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Separation of Cell Wall Components by Kraft Pulping and their Utilization for Oil Absorption

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In the conventional pulp and papermaking process, lignin in black liquor is mostly burned for energy. It has not been widely used as a functional polymer. To use both cellulose and lignin component, unique kraft cooking conditions were used in bamboo cooking in this study, and acid precipitation was used to extract lignin from the black liquor. Under different pH values, the precipitated lignins were characterized and compared by gel permeation chromatography (GPC), dynamic light scattering (DLS), and Fourier transform infrared spectroscopy (FTIR). Lignin dissolution in acidic conditions was studied. Pulps with high lignin content were used to synthesize oil absorption materials, which were prepared by grafting butyl methacrylate (BMA) onto the cellulose chain. Sodium silicate was used as an initiator, and 1,4-butane dioldimethacrylate (BDDMA) was used as a crosslinker. The structures of grafted copolymers were characterized by FTIR, scanning electron microscopy (SEM), and thermogravimetry (TG). The acid precipitation process was found to be effective and has important implications for the further lignin applications. The grafting reaction between pulps and BMA was successful. The silicone oil absorption capacity of the obtained materials was 15.3 g/g.

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INTRODUCTION

In China, the wastewater produced in pulp and papermaking processes ranks third after the oil chemical industry and metal smelting. Many small paper mills have been closed by the government due to concerns regarding the discharge of wastewater. Black liquor is the main source of pollution in the papermaking industry (Sridach 2010). A large amount of lignin in black liquor is burned for energy, rather than for potential higher-valued applications as a natural aromatic polymer. Using lignin to produce high value-added products has generated widespread interest (Nguyen *et al.* 2012; Baker and Rials 2013). Vander-Klashorst and Strauss (1986) separated alkali lignin from black liquor and developed phenolic resin, which reduces the consumption of petroleum products, produces a good economic benefit, and protects the environment. Kubo *et al.* (1996) modified alkali lignin by acetylation to change the hot melt property of lignin and then applied it in carbon fiber. Since lignins are functional polymers and have the potential for usage in composite materials, it is critical to separate lignin from the cell wall.

Alkali lignins in black liquor have different solubility in different pH, and they

can be recovered by the step-by-step acid precipitation of black liquor (Lourençon *et al.* 2015). This method provides a foundation from which all cell wall components have potential to be utilized effectively.

The spillage of petroleum is another serious pollution problem. In recent years, with the development of the petroleum industry and oil tanker accidents in the sea, there is a growing concern worldwide about the urgent need to control accidental and deliberate oil releases. Absorption materials are popular due to their capacity to collect and remove the oil from the oil spill site (Gao *et al.* 2012). Although the absorption materials are diverse, such kinds of absorption material are favorable, since they are fully biodegradable and have a minimum of adverse effects on the environment (Hubbe *et al.* 2013). Cellulose is one of the most available natural materials with a fascinating structure and properties. Since cellulose is biodegradable, renewable, and biocompatible, its derivatives are used for many applications including the optical films, pharmaceuticals, textiles, foodstuffs, as well as the formation of cellulose composites with synthetic polymers and biopolymers (Khan *et al.* 2016). Its application on absorption materials have been researched by many scholars and researchers (Chen *et al.* 2015; Mulyadi *et al.* 2016).

In this study, the sulfate-acid precipitation method was used to fractionate different molecular weights of lignin by controlling the pH value. In order to ensure better yield of both lignin and cellulose and separate completely, unique cooking conditions were used. The pulps were used to synthesize oil absorption materials, which were prepared by grafting butyl methacrylate (BMA) onto the cellulose chain. All cell wall components were converted into high value-added products effectively.

EXPERIMENTAL

Materials and Chemical Reagents

Bamboo originated from ShaoXing, ZheJiang Province, China. The chemical components of bamboo were as follows: moisture, 7.14%; Klason lignin, 24.4%; acid soluble lignin, 1.28%; cold water extractives, 11.2%; hot water extractives, 12.3%; 1% NaOH extractives, 34.4%; and ash, 1.3%. Bean stalk originated from YanCheng, JiangSu Province, China. Its chemical components were as follows: moisture, 9.84%; Klason lignin, 21.5%; acid soluble lignin, 0.99%; cold water extractives, 8.4%; hot water extractives, 10.2%; 1% NaOH extractives, 27.5%; and ash, 4.1%.

Sodium hydroxide (NaOH), sulphuric acid, butyl methacrylate (BMA), potassium sulfate (KPS), and 1,4-butane dioldimethacrylate (BDDMA) were supplied by Nanjing Chemical Reagent Co., Ltd (Nanjing, China).

Kraft Pulping Conditions

Bean stalk and bamboo chips were oven-dried to determine the moisture content (Sjöström and Alén 1999). Cooking conditions were modified as follows from previously published methods (Sarwar *et al.* 2008). 100 g (oven dried)/pan of bean stalk chips were installed under the solid-liquid ratio of 1:4. 19% sodium oxide dosage was used in the system. The sulfidity degrees for bean stalk and bamboo were 20% and 25% respectively. The cooking temperature and soaking time were 170 °C and 120 min. Under these conditions, the results showed better yield and lower kappa number.

Table 1. The Influence of Four Factors on the Cooking Results (Bamboo)

Sodium oxide dosage (%)	Sulfidity (%)	Cooking temperature (°C)	Soaking time (min)	Yield (%)	Residual alkali (g/L)	Kappa number
19	15	160	90	39.12	8.36	28.43
19	20	165	120	37.03	12.40	27.21
19	25	170	150	41.12	6.32	29.98
17	25	170	120	49.37	4.72	31.58
17	20	165	120	39.42	6.28	34.31
17	25	170	150	39.83	3.52	36.91
15	15	160	120	45.12	2.40	36.18
15	20	165	120	43.73	2.96	37.43
15	25	170	120	50.73	3.10	42.37

Classification and Purification of Black liquor

A certain amount of black liquor was stirred in a beaker, and 10% H_2SO_4 solution was slowly dropped into the mixture until pH was 6. The stirring status was maintained for 4 h at this pH. After waiting for the full reaction, the mixture was centrifuged for 15 min at 4000 rpm, and the precipitate was collected. The supernatant liquid was further neutralized stepwise with 10% H_2SO_4 solution until the pH value reached 5, 4, 3, and 2, and the precipitate was collected (Dong and Liu 2012; Wang and Chen 2013; Santos *et al.* 2014). In addition, with the same amount of black liquor, 10% H_2SO_4 was to neutralize the mixture with stirring until the pH directly fell to 2, the precipitate was collected by centrifugation. The collected lignin fractionations were freeze-dried and vacuum-dried. The samples collected from the above steps were refined by dioxane-acetone-diethyl ether prior to analysis.

Structural Analysis of Lignins

Lignins were analyzed by gel permeation chromatography (GPC) on a PL-GPC50 plus Integrated GPC system (Varian Inc. Company, Palo Alto, CA, USA) equipped with a Waters 2410 RID detector. Sepax Mono-GPC columns (100 Å, 300 Å, 500 Å, 10 mm ID × 300 mm) were connected, and tetrahydrofunan (THF) was used as an eluent (flow rate: 1.0 mL/min). Standard polystyrene beads were used to calibrate the weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity (M_w/M_n).

The chemical structure of lignins was evaluated by Fourier transform infrared spectroscopy (FTIR). The spectra were obtained on an FTIR spectrophotometer (Vertex 80, Bruker Co., Ltd, Saarbrücken, Germany) using a KBr disc containing 3% finely ground samples. The spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans.

Dynamic light scattering (DLS) measurements were performed at 298 K using a Malvern laser light scattering spectrometer (Malvern Instruments Co., Ltd, Malvern, UK) with a scattering angle of 90°. The light source had the power of 35 mW and a wavelength of 659 nm. Data analysis software was provided by the supplier. Before analysis, the solutions were passed through a 0.22 μm filter to remove any dust, and samples were allowed to stand for 12 h before data collection. Each measurement was repeated three times, and the average result was accepted as the final hydrodynamic diameters (D_h) when all the values fluctuated within reasonable experimental errors. All solutions were prepared in distilled water, and the pH of solutions was adjusted by 1 M

NaOH and HCl.

Preparation of Oil Absorption Material

As previously described (Maimaiti *et al.* 2014), the oil absorption material was prepared as follows. A total of 1 g (oven-dried) kraft pulp and 30 g deionized water were placed in a 250-mL four neck flask in an airtight nitrogen environment. After stirring and heating the solution to 75 °C for 5 min, butyl methacrylate and dimethyl 1,4-butanediol acrylate (BMA) were added. After 6 h, 0.025 g potassium persulfate was added; the mixture was filtered and washed with hot water and ethanol. The products were soaked in acetone solutions at room temperature and then washed with deionized water several times. After the suction filter, the products were dried at 60 °C, vacuum-dried, and used as BMA-grafted cellulose products. The properties of these oil absorption materials based on different raw materials were examined. The three raw materials were bagasse, bamboo pulp, and bean stalk pulp, respectively. The chemical composition and fiber length are shown in Tables 2 and 3.

Table 2. Chemical Composition Analysis of Bagasse, Bamboo Pulp and Bean Stalk Pulp

Sample	Moisture (%)	Ash (%)	Cellulose (%)	Holocellulose (%)	Lignin (%)
Bagasse	10.22	3.71	42.31	63.72	21.06
Bamboo pulp	5.26	0.63	76.38	93.41	5.43
Bean stalk pulp	5.61	2.14	79.21	92.16	4.36

Table 3. Average Properties of Bamboo Pulp and Bean Stalk Pulp Fiber

Raw material	Average length / μm	Average width / μm
Bamboo pulp fiber	61	14.0
Bean stalk pulp fiber	79	18.8

Characterization of Oil Absorption Material

Oil absorption capacity was tested as follows. Accurately measured dry oil absorption material in a 200-mesh nylon yarn bag was soaked in silicone oil. It was taken out for weighing after excess oil was removed every hour until the oil absorption capacity was saturated. The ratio of weight difference before and after the oil absorption and initial weight was named oil absorption capacity.

FTIR spectra were obtained on a Bruker VERTEX 80 spectrometer (Saarbrücken, Germany) using KBr discs. The spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans. The morphology was observed by an environmental scanning electron microscope (FEI Quanta 200, Suzhou, China) at 25.00 kV under vacuum. The thermal stability of the oil absorption material was investigated by TG/DTA 6200 (SEIKO Instruments Inc., Shanghai, China). Thermogravimetry (TG) was run at a heating rate of 10 °C/min in nitrogen, with a heating temperature range from 0 to 800 °C.

RESULTS AND DISCUSSION

Acid Precipitation Rules of Lignin Samples

Acid precipitation analysis was carried out on the bamboo and bean stalk black liquors. The fractionated lignin samples under pH value were weighed (Table 4). pH showed a great effect on the dissolution of alkali lignin; the unfractionated (pH was directly acidified to 2) samples had the largest lignin recovery. When the pH was 4, bean stalk alkali lignin was precipitated in great quantities. When the pH was between 4 and 5, bamboo alkali lignin was precipitated in great quantities. At other pH values, both kinds of alkali lignin were difficult to collect.

Table 4. Weight of Precipitated Lignins under Different pH Conditions

pH	6	5	4	3	2	pH directly to 2
Bamboo Lignin (to original lignin, w%)	5.91	17.08	35.03	1.15	0.16	66.41
Bean Stalk Lignin (to original lignin, w%)	1.23	0.75	13.87	0.79	0.14	18.92

Under the alkaline cooking conditions, lignin macromolecules cracked and became soluble in the liquor. At pH 7, lignin did not exist as sodium salt form, and it began to flocculate, possibly due to hydrogen bonding between the phenolic hydroxyl group and the carboxyl group. At pH 6, the solution assumed the suspended state. Most molecules did not settle into the precipitate. With increased acidity (pH 4 and 5), the higher molecular weight lignin precipitated first. With continued reduced pH, small molecules could not precipitate in strong acidic ionization. When the pH was modified to 2 directly, relatively large molecules precipitated, but their solubility was lower than the solubility of small molecules.

Molecular Weight of Lignin Fractionations

After different conditions of acid precipitation and purification, the bamboo alkali lignin and bean stalk alkali lignin were measured by GPC, and the molecular weight data is shown in Tables 2 and 3, respectively. With decreasing pH, both the number average molecular weight and weight average molecular weight became smaller. Thus, during the acid precipitation, molecular lignin was precipitated in turn. The larger molecular weight lignin was precipitated quickly, while smaller molecules precipitated slowly. Therefore, different molecules of lignins can be separated gradually. At the same time, the polydispersity index of both kinds of lignin also showed a decreasing trend, which indicated that the distribution of molecular weight of lignin can be narrowed by this method.

Table 5. Molecular Weight of Bamboo Lignins

pH	6	5	4	3	2	pH directly to 2
M_w	3282	2324	1883	1215	1172	2148
M_n	1240	1199	868	852	815	899
M_w/M_n	2.65	1.94	2.17	1.43	1.44	2.39

Table 6. Molecular Weight of Bean Stalk Lignins

pH	5	4	3	2	pH directly to 2
M_w	5590	3318	2451	1253	1753
M_n	923	1449	1143	798	814
M_w/M_n	6.06	2.29	2.11	1.57	2.13

FTIR Spectra of Lignin Fractionations

The FTIR spectra of bamboo lignins and bean stalk lignins are shown in Figs. 1 and 2. At around 3400 cm^{-1}, the stretching vibration absorption peaks of the hydroxyl were observed; near 1720 cm^{-1}, C=O vibration absorption peaks in acetyl and ester bond were observed.
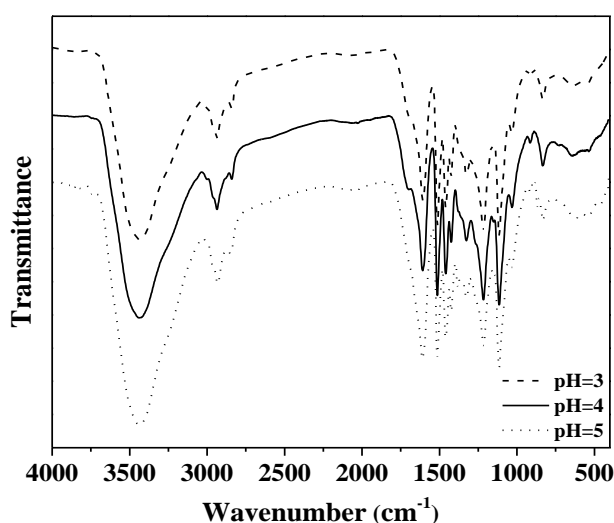
Fig. 1. FTIR spectra of bamboo lignins
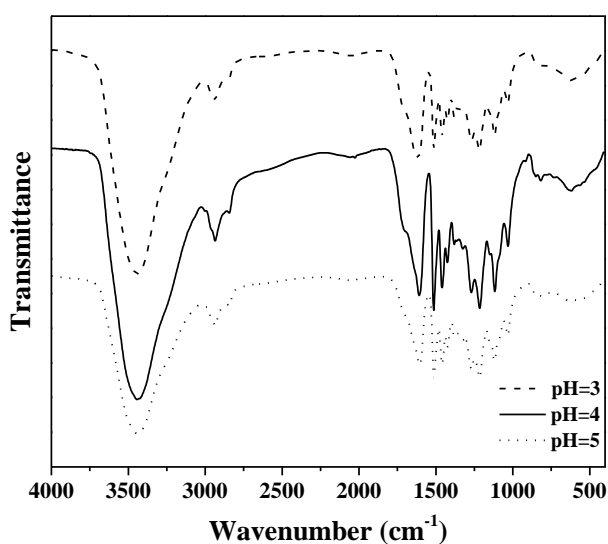
Fig. 2. FTIR spectra of bean stalk lignins

Aromatic ring vibration absorption peaks were shown at 1600 cm^{-1}, 1430 cm^{-1}, and 1510 cm^{-1}. The C-H bending vibration peaks were shown at 1030 cm^{-1}. And the peak at 860 cm^{-1} belonged to the guaiacyl group. However, there was no visible difference between fractionations on the FTIR spectra. This result suggested that there was no difference among the fractionations for lignin skeleton structure and the types of functional groups.

DLS Analysis of Lignin Fractionations

There are many hydroxyl groups in the alkali lignin structure, which causes strong intramolecular and intermolecular hydrogen bonding. Thus, alkali lignin is hardly soluble in water, but it is soluble in dilute alkaline solutions, alkaline or neutral solvents, and mixed solvents (dioxane, DMF, ethanol, acetone, *etc*.). In different solvents, or identical under different concentration and acidity, the ionization activity of hydroxyl and carboxyl functional groups can lead to changes in molecular size and agglomeration.

This study by DLS discussed two kinds of raw materials of alkali lignin (acid precipitated by pH 3, 4, and 5, respectively) in the concentration of 0.1 g/L and pH 8. The changes rules on particle sizes of the lignin molecules were measured, and the results are shown in Figs. 3 and 4.

Under the same concentration and pH, as for bean stalk lignin, the particle size distribution was in dozens to several thousand nanometers. In bamboo lignin, the particle size distribution was from 1000 nm to thousands of nanometers, and they were relatively more concentrated. The average particle size of bean stalk lignin was less than that of bamboo lignin because lignification degree of bean stalk was lower than bamboo due to its shorter growth cycle. At the same time, with the pH value of acid precipitation, the size of alkali lignin decreased gradually, which was consistent with the results that the molecular weight became smaller with decreasing pH. These results showed that the acid precipitation method can effectively fractionate lignins from black liquors. Therefore different molecular weight of lignins can by separated to satisfy the industry requirements through this method.
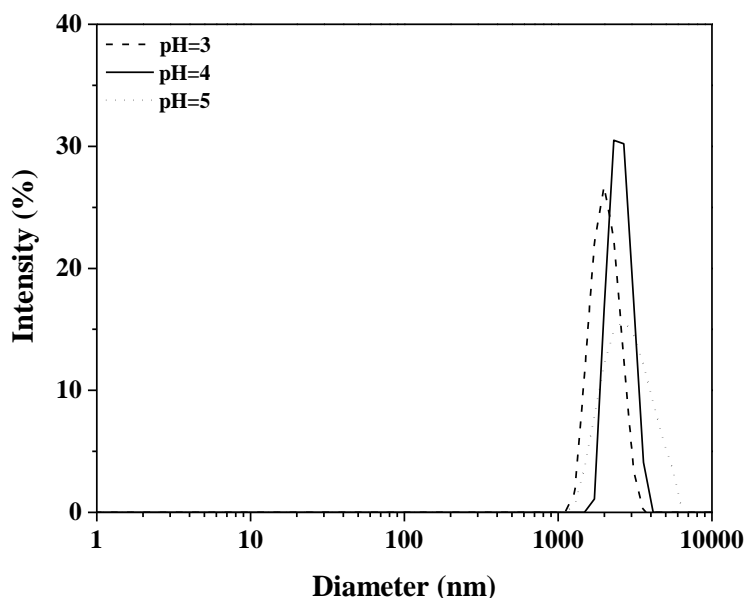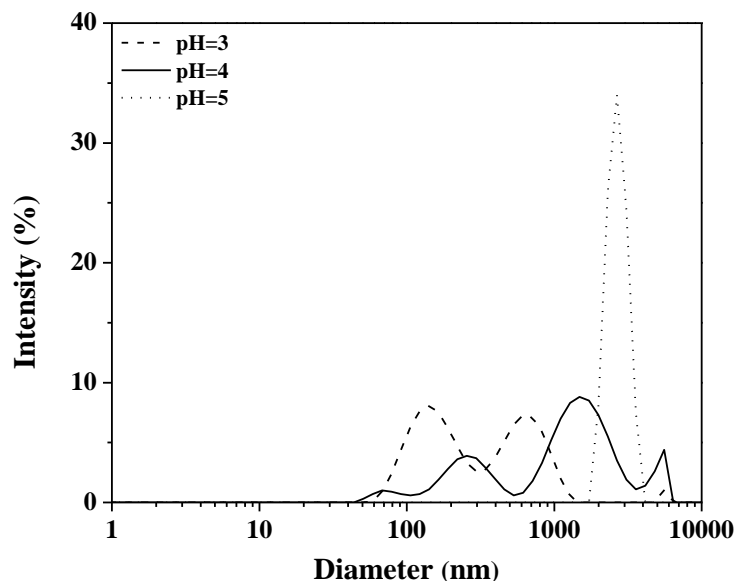

Fig. 3. DLS spectra of bamboo lignins

Fig. 4. DLS spectra of bean stalk lignins

Oil Absorption Capacity of Oil Absorption Material

The oil absorption capacity of raw materials and synthesized materials varied by different raw material, and the results are shown in Fig. 5. The oil absorption capacities of bagasse, bamboo pulp and bean stalk for toluene were about 4.62, 4.51, 5,63 g/g, respectively and for silicone oil the results were about 6.43, 6.12, 7.19 g/g, respectively. As for synthesized materials, BMA grafted bean stalk pulp had the highest oil absorption capacity (11.2 and 13.4 g/g for toluene and silicone oil) which was followed by BMA grafted bamboo pulp (9.3 and 11.4 g/g for toluene and silicone oil) and BMA grafted bagasse (8.2 and 9.2 g/g for toluene and silicone oil). Compared with raw materials, oil absorption capacities of synthesized materials were about twice as much as raw material, higher than coated kapok fiber (Wang *et al*. 2013). And the differences were caused by the fiber shapes of the raw materials.
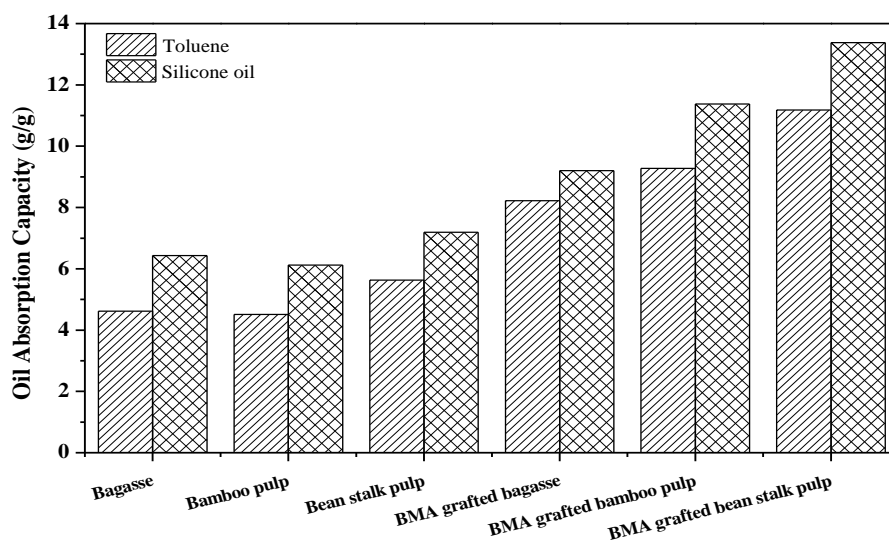
**Fig. 5.** Oil absorption capacity of raw materials and synthesized materials

The relationship between mixture mass ratio and silicone oil absorption capacities of synthesized materials was shown as Fig. 6. The results showed that, when mixture mass ratio of bagasse and bamboo pulp was 0.4:0.6, the oil absorption capacity reached the highest value (15.3 g/g), even higher than pure bean stalk pulp grafted by BMA. Therefore, bagasse mixed with bamboo pulp fiber would improve the surface area of the whole system, which increased the possibility of producing cellulose radicals and finally improved the properties of synthetic materials.
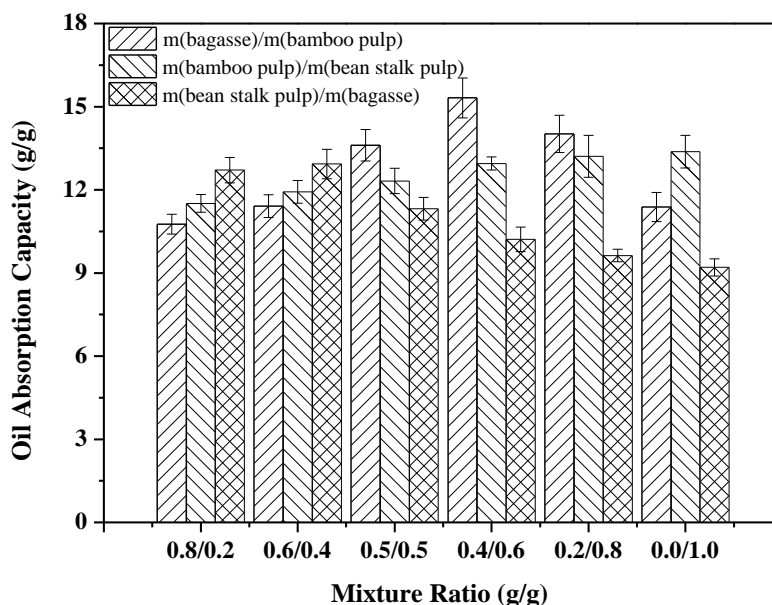
Fig. 6. Relationship between mixture mass ratio and silicone oil absorption capacity of synthesized materials

FTIR Spectra of Oil Absorption Material

The FTIR spectra of bamboo pulp, bean stalk pulp, bagasse, and their corresponding graft copolymers are shown in Figs. 7 through 9.
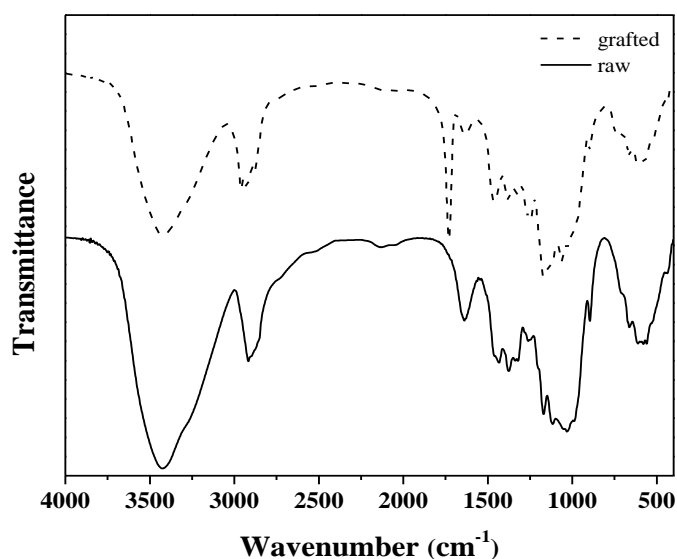
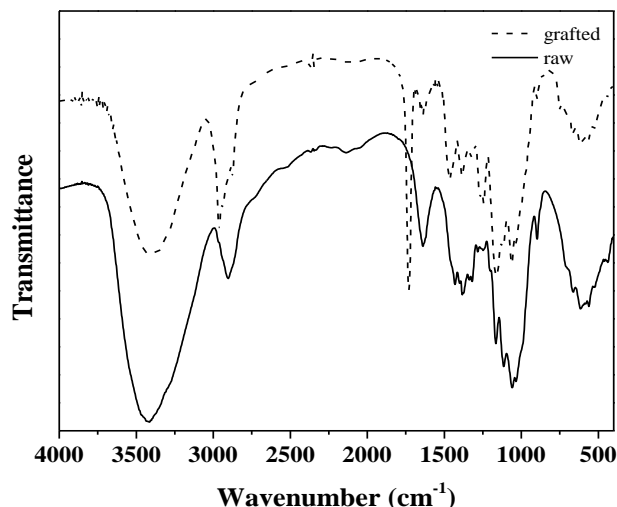**Fig. 7.** FTIR spectra of bamboo pulp and synthesized materials

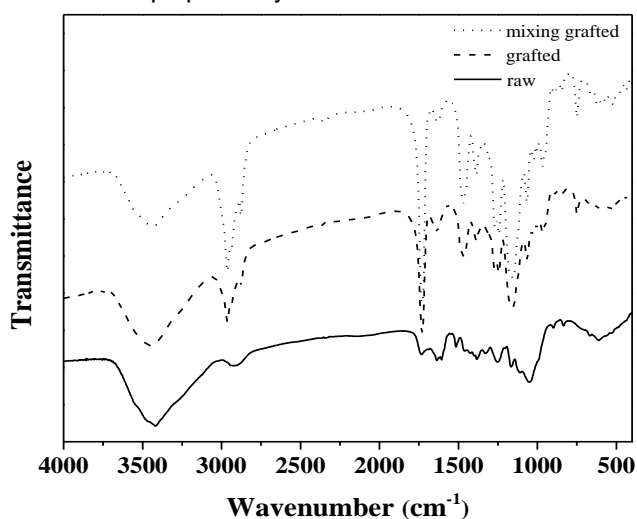**Fig. 8.** FTIR spectra of bean stalk pulp and synthesized materials

Fig. 9. FTIR spectra of bagasse and mixed fiber and synthesized materials

In the grafted pulps, several peaks were observed in addition to cellulose absorption characteristic peaks. For example, the C=O stretching vibration peak and C-O-C stretching vibration peak were observed at 1722 cm^{-1} and 1240 cm^{-1}. The R-O-C-strong absorption peak was detected at 1610 cm^{-1}. The characteristic absorption peak of long chain alkanes was observed at 2959 cm^{-1}, which indicated the existence of ester bonds in long chain alkanes. In contrast with the raw materials, the alcoholic hydroxyl absorption peak in 1030 to 1040 cm^{-1} decreased, and the C-O-C characteristic absorption peak in 1240 cm^{-1} was enhanced. This result indicated that there was a chemical reaction between hydroxyl groups on cellulose and the -C=O on butyl methacrylate, and hydroxy groups on cellulose were replaced by the methyl acrylic acid. Thus, FTIR spectra indicated that the graft modification was successful.

SEM Analysis of Oil Absorption Material

Chemical treatment can make the corresponding changes in the surface of the pulps. The surface morphologies of the raw materials (bamboo pulp, bean stalk pulp, and bagasse) and synthesized materials are shown in Figs. 10 through 12. Before the grafting

reaction, the surface of raw materials was smooth. After grafting by BMA, the product maintained the original fiber structure, but there was a large number of small convex marks, folds, and burrs on the fiber surface. This observation indicated that the butyl methacrylates were grafted successfully on the surface of the pulp, thereby the oil-wet hydrophobic ability was increased. At the same time, the BMA grafted bean stalk pulp products showed the roughest surface. Hence, its oil absorption capacity was the highest among bamboo pulp, bean stalk pulp, and bagasse.
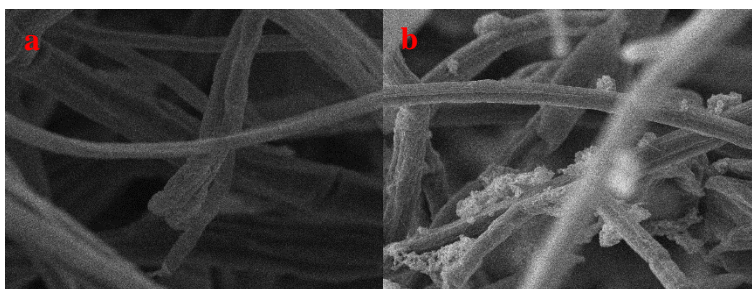
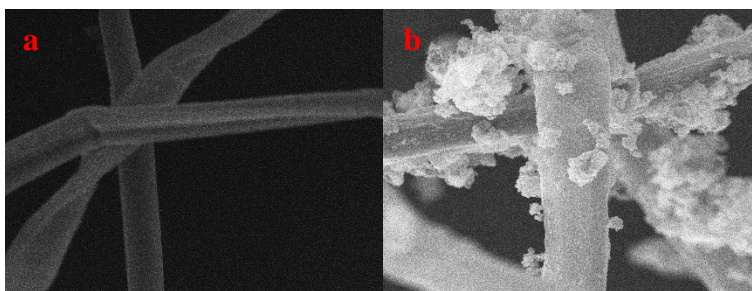**Fig. 10.** SEM photos of bamboo pulp (a) and synthesized material (b)

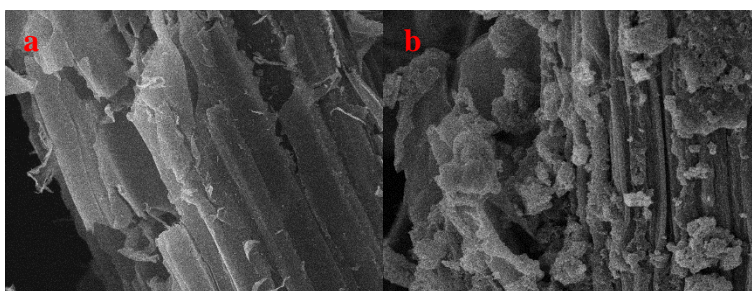**Fig. 11.** SEM photos of bean stalk pulp (a) and synthesized material (b)

Fig. 12. SEM photos of bagasse (a) and synthesized material (b)

TG Analysis of Oil Absorption Materials

The thermal behaviors of bamboo pulp, BMA grafted bamboo pulp, and BMA grafted bamboo pulp-bagasse are shown in Fig. 13. The onset temperature of bamboo pulp was 327.8 °C. After grafted by BMA, the onset temperature decreased to 322.5 °C, and the residual mass value decreased from 15.2% to 14.5%. The mixing grafting product grafted bagasse-bamboo pulp by BMA showed lower onset temperature (319.2 °C) and lower residual mass value (12.4%). The onset temperature was determined by the order state structure of the polymer. These slight differences indicated that the order state structure of cellulose was destroyed by grafting BMA. It implied that the grafting reaction was successful.
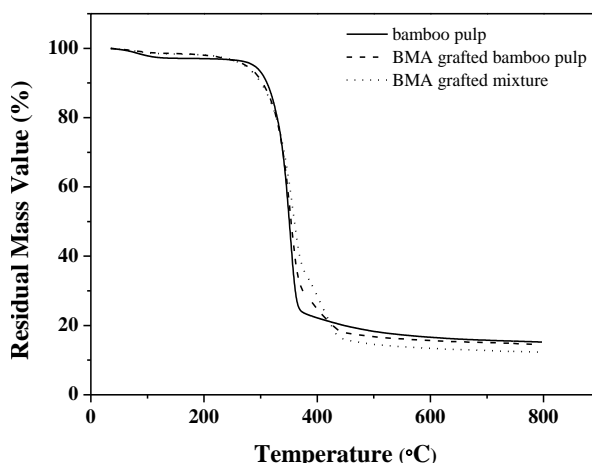
Fig. 13. TG curves of bamboo pulp, BMA grafted bamboo pulp and BMA grafted mixture

CONCLUSIONS

1. The different pH conditions greatly influenced the precipitation of alkali lignin. When the pH was between 4 and 5, bamboo alkali lignin and bean stalk alkali lignin were relatively easily precipitated. High (pH 6) or low (pH 2 and 3) pH changed the particle suspension in solution, which affected the precipitation.

2. The lignin structures of bean stalk and bamboo alkali lignin at all levels did not show obvious structural differences in the FTIR spectra. The DLS detection results showed that the bean stalk alkali lignin is smaller than the average particle size of bamboo alkali. The distribution of molecular weight could be narrowed by fractionation.

3. Both the bamboo pulp and bean stalk pulp were grafted successfully by BMA, and the products could be used as oil absorption materials. For pure raw material, BMA grafted bean stalk pulp showed the highest oil absorption capacity (13.4 g/g). For the mixed grafting, BMA grafted the mixture of bagasse and bamboo pulp showed the highest oil absorption capacity (15.3 g/g), which was higher than BMA grafted bean stalk pulp. The differences on oil absorption capacity of synthesized materials were caused by the fiber shapes of raw materials or the mixture system.

4. SEM analysis showed that the effect of grafting BMA on bean stalk pulp was better than that on bamboo pulp for the relatively longer fiber and rougher surface. TG analysis showed that the grafting reaction was successful.

5. All results indicated that cell wall components can separate completely though cooking and acid precipitation. Both lignin and pulp are applied on other industry site and alleviate the problem of water pollution, which can reduce the input of manpower and material resources.

ACKNOWLEDGMENTS

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