Concentration driven cocrystallisation and percolation in all-cellulose nanocomposites : supporting information

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Humidity-controlled dynamic mechanical analysis (RH-DMA) is a powerful tool that can be used to measure the loss and storage modulus of hydrophilic materials as a function of humidity, thereby providing an insight into the water-induced plasticisation mechanisms. In our study, we showed that the all-cellulose composites (ACC). In order to provide an insight into their peculiar behaviour dictated by their matrix but also by a percolated cellulose nanocrystal network acting as a reinforcement, a simple mathematical model in the form of a second order polynomial was fitted to the data (Figure S1).

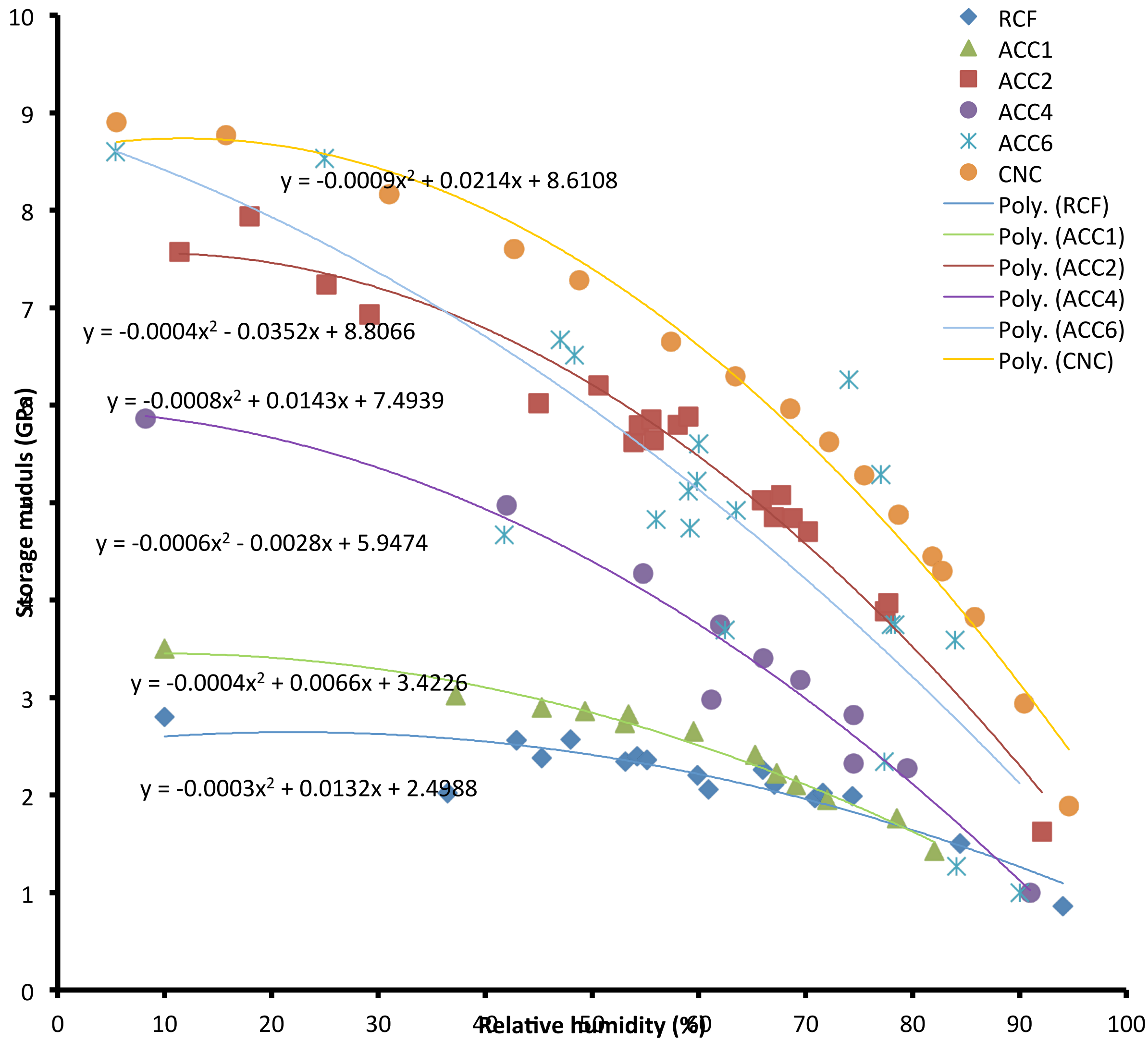

Figure S1. Storage modulus as a function of the relative humidity and second-order polynomial fits.

The Takayanagi model which sets in parallel and series different elements was originally devised to model a semi-crystalline polymer.[1] It can be used to describe the more general case of a composite with a percolated dispersed phase with a good degree of accuracy. This model was used several times with an excellent level of accuracy to describe composites reinforced with CNC.[2–4] A modified version was proposed in the form of:

$$E' = \frac{(1-2\psi+\psi X_r)E'_{RCF}E'_{CNC}+(1-X_r)\psi E'^{2}_{CNC}}{(1-X_r)E'_{CNC}+(X_r-\psi)E'_{RCF}} \qquad (1)$$

Where:

$$\psi = X_R\left(\frac{X_R-X_C}{1-X_C}\right)^{0.4} \qquad (2)$$

In this equation, E'_{RCF} and E'_{CNC} represent respectively the storage modulus of the CNC film and of RCF, ψ is the volume fraction of whiskers. X_R is the volume fraction of whiskers contributing to the load transfer and this value is back-calculated by fitting the second order polynomial describing the experimental data with the model data. The least square method and the solver toolbox in Microsoft Excel were used. X_C is the critical CNC percolation threshold; its value is equal to ~0.7/A where A is the aspect ratio of the CNC as deduced from imaging techniques. In general, the fitting was quite good as exemplified by the data calculated for ACC6 (Figure S2). The correlation coefficient between the model and the fitted data was acceptable and in general R was superior to 0.99. The value of Xc increased with the initial cellulose concentration, indicating an increasing contribution of the percolated CNC network in the dynamic mechanical behaviour.

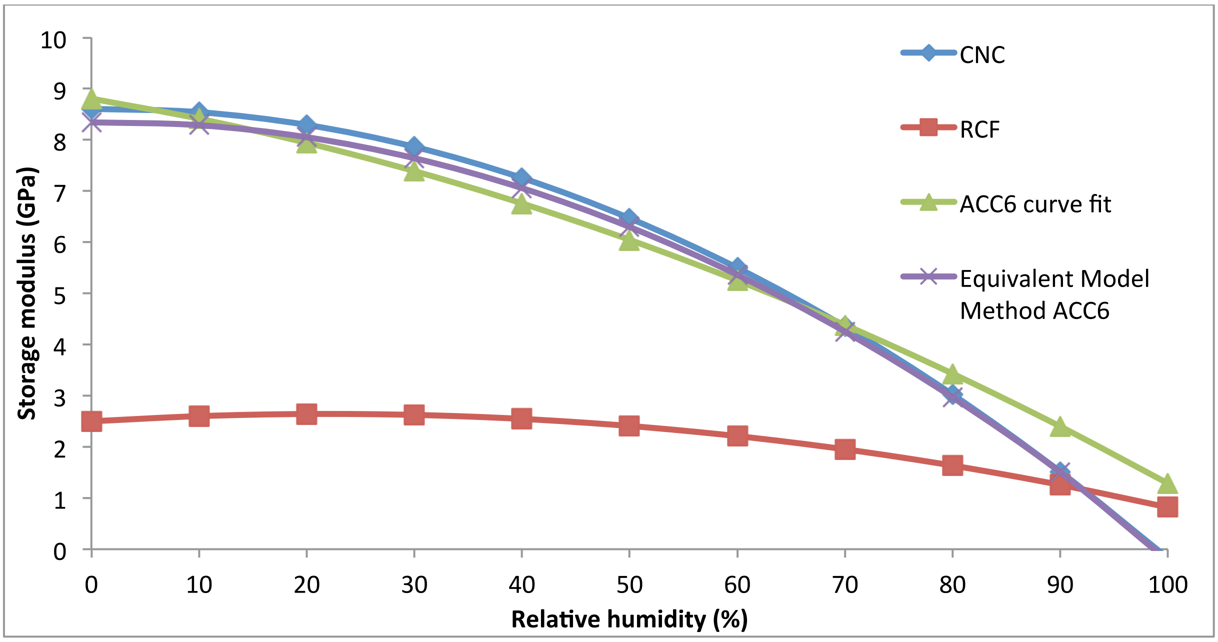

Figure S2. Example of a data fitted according to the percolation model.

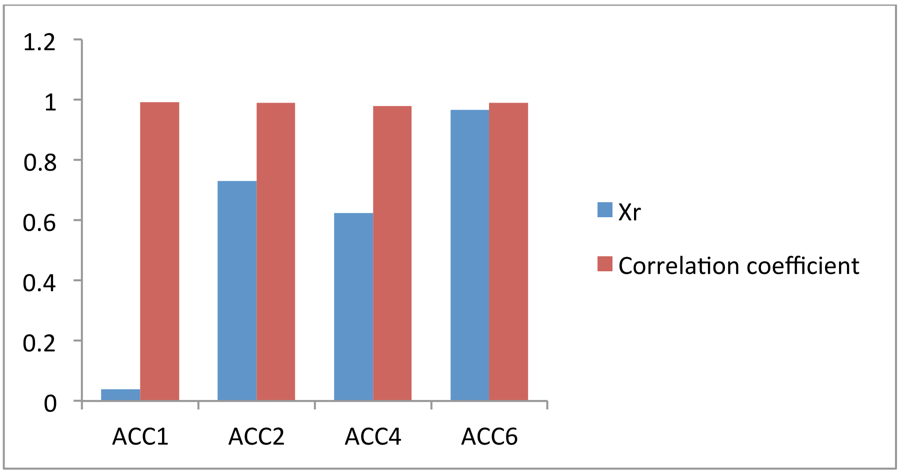

Figure S3. Correlation coefficient and volume fraction of the whiskers contributing to the observed mechanical properties as deduced from least-square fitting.

References:

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