

Preparation of artificial wood films with controlled biodegradability

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ABSTRACT: Artificial wood films containing cellulose, xylan, and lignin were easily prepared by the dissolution of wood components in 1-ethyl-3-methylimidazolium acetate followed by reconstitution with distilled water. The composition and characteristics of wood films were highly controllable and predictable through the variation of the concentration of each component in the wood solution. The water vapor solubility of the wood films was increased when the xylan content was increased and the content of lignin was decreased. The biodegradability of the artificial wood films was investigated with cellulase from *Trichoderma viride*. The relative degradability of the wood film prepared with 5% cellulose and 5% lignin was 42%, whereas that of the wood film made with 5% cellulose and 5% xylan was 189%. The biodegradability of cellulose in the wood films correlated well with the content of xylan and lignin, and it was enhanced when the xylan content was increased and the content of lignin was decreased. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42109.

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INTRODUCTION

Composites are engineered materials made from two or more constituents with different physical and/or chemical properties.¹ Biopolymer-based composites have received considerable attention in the biomedical and environmental fields recently because of their inherent biocompatibility and biodegradability.² Biopolymers are naturally obtainable macromolecules, such as polysaccharides, polyphenols, polyamides, and proteins. However, the preparation of biopolymer-based composites remains challenging, as many biopolymers have low solubility in conventional solvents.³

Lignocelluloses, which include agricultural residues, waste paper, forestry waste, and energy crops, have long been recognized as sustainable sources of biopolymer-based composites.^{4,5} Lignocelluloses consist of three major biopolymers with distinct chemical, physical, and structural properties: cellulose, hemicellulose, and lignin. Cellulose, a linear polysaccharide of glucose residues linked by β -(1 \rightarrow 4)-glycosidic bonds, is the most abundant renewable biopolymer. The cellulose content in lignocelluloses ranges from 41 to 50%.⁶ Cellulose has excellent thermal stability, mechanical stability, and biocompatibility.⁷ Hemicelluloses are heterogeneous, branched polymers of pentoses, hexoses, and acetylated sugars, with xyans being the most predominant

hemicellulose. Hemicelluloses are as common as cellulose but have a lower molecular weight and a wood content of 25–35%.⁸ Lignin is an aromatic network polymer composed of phenyl propanoid units; this aids in binding cellulose and hemicellulose together. Lignin is more hydrophobic than cellulose and hemicelluloses and has a wood content of 18–35%.⁹ Although lignin is usually considered waste material, a number of studies on lignin applications have been published in recent years.^{10,11} For the preparation of lignocellulose-based materials, the development of solvents with a high lignocellulose-dissolving ability is important, as lignocelluloses are very difficult to handle because of their crystalline structure.

We previously reported the preparation of artificial wood composites containing cellulose, xylan, and alkali lignin with ionic liquids (ILs).^{3,12–15} ILs are organic salts that typically melt at temperatures below 100°C. Interest in ILs stems from their potential applications as green solvents due to their high thermal stability and nonvolatility.¹⁶ In chemical processes, ILs exhibit excellent physical characteristics, including the ability to dissolve polar and nonpolar organic, inorganic, and polymeric compounds and lignocellulosic biomasses.¹⁷ In our previous studies,^{3,14,15} three major wood components were fully dissolved in 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) and successfully reconstituted into various forms, including hydrogel,

thin film, and microfiber. Artificial wood films showed smoother surface textures, higher water resistance, and higher tensile strengths than cellulose films. In particular, tailor-made wood composites with controllable properties, including hydrophilicity/hydrophobicity, dielectric constant, cohesiveness, and light protection, could be prepared.³ A variety of additives, such as poly(ethylene glycol), multiwalled carbon nanotubes, porphyrin, and poly(3-octylthiophene), can be entrapped in artificial wood composites by simple dissolution or dispersion of the additives in the solution containing the three wood components.^{3,14,15} Artificial wood composites can offer great opportunities for the development of environmentally friendly and biocompatible materials.

For the application of artificial wood composites, their biodegradation behavior as either bulk materials or components in composites may have a significant influence on the properties and durability of wood composites. In addition, the study of the biodegradability behavior of various wood composites can also be helpful for understanding the problems in the saccharification of lignocelluloses. The efficient hydrolysis of cellulose in lignocellulosic materials is the most important issue in the biorefinery of lignocelluloses.¹⁷

In this study, we prepared various artificial wood films by changing the ratio of cellulose, xylan, and lignin. The influence of each component in the wood solution on the characteristics, such as the composition and water solubility of the prepared films, was first investigated. The biodegradability of various artificial wood films was studied with cellulase from *Trichoderma viride*. The trend and controllability of the wood film biodegradability were investigated. Statistical analysis was also used to predict the biodegradability of the artificial wood films.

EXPERIMENTAL

Materials

Microcrystalline cellulose, xylan from birch wood (>90% xylose residues by high-performance anion exchange chromatography), alkali lignin, [Emim][Ac], glucose, cellulase from *T. viride*, and hexokinase-based glucose assay kit were obtained from Sigma-Aldrich (St. Louis, MO). Citric acid, sulfuric acid, and KNO₃ were purchased from Samchun Pure Chemical (Gyeonggi-Do, South Korea).

Preparation of Artificial Wood Films

To prepare a basic cellulose solution, 5% w/w of cellulose was dissolved in 5 mL (5.14 g) of [Emim][Ac] under stirring at 80°C for 3 h. Various contents of xylan (1–5%) and alkali lignin (1–5%) were added to the 5% cellulose solution, and the mixtures were stirred again at 80°C for 2 h to prepare the wood solution. The wood solution was coated onto glass slides with 0.45 mm thickness with an applicator (micrometer film applicator/1117, Mitutoyo, Japan). The coated wood solution was maintained at room temperature for 10 min and was then washed with water to reconstitute the wood components. Washing was conducted three times, and the absence of [Emim][Ac] was confirmed by the measurement of the optical density of the washing solution at 211 nm. To prepare artificial wood films,

the obtained wood hydrogel was dried in a vacuum oven at 60°C for 24 h to remove residual water.

Surface Characterization of the Artificial Wood Films

Artificial wood films dried *in vacuo* were sputter-coated with gold. The surfaces of the samples were studied with a scanning electron microscope (JSM 6308; JEOL; Japan).

Compositional Analysis of the Artificial Wood Films

The cellulose and xylan contents in all of the samples were determined by quantitative saccharification after acid hydrolysis and subsequent high-performance liquid chromatography analysis based on National Renewable Energy Laboratory procedure number 002.^{17,18} The samples (150 mg each) were treated with 72% v/v sulfuric acid at 30°C for 3 h and then diluted acid (4%) at 121°C for 1 h. The hydrolyzed products were analyzed by high-performance liquid chromatography (Young-Lin model YL9100, Korea) equipped with a refractive-index detector and an Aminex HPX-87P column (Bio-Rad) operated at 85°C. The mobile phase consisted of deionized water with a flow rate of 0.6 mL/min. The cellulose and xylan contents were calculated from the glucose and xylose contents multiplied by conversion factors of 0.90 and 0.88, respectively.¹⁷ Acid-insoluble lignin after acid hydrolysis was measured as the mass of insoluble residue remaining. The acid-soluble lignin was measured with an ultraviolet–visible spectrophotometer at 205 nm with an extinction coefficient value of 110 L g⁻¹ cm⁻¹.¹⁸

Water Vapor Solubility of the Artificial Wood Films

Artificial wood films were dried at 60°C for a minimum of 24 h in a vacuum oven to remove any moisture inherently present in the films. To determine the water vapor solubility of a film, 100 mg of the artificial wood film was equilibrated over a saturated salt solution of KNO₃ [water activity (a_w) = 0.94] in closed vessels for 7 days at 25°C until no further water uptake was observed. The water vapor solubility of the films was calculated on the basis of the difference between the initial and final film weights.

Biodegradation of the Artificial Wood Films by Cellulase

Artificial wood films containing 10 mg of cellulose were prepared for hydrolysis by cellulase. Cellulase-catalyzed hydrolysis reactions were performed in 4-mL vials on a shaking incubator at 150 rpm and 37°C. The reactions were carried out with a cellulase concentration of 17 U/mL in 1 mL of 50 mM citrate buffer (pH 5.0). Samples (70 μ L) were periodically removed and boiled for 3 min to quench the enzymatic reaction. After centrifugation of the boiled samples, the glucose concentration was measured with a glucose assay kit. The relative degradability for the artificial wood films was defined as the relative activity of cellulase for hydrolysis of cellulose in artificial wood films when the activity of cellulase for pure cellulose film was set to 100%.¹⁷

RESULTS AND DISCUSSION

Preparation of the Artificial Wood Films

Various wood-component-based hydrogels containing microcrystalline cellulose, xylan from birch wood, and alkali lignin could be prepared by the dissolution of the wood components in [Emim][Ac] and then their reconstitution in distilled water.

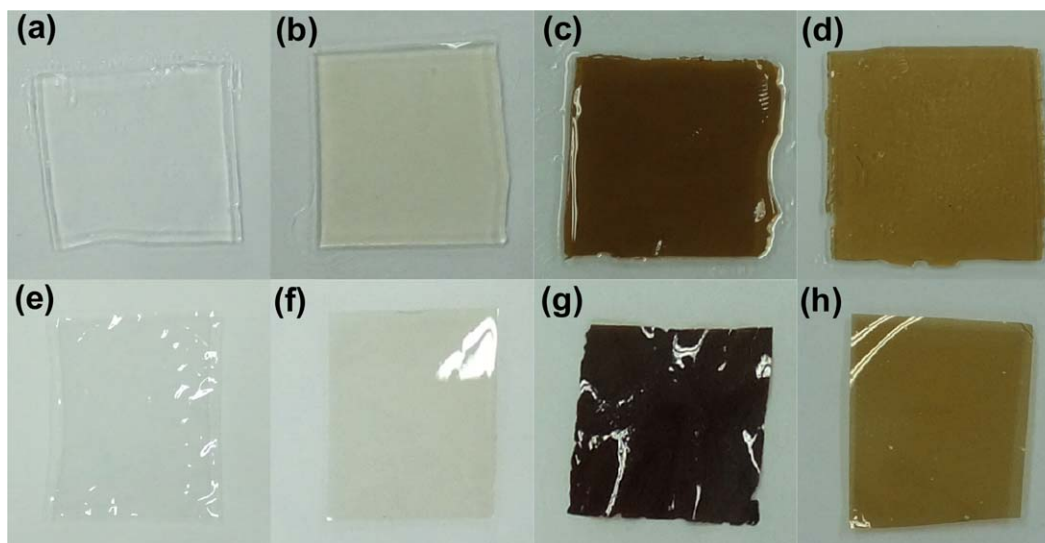


Figure 1. (a–d) Artificial wood hydrogels and (e–h) thin films with various compositions: (a,e) cellulose only, (b,f) cellulose/xylan (5/5 wt % in [Emim][Ac]), (c,g) cellulose/lignin (5/5 wt % in [Emim][Ac]), and (d,h) cellulose/xylan/lignin (5/3/2 wt % in [Emim][Ac]). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Transparent and flexible thin wood films were obtained by the drying of the hydrogels in a vacuum oven. Wood-component-based films containing cellulose, xylan, and alkali lignin are referred to as artificial wood films in this article.

Figure 1 shows the hydrogels and thin films of the artificial wood composites. Cellulose film [Figure 1(e)] was fully transparent, whereas the addition of xylan [Figure 1(f)] and lignin [Figure 1(g)] changed the color of the prepared films to slight yellow and brown, respectively. Neither pure xylan nor pure lignin could be reconstituted to hydrogel by dissolution with [Emim][Ac] and precipitation with distilled water because xylan is water soluble and lignin shows very low gel-forming ability.¹² However, when 3% xylan and 2% lignin were mixed with 5%

cellulose in [Emim][Ac], approximately 63 and 72% of xylan and lignin, respectively, were recovered in the prepared artificial wood hydrogel. Over 98% of cellulose was recoverable during the reconstitution process with water as an antisolvent. These results show that the strong gel-forming property of cellulose can aid in the preparation of wood-component-based artificial wood hydrogels.

Scanning electron microscopy images of various artificial wood films prepared by changes in the ratio of cellulose, xylan, and lignin are shown in Figure 2. The cellulose film [Figure 2(a)] had a slightly rougher surface than the cellulose/xylan/lignin (5/3/2) film [Figure 2(f)]. The surface of the cellulose film was smoothed by the addition of xylan [Figure 2(b)]. On the other

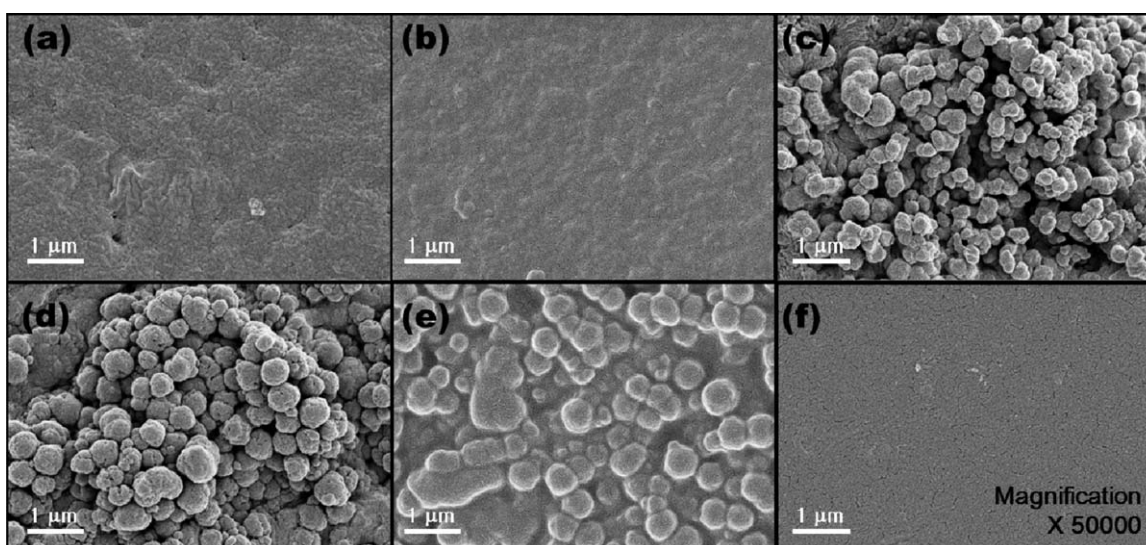


Figure 2. Scanning electron microscopy images of artificial wood films: (a) cellulose only, (b) cellulose/xylan (5/5 wt % in [Emim][Ac]), (c) cellulose/lignin (5/5 wt % in [Emim][Ac]), (d) cellulose/xylan/lignin (5/1/1 wt % in [Emim][Ac]), (e) cellulose/xylan/lignin (5/3/5 wt % in [Emim][Ac]), and (f) cellulose/xylan/lignin (5/3/2 wt % in [Emim][Ac]).

Table I. Compositions and Water Vapor Solubilities of the Artificial Wood Films

Biopolymer content in the wood solution the film	Composition of the prepared film				Total (%)	Water vapor solubility (%)
	Cellulose (%)	Xylan (%)	Acid-soluble lignin (%)	Residues (%) ^a		
Cel 5%	98.3	-	0.2	1.2	99.7	3.9
Cel 5% + Xyl 1%	80.8	7.9	0.7	4.7	94.1	4.7
Cel 5% + Xyl 2%	72.0	16.6	0.6	5.5	94.7	5.5
Cel 5% + Xyl 3%	64.3	24.3	0.6	5.0	94.2	7.1
Cel 5% + Xyl 4%	57.9	32.5	0.7	5.6	96.7	7.6
Cel 5% + Xyl 5%	50.7	41.9	0.6	5.5	98.7	9.3
Cel 5% + Lig 1%	81.0	-	0.7	14.6	96.3	3.5
Cel 5% + Lig 2%	75.8	-	0.7	20.3	96.8	2.9
Cel 5% + Lig 3%	69.6	-	0.8	26.6	97.0	2.6
Cel 5% + Lig 4%	61.6	-	0.9	35.3	97.8	2.2
Cel 5% + Lig 5%	58.4	-	0.9	38.3	97.6	1.2
Cel 5% + Xyl 1% + Lig 1%	72.6	12.4	0.7	10.1	95.8	3.6
Cel 5% + Xyl 1% + Lig 2%	65.0	10.8	0.8	14.9	91.5	3.3
Cel 5% + Xyl 1% + Lig 3%	61.5	10.0	0.9	22.3	94.7	2.5
Cel 5% + Xyl 1% + Lig 4%	55.8	7.8	0.9	29.7	94.2	1.9
Cel 5% + Xyl 1% + Lig 5%	54.9	7.1	1.1	36.4	99.5	1.4
Cel 5% + Xyl 3% + Lig 1%	62.4	23.6	0.7	9.1	95.8	6.1
Cel 5% + Xyl 3% + Lig 2%	58.8	22.1	0.8	16.2	97.9	5.3
Cel 5% + Xyl 3% + Lig 3%	55.3	19.7	0.8	22.3	98.1	4.8
Cel 5% + Xyl 3% + Lig 4%	52.3	16.8	0.9	28.9	98.9	3.7
Cel 5% + Xyl 3% + Lig 5%	46.3	14.9	0.8	32.4	94.4	3.3

Cel, cellulose; Xyl, xylan; Lig, lignin.

^aNonhydrolyzed compounds after sulfuric acid treatment. Most compounds were acid-insoluble lignin.

hand, precipitated lignin particles on the surface of cellulose were observed in the cellulose/lignin film [Figure 2(c)]. This surface heterogeneity of the cellulose/lignin film explained why the cellulose/lignin films became brittle with increasing lignin content.³ The heterogeneous surface of the cellulose/lignin film was made smoother by the addition of xylan [Figure 2(e)]. It is quite interesting that the cellulose/xylan/lignin film [Figure 2(f)] prepared with a ratio of 5/3/2 wt % in [Emim][Ac] showed the smoothest surface, as this ratio of each component is very similar to that in natural woods. In the previous study, the tensile strength of the cellulose/xylan/lignin (5/3/2) film was higher than those of the cellulose and functionalized cellulose films.³ The highest tensile strength of the cellulose/xylan/lignin (5/3/2) film could be understood by its smoothest surface morphology. Strong hydrogen bonding between cellulose, xylan, and lignin may have been the source of this improved tensile strength, as some hydroxyl groups of lignin are acidic and, therefore, prone to hydrogen-bonding interactions.

Composition of the Artificial Wood Films

To determine the effect of xylan and lignin on the artificial wood film composition, various films were prepared by changes in the contents of each component (Table I). The recovery yield of xylan and lignin was calculated from the compositions of the prepared

film. More than 98% cellulose was recovered from [Emim][Ac] solution in the form of hydrogel and thin films, as cellulose is completely immiscible in water. When xylan was added to the 5% cellulose solution to prepare the cellulose/xylan film, the composition of xylan in the reconstituted film ($c_{\text{xylan, film}}$; %) correlated well with the mass fraction of xylan among biopolymers in the [Emim][Ac] solution ($x_{\text{xylan, biopolymers in solution}}$; %). The content of xylan in total in the 15 films containing xylan ($n = 15$, where n is the number of films) was predicted well with the high coefficient of determination (r^2) value:

$$c_{\text{xylan, film}} = 0.744x_{\text{xylan, biopolymers in solution}} - 0.605 \quad (1)$$

$$(n = 15, r^2 = 0.933)$$

When the lignin was added to the 5% cellulose solution to prepare the cellulose/lignin film, the composition of total lignin (sum of acid-soluble lignin and residues) in the reconstituted film ($c_{\text{total lignin, film}}$; %) also correlated well with the mass fraction of lignin among the biopolymers in the [Emim][Ac] solution ($x_{\text{lignin, biopolymers in solution}}$; %):

$$c_{\text{total lignin, film}} = 0.788x_{\text{lignin, biopolymers in solution}} + 0.194 \quad (2)$$

$$(n = 15, r^2 = 0.948)$$

These results clearly show that the recovery yields of xylan and lignin in the reconstituted thin film were highly dependent on

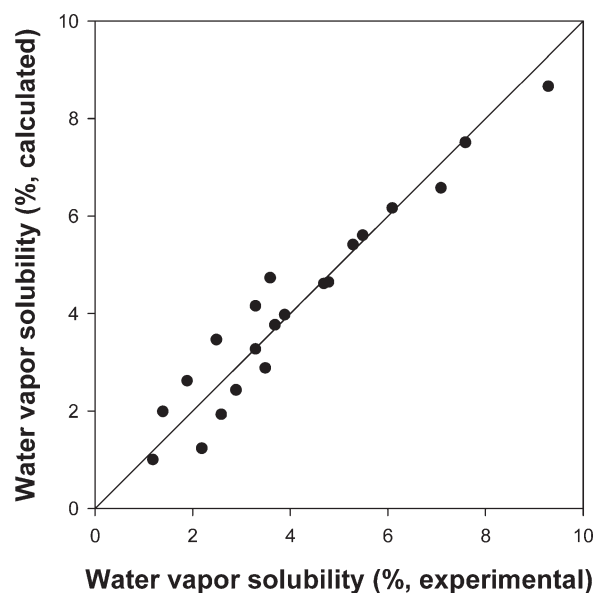


Figure 3. Measured and calculated water vapor solubility of artificial wood films.

the concentration of xylan and lignin in the film-forming solution.

Water Vapor Solubility of the Artificial Wood Films

The water vapor solubility of artificial wood films can highly influence the activity of cellulase, as cellulase acts under aqueous conditions. The water vapor solubilities of various wood films were determined under controlled a_w ($a_w = 0.94$) by saturated KNO_3 . When the water vapor solubility was correlated with the composition (percentage) of wood components, the r^2 values for cellulose, xylan, acid-soluble lignin, residues, and total lignin with the water vapor solubility (S_w) were 0.007, 0.762, 0.267, 0.573, and 0.571, respectively. The effect of the cellulose content in the film on the water vapor solubility was very weak. The most important component determining the water solubility of

wood films was xylan. Additionally, the water vapor solubility of films was highly predictable by linear regression with two parameters ($c_{\text{xylan, film}}$ and $c_{\text{total lignin, film}}$) with an r^2 value of 0.926 [eq. (3)]. Figure 3 shows the correlation between the measured and calculated water vapor solubilities of the artificial wood films:

$$S_w = 4.07 (\pm 0.37) + 0.12 (\pm 0.01) c_{\text{xylan, film}} - 0.08 (\pm 0.01) c_{\text{total lignin, film}} \quad (n = 21) \quad (3)$$

This equation clearly shows that increased xylan and total lignin contents in the films could increase and decrease, respectively, the water vapor solubility of the films.

Biodegradability of the Artificial Wood Films by Cellulase

The artificial wood films could be degraded by cellulase, as shown in Figure 4. The relative degradability of the wood film was significantly increased by the addition of xylan to a solution of 5% cellulose. The relative degradability was increased by approximately 17% per 1% addition of xylan ($n = 6$, $r^2 = 0.99$). The relative degradability of the cellulose/xylan film prepared with a 5/5 wt % solution was 189% higher than that of film containing only cellulose. On the other hand, the addition of 1% lignin to the 5% cellulose solution significantly decreased the relative degradability of the cellulose/lignin film up to 65%, and the relative degradability was gradually decreased by the addition of more lignin at a ratio of approximately 5.5% per 1% addition of lignin ($n = 5$, $r^2 = 0.99$). The relative degradability of the cellulose/lignin film prepared with a 5/5 wt % solution was 42% lower than that of the cellulose-only film. The addition of 1% lignin to the 5/1 or 5/3 wt % cellulose/xylan solution did not change the relative degradability of the prepared wood films. The addition of more than 2% lignin to the 5/1 and 5/3 wt % cellulose/xylan solutions gradually decreased the relative degradability at rates of 12 and 16% per 1% addition of lignin, respectively ($r^2 = 0.99$). When the relative degradability of the wood film was correlated to the wood-component content in the film, the r^2 values for cellulose, xylan, acid-soluble lignin, residues, and total lignin with relative

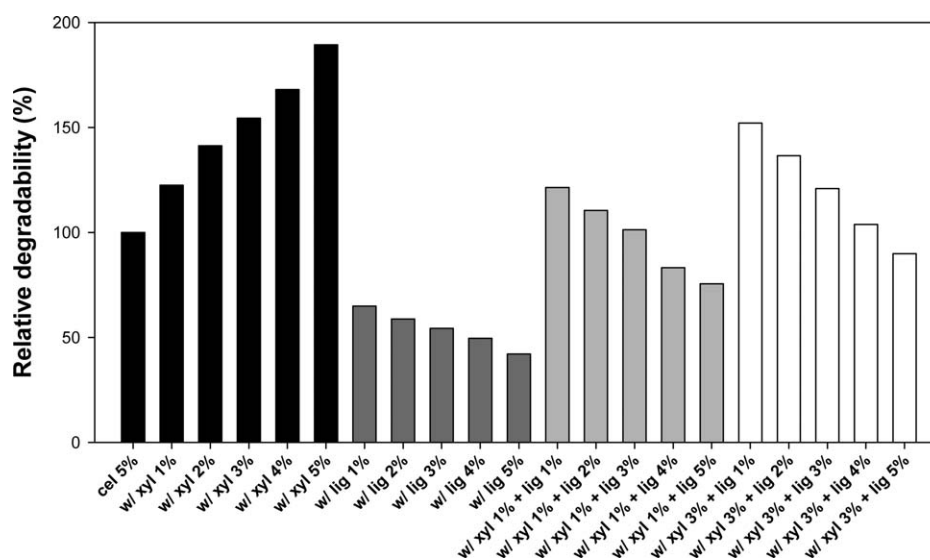


Figure 4. Relative degradability of the artificial wood films by cellulase.

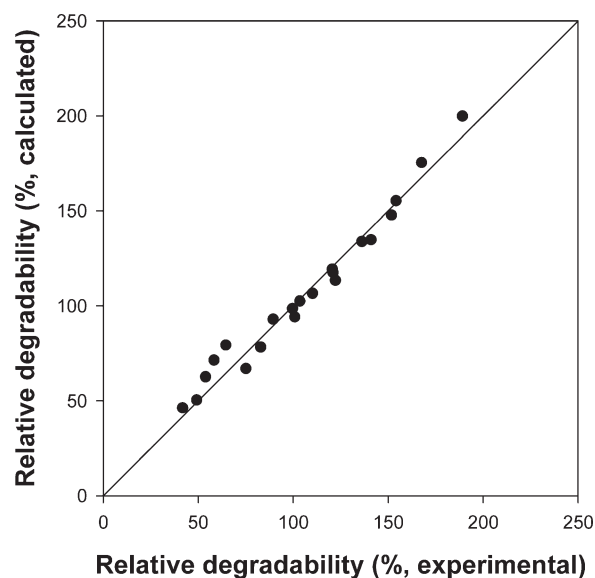


Figure 5. Measured and calculated relative degradability of the artificial wood films.

degradability were 0.026, 0.838, 0.160, 0.551, and 0.546, respectively. The effect of the cellulose content in the films on the relative degradability was very weak. The most important component determining the relative degradability of the wood films was xylan. Additionally, the relative degradability of the films ($D_{\text{cellulase}}$) was highly predicted by linear regression with two parameters ($c_{\text{xylan, film}}$ and $c_{\text{total lignin, film}}$) with an r^2 value of 0.971 [eq. 4]. Figure 5 shows the correlation between the measured and calculated $D_{\text{cellulase}}$ values:

$$D_{\text{cellulase}} = 100.19 (\pm 4.50) + 2.57 (\pm 0.16)c_{\text{xylan, film}} - 1.38 (\pm 0.15)c_{\text{total lignin, film}} \quad (n = 21) \quad (4)$$

This equation clearly shows that the contents of xylan and total lignin in the prepared wood films increased and decreased, respectively, the $D_{\text{cellulase}}$ values.

The enhancing effect of xylan on the cellulase activity for cellulose in the artificial wood films may have been caused by the highly increased hydrophilicity of the films. As described previously, the water solubility of cellulose-based wood films is an important factor in determining the relative degradability of the films by cellulase because cellulases act under aqueous conditions. $D_{\text{cellulase}}$ correlated well with the water vapor solubility of the film at an r^2 value of 0.839 ($n = 21$). Generally, the biodegradability of the films increased with increasing water vapor solubility of films. Xylan was the most important factor in determining the water vapor solubility of the artificial wood films [eq. (3)]. Therefore, the xylan-induced increased biodegradability of the artificial wood film may have been caused by the increased water vapor solubility of the wood film. In recent, Kumar and Wyman¹⁹ reported that xylan and its oligomers inhibited cellulase activity. However, in this study, the increased hydrophilicity of the artificial wood films by the addition of xylan was a more influencing factor in the determination of the biodegradability of the films. On the other hand, inhibitory effect of lignin on the cellulase activity is well known.²⁰ The

presence of lignin in an artificial wood film may have inhibited the cellulase activity, although the structure of wood film containing lignin was physically more brittle than that of the cellulose film. The inhibitory effect of lignin on the cellulase activity could be overcome by an increase in the xylan content in the artificial wood films. These results show that the biodegradability of the artificial wood film could be easily controlled through the adjustment of the content of each wood component.

CONCLUSIONS

Artificial wood films containing various ratios of cellulose, xylan, and alkali lignin were prepared simply with [Emim][Ac]. The xylan and lignin content significantly changed the hydrophobicity and biodegradability of the artificial wood films. The composition, water vapor solubility, and biodegradability of the prepared films were highly predictable by multiparameter linear equations. The extremely controllable properties of the artificial wood films add to their potential as basic materials for environmental, biomedical, and bioelectronic fields.

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