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Correlation between stiffness of sheets prepared from cellulose whiskers and nanoparticles dimensions

Julien Bras, David Viet[1], Cécile Bruzzese, Alain Dufresne*

The International School of Paper, Print Media and Biomaterials (Pagora), Grenoble Institute of Technology, BP 65, F-38402 Saint Martin d'Hères Cedex, France

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ABSTRACT

Impressive mechanical properties of cellulose nanocrystals or whiskers have generated great interest from the scientific community as shown by the huge amount of recent literature in this field. It makes them ideal candidates for the processing of polymer nanocomposites. Their outstanding reinforcing capability is classically ascribed to a mechanical percolation phenomenon. At sufficiently high temperature, the stiffness of the materials depends only on the volume fraction of the percolating rigid phase and stiffness of the percolating network. The effect of the first parameter has been well investigated in the literature but surprisingly no report is found about the latter. Tensile tests were performed on films prepared by water evaporation of a series of cellulose whiskers suspensions. Interestingly, our experimental data show that a correlation exists between the stiffness of the films and aspect ratio of the constituent rod-like nanoparticles.

1. Introduction and background

Since the first announcement in 1995 of using cellulose nanocrystals or whiskers as a reinforcing phase in a polymeric matrix (Favier et al., 1995), they were extensively used in association with several kinds of matrices, including synthetic and natural polymers. In this pioneering study, mixtures of tunicin whiskers and latex obtained by the copolymerization of styrene and butyl acrylate (poly(S-co-BuA)) were cast and evaporated. It led to nanocomposite materials with drastically enhanced mechanical properties, especially above the glass transition temperature of the matrix. These outstanding mechanical properties were well understood by virtue of the formation of a continuous network of whiskers. The formation of this rigid network, resulting from strong interactions between whiskers was assumed to be governed by a percolation mechanism. This hydrogen-bonded network also induced a thermal stabilization of the composite up to 500 K, the temperature at which cellulose starts to decompose. Any factor that perturbs the formation of this percolating network directly affects the reinforcing effect of cellulose nanocrystals (Azizi Samir, Alloin, & Dufresne, 2005). Afterwards a huge amount of literature has been devoted to nanocellulose, i.e. cellulose whiskers of microfibrils, reinforced nanocomposites that become a topical subject.

The mechanical behavior of these nanocomposite films was well predicted from a percolation approach. Even if significantly oversimplified, a good agreement between experimental and predicted data was reported when using the series-parallel model of Takayanagi, Uemura, and Minami (1964) modified to include a percolation approach. In this approach, the elastic tensile modulus E_c of the composite is given by the following equation:

$$E_c = \frac{(1 - 2\psi + \psi v_R)E_S E_R + (1 - v_R)\psi E_R^2}{(1 - v_R)E_R + (v_R - \psi)E_S} \quad (1)$$

where E_S and E_R refer to the tensile modulus of the soft and rigid phase, respectively, and v_R is the volume fraction of the reinforcing phase. The adjustable parameter, ψ, involved in the Takayanagi et al. model corresponds to the volume fraction of the percolating rigid phase. With b being the critical percolation exponent, ψ can be written as:

$$\begin{aligned} \psi &= 0 && \text{for } v_R < v_{Rc} \\ \psi &= v_R\left(\frac{v_R - v_{Rc}}{1 - v_{Rc}}\right)^b && \text{for } v_R > v_{Rc} \end{aligned} \quad (2)$$

where $b = 0.4$ for a 3D network (de Gennes, 1979; Stauffer, 1985) and v_{Rc} is the percolation threshold.

At high temperatures, i.e. when the stiffness of the polymeric matrix could be assumed to be much lower than the one of the reinforcing phase ($E_S \sim 0$), the calculated stiffness of the composites

* Corresponding author. Present address: Universidade Federal de Rio de Janeiro (UFRJ), Departamento de Engenharia Metalúrgica e de Materiais, Coppe, Rio de Janeiro, Brazil.
E-mail address: Alain.Dufresne@pagora.grenoble-inp.fr (A. Dufresne).
[1] Present address: The Green Factory, 27 rue Chanez, 75016 Paris, France.

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Table 1
Experimental pretreatment conditions of the fibers.

Sources	Washing step	Bleaching step	Ref.
Capim Dourado	NaOH 4%/80 °C/2 h	Acetate buffer/sodium chlorite/80 °C	Siqueira, Abdillahi, Bras, and Dufresne (2010)
Cotton	NaOH 5%/80 °C/4 h	Acetate buffer/sodium chlorite/80 °C	de Souza Lima and Borsali (2004)
Hardwood			Beck-Candanedo, Roman, and Gray (2005)
Luffa Cylindrica	NaOH 2%/80 °C/2 h	Acetate buffer/sodium chlorite/80 °C	Siqueira, Bras, and Dufresne (2010)
Palm Tree Rachis	NaOH 2%/80 °C/2 h	Acetate buffer/sodium chlorite/70 °C	Bendahou, Habibi, Kaddami, and Dufresne (2009)
Ramie	NaOH 2%/80 °C/2 h	No bleaching step	Habibi and Dufresne (2008)
Sisal	NaOH 2%/80 °C/2 h	Acetate buffer/sodium chlorite/80 °C	Siqueira, Bras, and Dufresne (2009)
Sugar Cane Bagasse	NaOH 5%/80 °C/4 h	Acetate buffer/sodium chlorite/80 °C	Hassan et al. (2009)

is simply given by:

$$E_c = \psi E_R \quad (3)$$

Therefore, the predicted modulus depends on the volume fraction of the percolating rigid phase, ψ, which is directly related to the volume fraction and geometrical characteristics of the reinforcing phase. This parameter is directly related to the origin of cellulose and its effect has been reported in the literature (Dufresne, 2006).

The other parameter involved in the prediction of the composite's modulus (Eq. (3)) is the modulus E_R of the percolating cellulosic nanoparticles network. It is obviously different from the one of individual whisker and depends on the preparation procedure and obviously nature and strength of inter-particle interactions. This modulus can be assumed to be similar, in principle, to the one of a paper sheet for which the hydrogen bonding forces provide the basis of its stiffness. It can be experimentally determined from tensile tests performed on films prepared from the evaporation of a suspension of nanocrystals. Very few data are reported in the literature. For tunicin (Favier, Chanzy, & Cavaillé, 1995) and wheat straw cellulose whiskers (Helbert, Cavaillé, & Dufresne, 1996), the tensile modulus was around 15 GPa and 6 GPa, respectively.

The apparent tensile modulus of a tunicin whiskers network was also calculated by a 3D finite elements simulation (Bréchet et al., 2001; Favier et al., 1995). The linking elements were considered as beams with adjustable stiffness. All the calculated values were lower than 1 GPa. For link modulus values below 1 GPa, the network modulus was found to increase with increasing whisker concentration and seemed to increase linearly with the link modulus. For higher linking modulus, the modulus of the percolating network tends toward the value for totally rigid links. It was shown that rather tight bonds between the whiskers are needed to reproduce a sufficient rigidity of the material, which is possible by the hydrogen bonds that can be created when whiskers come into contact.

A huge quantity of different natural fibers can be found throughout the world, leading to broad range of aspect ratios (L/d, L being the length and d the diameter) of cellulosic whiskers. This should influence several parameters such as percolation threshold but also intrinsic mechanical properties. A way to predict these properties could limit testing of different sources.

The present study reports a benchmarking of cellulose whiskers from different sources, and shows the impact of the geometrical characteristics on the specific mechanical properties of the percolating network. Even if other factors are controlling the mechanical properties of this network, such as porosity, density, orientation and organization of the nanoparticles, it seems that a weak correlation exists between the aspect ratio of the whiskers and mechanical stiffness of the mat.

2. Experimental

2.1. Materials

Different natural fibers have been used in this study to prepare cellulose whiskers, viz. bleached cotton fibers (*Gossypium* sp.), native sisal fibers (*Agave Sisalana*) originating from Brazil (Mariana, Minas Gerais), native *Luffa Cylindrica* fibers originating from Brazil (Belo Horizonte, Minas Gerais), native Capim Dourado fibers were brought back from the Jalapão region, Tocantins State, Brazil, native date palm tree fibers (*Phoenix dactylifera*) originating from Morocco (Marrakech), treated ramie fibers (Stucken Melchers GmbH & Co., Germany), hardwood (Tembec, Saint Gaudens, France), and sugarcane bagasse fibers originating from Egypt (Cairo). Sulfuric acid (≥95 wt%) was used as purchased from Aldrich.

2.2. Methods

2.2.1. Pretreatments of the fibers

Unbleached fibers were cut with a FRITSCH Pulverisette mill, until fine particulate fibers were obtained. Then, the fibers were treated with a NaOH solution at 80 °C under mechanical stirring. The concentration of the solution and duration of the treatment varied depending on the source of cellulose. The experimental conditions are reported in Table 1. This treatment was done 3 times, in order to purify cellulose by removing other constituents present in the fibers. After each treatment, the fibers were filtered and washed with distilled water until the alkali was completely eliminated.

A subsequent bleaching treatment was carried out to whiten the fibers. The solution used in this treatment was made by equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water) and distilled water. The bleaching treatment was performed for 4 h under mechanical stirring and was repeated 4 times. After each treatment the fibers were filtered and washed with distilled water. The precise bleaching conditions are reported in Table 1.

2.2.2. Preparation of cellulose whiskers

The acid hydrolysis treatment was achieved with sulfuric acid (pre-heated) under mechanical stirring. The experimental conditions varied depending on the source of cellulose and are reported in Table 2. The fiber content was in the range 4–6 wt%. The suspension was diluted with ice cubes or cold water to stop the reaction and washed until neutrality by successive centrifugations at 10,000 rpm at 10 °C for 10 min each step and dialyzed against distilled water. Afterwards the cellulose whiskers suspension was homogenized by using an Ultra Turax T25 homogenizer for 5 min and filtered using glass filter n°1. Some drops of chloroform were added to the suspension which was stored at 4 °C until use.

2.2.3. Preparation of cellulose whisker films

Films for tensile tests were obtained by water evaporation of aqueous suspensions of cellulose whiskers. The aqueous suspensions were cast in Teflon molds and allowed to evaporate at 30 °C in a ventilated oven. Films, around 10–20 μm thick, were conditioned at 25 °C and 50% relative humidity (RH) for at least 24 h before testing.

2.2.4. Tensile tests

Tensile tests were carried out with a RSA3 (TA Instruments, USA) equipment with a 100 N load cell. Measurements were performed

Table 2
Experimental hydrolysis conditions used for the preparation of cellulose whiskers.

Source	H_2SO_4 conc. (wt%)	Duration (min)	T (°C)	Acid-to-pulp ratio	Quenching	Purification	Ref.
Capim Dourado	65	60	50	5	Ice	Dialysis/filtration	Siqueira, Abdillahi, et al. (2010)
Cotton	64	45	45	10	10-Fold water	Dialysis/mixed bed resin/filtration	de Souza Lima and Borsali (2004)
Hardwood							Beck-Candanedo et al. (2005)
Luffa Cylindrica	65	40	50	5	Ice	Dialysis/filtration	Siqueira, Bras, et al. (2010)
Palm Tree Rachis	65	45	45	5	Ice	Dialysis/filtration	Bendahou et al. (2009)
Ramie	65	30	55	5	Ice	Dialysis/filtration	Habibi and Dufresne (2008)
Sisal	65	40	50	5	Ice	Dialysis/filtration	Siqueira et al. (2009)
Sugar Cane Bagasse	60	150	60		Ice water	Dialysis/mixed bed resin/filtration	Hassan et al. (2009)

at 25 °C with a cross-head speed of 10 mm min^{-1}. The samples were prepared by cutting strips from the films 20 mm long and the distance between jaws was 10 mm, whereas the width and the thickness of the samples were measured before each measurement. Five samples were used to characterize each nanocomposite film.

3. Results and discussion

Any material containing cellulose can be used to prepare aqueous suspensions of cellulose whiskers but the dimensions of the constitutive rod-like nanoparticles depend on the source of cellulose. Also, the dimensions depend on the exact preparation conditions. When starting from native lignocellulosic fibers, the first step consists in a washing treatment with NaOH followed by a bleaching step using acetate buffer and sodium chlorite in order to purify cellulose by removing other constituents such as hemicellulose and lignin. This first step is crucial and need to be performed carefully. The experimental conditions have to be adjusted depending on the source of cellulose (Table 1).

Cellulose is a semicrystalline polymer and the amorphous regions act as structural defects and are responsible for the transverse cleavage of the microfibrils into short monocrystals under acid hydrolysis (Azizi Samir et al., 2005; Battista, Coppick, Howsmon, Morehead, & Sisson, 1956; Marchessault, Morehead, & Joan Koch, 1961). It is ascribed to the faster hydrolysis kinetics of amorphous domains compared to crystalline ones. The hydronium ions penetrate the cellulosic material in the amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds releasing individual crystallites. The geometrical characteristics of cellulose whiskers depend on the origin of cellulose and acid hydrolysis conditions such as time, temperature and purity of the material. The acid hydrolysis conditions (temperature, time, and acid concentration) need to be controlled and adapted for each source (Table 2). The resulting aqueous suspension does not precipitate nor flocculate when using H_2SO_4. It is ascribed to the electrostatic repulsion between the negatively charged particles on their surface. The suspension is subsequently diluted with water or ice and then washed several times by centrifugation. Dialysis, filtration or addition of a mixed bed resin, depending on the process, allows removing the free acid from the dispersion. After reaching the neutral pH, complete dispersion is obtained by a sonication step.

The most studied cellulose source is cotton with about 600 scientific papers listed in June 2008 (Viet et al., 2009). The main reason is the high cellulose content of cotton that results in a higher yield when preparing cellulose whiskers and avoids intensive purification of cellulose. For all other sources, the number of scientific papers is generally lower than 30.

Determination of the whiskers content can be done by weighing samples of the suspension before and after drying. Viscous suspensions are obtained as soon as the concentration of nanoparticles is higher than few percents, which exact value depends on their geometrical dimensions.

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) are generally used to determine the structure and the morphology of cellulose nanocrystals. These two techniques have been compared (Kvien, Tanem, & Oksman, 2005). It was shown that AFM overestimated the width of the whiskers due to the tip-broadening effect. Scanning electron microscopy (SEM) could be used to have a quick examination in order to have an overview of the sample. The resolution is simply insufficient for more detailed information. Therefore, the best method to identify individual whiskers and enables the determination of nanocrystals size and shape is TEM.

The geometrical characteristics reported for nanocrystals from different sources are reported in Table 3. The length is generally of the order of few hundred nanometers and the width is around few nanometers. From these values, the aspect ratio L/D can be determined, as well as the percolation threshold (v_{Rc}) that can be calculated from the following relation (Azizi Samir et al., 2005; Dufresne, 2006):

$$v_{Rc} = \frac{0.7}{L/d} \quad (4)$$

Films were prepared by casting and evaporating aqueous suspensions of cellulose whiskers from different origins. Tensile tests have been performed on the ensuing films in order to determine the Young's modulus from the maximum slope of the stress–strain curves. Fig. 1 shows typical stress–strain curves obtained for films prepared from cellulose whiskers from three different origins, viz. date palm tree, *Luffa Cylindrica* and sugar cane bagasse. It is clearly seen that the Young's modulus is higher for date palm tree than for *Luffa Cylindrica* and sugar cane bagasse whiskers. The average aspect ratio is 42.6, 46.5 and 12.9, respectively. The Young's modu-

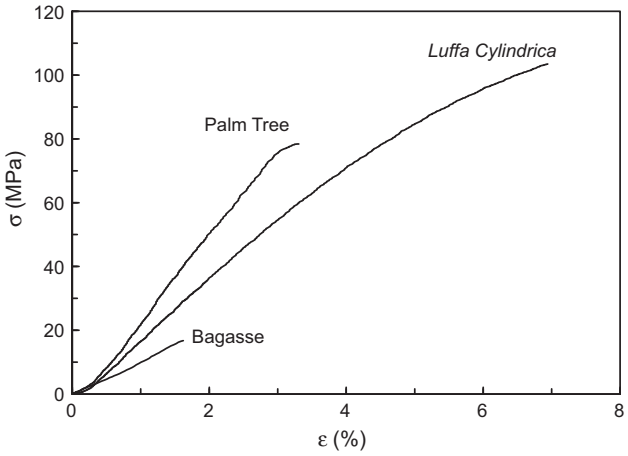

Fig. 1. Typical stress–strain curves obtained for films prepared from date palm tree, *Luffa Cylindrica* and sugar cane bagasse cellulose whiskers.

Table 3
Average geometrical characteristics of cellulose whiskers from various sources: length (L), width (D), aspect ratio (L/D), percolation threshold (v_{Rc}) and Young's modulus (E) determined from a tensile test performed on a cast/evaporated whiskers film.

Source	L (nm)	D (nm)	L/D	Ref.	v_{Rc} (vol.%)	E (GPa)
Capim Dourado	300 ± 93	4.5 ± 0.86	67	Siqueira, Abdillahi, et al. (2010)	1.0	10.9 ± 1.6
Cotton	170	15	11.3	de Souza Lima and Borsali (2004)	6.2	2.13 ± 0.32
Hardwood	200	10	20	Beck-Candanedo et al. (2005)	3.5	0.40 ± 0.06
Luffa Cylindrica	242	5.2	46.5	Siqueira, Bras, et al. (2010)	1.5	2.41 ± 0.31
Palm Tree Rachis	260	6.1	42.6	Bendahou et al. (2009)	1.6	7.70 ± 1.15
Ramie	134	10.8	12.4	Habibi and Dufresne (2008)	5.6	0.46 ± 0.07
Sisal	215	5	43	Siqueira et al. (2009)	1.6	8.50 ± 1.27
Sugar Cane Bagasse	96.7	7.5	12.9	Hassan et al. (2009)	5.4	1.50 ± 0.24
Tunicin	1000	15	66.7	Favier et al. (1995)	1.0	15*
Wheat Straw	225	5	45	Helbert et al. (1996)	1.6	6**

*, **: Young's moduli values taken from literature.

lus values obtained for films prepared from cellulose whiskers from various origins are report in Table 3. The ultimate properties were not considered because of the brittleness of the samples and highly scattered data.

Fig. 2 shows the evolution of the Young's modulus of the cellulosic whiskers film determined from the tensile tests as a function of the aspect ratio of the constituting whiskers. It seems that a weak correlation exists between these two parameters. Higher aspect ratios result in higher stiffness of the films. It could be possibly ascribed to stronger H-bonding interactions between high aspect ratio nanoparticles. However, it is worth noting that other factors are controlling the mechanical properties, among which are the porosity and density of the film. We have seen for instance that the porosity and density of a sisal cellulose whiskers film were around 62% and 0.9 g cm^{-3}, respectively (Belbekhouche et al., 2010). When increasing the aspect ratio of the cellulosic nanoparticles, it is believed that the density of the film decreases and therefore it becomes more difficult to have rods close packed (except in chiral nematic-type structures) and this should be a factor reducing the H-bonding strength. Nevertheless the stiffness of the film is found to increase with the apect ratio of the whiskers. The measured initial tensile modulus must be a function of the modulus of the individual whiskers, strength of the inter-whiskers bonds as well as bonded area. It is worth noting that the wet-laying process ensures whisker-to-whisker contact, but such contacts might be less evident after dispersion in a matrix. Clearly there will be more whisker–whisker contacts in a solid film of whiskers than in a composite, which modulus depends upon the environment, especially as it impacts hydrogen bonding. Another issue that arises when measuring the modulus of a dried film is that the whiskers in the film are not randomly oriented. Simply viewing the film through crossed polars confirms this, as does the large number of reports on the chiral nematic structure of nanocrystal films. Eqs. (1) and (3) assume a random orientation of whiskers in the composite. Of course, the value of E_R is much more complex than the complexity shown in these equations. However, it gives a clear indication of whisker–whisker interactions. In addition, the high dispersion of whisker dimensions was not included in this analysis.

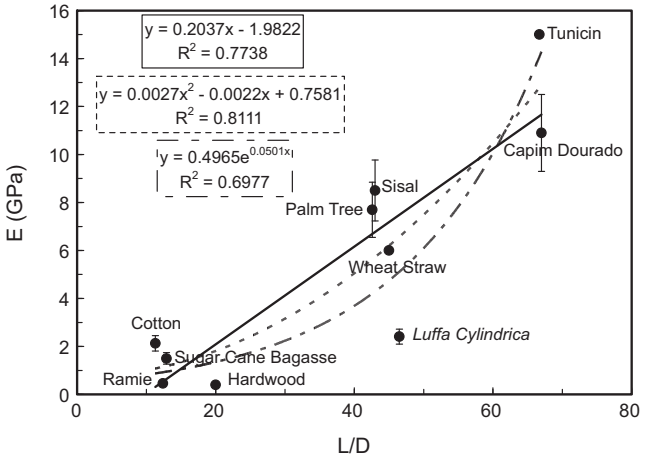

Fig. 2. Evolution of the Young's modulus of the cellulosic whiskers film determined from tensile tests as a function of the aspect ratio of the constituting whiskers.

The data have been fitted using a linear (continuous line), second order polynomial (dashed line) and exponential regression (hybrid line). The equations and correlation factors corresponding to these regressions are reported in Fig. 2. The correlation factors are not so good but the relationship between these two parameters is real. It is worth noting that films were thin and very brittle rendering the tensile measurements fastidious. Additional measurements with nanoparticles of different aspect ratios should be performed to refine the observed tendencies. Refining tendencies would allow deducing Young's modulus values only from the knowledge of the aspect ratio of the nanoparticles limiting experiments.

4. Conclusion

Tensile tests were performed on films prepared by water evaporation of a series of cellulose whiskers suspensions. Interestingly, it is shown that their tensile modulus increases when increasing the aspect ratio of the nanoparticles. It is an indication that the modulus of a film of pure whiskers depends on some extent upon aspect ratio. Even if the estimation of the modulus of the percolating whisker network from the modulus of a film of pure whiskers is questionable it proves that it is important to choose high aspect ratio whiskers to have an efficient reinforcing effect of a polymeric matrix. It results in an obvious reduction of the percolation threshold allowing reduction of the filler content necessary to reach an effective reinforcing effect, and higher stiffness of the percolating cellulosic network. However, the present conclusion should be taken with care since many other factors are controlling the mechanical properties of the whisker films, such as porosity and density of the films, as well as morphology of the mats, i.e. orientation and organization of the rod-like nanoparticles.

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