Convection-assisted assembly of cellulose nanowhiskers embedded in an acrylic copolymer

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Supporting material

XPS results

For the quantitative evaluation of CNW influence on thin film compositions, resulting ultrathin films were examined by XPS analysis. Thin films of CNW/poly(EHA-co-GMA) nanocomposites with loadings of 0, 20, 50 and 100 % of CNW deposited on silicon substrate with a speed rate of 4.8 $m.h^{-1}$ were evaluated by XPS analysis.

Low-resolution survey measurements providing information on elemental concentrations within the topmost 10 nm of the sample surface was first performed. The atomic compositions based on the relative peak area in the survey scans of the investigated samples are summarized in Table S1. Neat copolymer contains 80 % of carbon and 20 % of oxygen whereas as pristine CNW contains 60 % of carbon and 40 % of oxygen. The sample loaded with 20 % of CNW contains the same amount of carbon and oxygen than poly(EHA-co-GMA). Intermediate value of carbon and oxygen (respectively 70 and 30 %) between pure copolymer and pristine CNW is obtained for the 50 % CNW loading sample. Few percentage of silicon has been found probably due to some residual grease contamination during copolymer synthesis.

Table S1. Atomic concentration of thin films with different CNW concentration

% CNW	% C	% O
0	79.9	20.1
20	79.3	20.7
50	70	30
100	60.2	39.8

High-resolution XPS was also carried out on carbon 1s, which provide more information on carbon chemistry. Differences in the molecular environment of carbon show up as shifts in the carbon C1s binding energy. As a result, the carbon signal can be resolved into four distinct peaks, each reflecting the local chemical environment of the carbon atoms. Carbon bonded only to other carbon atoms (or hydrogen) has a binding energy of 285 eV. As the number of carbon–oxygen bonds increases, the chemical binding energy is shifted to higher values. Figure S1 depicts the C1s spectra of the different films. Typical peaks of P(EHA-co-GMA) and CNW correspondent to C-C (C1), C-O (C2), O-C-O (C3) and O=C-O (C4) at respectively 285, 286-286.5, 288 and 289 eV are observed. The relative peak areas from the fitted C1s spectra are listed in Table S2. These results revealed by XPS show contributions of both CNW and copolymer meaning that CNW are well incorporated within the polymeric matrix.

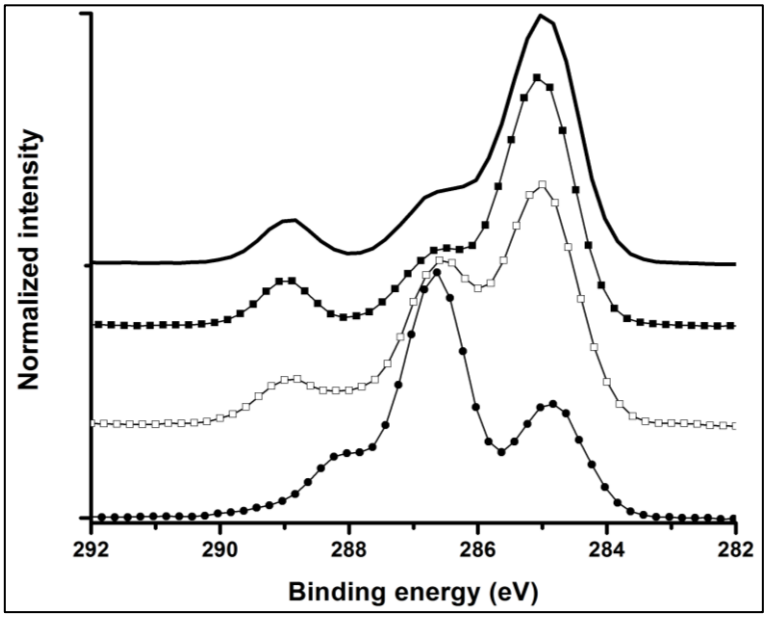

Figure S1. C1s peaks of thin films with : (-) 0 % of CNW, (■) 20 % of CNW, (□) 50 % of CNW and (●) 100 % of CNW.

Table S2. Relative carbon composition of thin films with different CNW loadings

% CNW	C1	C2	C3	C4
0	69.6	21.4	-	9
20	69	21.5	-	9.5
50	54	34.7	3.1	8.2
100	29	49.8	21.2	-

Vectorization

AFM images were subjected to Gwyddion software in order to estimate relative orientation of CNW and the possible correlation with good mechanical properties observed above. For this AFM images presented above have been considered. One example of the vectorizations performed is presented at Figure S2. As it can be seen almost all the single CNW have been assigned to a vector. The angles of the vectors with respect to the withdrawal direction were calculated by Gwyddion software and different categories have been assigned to the CNW in

function of the angles (0-20 °; 20-40 °; 40-60 ° and 60-90 °). Considering symmetry conditions for the angles between 0 and 90 °, and 90 and 180 ° the respective number of CNW counted at the given angle were added to the number collected for the 0 to 90 ° angle range. The histograms (number % of CNW) for a given angle range were obtained. Typically, several hundreds of CNW were counted in each image analysis.

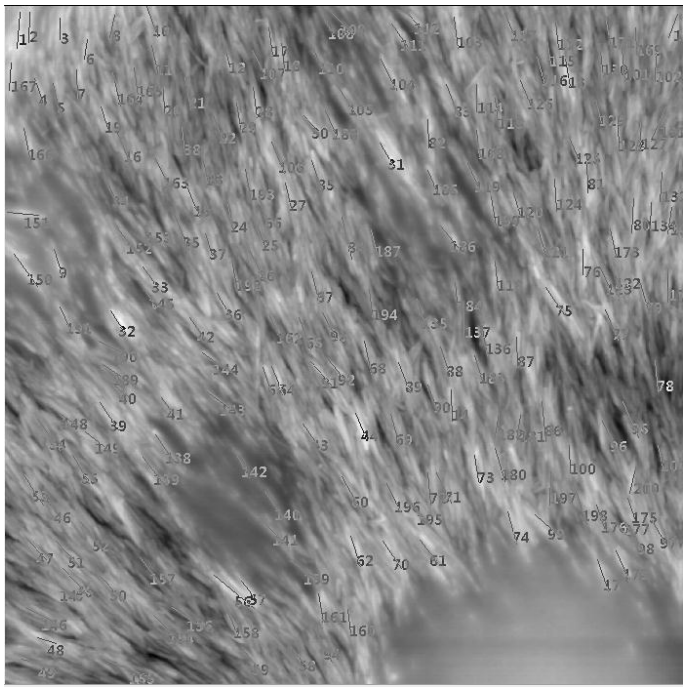

Figure S2. Vectorization of the coating loaded with 50 % of CNW with Gwyddion software