

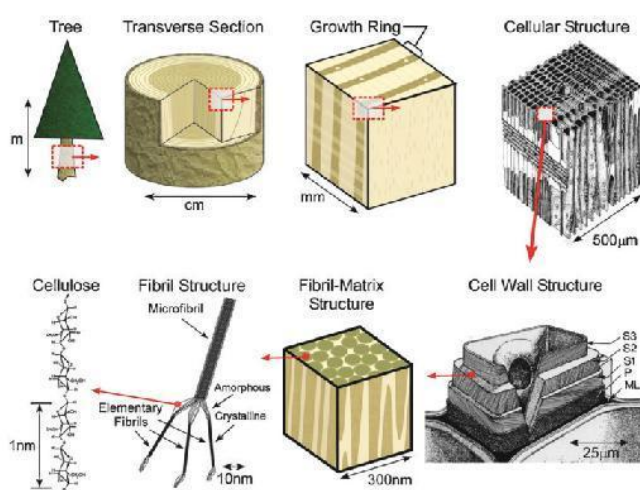
CELLULOSE CHARACTERISTICS : FROM MICRO TO NANO

by Syeed SaifulAzry, Luqman Chuah Abdullah and Paridah Md Tahir



Introduction

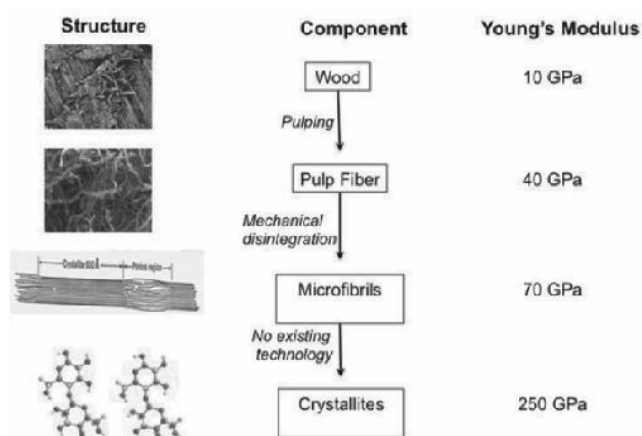
Cellulose characteristics very much depending on hierarchical structure design that spans nanoscale to macroscopic dimensions as illustrated in Figure 1. It possesses several attributes such as a fine cross section, the ability to absorb moisture, high strength and durability, high thermal stability, good biocompatibility, relatively low cost and low density yet good mechanical properties (Roy et al., 2009). However, cellulose fibres properties are strongly influenced by many factors, which differ from different parts of a plant as well as from different plants (Siquera, Bras, & Dufresne, 2010). Due to this inuniformity and some of cellulose natural characteristics (i.e high hydrophilicity, poor dimensional stability, easily attack by insects and fungi), its promotes endless efforts especially by scientist to improve and modify drawbacks that associate with cellulose in original form. The improvement and modification of cellulose can be done physically and/or chemically depending on properties that desired to be improved.



Source : Dufresne, 2013

Figure 1 : Illustration of cellulose hierarchical structure

The hierarchical structure design of cellulose fibres exhibit uniqueness to it properties. The mechanical performance of cellulose fibre increase tremendously as it is downscaled from macro to nano level. As illustrated in Figure 2, the modulus of wood in original form is about 10Gpa. It increase to 40GPa after separated and downsize into pulps and further to 70 GPa at microfibrill form and 250 Gpa as in crystalite (nano) form (Silva et al, 2015). In fact, at the nanoscale level, some material properties are affected by the laws of atomic physics rather than behaving as traditional bulk materials do. Their extremely small features size is of the same scale as the critical size for some physical phenomena, such as light (Brinchi, et al., 2013). This makes cellulose fibre at nanoscale open a wide range of possible properties to be



Source : Silva et al., 2015

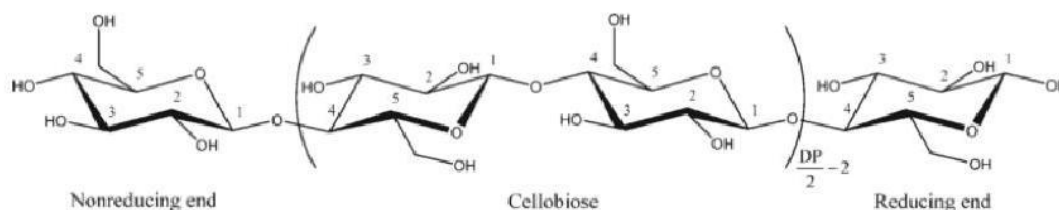
Figure 2 : Correlation between structure, process, component and modulus

discovered. Generally, the size of nanocellulose fibres are in the range from 2 to 20 nm in diameter, and a length of more than a few micrometers.

Cellulose structure and arrangement

Cellulose molecular structure

The cellulose molecule is a linear homopolysacchride that composed of D-anhydroglucopyranose units linked together by β -1,4-glycoside bonds. The molecular structure of cellulose shown in Figure 3.



Source : Habibi, Lucía, & Rojas, 2010

Figure 3 : Structure of cellulose with carbon atom numbering with hemiacetal at the reducing end and free hydroxyl group at C4 as non-reducing end

As illustrated in Figure 3, cellulose is 1,4-linked glucans that has one reducing end containing an unsubstituted hemiacetal, and one non-reducing end containing an additional hydroxyl group at C4. Each monomer attached with three hydroxyl groups where C6-OH act as primary group and C1-OH and C2-OH as secondary group (Wertz, Bédoué, & Mercier, 2010). These hydroxyl groups will determine the cellulose reactivity. Generally, the reactivity of these hydroxyl groups can be expressed as $\text{OH-C6} \gg \text{OH-C2} > \text{OH-C3}$ (Roy et al., 2009). Besides, these groups are responsible for the formation of strong hydrogen bonding inter- and intra-cellulose molecule chain (Figure 4). The hydrogen bonding will attributes to cellulose important properties especially its (i) multi-scale microfibrillated structure, (ii) hierarchical organization (crystalline vs. amorphous regions), and (iii) highly cohesive nature (with a glass transition temperature higher than its degradation temperature (Lavoine et al., 2012).

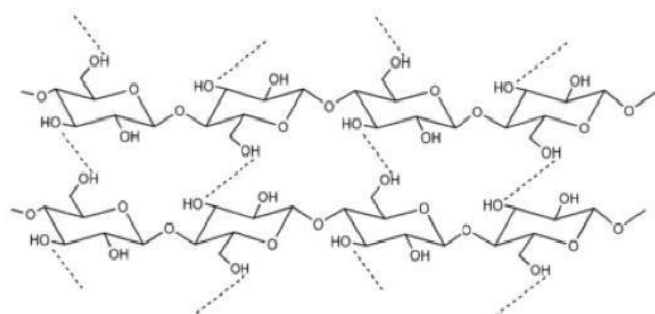


Figure 4 : Hydrogen bonding in cellulose molecules
(a) Intramolecular; (b) Intermolecular

Cellulose polymerization and packing assemblies

The degree of polymerization of native cellulose from various sources is ranging from 1000 to 30,000, which corresponds to chain lengths from 500 to 15000 nm (Ioelovich, 2008). As mentioned earlier, cellulose is a hierichal structure. It has a complex, multi-level from macro to nano-scale architecture. It assemble from packing bundles of elementary fibrils that have size 3-15 nm in diameter and length about 1 μ m. These packing

assemblies of elementary fibrils consist of 60-80% of ordered domain and remaining as disordered domain. Ordered domains also called as crystalline region contains highly ordered and very minimal defect crystallite chains having length in range of 50-150 nm. Meanwhile, disordered domain which commonly known as amorphous region is 25-50 nm (Ioelovich, 2008).

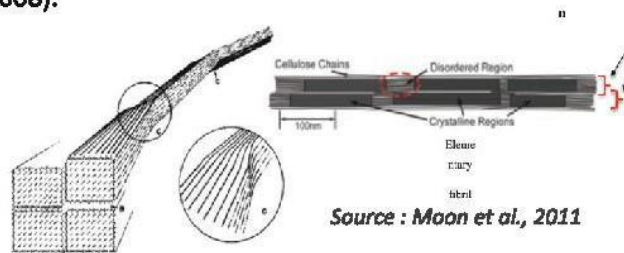


Figure 5: Illustration on the microstructure of the microfibril a) cross-section view of microfibril that comprise elementary fibrils bundle b) single elementary fibril c) amorphous region/defects due to distorted by internal strain in the fibre and proceed to tilt and twist d) side-view of microfibrils and elementary fibril bundles

The amorphous regions are scattered along the microfibrils. One of well accepted theory of how amorphous region occurs was due to microfibrils are distorted by internal strain in the fibre and proceed to tilt and twist and producing chain dislocations/defects on segments along the elementary fibril packings as illustrated in Figure 5 (Habibi et al., 2010).

Cellulose polymorph and packing arrangement

There are six crystalline polymorphs of pure cellulose with different packing arrangements ; cellulose I, II, III, III_{II} IV_I and IV_{II} (O'sullivan, 1997). Cellulose I also called as native cellulose because its the most cellulose polymorphs that found in nature. Naturally, within the same microfibril, cellulose I coexists in two crystal phase suballomorphs, cellulose I α and cellulose I β . Cellulose I α is richly found in algae and bacterial cellulose, whilst cellulose I β dominantly in higher plant and tunicate (Wertz et al., 2010). Phase I α has a triclinic unit cell containing one chain, whereas cellulose I β is

represented by a monoclinic unit cell containing two parallel chains (Nishiyama et al., 2002). These were by measured it vectors (a, b and c) and vectors angle. Thus, its attributes to displacement of adjacent chains of cellulose molecular unit arrangement whether it diagonally shifted for cellulose I α or a staggered for cellulose I β . (Wertz et al., 2010). Figure 6 shows schematic drawing and measurement of the cellulose unit coordinate systems for cellulose I α and I β .

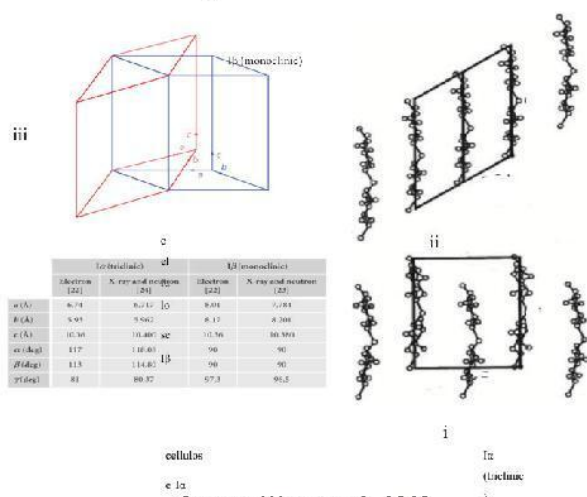


Figure 6 : Cellulose I α (triclinic) and I β (monoclinic) coordinate systems (i) Cellulose unit orientation; (ii) Measurement of vectors and angle; (iii) View of five cellulose chains viewed orientation and arrangement.

Reference

Abdul Khalil, H. P. S., Bhat, a. H., & Ireana Yusra, a. F. (2012). Green composites from sustainable cellulose nanofibrils: A review. Carbohydrate Polymers, 87(2), 963–979.

Brinchi, L., Cotana, F., Fortunati, E., & Kenny, J. M. (2013). Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications. Carbohydrate Polymers, 94(1), 154–169.

Dufresne, A. (2013). Nanocellulose: A new ageless bionanomaterial. Materials Today, 16, 220–227.

Habibi, Y., Lucia, L. a, & Rojas, O. J. (2010). Cellulose Nanocrystals : Chemistry, Self-Assembly, and Applications. Chemical Reviews, 110, 3479–3500.

Ioelovich, M. (2008). Cellulose as a nanostructured polymer: A short review. BioResources, 3(4), 1403–1418.

Klemm, D., Heublein, B., Fink, H.-P. and Bohn, A. (2005). Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angewandte Chemie International Edition, 44(22): 3358–3393.

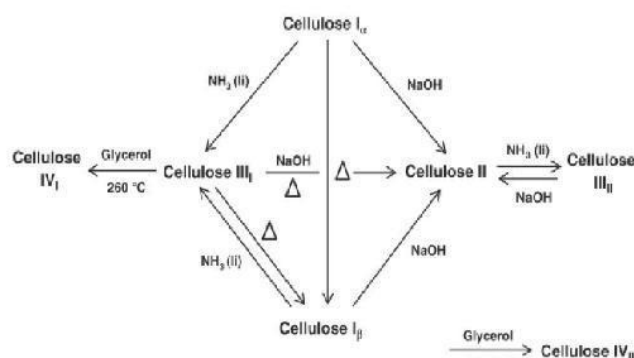
Lavoine, N., Desloges, I., Dufresne, A., & Bras, J. (2012). Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. Carbohydrate Polymers, 90(2), 735–764.

Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). Cellulose nanomaterials review: structure, properties and nanocomposites. Chemical Society Reviews, 40(7), 3941–3994.

Nishiyama Y, Langan P, Chanzy H. Crystal structure and hydrogen-bonding system in cellulose 1 beta from synchrotron X-ray and neutron fiber diffraction. J Am Chem Soc (2002) 124:9074-9082.

O'sullivan, A. (1997). Cellulose: the structure slowly unravels. Cellulose, 4(3), 173–207.

Cellulose polymorphs are intertransform as shown in Figure 7. Some of polymorph are irreversible once been transformed into different polymorph i.e cellulose II. The transformation of cellulose II from cellulose I can be done by two distinct routes: mercerization (alkali treatment) and regeneration (solubilization and subsequent recrystallization). Celluloses III α and III β can be formed from celluloses I and II, respectively, by treatment with liquid ammonia, and the reaction is reversible. Celluloses IV α and IV β can be obtained by heating celluloses III α and III β , respectively. (Klemm et al., 2005; O'Sullivan, 1997; Abdul Khalil et al., 2012;



Source : wustenberg, 2015

Figure 7 : Transformation of cellulose into its various polymorphs

Roy, D., Semsarilar, M., Guthrie, J. T., & Perrier, S. (2009). Cellulose modification by polymer grafting: a review. Chemical Society Reviews, 38(7), 2046–2064.

Silva, T. C. F., Silva, D., & Lucia, L. A. The Multifunctional Chemical Tunability of Wood-Based Polymers for Advanced Biomaterials Applications. In: Kumar Thakur, V., & R Kessler, M. Green Biorenewable Biocomposites : From Knowledge to Industrial Applications. Apple Academic Press Inc. (2015). p 427-460

Siqueira, G., Bras, J. and Dufresne, A. (2010). Cellulosic Bionanocomposites: A Review of Preparation, Properties and Applications. Polymers, 2(4): 728-765.

Wertz, J.-L., Bédoué, O., & Mercier, J. P. (2010). Cellulose Science and Technology. EPFL Press. Taylor & Francis.. p. 359

Wustenberg, T. (2015). Cellulose and Cellulose Derivatives in the Food Industry : Fundamentals and Application. Weinheim, Germany: Wiley-VCH.

Author:

Mr. Syeed SaifulAzry Osman El-Edrus

Research Officer

Laboratory of Biocomposite Technology

Institute of Tropical Forestry and Forest Products (INTROP)

Universiti Putra Malaysia

Email: saifulazry@upm.edu.my