

Electronic Supplementary Information (ESI)

Rheological characteristics of novel cellulose/superbase-derived ionic liquid solutions and coagulation process towards regenerated cellulose films

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Keywords: *Superbase-derived ionic liquids; Cellulose solution; Rheological behavior;*

Regeneration mechanism; Regenerated cellulose materials

Results and discussion

Thermal stability of [DBUH][CH₃CH₂OCH₂COO]

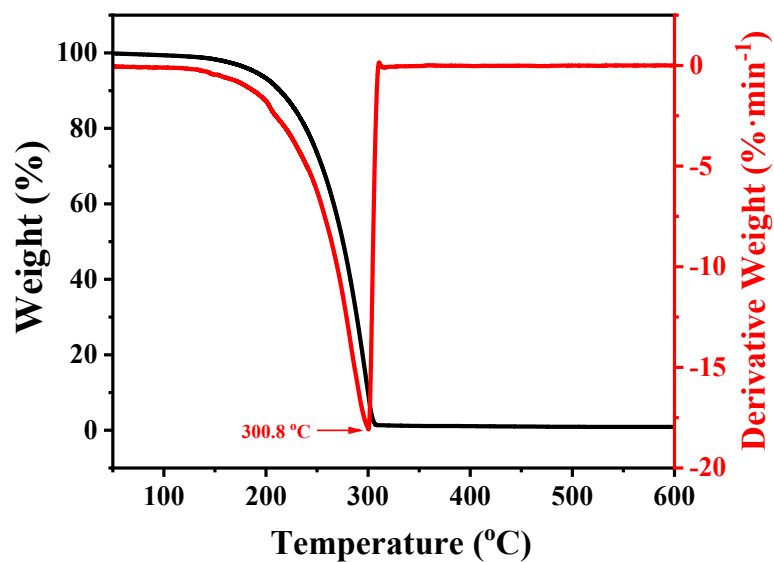


Fig. S1 TGA and DTG curves of [DBUH][CH₃CH₂OCH₂COO]

Images obtained by polarizing microscope

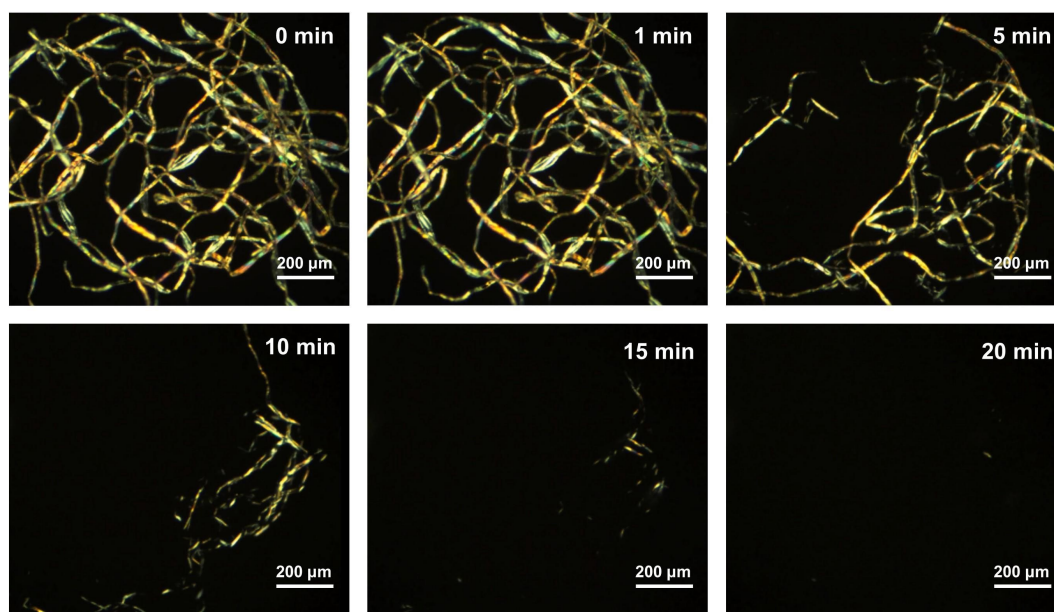


Fig. S2 Polarized light microscopy images displaying the dissolution of pulp fibres in [DBUH][CH₃CH₂OCH₂COO] at 80 °C.

NMR analysis on molecular interactions of cellobiose with [DBUH][CH₃CH₂OCH₂COO]

The [DBUH][CH₃CH₂OCH₂COO]/cellobiose/DMSO-d₆ was utilized to ¹³C NMR analysis. The comparative ¹³C NMR results of pure solvent and cellobiose solution are shown in **Fig. S3** with corresponding schematic structures. The chemical shifts obtained from ¹³C NMR spectra are summarized in **Table S1**. The ¹H NMR spectra of cellobiose, pure solvent and cellobiose solution are presented in **Fig. S4-S6**, respectively. The chemical shifts assigned to the carbons in [DBUH][CH₃CH₂OCH₂COO] were changed with the addition of cellobiose, indicating the changes in the chemical environment of [DBUH][CH₃CH₂OCH₂COO] and implying the interaction between [DBUH][CH₃CH₂OCH₂COO] and cellobiose. In the ¹³C NMR study, significant changes in the signals of C₂, C₆, C₇, C₉ and C₁₁ atoms in [DBUH]⁺ were observed, which was ascribed to the strong hydrogen-bonding interaction between [DBUH]⁺ and the oxygen atoms in cellobiose. Meanwhile, the results implied that the protonated [DBUH]⁺ acted as a hydrogen bond donor in the system. It is well known that carboxylate anion is a hydrogen bond acceptor. The signals of C₁₂ in the system moved downfield from 172.90 to 173.49 ppm with the addition of cellobiose, corresponding to the decreased electron cloud density around C₁₂. This result indicated the hydrogen-bonding interaction between the O atoms on carboxylate groups in [CH₃CH₂OCH₂COO]⁻ and H atoms on -OH groups in cellobiose. Particularly, the chemical shift assigned to the C atom (C₁₄) moved from 64.68 to 64.83 ppm, implying that the ethoxy group also acted as a hydrogen bond acceptor to interact with cellobiose.

Conversely, the above interactions weakened the electron-withdrawing ability of carboxy and ethoxy groups to $-\text{CH}_2-$ in $[\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]^-$, resulting in the up-field shift of the C_{13} atom from 70.58 to 70.42 ppm in ^{13}C NMR signals.

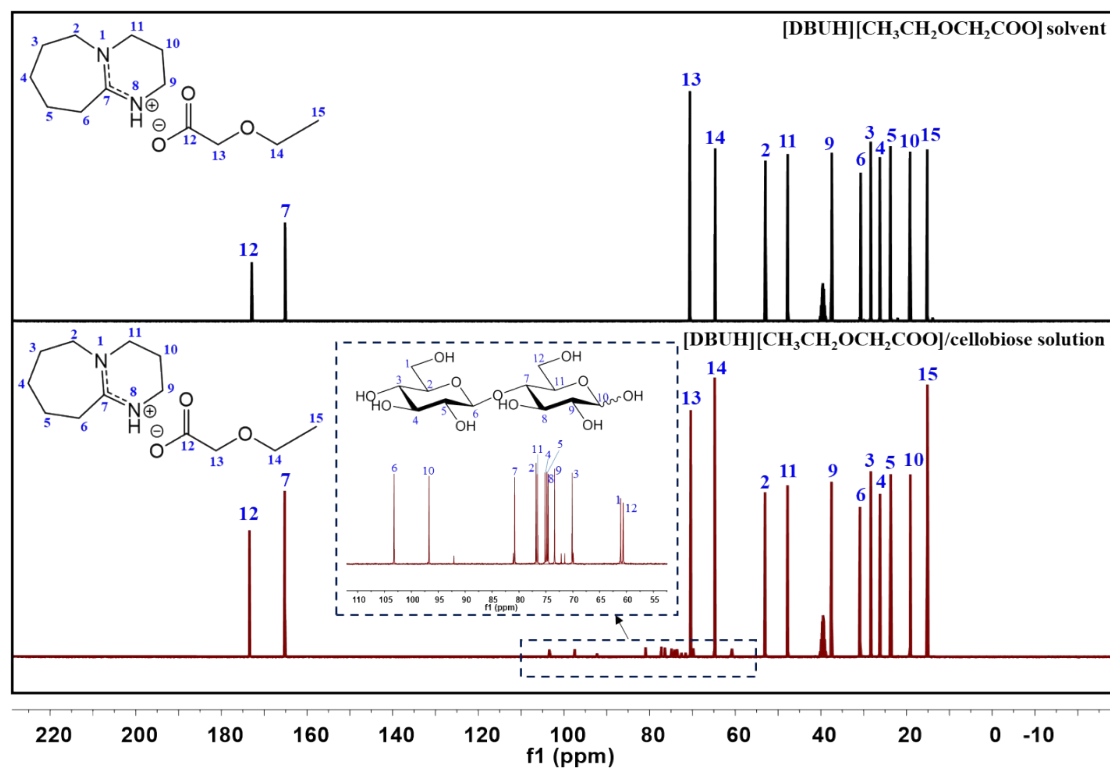


Fig. S3 Comparison of the ^{13}C NMR spectra of $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ and cellobiose/ $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ solution.

Table S1 ^{13}C NMR chemical shifts of $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ and cellobiose/ $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ solution

Atomic number	Pure solvent chemical shifts f1/ppm	Cellobiose solution chemical shifts f1/ppm	$\Delta\text{f1/ppm}$
12	172.90	173.49	-0.59
7	165.15	165.23	-0.08
13	70.58	70.42	0.16
14	64.68	64.83	-0.15
2	52.94	53.07	-0.13
11	47.74	47.81	-0.07

9	37.46	37.54	-0.08
6	30.70	30.90	-0.2
3	28.36	28.36	0
4	26.24	26.21	0
5	23.75	23.72	0.03
10	19.17	19.15	0
15	15.16	15.15	0.01

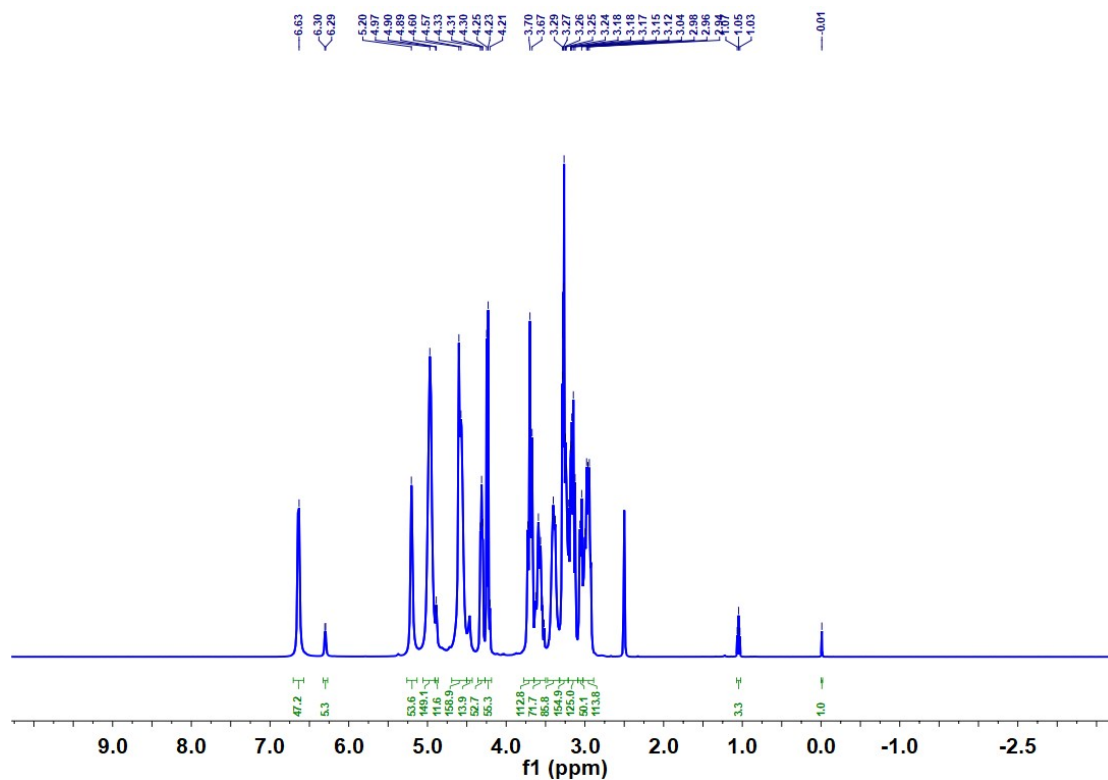


Fig. S4 ^1H NMR chemical shifts of cellobiose, DMSO-d_6 as external reference.

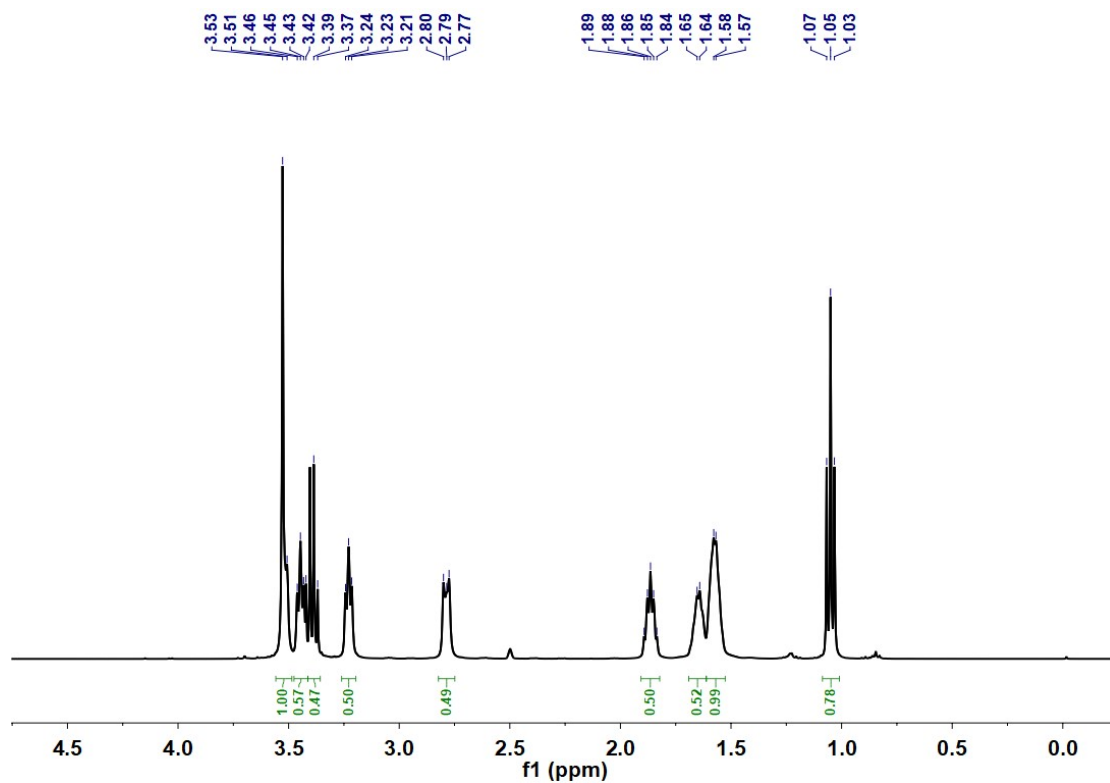


Fig. S5 ^1H NMR chemical shifts of $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ solvent, DMSO-d_6 as external reference.

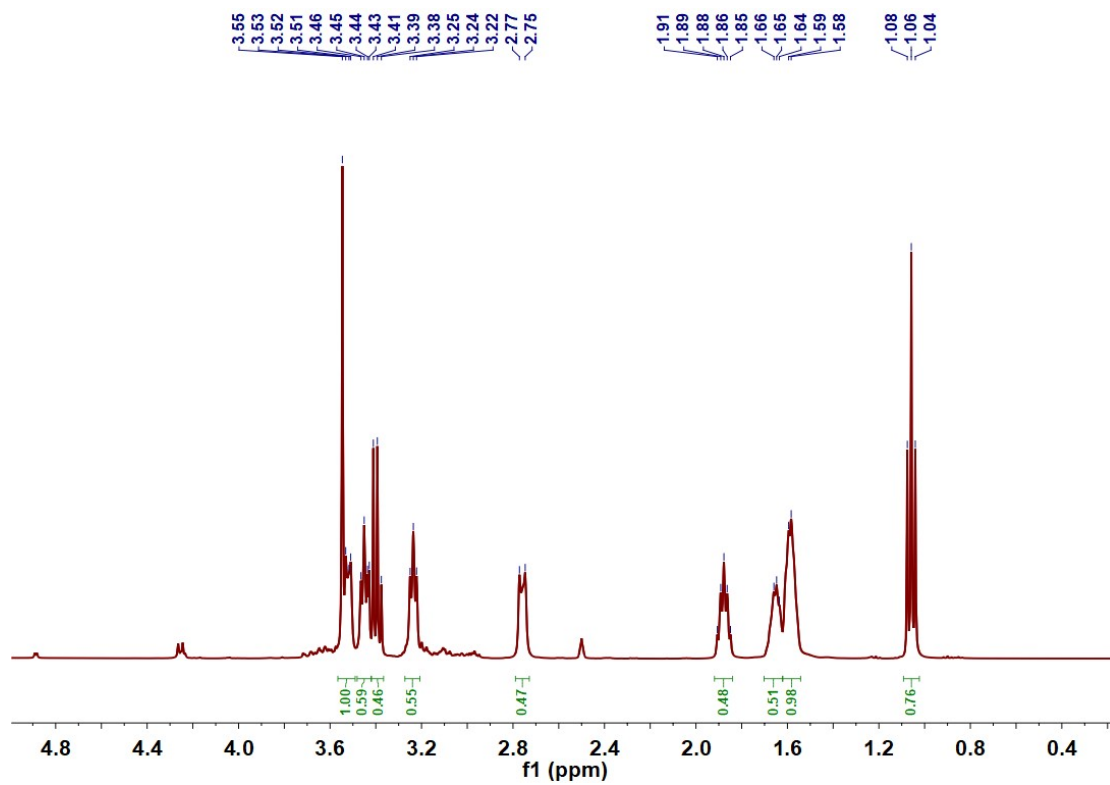


Fig. S6 ^1H NMR chemical shifts of cellobiose/ $[\text{DBUH}][\text{CH}_3\text{CH}_2\text{OCH}_2\text{COO}]$ solution, DMSO-d_6

as external reference.

¹H NMR data of [DBUH][CH₃CH₂OCH₂COO]

Pure [DBUH][CH₃CH₂OCH₂COO] solvent:

¹H NMR (400 MHz, DMSO-d₆) δH 3.53-3.37 (8H, m), 3.24 (2H, t), 2.75 (2H, d), 1.89-1.84 (2H, m), 1.65-1.57 (6H, m), 1.05 (3H, t).

[DBUH][CH₃CH₂OCH₂COO]/cellobiose:

¹H NMR (400 MHz, DMSO-d₆) δH 3.55-3.38 (8H, m), 3.24 (2H, t), 2.75 (2H, d), 1.91-1.85 (2H, m), 1.66-1.58 (6H, m), 1.06 (3H, t).

Table S2 The fitted values of η_0 for DWP solutions with different DWP concentrations at 80 °C

Model	Cross				
Equation	$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + K\dot{\gamma}^m}$				
DWP concentration/wt%	4	6	8	10	12
η_0	3.2±0.1	23.9±0.7	115.4±2.0	632.7±20.7	1396.1±72.7
R^2	0.998	0.996	0.998	0.992	0.994

Table S3 The fitted values of η_0 for 12 wt% DWP solutions at different temperatures

Model	Cross				
Equation	$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + K\dot{\gamma}^m}$				
temperature/°C	50	60	70	80	90
η_0	7786.5±621.6	3320.2±156.1	1786.3±74.2	1396.1±72.7	821.1±40.8
R^2	0.998	0.997	0.990	0.994	0.992

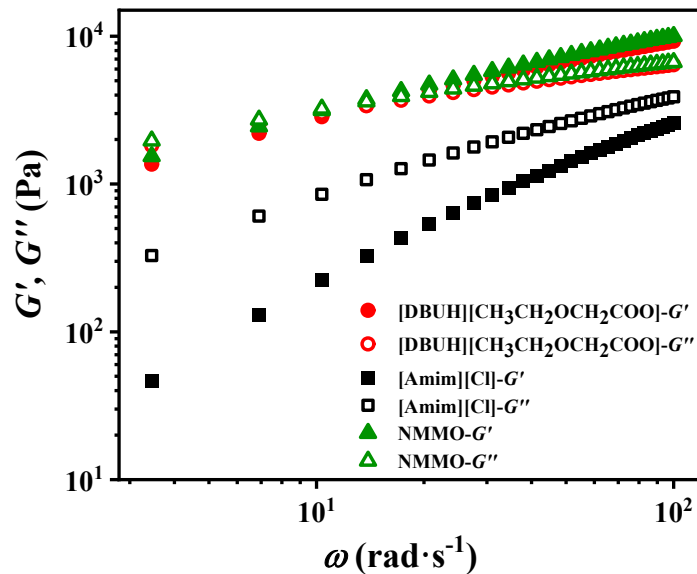


Fig. S7 Curves of dynamic frequency sweep for 12 wt% DWP/[DBUH][CH₃CH₂OCH₂COO], DWP/AmimCl, and DWP/NMMO solutions at 80 °C, respectively.

Table S4 Parameters related to the TGA curves of raw DWP and RC films prepared in various coagulation baths

Code	Initial thermal decomposition T (°C)	Maximum thermal decomposition T (°C)	Residual mass at 600 °C (%)
DWP	238	359	5.1
E-film	247	335	14.6
AE-film	236	318	16.7
DW-film	201	285	18.3

Table S5 Parameters related to the stress-strain curves of RC films prepared in various coagulation baths

Code	Thickness (μm)	Tensile strength (MPa)	Strain (%)
E-film	34 ± 3	120.0 ± 5.9	12.0 ± 3.7
AE-film	33 ± 2	83.7 ± 5.7	5.0 ± 1.9
DW-film	30 ± 2	63.0 ± 5.1	2.8 ± 2.3

Table S6 The maximum values of haze in the range of 400-800 nm for RC films prepared in various

coagulation baths

Code	E-film	AE-film	DW-film
Haze (%)	4.9 ± 1.1	8.1 ± 1.0	8.7 ± 2.3

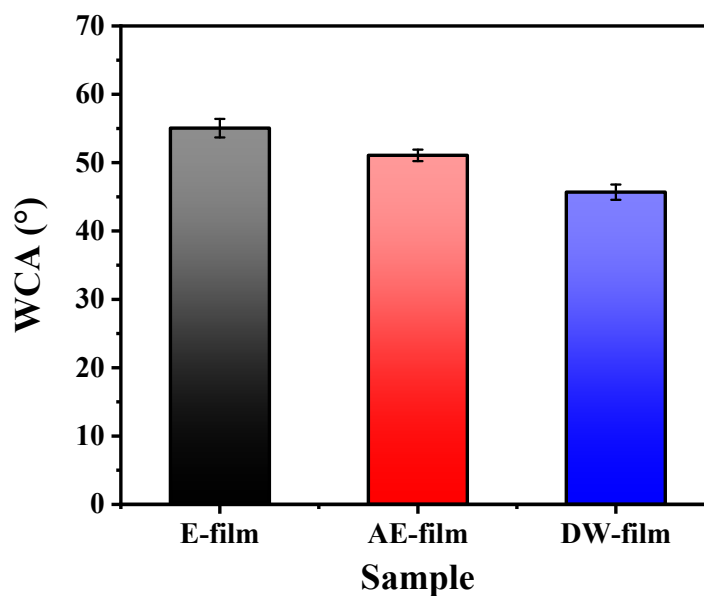


Fig. S8 WCAs of cellulose films regenerated from ethanol, 50% aqueous ethanol and deionized water, respectively.

Table S7 Parameters related to the XRD curves of raw DWP and RC films prepared in various coagulation baths

Code	Lattice planes				Crystalline form	Crystallinity (%)
	1-10	110	200/020	004		
DWP	15.2°	16.5°	(200)22.5°	34.5°	I	49.0±2.0
E-film	12.5°	19.9°	(020)20.5°	–	II	38.8±2.1
AE-film	12.1°	20.0°	(020)21.2°	–	II	36.8±1.9
DW-film	12.2°	20.0°	(020)21.3°	–	II	36.2±1.5

Experimental

Synthesis of [DBUH][CH₃CH₂OCH₂COO]

[DBUH][CH₃CH₂OCH₂COO] was synthesized by acid-base neutralization. Briefly, DBU was mixed with n-Hexane in a 1:3 mass ratio, and then 0.95 mol of CH₃CH₂OCH₂COOH (relative to DBU) was added to the mixture. The reaction was carried out under mechanical stirring for over 5 hours at 30 °C under the nitrogen atmosphere. The [DBUH][CH₃CH₂OCH₂COO] deposited on the bottom of the flask was separated and repeatedly washed with n-Hexane to remove the unreacted DBU. The high-purity [DBUH][CH₃CH₂OCH₂COO] was obtained by drying at 80 °C for 1 h under a nitrogen flow. It was worth noting that the n-Hexane and unreacted DBU in the washing process could be repeatedly used after being distilled and recycled.

Solubility of DWP in [DBUH][CH₃CH₂OCH₂COO]

The solubility of DWP in [DBUH][CH₃CH₂OCH₂COO] at different temperatures was determined as follows. The DWP (0.8 g) was added into a 50 mL flask which contained preheated [DBUH][CH₃CH₂OCH₂COO] (20 g) and stirred magnetically at the given temperature. Additional DWP was added after complete dissolution, as observed by PLM. This procedure was repeated until the additional added DWP was not dissolved even after more than 2 h. The maximum solubility of cellulose, expressed in g/100 g of the solvent, was determined by the ratio of the mass of DWP dissolved in [DBUH][CH₃CH₂OCH₂COO] to that of its solution. The dissolution experiments were repeated for three times.