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Electronic Supplementary Information

Benzoylation of microfibrillated cellulose-hydroxyapatite composites for green and water-resistant mechanical materials

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Table S1. The density and the mechanical properties of the molded composites benzoylated at various temperatures.[a]

Benzoylation temp.	density (g/cm^3)	Bending strain (%)	Bending strength (MPa)	Elastic modulus (GPa)	Work of fracture (J/m^2)	N^b
50 °C	1.7 ± 0.2	1.1 ± 0.1	65.5 ± 1.8	6.5 ± 0.5	320 ± 90	3
70 °C	1.76 ± 0.19	1.13 ± 0.16	81.3 ± 0.99	7.74 ± 0.24	400 ± 130	2
100 °C	1.59 ± 0.13	1.3 ± 0.30	74.0 ± 1.9	6.0 ± 0.5	400 ± 260	4
110 °C	1.51 ± 0.14	1.5 ± 0.2	65.7 ± 1.2	4.5 ± 0.2	400 ± 180	3
120 °C	1.53 ± 0.06	1.3 ± 0.12	56.6 ± 0.8	4.8 ± 0.2	310 ± 50	3
130 °C	1.52 ± 0.05	1.4 ± 0.2	56 ± 1.6	4.4 ± 0.2	330 ± 120	3
150 °C	1.52 ± 0.04	1.58 ± 0.05	61.6 ± 0.4	4.27 ± 0.10	410 ± 30	3

a The standard errors of the mean. b Number of determinations.

Table S2. The density and the mechanical properties of the molded composites benzoylated at various temperatures after the compacts were immersed in water at 25 °C for 24 h.[a]

Benzoylation temp.	density (g/cm^3)	Bending strain (%)	Bending strength (MPa)	Elastic modulus (GPa)	Work of fracture (J/m^2)	N^b
50 °C	1.5 ± 0.3	2 ± 1	5.2 ± 1.9	0.12 ± 0.4	90 ± 350	2
70 °C	1.55 ± 0.09	4 ± 1.1	14.3 ± 0.6	0.4 ± 0.4	270 ± 360	2
100 °C	1.5 ± 0.11	2.1 ± 0.4	10.6 ± 1.4	0.6 ± 0.3	120 ± 40	3
110 °C	1.55 ± 0.07	1.3 ± 0.2	38.4 ± 1.1	3.3 ± 0.4	210 ± 30	3
120 °C	1.56 ± 0.02	1.2 ± 0.14	26.6 ± 0.9	2.4 ± 0.16	140 ± 50	3
130 °C	1.54 ± 0.03	1.23 ± 0.09	34.7 ± 1.0	3.1 ± 0.2	180 ± 40	3
150 °C	1.55 ± 0.06	0.74 ± 0.09	20.0 ± 0.6	2.9 ± 0.3	60 ± 30	3

a The standard errors of the mean. b Number of determinations.

Table S3. The water absorption ratio, $(w_{wet} - w_{dry})/w_{dry}$, after the compacts were immersed in water at room temperature for 24 h.

Benzoylation temp.	$(w_{wet} - w_{dry})/w_{dry}$, %[a]	N[b]
50 °C	28 ± 7.3	2
70 °C	38 ± 0.9	2
100 °C	21 ± 2.0	3
110 °C	6.1 ± 0.4	3
120 °C	10 ± 0.5	3
130 °C	6.9 ± 1.3	3
150 °C	5.4 ± 1.3	3

a Standard error of the mean is shown. b N: number of determinations.

Table S4. Mole fractions (%) of carbon, oxygen, calcium and phosphorous of the fracture surface of the compact benzoylated at 130 °C determined with energy dispersive X-ray spectroscopy. For SEM images, see Figures S4 and S5.

	Before water immserion	After water immersion	Calculated values[a]
C	55.6	54.7	50.9
O	37.4	37.3	38.9
Ca	4.5	5.2	6.4
P	2.5	2.9	3.8

a Calculated based on the molecular formula, $C_6H_7O_2(OH)_{3-x}(OCOC_6H_5)_x \cdot \alpha Ca_{10}(PO_4)_6(OH)_2$, with $x = 1.14$ and $\alpha = 0.175$.

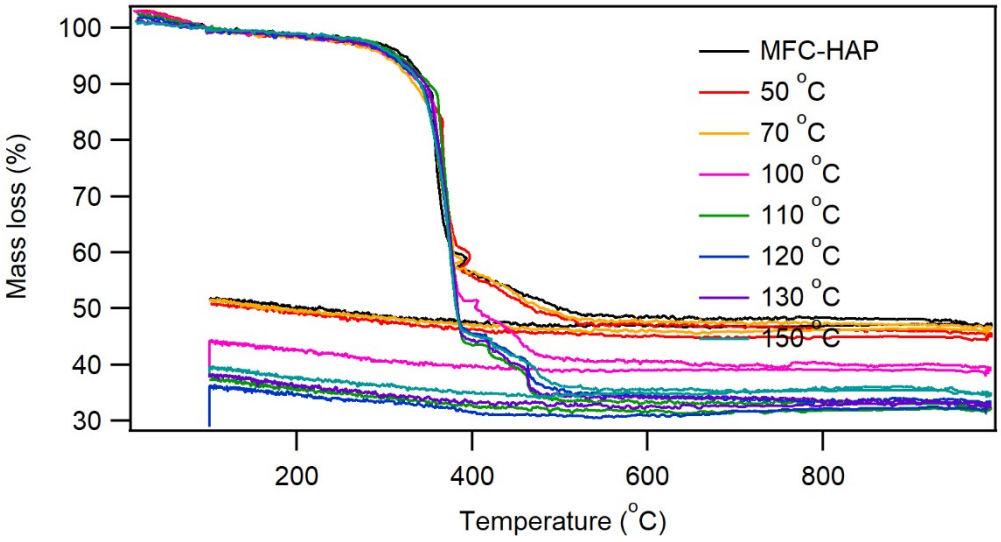

Figure S1. TG traces of the MFC-HAP composite and the benzoylated composites.

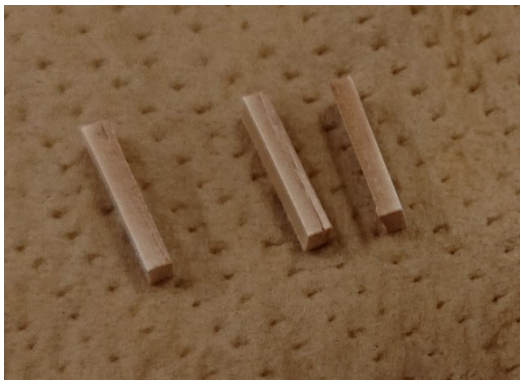

Figure S2. A photograph of the molded composite, benzoylated at 100°C, after being immersed in water at room temperature for 24 h.

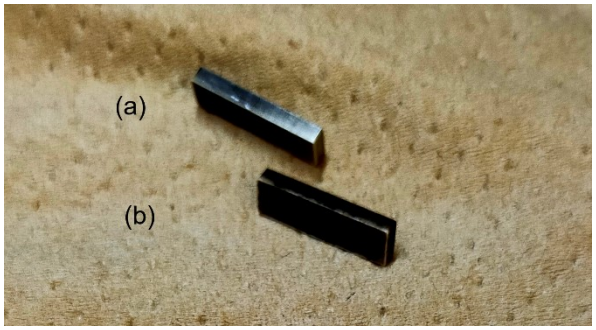

Figure S3. A photograph of the molded composites, benzoylated at 130 °C (a) and at 150 °C (b), after being immersed in water at room temperature for 24 h.

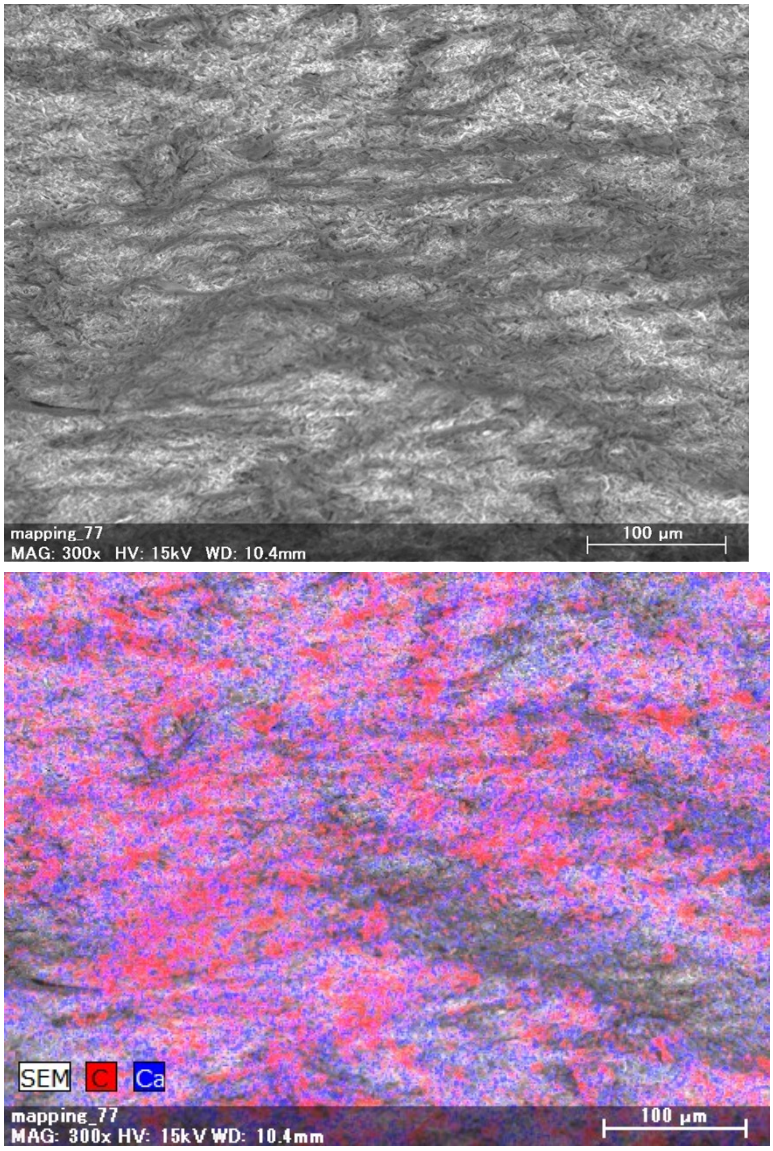

Figure S4. Cross-sectional SEM images and elemental mapping with energy dispersive X-ray spectroscopy at an acceleration voltage of 15 kV (calcium in blue and carbon in red) of the fracture surface of the compacts before water immersion. The composite was benzoylated at 130 °C. EDS was performed by TM3030/EDS system (Quantax70) using the following conditions: working distance = 9800 µm, emission current = 48600 nA, filament current = 1850 mA, count time = 180 sec.

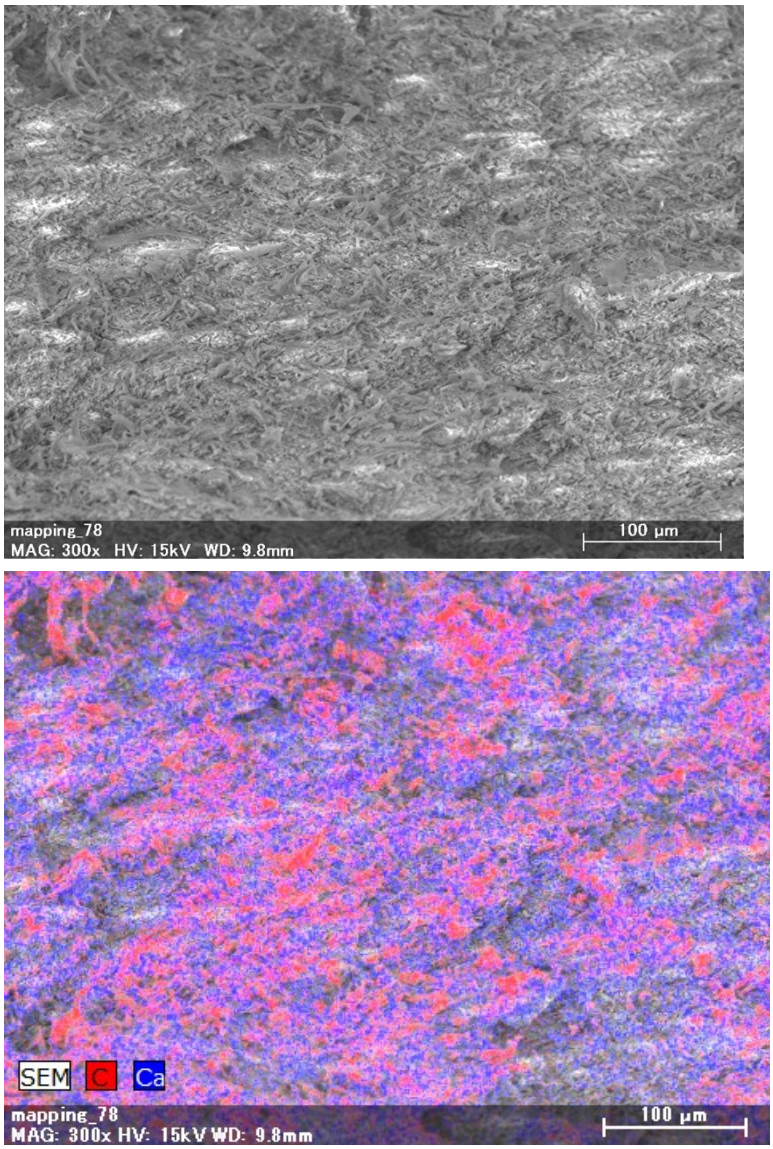

Figure S5. Cross-sectional SEM images and elemental mapping with energy dispersive X-ray spectroscopy at an acceleration voltage of 15 kV (calcium in blue and carbon in red) of the fracture surface of the compacts after water immersion. The composite was benzoylated at 130 °C.

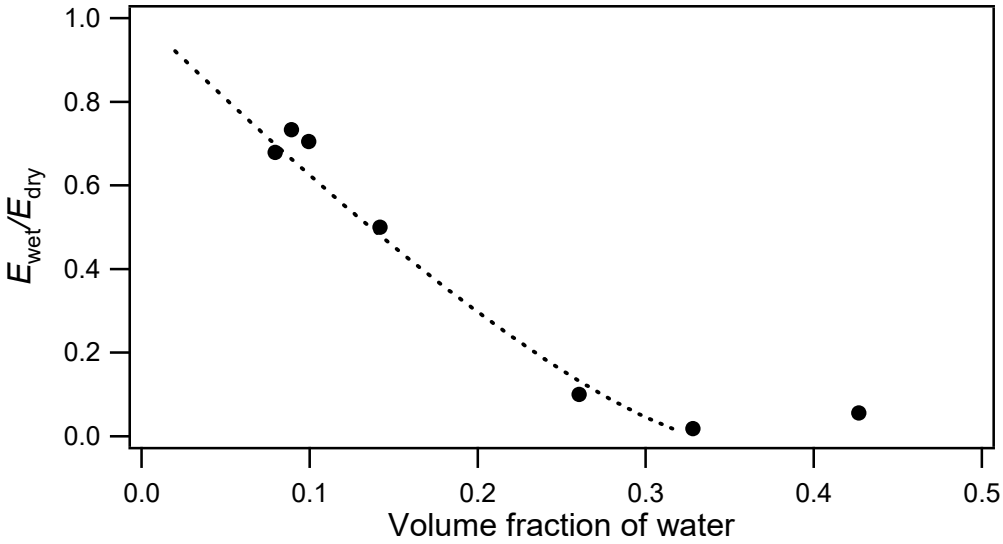

Figure S6. Plot of the ratios of elastic modulus of benzoylated MFC-HAP composites after immersion in water (E_{wet}) to that before immersion (E_{dry}) against the volume fraction of water. By fitting the data to the equation to $E_{wet}/E_{dry} = (1 - a\phi)^n$ using the least-squares method, values of $a = 3.0 \pm 0.5$, $n = 1.3 \pm 0.4$ were obtained. The curve calculated with these parameters is presented in the figure.

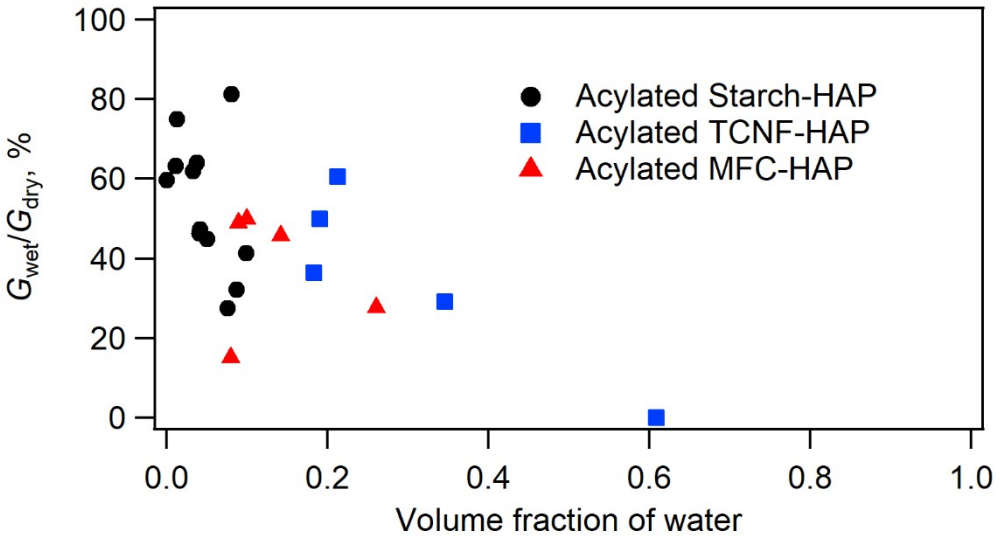

Figure S7. Plot of the ratios of the work of fracture of acylated polysaccharide-HAP composites after immersion in water (G_{wet}) to that before immersion (G_{dry}) against the volume fraction of water for acylated starch-HAP, TCNF-HAP, and MFC-HAP composites.