Supplementary information for:

Well-dispersed cellulose nanocrystals in hydrophobic polymers by *in-situ* polymerization for synthesizing highly reinforced bio-nanocomposites

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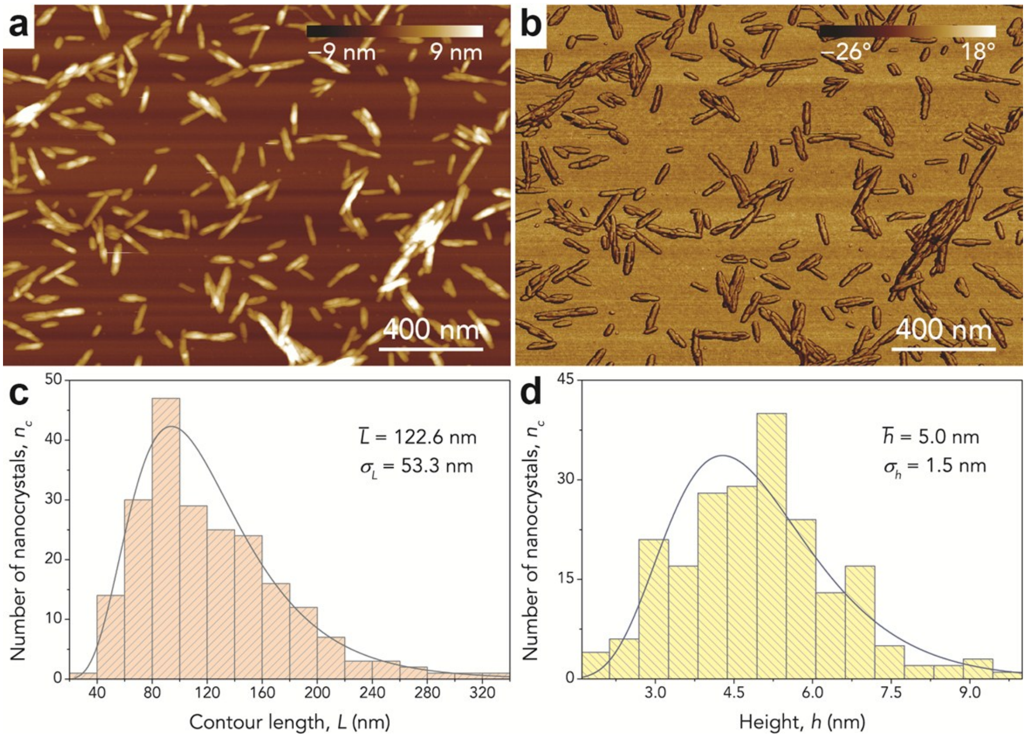

Fig. S1 (a) AFM height image and (b) AFM phase image of the CNC used in this study. (c) Length and (d) diameter distributions of the CNC obtained according to the AFM images. (with permission from Elsevier, copyright 2016).[1]

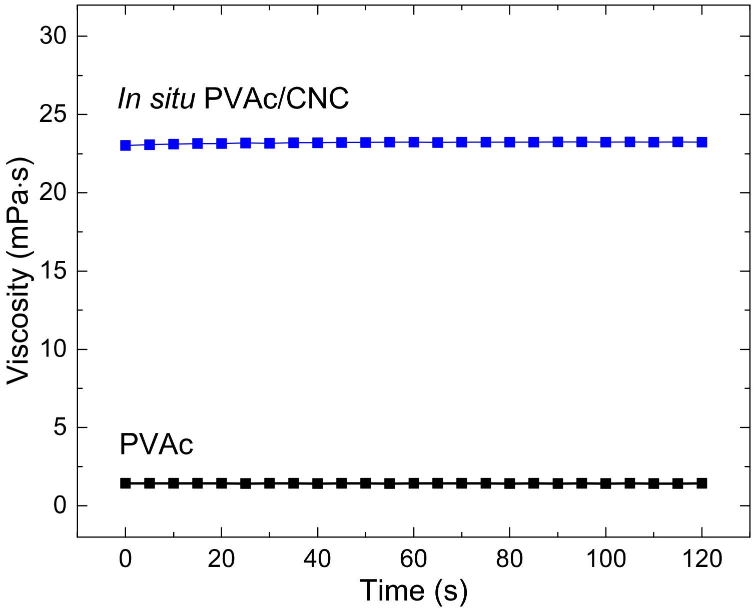

Fig. S2 Viscosities of the aqueous PVAc and *in-situ* PVAc/CNC latexes with 15 wt% of solid content at room temperature.

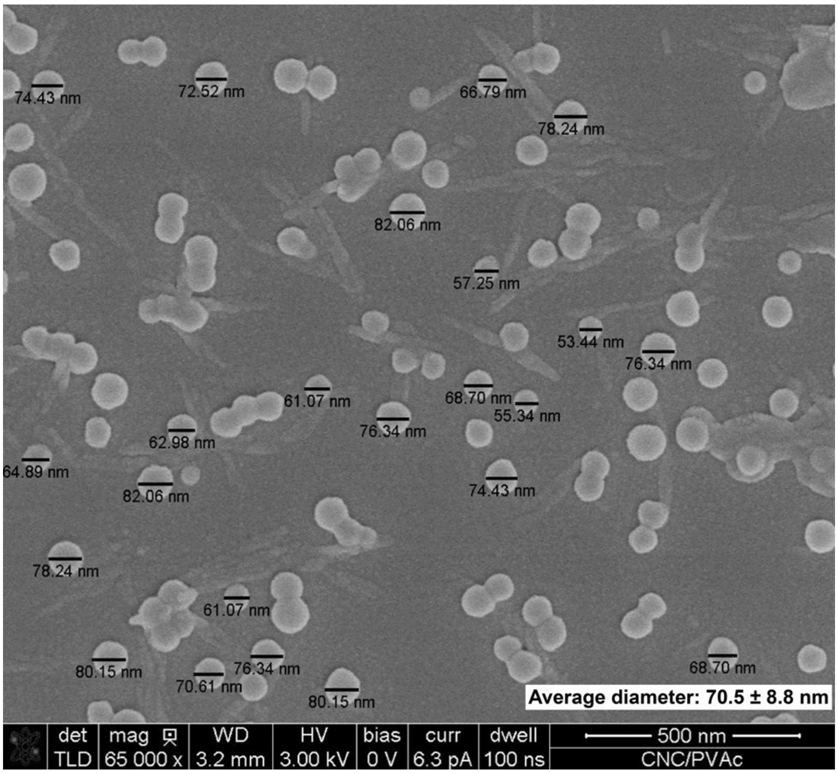

Fig. S3 Diameter of the PVAc particles in the *in-situ* PVAc/CNC latex after drying measured using ImageJ according to the SEM image. The weight ratio of PVAc to CNC is 80:20.

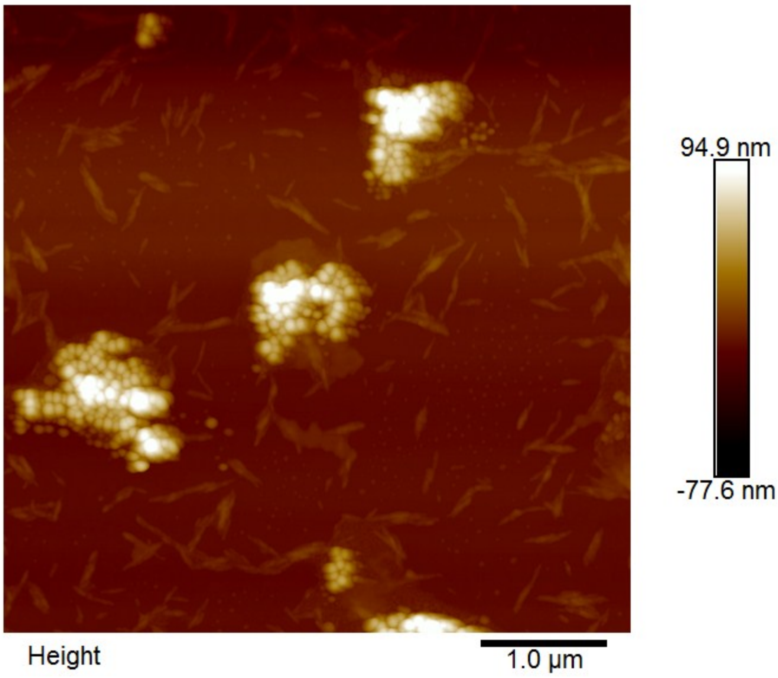

Fig. S4 5×5 µm AFM height image of the mixed PVAc/CNC latex after drying. The weight ratio of PVAc to CNC is 80:20.

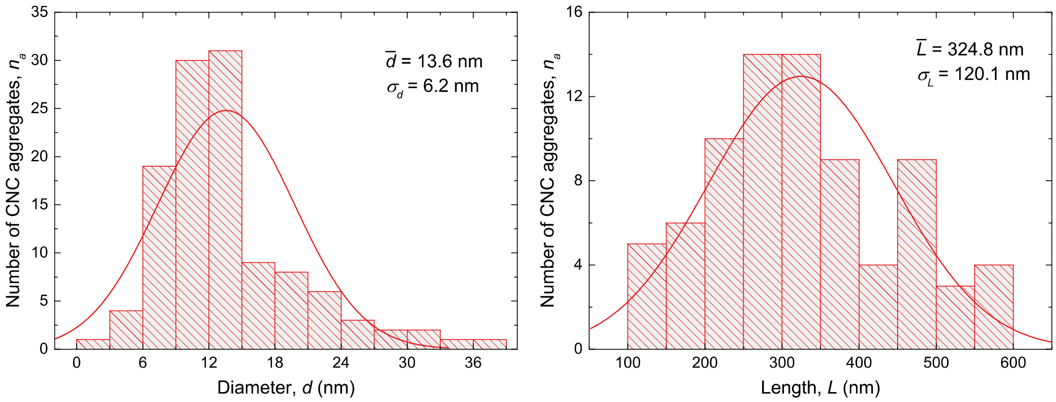

Fig. S5 Diameter (left) and length (right) distributions of the CNC aggregates in the mixed PVAc/CNC sample measured using software "FibreApp"[2] according to the AFM height images.

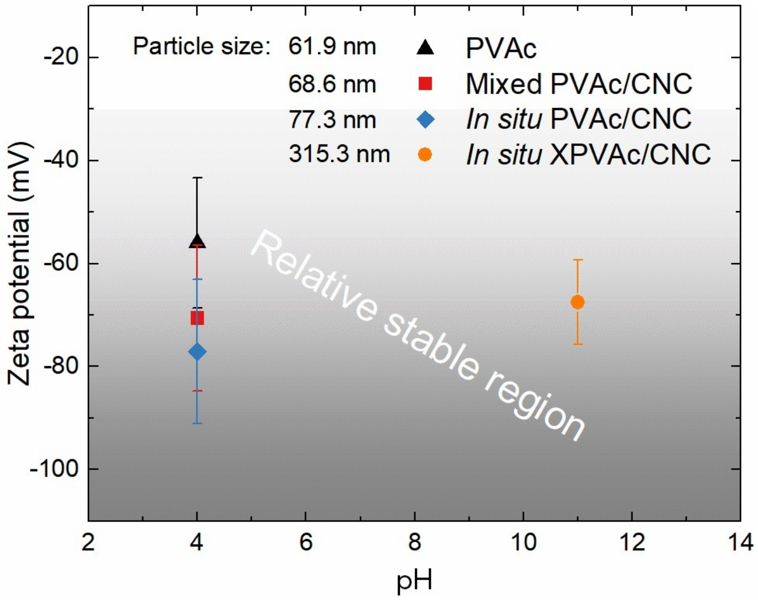

Fig. S6 Zeta potentials and particle sizes of the PVAc, *in-situ* and mixed PVAc/CNC and *in-situ* XPVAc/CNC latexes.

Calculation of the length efficiency (η_l) of reinforcement in nanocomposites:[3]

$$\eta_l = 1 - \frac{\tanh(\beta L/2)}{\beta L/2} \qquad \text{(S1)}$$

where,

$$\beta = \frac{2}{d}\sqrt{\frac{2G_m\eta_i}{E_f ln(2R/d)}}$$

where L, d and E_f stand for the length, diameter and the elastic modulus of the reinforcement, respectively, G_m is the shear modulus of the matrix calculated as $G_m = E_m/2(1+\nu)$, where E_m and v are the elastic modulus and Poisson ratio of the matrix, respectively, and R can be expressed as $R = d/2\sqrt{K_R/v_f}$, where K_R is equal to π/4 for square packing[4] and v_f is the volume fraction of the reinforcement. Since there is few covalent bond between CNC and PVAc matrix in the *in-situ* and mixed nanocomposites without crosslinking, an interaction factor, η_i, is taken into consideration and the value of it is determined as 0.6 according to the experimental data.

Table S1 Compositions of all samples investigated in this study. The ratio of GTA to polymer (including CNC and PVAc) in each sample was maintained the same (GTA:Polymer = 5:95).

Sample coding	CNC (wt%)	PVAc (wt%)	Borax (wt%)	GTA (wt%)	PLA (wt%)
PVAc	0	95	0	5	/
XPVAc	0	93.6	1.5	4.9	/
Mixed PVAc/5CNC	5	90	0	5	/
In-situ PVAc/5CNC	5	90	0	5	/
In-situ XPVAc/5CNC*	5	88.6	1.5	4.9	/
Mixed PVAc/10CNC	10	85	0	5	/
In-situ PVAc/10CNC	10	85	0	5	/
In-situ XPVAc/10CNC*	10	83.6	1.5	4.9	/
Mixed PVAc/15CNC	15	80	0	5	/

In-situ PVAc/15CNC	15	80	0	5	/
In-situ XPVAc/15CNC[*]	15	78.6	1.5	4.9	/
Mixed PVAc/19CNC	19	76	0	5	/
In-situ PVAc/19CNC	19	76	0	5	/
In-situ XPVAc/19CNC[*]	19	74.6	1.5	4.9	/
PLA/PVAc	0	10	/	/	90
Mixed PLA/PVAc/0.1CNC	0.1	9.9	/	/	90
In-situ PLA/PVAc/0.1CNC	0.1	9.9	/	/	90

[*] Samples coding with “X” indicates that the sample was crosslinked by borax.

Table S2 Mechanical properties of all samples measured by tensile testing in this study.

Sample coding	Elastic modulus (GPa)	Ultimate strength (MPa)	Elongation at break (%)	Toughness (MJ/m^3)
PVAc	0.52 ± 0.02	11.14 ± 0.35	252.4	19.62
XPVAc	0.98 ± 0.01	20.67 ± 0.36	105.5	13.44
Mixed PVAc/5CNC	0.67 ± 0.04	13.06 ± 0.68	122.1	11.43
In-situ PVAc/5CNC	0.79 ± 0.03	15.15 ± 0.18	166.1	16.93
In-situ XPVAc/5CNC	1.04 ± 0.03	21.81 ± 0.76	82.6	11.44
Mixed PVAc/10CNC	0.85 ± 0.03	16.61 ± 0.47	169.0	19.34
In-situ PVAc/10CNC	0.95 ± 0.05	17.81 ± 1.09	179.5	21.50
In-situ XPVAc/10CNC	1.09 ± 0.03	22.04 ± 0.31	12.4	2.23
Mixed PVAc/15CNC	1.03 ± 0.04	18.33 ± 0.78	119.4	16.36
In-situ PVAc/15CNC	1.04 ± 0.08	19.21 ± 0.65	84.8	12.46
In-situ XPVAc/15CNC	1.25 ± 0.02	24.89 ± 0.41	24.4	4.70
Mixed PVAc/19CNC	0.94 ± 0.08	16.73 ± 0.36	31.1	4.63
In-situ PVAc/19CNC	0.98 ± 0.02	16.92 ± 0.55	61.0	9.14
In-situ XPVAc/19CNC	1.27 ± 0.06	24.58 ± 0.76	15.1	3.05
PLA/PVAc	1.94 ± 0.03	46.48 ± 0.91	5.2	1.63

Mixed PLA/PVAc/0.1CNC	2.12 ± 0.03	53.20 ± 0.80	5.4	2.08
In-situ PLA/PVAc/0.1CNC	2.20 ± 0.05	57.18 ± 1.08	9.3	4.13

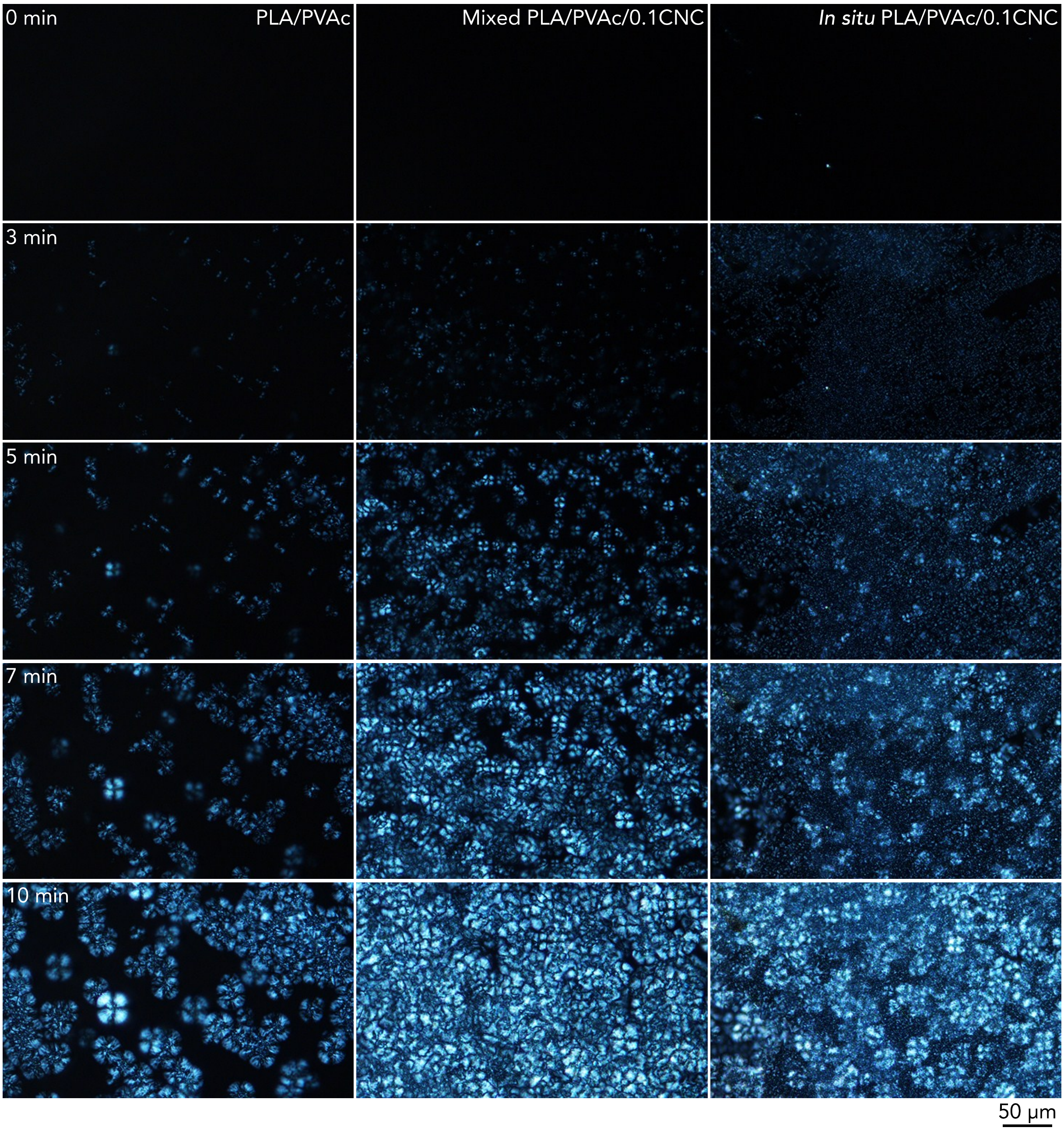

Fig. S7 POM images of the PLA/PVAc, mixed PLA/PVAc/0.1CNC and *in-situ* PLA/PVAc/0.1CNC. The samples were heated to 190 °C and then annealled at 110 °C, and the images were captured at 0, 3, 5, 7 and 10 min during the annealing.

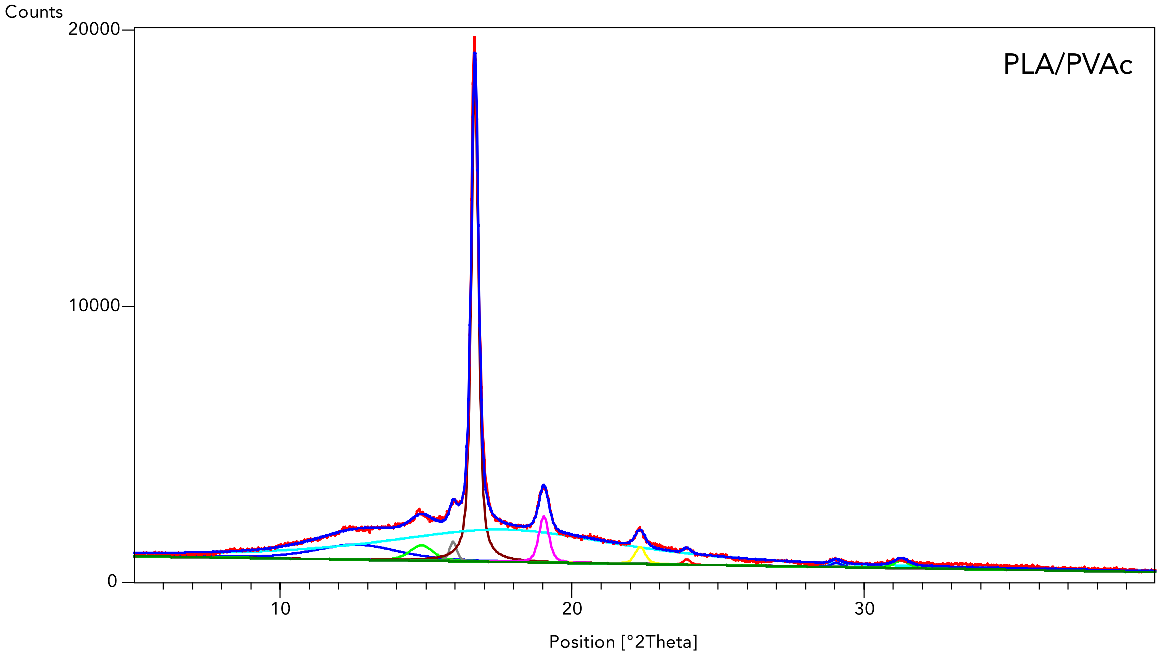

Fig. S8 XRD scattering curve of the PLA/PVAc deconvoluted using the software PANalytical Highscore Plus.

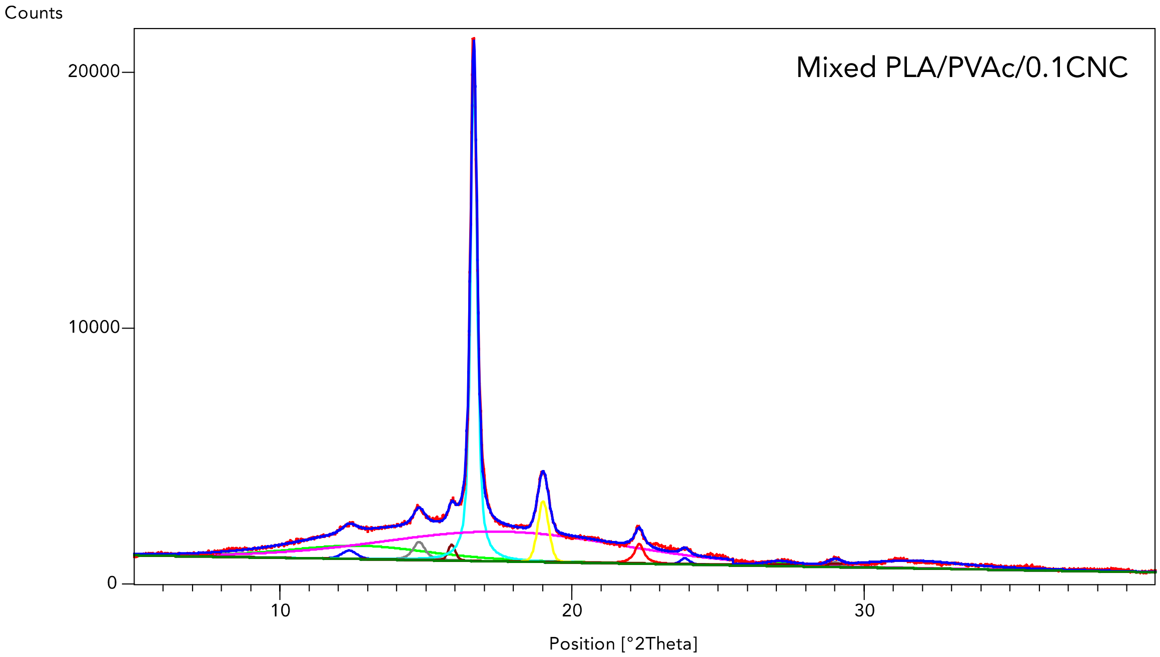

Fig. S9 XRD scattering curve of the mixed PLA/PVAc/0.1CNC deconvoluted using the software PANalytical Highscore Plus.

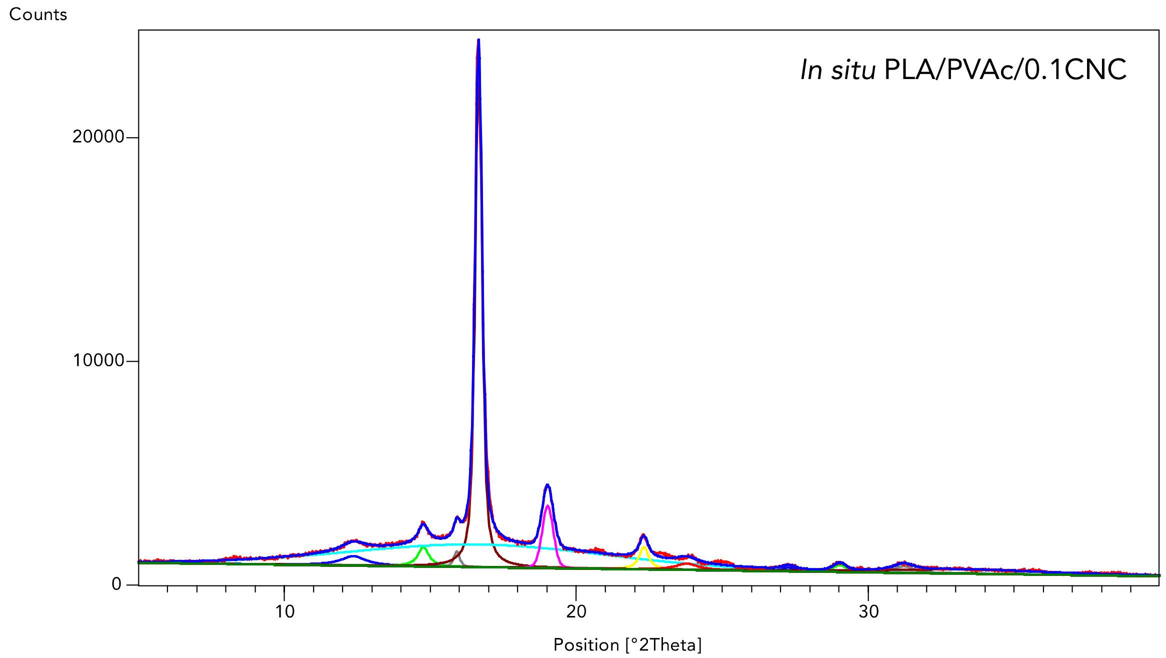

Fig. S10 XRD scattering curve of the *in-situ* PLA/PVAc/0.1CNC deconvoluted using the software PANalytical Highscore Plus.

Table S3 Relative crystallinity (X_c) of PLA in the samples evaluated using DSC and XRD, respectively.

Sample coding	X_c (%) from DSC	X_c (%) from XRD
PLA/PVAc	21.2	30.9
Mixed PLA/PVAc/0.1CNC	42.2	35.8
In-situ PLA/PVAc/0.1CNC	45.5	43.3

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