**Prediction of the equilibrium moisture content based on the chemical composition and crystallinity of natural fibres**

Delphine E.C. Depuydta, Nick Sweygersb, Samuel Eyleyc, Wim Thielemansc, Lise Appelsb, Jan Ivensd, Aart W. van Vuurea

aKU Leuven, dept. Materials Engineering; Campus Groep T, Composite Materials Group, Andreas Vesaliusstraat 13, 3000 Leuven, Belgium

delphine.depuydt@kuleuven.be, aartwillem.vanvuure@kuleuven.be, [www.composites-kuleuven.be](http://www.composites-kuleuven.be/)

bKU Leuven, dept. Chemical Engineering;  Process and Environmental Technology Lab, Jan Pieter de Nayerlaan 5, 2860 Sint-Katelijne-Waver, Belgium

[nick.sweygers@kuleuven.be](mailto:nick.sweygers@kuleuven.be), [lise.appels@kuleuven.be](mailto:lise.appels@kuleuven.be), iiw.kuleuven.be/onderzoek/petlab

cKU Leuven, dept. Chemical Engineering; Renewable materials and nanotechnology research group, Etienne Sabbelaan 53 - box 7659, 8500 Kortijk, Belgium

[Samuel.eyley@kuleuven.be](mailto:Samuel.eyley@kuleuven.be), [wim.thielemans@kuleuven.be](mailto:wim.thielemans@kuleuven.be),

www.kuleuven-kulak.be/nl/onderzoek/key-areas/onderzoeksgroepen/rmnt

dKU Leuven, dept. Materials Engineering; Technology Campus De Nayer, Composite Materials Group, Jan De Nayerlaan 5, 2860 Sint-Katelijne-Waver, Belgium

jan.ivens@kuleuven.be, [www.composites-kuleuven.be](http://www.composites-kuleuven.be/)

**Keywords:** natural fibres, equilibrium moisture content, crystallinity, chemical composition

**Abstract**

The presented work investigates the relationship between the chemical composition and crystallinity of natural plant fibres and the equilibrium moisture content. Data from literature were verified with experimental data and were used to fit the model.

# Introduction

One of the challenges natural fibre reinforced composites face, is to reduce moisture induced degradation. In order to do so, more insight in the moisture absorption is needed. One way to study the moisture sorption behavior is by dynamic vapor sorption measurements, as in the work of Hill et al. [1] where several moisture sorption curves for different natural fibres were measured. From this work it becomes clear that different fibres show different sorption behavior. Moreover, equilibrium moisture contents (EMC) were found to be higher for fibres with high lignin contents. The hypothesis was that this might be related to the ability of the lignin network to deform to accomodate water within the cell wall. However, the current authors would like to investigate the influence of all plant fibre constituents on the EMC, in order to gain deeper understanding in the relationship between the equilibrium moisture content and the chemical composition and/or crystallinity of the fibre.

# Materials and Methods

Moisture sorption curves of different natural fibres: bamboo, flax, hemp, jute, coconut and spruce, were recorded via dynamic vapor sorption experiments (DVS). The equipment used, consisted of a Cahn microbalance, a temperature-controlled housing and mass flow controllers that control the appropriate flow of the wet and dry N2 gas. The benefit of this technique is the control over both the relative humidity and the temperature (i.e. 21°C). The fibres were first milled to a powder with a size < 250 µm. Approximately 5-10 mg of the natural fibre dust was used. The sample was first dried to a relative humidity (RH) of 0%; subsequently, the humidity was changed in steps of 10 % RH, except at the extremes where steps of 5 % were used(0, 5, 10, 20 … 80, 90 , 95 %). Every subsequent step was initiated when the change of the sample mass as a function of time was lower than 0.02 mg/min. A desorption curve with equal levels of RH was realized till full desorption. The moisture content was calculated according to the following equation:

(1)

Where meq is the mass of the sample at equilibrium and md the mass of the dry sample reached after the first drying stage. From the sorption curves the datapoint in the desorption cycle at a RH of 50% is used for the analysis of the different fibres.

To determine the chemical composition, i.e. the lignin, cellulose and hemicellulose content, an adapted Van Soest method in-house developed by Sweygers et al. [2] was used. Fibres were milled to powder in the same way as described for the DVS measurements. In a first step, a neutral detergent at 100°C was applied, thereby extracting the digestible cell contents (soluble sugars, starch) while the hemicellulose, cellulose and lignin fractions remain. In a second step, the residual content was treated with sodium chloride and acetic acid at 75°C in a water bath; the loss in matter is attributed to the lignin fraction. The remaining fraction, being the holocellulose, is treated with a mildly acidified detergent at 100°C, which only leaves cellulose as the sole particulate matter. The ash content is determined by heating the fibre particles for 2h at 550°C in a muffle furnace. The residual inorganic matter is the ash content. The cellulose, hemicellulose and lignin percentages mentioned in this report were determined by substracting the ash content and extractives from the total batch, and rescaling the former components to a total of 100 %.

The crystallinity of the natural fibres was determined via X-ray diffraction, with the test conditions listed in Table 1. Fibres were razor cut to a length < 0.6mm. Tests were performed on a Bruker D8 Advance goniometer, equipped with a Lync Eye-XE-T detector. Samples were analysed in a zero “background sample holder”. Rietveld refinement was carried out based on the the cellulose I beta structure published by Nishiyama et al. [3] using Topas Academic v6 software with subtraction of instrumental background (collected using an empty sample holder). The crystallinity index was then determined using the method described by Thygesen et al. [4] whereby the crystalline and amorphous contributions to the diffraction pattern are determined by integration of the fitted profile. For cellulose, the unit cell parameters a, b, c and gamma, 1 scale factor, a Lorentzian peak broadening parameter and a preferred orientation parameter (001 direction) were optimized during the refinement procedure. The amorphous contribution to the diffractogram was modelled using an hkl phase based on the P4 space group with a = 2 Å, c = 55 Å and with a peak width set to the equivalent for a 1 nm crystallite size. All unit cell parameters and intensities of individual hkl’s for this phase were allowed to vary freely during the refinement. A zero-shift parameter common to all phases was also refined. The crystallinity index is then calculated accoriding to the following equation (Eq. 1) where IC is the crystalline intensity, s is the scattering vector, and s1 and s0 represent the scattering vector at 2θ = 5° and 2θ = 60° respectively.

(1)

**Table 1** Settings of X-ray diffractometry

|  |
| --- |
| Xray: Cu Kα, 40 kV, 40mA; Line focus |
| Divergence slit: 0.1 mm |
| Receiving slit: none |
| Sampling time: 0.1 s |
| Step angle: 0.04° |
| Scan area: 5° ≤ 2θ ≤ 60° |

Supplemented with data from literature a data set was created as shown in Table 2. The equilibrium moisture content was determined for the moisture desorption curve at a relative humidity (RH) of 50% according to the work of Hill et al. [1]. Values for the chemical composition of the fibres and the crystallinity were collected from literature [5-8]. Crystallinity being determined as the amount of crystalline cellulose in 100 g dry material. A linear law is fitted through the data, either with one or multiple factors.

# Results and Discussion

## Dataset

Table 2 gives an overview of the data available in literature on the chemical composition, crystallinity and moisture sorption of natural fibres. The chemical components present in natural fibres are moisture sensitive, ranked from the highest contributor to the lowest one: hemicellulose, non-crystalline cellulose, lignin and crystalline cellulose [9]. The amount of amorphous cellulose can be calculated by subtracting the crystallinity from the cellulose content. However, this value is not found in literature. When considering the data from literature it can be seen that for a few cases the crystallinity exceeds the amount of cellulose. This can not be the case and can be attributed to the fact that the chemical compostion and crystallinity were often not determined in the same work, as well as the different techniques used to determine both and the error on these techniques. Therefore the authors decided to redo the measurements on 6 selected natural fibres. An adapted Van Soest method was used to determine the chemical composition and Rietveld refined was selected as the most accurate method to determine crystallinity, as mentioned in the work of Theygesen et al. [4]. The results from the measurements are listed in Table 3. However from the values it can be seen that the current method used in the Rietveld refinement tends to overestimate the crystallinity, as becomes clear by the abnormalities for the bamboo but most particulary for the jute fibre. Therefore, for this analysis the amorphous cellulose content will not be used, but the amorphous content instead (100%-crystallinity). Further research will optimize the Rietveld refinement for these natural fibres.

**Table 2** Literature overview of the chemical composition and crystallinity of natural fibres. The values between brackets, are the averages used for the calculation.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Crystallinity (%) | REF | EMC\* (%) | REF |
| Flax | 62-81 (72) | 14-21 (18) | 2-5 (4) | 70 (70) | [5, 6] | 7,5 | [1] |
| Coir | 35-44 (40) | 0,2-15,4 (8) | 33-45 (39) | 25-33 (29) | [7, 8] | 10 | [1] |
| Hemp | 57-92 (75) | 5-22 (14) | 3-13 (8) | 60-88 (74) | [7, 8] | 8 | [1] |
| Jute | 51-84 (68) | 12-24 (18) | 5-14 (10) | 78 (78) | [7, 8] | 9,5 | [1] |
| Sitka Spruce | 45 (45) | 25 (25) | 30 (30) | 34-52 (43) | [1, 7, 10] | 11 | [1] |
| Cotton | 82-96 (89) | 2-6 (4) | 0-1,6 (1) | 70-91 (81) | [5, 6, 11] | 6,5 | [1] |
| Bamboo | 26-43 (35) | 15-30 (23) | 21-31 (26) | 44-46 (45) | [5, 6] | 9,7 | \*\* |

\*In the desorption cycle, RH 50%

\*\*Own measured experimental data point

**Table 3** Experimentally determined values in this research. The values between brackes, are the averages used for the calculation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Crystallinity (%) | EMC\* (%) |
| Flax | 92 | 6 | 2 | 79;84 (82) | 7,4 |
| Coir | 48 | 17 | 35 | 37;41 (39) | 10 |
| Hemp | 90 | 7 | 3 | 82;80 (81) | 8,5 |
| Jute | 69 | 16 | 14 | 78;78 (78) | 9,7 |
| Spruce | 55 | 17 | 28 | 58;52 (55) | 10,7 |
| Bamboo | 66 | 10 | 24 | 67;69 (68) | 9,7 |

\*In the desorption cycle, RH 50%

## One factor fit

A first fit is done by linking the EMC to the amorphous content (=100%-crystallinity). Figure 1 shows the plots for both data sets. The intercept was forced to zero, with the assumption that if no amporhous content is present, no water will be absorbed in the structure. A R-square value of 0.89 and 0.87 is found for the dataset comprised out of literature data and experimental data respectively. However, to analyse the fitted model, the standard error of the regression (S) needs to be considered as well, S is found to be 3.21 % and 3.76 % for the literature and experimental data set respectively. This means that on average the observed values fall 3.5% from the regression line. Considering the EMC in this research, this value is large, indicating a poor fit.

**Figure 1** Plot of the equilibrium moisture content versus the amorphous content for the values found in literature and the experimental measured ones.

## Multiple factor fit

A fit is performed containing the main consituents present in the fibre: cellulose, hemicellulose and lignin. This results in the relationship in formula 1 for the data from literature and in formula 2 for the experiments performed in this work. The coefficients give a weight to the contribution of each factor. It is known that some chemical constituents of the fibres are more prone to moisture sorption than others. This seems to be reflected in the coefficients found in this research, where hemicellulose has the highest contribution, as would be expected from literature [9]. Both fits show a high R-square and Adjusted R-square value, though caution should be taken since less than 10 datapoints were used to fit the equations. The standard error of the regression is smaller than in the single factor fit, and seems acceptable. More calculations on the statistic significancy and robustness of the fit will be made.

(1)

**Table 4** Statistical analysis of the fit.

|  |  |  |  |
| --- | --- | --- | --- |
|  | S | R-square | R-square adjusted |
| Formula 1 | 0.53 | 99.81 | 99.66 |
| Formula 2 | 0.58 | 99.81 | 99.62 |

# Conclusion

First simulations, give indication of a relationship between the EMC and the different chemical components of the fibres. To draw a conclusion about the true predictiveness of the EMC depending on the chemical consituents, further investigation is needed. The Rietveld refinement, to determine crystallinity will be closer investigated, so that a fit can be made containing the amorphous cellulose as parameter instead of the total amount of cellulose. The robustness of the models will still be further analysed.

**Acknowledgements**

The authors would like to thank the Impulse Fund KU Leuven – Belgium (BOF/IMP14/034).

**References**

[1] C. A. S. Hill, A. Norton, G. Newman. The Water Vapor Sorption Behavior of Natural Fibers. Journal of Applied Polymer Science. 2009;112(3):1524-37.

[2] Nick Sweygers, Matthijs H. Somers, Lise Appels. Optimization of hydrothermal conversion of bamboo (Phyllostachys aureosulcata) to levulinic acid via response surface methodology. Journal of Environmental Management. 2018;219:95-102.

[3] Yoshiharu Nishiyama, Paul Langan, Henri Chanzy. Crystal Structure and Hydrogen-Bonding System in Cellulose Iβ from Synchrotron X-ray and Neutron Fiber Diffraction. Journal of the American Chemical Society. 2002;124(31):9074-82.

[4] A. Thygesen, J. Oddershede, H. Lilholt, A. B. Thomsen, K. Stahl. On the determination of crystallinity and cellulose content in plant fibres. Cellulose. 2005;12(6):563-76.

[5] M.J. John, T. Sabu. Natural Polymers Volume 1 : Composites. Cambridge: The Royal Society of Chemistry; 2012.

[6] J. Müssig. Industrial Applications of Natural Fibres. West Sussex: John Wiley & Sons, Ltd; 2010.

[7] N. Chand, M. Fahim. Tribology of natural fiber polymer composites. Cambridge: Woodhead Publishing and Maney Publishing.

[8] L. Y. Mwaikambo, M. P. Ansell. Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. Journal of Applied Polymer Science. 2002;84(12):2222-34.

[9] C. Baillie. Green composites, polymer composites and the environment. Cambridge, England: Woodhead Publising Limited; 2000.

[10] D.D. Stokke, Q. Wu, G. han. Introduction to Wood and Natural Fiber Composites. West Sussex, United Kingdom: John Wiley & Sons; 2014.

[11] Y. Kubojima, M. Wada, Y. Suzuki, M. Tonosaki. Real-time measurement of vibrational properties and fine structural properties of wood at high temperature. Wood Science and Technology. 2001;35(6):503-15.