

Fabrication and Characterization of Hydrophobic Cellulose Nanofibrils/Silica Nanocomposites with Hexadecyltrimethoxysilane

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1. Morphology of the CNF

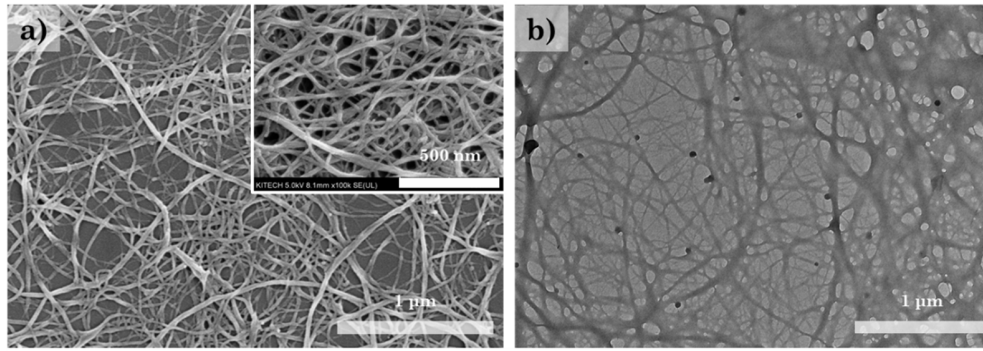


Figure S1. Morphology of the CNF investigated via (a) SEM and (b) TEM.

2. Calculation of the CNF, CNF/Silica, and Poly-HDTMS Content of the CNF Composites

Table S1 shows the elemental composition of the CNF surface before and after modification with TEOS and HDTMS obtained via XPS. The CNF, silica, and HDTMS content was calculated using the following equations based on each XPS elemental analysis. Here, the Si coefficient (k) of HDTMS was assumed to be 1.

$$CNF = (C_6H_{10}O_5)_n = x, 162.14 \text{ g/mol}$$

$$Silica = SiO_2 = y, 60.08 \text{ g/mol}$$

$$HDMTS = CH_3(CH_2)_{15}SiO_k = z, 269.58 \text{ g/mol (Assuming } k = 1)$$

$$C = 6x + 16z$$

$$O = 5x + 2y + kz$$

$$Si = y + z$$

$$z = \frac{(6O - 5C - 12Si)}{(6k - 92)}$$

$$x = \frac{(C - 16z)}{6}$$

$$y = Si - z$$

Table S1. Surface composition of the samples measured via XPS.

Samples	Atomic percentage (%)			CNF(wt%)	Silica(wt%)	HDTMS (wt%)
	C	O	Si			
CNF	56.20	43.80	-	100.00	-	-
CNF/silica	29.20	54.65	16.15	44.85	55.15	-
h-sCNF 0.1	33.94	50.97	15.05	40.65	51.18	8.17
h-sCNF 0.5	52.82	35.78	11.40	30.14	34.04	35.82
h-sCNF 1.0	57.14	31.85	11.01	24.98	31.09	43.92
h-sCNF 2.0	64.82	25.66	9.52	20.29	23.53	56.18
h-CNF 0.4	67.30	30.55	2.15	60.53	-	39.46
h-CNF 0.8	66.71	31.37	1.92	65.27	-	34.73

3. Calculation of the CNF, CNF/silica, and Inorganic/Organic HDTMS Content of the CNF Nanocomposites

The inorganic/organic HDTMS amount was calculated using the CNF, silica, and HDTMS amount based on the XPS analysis shown in Table S2 and the thermal degradation properties (T_{max}) obtained from the TGA. Here, the inorganic/organic HDTMS content of h-CNF and h-sCNF samples was calculated according to the ash content of the CNF and CNF/silica nanocomposites. Firstly, the T_{max} value of CNF/silica was 57.41 wt%, which is about 2.26 wt% higher compared with the silica content of the CNF due to the insulating effect of the silica nanoparticles. Therefore, the ash content of the CNF/silica nanocomposites was assumed to be 2.26 wt%.

$$\begin{aligned} \text{Ash of CNF/silica, } a &= T_{max, \text{CNF/silica}} - \text{Silica content}_{\text{CNF/silica, XPS}} \\ &= 57.41 - 55.15 = 2.26 \text{ wt\%} \end{aligned}$$

$$\text{Ash of CNF, } b = T_{max, \text{CNF}} = 0.88 \text{ wt\%}$$

$$\text{Inorganic HDTMS}_{h\text{-sCNF}} = T_{max, h\text{-sCNF}} - \text{Silica content}_{h\text{-sCNF, XPS}} - 2.26$$

$$\text{Organic HDTMS}_{h\text{-sCNF}} = \text{HDTMS}_{h\text{-sCNF, XPS}} - \text{Inorganic HDTMS}_{h\text{-sCNF}}$$

$$\text{Inorganic HDTMS}_{h\text{-CNF}} = \text{HDTMS}_{h\text{-CNF, XPS}} - T_{max, h\text{-CNF}} - 0.88$$

$$\text{Organic HDTMS}_{h\text{-CNF}} = \text{HDTMS}_{h\text{-CNF, XPS}} - \text{Inorganic HDTMS}_{h\text{-CNF}}$$

Table S2. Thermal degradation properties (T_{max}) and amount of the CNF, silica, and inorganic/organic HDTMS.

Samples	TGA	XPS		Inorganic HDTMS (wt%)	Organic HDTMS (wt%)
	T_{max} (wt%)	Silica (wt%)	HDTMS (wt%)		
CNF	0.88	-	-	-	-
CNF/silica	57.41	55.15	-	-	-
h-sCNF 0.1	55.02	51.18	8.17	1.58	6.59
h-sCNF 0.5	50.77	34.04	35.82	14.47	21.35
h-sCNF 1.0	46.54	31.09	43.92	13.19	30.73
h-sCNF 2.0	38.03	23.53	56.18	12.24	43.94
h-CNF 0.4	14.34	-	39.46	13.46	26.00
h-CNF 0.8	17.93	-	34.73	17.05	17.68

4. Thermal Properties of the CNF/Silica and HDTMS-Modified CNF/Silica Nanocomposite

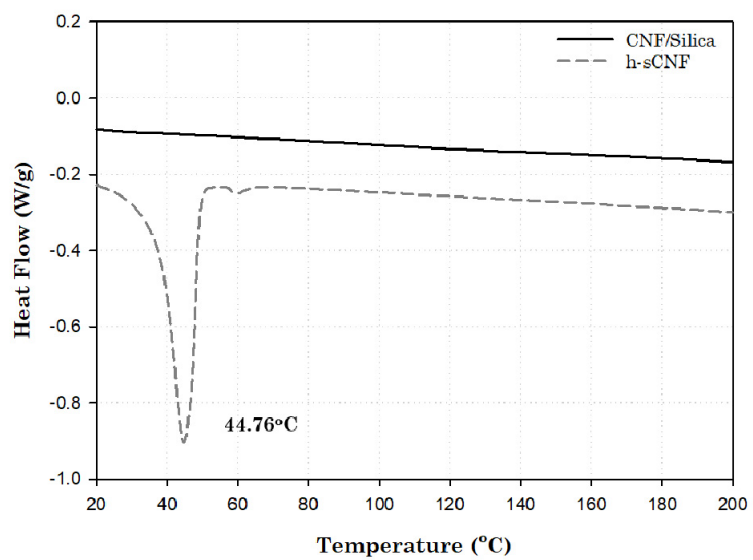


Figure S2. DSC curves of the CNF/silica and HDTMS-modified CNF/silica nanocomposites.