

Flame-retardant thermoplastics derived from plant cell wall polymers by single ionic liquid substitution

著者	Nishita Ryunosuke, Kuroda Kosuke, Ota Shohei, Endo Takatsugu, Suzuki Shiori, Ninomiya Kazuaki, Takahashi Kenji
著者別表示	黒田 浩介, 仁宮 一章, ?橋 憲司
journal or publication title	New Journal of Chemistry
volume	43
number	5
page range	2057-2064
year	2019-03
URL	http://doi.org/10.24517/00056097

doi: 10.1039/C8NJ04797A



Flame-retardant thermoplastics derived from plant cell wall polymers by single ionic liquid substitution

Ryunosuke Nishita^a, Kosuke Kuroda^{*a}, Shohei Ota^a, Takatsugu Endo^b, Shiori Suzuki^a, Kazuaki Ninomiya^c, and Kenji Takahashi^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Three components of plant cell walls—cellulose, hemicellulose and lignin—were converted to flame-retardant thermoplastics by adducting only single ionic liquid species *via* covalent bonds. They showed thermoplasticity and formed thin films by hot pressing. They also showed flame retardancy and self-extinguished the fire during burning. The properties of the samples depend on the cation species of ionic liquids adducted and thus are controllable. In the present study, more than 66% of the hydroxyl groups present on the polymers were maintained after derivatisation; they thus have the potential for further functionalisation for moulding and practical use and so on, in addition to flame retardancy and thermoplasticity.

Introduction

Cellulose, hemicellulose, and lignin are produced as main components of cell walls and have accumulated in large quantities on the earth. They have attracted attention as candidates to produce new materials for the replacement of petroleum-based materials. Researches regarding cellulose especially have progressed for these decades and cellulose has been converted to thermoplastics through acylation.^{1–4} On the other hand, flame retardancy is well known as an important property for thermoplastics to save our lives, but cellulosic materials are known to be flammable materials. Therefore, there is strong demand for flame-retardant thermoplastics derived from cellulose.

Addition of flame retardancy to plant-derived polymers has been reported.^{5,6} For example, boric acid flame retardants are added to cellulose plastics.⁷ The flame retardants form foam layers on the surfaces of the materials to prevent heat and air from passing to the interior part of the materials when the plastics are heated.⁵ The phosphoric acid-type flame retardants also form char layers composed of polyphosphate on the surfaces of the materials, in addition to radical trap by PO-radicals in gas phase.^{8,9} It is noted that some of the phosphoric acid-type flame retardants also play a role as plasticisers.¹⁰ However, such flame retardants easily bleed out because they are only mixed with the polymers.

Introduction of flame retardants *via* covalent bonds is one of methods to prevent bleeding out of the flame retardants. For example, phosphoric acid-type flame retardants can be

covalently bonded to the hydroxyl groups of carbohydrates and has been reported to improve the flame retardancy of wood powders.⁸ In addition, Aoki *et al.* have produced a flame-retardant thermoplastic from cellulose by two steps: adduction of a phosphoric acid-type flame retardant to the residual hydroxyl groups of a cellulose-derived thermoplastic, cellulose propionate (CP).¹¹ The cellulose plastic synthesised *via* this method, however, cannot be further functionalised because almost all of the hydroxyl groups have been substituted by the flame-retardant group (phosphoric acid) and plasticiser-group (acyl group) and thus there are no more reactive groups. Therefore, further control of other properties of the cellulose plastic that are important for moulding and practical use (*e.g.* physico-chemical properties such as solubility and viscosity, and mechanical properties such as tensile strength, bending strength, and elastic modulus). For this reason, the current cellulose-derived flame-retardant thermoplastics have limited applications, and they are not recognised as a suitable alternative to petroleum-derived plastics. If a certain number of hydroxyl groups could be maintained on cellulose after the addition of thermoplasticity and flame retardancy, the cellulose-derived flame-retardant thermoplastic can be further functionalised by substitution with other kinds of functional groups and thus may have the potential to correspond to or surpass petroleum-derived plastics. We here propose the introduction of a single substituent that can impart both thermoplasticity and flame retardancy to cellulose, to maintain the hydroxyl groups after derivatisation.

We focused on ionic liquids as substituents, to impart thermoplasticity and flame retardancy to cellulose simultaneously. Ionic liquids are salts that are liquid below 100 °C. Ionic liquids have been reported to function as plasticisers or flame retardants when mixed with polymers.¹² For example, cellulose does not show softening point because cellulose chains are strongly bound by hydrogen bonding. Ionic liquids act as plasticisers by mixing with cellulose, through

^a Faculty of Biological Science and Technology, Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^b Faculty of Science and Engineering, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe-shi, Kyoto 610-0394, Japan

^c Institute for Frontier Science Initiative, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

disrupting hydrogen bonds and increasing the free volume to make free space for cellulose molecules' moving.¹³ Different ionic liquid species are known to impart flame retardancy by mixing with plastics or impregnating wood.^{14–17} Based on these reports, suitably designed ionic liquids are expected to function as both plasticisers and flame retardants. Furthermore, ionic liquids do not bleed out if they adduct to cellulose as substituents.

In this study, we selected 1-ethyl-3-methylimidazolium methylphosphonate ($[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$, see Fig. 1), as it can dissolve cellulose^{18–25} and the $[(\text{MeO})(\text{H})\text{PO}_2]$ anion can be bound by the hydroxyl group of cellulose by an esterification reaction at high temperatures.²⁶ Substitution of the hydroxyl group was further expected to show another effect in addition to the influence of just mixing ILs; the decrease in hydroxyl groups leads to further disruption of the hydrogen bond network of cellulose, resulting in a decrease in the softening point²⁷. From a flame retardancy perspective, $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ was expected to show not only the flame-retarding effect of the ionic liquid itself but also a flame-retardant effect as a phosphoric acid-type compound, as well as other phosphorus-containing ILs^{14,15}. It has also been reported that if phosphoric acid-type flame retardants are covalently introduced to the 6 position of cellulose, the process of char formation is further improved.^{5,11}

This method has the two more advantages: single step reaction (the previous flame-retardant thermoplastic⁹ has two steps) and allowing control of the degree of substitution. Latter one enables to control the resulting properties of the plastics, because it has been reported that some of the propionyl groups already introduced are eliminated when introducing a phosphoric acid-type flame retardant into the CP in the case of two-step production.¹¹

The present method can be applied to the other polymers derived from plant cell walls, namely, hemicellulose and lignin, because they also have hydroxyl groups. In this study, all three kinds of "flame-retardant cell-wall-derived thermoplastics" were developed, while maintaining a certain number of hydroxyl groups.

Results and Discussion

Flame-retardant cell-wall-derived thermoplastics with imidazolium-based ionic liquid

The residual weight of $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ at 400 °C upon thermogravimetric analysis (TGA) under air atmosphere was preliminarily checked as an index of flame retardancy⁸ (Fig. S1). The residual weight was 41%, while $[\text{C}_2\text{mim}]\text{Br}$ (the same cation and bromide anion) showed only 2%. The residual

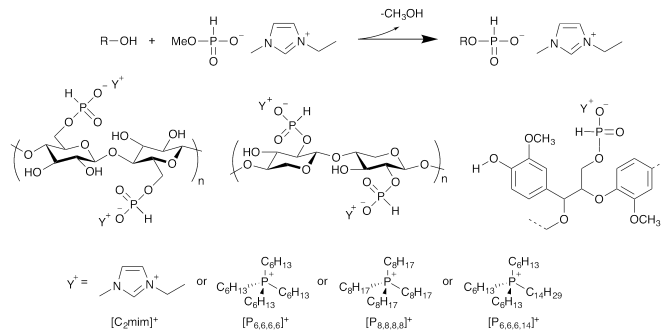


Fig. 1 The reaction scheme of substitution of cellulose, xylan, and lignin by $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$, and the structures of the ionic liquid-substituted cellulose, xylan, and lignin.

weight is attributed to char formation of $[(\text{MeO})(\text{H})\text{PO}_2]$ anion. This result shows the flame retardancy of $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ mainly based on $[(\text{MeO})(\text{H})\text{PO}_2]$ anion (although actually $[\text{C}_2\text{mim}]$ cation was also found to involve flame retardancy in burning test (details later)).

Cellulose, xylan, and lignin were respectively added to $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ and were substituted with $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ ($[\text{C}_2\text{mim}]^+\text{cellulose}$, $[\text{C}_2\text{mim}]^+\text{xylan}$, $[\text{C}_2\text{mim}]^+\text{lignin}$; structures are shown in Fig. 1). Lignin required longer reaction time (3 h), because the reaction hardly proceeded within 1 h.

In the ^1H NMR spectrum of $[\text{C}_2\text{mim}]^+\text{cellulose}$, peaks derived from $[\text{C}_2\text{mim}]$ cations were observed at 1.37, 3.84, 4.19, 7.75, 7.83, and 9.43 ppm, while peaks derived from $[(\text{MeO})(\text{H})\text{PO}_2]$ anions were observed at 6.09 and 7.05 ppm (Fig. S2). Furthermore, the signal attributed to the methyl group of the $[(\text{MeO})(\text{H})\text{PO}_2]$ anion (around 3.2 ppm) was not observed in the spectrum of $[\text{C}_2\text{mim}]^+\text{cellulose}$. These results strongly suggest that the $[(\text{MeO})(\text{H})\text{PO}_2]$ anion was covalently introduced into the cellulose, accompanied by removal of the methyl group of the $[(\text{MeO})(\text{H})\text{PO}_2]$ anion. $[\text{C}_2\text{mim}]^+\text{xylan}$ and $[\text{C}_2\text{mim}]^+\text{lignin}$ were confirmed to have been synthesised as well as $[\text{C}_2\text{mim}]^+\text{cellulose}$ (see Fig. S2).

Introduction of $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ into each of the three components of plant cell walls was also confirmed by FT-IR (Fig. S3). The peaks derived from the P-O-C bond at 821 cm^{-1} , P=O bond at 1211 cm^{-1} , and C=N bond at 1571 cm^{-1} were detected in $[\text{C}_2\text{mim}]^+\text{cellulose}$ but not in the unreacted polymer.^{28,29} The peaks derived from these bonds were also detected in $[\text{C}_2\text{mim}]^+\text{xylan}$ and $[\text{C}_2\text{mim}]^+\text{lignin}$ (see Fig. S3). These results indicated that $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ was introduced to each component of plant cell walls.

The substitution ratios of hydroxyl groups of cellulose, xylan, and lignin with $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ were detected by ^{31}P NMR. Their substitution ratio was 33, 32, and 14%, respectively, against number of the hydroxyl groups. Namely, they maintain 67, 68, 86% of the hydroxyl groups, respectively, after derivatisation.

Characteristics of the samples are shown in Table 1. All three samples were able to form thin films when subjected to

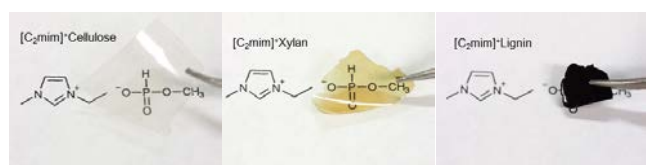


Fig. 2 Thin films of [C₂mim]⁺cellulose (left), [C₂mim]⁺xylan (centre), and [C₂mim]⁺lignin (right) after hot pressing.

hot pressing (Fig. 2). The films of [C₂mim]⁺cellulose and [C₂mim]⁺xylan were flexible and transparent, while the film of [C₂mim]⁺lignin was hard and not transparent. We developed thermoformable films from the three types of polymers derived from plant cell walls with [C₂mim]⁺[(MeO)(H)PO₂] at a low substitution ratio ($\leq 33\%$).

Thermal properties of the polymers regarding thermoplasticity were investigated (Table 1). The softening points of the samples were briefly checked while elevating the temperature. Both [C₂mim]⁺cellulose and [C₂mim]⁺xylan were remarkably softened at about 160 and 170 °C, respectively. On the other hand, the clear softening point of [C₂mim]⁺lignin was not observed (namely, it was still hard up to 250 °C). However, it seems that the fluidity of the molecules of [C₂mim]⁺lignin was improved by heating because [C₂mim]⁺lignin formed a thin film upon hot pressing. TGA was conducted under air to investigate the thermal decomposition temperature (the temperature when the residual weight is 95%). [C₂mim]⁺cellulose and [C₂mim]⁺xylan showed decomposition temperatures of 230 and 235 °C (full TGA curves in Fig. S4). Thus, these samples showed potential for use as thermoplastics, because the thermal decomposition temperature was higher than the softening points (160 °C and 170 °C). [C₂mim]⁺lignin showed a decomposition temperature of 269 °C, which was slightly higher than those of polysaccharide derivatives.

Thermal properties of the polymers regarding flame retardancy were investigated (see Table 1). The residual weight of each sample at 400 °C upon TGA under air atmosphere was checked as an index of flame retardancy⁸ (see Fig. S4). As mentioned above, phosphoric acid-type flame retardants are effective for blocking oxygen and heat by generation of polyphosphate as char when combusted.⁸ The residual weight of untreated cellulose at 400 °C was 11%. The residual weight of CP, which is a typical cellulose plastic, CP at 400 °C was 12%, equivalent to that of untreated cellulose. By contrast, the residual weight of [C₂mim]⁺cellulose was 52%, suggesting flame retardancy. Furthermore, the residual weight of [C₂mim]⁺cellulose (52%) is larger than each residual weight of untreated cellulose (11%) and that of [C₂mim]⁺[(MeO)(H)PO₂] (41%). The increase should be attributed to the effect of immobilised phosphoric acids on cellulose. The immobilised phosphoric acids on cellulose promotes carbonisation of the polysaccharides when exposed to high temperatures.^{5,8,9} The residual weight at 400 °C of the flame-retardant cellulose previously reported (*i.e.* the cellulose derivative prepared by introduction of the phosphoric acid-type flame retardant into CP through two steps, as mentioned in introduction section) was 30–40%.⁹ Based on these results, [C₂mim]⁺cellulose showed not only thermoplasticity and flame retardancy while

maintaining many hydroxyl groups, but also better flame retardancy compared with the flame-retardant plastic previously reported. As a just reference, a TGA curve of [C₂mim]⁺cellulose measured under N₂ was shown in Fig. S5. The residual weight of [C₂mim]⁺xylan was 48% at 400 °C, whereas that of untreated xylan was 39%, indicating an improvement in flame retardancy. The improved value was similar to that of [C₂mim]⁺cellulose. The residual weight of [C₂mim]⁺lignin was 74% at 400 °C, whereas that of untreated lignin was 67%. The small difference was presumably due to the flame retardancy of unreacted lignin. Together, these results confirm that each of the three components of plant cell walls substituted with [C₂mim]⁺[(MeO)(H)PO₂] shows flame retardancy upon TGA.

It is noted here that the thermal decomposition temperature of un-derivatised cellulose was 306 °C, and that of [C₂mim]⁺cellulose was 230 °C. A decrease in decomposition temperature of [C₂mim]⁺cellulose can be explained by decomposition and simultaneous char formation temperature of [C₂mim]⁺[(MeO)(H)PO₂] (see also Fig. S1).^{30, 31} The thermal decomposition temperature of un-derivatised xylan was 235 °C, and there was almost no change after substitution with [C₂mim]⁺[(MeO)(H)PO₂] (228 °C). This was probably because the original decomposition temperature of untreated xylan was near the thermal decomposition temperature of the phosphorus component. The decomposition temperature of lignin also showed a slight difference before and after derivatisation (256 and 269 °C). The reason for not decreasing the decomposition temperature to around 230 °C may be the low conversion ratio (14%).

The samples were then burned (Fig. 3 shows the photos of the samples after burning, and movies regarding CP and [C₂mim]⁺cellulose are shown in movies 1–4, ESI). When the film of the CP was in contact with the flame of an alcohol lamp, it burned completely with dripping and with slight char formation. On the other hand, when three [C₂mim]⁺samples were in contact with the flame of the alcohol lamp, combustion started but a char layer immediately formed and self-extinguished the fire. We concluded that this was caused by the flame-retardant effect of [C₂mim]⁺[(MeO)(H)PO₂], because this behaviour is consistent with that of phosphoric acid-type flame retardants. The formed char layers on the samples have foamed structure; foamed char layer is generally quite effective to show flame-retardancy because it shuts heat out. The scanning electron microscope (SEM) images of the samples showed the fine cells divided by thin char layers (Fig. S6). The foamed char layer is the characteristics of intumescent flame-retardants and



Fig. 3 Char formation of the thin films of [C₂mim]⁺cellulose (left), [C₂mim]⁺xylan (centre), and [C₂mim]⁺lignin (right) after burning and extinguishing the fire.

Table 1 Characteristics of plant-based polymers before and after derivatisation with the ionic liquids.

^aThey have the same conversion ratio as the [C₂mim]⁺ polymers because we conducted only exchange the free cation species. ^bNot evaluated because the samples did not form thin films. ^cThe film was not miscible with

	Cation	Conversion ratio	Film formation	Film character	Miscibility in water	Softening point	Thermal decomposition	Residual weight (at 400 °C)	Char formation	Fire suppression ability
Cellulose propionate	–	89 %	✓	Soft	Not miscible	160 °C	301 °C	12 %	Slightly formed	Completely burned
Cellulose	–	–	Not formed	– ^b	Not miscible	– ^d	313 °C	11 %	– ^b	– ^b
	[C ₂ mim] ⁺	33%	✓	Soft	Miscible	160 °C	230 °C	52 %	✓ (foam)	✓
	[P _{6,6,6,6}] ⁺	(33%) ^a	Not formed	– ^b	Not miscible	140 °C	234 °C	57 %	– ^b	– ^b
	[P _{8,8,8,8}] ⁺	(33%) ^a	✓	Hard	Not miscible	140 °C	248 °C	62 %	✓	✓
	[P _{6,6,6,14}] ⁺	(33%) ^a	✓	Hard	Not miscible ^c	120 °C	243 °C	62 %	✓	✓
Xylan	–	–	Not formed	– ^b	Not miscible	– ^d	235 °C	39 %	– ^b	– ^b
	[C ₂ mim] ⁺	32 %	✓	Soft	Miscible	170 °C	228 °C	48 %	✓ (foam)	✓
	[P _{6,6,6,6}] ⁺	(32%) ^a	Not formed	– ^b	Not miscible ^c	130 °C	228 °C	47 %	– ^b	– ^b
	[P _{8,8,8,8}] ⁺	(32%) ^a	Not formed	– ^b	Not miscible ^c	130 °C	232 °C	57 %	– ^b	– ^b
	[P _{6,6,6,14}] ⁺	(32%) ^a	✓	Hard	Not miscible ^c	120 °C	223 °C	59 %	✓	✓
Lignin	–	–	Not formed	– ^b	Miscible	– ^d	256 °C	67 %	– ^b	– ^b
	[C ₂ mim] ⁺	14 %	✓	Hard	Miscible	– ^d	269 °C	74 %	✓ (foam)	✓
	[P _{6,6,6,6}] ⁺	(14%) ^a	✓	Hard	Not miscible	190 °C	287 °C	61 %	✓	✓
	[P _{8,8,8,8}] ⁺	(14%) ^a	✓	Hard	Not miscible	140 °C	250 °C	71 %	✓	✓
	[P _{6,6,6,14}] ⁺	(14%) ^a	✓	Hard	Slightly miscible	– ^d	225 °C	71 %	✓	✓

water but broken and dispersed in water. ^dNot detected.

formed by simultaneous char formation and gas generation. The gas is presumably generated by decomposition of imidazolium cation since it contains N atoms like melamine, which is a popular nitrogen-type flame-retardant. The char layer was additionally confirmed to include P atoms by using SEM-energy dispersive X-ray spectroscopy (EDX) (Fig. S7): the char layer includes polyphosphate. Utilisation of typical ILs as intumescent flame retardants has not been reported, to the best of our knowledge.

We here developed flame-retardant thermoplastics from the three types of polymers derived from plant cell walls with $[C_2mim][(MeO)(H)PO_2]^+$ at a low substitution ratio ($\leq 33\%$). Enabling to satisfy both flame retardancy and thermoplasticity at the low substitution is clearly attributed to functionalisation by only single species, $[C_2mim][(MeO)(H)PO_2]^+$. On the other hand, $[C_2mim]^+$ lignin did not show clear macroscopic softening behaviour upon the experiment for checking the softening point, although it could form a thin film with hot pressing.

Flame-retardant cell-wall-derived thermoplastics with phosphonium-based ionic liquid

We considered whether lignin could be macroscopically softened further through more precise design of ionic liquids. In this study, we focused on phosphonium cations with long alkyl chains. The phosphonium cations have high molecular weights and bulky structures; thus, they were expected to have large free volumes and increase the free volume of lignin through substitution. Consequently, derivatisation with the phosphonium cations was expected to increase the thermal fluidity of the lignin molecules and decrease the softening point.¹¹ Thus, the softening points of the lignin derivatised with long-alkyl-chain phosphonium cations were investigated, with a focus on the alkyl chain length of the phosphonium cations (length itself and its symmetry/asymmetry) and the consequent size of the free volume. Furthermore, derivatisation with the phosphonium cations was also expected to drastically control various properties of the biopolymers. For example, substitution with phosphonium cations would make the polymers hydrophobic while the imidazolium-type polymers were hydrophilic.

The cations of $[C_2mim]^+$ cellulose, $[C_2mim]^+$ xylan, and $[C_2mim]^+$ lignin were exchanged with tetrahexylphosphonium ($[P_{6,6,6,6}]^+$), tetraoctylphosphonium ($[P_{8,8,8,8}]^+$), and trihexyl(tetradecyl)phosphonium ($[P_{6,6,6,14}]^+$) (the structures are in Fig. 1). Both the $[P_{8,8,8,8}]$ cation and $[P_{6,6,6,14}]$ cation has 32 carbon atoms but they are symmetric and asymmetric, respectively. The fractional free volumes of the ionic liquids have not been reported and we calculated in this study. The fractional free volumes of $[C_2mim][(MeO)(H)PO_2]^+$, $[P_{6,6,6,6}][(MeO)(H)PO_2]^+$, $[P_{8,8,8,8}][(MeO)(H)PO_2]^+$, and $[P_{6,6,6,14}][(MeO)(H)PO_2]^+$ were 0.311, 0.363, 0.369, and 0.367, respectively. The higher fractional free volumes of phosphonium salts may indicate the potential to decrease the softening points of polymers, including lignin. The abbreviations used for the derivatives are $[P_{8,8,8,8}]^+$ cellulose and so on.

Characteristics of the samples are shown in Table 1. $[P_{8,8,8,8}]^+$ and $[P_{6,6,6,14}]^+$ cellulose were able to form thin films with hot

pressing and $[P_{6,6,6,14}]^+$ cellulose was brittle (the photos are shown in Fig. S8). On the other hand, $[P_{6,6,6,6}]^+$ cellulose was not able to form films with hot pressing. In the case of xylan, $[P_{6,6,6,14}]^+$ xylan was able to form thin films with hot pressing, while it was brittle, but $[P_{6,6,6,6}]^+$ and $[P_{8,8,8,8}]^+$ xylan were not. In the case of lignin, $[P_{6,6,6,6}]^+$, $[P_{8,8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ lignin were all able to form thin films with hot pressing, while the $[P_{8,8,8,8}]^+$ lignin film was brittle. All samples substituted with long-alkyl-chain phosphonium cations were harder (*i.e.*, less flexible) than the $[C_2mim]^+$ samples. In summary, $[P_{8,8,8,8}]^+$ and $[P_{6,6,6,14}]^+$ cellulose; $[P_{6,6,6,14}]^+$ xylan; and $[P_{6,6,6,6}]^+$, $[P_{8,8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ lignin formed thin films.

Thermal properties with respect to thermoplasticity were investigated (see Table 1). While $[C_2mim]^+$ cellulose was markedly softened at about 160 °C, $[P_{6,6,6,6}]^+$, $[P_{8,8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ cellulose were markedly softened at about 140, 140, and 120 °C, respectively (although $[P_{6,6,6,6}]^+$ cellulose did not form a film with hot pressing). The increase of the thermal fluidity of the samples may be due to the long-alkyl-chain phosphonium cations of the bulky structures, which have large free volume (0.311 for $[C_2mim][(MeO)(H)PO_2]^+$ vs. 0.363–0.369 for phosphonium $[(MeO)(H)PO_2]^+$). Therefore the phosphonium-type ionic liquids consequently increased the free volume of the derivatised polymers. The softening points of $[P_{6,6,6,6}]^+$ cellulose and $[P_{8,8,8,8}]^+$ cellulose were the same, because there was no substantial difference between the fractional free volumes of $[P_{6,6,6,6}][(MeO)(H)PO_2]^+$ and $[P_{8,8,8,8}][(MeO)(H)PO_2]^+$ (0.363 vs. 0.369). Further investigation is required to explain the lower softening point of $[P_{6,6,6,14}]^+$ cellulose despite the similar fractional free volume ($[P_{6,6,6,14}][(MeO)(H)PO_2]^+$: 0.367).

In the case of xylan, while $[C_2mim]^+$ xylan was markedly softened at about 190 °C, $[P_{6,6,6,6}]^+$, $[P_{8,8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ xylan were markedly softened at about 130, 130, and 120 °C, respectively; that is, they showed the same tendency as the cellulose derivatives. In the case of lignin, $[P_{6,6,6,6}]^+$, and $[P_{8,8,8,8}]^+$ lignin were markedly softened at about 190 and 140 °C, whereas $[C_2mim]^+$ lignin did not show macroscopic softening behaviour, as mentioned above. On the other hand, the softening of $[P_{6,6,6,14}]^+$ lignin was not confirmed, although it formed a thin film upon hot pressing. Thus, totally different behaviours were observed for the lignin derivatives compared to the polysaccharide derivatives, which cannot be explained by the effects of free volume. The differences were probably because lignin has a three-dimensional structure, whereas polysaccharides basically have straight-chain structures (although xylan has very short branches). It might be necessary to confirm the increase in the free volumes of the polymers substituted by the ionic liquids, in order to elucidate these behaviours. However, such investigation is too complex to attempt at this early stage because of the complex structure of lignin. As a summary of this experiment, it was possible to lower the softening point by introducing long-chain phosphonium cations.

TGA was conducted under air to investigate the thermal decomposition temperature (see Table 1 and Fig. S4). $[P_{6,6,6,6}]^+$, $[P_{8,8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ cellulose showed decomposition temperatures of 234, 248, and 243 °C, respectively, which were

sufficiently higher than their softening points (while $[P_{6,6,6}]^+$ cellulose did not form a film with hot pressing). $[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ xylan showed decomposition temperatures of 228, 232, and 223 °C, respectively, which were also higher than their softening points (while $[P_{6,6,6}]^+$ and $[P_{8,8,8}]^+$ xylan did not form films with hot pressing). $[P_{6,6,6}]^+$ and $[P_{8,8,8}]^+$ lignin showed decomposition temperatures of 287 and 250 °C, which were higher than their softening points. $[P_{6,6,6,14}]^+$ lignin showed a decomposition temperature of 225 °C, while its softening point could not be determined (although it formed a thin film with hot pressing).

The residual weight of the samples at 400 °C was determined by using TGA (see Table 1 and Fig. S4). The residual weights of $[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ cellulose were 57, 62, and 62%, respectively, suggesting higher flame retardancy compared with that of $[C_2mim]^+$ cellulose (52%). The residual weights of $[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ xylan were 47, 57, and 59%, respectively, suggesting also higher flame retardancy compared with that of $[C_2mim]^+$ xylan (48%). The residual weights of $[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ lignin were 61, 71, and 71%, respectively, suggesting lower or similar flame retardancy compared with that of $[C_2mim]^+$ lignin (74%). Based on these results, the flame retardancy of the derivatives with long-alkyl-chain phosphonium cations was confirmed by TGA.

The samples were then burned (Fig. S9 shows the photos of the samples after burning). When the films of $[P_{8,8,8}]^+$, $[P_{6,6,6,14}]^+$ cellulose, $[P_{6,6,6,14}]^+$ xylan, $[P_{6,6,6}]^+$, and $[P_{8,8,8}]^+$ lignin made contact with the flame of the alcohol lamp, combustion started but a char layer was immediately formed and then the fire was self-extinguished. The actual flame retardancy of the derivatives with long-alkyl-chain phosphonium cations was confirmed.

The formed char layers were smooth, not foamed structure (see Fig. S9, and a SEM image for $[P_{8,8,8}]^+$ cellulose is shown in S10). Therefore, the phosphonium-type ILs did not work as intumescent flame retardants. It is due to the absence of N atom in the phosphonium cations unlike imidazolium cations. On the other hand, phosphine is also known as phosphorus-type flame retardants and phosphonium cations may play a role of such flame retardants. SEM-EDX indicates that the char layer contains polyphosphate (Fig. S11).

Solubility of the polymers in water was investigated to determine the controllability of properties of the polymers. $[C_2mim]^+$ cellulose was miscible in water. On the other hand, the cellulose derivatives produced by exchanging the cation for phosphonium cations ($[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$) were immiscible in water. Notably, the film of $[P_{6,6,6,14}]^+$ cellulose was broken when immersed in water, which may indicate relatively weak entanglement of the polymer chains in $[P_{6,6,6,14}]^+$ cellulose. $[P_{6,6,6}]^+$, $[P_{8,8,8}]^+$, and $[P_{6,6,6,14}]^+$ xylan were immiscible in water, whereas $[C_2mim]^+$ xylan was miscible. These films were also broken in water, similar to $[P_{6,6,6,14}]^+$ cellulose. In the case of lignin, $[P_{6,6,6}]^+$ and $[P_{8,8,8}]^+$ lignin were immiscible in water, whereas $[C_2mim]^+$ lignin was miscible. On the other hand, $[P_{6,6,6,14}]^+$ lignin partially dissolved in water. The hydrophobicity of ions generally becomes stronger when increasing the alkyl chain length, but these results showed a different tendency.

Therefore, we considered the possibility that the cation was not introduced 1:1 relative to the anion. However, the ratio of anion to cation was measured using ^{31}P NMR and was found to be 1:1. Further investigation is necessary to clarify why $[P_{6,6,6,14}]^+$ lignin was partially soluble in water. In summary, it was possible to add hydrophobicity to the cellulose, xylan, and lignin derivatives by substituting with long-alkyl-chain phosphonium cations, suggesting that the properties of the polymers can be controlled by introduction of different cation species. There is much room to design the properties of the biopolymers because there are various cations such as ammonium, pyridinium, and many inorganic cations.

The results above show that introduction of a long-chain phosphonium cation enables adduction of hydrophobicity and control of softening temperature. Although some of samples are not amenable to forming films, at least by hot pressing (we have not attempted solution casting), they can be used as composites. For instance, such polymers can be used as high-molecular-weight flame retardants. Low-molecular-weight flame retardants have problems, e.g. bleeding out and damaging the human body via volatilisation. By contrast, flame-retardant polymers do not readily bleed out owing to entanglement with polymer matrices and have low toxicity owing to their non-volatility.

Conclusions

Thermoplasticity and flame retardancy can be simultaneously imparted to each of the three components of plant cell walls, while maintaining more than 66% of the hydroxyl groups of the polymers, by substituting with $[C_2mim][[(MeO)(H)PO_2]]$. $[C_2mim]^+$ cellulose, $[C_2mim]^+$ xylan, and $[C_2mim]^+$ lignin formed thin films and their residual weights at 400 °C were 52, 48, and 74%, higher than those of the underivatized cellulose, xylan and lignin (10, 39 and 67%, respectively), showing high flame retardancy. In actual combustion test, they extinguished the fire before completely burned. Long-alkyl-chain phosphonium cations were introduced into each polymer instead of $[C_2mim]^+$ cation to control the softening point and other properties such as hydrophobicity. It was confirmed that the softening point of long-alkyl-chain phosphonium cation polymers can be controlled while maintaining flame retardancy equivalent to that of the $[C_2mim]^+$ samples. In addition, almost all the long-alkyl-chain phosphonium cation-based polymers became hydrophobic, clearly indicating that the design of the cation species results in control of their properties.

Experimental

Materials and Equipment

$[C_2mim][[(MeO)(H)PO_2]]$, methanol, hexane, nitric acid, 0.1 mol/L silver nitrate solution, and dichloromethane were purchased from Kanto Chemical Co., Inc. and used as received. Filter paper (No. 5C) derived from cellulose was purchased from Advantec Co., Ltd. and used as received. Xylan from beech wood was purchased from Apollo Scientific Co., Ltd. and used as

received. Alkali lignin (low-sulfonate content), trihexyltetradecylphosphonium bromide, Amberlite IRN 77A hydrogen form, and Amberlite IRN 78A hydroxide form were purchased from Sigma-Aldrich Co., LLC, and used as received. Triethyl phosphate, trihexylphosphine, 1-bromohexane, tetra-*n*-octylphosphonium bromide, and dimethyl phosphite were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Dialysis membrane (MWCO 1,000) was purchased from Funakoshi Co., Ltd and used as received. ^1H and ^{31}P NMR were measured with JEOL ECA-600. FT-IR were measured with Thermo Scientific NICOLETis10. Thermogravimetric analysis were measured with Shimadzu DTG-60AH. Softening point were measured with ATM-01, AS ONE.

Synthesis of $[\text{C}_2\text{mim}]^+$ three each component of plant cell walls

Cellulose, hemicellulose, and lignin (0.5 g), respectively, were mixed with $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ (5 g) and then heated in an oil bath at 160 °C for different periods of time (cellulose and xylan: 1 h, lignin: 3 h). After the reaction, the resulting mixture was cooled to room temperature and diluted with 20 ml of water (for cellulose and xylan) or methanol (for lignin). Dialysis was performed to remove the unreacted $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ in 500 ml water or methanol for three times. The resulting dialysed solution was dried under reduced pressure. After drying $[\text{C}_2\text{mim}]^+$ cellulose, $[\text{C}_2\text{mim}]^+$ xylan, and $[\text{C}_2\text{mim}]^+$ lignin were obtained.

The substitution ratios of the hydroxyl groups of the biopolymers with $[\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2]$ were measured by ^{31}P NMR. Triethyl phosphate was added as a standard for quantification. Each substitution ratio of $[\text{C}_2\text{mim}]^+$ cellulose and $[\text{C}_2\text{mim}]^+$ xylan was obtained as follows. First, we calculated DS from the following equation.

$$\text{Substitution ratio (\%)} = \frac{\text{Triethyl phosphate (g)} \times \text{peak ratio}}{\text{Molecular weight (MW) of triethyl phosphate}} \times \frac{[\text{C}_2\text{mim}]^+ \text{ sample added (g)} \times \text{Degree of substitution (DS)}}{\text{MW of one unit of cellulose or xylan} + (\text{MW of } [\text{C}_2\text{mim}][(\text{MeO})(\text{H})\text{PO}_2] - 32) \times \text{DS}}$$

Where the peak ratio represents the integrated value of the phosphorus atoms in the anionic moiety of the sample when the integrated value of triethyl phosphate is 1.0. Then, the substitution ratio can be expressed by the following equation.

$$\text{Substitution ratio (\%)} = \frac{\text{DS}}{\text{Maximum value of the DS (3 or 2)}} \times 100$$

Where the maximum values of DS is 3 for cellulose and 2 for xylose.

The substitution ratio of $[\text{C}_2\text{mim}]^+$ lignin was obtained by the following equation.

$$\text{Substitution ratio (\%)} = \frac{\text{Triethyl phosphate (g)} \times \text{peak ratio}}{\text{MW of triethyl phosphate (mol/g)}} \times \frac{1}{\text{OH content of untreated lignin (mol/g)}} \times 100$$

The OH content of untreated lignin we used was 4.26×10^{-3} (mol/g), measured as reported^{32, 33}.

Synthesis of tetrahexylphosphonium bromide ($[\text{P}_{6,6,6,6}]\text{Br}$)

Trihexylphosphine (6.29 g, 0.022 mol) and 1-bromohexane (4.17 g, 0.025 mol) were added to hexane at room temperature under argon atmosphere. The resulting mixture was stirred for 24 h at 160 °C. The resulting liquid was washed repeatedly with hexane. The liquid was dried under reduced pressure at room temperature for 24 h to yield $[\text{P}_{6,6,6,6}]\text{Br}$ as a solid.

^1H NMR (600 MHz, DMSO-*d*₆; Me₄Si) δ = 2.01-2.25 (m, 8H, $\text{PCH}_2(\text{CH}_2)_4\text{CH}_3$), 1.38-1.45 (m, 8H $\text{PCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.31-1.36 (m, 8H, $\text{P}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.11-1.28 (m, 16H; $\text{P}(\text{CH}_2)_3(\text{CH}_2)_2\text{CH}_3$), 0.83 (t, *J* = 5.7 Hz, 12H, $\text{P}(\text{CH}_2)_5\text{CH}_3$).

Synthesis of [phosphonium]⁺three each component of plant cell walls

Here we describe the example of $[\text{P}_{8,8,8,8}]^+$ cellulose. The cation of $[\text{C}_2\text{mim}]^+$ cellulose (0.1 g) was converted into a proton by mixing the aqueous solution of the imidazolium salt and cation exchange resin (Amberlite IRN 77). The bromide anion of $[\text{P}_{8,8,8,8}]\text{Br}$ was converted to hydroxide by mixing the water/methanol solution of the bromide salt with anion exchange resin (Amberlite IRN 78). An equimolar amount of $[\text{H}]^+$ cellulose relative to $[\text{P}_{8,8,8,8}][\text{hydroxide}]$ was added. Dialysis was performed to remove the unreacted $[\text{P}_{8,8,8,8}][\text{hydroxide}]$ in 500 ml methanol for three times. The resulting liquid was dried under reduced pressure at room temperature for 24 h to yield $[\text{P}_{8,8,8,8}]^+$ cellulose.

^1H NMR (600 MHz; DMSO-*d*₆; Me₄Si), δ = 6.97 and 6.02 (s, 1H, *P-H*), 2.10-2.15 (m, 8H, $\text{PCH}_2(\text{CH}_2)_6\text{CH}_3$), 1.39-1.45 (m, 8H, $\text{PCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.31-1.35 (m, 8H, $\text{P}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.22-1.26 (m, 32H, $\text{P}(\text{CH}_2)_3(\text{CH}_2)_4\text{CH}_3$), 0.83 (t, *J* = 7.0 Hz, 12H, $\text{P}(\text{CH}_2)_7\text{CH}_3$), and many cellulose backbone signals (Fig. S12).

The introduction of $[\text{P}_{8,8,8,8}]^+$ cellulose was also confirmed by the FT-IR spectrum (Fig. S2). Peaks derived from the C-H bond of phosphonium cation at 2854 and 2924 cm^{-1} were detected in the spectrum of $[\text{P}_{8,8,8,8}]^+$ cellulose, in addition to the P-O-C bond at 821 cm^{-1} and the P=O bond at 1211 cm^{-1} .

All the other samples were synthesised using the same method and the synthesis was confirmed in the same way for the other samples (Fig. S2, 13, and 14).

Calculation of free volumes of ionic liquids

To calculate the free volumes of the ionic liquids, density functional theory (DFT) calculations were used, as reported.³⁴ We write the method briefly here. DFT calculations for the ionic liquids were performed by using the Gaussian 09 program package.³⁵ Full geometry optimization (gas phase) were conducted by using 6-311+G(d,p) basis sets based on Becke's three-parameter hybrid method³⁶ with LYP correlation (B3LYP).^{37, 38} Ionic volumes of the ionic liquids were estimated³⁹ and can be considered as the van der Waals volume of the ionic liquids.⁴⁰ We used the density of the $[\text{phosphonium}][(\text{MeO})(\text{H})\text{PO}_2]$ for the calculation. The synthesis of the $[\text{phosphonium}][(\text{MeO})(\text{H})\text{PO}_2]$ is described below.

Synthesis of [phosphonium][(MeO)(H)PO₂]

Here we describe the example of [P_{8,8,8,8}][(MeO)(H)PO₂]. The bromide anion of [P_{8,8,8,8}]Br (10 g) was converted to hydroxide by mixing a [P_{8,8,8,8}]Br/water/methanol solution with anion exchange resin (Amberlite IRN 78). An excess amount of dimethyl phosphite relative to [P_{8,8,8,8}][hydroxide] (5 eq) was added. The resulting liquid was dried *in vacuo* and dissolved in dichloromethane. The solution was washed repeatedly with water. The dichloromethane layer was dried *in vacuo* at room temperature to yield [P_{8,8,8,8}][(MeO)(H)PO₂]. [P_{6,6,6,6}][(MeO)(H)PO₂] and [P_{6,6,6,14}][(MeO)(H)PO₂] were synthesised using the same method.

¹H NMR (600 MHz; DMSO-*d*₆; Me₄Si), δ = 6.88 and 5.95 (s, 1H, PH), 3.16 (d, J = 11.7 Hz 3H, POCH₃), 2.10–2.15 (m, 8H, PCH₂(CH₂)₆CH₃), 1.39–1.45 (m, 8H, PCH₂CH₂(CH₂)₅CH₃), 1.31–1.36 (m, 8H, P(CH₂)₂CH₂(CH₂)₄CH₃), 1.22–1.26 (m, 32H, P(CH₂)₃(CH₂)₄CH₃), 0.83 (t, J = 7.0 Hz, 12H, P(CH₂)₇CH₃). Synthesis was confirmed in the same way for the other samples.

Conflicts of interest

These are no conflicts to declare.

Acknowledgements

This research was supported in part by the COI program "Construction of next-generation infrastructure using innovative materials—Realization of a safe and secure society that can coexist with the Earth for centuries", which is supported by Ministry of Education, Culture, Sports, Science and Technology-Japan (MEXT) and Japan Science and Technology (JST), the Advanced Low Carbon Technology Research and Development Program (ALCA, No. JPMJAL1104) and the Cross-ministerial Strategic Innovation Promotion Program (SIP) of JST. This study was also partly supported by KAKENHI (18K14281 from the Japan Society for the Promotion of Science) and Leading Initiative for Excellent Young Researchers (from MEXT).

References

- K. J. Edgar, C. M. Buchanan, J. S. Debenham, P. A. Rundquist, B. D. Seiler, M. C. Shelton and D. Tindall, *Prog. Polym. Sci.*, 2001, **26**, 1605–1688.
- D. Klemm, B. Heublein, H.P. Fink, and A. Bohn, *Angew. Chem. Int. Ed.*, 2005, **44**, 3358–3393.
- T. Mekonnen, P. Mussone, H. Khalil, and D. Bressler, *J. Mater. Chem. A.*, 2013, **1**, 13379–13398.
- P. M. Kosaka, Y. Kawano, H. M. Petri, M. C. A. Fantini, and D. F. S. Petri, *J. Appl. Polym. Sci.*, 2007, **103**, 402–411.
- B.K. Kandola, A.R. Horrocks, D. Price, and G. V. Coleman, *J. Macromol. Sci. Part C Polym. Rev.*, 1996, **36**, 721–794.
- S.L. Levan, J.E. Winandy, *Wood Fiber Sci.*, 1990, **22**, 113–131.
- K. Xie, A. GaO, and Y. Zhang, *Carbohydr. Polym.*, 2013, **98**, 706–710.
- R. Stevens, S.Daan, Es. Van, R. Bezemer, and A. Kranenbarg, *Polym. Degrad. Stab.*, 2006, **91**, 832–841.
- B. Scharrel, *Materials*, 2010, **3**, 4710–4745.
- G.-L. Wei, D.-Q. Li, M.-N. Zhuo, Y.-S. Liao, Z.-Y. Xie, T.-L. Guo, J.-J. Li, S.-Y. Zhang and Z.-Q. Liang, *Environ. Pollut.*, 2015, **196**, 29–46.
- D. Aoki and Y. Nishio, *Cellulose*, 2010, **17**, 963–976.
- S. Marceneiro, Q. Hu, A. M. A. Dias, I. Lobo, I. Dias, E. Pinho, M. G. Rasteiro, and H. C. Sousa, *Ind. Eng. Chem. Res.*, 2014, **53**, 16061–16071.
- J. Wu, J. Bai, Z. Xue, Y. Liao, X. Zhou, and X. Xie, *Cellulose*, 2015, **22**, 89–99.
- X. Yang, N. Ge, L. Hu, H. Gui, Z. Wang, Y. Ding, *Polym. Adv. Technol.* **2013**, **24**, 568–575.
- R. Sonnier, L. Dumazert, S. Livi, T. K. L. Nguyen, J. Duchet-Rumeau, H. Vahabi, P. Laheurte, *Polym. Degrad. Stab.* **2016**, **134**, 186–193.
- H. Miyafuji and Y. Fujiwara, *Holzforschung*, 2013, **67**, 787–793.
- S. Han, J. Li, S. Zhu, R. Chen, Y. Wu, X. Zhang, and Z. Yu, *Bioresources*, 2009, **4**, 825–834.
- R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
- H. Wang, G. Gurau and R. D. Rogers, *Chem. Soc. Rev.*, 2012, **41**, 1519–1537.
- A. Brandt, J. Grasvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550–583.
- H. Ohno and Y. Fukaya, *Chem. Lett.*, 2009, **38**, 2–7.
- M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
- I. Kilpeläinen, H. Xie, A. King, M. Granstrom, S. Heikkinen and D. S. Argyropoulos, *J. Agric. Food Chem.*, 2007, **55**, 9142–9148.
- J. Song, H. Fan, J. Ma, and B. Han, *Green Chem.*, 2013, **15**, 2619–2635.
- K. Ohira, Y. Abe, M. Kawatsura, K. Suzuki, M. Mizuno, Y. Amano and T. Itoh, *ChemSusChem*, 2012, **5**, 388–391.
- H. T. Vo, Y. J. Kim, E. H. Jeon, C. S. Kim, H. S. Kim and H. Lee, *Chem. Eur. J.*, 2012, **18**, 9019–9023.
- A. Pinkert, K.N. Marsh, S.S. Pang, and M.P. Staiger, *Chem. Rev.*, 2009, **109**, 6712–6728.
- D.M. Suflet, G. C. Chitanu, and V. I. Popa, *React. Funct. Polym.*, 2006, **66**, 1240–1249.
- J. L. E. Campbell, K. E. Johnson, and J. R. Torkelson, *Inorg. Chem.*, 1994, **33**, 3340–3345.
- I. Šimkovic, and K. Csomorová, *Polym. Degrad. Stab.*, 2003, **80**, 519–523.
- W.D. Ellis, R.M. Rowell, S.L. Levan, R.A. Susott, *Wood Fiber Sci.*, 1987, **19**, 439–445.
- S. Suzuki, Y. Shibata, D. Hirose, T. Endo, K. Ninomiya, R. kakuchi, and K. Takahashi, *RSC Adv.*, 2018, **8**, 21768–21776.
- A. Granata, and D. S. Argyropoulos, *J. Agric. Food Chem.*, 1995, **43**, 1538–1544.
- T. Endo, S. Nemugaki, Y. Matsushita, Y. Sakai, H. Ozaki, Y. Hiejima, Y. Kimura, K. Takahashi, *Chem. Phys.*, 2016, **472**, 128–134.
- Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian, Inc., Wallingford CT, 2013.
- A. D. J. Becke, *Chem. Phys.*, 1993, **98**, 5648–5652.
- C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, B, 1988, **37**, 785–789.
- B. Miehllich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206.
- D. F. Parsons and B. W. Ninham, *J. Phys. Chem. A*, 2009, **113**, 1141–1150.
- T. Endo, H. Murata, M. Imanari, N. Mizushima, H. Seki, S. Sen, and K. Nishikawa, *J. Phys. Chem. B*, 2013, **117**, 326–332.