Non-flammable and Moisture-permeable UV Protection Film Only from Plant Polymer and Clay Mineral

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Complete List of Authors:	Shikinaka, Kazuhiro; National Institute of Advanced Industrial Science and Technology, Research Institute for Chemical Process Technology Nakamura, Masaya; Forestry and Forest Products Research Institute, Navarro, Ronald R.; Forestry and Forest Products Research Institute Otsuka, Yuichiro; FFPRI, Biomass Chemistry

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Kazuhiro Shikinaka,*[a] Masaya Nakamura, [b] Ronald R. Navarro[b] Yuichiro Otsuka[b]

Here, we propose a novel technique that combines the lignin nanoparticles and clay minerals into transparent, non-flammable and moisture-permeable UY protection films without requiring a petroleum-based component. The preparation process is entirely free of hazardous chemicals. The film's function can be tuned by varying the botanical origin of lignin.

Departure from petroleum-based materials science is vital to sustainable social and economic development.[1] Plant polymers, polysaccharides, and lignin are promising alternatives to petroleum resources.[2] Lignin is particularly promising for composite functional materials production, as its physical and chemical properties are uniquely adapted to the structural, defensive, and water transport functions in plants. However, the lignin in functional materials production has usually been chemically reacted during the extraction process, which modifies its native properties. Furthermore, lignin is usually combined with petroleum-based compounds to create a variety of composite products such as heatproof fillers.[3,4]

Here, we present a novel technology that combines non-deteriorated lignin and clay minerals[5] into all-natural film composites, without requiring a petroleum-based component. The self-standing thin film was obtained through a simple one-step procedure involving knife-casting of lignin mixed with water-dispersed natural clay minerals. The produced film exhibits an excellent UV protection property (UVA transmittance 1.2%) and is highly non-flammable (class V-0 in the UL94 standard). Of equal interest from a durability perspective, the optical and physical properties of lignoclaist depend on the plant species from which the native lignin was extracted. The lignoclaist production process will not only enable the industrial utilization of plant and mineral resources as novel alternatives to petroleum compounds but will also promote research on plant biomass functions, which can impart important properties to composite materials.

[a] Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Nigatake, 4-2-1, Miyagino-ku, Sendai 983-8551, Japan, E-mail: kaz.shikinaka@aist.go.jp.
[b] Forestry and Forest Products Research Institute, Matsunosato, 1, Tsukuba 305-8687, Japan.
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Claist® is a thin film consisting of platelet clay mineral and organic polymer. The densely stacked platelets of clay mineral confer various functionalities, such as high gas-barrier capacity.[6] Recently, thin films consisting of clay mineral, poly(ethylene glycol)-modified lignin, and a petroleum-derived synthetic cross-linking reagent have been prepared by the claist® fabrication process.[7] The opaque, deep-black color of the film is attributable to the lignin derivative obtained through acid-catalyzed solvolysis. Furthermore, the product is estimated a poor flame retardant owing to the presence of poly(ethylene glycol) and organic cross-linking reagent. Additionally, the preparation process of the film is not eco-friendly due to need of treatment by organic solvent and long-time ignition.

Using the claist® fabrication technique, we attempt to create an all-natural (clay mineral and plant polymer only) thin film with novel functionality. To achieve this task, non-deteriorated lignin prepared by simultaneous enzymatic saccharification and comminution (SESC) of plant biomass that we have previously developed[8] was added as a component. SESC-prepared lignin is a nano-particulate colloid platelet that disperses in water and is miscible in other solid components such as synthetic polymers.[9]

In this work, we found that SESC-prepared lignins from Japanese cedar and rice straw (hereafter denoted as cedar and straw, respectively, for simplicity) were also finely miscible with clay minerals such as Li^+ montmorillonite (MMT; natural smectite) in a water dispersion. After water evaporation from a knife-casted mixture of SESC lignin and clay mineral, a self-standing thin transparent film is formed (Fig. 1). This film is easily penetrated by moisture vapor because the clay mineral (smectite) is hydrophilic.[10] During thermal heating, the Li^+ MMT becomes hydrophobic by the Hoffman–Klemen effect.[11,12] which defines the partial migration of interlayer Li^+ ions within the Li^+ MMT silicate sheets. Consequently, the number of hydrous ions is reduced, and the film is waterproofed. In this specific case, annealing at 150 °C for 2 h produced a film (termed *lignoclaist*) that remained un-swollen after 2 months in pure water. Contact angle of lignoclaist (Table 1) is smaller than 90° that indicates a hydrophilic nature of lignoclaist despite of its waterproof character. Although lignoclaist can also be produced from synthetic smectite (*e.g.*, Li^+ stevensite and saponite), the resulting materials are very brittle because synthetic smectite particles are smaller than their natural

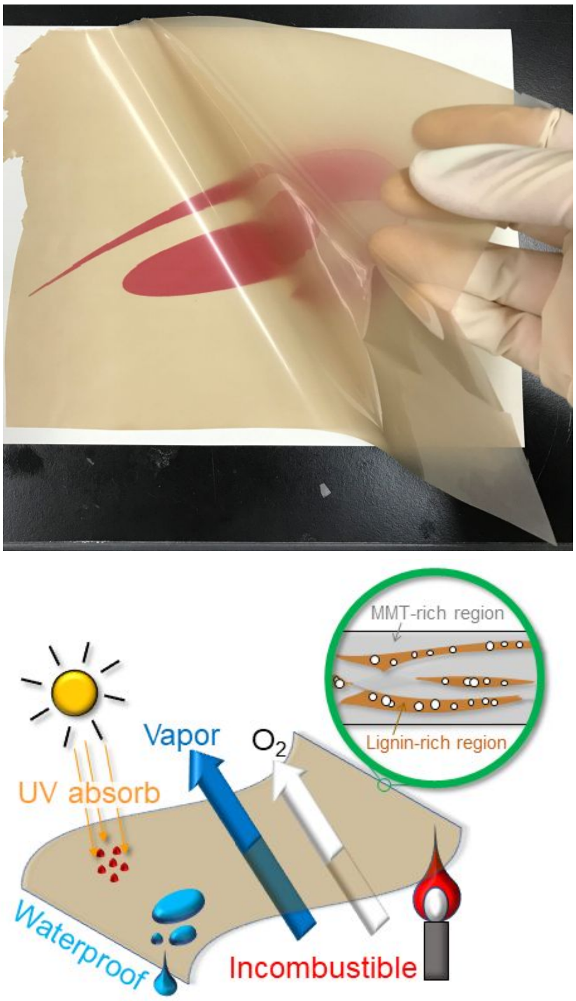

Fig. 1 (a) Photograph of typical lignoclaist with approx. A4-paper size prepared from clay mineral and straw lignin (Li^+MMT:SESC lignin = 8:2 w/w%). (b) Schematic of the structure and functionalities of lignoclaist. In the thin transparent film, SESC lignin (20 wt.%, diameter several tens of nm[9]) and Li^+MMT platelets (80 wt.%, diameter several μm[6]) form layered structure in that there are many holes on the lignin's layers.

counterparts. Therefore, self-standing transparent thin films cannot be formed from synthetic smectite.

Lignoclaist exhibits various attractive properties for industrial application. First, despite its transparency, its UV-blocking ability is excellent (56% of total light transmittance (TL-T)); second, the film is extremely thin (26 μm). The UVA and UVB transmittances (UVA-T and UVB-T, respectively) of lignoclaist prepared from straw lignin are 1.2% and 0%, respectively. Therefore, lignoclaist is an excellent UV protection film for living organisms and material protection. The low UV transmittance is attributable to the phenols, ketones, and other chromophores in the polyphenol structure of the lignin component.[13–15] In fact, lignoclaist (even in the thin-film state) offers stronger UV protection than other lignin-and/or petroleum-based materials,[16–20] probably because the SESC process preserves the UV-blocking functional groups of natural lignin, whose UV-blocking property surpasses that of petroleum-derived materials. The aparition of radicals by terminal decomposition[21] maybe help to increase the UV protection property of lignoclaist. The high UV-blocking property is important for eco-friendly UV protection mulch for the agricultural industries.

Natural lignin is non-flammable owing to its non-thermally decomposable phenolic framework.[22] Furthermore, the guaiacol groups in lignin scavenge the radicals such as formed by thermal decomposition of the polymer.[23] Consequently, SESC lignin acts as an excellent heatproof filler in synthetic polymers,[9] and lignoclaist is expected to offer comparable thermal stability. The flame retardant grade of lignoclaist is V-0 in the UV94 standard, similar to that of ordinary engineering plastics (*e.g.,* the fluorocarbons and poly(vinyl chloride)), so lignoclaist is a suitable house-construction material. It must be emphasized that lignoclaist is naturally non-flammable and requires no additional halogen or phosphorus compounds. Furthermore, in ordinary claist®, non-flammability is conferred only by the special combination of clay mineral and synthetic polymer.[24]

Lignoclaist also readily transmits moisture and gas. The moisture vapor transmission rate (MVTR) and oxygen transmission rate (OTR) of lignoclaist composed of Li^+MMT and SESC-prepared cedar lignin (molar ratio 8:2) are 873 g m^{-2} day^{-1} and 406 cm^3 m^{-2} day^{-1} atm^{-1}, respectively, much higher than those of ordinary claist®[6] used as a gas-barrier film. The high moisture/gas transmittance is attributable to the porous structure of SESC-lignin rich layers in the lignoclaist which was revealed by transmission electron microscopic (TEM) image (Fig. 2). From TEM image and X-ray diffraction results (Fig. S1), Li^+MMT clay

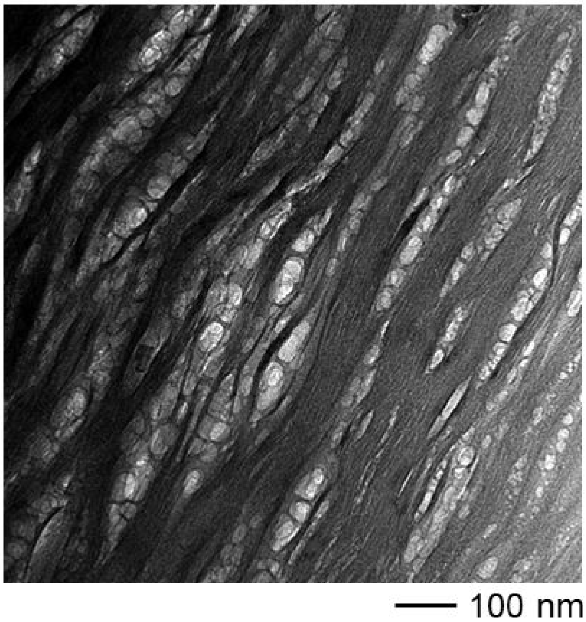

Fig. 2 Typical TEM image of lignoclaist prepared from clay mineral and cedar lignin (Li^+MMT:SESC lignin = 8:2 w/w%). In TEM image, black layered part and grey amorphous part are aggregation of Li^+MMT platelets and SESC lignin, respectively. There are many holes in the aggregated part of SESC lignin that induces the high moisture/gas transmittance of lignoclaist. SESC lignin itself can form inhomogeneous film by cast drying of its water dispersion. In the lignoclaist, layers of clay platelets support homogeneous film formation of SESC lignin.

Table 1 Physical properties of lignoclaist consisting of SESC lignin extracted from cedar or straw (Li^+MMT:SESC lignin = 8:2 w/w%).

	Thickness [μm]	Contact Angle (°)	TL-T [%]	Haze [%]
Cedar	24	42.7	56	41
Straw	26	58.7	56	57

	UVA-T [%]	UVB-T [%]	Flame retardant grade	MTVR [g m^{-2} day^{-1}]
Cedar	2.0	0	V-0	873
Straw	1.2	0	V-0	1092

	OTR [cm^3 m^{-2} day^{-1} atm^{-1}]	Mandrel bent radius [mm]	Young's modulus [GPa]
Cedar	406	1	1.29
Straw	52.8	< 1	0.77

	Fracture or yield stress [MPa]	Fracture or yield strain [%]
Cedar	480 (Fracture)	6 (Fracture)
Straw	423 (Yield)	105 (Yield)

platelets and SESC lignin nanoparticles are mainly formed separate layers in the lignoclaist. Furthermore, SESC lignin-rich layers have many nano-sized pores that causes the high moisture/gas transmittance properties of the lignoclaist. The high MVTR and OTR values are important for realizing breathable, waterproof lignoclaist materials for the housing and textile industries. Additionally, the coexistence of porous structure and waterproof nature encourages utilization of lignoclaist for battery separator. The ordinary claist® have never exhibited transmitting of moisture and gas, *i.e.,* that have been used as functional film with high gas barrier properties.[6] Therefore, the lignoclaist also shows a new departure for material utilization of claist®.

The lignoclaist is consisted of only clay mineral and SESC lignin. The preparation procedure of claist® by other lignin derivatives such as poly(ethylene glycol)-modified lignin[7] and alkaline lignin[25] needed additional toxic reagents (*e.g.,* organic cross-linker and organic solvent). Furthermore, as mentioned above, these claist® showed moisture/gas barrier properties that are given by dense multilayered parallel stacking structure of clay minerals.[7] Thus, the high moisture/gas transmittance nature of lignoclaist is totally specific property relative to ordinary claist®.

The contact angle, UV transmittance, MTVR, OTR, Mandrel bent radius, and tensile mechanical properties of lignoclaist depend on the botanical origin of the SESC lignin. The physical characteristics of lignoclaist consisting of SESC lignin extracted from cedar and straw are listed in Table 1. Mandrel bent radius of lignoclaist is smaller than that of previous claist® consisting of poly(ethylene glycol)-modified lignin.[7] The mechanical strength (*i.e.,* mandrel bent radius, Young's modulus, and fracture/yield stress/strain) of lignoclaist differs depending of botanical origin of SESC lignin. The lignoclaist consisting of SESC lignin extracted from cedar was fractured at 6% of strain, by contrast, the lignoclaist consisting of SESC lignin extracted from straw did not exhibit clear fracture point under our experimental condition. The tensile fracture stress of lignoclaist is close to that of nanocellulose/platelet clay composites with excellent mechanical properties.[26] Furthermore, the UVA-T of lignoclaist from SESC lignin extracted from straw (1.2%) is smaller than that from SESC lignin extracted from cedar (2.0%). According to previous literature,[27] the monomer composition of lignin (*i.e.,* the molar ratio of guaiacol (G), syringol (S), and phenol (P)) differs among plant species. Although lignin extracted from cedar is almost a homopolymer of vanillin (G:S:P = 1.00:0.00:0.05), lignin extract from straw is a copolymer of all three monomers (G:S:P = 1.00:0.67:0.52).[27] Furthermore, lignin extracted from straw possesses *p*-coumarate esterified[28] and tricin units,[29] that is, conjugated double bonds, that spread the conjugate system[30] through the lignin framework.[31] The wider spread of the π-conjugated system in the phenolic lignin framework of straw, enabled by the additional conjugated double bonds and the more variable bonding patterns between the monolignols, should increase the UV adsorption of the lignoclaist prepared from this material. Other literatures have denoted that the physical properties (*e.g.,* the electrical property[32]) of lignin derivative are determined only on their extraction procedures (*e.g.,* kraft pulping and alkaline cooking) and are independent of plant species. However, the plant species appear to dictate the properties of SESC lignin, possibly because the mild extraction process preserves the original and unique characteristics of the native lignin materials. Indeed, by studying the properties of SESC lignin, we could better understand how their true structures relate to their varied functions in plant tissues.

Conclusions

In conclusion, we have developed an all-natural functional thin film called "lignoclaist" only from components of mineral and plant. The product was prepared by an environmentally friendly process, that is, by purification and mixing of mineral and plant components without hazardous petroleum-derived chemicals.[8,33] Lignoclaist exhibits various novel functions such as excellent UV protection, non-flammability, and moisture/gas transmittancy. The optical and physical properties of lignoclaist depend on the plant species of the extracted SESC lignin component and largely reflect the structural characteristics of the plant lignin.

Lignoclaist production would not only encourage the utilization of mineral and plant components as high-value industrial materials (*e.g.,* non-flammable UV protection agricultural film) but would also reduce the environmental load of extracting limited petroleum-based resources. Ultimately, the replacement of petroleum-based resources with natural resources is expected to establish a novel field of "Agricultural Industry".

Conflicts of interest

There are no conflicts to declare.

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We propose transparent, non-flammable sunscreen films consisting of only lignin and clay minerals without petroleum-based hazardous components.