Supporting Information

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

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Experimental Section

Chemicals: Li^+ MMT (Kunipia M by Kunimine Industries Co., Ltd., Japan; cation exchange capacity = 99.8 meq per 100 g; layer distance = 1.23 nm), was used as purchased (20 w/w% of hydrogel). The SESC-prepared lignin was extracted from Japanese cedar and rice straw as platelet-like nanoparticles of approximate diameter 40 nm. The extraction method is reported in our previous literature.[S1,S2] Ultrapure water, purified in a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany), was used throughout the study.

Preparation of lignoclaist: Lignoclaist was prepared as follows: 40 g of Li^+ MMT hydrogel was dispersed in 105.4 g of ultrapure water in a homogenizer operated at 6,000 rpm for 15 min. The SESC-prepared lignin water dispersion at a certain concentration was dropped into the Li^+ MMT dispersion while stirring. The stirring was continued for 25 min. The stirred mixture was cooled at room temperature for 30 min and then mixed at 2,000 rpm for 5 min using a planetary centrifugal mixer (ARE-250 Thinly Co., Ltd., Japan). Finally, the mixture was passed through a sieve with a 53 μm mesh and then degassed at 2,200 rpm for 10 min, again using a planetary centrifugal mixer. The resultant gel-like mixture was cast onto a polyethylene terephthalate (PET) sheet by a film-casting knife (of clearance gap 0.6 mm) and dried in ambient conditions for approximately 1 day. The dried films were removed from the PET sheet and then annealed at 150 °C for 2 h, yielding the lignoclaist product.

Measurement of surface properties: The contact angle was measured by an automatic contact angle gauge equipped with SmartContact analysis software (Smart Contact PRO 100, Excimer Inc., Japan), according to the tangent method.

Measurement of optical properties: The total light transmittance and haze value were measured by a haze meter (NDH5000, Nippon Denshoku Ind. Co., Ltd., Japan). The transmittance at 200–800 nm was estimated in a UV–vis spectrophotometer (U-2910, Hitachi High-Technologies, Co., Japan). The average UVA and UVB transmittances were estimated within the 315–400 and 290–315 nm ranges, respectively, according to AS/NZS4399. (The average UVB transmittance of all samples was 0%.)

Measurement of thermal properties: The thermo-gravimetric (TG) analysis was conducted by a Rigaku Thermo plus EVO2 TG8121 system heated at 10 °C min^{-1} under a nitrogen atmosphere. The flame retardance was estimated by the 20 mm vertical burning test, according to the UL-94 vertical method following the ISO 1210 protocol.

Measurement of moisture/gas transmittance properties: The moisture vapor transmission rates (MVTRs) were estimated by the gravimetric (dish) method according to ISO 2528. The oxygen transmission rates (OTR) were measured at 40 °C and 90 RH% by a coulometric oxygen permeability measuring apparatus (OX-TRAN 2/22L, Mocon Inc., USA), following the ISO 15105-2 protocol.

Measurement of mechanical properties: To elucidate the flexibility, Mandrel tests were conducted by the TQC Cylindrical Bend Test using the 100MM INCL MANDREL Set (IMPERIAL) in accordance with ISO 1519. The tensile stress–strain curves were obtained by a JTT LSC-005/30 type tensile tester (Tokyo Koki Testing Machine Co., Ltd., Japan).

Transmission electron microscopy (TEM): TEM observation were performed using a JEM-2100F (JEOL, Tokyo, Japan) at an acceleration voltage of 200 kV. The ultrathin sample of film (~ 100 nm) was prepared by argon ion milling using an ion slicer (EM-09100IS, JEOL). The digital TEM data were obtained using a slow-scan charge-coupled device (CCD) camera

(Gatan USC1000XP, Gatan Inc.) and converted into images with a frame size of 1024 × 1024 pixels.

Measurement of X-ray diffraction: The X-ray diffraction (XRD) patterns were collected using a Rigaku Smart Lab X-ray diffractometer with Cu Kα radiation, a Cu Kβ filter, a 2.5° Soller slit, and a non-reflecting rotation stage. The collected count range was 2θ = 2–20° in 2θ increments of 0.02°.

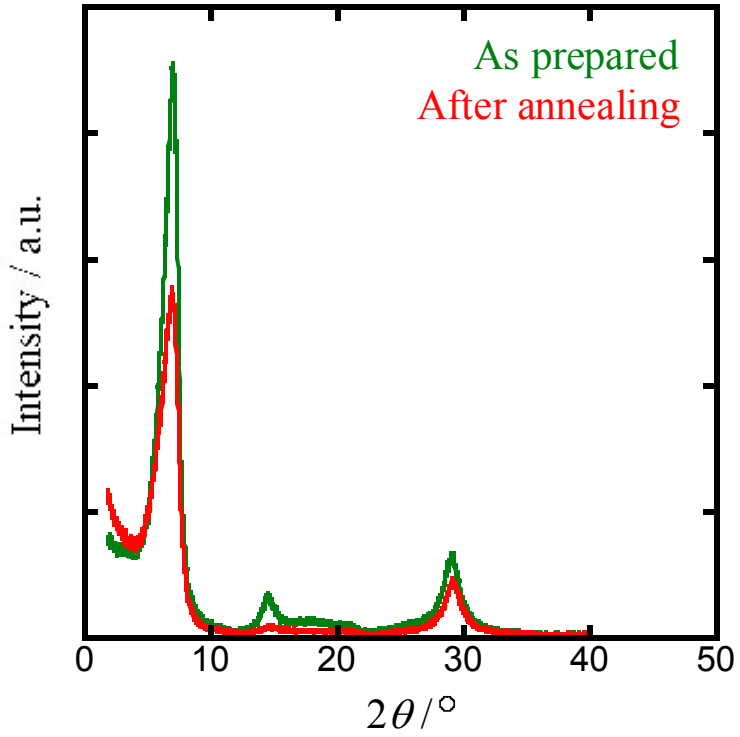

Fig. S1. X-ray diffraction (XRD) pattern of typical clay–lignin thin film (as prepared from straw) and lignoclaist film (after annealing at 150 °C for 2 h). Li^+MMT:SESC lignin from straw = 8:2 w/w%. In ordinary claist®, heat annealing aggregates the Li^+MMT in the claist® and then reduces the charge in Li^+MMT.[S3] Consequently, the lowest 2θ peak (the basal (001) reflection of the Li^+MMT in claist®) shifts to a smaller 2θ region. However, as shown in this figure, the lowest 2θ peak of lignoclaist is not shifted after heat annealing, indicating the emergence of ion-deficient layers between the Li^+MMT due to migration of Li^+ ions. Thus, the SESC-prepared lignin nanoparticles with diameters of several tens of nm[S2] don't insert between the Li^+MMT platelets with diameters of several μm. As shown in TEM image (Fig. 2), the Li^+MMT platelets and SESC-prepared lignin nanoparticles form layered structure individually in the lignoclaist.

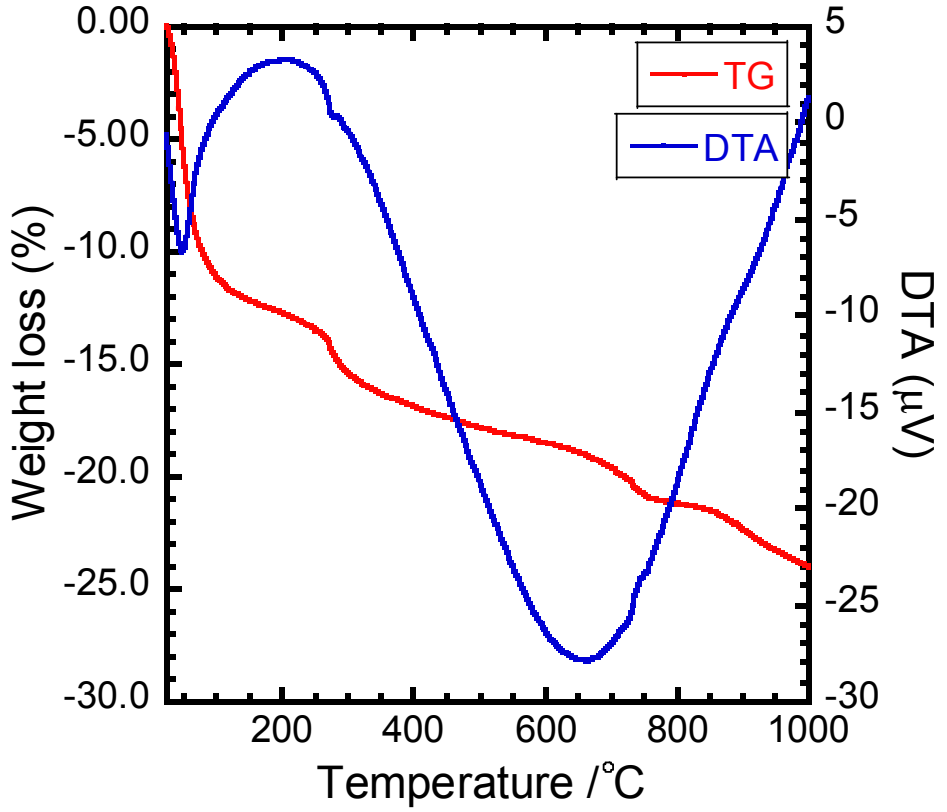

Fig. S2 TG result of typical lignoclaist (Li^+MMT:SESC lignin from straw = 8:2 w/w%).

REFERENCES

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