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FORMING OF NATIVE STARCH/WOOD COMPOSITES

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ABSTRACT

Due to their excellent native mechanical properties, several biosourced materials are promising candidates as raw materials for manufacturing biocomposites with enhanced mechanical properties. However, classical composite forming techniques generally induce irreversible degradation of both structural and mechanical native properties of such materials. In this study, thermo-compression and ultrasonic compression moulding were used to form composite materials made up of starch powder and softwood pulp reinforcement fibres. The objective was to find a window of forming parameters enabling the preservation of the native structure and excellent mechanical properties of starch granules. The best set of investigated forming parameters (pressure, temperature, and starch powder moisture content) allowed us to obtain composite samples with good mechanical properties. For instance, their Young modulus ranged from 4 to 6 GPa and their mechanical strength from 30 to 70 MPa, depending on fibre content. The two processing techniques produced composite samples with similar mechanical properties but distinct microstructures. While a better control of the microstructure is achieved using thermo-compression moulding in terms of both coalescence of starch granules and crystallinity, ultrasonic compression moulding allows a significant gain in processing time.

1 INTRODUCTION

The need for sustainable materials in the field of polymer-matrix composite materials leads to a growing use of biopolymer matrices and bio-based reinforcement fibres. Several bio-based components exhibit excellent native mechanical properties and are promising candidates as raw materials for biocomposites with enhanced mechanical properties. Among bio-based materials, agro-polymers such as plant and wood fibres offer excellent specific mechanical properties. Starch granules also exhibit excellent native mechanical properties because of their nanoscale semi-crystalline structure [1, 2]. Starch and wood fibres are also widespread in several industrial domains, meaning that their extraction chains are well established and their cost is limited. However, classical composite forming processes such as extrusion and injection result in a complete modification of the structure of thermoplastic-like matrices because of the melting, cooling, possible recrystallization, and degradation processes of these polymers. For starch powders, such thermal variations induce a modification of the

native crystallographic properties resulting in a degradation of mechanical properties.

In this study, we investigated the manufacturing of biocomposites using two different processing techniques: thermo-compression moulding (TCM) and ultrasonic compression moulding (UCM) [3]. In both techniques, starch was used as a powder-like polymer matrix that was mixed with wood pulp fibres. The objective was to evaluate the suitability of both techniques for preserving the structural properties of the biocomposite constituents and for obtaining interesting final mechanical properties. This study focuses on the influence of the two forming techniques on the structural and mechanical properties of the composites after forming.

2 MATERIALS

2.1 Starch

Two different natures of starch powders were used. These starches differed in both their amylopectin/amylose ratio and their crystalline structure:

• waxy maize starch C*Gel 04201 from Cargill: 99% of amylopectin and A-type crystalline structure,

• amylo-maize starch N-460 from Roquette with 50% of amylopectin and B-type crystalline structure.

2.2 Pine wood fibres

Lignocellulosic fibres were obtained from two pine wood fibre pulps:

• a chemo-thermomechanical pulp (CTMP),

• a bleached chemical kraft pulp (CB).

The CB pulp was refined using a PFI mill (10,000 rotations). The dewatering properties of the pulp fibres was assessed using a Schopper Riegler index testing device, and a fibre and shive analyser MorFi from TechPap (Grenoble, France). Results are gathered in Table 1 and show, as expected, that the such-treated CB pulp is much more fibrillated than the CTMP pulp.

Pulp	Mean fibre length [µm]	Mean fibre width [µm]	Fibrillation index [%]	Fine content [% in area]	Schopper Riegler Index
CTMP	845	40.9	1.65	6.09	16
CB	1085	33.1	0.94	3.51	58

Table 1: Morphological properties and Schopper Riegler index of pine wood pulp fibres.

3 PROCESSING

3.1 Preform manufacturing

In order to obtain an adequate dispersion of fibres into the powder starch matrix, semi-products were manufactured in the form of sheets. First, the appropriate amount of pulp was weighed. This amount depended on the targeted fibre content, such that the total weight (starch and fibres) was 10 g for all samples. Then, the pulp was immersed in 1 L of distilled water. The preparation was mixed for 5 min in a domestic blender to separate single fibres. Then, starch powder was added and slowly stirred with fibres for 20 min to obtain a homogeneous suspension. Preform sheets were obtained by filtering the suspension using a Rapid Köthen sheet former and a 1 µm filter cloth. Then, sheets were oven-dried at 40°C overnight and cut into layers matching the dimensions of the moulds corresponding to each forming technique. Finally, the moulds were filled with a stack of starch/fibres layers until a given mass (constant for each technique) was reached.

3.2 Thermo-compression moulding (TCM)

TCM induces the coalescence of granules and fibres by conduction heating in quasi-static

compression conditions. A processing temperature of 100°C was applied to the thermo-regulated plates of the moulding press while the compression stress was kept at 100 MPa for 60 min. For this technique, a stainless steel rectangular mould with dimensions of 80 × 10 mm² was designed. Rectangular layers of semi-products were stacked into the mould cavity to reach a mass of 4.80 (± 0.05) g. After moulding, samples were stored at least four days in a climate controlled room at 23°C and 50% of relative humidity before characterisation was undertaken.

3.3 Ultrasonic compression moulding (UCM)

The aim of UCM is to induce the coalescence of granules and fibres by localized heating under the effect of inter-particle friction [4, 5, 6]. This technique consists of simultaneously applying a constant average compression stress of 15 MPa and a forced 20-kHz vibration of 60 µm amplitude during 0.70 s. A schematic view of the device is shown in Figure 1. For UCM, the mould was made of stainless steel and was a 32 × 4 mm² oblong cavity. The filling technique was similar to the aforementioned technique for thermo-compression, and the targeted material weight was 300 (± 15) mg. After moulding, samples were stored at least twelve hours in a climate controlled room at 23°C and 50% of relative humidity before characterisation was undertaken.

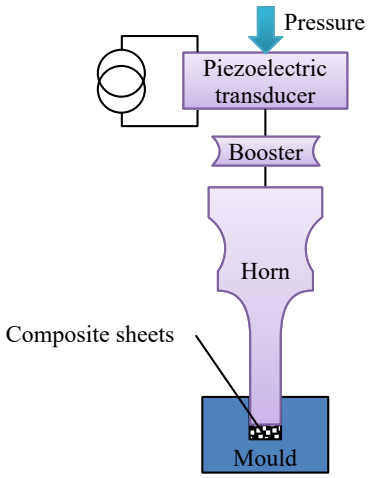

Figure 1: Schematic representation of the ultrasonic compression machine.

4 CHARACTERISATION METHODS

4.1 Density and porosity measurements

The determination of the bulk density d_{bul} of samples was based on mass and volume measurements. Their mass m was measured using a Mettler Toledo ME204 balance. Their thickness and width were assessed using a Mitutoyo Digimatic 293-821 micrometer. Three measurements along the length of samples were used to define the mean value of these two dimensions. The length was assessed using a Mitutoyo Absolute Digimatic 500-181 calliper. Finally, the volume V of samples was calculated using these measured dimensions making the assumption of a plane-parallel geometry. The density d_{bul} is the ratio of m over V.

A helium pycnometer (Accupyc 1330, Micromeritics Instrument Corporation, USA) was used to measure the absolute density of starch granules d_{sta} and wood fibres d_{fib}. The determination of volume is based on the reduction of the gas capacity of a chamber where the sample is placed. In practice, the device measures the pressure drop when the sample chamber is connected to an expansion chamber. All experiments were conducted in triplicate.

The values of d_{sta} for waxy and amylo-maize starches were 1.495 and 1.488, respectively. The values of d_{fib} for CTMP and CB pulps were 1.486 and 1.542, respectively.

The porosity of composites Φ was evaluated from their bulk density d_{bul} and absolute

density d_{abs}, as follows:

$$\Phi = 1 - \frac{d_{bul}}{d_{abs}} \tag{1}$$

where the absolute density of composites d_{abs} was determined from the absolute density of its constituents (d_{sta} and d_{fib}) and the weight fibre content w, as follows:

$$d_{abs} = \frac{d_{sta}\, d_{fib}}{w\, d_{sta} + (1 - w)\, d_{fib}} \tag{2}$$

4.2 Bending tests

Mechanical properties of composites were determined by three-point bending tests. An Instron 5965 testing machine was used with a 5 kN force sensor. Considering the low stress levels, the deformation of the testing machine was neglected, and strain calculations were based on the crosshead displacement. Experiments were performed using a crosshead velocity of 2 mm min^{-1} in accordance with ISO178 standard. All experiments were conducted in triplicate.

4.3 Scanning electron microscopy (SEM)

The morphology of the cross section of some samples was analysed with an environmental scanning electron microscope (ESEM) FEI™ Quanta 200. The cross sections were obtained by breakage of samples in liquid nitrogen. They were metallised with an Emitech K550X gold-palladium coating device.

4.4 X-Ray diffraction (XRD)

XRD analysis was conducted on starch only. Native starch and compacted starch materials ground to a fine powder were poured into glass capillaries of 1.5 mm outer diameter. The capillaries were flame-sealed and exposed to X-ray in a vacuum chamber using a Philips PW3830 generator operating at 30 kV and 20 mA (Ni-filtered CuKα radiation, λ = 0.1542 nm). Two-dimensional diffraction patterns were recorded on Fujifilm imaging plates. The plates were read off-line using a Fujifilm BAS 1800-II bio-imaging analyser. The resulting digitized ring patterns were radially averaged in order to get diffraction profiles.

5 RESULTS AND DISCUSSION

5.1 Visual aspects and handling of samples

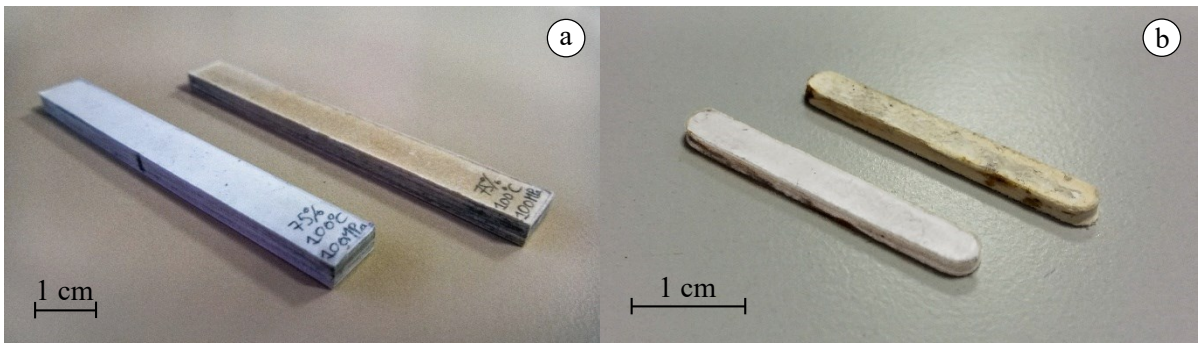

Figure 2: Composites obtained by thermo-compression moulding (a) and ultrasonic compression moulding (b) with CB (foreground) and CTMP (background).

The visual aspect of the different materials mainly depended on the nature of reinforcement (Figure 2). CB reinforced composites were totally white, while CTMP reinforced composites were light-brown due to the presence of lignin in CTMP fibres. For both processing techniques, the aspect of both sides of samples was consistently slightly different. The side in contact with the punch was a bit brighter than the opposite side (bottom of the mould), probably because of a smoother surface.

Samples obtained using both forming techniques were strong enough to be easily handled without failure, indicating that both forming techniques enabled to produce samples with a good cohesion between the constituents.

5.2 Crystallographic properties of starch

The crystalline structure of waxy maize starch samples was assessed by XRD before and after forming. In order to avoid undesired diffraction peaks originating from fibre constituents, starch samples were fabricated in the same conditions than composite samples, except that the moulds were directly filled with starch powder only before TCM or UCM processing. Starch samples had the same mass as composite samples. Figure 3 shows the XRD patterns of as-received starch, after TCM forming and after UCM forming. The diffractogram of the as-received starch exhibited typical diffraction peaks for waxy maize starch (A-type). The same diffraction peaks were observed for starch processed by TCM, with an amplitude slightly smaller, indicating a slight decrease in the overall crystallinity of TCM-processed starch. For starch processed by UCM, the same decrease was observed; but much more pronounced. However, UCM-processed starch was not totally amorphous. AS a result, both TCM and UCM forming techniques produced cohesive samples (*i.e.* the coalescence/welding of starch granules was successfully obtained) without completely modifying their crystalline structure (*i.e.* without melting them).

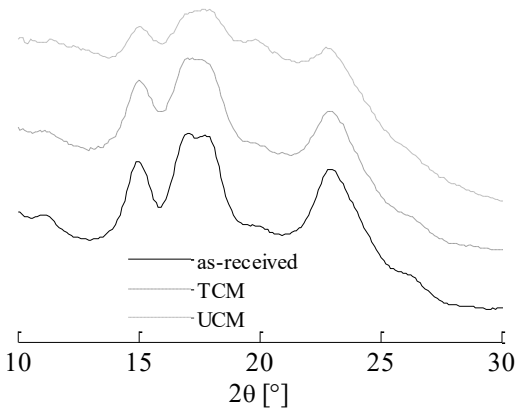

Figure 3: XRD patterns of waxy starch before and after thermo-compression and ultrasonic mouldings.

Thus, both techniques fulfilled the initial objective of this study: starch granules were welded, and their native crystalline properties were partially preserved. However, UCM induced larger changes in the crystalline structure of samples compared to TCM.

5.3 Structural properties: porosity and morphology

Figure 4 shows the evolution of the porosity of composites as a function of the weight fibre content for both moulding techniques. The porosity of TCM-processed samples was globally lower than the porosity of UCM-processed samples. This difference in porosity could be related to the difference in the compression stress between the two forming techniques: 100 MPa and 15 MPa for TCM and UCM, respectively. For both forming techniques, the porosity also slightly increased with the fibre content. For a given type of starch matrix, samples made of CTMP fibres showed a higher porosity than samples made of CB fibres. This increase in the porosity could be attributed to the usually higher stiffness of CTMP fibres compared to CB fibres [7]. This effect could also be enhanced by the refining

treatment of CB fibres. The influence of the nature of the starch chosen for the samples matrix was not clear. For TCM and a given type of reinforcement fibres, samples that were made of amylo-maize starch exhibited a higher porosity than samples made of waxy maize starch. This effect could be attributed to different compaction and coalescence behaviours of both starch granules. However, this trend was not observed for UCM, the nature of fibre reinforcement probably being predominant.

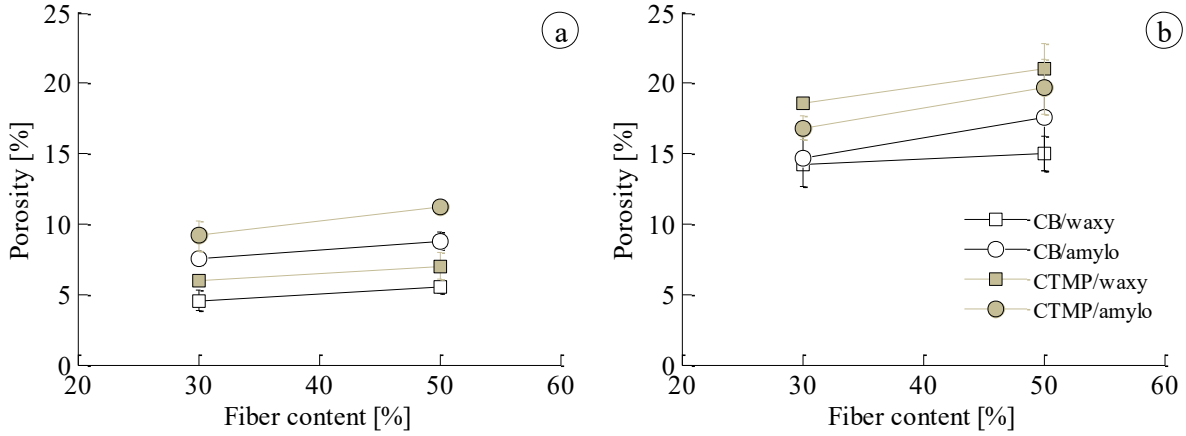

Figure 4: Porosity of pulp/starch composites as a function of fibre content processed by thermo-compression moulding (a) and ultrasonic compression moulding (b)

Figure 5 shows SEM images of failure surfaces of cryo-fractured samples. Although the interpretation of these images is difficult because of the important roughness of failure surfaces, several differences were found between TCM and UCM samples for both types of fibres. The through-thickness distribution of fibres into matrix appeared to be more homogeneous for CB composites than for CTMP composites. CTMP samples exhibited a layered structure. The origin of this structure was attributed to heterogeneity in the thickness of the preform sheets during the process described in section 3.1. The Schopper Riegler index showed that the dewatering of pulp fibre suspensions was easier for CTMP fibres than for CB fibres. This implies that the permeability of the CTMP fibre network was larger than that of CB fibres, suggesting larger pores in the CTMP fibre network. Consequently, it is probable that during the filtering step of the preform manufacturing, starch granules could penetrate more easily the CTMP fibre network and settle against the filtering cloth, inducing a significant segregation effect. In the case of CB fibres, granules are more likely trapped in the small pores of the CB fibre network, leading to a more homogeneous distribution.

Besides, TCM samples exhibited a more homogeneous structure than UCM samples. The microstructure of samples that were fabricated by UCM depended on the distance from the application of the ultrasounds (*i.e.* from the horn of the ultrasonic machine). Basically, welding of starch and fibres was improved in the vicinity of the horn. As a result, the porosity of the samples was most probably heterogeneous in the thickness of the sample. The most porous zones were generally located at the bottom of the mould, opposite from the horn.

Debonding between fibres and starch matrix was also observed at some locations for TCM samples. This phenomenon was not obvious for UCM samples where the fibres could not be easily distinguished from the starch matrix.

To summarise, SEM observations indicated that preform manufacturing could induce significant through-thickness heterogeneities in the structure of the samples. The fibre distribution was more heterogeneous for CTMP fibres than for CB fibres. This could be possibly attributed to the difference in the dewatering properties of both pulps. The morphology and mechanical properties of both types of fibres also affected the overall porosity of the processed composites. Both techniques also certainly induced significant porosity gradients. The visual aspect of the fracture surfaces also suggested that the nature of bonding between the fibres and the starch matrix was certainly different in the two forming techniques.

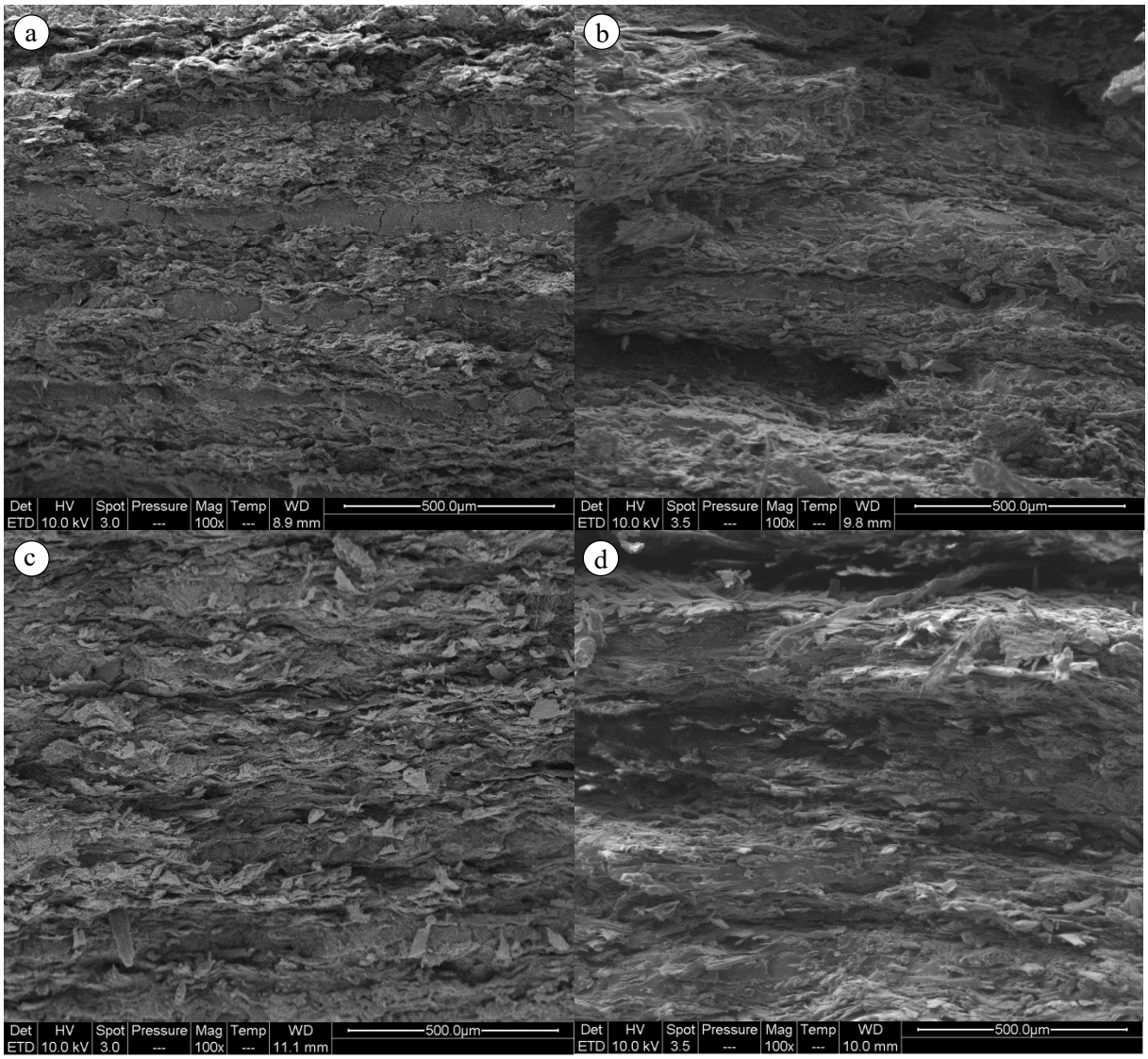

Figure 5: Cryo-fracture surface of 50%/50% pine pulp/waxy starch composites. (a) TCM – CTMP, (b) UCM – CTMP, (c) TCM – CB, (d) UCM – CB

5.4 Mechanical properties

Figure 6 shows the Young moduli of composites as a function of fibre content. For both processing techniques, their moduli ranged between 4 and 6 GPa. The effect of the increase in fibre content varied significantly for all studied composites. The moduli of materials that were fabricated by TCM were almost systematically higher than those fabricated by UCM. This effect could be attributed to the lowest porosity of TCM composites, which is consistent with the observed structural properties. However, porosity was not the only parameter which had a significant effect on the Young modulus. For example, for CB fibres, the composites that exhibited the largest Young moduli were made of amylo-maize starch, although they had a higher porosity than waxy maize starch composites. Thus, the variety of starch used as a matrix also affected the elastic properties of composites. This effect could be attributed to both mechanical properties of starch, and interfacial properties between fibres and starch matrices. For CTMP fibres, the larger modulus of composites that exhibited the largest Young moduli had the lowest porosity.

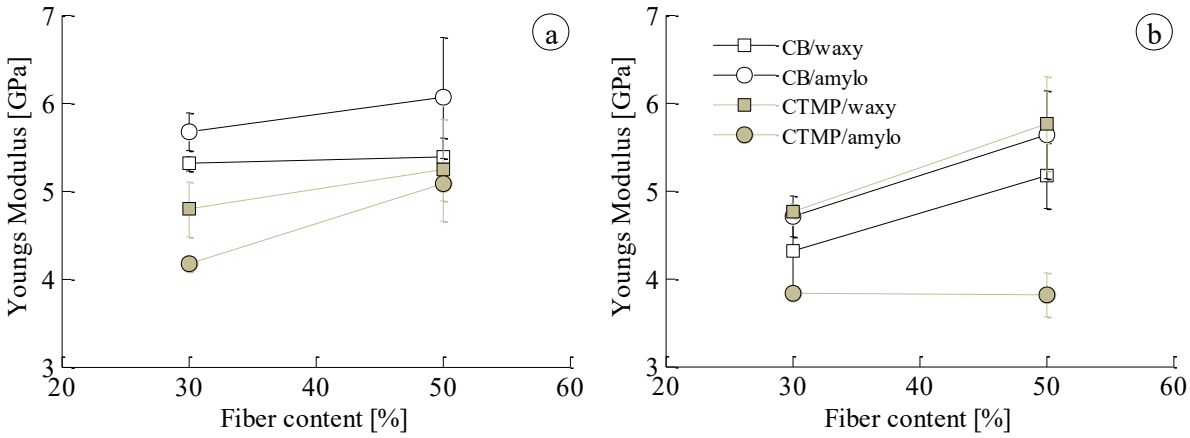

Figure 6: Young modulus of pulp/starch composites as a function of fibre content for (a) thermo-compression moulding, and (b) ultrasonic compression moulding.

Figure 7 shows the ultimate stress of composites, which was defined as the maximum stress reached during bending tests. For both forming techniques, the ultimate stress ranged between 30 and 70 MPa. The effect of the fibre content on this property was very limited. However, it seems that materials reinforced with CTMP offer a poorer strength. The potential origin of this behaviour could be the higher porosity of CTMP reinforced composites, the smaller aspect ratio of CTMP fibres as well as the starch-fibre interface properties. For TCM, Figure 6.a and Figure 7.a show that the ultimate stress and Young moduli exhibited the same trend when varying the composite constituents (*i.e.* for CB fibres, better mechanical properties for amylo-maize starch matrix, whereas for CTMP fibres, better mechanical properties for waxy starch matrix). For UCM, the effect of the nature of fibres was limited, except for amylo-maize starch with CTMP fibres for which the mechanical properties were worse in all cases.

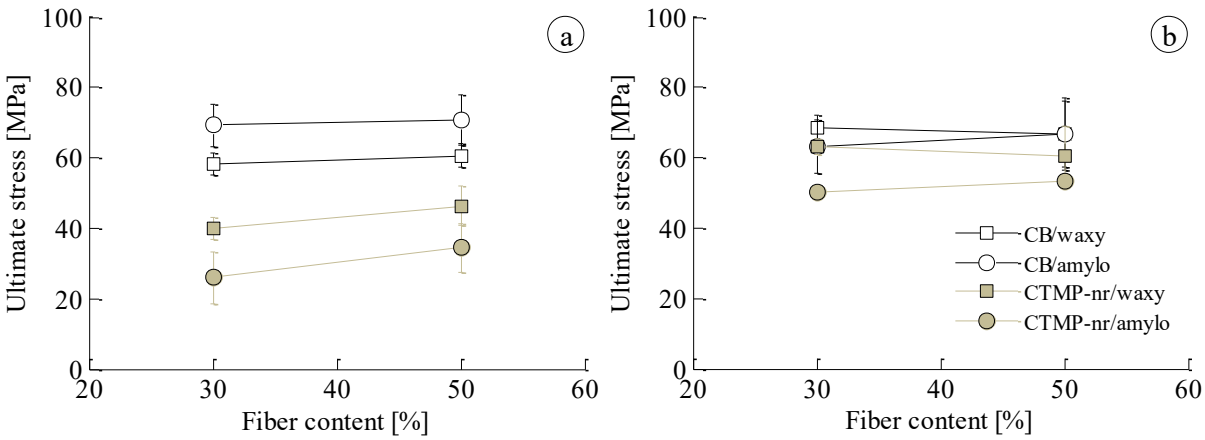

Figure 7: Ultimate strength of pulp/starch composites as a function of fibre content for (a) thermo-compression moulding, and (b) ultrasonic compression moulding.

Figure 8 shows the strain of samples at ultimate stress. This strain ranged from 1 to 8%. The effect of fibre content on this property was limited. Similarly to the ultimate stress, the strain at ultimate stress was more dependent on the nature of the composite constituents for TCM than UCM. Nevertheless, for both processing techniques, CB fibres led to an increase in the ductility of the composite compared with CTMP fibres. Regarding the influence of the matrix, the comparison of Figure 7 and Figure 8 suggests that waxy maize starch provided a better ductility than amylo-maize, which offered a better strength.

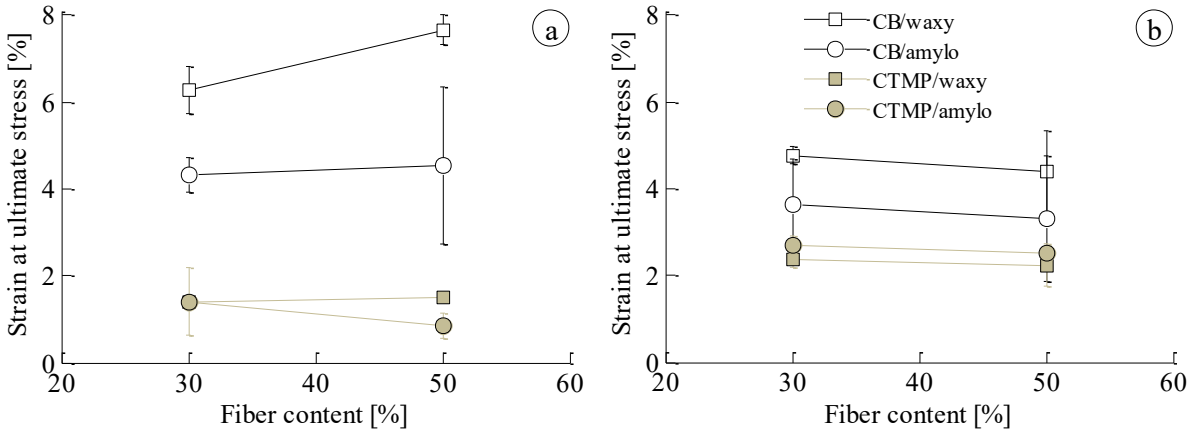

Figure 8: Strain at ultimate strength of pulp/starch composites as a function of the fibre content for thermo-compression moulding (a), and ultrasonic compression moulding (b).

CONCLUSION

Biocomposites based on native starch and softwood thermomechanical (CTMP) and bleached chemical kraft (CB) pulp fibres were obtained using two forming techniques: thermo-compression moulding (TCM) and ultrasonic compression moulding (UCM). Composite samples were characterised using three-point bending tests, SEM and XRD. Both forming techniques produced samples with good cohesion between basic constituents. For all forming techniques and constituents, composite samples presented interesting mechanical properties: Young moduli ranged from 4 to 6 GPa, flexural strength from 30 to 70 MPa, and strain at ultimate stress from 1 to 8%. XRD showed that the native crystallinity of starch granules was partially preserved, especially for TCM. Structural analysis also showed that the porosity of TCM samples was lower than that of UCM for which the compression stress was lower. Porosity was higher with CTMP fibres than CB fibres, probably because of their higher stiffness, whereas the effect of starch variety was not clear. SEM images also showed some defects such as cracks, heterogeneous distribution of fibres, and poor fibre-matrix adhesion. The heterogeneity in the fibre distribution could be attributed to dewatering properties of fibre-starch-water suspensions used to make composites preforms. The effects of moulding, starch variety and nature of fibres on the mechanical properties were also studied. Mechanical properties of UCM-processed samples were very similar, but not as good as TCM-processed samples. This behaviour was attributed to the larger porosity of UCM samples. CB fibres provided better mechanical properties compared to CTMP fibres. Ductility was particularly enhanced by the use of CB fibres. The effect of starch variety was more complex and also seemed to depend on the type of fibres. It is noteworthy that UCM provides a very fast and low-energy solution to process biocomposites, leading to samples with mechanical properties very close to TCM.

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