 \$/g) were 27 times lower compared to commercial carbon nanofiber (343.4 \$/g) available in a similar form. This price difference presents an opportunity to further development of carbon nanofiber for industrial application, although intensive research and development are still required.

Keywords Sugarcane bagasse · Lignin · Electrospinning · Carbon nanofiber · A sugar industry

1 Introduction

In Thailand, the sugar industry has the potential to generate 30 million tons of bagasse a year or around 7.5 million tons of available lignin [1]. Currently, sugarcane bagasse is used for cogeneration processes within the factory and the surplus is sold to community electrical plants [2]. To use this agricultural by-product more efficiently, a concept of separating and using lignin to produce higher value products before returning delignified bagasse for energy

production was considered. Structurally, agricultural residues such as bagasse and cereal straw are more porous than wood materials; thus, recovering lignin could be performed economically and in an environmentally friendly manner [3]. In addition, with slight lower heat building capacity of around 5–19% compared to normal bagasse, delignified bagasse could still be used for energy production [4].

Lignin has been extensively studied to produce higher value products than combustion for energy such as

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antimicrobial agents, UV-blocker in textiles and biomaterial [5]. Due to the high carbon content, lignin from various sources is also the most-studied biological resource for carbon fiber (CF) precursor [6–9]. For commercial CF, almost 80% use polyacrylonitrile (PAN), a linear polymer derived from petroleum as a precursor, while 20% use rayon and petroleum pitch [10]. Due to its suitable chemical structure, PAN carbon fiber offers excellent mechanical properties [11]. However, carbon fiber produced from PAN is expensive and the main production cost is from PAN itself; thus, PAN application is limited to products where performance is a primary concern. Currently, lignin-CF is not commercially available as it offers lower mechanical performance with production limitations [12]. Here, an alternative use of bagasse lignin-CF was explored to develop bagasse lignin as a cost-effective precursor for CF production. The chosen fabrication technique was electrospinning as it is simple, requires less equipment and can be easily scaled-up. Surface morphology, surface area and electrical conductivity of the obtained electrospun fibers were studied. Technical and financial feasibility studies were also conducted to determine suitability for the Thai CF market. The study was carried out in the laboratory of the Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart University, Bangkok, Thailand during June 2016 to June 2017.

2 Materials and methods

2.1 Lignin preparation

The bagasse sample was kindly provided by Mitr Phu Khieo Sugar Mill, Chaiyaphum Province, Thailand and dried at 50 °C in a ventilated oven until constant dry weight was obtained. Lignin was isolated from the dried bagasse under a mild condition of alkali hydrolysis with ratio of dried bagasse and 1%NaOH solution 1:12 (w/v). The mixture was heated to 105 °C for 2 h by autoclave. After bagasse removal by filtration, pH of the filtrate was adjusted to 2 with 50% H₂SO₄ and the precipitated lignin was separated through filter paper. The obtained lignin was washed with deionized water to remove impurities and dried in a ventilated oven at 50 °C overnight for further experiment. The yield of bagasse lignin obtained was 25.5 ± 1.28% (w/w dry bagasse).

2.2 Lignin molecular weight characterization

The molecular weight of lignin was determined by gel permeation chromatography (GPC) (Waters e295 Separations Modules, Water Corporation, USA). Solubility of lignin in tetrahydrofuran (THF), a solvent used for GPC systems was

increased by subjection to acetylation reaction. A 100 ml aliquot of pyridine and acetic anhydride was mixed at room temperature for 10 min before adding 2 g of lignin powder and stirring for 72 h at 300 rpm using a magnetic stirrer to obtain acetylated lignin. Then, the supernatant was filtered through a membrane (nylon 66, pore size 0.45 µm) to remove the residue from the reaction. Lignin solution was injected into cold water (4 °C) to precipitate acetylated lignin. The powder was collected and dried in an oven at 80 °C for 3 h or until the weight was constant. Acetylated lignin was mixed with THF for molecular weight analysis. A solution of 2 mg/ml lignin in THF was prepared and filtered through a membrane (nylon 66, pore size 0.45 µm) prior to injection. The GPC system was equipped with a PLgel 10 µm mixed B2 column and refractive index (RI) detector (model 3580, Viscotek). Injection volume of the sample was 100 µl with a flow rate of solvent set at 10 ml/min at 35 °C. Calibration was performed under the same GPC condition using polystyrene as a standard (MW 1220–1,214,000 Dalton).

2.3 Fabrication of lignin fiber using electrospinning

Electrospinning is a widely reported method to prepare polymeric fibers [13] including CF with diameters ranging from nanometers to micrometers. Here, lignin alone dissolved in dimethylsulfoxide (DMSO) solution was found unsuitable for fabrication due to its heterogeneity and branching structure that was not ideal for the fiber forming process. Thus, electrospun fiber was prepared from a mixture of lignin-PAN solution. Bagasse lignin solution was prepared in dimethylsulfoxide (DMSO) at a 5 wt% concentration and the same concentration of polyacrylonitrile (PAN) solution was prepared in dimethylformamide (DMF). Lignin and PAN polymer solutions were mixed at the ratio of 1:3 by weight to obtain fiber containing 25% lignin on a dry weight basis. This mixture was selected as no precipitation occurred during and after mixing. The mixed solution was pumped into the electrospinning system at a rate of 60 ml/min, with the tube placed 20 cm above the collector. The applied voltage was kept constant at 40 kV during fabrication.

2.4 Thermal treatment condition

Fiber from the lignin-PAN mixture was thermostabilized by heating from room temperature to 250 °C at a heating rate of 5 °C/min in a tube furnace (Lenton, Model 12/25/250, England). The stabilized fiber was further carbonized in the same tube furnace from 250 to 800 °C with a heating rate of 5 °C/min to promote polymer chain alignment.

2.5 Scanning electron microscopy (SEM)

Surface morphology of lignin carbon fiber was studied by scanning electron microscopy (SEM) using a Quanta 450FEI at 20 kV.

2.6 BET surface area measurement

Surface area analysis of the fiber sheet was performed using Brunauer Emmett Teller (BET) (Micromeritics, 3Flex Surface Characterization Analyzer, Georgia, USA) under nitrogen gas. Single point surface area at $p/p_0 = 0.299$, isothermal 77.0 K and sample constant density were used as condition and assumption for the analysis.

2.7 Electrical conductivity measurement

A two-point probe digital multimeter (Fluke, USA) was used to identify the electrical conductivity of the fiber sheet. Due to the low speed of the conveyor belt used for collecting fiber sheets, the fibers were randomly collected on a collector, as shown in Fig. 1a. Without obvious

direction, an analysis was performed by randomly attaching a metal probe to the sheet surface and the average reading value was used for analysis.

2.8 Financial feasibility study and market survey

The financial feasibility of CNF fabrication from bagasse lignin/PAN mixture was determined. Production cost at laboratory scale was calculated from direct material, direct labor and manufacturing overheads during the fabrication process.

3 Results and discussion

3.1 Molecular weight of bagasse lignin and morphology of electrospun nanofiber

The average molecular weight (M_w) of lignin from bagasse is 7500 g/mol with a polydispersity index of 3.14. The obtained bagasse lignin alone was not able to form fiber by the electrospinning process thus PAN ($M_w = 150,000$ g/

Fig. 1 Bagasse lignin-PAN fiber on aluminum foil collector (a) and SEM images of bagasse lignin-PAN fiber (bar length: 5 μm) before carbonization (b) and the obtained bagasse lignin-PAN CNF (bar length: 5 μm) (c)

mol) was used as a backbone polymer to assist in fiber formation. Generally, the comonomers are widely used in PAN-based polymer precursors. A formulation using acrylonitrile (AN) monomer and various acids such as itaconic and methacrylic was reported to improve CF properties by reducing interaction between the highly polar nitrile groups which increased segment mobility and crystalline orientation [10]. Therefore, a solution of bagasse lignin was mixed with PAN solution and the obtained fiber contained 25% lignin on a dry weight basis. Submicron electrospun fiber with lignin content greater than 25% could be also obtained but a larger proportion of DMSO from an increasing of lignin solution ratio during mixing affected fiber processing. In this regard, wetted fiber was received and not suitable for further processing. Morphology of lignin-PAN fiber randomly collected from the collecting tray (Fig. 1a) was further determined by SEM. Diameter of the electrospun fiber before thermostabilization was 263 nm and bead-like structure was randomly appeared in fiber filaments as shown in Fig. 1b. This structure could be attributed to an unstable electrospinning jet caused by solvent viscosity and low volatility. Similar result was reported in the study of Leite et al. [14], where DMSO was also used for bagasse lignin solubilization. It was also mentioned that DMSO was the only one among studied solvents (ethanol, methanol and toluene) that could provide adequate lignin concentration for electrospinning. The diameter of carbonized lignin-PAN fiber was 171 nm; and it was denoted as carbon nanofiber (CNF) (Fig. 1c).

3.2 Surface area of bagasse lignin-PAN CNF

Surface area of obtained bagasse lignin-PAN CNF was 414 m²/g. This value was consistent with the usual range of carbon nanofiber previously reported (20–1200 m²/g) [15–17]. From this experiment, addition of bagasse lignin in the structure resulted in a higher surface area compared to PAN alone (346 m²/g). An observed higher surface area could possibly relate to a topological defects and structural disorder of CNF introduced by addition of lignin as described in the work of Jin et al. [18]. Similar observation was also made for carbon fiber derived from bio-based precursors. Its lack of graphitic crystallinity was found to facilitate the generation of internal pores and large specific surface area [19]. The major advantage of nanofiber which is a large surface area to volume ratio has long recognized by industrial utilization such as catalyst support. A recent study demonstrated the use of simplified catalyst support from carbon nanofiber with a stainless steel filter in order to improve reaction efficiency through multiple layered of carbon nanofiber with an embedded metallic catalyst [20]. This could be considered as one of the alternative applications of lignin-CNF.

3.3 Electrical conductivity of bagasse lignin-PAN CNF

Electrical conductivity is one of the main characteristic that used to characterize electrode and electrical energy storage system and devices. It is important to quantify this parameter as a way to elucidate product performance. Recent information summarized by Kumar et al. [21] indicated that electrospun CNF with various unique properties such as lightweight, high surface area and good thermal and electrical conductivity could be potentially used for different non-structural applications for instances energy conversion and storage, sensing and diagnostics and micro/nano electromechanical system. The average electrical conductivity of PAN-CNF and bagasse lignin-PAN CNF were 0.0018 S/cm and 0.0006 S/cm, respectively (Fig. 2). A porous structure of electrospun carbon nanofiber was reported to influence electrical properties of the sample as it increases overall surface area which is the pathway for ion diffusion and absorption. Consequently, it influences navigation of electrical current on nanofiber surface determined by electrical conductivity [22, 23]. However, it was not the case for bagasse lignin-PAN CNF which had a higher surface area than PAN-CNF. The addition of bagasse lignin as 25% replacement of PAN was found to reduce electrical conductivity of CNF by 60% as compared to PAN alone. Though lignin cyclization and electrical properties is not yet fully understood [6], increasing of carbonization temperature of electrospun lignin nanofiber sheet was reported to directly increase electrical properties of the obtained CNF by promoting the order of carbon atom reorganization [24]. This could be an approach for further study to improve bagasse lignin-PAN CNF electrical conductivity.

3.4 Financial feasibility study and market survey

Details of cost for 1 kg of bagasse lignin-PAN CNF production are presented in Table 1. The price of bagasse lignin obtained from lignin extraction at the lab-scale unit according to our non-published results was \$0.22/g solid lignin while the unit price of other materials was that of commercial products.

Total CNF production cost was 12,367.96 \$/kg or 12.4 \$/g. The cost structure at a laboratory scale as presented in Fig. 3 showed that more than 80% of the total was from raw material, with the price of PAN at around 60% of total raw material cost. Due to the much lower unit price of lignin, increasing its proportion in the mixture could significantly decrease CNF production cost. Nevertheless, properties and financial feasibility of CNF

Fig. 2 Electrical conductivity of bagasse lignin-PAN CNF and PAN-CNF compared to a reference graphite **Table 1** Cost structure of 1 kg bagasse lignin-PAN CNF production in a laboratory scale

List	Cost (USD)
Raw material/quantity used	10,203.85
Polyacrylonitrile (PAN) 1.85 kg	7743.93
Dimethylformamide (DMF) 16.62 kg	291.81
Bagasse lignin 0.62 kg	133.94
Dimethylsulfoxide (DMSO) 5.54 kg	173.70
Oxygen gas 43.08 m ³	1447.46
Nitrogen gas 0.86 m ³	413.01
Labour	1736.96
Utility	119.79
Depreciation	110.89
Total	12,171.49

Remarks: Foreign exchange rates as of 22 April 2019 is 31.886 Baht/US Dollar

with lignin mixture must be evaluated to identify a suitable application and cost-effective production for such a market.

A market survey discovered that the CF market is ideal for structural applications where high mechanical strength is required [25, 26]. In Thailand, surveyed information indicated that medium-performance CF is mainly imported and used for the automotive industry and fiberglass replacement. This market has grown steadily during the last 5 years. CNF is less popular for structural application due to high production cost and low product yield [22].

Nevertheless, it received significant attention for energy storage and conversion application due to their electrical conductivity, high surface areas and ability to incorporate catalyst materials [27]. Currently, there are no factories that produce either CF or CNF in Thailand. It was found that commercialization of CF is mainly through the Japanese Joint Venture Company and distributors who import CF or CNF from different producing countries such as Japan, Korea, China or the United States. Total imported CF articles, reported by the Information and Communication Technology Center with the cooperation of the Customs Department of Thailand in 2017 amounted to 126 tons with a value of around \$4.2 million, and 80% of total imports were from Japan. A significant amount of financial investment for production technology and industrial equipment is required by Thai companies and distributors to establish this industry in Thailand.

4 Conclusions

Applications of obtained CNF have not yet been targeted as further research and development of fiber modification is required. Nevertheless, certain properties such as high surface area and conductivity allow bagasse lignin-based composite electrospun nanofiber to be applied without high-temperature treatment such as for heavy metal entrapment and catalyst support. CNF production from bagasse lignin at the laboratory scale indicated the potential to produce low-cost lignin-based CNF. Only

Fig. 3 Structure of CNF production cost from bagasse lignin-PAN mixture in laboratory scale

25% of bagasse lignin replacement in the formulation could reduce total production cost by 16%. In addition, electrospinning was found to be a promising technique for scale up as it is simple, low cost and requires less equipment, with a small carbon footprint. Despite a number of challenges, lignin-incorporated CNF could be an effective approach to increase the overall value of both lignin utilization and the sugar industries.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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