Electronic Supplementary Information

Fabrication of biological cushioning materials with natural wood structure by an ionic liquid-based sustainable chemistry approach

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Materials and methods

Materials

Test pieces (15, 15, and 5 mm in the tangential, radial, and longitudinal directions, respectively) were prepared from *Cryptomeria japonica* (*C. japonica*) D. Don planted and undertook by Kyushu University Kasuya Research Forest in Japan. We obtained a permission from Kyushu University Forest, and collected experiment specimens in accordance with relevant guideline and legislation. Identification of these specimens was carried by Hiroki Sakagami. No voucher specimen in this study was collected and deposited in a publicly available herbarium. These specimens were successively cut from an air-dried long stick sample more than 40 cm in length in the fiber direction of the sapwood to ensure similar growth ring structures for all specimens. The growth rings of the specimens were parallel and perpendicular to the radial and tangential surfaces, respectively. We evaluated fifteen clear specimens selected from a total of 43 specimens obtained from a long stick to eliminate the defective specimens such as knots or cracks. The average density under air-dried conditions was 400 kg m^{-3} (standard deviation: 9.5 kg m^{-3}). The IL used in this study was 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) (≥ 95 %), which was purchased from Sigma-Aldrich Co. LLC, Japan. An aqueous solution of [BMIM][OAc] was prepared by dilution to 30 wt% using distilled water. The IL concentration was determined by the cell wall volume ratio calculated from the density and specific gravity of *C. japonica*.

ESW preparation

As a first step, test pieces kiln-dried at 105 °C for 24 h were saturated with 30 wt% [BMIM][OAc] aqueous solution. This was achieved by repeatedly submerging the pieces in their respective solutions under atmospheric and vacuum conditions (ca. 1.3×10^3 Pa) for four days until no air bubbles emerged from the pieces under vacuum conditions. Subsequently, the [BMIM][OAc] aqueous solution-saturated test pieces were heated at 105 °C for 48 h after 24 h of drying at room temperature. The prepared ESW specimens were conditioned at 20 °C and 60 % relative humidity for 24 h before compression testing.

Specimen preparation for comparative experiments

Air-dried control specimens were prepared by kiln-drying of the test pieces at 105 °C for 24 h. Those were conditioned at 20 °C and 60 % relative humidity for 24 h prior to compression testing. In the same way as the ESW preparation, water-absorbed specimens were prepared, but the distilled water, not [BMIM][OAc] aqueous solution, was used for the process. The resulting water-absorbed specimens were immediately subjected to compression tests.

Compression test

All specimens were compressed in the radial direction with a universal testing machine (AG-110kN, Shimazu, Kyoto, Japan). Specimens were compressed by different two methods: at a speed of 2 mm min^{-1} until 1000 N of compression force; and at a speed of 2 mm min^{-1} until 50 % of the original radial length. The radial length of the specimens during compression was calculated from the crosshead position of a universal testing machine. The radial length of the specimen was measured after the

compression force was removed. The compression ratio and retention were calculated using Eqs. (1) and (2), respectively.

$$\text{Compression ratio (\%)} = (R_0 - R) / R_0 \times 100 \quad (1)$$

where R_0 and R are the radial lengths of specimens before and after compression, respectively, calculated from the crosshead position.

$$\text{Retention of radial length (\%)} = R_f / R_0 \times 100 \quad (2)$$

where R_f is the radial length immediately after the compression force was removed.

FT-IR analysis

Thin tangential sections with a 30 μm thickness were cut from the ESW and air-dried control specimens using a sliding microtome for conducting Fourier transform infrared spectrophotometer (FT-IR) analysis. A small-sized trimmed section was placed between the KBr plates and analyzed using FT-IR spectroscopy (FT/IR-620, JASCO, Tokyo, Japan) under the vacuum. A section of ESW after washing with distilled water and an IL of [BMIM][OAc] was also analyzed.

SEM observation

Small-sized specimens (5 mm^3) were cut from the rest of 15 × 15 × 5 mm specimens. The same procedure was used for preparing ESW after the cross section for observation were smoothened with a sliding microtome. The cross shape of the tracheid cells in the same area was evaluated under three conditions: the completely vacuum-dry condition before impregnating with aqueous [BMIM][OAc] solution; the saturated condition with [BMIM][OAc] IL remained after drying aqueous [BMIM][OAc] solution; and the softened condition for the ESW preparation. Additionally, the morphology of the crushed tracheid of ESW was observed before compression, at 20 %, 50 % compression ratios and after unloading. The microstructure of the wood cells was observed using a scanning electron microscope (SEM) (SU3500, Hitachi High-Tech, Tokyo, Japan). Backscattered electron images were captured at an accelerating voltage of 15 kV under a low-vacuum condition at 90 Pa.

Caption for Movie S1

Movie S1 Morphological change of the ESW prepared in this research during a compression test at a speed of 2 mm min^{-1} until 50 % compression ratio and after unloading.

Table S1 Summary of specimen preparation processes used in this research

	ESW (n = 9)	**Water-absorbed (n = 3)**	**Air-dried control (n = 3)**
Step 1	Dried for 24 h at 105 °C	Dried for 24 h at 105 °C	Conditioned for 24 h at 20 °C and 60 % relative humidity
Step 2	Injected with 30 wt. % aqueous [BMIM][OAc] solution under repeating atmospheric and vacuum conditions	Injected with water under repeating atmospheric and vacuum conditions	-
Step 3	Dried for 24 h at room temperature	-	-
Step 4	Dried for 48 h at 105 °C	-	-
Step 5	Conditioned for 24 h at 20 °C and 60 % relative humidity	-	-

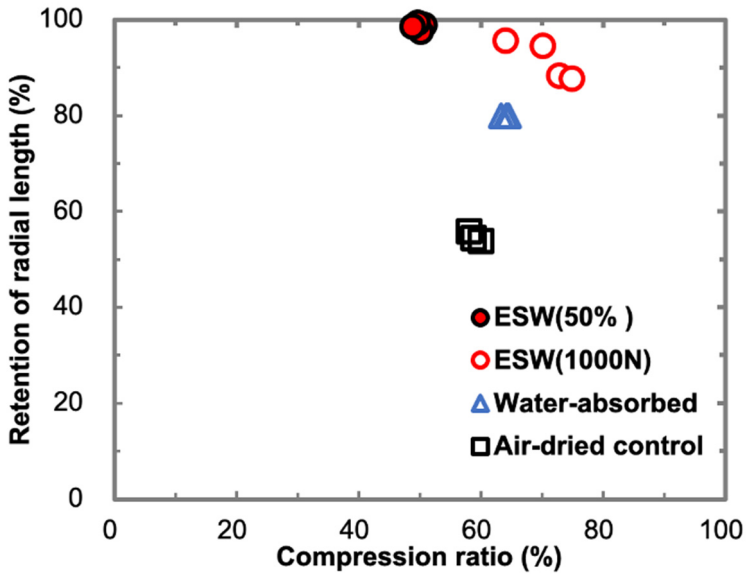

Fig. S1 Retention of radial length of (circles, full at 50 % compression ratio and empty at 1000 N) ESW, (triangles) water-absorbed and (squares) air-dried control specimens at different compression ratios.

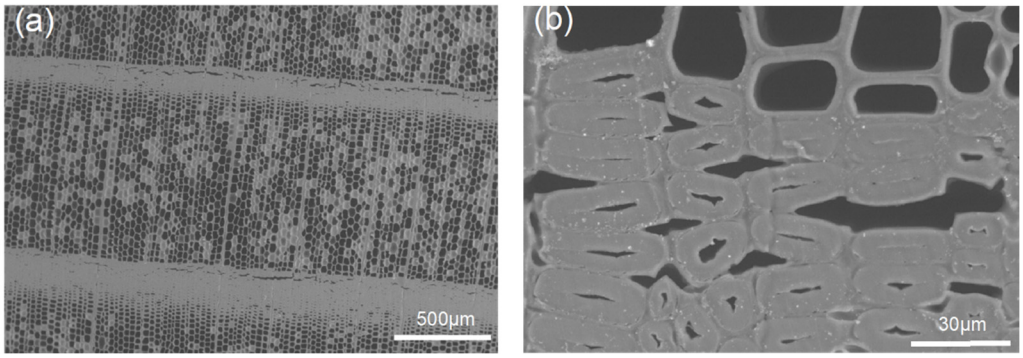

Fig. S2 (a) SEM image of the cross-section view of a typical ESW specimen. (b) Enlarged SEM image at latewood region shown in Fig. S2a.

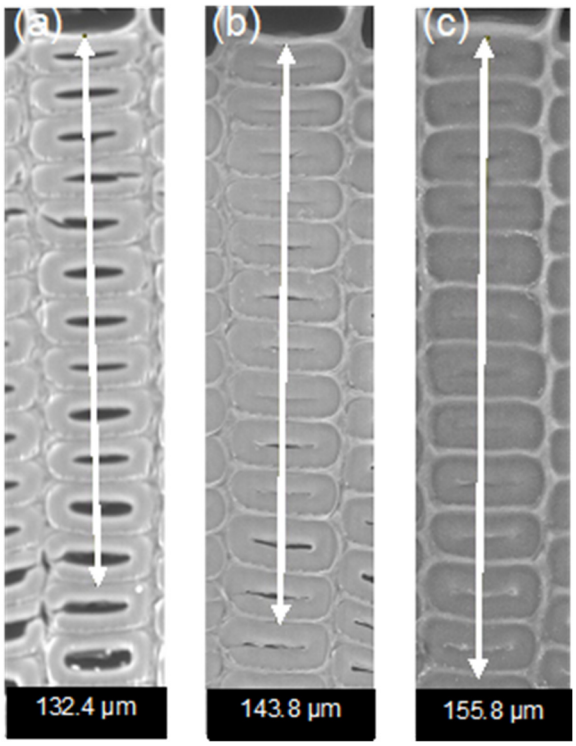

Fig. S3 SEM images of latewood cells in (a) the completely vacuum-dry condition before impregnating with aqueous [BMIM][OAc] solution, (b) the saturated condition with [BMIM][OAc] IL remained after drying aqueous [BMIM][OAc] solution and (c) the softened condition for the ESW preparation. Radial length of twelve latewood cells is given at the bottom of each SEM image.