

Controlled Allocation of Aromatic/Aliphatic Substituents to Polysaccharides and Lignin in Sugarcane Bagasse via Successive Homogeneous Transesterification Using Ionic Liquid

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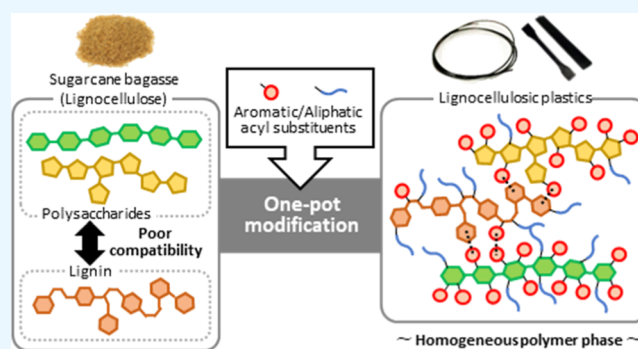
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ABSTRACT: Lignocellulosic agricultural waste is an abundant renewable feedstock that can be utilized as a sustainable source of biomass-based plastics. Ideally, it is used without discarding any components, including cellulose, hemicellulose, and lignin. However, their utilization as lignocellulose-based plastics has been limited because of the low compatibility between the polysaccharides and lignin derivatives and the resulting poor mechanical properties of the final products. Here, we demonstrate a facile but highly controllable conversion of sugarcane bagasse into valuable thermoplastics by utilizing the excellent solubility and unique organocatalytic abilities of an ionic liquid, 1-ethyl-3-methylimidazolium acetate. In a homogeneous and one-pot chemical modification reaction system, the substitution ratio of an aromatic benzoyl group to an aliphatic hexanoyl group in the bagasse derivative was adjusted by the ratio of acyl reagents used. Moreover, the allocation of these two acyl groups to polysaccharide and lignin components in bagasse was successfully controlled only by exchanging the order of the acyl reagents introduced into the reaction system. The controlled introduction of the acyl groups into bagasse achieved a homogeneous polymer phase in the resultant multicomponent hot-pressed film, resulting in enhanced mechanical properties such as sufficient tensile strength (~ 20 MPa) and excellent ductility with a high strain energy density (~ 5 MJ m^{-3}).



1. INTRODUCTION

Lignocellulosic biomass is composed of polysaccharides (cellulose and hemicellulose) and an aromatic polymer (lignin). It has been expected as an abundant renewable feedstock for the production of goods and commodities for our society toward switching off the current fossil-dependent industry. Among many lignocellulose species, agricultural waste such as sugarcane bagasse can be obtained at low cost in large quantities from the sugar and alcohol industries,¹ and has been strongly demanded for its high-value added utilization. However, there are still challenges and technical limitations that must be overcome, particularly on an efficient and sustainable conversion of its major components. Moreover, the technology development for valorization of lignocellulosic waste must follow green chemistry practices toward eco-friendly processes; otherwise, no environmental leverage over traditional petrochemical technologies will be acquired.²

In this context, ionic liquids (ILs) are promising media for lignocellulose processing owing to their excellent solubility^{2–6} and organocatalytic abilities for various chemical modification reactions.^{7–9} Recently, our group has demonstrated direct conversion of bagasse into lignocellulose-based thermoplastics

via homogeneous transesterification using an IL, 1-ethyl-3-methylimidazolium acetate (EmimOAc), as both a solvent and catalyst.^{10,11} Two kinds of vinyl esters were successively added to the homogeneous reaction system, and all the hydroxy (OH) groups in bagasse were substituted with long/short chain-mixed aliphatic acyl groups in the desired ratios. In particular, decanoylated and per-acetylated bagasse exhibited excellent thermal moldability; there was a sufficient gap between the temperatures of thermal decomposition and melt flow, and it was readily applied to hot pressing and injection molding. However, this aliphatic-acylated bagasse was fragile owing to its poor ductility, which has remained an issue in the material design.¹¹

The bagasse derivative is a composite material in which polysaccharide and lignin derivatives are naturally blended. Thus, the brittleness of the aliphatic-acylated bagasse might be

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attributed to the poor compatibility between its constituents,¹² as implied by the “sea-island” internal structure formed in the hot-pressed film (Figure S1). Introducing an aromatic group into the polysaccharide-OH groups can improve the compatibility with lignin,^{13,14} which was preliminary verified by our investigation of decanoylated and per-benzoated bagasse (Figure S2). However, the homogeneous reaction of bagasse concurrently involved the modification of lignin-OH groups with the aromatic substituent, which caused embrittlement of the product (Figure S3), perhaps owing to the excessively enhanced π - π interactions between the lignin derivatives.^{15–17} Thus, we propose a new synthetic strategy for the homogeneous reaction of bagasse, offering preferential modification of polysaccharides with an aromatic acyl group while minimizing the substitution of lignin.

EmimOAc has a unique catalytic ability in transesterification of lignin-OH groups with vinyl esters as acyl donors. In precise, it can catalyze acylation of both aliphatic OH (R-OH) and aromatic OH (Ar-OH) groups and also catalyze selective deacylation of the aromatic moiety.¹⁸ In this dual catalytic system, selective acylation of the R-OH group in lignin while leaving the Ar-OH group intact was achieved by a one-pot process^{19,20} without any requirement for conventional multi-step protection and deprotection processes.²¹ Applying this synthetic strategy to the homogeneous reaction of bagasse, it is predicted that an aromatic acyl group, derived from an initially added vinyl ester, will preferentially substitute the R-OH groups of polysaccharides and lignin. The residual OH groups, including the Ar-OH group of lignin, can be per-acylated with another vinyl ester that is subsequently added to the reaction system. Consequently, these successive reactions in one-pot can control the molar ratio of the two acyl substituents and their allocation to the polysaccharides and lignin in bagasse.

This study demonstrated the direct chemical modification of bagasse with the desired ratio and allocation of aromatic/aliphatic-mixed acyl groups, producing a lignocellulose-based thermoplastic with improved compatibility among its polymeric components and enhanced mechanical properties. First, the reactivities of the R-OH and Ar-OH groups in EmimOAc-catalyzed transesterification with aromatic/aliphatic-type vinyl esters were elucidated using a model reaction system. Then, the allocation of the aromatic/aliphatic-mixed acyl groups to each lignocellulose component was controlled in a one-pot homogeneous transesterification of bagasse using EmimOAc. Furthermore, the effects of the molar ratio and distribution of the two acyl groups on the material properties of the products were investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Sugarcane bagasse was purchased from Sanwa Cellulose Co. Ltd. (Yokkaichi, Japan). It was milled using a grinder mill (Y-308B, Osaka Chemical Co. Ltd., Osaka, Japan) and sifted to sort particles smaller than 250 μ m. The obtained bagasse powder was washed by Soxhlet extraction with dichloromethane (150 mL, purity >99%, Kanto Chemical Co. Inc., Tokyo, Japan) at 60 °C for at least 16 h. The washed bagasse was then dried in a vacuum oven at 70 °C until a constant weight was achieved.

1-Ethyl-3-methylimidazolium acetate (EmimOAc, $\geq 95\%$; initial water content, 0.05 wt %) was obtained from Nippon Nyukazai Co. Ltd. (Tokyo, Japan) and used without further purification. Dimethyl sulfoxide (DMSO, anhydrous, $\geq 99.9\%$) was purchased from Sigma-Aldrich Co. LLC (St. Louis, MO,

USA). Vinyl benzoate (VBz, >99%) and vinyl hexanoate (VHe, >99%) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). DMSO-*d*₆ (99.9 atom % D) containing 0.03 vol % tetramethylsilane (TMS) was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Phenol and 2-phenylethyl alcohol (2-PA) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). The reagents, including EmimOAc, for model experiments using in situ ¹H nuclear magnetic resonance (NMR) were always stored and used in a glovebox. All other chemicals were commercially available and used as received unless otherwise stated.

2.2. One-Pot Two-Step Homogeneous Transesterification of Bagasse. Bagasse was homogeneously substituted with a predetermined molar ratio of two kinds of acyl groups according to the synthetic method described in our previous report.¹¹ First, purified and dried bagasse (6.0 g, 6 wt %/EmimOAc) in EmimOAc (100 g) was vacuum-dried at 80 °C for 24 h. DMSO (150 mL) was then added to the mixture under an Ar atmosphere, and the bagasse was completely dissolved at 110 °C for 16 h. A predetermined amount of vinyl ester (VBz or VHe) was added to the homogeneous reaction solution and reacted at 80 °C for 30 min. An excess amount (3.0 equiv/[OH]) of another vinyl ester (VHe or VBz) was subsequently added and reacted at 80 °C for an additional 30 min. The resulting viscous mixture was poured into distilled water (6 L), and the precipitate was vacuum-filtered and repeatedly washed with distilled water. The obtained bagasse derivative was freeze-dried for 2 d and then vacuum-dried at 80 °C for 24 h. The amounts of the acyl reagents used for the reactions are summarized in Table S1.

2.3. Subsequent Fractionation of Polysaccharide and Lignin Derivatives. To determine the allocation of the two acyl groups on the polysaccharides and lignin in bagasse, each derivative was fractionated from the acylated bagasse according to the separation method described in our previous report.¹⁰ First, 200 mg of the dried acylated bagasse was stirred in methanol (MeOH, 10 mL) at 50 °C for 1 d. The MeOH-insoluble fraction was separated by vacuum filtration and then vacuum-dried at 70 °C for 24 h to yield the polysaccharide derivative. The MeOH filtrate was concentrated by rotary evaporation at 40 °C, and the MeOH-soluble fraction was then vacuum-dried at 70 °C for 24 h to yield the lignin derivative.

2.4. Chemical Structural Analyses. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Scientific Nicolet iS10 spectrophotometer (Thermo Fisher Scientific Inc., Tokyo, Japan) equipped with an attenuated total reflection (ATR) unit. The measured wavenumber range was 4000–400 cm^{-1} , and 64 scans were accumulated per spectrum. A resolution of 4 cm^{-1} was maintained throughout the measurements, and the signal-to-noise ratio was 35 000:1.

¹H NMR spectra were recorded in deuterated solvents on a JNM-ECA 600 spectrometer (JEOL Ltd., Tokyo, Japan) at the Advanced Research Center in Kanazawa University. All NMR spectra were analyzed using Delta NMR (JEOL Ltd., Tokyo, Japan), and the chemical shifts [δ , parts per million (ppm)] were referenced against TMS ($\delta = 0$ ppm) as the internal standard.

Degrees of substitution (DS) with the two acyl groups and residual OH content of the acylated bagasse were estimated by NMR analyses according to a previously reported method.¹¹ First, quantitative ¹H NMR (¹H qNMR) was performed for the acylated bagasse (20.0 mg) using an internal standard of 1,4-bis(trimethylsilyl)benzene-*d*₄ (1,4-BTMSB-*d*₄) at a prede-

terminated concentration (0.40 g L⁻¹) in CDCl₃. The content (mmol g⁻¹) of each acyl group in the acylated bagasse was calculated from the integral ratio of the peak areas corresponding to the 1,4-BTMSB-*d*₄ and acyl group. Next, to quantify the unreacted OH content, quantitative ³¹P NMR (³¹P qNMR) was performed for the per-phosphitylated acylated bagasse using a predetermined concentration of internal standards in accordance with previous studies.^{22–24} Finally, the DS of the acylated bagasse was calculated from the concentration ratio of the two acyl groups and unreacted OH groups.

The molar mass distributions of the polysaccharide and lignin derivatives, prepared in Section 2.3, were determined by size exclusion chromatography (SEC) based on polystyrene standards (Tosoh Co. Ltd., Tokyo, Japan). The SEC measurements were carried out using a Prominence UFLC system with a refractive index detector (Shimadzu Co. Ltd., Kyoto, Japan) at 40 °C using two columns of KF806M (Showa Denko K. K., Tokyo, Japan). 0.01 M LiBr in *N,N*-dimethylformamide (DMF) was used as an eluent at a flow rate of 0.5 mL min⁻¹.

2.5. Thermal Analyses. Thermogravimetric analysis was performed using a DTG-60AH/FC-60A/TA-60 (Shimadzu Co. Ltd., Kyoto, Japan) in the temperature range of 50–500 °C at a heating rate of 10 °C min⁻¹ under a N₂ flow at 50 mL min⁻¹. Prior to these measurements, 10 mg of each sample was dried at 120 °C for 2 h. The thermal decomposition temperature (*T*_d) was considered the onset of significant (≥5%) weight loss (*T*_{d-5%}).

A melt-flow tester (CFT-500EX, Shimadzu Co. Ltd., Kyoto, Japan) was used to evaluate the thermal processability of the acylated bagasse. The dried sample (1 g) was loaded into a barrel and roughly pressed with a piston (diameter: 10 mm). After preheating at 50 °C for 300 s, a constant pressure of 4.9 MPa was applied to the piston at a heating rate of 3 °C min⁻¹. *T*_{flow} was defined as the temperature at which the sample was melted and extruded from the equipped die (diameter: 1.0 mm and length: 10 mm). The temperature at which the piston moved downward by 5 mm through the melt-flowing of each sample was defined as *T*_{offset}.

2.6. Hot Press Molding into Films and Tensile Tests. The acylated bagasse powder was vacuum-dried at 70 °C for 24 h, transferred into a twin-screw micro compounder (DCM Xplore MCS, Xplore Instruments BV, Sittard, The Netherlands), and kneaded for 5 min at 60 rpm. The operating temperature of the extruder was set to a temperature of *T*_{flow} + 10 °C. The kneaded sample was subsequently pelletized to a size of approximately 5 mm. The prepared pellet (2 g) was vacuum-dried for 24 h at 70 °C and subjected to thermal molding into a film using a hot press machine (IMC-180, Imoto Co. Ltd., Kyoto, Japan). The pellet sample was melted at a predetermined temperature of *T*_{flow} + 10 °C for 7 min, and then pressed under a constant pressure of 40 kN for 3 min. The resultant film was cut into a dumbbell shape using a punching machine (IMC-1948, Imoto Co. Ltd., Kyoto, Japan) following JIS K 7139.

The mechanical properties of the acylated bagasse film were investigated by tensile testing using a universal testing machine (AG-SkNX, Shimadzu Co. Ltd., Kyoto, Japan) at a crosshead speed of 5 mm min⁻¹ and an intergrip distance of 58 mm. The tensile test was repeated more than seven times, and the tensile properties were evaluated as the average of at least five tests.

2.7. In Situ ¹H NMR Analysis of Transesterification of Model Compounds. A molar equivalent mixture of 2-PA and phenol was used as a model substrate for lignin containing both R-OH and Ar-OH groups. The reactivity of each OH group in the EmimOAc-catalyzed transesterification with VBz and VHe was investigated by in situ ¹H NMR analysis according to our previously reported method.^{18,19}

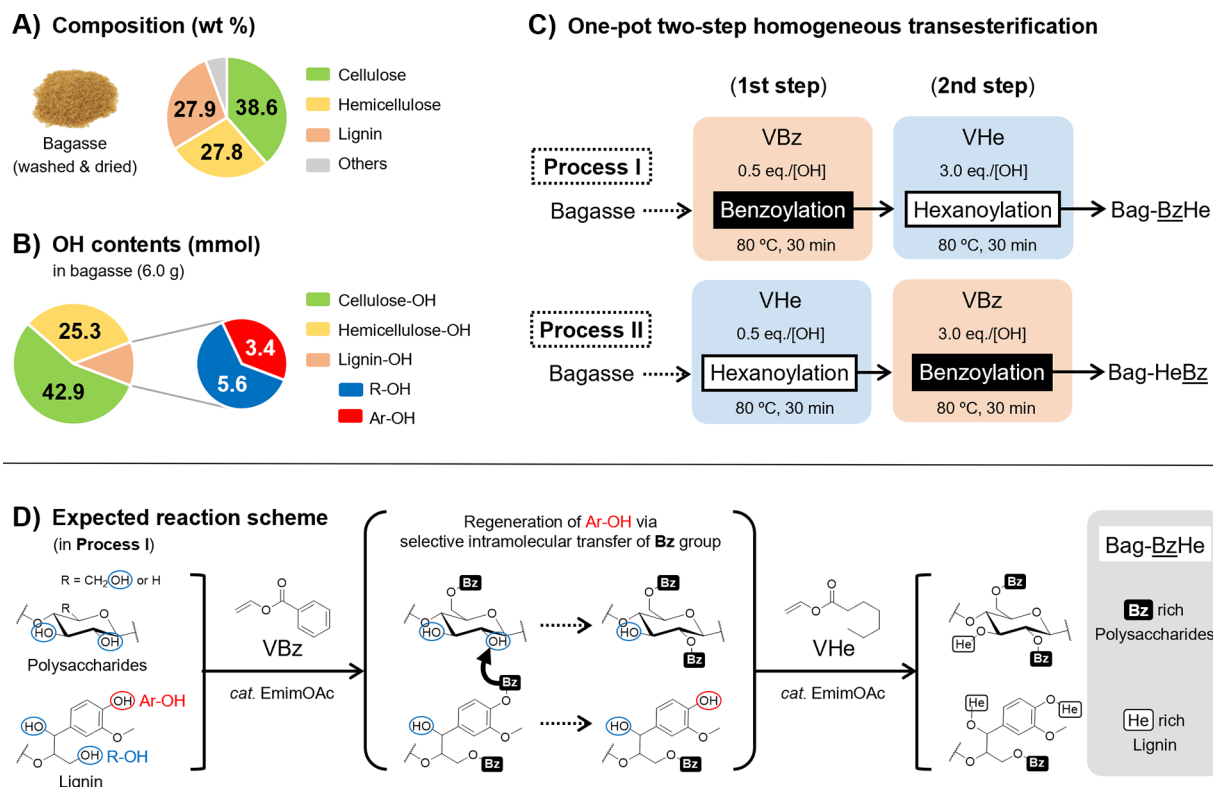
In a glovebox filled with Ar gas and less than 10 ppm of water, dried EmimOAc (108.9 mg, 0.64 mmol), 2-PA (60.2 mg, 0.64 mmol), and phenol (78.2 mg, 0.64 mmol) were weighed into a 9 mL vial and dissolved in DMSO-*d*₆ (1.5 mL). VBz (88.6 μL, 0.64 mmol) or VHe (102.6 μL, 0.64 mmol) was added to the vial and quickly stirred. The ¹H NMR spectrum of the resultant solution was immediately recorded at room temperature (22 °C) over 80 scans; the obtained spectrum was regarded as the reaction time of 0 min. Then, the measurement temperature was increased to 80 °C, and another ¹H NMR spectrum was recorded at 80 °C in 80 scans; the obtained spectrum was regarded as the reaction time of 10 min. The measurement was subsequently repeated until 600 min at 80 °C. The concentration and conversion of each model compound were estimated from the integral ratio of the peak areas derived from the corresponding protons.

3. RESULTS AND DISCUSSION

3.1. Synthetic Strategy of Aromatic/Aliphatic-Mixed Acylated Bagasse. The washed and dried bagasse consisted of 66.4 wt % of polysaccharides and 27.9 wt % of lignin (Scheme 1A).²⁴ The polysaccharides in bagasse consist of cellulose and xylan-based hemicellulose,^{25,26} and their total R-OH content including primary and secondary alcohols was estimated as 68.2 mmol per 6.0 g of bagasse. Meanwhile, the lignin contained approximately 5.6 mmol of R-OH and 3.4 mmol of Ar-OH groups (Scheme 1B), based on our previous report ([R-OH] = 3.32 mmol g⁻¹ and [Ar-OH] = 2.02 mmol g⁻¹).¹⁸ These compositional results indicate that the bagasse is rich in R-OH groups, mainly derived from the polysaccharides.

In our previous studies,^{10,11} the DS of two acyl groups in the bagasse derivative was controlled by a one-pot, two-step homogeneous reaction system using EmimOAc, where the two acyl reagents were successively fed. In precise, the DS of the two acyl groups depended on the amount of the first acyl reagent added, and the residual OH groups were subsequently per-acylated with a second acyl reagent. In this study, it was assumed that by changing the order of addition of the two acyl reagents, allocation of the substituents to polysaccharides and lignin in bagasse could be controlled.

When an aromatic acyl donor (i.e., VBz) is added in the first step, as shown in process I (Scheme 1C), EmimOAc catalyzes the acylation of both R-OH and Ar-OH groups. Subsequently, it also catalyzes selective transesterification of the resultant Ar-OH-substituted benzoyl (Bz) groups with the available proton donors remained in the reaction system.^{18–20} Therefore, the Ar-OH group in lignin can be regenerated via intra- and intermolecular transfer of the Bz group to the residual R-OH groups (Scheme 1D). As a result, the abundant R-OH groups in the polysaccharides should be preferentially benzoylated in the first step. Subsequently, the residual R-OH groups in the resultant Bz-rich polysaccharide derivative and lignin containing the free Ar-OH groups can be per-acylated by the addition of another aliphatic acyl donor (i.e., VHe), resulting in the hexanoyl (He)-rich lignin derivative. In contrast, by changing the order of addition of these vinyl esters, as shown in process

Scheme 1. Schematic Representation of the Synthetic Strategy in This Study^a

^a(A) Composition of washed and dried bagasse; (B) the estimated R-OH and Ar-OH contents of cellulose, hemicellulose, and lignin in 6.0 g of bagasse, based on the hypothesis that the hemicellulose was only composed of xylan;¹¹ (C) two types of procedures with different orders of addition of vinyl esters in the EmimOAc-catalyzed one-pot, two-step transesterification reactions (process I and process II); and (D) expected reaction mechanism in process II for the preferential benzoylation of R-OH groups of polysaccharides in bagasse.

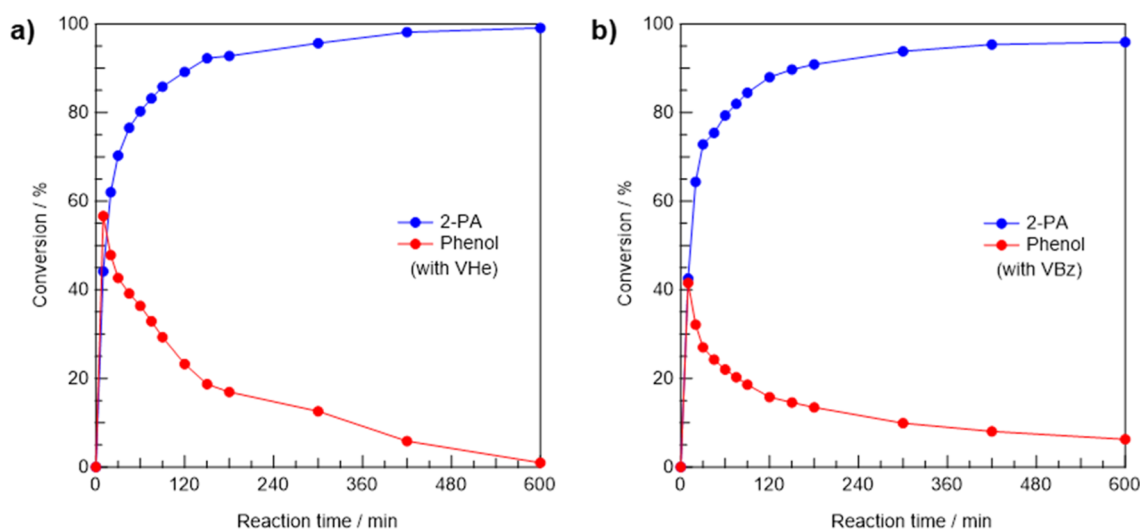


Figure 1. In situ ¹H NMR analysis for successive transesterification reactions of the mixture of phenol (0.64 mmol) and 2-phenylethyl alcohol (2-PA, 0.64 mmol) with a molar equivalent of (a) VHe or (b) VBz (each 0.64 mmol) catalyzed by a molar equivalent of EmimOAc (0.64 mmol) in 1.5 mL of DMSO-*d*₆ at 80 °C for 10 h.

II (Scheme 1C), He-rich polysaccharide and Bz-rich lignin derivatives can be obtained.

In the above synthetic strategy, He group was selected as the aliphatic acyl group in combination with Bz group because the benzoylated and per-hexanoyl bagasse showed superior tensile strength to that of benzoylated and per-decanoylated bagasse in our preliminary study (Figure S4). Although benzoylated

and per-acetylated bagasse was also prepared, the tensile testing was not performed because it could not be thermally molded (Figure S5 and Table S2).

3.2. Verification of Preferential Acylation of R-OH by Model Experiments. The strategy described in Section 3.1 was verified by in situ ¹H NMR analysis of transesterification reactions using a molar equivalent mixture of phenol and 2-PA

as the model substrates for Ar-OH and R-OH groups, respectively. As shown in Figure 1, approximately 60 and 40% of phenol were initially acylated by VHe and VBz, respectively, but almost all the generated phenyl esters were deacylated within 10 h. Meanwhile, 2-PA was gradually acylated, and the conversion reached almost 100% in both cases using VHe and VBz. Since the molarity of VHe and VBz added into each reaction system was equivalent to that of either phenol or 2-PA, it was stoichiometrically demonstrated that the intermolecular transfer of the acyl groups to 2-PA via phenol occurred under the EmimOAc catalysis. These results indicate that the transesterification reactions of (1) vinyl ester and phenol (or 2-PA) and (2) the resultant phenyl ester and 2-PA successively occurred, regardless of the types of vinyl esters used. More importantly, the generated 2-phenylethyl ester is resistant to the EmimOAc-catalyzed deacylation,^{18–20} and thus, the acyl groups are only transferred from the Ar-OH to R-OH groups.

To enable real-time monitoring of the reactions by ¹H NMR, the concentrations of the substrates and EmimOAc catalyst in these model experiments were set to be much lower than those applied in the bagasse reaction. In particular, for the dissolution of bagasse, EmimOAc should be used in excess as the solvent;^{27,28} thus, the acylation and subsequent acyl transfer from Ar-OH to R-OH groups in the bagasse reaction are expected to proceed much faster than in the model reactions (Figure 1).

3.3. Investigation of Controlled Allocation of Bz/He Groups on Polysaccharides and Lignin. First, bagasse was benzoylated with 0.5 equiv/[OH] of VBz and successively peracylated with excess VHe (3.0 equiv/[OH]) to obtain Bag-BzHe. For comparison, Bag-HeBz was prepared in the opposite manner with 0.5 equiv/[OH] of VHe and excess VBz. The polysaccharide and lignin components of each acylated bagasse were further separated as the MeOH-insoluble and MeOH-soluble fractions, respectively. Their molar mass distributions were distinct (Figure 2), and no clear difference was observed between the fractions derived from Bag-BzHe and Bag-HeBz.

The molar ratio of the Bz to He groups in each derivative was estimated by ¹H NMR analysis (Figure 3), and is

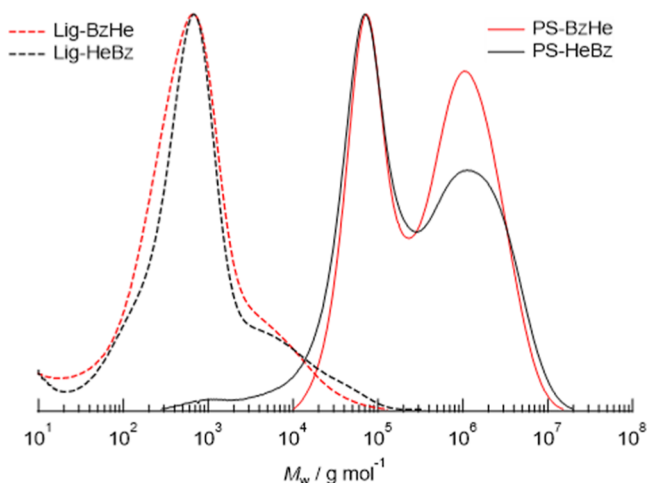


Figure 2. Molar mass distributions of the bagasse-derived polysaccharide (PS-) and lignin (Lig-) derivatives substituted with Bz and He groups, determined by SEC measurements in 0.01 M LiBr/DMF as an eluent using polystyrene standards.

summarized in Table 1. In the spectra of the polysaccharide derivatives (PS-BzHe and PS-HeBz), there were broad chemical shifts derived from protons of the sugar backbone in the range of 3–5.5 ppm^{10,24} and the distinctive signals of the Bz and He groups at 7.2–8.2 and 0.5–2.3 ppm, respectively. Conversely, the spectra of the lignin derivatives (Lig-BzHe and Lig-HeBz) showed a variety of signals due to the many aromatic and aliphatic protons in lignin structures, and their assignments, annotated on the spectra (Figure 3), were predicted based on β -O-4-linked artificial lignin measured in CDCl₃.²⁹ Comparing the spectra of the two lignin derivatives, the signal intensity of the Bz group of Lig-BzHe was lower than that of Lig-HeBz, while the intensity of the multiple signals derived from the He group of Lig-BzHe was greater than that of Lig-HeBz. In particular, the intensity of a signal at 2.2–2.4 ppm, attributed to the proton (*) in the He group substituted on Ar-OH groups, was higher for Lig-BzHe than Lig-HeBz. These results suggest that the benzylation of the Ar-OH groups in lignin was suppressed by the initial addition of VBz to the reaction system, and the degree of per-hexanoylation consequently increased.

As shown in Table 1, the Bz/He ratio of Lig-BzHe was 0.3, whereas that of PS-BzHe was 1.1. In contrast, Lig-HeBz showed a much higher Bz/He ratio (1.9) than Lig-BzHe, suggesting that the acyl group derived from the vinyl ester added in the second step predominantly reacted at the lignin-OH groups. In contrast, PS-HeBz showed a slightly lower Bz/He ratio of 0.9 than PS-BzHe, and thus, the allocation of the two acyl groups on the polysaccharides was found to be hardly affected by the addition order of the vinyl esters. This might be owing to the much larger R-OH content of the polysaccharides, compared to the total OH content of lignin.

3.4. Effects of Allocation and DS Ratio of Bz/He Groups on Thermal and Mechanical Properties. As discussed in Sections 3.2 and 3.3, the benzylation of the lignin-OH groups in bagasse was moderately suppressed by the initial addition of VBz into the reaction system. Then, several kinds of Bag-BzHe with different DS ratios of Bz/He groups were prepared by changing the amount of VBz added. The chemical structures of the Bag-BzHe series and Bag-HeBz as a reference were confirmed by ATR-mode FT-IR and ¹H qNMR (Figures S6 and S7), and the DS of the Bz/He groups and the residual OH content were determined using ³¹P qNMR analysis after per-phosphitylation of the acylated bagasse (Figure S8). As summarized in Table 2, all the acylated bagasse contained less than 5% unreacted OH groups. The DS of the Bz group varied from 5 to 48, while that of the He group ranged from 94 to 51. In each abbreviation for the acylated bagasse, Bag-R1R2(X), the number X in the parentheses corresponds to the DS (mol %) of the acyl group of R2, introduced in the second step.

The effects of the allocation and DS ratio of Bz/He groups on the thermal processability of the acylated bagasse were investigated by TG and melt-flow measurements (Figure 4). The Bag-BzHe series and Bag-HeBz exhibited similar TG curves, and the $T_{d-5\%}$ was in the range of 234–251 °C, suggesting that the thermal stability might not depend on the Bz/He ratio and their allocation. Although any clear correlation with the different Bz/He ratios was not observed for both T_{flow} and T_{offset} , the Bag-BzHe series was found to start melt-flowing at a much lower temperatures range of 122–143 °C than those for Bag-DeAc series and Bag-BzAc(71) (Figure S5). In precise, the thermal processability of thermoplastics can

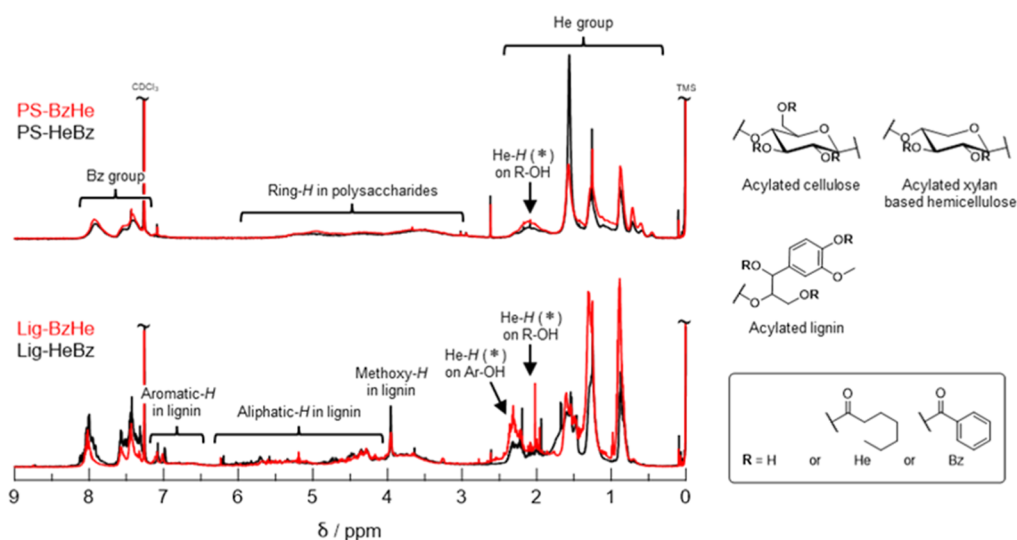


Figure 3. ^1H NMR spectra of the bagasse-derived polysaccharide and lignin derivatives substituted with Bz and He groups, which were fractionated from Bag-BzHe and Bag-HeBz. The concentration of the product in CDCl_3 used for the measurements was consistent with the displayed scale of the obtained spectra.

Table 1. Molar Ratios of Bz/He Groups in the Polysaccharide and Lignin Derivatives Fractionated from Bag-BzHe and Bag-HeBz

entry	origin	fraction	Bz/He ratio
PS-BzHe	Bag-BzHe	MeOH-insoluble	1.1
Lig-BzHe		MeOH-soluble	0.3
PS-HeBz	Bag-HeBz	MeOH-insoluble	0.9
Lig-HeBz		MeOH-soluble	1.9

Table 2. Thermal Properties of Bagasse Derivatives with Different DS Ratios of Bz/He Groups

entry	DS/mol %			thermal property/ $^{\circ}\text{C}$			
	Bz	He	OH	$T_{\text{d-5\%}}$	T_{flow}	T_{offset}	$\frac{\Delta T_{\text{d-5\%}}}{T_{\text{flow}}}$
Bag-HeBz(53)	53	42	5	251	136	173	115
Bag-BzHe(51)	48	51	1	234	122	157	112
Bag-BzHe(74)	22	74	4	250	143	181	107
Bag-BzHe(82)	14	82	4	242	133	179	109
Bag-BzHe(90)	9	90	1	239	126	164	113
Bag-BzHe(94)	5	94	1	234	138	182	96

be evaluated from the gap between the decomposition temperature and melting/thermal-flowing temperature.^{30,31} For instance, cellulose, featuring an intensive hydrogen-bonded structure, has a much higher melting temperature than its decomposition temperature, resulting in its significantly poor thermal processability. Similarly, lignocellulosic biomass, including bagasse, cannot be melted and is not suitable for thermal molding. However, the Bag-BzHe series can be considered to have excellent thermal processability because there is a sufficient gap over 100 $^{\circ}\text{C}$ between their $T_{\text{d-5\%}}$ and T_{flow} (Table 2).

The hot-pressed films of Bag-BzHe series and Bag-HeBz(53) were subjected to tensile testing (Figure 5). Bag-HeBz(53) containing the Bz-rich lignin derivative, as demonstrated in Section 3.3, showed the highest tensile strength (20 MPa) and elastic modulus (1.4 GPa) but the lowest elongation at break of only 2% that resulted in its poor strain energy density (0.17 MJ m^{-3}). The rigid and brittle properties of the Bag-HeBz(53)

might be attributed to the enhanced π - π interactions between the benzoated lignin moieties.^{16,32,33} On the other hand, Bag-BzHe(51) showed a comparably high tensile strength (18 MPa) and a 5-fold higher elongation at break (10%), which contributed to a 10 times higher strain energy density (1.6 MJ m^{-3}) than that of Bag-HeBz(53). This drastic improvement in ductility of the acylated bagasse should result from our synthetic strategy that appropriately suppresses the benzylation of lignin, while polysaccharides are sufficiently benzyolated.

With increasing the DS of the flexible He group,^{34,35} the elongation at break of the Bag-BzHe series was further increased to 60%, and Bag-BzHe(90) showed the highest strain energy density of 4.8 MJ m^{-3} , which is 3 times higher than that of Bag-BzHe(51) and 28 times higher than that of Bag-HeBz(53). These results indicate that the mechanical properties of the acylated bagasse can be controlled by adjusting the molar ratio and also the allocation of the aromatic/aliphatic-mixed acyl groups. Although the tensile strengths of the Bag-BzHe series were inferior to those of the previously reported bagasse benzoate,³⁶ the ductility of the Bag-BzHe series exceeds that of the bagasse benzoate because of its poor elongation at break ($\sim 2\%$). Moreover, the stiffness of the bagasse benzoate can be attributed to the relatively abundant residual OH groups and the resulting hydrogen bonding.³⁷ Hence, the OH content in the Bag-BzHe series should be further considered as an important factor for the material design to improve their tensile strengths. Using other thermal molding processes, such as melt spinning,^{38,39} can also be effective for the Bag-BzHe series, which may lead to highly orientated polymer chains by exploiting their excellent melt-flow characteristics.

4. CONCLUSIONS

To improve the compatibility of polysaccharides (cellulose and hemicellulose) and lignin, bagasse was successively modified with aromatic and aliphatic acyl groups in the desired ratio and allocation. The combination of the acylsubstituents was optimized as benzoyl (Bz) and hexanoyl (He) groups through our systematic investigation (see the Supporting Information).

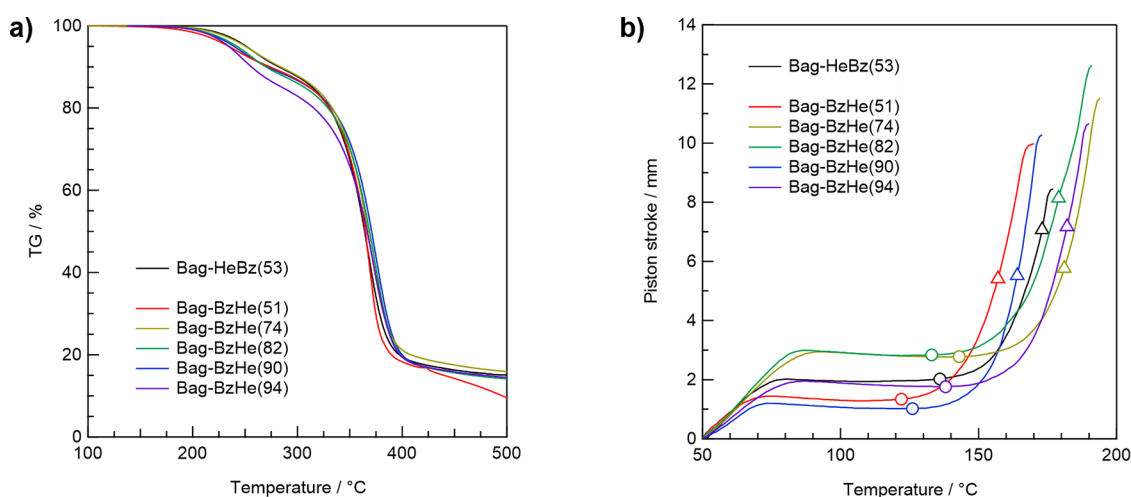


Figure 4. (a) TG and (b) melt-flow curves of Bag-BzHe series and Bag-HeBz. In the melt-flow curves, the symbol \circ indicates the T_{flow} , while the symbol \triangle indicates the T_{offset} .

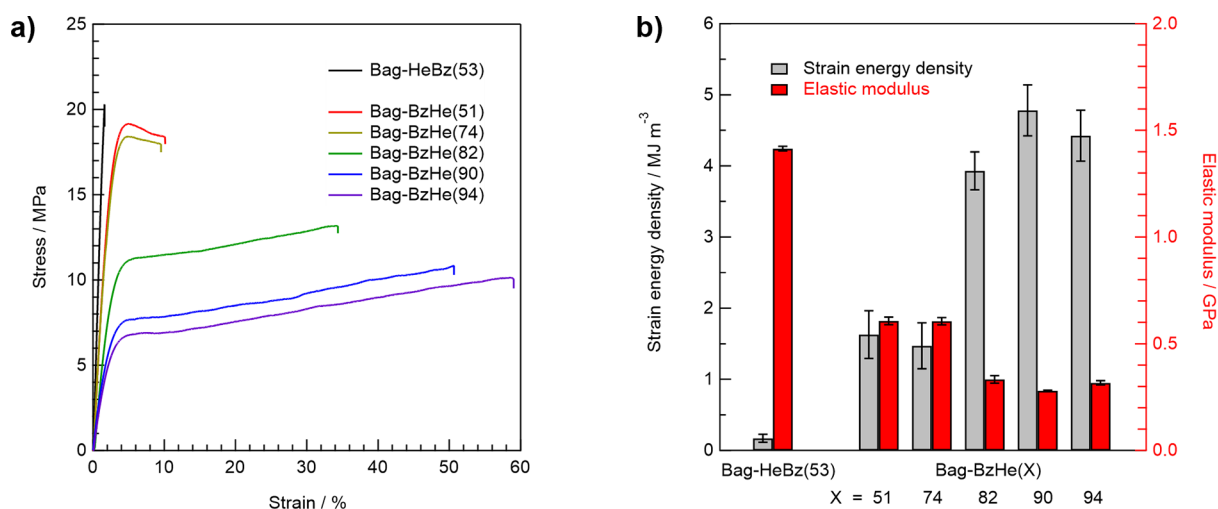


Figure 5. (a) Stress–strain curves obtained in tensile testing of the hot-pressed films of Bag-BzHe series and Bag-HeBz(53) and (b) the average strain energy density and elastic modulus.

Consequently, the undesired phase separation in the internal structure of the only aliphatic-acylated bagasse film was successfully prevented owing to the enhanced π -electron interactions between the partially benzyolated polysaccharide and lignin derivatives in Bag-HeBz. However, excessive benzyolation of the lignin led to the brittleness of Bag-HeBz. Thus, the polysaccharides in bagasse were preferentially benzyolated, while lignin benzyolation was moderately suppressed by exploiting the unique catalytic ability of EmimOAc, followed by hexanoylation of the residual OH groups in one-pot. By controlling the allocation and DS ratio of the Bz/He groups, the acylated bagasse films exhibited the improved tensile strength (~ 20 MPa) and/or excellent ductility, as indicated by their high strain energy density (~ 5 MJ m^{-3}). It should be noted that this is the first one-pot reaction system for lignocellulose that can control the DS of the two acyl groups and their allocation to each polymeric component. This progress, including the elucidation of the effects of aromatic/aliphatic-mixed acyl groups on the material properties of acylated bagasse, provides a valuable synthetic methodology, enabling more advanced material designs for lignocellulose-based thermoplastics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c00369>.

Synthetic conditions, DS, and residual OH content for all the acylated bagasse; FT-IR and NMR spectra for Bag-HeBz and Bag-BzHe series; SEM images; and tensile and thermal properties of hot-pressed films of the acylated bagasse samples (PDF)

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Author Contributions

The manuscript was written with the contributions of all authors. All authors approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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