Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Cellulose nanofibrils efficiently improve mechanical, thermal and oxygen-barrier properties of all-cellulose composites by nano-reinforcement mechanism and nanofibril-induced crystallization

Quanling Yang,[a] Tsuguyuki Saito,[a] Lars A. Berglund[b] and Akira Isogai*[a]

[a]Department of Biomaterials Science, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan. E-mail: aisogai@mail.ecc.u-tokyo.ac.jp

[b]Wallenberg Wood Science Centre, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

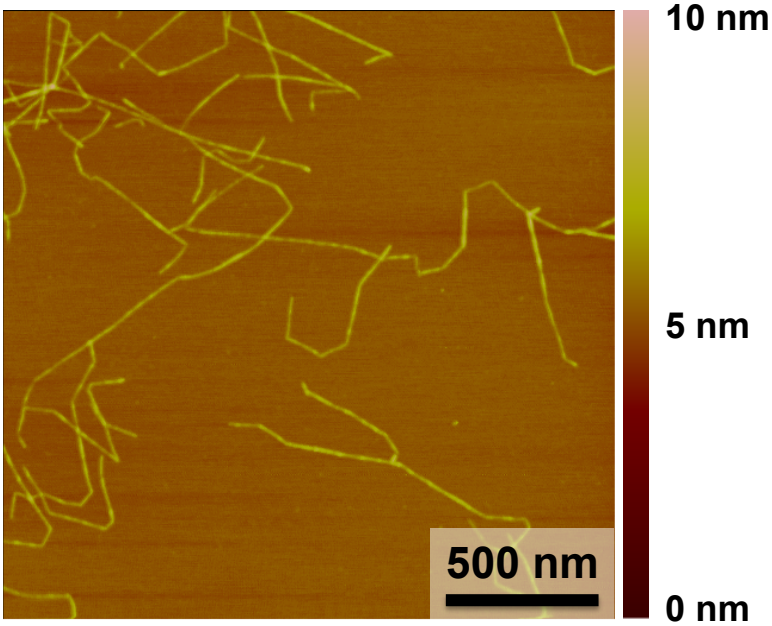

Fig. S1 A typical AFM image of TOCN elements.

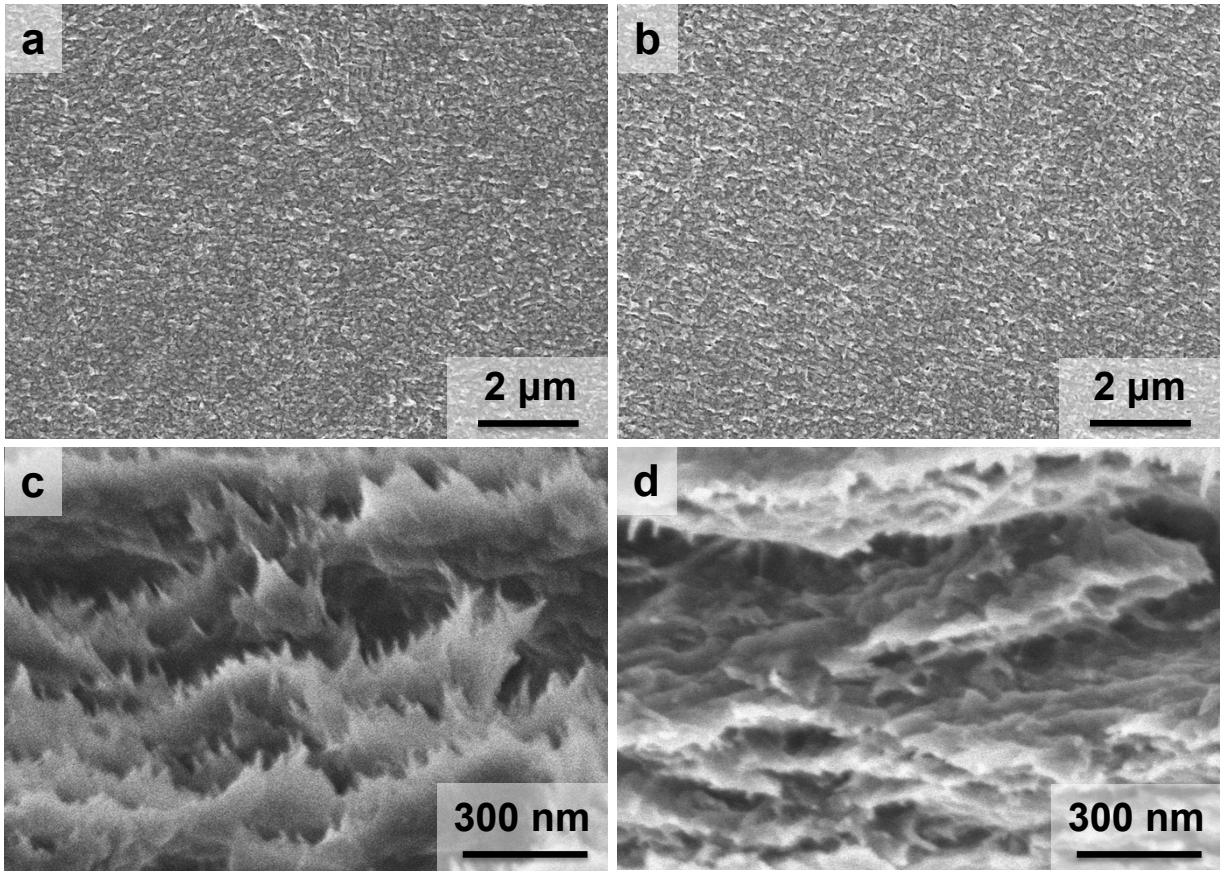

Fig. S2 SEM images of surfaces (a, b) and cross-sections (c, d) of AUC-only (a, c) and TOCN–1.0/AUC (b, d) films.

Two-dimensional X-ray diffraction analysis

Two-dimensional X-ray diffraction pattern of the TOCN–1.0/AUC film was obtained with a rotating anode X-ray generator, RotaFlex RU-200BH (Rigaku), using nickel-filtered Cu Kα radiation (0.15418 nm) operated at 50 kV and 100 mA. The X-ray beam was irradiated to the film cross-section parallel to the film surface. The pattern was recorded on a flat-plate imaging plate (Fuji Film BAS-IP SR 127) using an evacuated camera. Sodium fluoride (d = 0.23166 nm) was dusted on the sample to provide a calibration. From the azimuthal intensity distribution graphs for the (1 −1 0) reflection of cellulose II, Herman's orientation parameter (*f*) was calculated according to a previously reported method.[S1]

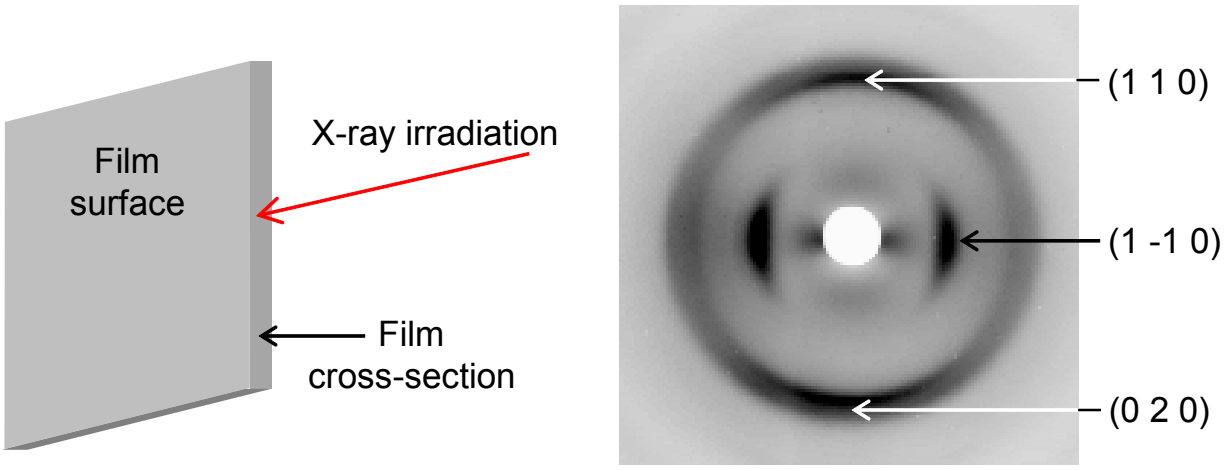

Fig. S3 Two-dimensional X-ray diffraction diagram of the TOCN–1.0/AUC film. The X-ray beam was irradiated parallel to the film surface.

Calculation for predicting Young's modulus of composites

The Halpin-Tsai model was used for predicting Young's modulus (E_{HT}) of composite films consisting of short fibers randomly oriented in the in-plane direction.[S2] In this model, we assume that short fibers form lamina in the matrices. The longitudinal modulus of TOCN (E_{fL}) was regarded as 134 GPa[S3] and its transverse modulus (E_{fT}) was regarded as 24.8 GPa.[S4] The modulus of AUC matrix (E_m) determined from the tensile test data in this study was 3.2 GPa. The average TOCN length (l_f) and width (d_f) of 1158 nm and 2.7 nm, respectively, were obtained from 50 TOCN elements in the AFM images from this study (see text). The volume fraction of TOCN (V_f) in composites was calculated, assuming that the densities of TOCN and bulk AUC film are 1.6 and 1.4 g cm^{-3}, respectively.[S5,S6]

$$E_{HT} = \left[\frac{3}{8} \times \frac{1 + 2(l_f / d_f)\eta_L V_f}{1 - \eta_L V_f} + \frac{5}{8} \times \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right] E_m$$

$$\eta_L = \frac{(E_{fL} / E_m) - 1}{(E_{fL} / E_m) + 2(l_f / d_f)}$$

$$\eta_T = \frac{(E_{fT} / E_m) - 1}{(E_{fT} / E_m) + 2}$$

Calculation for predicting tensile strength of composites

A simple model was used to roughly and empirically estimate the tensile strength (σ) of the TOCN/AUC composite films. The tensile strength of TOCN (σ_f) was regarded as 3 GPa.[S7] The tensile strength of AUC matrix (E_m) determined from the tensile test data in this study was 111 MPa. The same densities of the TOCN and AUC matrix as described above were used to calculate the volume fraction of TOCN (V_f).

$$\sigma = V_f \sigma_f + (1 - V_f)\sigma_m$$

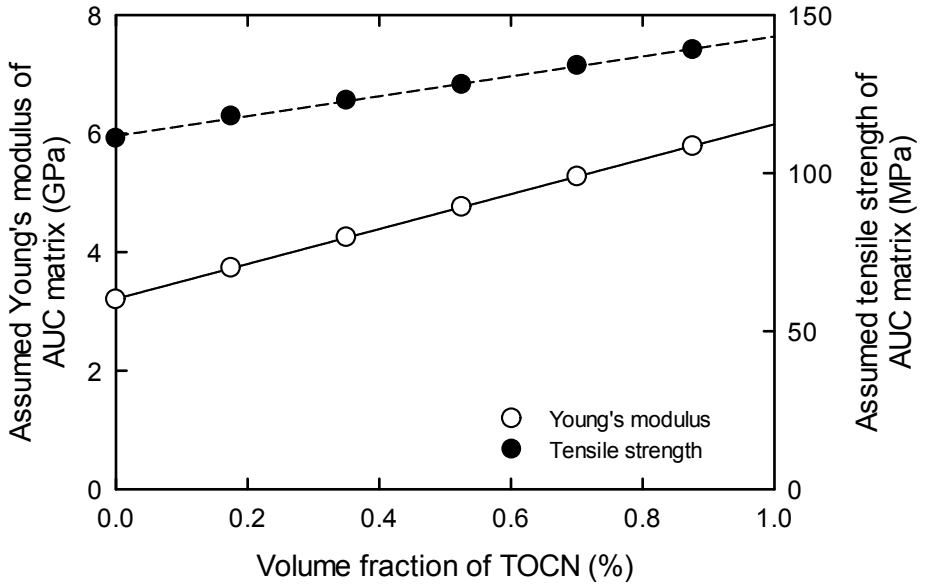

Fig. S4 Relationships between the volume fraction of TOCN in the composite films and the assumed values for AUC matrix modulus and strength required in order for the present modeling predictions to fit experimental data for the composites.

REFERENCES

(S1) H. Sehaqui, N. Mushi, S. Morimune, M. Salajkova, T. Nishino and L. A. Berglund, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1043–1049.

(S2) R. Guzmán de Villoria and A. Miravete, *Acta Matter.*, 2007, **55**, 3025–3031.

(S3) I. Sakurada, Y. Nukushima and T. Ito, *J. Polym. Sci.*, 1962, **57**, 651−660.

(S4) A. Pakzad, J. Simonsen, P. A. Heiden and R. S. Yassar, *J. Mater. Res.*, 2012, **27**, 528−536.

(S5) Y. Nishiyama, P. Langan and H. Chanzy, *J. Am. Chem. Soc.*, 2002, **124**, 9074–9082.

(S6) Q. Yang, H. Fukuzumi, T. Saito, A. Isogai and L. Zhang, *Biomacromolecules*, 2011, **12**, 2766–2771.

(S7) T. Saito, R. Kuramae, J. Wohlert, L. A. Berglund and A. Isogai, *Biomacromolecules*, 2013, **14**, 248−253.