ACS Sustainable Chemistry & Engineering

Research Article

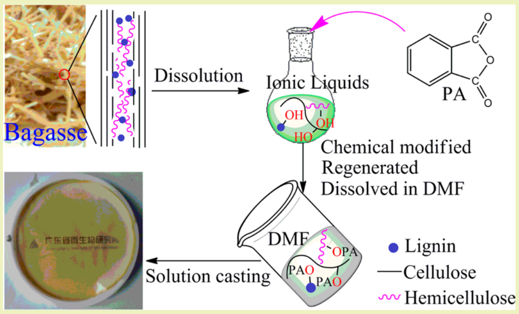
pubs.acs.org/journal/ascecg

Transforming Sugarcane Bagasse into Bioplastics via Homogeneous Modification with Phthalic Anhydride in Ionic Liquid

Ming-Jie Chen and Qing-Shan Shi*

State Key Laboratory of Applied Microbiology Southern China, Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Institute of Microbiology, Guangzhou 510070, China

ABSTRACT: The major challenges for directly converting lignocellulosic biomass into available materials in place of synthetic polymer materials are the complex chemical−physical structure and the narrow processing windows of the resources. In the present study, homogeneous chemical modification of sugarcane bagasse with phthalic anhydride was taken to be an improved strategy to meet the challenges. FT-IR and liquid-state NMR spectra confirmed the chemical structure of the sugarcane bagasse phthalates. Sugarcane bagasse phthalates with weight percentage gain higher than 32.9% were readily dissolved in organic solvents, and film materials were prepared by solution casting from the sugarcane bagasse phthalates. Thermogravimetric analysis and differential scanning calorimetry was applied to study the thermal behaviors of the sugarcane bagasse phthalates. Scanning electron microscope, atomic force microscopy and tensile testing were applied to study the morphologies and mechanical properties of the films. The results indicated that sugarcane bagasse was plasticized by homogeneous chemical modification with phthalic anhydride.



KEYWORDS: *Biomass, Ionic liquid, Bioplastics, Biobased materials, Chemical modification*

■ INTRODUCTION

The concepts of green chemistry and sustainability have been directing the development of chemical and material industries. The growing global environment concern drives researchers to develop energy, chemicals, and materials from renewable resource replacing, or partially replacing traditional ones from petroleum resources.[1]

Polymeric materials, such as polymer films, are of the most important products used in all areas of daily life and worldwide industries.[2] Over the last decades, a great number of scientific efforts were made to design, synthesize, and produce sustainable or green polymers, and the pursuit of green polymer will continue for the next decade.[3] However, these efforts are limited to develop polymer materials from monomers, polysaccharides, and all kinds of isolated fractions derived from biomass.[4] The processes in producing monomers and isolated fractions from biomass always involve in hazardous chemicals, high cost, and complex procedures. It would be more interesting to pursue materials directly from biomass without pretreatment or prior separations to replace synthetic polymer materials for traditional applications.

Lignocellulosic biomass in the form of plant, (such as wood, straw, grass, bagasse etc.) represents the most abundant biomass resource on the earth. Research toward converting lignocellulosic biomass into energies, fuels, and platform chemicals has expanded tremendously in this century.[5] However, because of the complex chemical structure and narrow processing window of lignocellulosic biomass, few studies on directly transforming those resources to materials in replacing of synthetic polymers have been reported.

Ionic liquids (ILs) were found to be excellent green solvents for lignocellulosic biomass and subsequently used for the processes of lignocellulosic biomass.[6,7] Composite fiber and aerogel materials were prepared upon dissolving wood in ILs.[8] Aliphatic wood esters were also synthesized by homogeneous reaction in ILs, and wood plastics composites were synthesized by blending aliphatic wood esters with poly(styrene) and poly(propylene).[9,10] Even though, these efforts suffered from one or more of the following disadvantages: poor performances, no improvement on the processing properties of lignocelllulosic biomass, not fully biobased and biodegradable.[8−10]

Fully biobased film materials directly from sugarcane bagasse without any additives were reported in a previous study.[11] The sugarcane bagasse films showed as high mechanical strength as those of cellulose−starch−lignin composites.[12] However, the sugarcane bagasse films tend to craze due to brittle fracture, and it is difficult to form a continuous film without any cracks unless complicated processes are applied.[11] Novel technologies for preparing film materials with enhanced pliability and processing property directly from sugarcane bagasse are to be developed.

Received: July 14, 2015
Revised: August 13, 2015
Published: August 17, 2015

DOI: 10.1021/acssuschemeng.5b00685
ACS Sustainable Chem. Eng. 2015, 3, 2510−2515

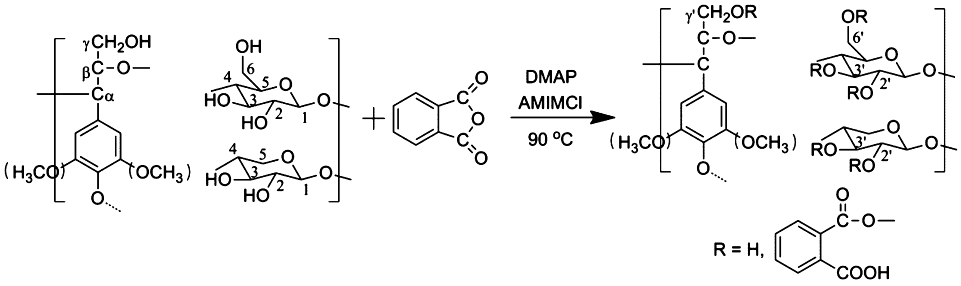


Figure 1. Chemical modification of sugarcane bagasse with PA in AMIMCl.

Chemical modification was shown to be an effective technique to enhance the film forming properties of cellulose and hemicellulose.[13,14] Thermoplastic materials were synthesized by esterified modification of cellulose. The cellulose esters exhibited plasticized behaviors due to the destruction of inter- and intramolecular hydrogen bonding in cellulose.[15] Sugarcane bagasse is a natural composite of lignin, hemicellulose, and cellulose with plenty of hydroxyl groups, which could be substituted by ester groups to enhance the materials properties of sugarcane bagasse. In the present study, homogeneous esterification of sugarcane bagasse with phthalic anhydride using 1-allyl-3-methylimidazium chloride (AMIMCl) as the reaction medium was studied. The chemical structure of modified sugarcane bagasse was confirmed by FT-IR and liquid-state NMR. Fully biobased film materials were prepared from the sugarcane bagasse phthalates. The surface and bulk morphology of the sugarcane bagasse phthalate films was studied by SEM and AFM. The mechanical properties of the films were discussed.

■ EXPERIMENTAL SECTION

Materials. Sugarcane bagasse was obtained from a local factory (Jiangmen, China). It was washed with hot water (80 °C), and dewaxed with toluene–ethanol (2:1, v/v) with Soxhlet extractor for 12 h. The dewaxed sugarcane bagasse was ground and screened to prepare particles of 250–425 μm size, and then ball-milled with a planetary ball miller (Nanjing Chishun Science & Technology Co., Ltd.) for 4 h, and dried in a vacuum oven set at 50 °C for 24 h. Component analysis according to ref 16 for sugarcane bagasse showed that it contained 78.4% carbohydrates and 21.6% lignin.

AMIMCl was purchased from Shanghai Cheng Jie Chemical Co. Ltd., Shanghai, China. Phthalic anhydride (PA), 4-dimethylaminopyridine, and *N*,*N*-dimethylformamine (DMF) were purchased from Aladdin Industrial Inc. Shanghai, China. Ethanol was purchased from Guangzhou Jinhuada Chemical Reagent Co., Ltd. Guangzhou, China. All of the chemicals were analytical-reagent and used as received.

Dissolution of Sugarcane Bagasse in AMIMCl. Ball-milled sugarcane bagasse (1 g) was dispersed in 19 g of AMIMCl under magnetic stirring at room temperature. The mixture of sugarcane bagasse/AMIMCl was stirred at 110 °C for 5 h under the protection of N_2 to guarantee complete dissolution.

Typical Chemical Modification of Sugarcane Bagasse. PA (3 g) and 4-methylaminopyridine (0.15 g, 5/100 w/w to PA) were added to the solution. The resulting mixture was stirred at 90 °C for 90 min under N_2 atmosphere. Isolation was carried out by precipitation of the product into 500 mL of ethanol. The sugarcane bagasse phthalate was obtained after filtration and washing with ethanol, and subsequently vacuum-dried at 50 °C for 24 h.

Preparation of Sugarcane Bagasse Phthalate Film. Sugarcane bagasse phthalate (0.6 g) was dissolved in 10 mL of DMF. The obtained solution was cast onto a polytetrafluoroethene mold and subsequently dried in a cabinet oven with air circulation at 50 °C for 12 h to obtain the sugarcane bagasse phthalate film.

Characterization. The weight percentage gain (WPG) was calculated according to

$$\text{WPG} = (M_1 - M_0)/M_0 \times 100$$

M_0 and M_1 are the vacuum-dried weights of the sugarcane bagasse before and after chemical modification, respectively.

FT-IR spectrum were collected on an FT-IR spectrophotometer (Bruker) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken of each sample recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} in the absorption mode.

The NMR spectra of sugarcane bagasse phthalates were recorded from 40 mg samples in 0.5 mL of DMSO-d_6 on a Bruker Avance III 600 spectrometer (Germany).

The detailed parameters for ^{13}C NMR analysis were: Number of scans, 5800. Receiver gain, 187. Acquisition time, 0.9088 s. Relaxation delay, 1.5 s. Pulse width, 12.0 s. Spectrometer frequency, 150.91 MHz. Spectral width, 36057.7 Hz.

The detailed parameters for HSQC analysis were: Number of scans, 20. Receiver gain, 187. Acquisition time, 0.0852 s. Relaxation delay, 1.5 s. Pulse width, 11.0 s. Spectrometer frequency, 600.17/150.91 MHz. Spectral width, 12 019.2/35 971.2 Hz.

The thermogravimetric analysis (TGA) was performed on a Q500 theromgravimetric analyzer (TA Instruments, USA) in nitrogen atmosphere. Sample weight: 9–10 mg. Heating rate: 10 °C/min. Differential scanning calorimetry (DSC) was conducted on a TA Q500 analyzer (TA Instruments, USA) in nitrogen atmosphere. Sample weight: 4–5 mg. Heating rate: 10 °C/min.

Tensile testing was performed with Instron Universal testing machine 5565 fitted with a 100 N load cell. The samples were cut in the rectangular specimens with a width of 15 mm and length of 70 mm, and five replicate specimens were tested. The initial distance between the grips was 30 mm, and the grips were separated at the rate of 1 mm/min.

For SEM analysis, the films were fixed on a metal stub using carbon tape and coated with gold. LEO 1530VP (LEO, Germany) with an accelerating voltage of 10 kV was used to obtain the secondary electron images.

Atomic force microscopy (AFM) analysis was performed on a Nanoscope IIIa (Digital Instruments Inc., USA) according to previous literature.[17] Scan sizes of 1.5 × 1.5 μm were employed.

■ RESULTS AND DISCUSSION

Chemical Modification of Sugarcane Bagasse. In the efforts to enhance the film properties of sugarcane bagasse, homogeneous chemical modification of sugarcane bagasse with PA in AMIMCl was performed (Figure 1). Previous studies showed that it was an effective way to control the WPG by stoichiometric methods.[18] In the present study, a series of samples varying in WPG were prepared by adjusting the PA/sugarcane bagasse ratio from 1:1 to 5:1 g/g (Table 1). Although the PA/sugarcane bagasse ratio was lower than 3:1 g/g, the homogeneous modification was inefficient with low WPG (lower than 10%), and the modified sugarcane bagasse was not dissoluble in any conventional solvents as unmodified sugar-

DOI: 10.1021/acssuschemeng.5b00685
ACS Sustainable Chem. Eng. 2015, 3, 2510–2515

Table 1. Preparation of Modified Sugarcane Bagasse and Solubility Testing

			solubility[b]			
entry	PA dosage[a] (g/g)	WPG (%)	DMSO	DMF	acetone	$CHCl_3$
PA0	0:1	−2.18	−	−	−	−
PA1	1:1	5.58	−	−	−	−
PA2	2:1	9.08	−	−	−	−
PA3	3:1	32.9	+	+	−	−
PA4	4:1	96.1	+	+	−	−
PA5	5:1	126	+	+	−	−

[a] PA dosage is the mass ratio of PA to sugarcane bagasse. [b] + soluble, − insoluble.

cane bagasse did. The WPG increased dramatically to 32.9%, and further increased to 126%, as the PA/sugarcane bagasse ratio increased to 3:1 g/g, and subsequently to 5:1 g/g, indicating that the WPG values could be controlled by varying the PA/sugarcane bagasse ratio. Excitingly, the modified sugarcane bagasse with WPG higher than 32.9% (including 32.9%) was dissoluble in DMSO and DMF, which made it possible to transform further the modified sugarcane bagasse into novel available materials. The results indicated that PA/sugarcane bagasse ratio should be larger than 3:1 g/g to prepare samples with ideal processing properties.

FT-IR Studies of the Modified Sugarcane Bagasse. The chemical changes of sugarcane bagasse during homogeneous chemical modification were monitored using FT-IR analysis. Peak assignments were according to the literature.[19,20] As shown in Figure 2, the intensity of the O−H bond signal in lignin and polysaccharides at 3420 cm^{-1} reduced with the increase of WPG from 5.58% to 126%, indicating the substitution of O—H group by phthalic group. The peak at 1735 cm^{-1} was associated with the C=O bond of acetyl group from hemicellulose for unmodified sugarcane bagasse. The intensity of the peak at 1735 cm^{-1} increased significantly with the increasing WPG due to the introduction of C=O upon chemical modification. This peak shifted to 1718 cm^{-1} (PA5 with WPG of 126%) gradually due to the introduction of phthalic esters formed between the PA and sugarcane bagasse. The peak at 745 cm^{-1} represents C—H deformation vibration of 1,2-disubstituted benzene (phthalic group), and the band intensity increased with the increasing WPG. Those results from FT-IR studies suggested the successful modification of sugarcane bagasse with PA. The peaks at 1605 and 1515 cm^{-1} are assigned to the vibrations of aromatic skeleton in lignin. The peak at 1375 cm^{-1} is related to C−H deformation in cellulose and C—H_3 deformation of acetyl group in hemicellulose. The peak at 897 cm^{-1} is attributed to C—H deformation of β-glycosidic linkage in cellulose. All of those peaks remained prominent in the modified sugarcane bagasse samples, suggesting the skeleton of sugarcane bagasse fractions was not modified during the homogeneous modification with PA in AMIMCl.

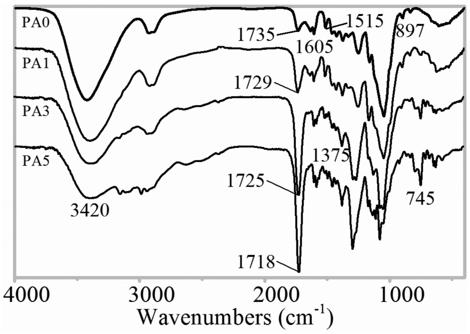


Figure 2. FT-IR spectra of the modified sugarcane bagasse.

Liquid-State NMR Analysis of the Modified Sugarcane Bagasse. To confirm further the chemical structure of the sugarcane bagasse derivatives, the liquid-state NMR spectra of modified sugarcane bagasse were obtained in DMSO-d_6. Signal assignments were according to the literature.[21,22] The carbon signals at 170−168 ppm originated from the carbonyl groups (C=O) in the ^{13}C NMR spectrum. There were three peaks at 169.63, 168.55, and 168.03 ppm (Figure 3), corresponding to acetyl groups ($CH_3\underline{C}OOR$) in hemicellulose, aromatic carboxyl groups (Ar-$\underline{C}$OOH) and aromatic ester (Ar-$\underline{C}$OOR), respectively. The characteristic peaks of aromatic carboxyl groups and aromatic ester suggested the phthalic groups were successfully attached onto sugarcane bagasse through ester bonds. ^{13}C NMR signals at 135.08 ppm were originated from the phthalic group. These results provided further evidence on the successful modification of sugarcane bagasse with PA. Figure 4 is the HSQC spectrum revealing carbohydrate regions of

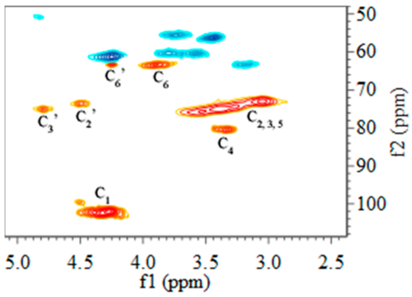


Figure 4. HSQC spectrum of PA5 (WPG = 126%) in DMSO-d_6 revealing carbohydrate regions.

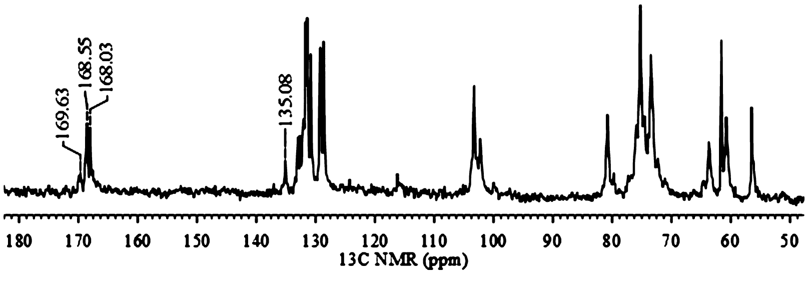


Figure 3. Liquid-state ^{13}C NMR spectrum of PA5 (WPG = 126%) in DMSO-d_6.

PA5. The results suggested that hydroxyl groups of C_2, C_3, and C_6 in carbohydrates took part in the chemical reactions. The hydroxyl groups were partially substituted with phthalic group, as both signals for substituted (C_2', C_3', and C_6') and nonsubstituted (C_2, C_3, and C_6) carbohydrates were presented.

Thermal Analysis of the Modified Sugarcane Bagasse. TGA analysis was performed to study the thermal stability of the modified sugarcane bagasse (Figure 5). The onset of weight loss temperature for the control sample (PA0) was 250 °C, and it decreased to 200 °C for PA1 (WPG = 5.58%) and PA3 (WPG = 32.9%), and further decreased to 175 °C for PA5 (WPG = 126%). The hydrogen bonds that held cellulose, hemicellulose and lignin molecular chains together were broken down upon the chemical modification, due to the substitution of hydroxyl groups by phthalic anhydrides. The decrease of the thermal stability of sugarcane bagasse upon homogeneous chemical modification may be due to the destruction of hydrogen bonding. The weight residues of modified sugarcane bagasse at 700 °C were 23.7%, 28.1, and 22.5% for PA1, PA3, and PA5, respectively, much higher than that of 12.0% for the control sample (PA0). The TGA analysis implied that there were different thermal degradation mechanisms between chemically modified sugarcane bagasse and unmodified sugarcane bagasse due to the substitution of the hydroxyl groups. It is well-known that large amounts of water are produced due to the presence of hydroxyl groups[23] during the thermal degradation of plant materials, which is not the case for chemically modified sugarcane bagasse as the hydroxyl groups are substituted. DSC studies were carried out to determine the glass transition temperatures (T_g) of the modified sugarcane bagasse (Figure 6). The unmodified sample (PA0) and PA1 showed no T_g value in the temperature range of the DSC scans. The T_g value of PA2 (WPG = 9.08%) was at 175 °C, and it decreased to 133 °C as the WPG increased to 126%, suggesting the plasticizing effect of homogeneous chemical modification on sugarcane bagasse.

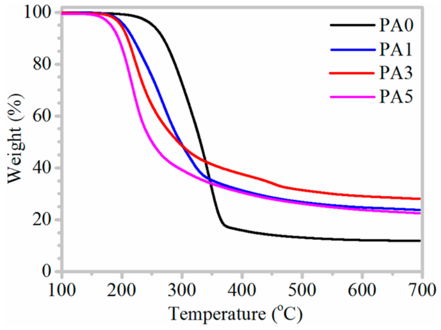


Figure 5. TGA curves of the sugarcane bagasse phthalates.

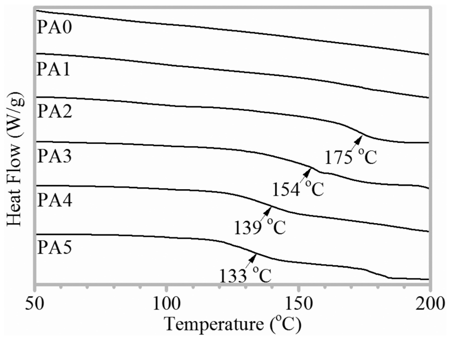


Figure 6. DCS curves of the sugarcane bagasse phthalates revealing the T_g value.

Films Preparation. There are two major challenges in forming film materials directly from lignocellulsic materials, including the insolubility of lignocellulosic biomass and a large amount of nonfilm forming fractions (lignin and hemicellulose). To meet the two challenges, homogeneous esterification of sugarcane bagasse with PA in IL was taken as an improved strategy. The present research showed that sugarcane bagasse phthalates had good solubility in DMF and DMSO, due to the destruction of hydrogen bonding in polysaccharides by homogeneous esterification. Sugarcane bagasse phthalate films were readily prepared without any cracks or collapses upon drying by solution casting using DMF as the solvent, suggesting the efficiency of homogeneous chemical modification to meet the challenges in transforming sugarcane bagasse into bioplastics.

Mechanical Properties of the Films. The mechanical property of film materials is very important in application to prevent films cracking and can be tailored by chemical modification.[24] Tensile test was conducted to determine mechanical properties of the sugarcane bagasse phthalate films (Table 2 and Figure 7). The stress–strain curves of sugarcane bagasse phthalate films displayed a typical semi-crystalline polymer model as those of crude sugarcane bagasse.[11] The tensile strength and young's modulus of PA3 (WPG = 32.9%) were more or less the same as that of crude sugarcane bagasse film prepared by dissolving in DMSO/LiCl and subsequently coagulated with acetone/water.[11] However, the sugarcane bagasse phthalate (PA3 with WPG 32.9%) film showed much lower elongation at break, which may be due to the degradation of sugarcane bagasse fractions during chemical modification[25] and the low degree of substitution of hydroxyl groups. The tensile strength and Young's modulus decrease dramatically with increasing WPG from 32.9% to 126%, while the elongation at break increased from 2.35% to 21.7%. It is suggested that sugarcane bagasse is considerably plasticized by the introduction of phthalic group.

Table 2. Mechanical Properties of the Sugarcane Bagasse Phthalate Films

entry	thickness (μm)	tensile strength (MPa)	elongation at break (%)	Young's modulus (MPa)
PA3	54.7 ± 4.0	30.6 ± 3.6	2.35 ± 0.17	1680 ± 150
PA4	59.6 ± 9.4	7.56 ± 1.06	12.1 ± 1.3	330 ± 28
PA5	58.2 ± 7.6	3.55 ± 0.31	21.7 ± 2.7	51.3 ± 3.7

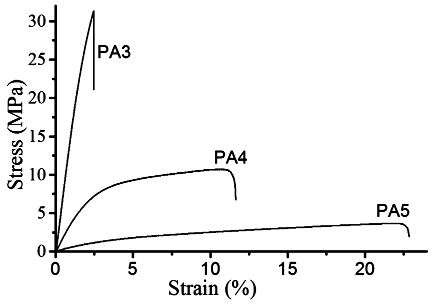


Figure 7. Strain–stress curves of the sugarcane bagasse phthalate films.

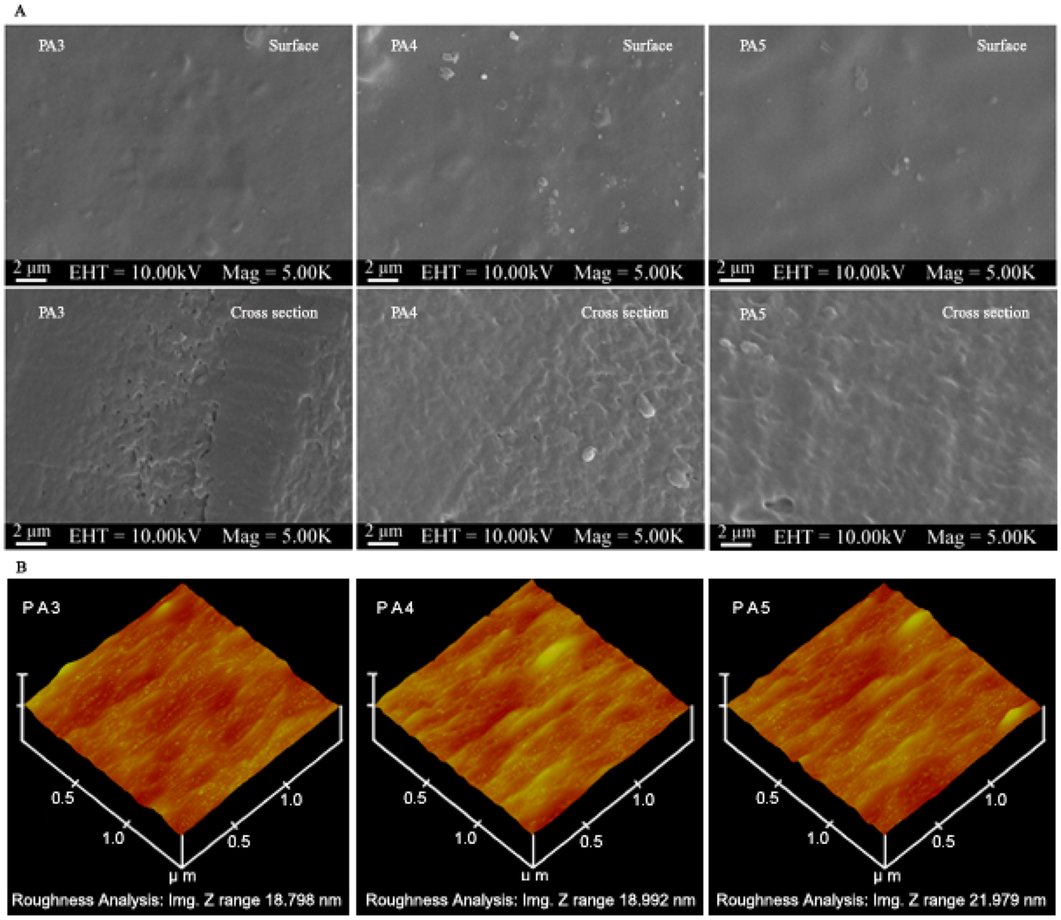


Figure 8. Morphology analysis of the sugarcane bagasse phthalate films. (A) SEM images. (B) AFM images.

Morphology Studies by SEM and AFM. The morphologies of the sugarcane bagasse phthalates films were observed using SEM, and the images are shown in Figure 8A. A homogeneous structure for both the surface and cross sections of the films was observed in the SEM images, which was quite similar to those of crude sugarcane bagasse films.[11] It is suggested that chemical modification with PA does not change the microstructure of sugarcane bagasse films. AFM analysis was performed to further study the morphologies of the sugarcane bagasse phthalates films at nanoscale (Figure 8B). The surface of the films is homogeneous, and shows no relationship to the WPG. The roughness analysis was performed on 1.5 μm × 1.5 μm areas. The roughness values of PA3, PA4, and PA5 were 18.798, 18.992, and 21.979 nm, respectively, which suggested that the morphologies of the sugarcane bagasse phthalates films are independent of WPG.

■ CONCLUSION

Sugarcane bagasse phthalates were successfully prepared using AMIMCl as reaction media. NMR studies suggested that hydroxyl groups of C_2, C_3, and C_6 in polysaccharides were partially substituted by phthalic groups. Sugarcane bagasse phthalates showed good solubility in organic solvents and film materials were prepared by solution casting. The phthalic group serves as the inner plasticizer for sugarcane bagasse. The sugarcane bagasse phthalate films showed a homogeneous architectural structure. However, the tensile strength of sugarcane bagasse phthalate films decreased with increasing WPG, and it would be interesting to develop novel strategies to improve the flexibility of sugarcane bagasse without losing in strength.

■ AUTHOR INFORMATION

Corresponding Author

*Q.-S. Shi. Tel.: +86 20 87137652. E-mail: shiqingshan@hotmail.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Scientific and Technological Project of Guangdong Province (No. 2013B010102016), the Guangdong Natural Science Fund (2014A030313665) and the National Science Foundation of China (21401028).

■ REFERENCES

(1) Pfaltzgraff, L. A.; bruyn, M. D.; Cooper, E. C.; Budarin, V.; Clark, J. H. Food waste biomass: a resource for high-value chemicals. *Green Chem.* **2013**, *15*, 307−314.

(2) Fried, J. R. *Polymer Science and Technology*, second ed.; Chemical Industry Press: Beijing, 2005.

(3) Miller, S. A. Sustainable Polymers: Opportunities for the next decade. *ACS Macro Lett.* **2013**, *2*, 550−554.

(4) Belgacem, M. N., Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*; Elsevier Ltd.: Amsterdam, 2008.

(5) Peng, P.; She, D. Isolation, structural characterization, and potential applications of hemicelluloses from bamboo: A review. *Carbohydr. Polym.* **2014**, *112*, 701−720.

(6) Kilpeläinen, I.; Xie, H.; King, A.; Granstrom, M.; Heikkinen, S.; Argyropoulos, D. S. Dissolution of wood in ionic liquids. *J. Agric. Food Chem.* **2007**, *55*, 9142−9148.

(7) Stark, A. Ionic liquids in the biorefinery: a critical assessment of their potential. *Energy Environ. Sci.* **2011**, *4*, 19−32.

(8) Sun, N.; Li, W.; Stoner, B.; Jiang, X.; Lu, X.; Rogers, R. D. Composite fibers spun directly from solutions of raw lignocellulosic biomass dissolved in ionic liquids. *Green Chem.* **2011**, *13*, 1158−1161.

(9) Xie, H.; King, A.; Kilpelainen, I.; Granstrom, M.; Argyropoulos, D. S. Thorough chemical modification of wood-based lignocellulosic materials in ionic liquids. *Biomacromolecules* **2007**, *8*, 3740−3748.

(10) Xie, H.; Jarvi, P.; Karesoja, M.; King, A.; Kilpelainen, I.; Argyropoulos, D. S. Highly compatible wood thermoplastic composites from lignocellulosic material modified in ionic liquids: Preparation and thermal properties. *J. Appl. Polym. Sci.* **2009**, *111*, 2468−2476.

(11) Chen, M.; Zhang, X.; Liu, C.; Sun, R.; Lu, F. Approach to renewable lignocellulosic biomass film directly from bagasse. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1164−1168.

(12) Wu, R. L.; Wang, X. L.; Li, F.; Li, H. Z.; Wang, Y. Z. Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresour. Technol.* **2009**, *100*, 2569−2574.

(13) Alekhina, M.; Mikkonen, K. S.; Alén, R.; Tenkanen, M.; Sixta, H. Carboxymethylation of alkali extracted xylan for preparation of bio-based packaging films. *Carbohydr. Polym.* **2014**, *100*, 89−96.

(14) Muller, Y.; Tot, I.; Potthast, A.; Rosenau, T.; Zimmermann, R.; Eichhorn, K.-J.; Nitschke, C.; Scherr, G.; Freudenberg, U.; Werner, C. The impact of esterification reactions on physical properties of cellulose thin films. *Soft Matter* **2010**, *6*, 3680−3684.

(15) Crepy, L.; Chaveriat, L.; Banoub, J.; Martin, P.; Joly, N. Synthesis of cellulose fatty esters as plastics-influence of the degree of substitution and the fatty chain length on mechanical properties. *ChemSusChem* **2009**, *2*, 165−170.

(16) Lan, W.; Liu, C.-F.; Sun, R.-C. Fractionation of Bagasse into Cellulose, Hemicelluloses, and Lignin with Ionic Liquid Treatment Followed by Alkaline Extraction. *J. Agric. Food Chem.* **2011**, *59*, 8691−8701.

(17) Orelma, H.; Filpponen, I.; Johansson, L. S.; Laine, J.; Rojas, O. J. Modification of cellulose films by adsorption of CMC and chitosan for controlled attachment of biomolecules. *Biomacromolecules* **2011**, *12*, 4311−4318.

(18) Chen, M.; Chen, C.; Liu, C.; Sun, R. Homogeneous modification of sugarcane bagasse with maleic anhydride in 1-butyl-3-methylimidazolium chloride without any catalysts. *Ind. Crops Prod.* **2013**, *46*, 380−385.

(19) Popescu, C.-M.; Popescu, M.-C.; Vasile, C. Structural analysis of photodegraded lime wood by means of FT-IR and 2D IR correlation spectroscopy. *Int. J. Biol. Macromol.* **2011**, *48*, 667−675.

(20) Hase, Y.; Davanzo, C. U.; Kawai, K.; Sala, O. The vibrational spectra of phthalic anhydride. *J. Mol. Struct.* **1976**, *30*, 37−44.

(21) Lu, F.; Ralph, J. Non-degradative dissolution and acetylation of ball-milled plant cell walls: high-resolution solution-state NMR. *Plant J.* **2003**, *35*, 535−544.

(22) Kim, H.; Ralph, J. A gel-state 2D-NMR method for plant cell wall profiling and analysis: a model study with the amorphous cellulose and xylan from ball-milled cotton linters. *RSC Adv.* **2014**, *4*, 7549−7560.

(23) Meszaros, E.; Jakab, E.; Varhegyi, G.; Szepesvary, P.; Marosvolgyi, B. Comparative study of the thermal behavior of wood and bark of young shoots obtained from an energy plantation. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 317−328.

(24) Fundador, N. G. V.; Enomoto-Rogers, Y.; Takemura, A.; Iwata, T. Syntheses and characterization of xylan esters. *Polymer* **2012**, *53*, 3885−3893.

(25) Köhler, S.; Heinze, T. Efficient synthesis of cellulose furoates in 1-N-butyl-3-methylimidazolium chloride. *Cellulose* **2007**, *14*, 489−495.