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# Nanocellulose from Curava Fibers and their Nanocomposites

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*Cellulose nanofibres are environmentally benign and have unique features compared to macro scales. Nowadays, many efforts have been made in developing potential composite products with improved properties. However, the manufacturing of nanocomposites with natural fibres has been a challenging task due to the difficulty encountered in order to aggregate the nanofibres. In this paper, curaua fibres were utilized for isolation of nanofibres. Polyvinylalcohol (PVA) was chosen as the matrix due to its excellent film forming, packaging capacity and its hydrophilic nature, which enhances the interfacial compatibility between the natural fibre and the matrix. The composite is prepared by solution casting technique.*

**Keywords** Curaua; nanocellulose; nanocomposites; polyvinylalcohol

## Introduction

The natural fibre extracted from different sources has shown promising results as reinforcement to thermoplastics. When isolated into nano scale, these fibres have shown values of tensile strength and modulus comparable to glass fibre [1]. Furthermore, various other lignocellulosic fibres present potential for use in polymer matrix composites, such as banana fibres, piassava and luffa, among others. However, the main challenge for the use of these fibres is the development of a fibre/matrix interface and good dispersion with increased mechanical properties.

Natural fibres are lightweight material, with properties of high specific modulus, non-abrasive in the processing equipments, renewable, biodegradable and recyclable that allows them to compete against other man-made materials like fossil materials and fibreglass.

The rapid growth of natural fibre composites is related to economic, technological, social and environmental issues. Due to the increased consumption of plastics

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and the limited availability of wood revealed the need to invest in new technologies in order to produce a high performance material from renewable sources.

There are different sources of lignocellulosics fibres that occur naturally throughout tropical and sub-tropical America (e.g., Piteira), others are cultivated commercially (sisal) and others in some areas are considered residues (e.g., rice hulls, Typha and wheat straw) representing a potential large source for nanofibres production.

Through the context presented, nanocomposites stand out as a new class of materials and have attracted growing interest because of their peculiar and fascinating properties as well as their unique applications in some industrial sectors. The composites are nominated nanocomposites when at least one of the components is at nanometer scale, it means, less than 100 nm. Because of having well dispersed nano-sized particles in the composites, they exhibit remarkably improved mechanical, thermal, and physicochemical properties with very low levels of reinforcement (usually less than 5%) and have a little impact on the optical property when compared to pure polymers or conventional composites. Overall nanocomposites present increase in Young's modulus, storage modulus, thermal stability, barrier properties to gas, and good flame retardance. Moreover, they have a higher value of heat distortion temperature (HDT) at up to 300°C, and thus extend the use of composites in an atmosphere of higher temperature. The composites have been used in highly technical fields and as substitutions for types of polymeric materials.

Among the potential applications for nanocellulose may be mentioned: paper and paperboard, bionanocomposites in foods, cosmetics, medical, optical devices, pharmaceuticals, chemicals with dispersion and emulsion and oil recovery.

New types of nanoparticles (nanofiller superconductivity and magnetic particles) have been reported and their ability to form nanocomposites with improved properties has been proposed. Moreover, recent advances in the production of bio-fibres, fibre microfibrils or nano size, make the manufacture of composites/nanocomposites with high performance possible [2,3].

It is important to note that natural nanofibres have a modulus greater than steel and this is particularly important for the automotive industry aimed at reducing overall vehicle weight. Another positive aspect of nanofibres derived from natural fibres is the possibility to meet the requirements of the ISO 14,000. And in this regard, the fibre-reinforced composites are much better on the issues of energy consumption, emission of effluent toxicity to workers and consumers, easy disposal, and repetitive recyclability.

The properties of nanocomposites depend on the chemistry of polymer matrices, nature of the nanofiller and also the processing technique. Nanotechnology shows up today as an inherently interdisciplinary field encompassing chemistry, physics, biology and engineering. This area has made significant scientific advances in recent years.

It has been reported that nanoreinforcements can increase the resistance without sacrificing the elongation of the material. In some cases, the nanoreinforcements have shown increasing resistance and modulus at the same time. The reason for the improvements is reported that nano-sized reinforcements have a surface area much larger than the conventional microcomposites and defects in the array are reduced at the nano-scales. Moreover, the polymers do not lose their transparency, because the fibres or particles with a diameter less than 1/10 of visible light are not affected by light scatter. These properties have motivated scientists to develop composites for the next generation of composite materials [4].

The studies in nanocomposites are not only made with clays and layered silicates. Cellulose nanocrystals have attracted significant attention in recent years as a nanoreinforcement potential in different polymers. Grunert and Winter [2] for example, using nanocrystals of cellulose obtained by acid hydrolysis of cellulose microfibrils, to obtain nanocomposites with cellulose acetate butyrate [5] observing a modulus of 138 GPa for the crystalline phase and a surface area of several hundred $m^2/g$ cellulose nanocrystals have been potential for significant reinforcement in thermoplastic polymers. The only restriction on the use of nanocellulose crystals as reinforcement is their incompatibility with a thermoplastic matrix which is typically more hydrophobic.

Studies conducted by Seydibeyoglu and Oksman [4] on composites containing polyurethane and cellulose microfibrils with the addition of 16.5% of the cellulose nanofibres increased the resistance by approximately 500% and the modulus by 3000%.

Another important reason for the extensive use of cellulose as an attractive reinforcement material due to its high density of –OH groups on the surface trying to join the adjacent –OH groups by hydrogen bonds. These results in agglomeration of nanofibres, where high energy is required to overcome this strong hydrogen bond. Often, in order to reduce the interactions between hydroxyl groups, the nanofibres obtained after chemical and mechanical treatments are kept in suspension in water and consequently, its use is restricted mostly to water-soluble polymers. Therefore, nanofibres of cellulose have not been extensively used in thermoplastics due to large surface area of the nanofibres, they can agglomerate easily and thus many of the beneficial properties sought are lost [6]. Some attempts have been made in order to modify its surface to improve dispersion in non-polar solvents [7].

Bei Wang and Mohini Sain [6] observed the use of an aqueous emulsion of ethylene-acrylic oligomer can improve the compatibility and dispersion of cellulose nanofibres in non-polar polymers such as PP, PE. Other treatments have been used to achieve dispersion of nanofibres and nanocrystals in solvents other than water through the use of surfactant and polyethylene glycol graft. However, there is a decrease in using modified cellulose crystals, since they will have less reinforcing effect than unmodified crystals [8].

The cellulose microfibrils (fibril elementary strings attached) can be extracted from the cell walls by 3 different procedures: simple mechanical methods, a combination of chemical and mechanical methods or enzymatic methods. A purely mechanical process can produce thinner fibrils with several microns in length and diameter between 20 and 90 nm. However, these nanofibres with similar structure to a network lead to a reduction in resistance. The chemical-mechanical process will also produce thinner cellulose fibrils, with a diameter ranging from 5 to 60 nm. This chemical-mechanical pulp treated can be considered as nanomaterial presenting elements that are highly expanded in terms of surface area. Depending on the materials and techniques of defibrillation, the degree of the polymerization, morphology and aspect ratio of nanofibres will differ [6,9].

Curaua fibre was identified as a very good fibre among native natural fibres in Brazil, which contains a large amount of cellulose of 70% and low lignin content to be utilized as an excellent source of the nanofibres [10] and one of its most impressive Curaua properties is its fineness index (denier), allied with excellent mechanical properties [11].

In this work, for the first time, curaua fibre was chosen as raw material to prepare the nanofibres not only due to its good mechanical properties as well as is an innovative fibre to be used for nanocomposite application. In this article, the preliminary studies are conducted in order to prove the reinforcement effect of prepared nanofibres in the PVA matrix.

In order to produce a biodegradable composite, Polyvinyl Alcohol (PVA), a water soluble polymer, was chosen as the matrix to produce the nanocomposite film by solution casting technique [12]. PVA has excellent film forming capacity and excellent optical properties, and its hydrophilic nature could enhance the interfacial compatibility between the fibre and matrix. The application of cellulose nanofibres with PVA finds application in the field of pharmaceuticals, medicine, packaging, etc.

The use of nanocellulose extracted from curaua fibre has been studied for the first time looking at the potential application for development of high strain nanocomposite film. Yano and his co-works have published several papers about the optical properties of wood-cellulose in several matrices, including PVA, acrylic resin, tricyclodecane dimethanol dimethacrylate (TCDDMA), aiming to use nanocellulose as a reinforcement agent for optically transparent resins, which are of significant interest to the optoelectronics industry [13,14]. The potential applications of the film obtained was not objective about this paper, but just show the use of curaua fibres as a reinforcement agent for the PVA matrix.

## Experimental

### *Materials*

Curaua fibres were obtained from Pematec Triangel Co. located in the city of Santarém, state of Pará, Brazil. The fibres were extracted from the leaves, using a traditional decortication equipment, largely used in sisal and curaua fibres extraction. This equipment works by scrapping the leaves longitudinally. After the fibres were extracted from the leaves they were dried at room conditions, cleaned mechanically by a beating process and then ready for chemical and mechanical process to obtain the nanofibres. Polyvinylalcohol (Celvol 165SF) was provided by Celanese Chemicals.

### *Pretreatment of Curaua Fibres*

The fibre bundles were cut into approximately 3 cm in length and washed for several times. Then the bundles were immersed in distilled water for overnight.

Pulping process was carried out in order to remove the lignin and hemicelluloses. The alkaline treatment with 17 wt% of NaOH was introduced to the fibre at a ratio of 10:1 (sodium hydroxide solution:fibre) at 80°C for 3 hours with constant stirring. After soaking with NaOH, the NaOH solution was removed and the fibre was washed with deionized water.

The bleaching process was done two times with the purpose of remove all remaining lignin. For the first bleaching, 0.3% of acetic acid solution were used to adjust the pH to 3.5. $NaClO_2$ was added until the final concentration reaches 2% in the solution containing the fibres, stirring for 3 h at 78°C approximately. The second bleaching process was performed with chlorine di-oxide at pH 3.3, using $NaClO_2$. This treatment was carried out for 3 h at 78°C under stirring, and it is similar as described in Jonoobi *et al.* [15]. The fibres were washed again with deionized water.

### *Nanofibre Production*

The mechanically defibrillating process was used to further reduce the fibre size. The chemically treated curaua fibres were crushed using a refiner for 3 times at 8,000 r.p.m, and defibrillated in a disintegrator for 15 minutes using water as the vehicle. Wet fibre mats were made from the fibre suspension with 24 g of dried pulp per mat. The mat was passed through a refiner aiming to further defibrillate the fibres. Then, the refined pulp was cryo-crushed following the process as used by Alemdar *et al.* [16].

The resulting powder was placed again in the disintegrator with 2 L water for 15 minutes and filtered in mash of 300 mesh. The bottom part of the filtered sample was treated using a high pressure defibrilizer under the pressure of above 400 bars. The suspension obtained is shown in Figure 1.

### *Preparation of Nanofibre and Nanocomposite Films*

In order to prepare the nanofibre film, the suspension was filtered at 0.1 μm aiming to remove all the remaining water. The retained materials was put in the middle of absorbent paper sheets, pressed at 50 bars and let to dry at room temperature for 24 hours.

Polyvinylalcohol – PVA was dissolved in 150 mL deionized water and mixed with a suspension of nanofibres for 3 hours under low heating conditions to promote better mixing. The fibre loading in fibre-PVA mixture was 4–5% of the quantity of PVA, after the solution was completely dissolved, it was homogenized. Then the process of solution casting was carried out to prepare composite film for 48 h at room temperature until the film was totally dried. Pure PVA film and nanofibre film were also produced for comparing purpose. This procedure was very similar to described by Roohani *et al.* [17].

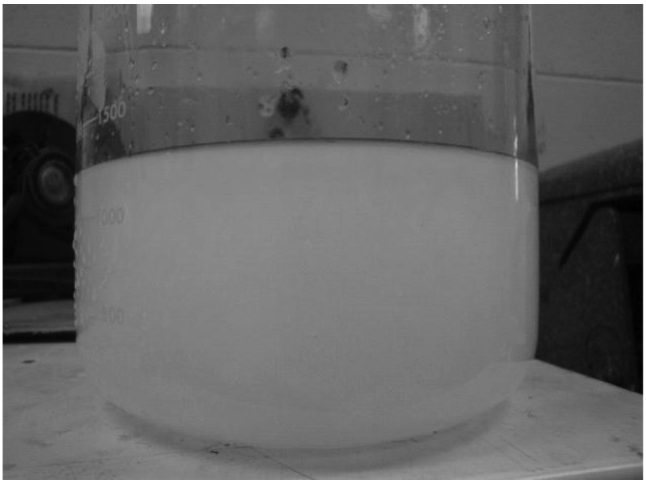

**Figure 1.** Suspension of nanofibres.

### *Characterization*

The following analyses were carried out with the original fibres before any treatment:

1. Chemical characterization was done following Standard TAPPI with the test methods T203, T204, T222, T249, and T235 for 3 samples.
2. The fibres were analyzed to understand their morphology and to measure their diameters with the purpose of indentifying the quality of the fibres.
3. The performance of single fibres was tested following the ASTM D3822 standard – Tensile Properties of Single Textile Fibres.
4. Fibre diameters correspond to an average of ten measures along the fibre length. Measures were carried out in the images of the fibres were collected with an ocular 4X designed and mounted in a Hyperion microscope from Bruker Optics (USA). The fibre morphology was examined using a Shimadzu SSX-550 Scanning Electron Microscope (SEM). The fibres were gold sputter coated before the analysis.

The nanofibres were characterized by:

1. ESEM – Environmental Scanning Electron Microscopy.
2. The diameters were measured using the program MatLab.
3. The nanofibre, PVA and the nanocomposites films produced were tested for their mechanical performance according to Standard ASTM D638 (tensile tests for plastics), and the thickness of all the samples produced were measured with a micrometer caliper. Every treatment was tested using six samples.

## Results and Discussion

### *Characterization of Curaua Fibres*

In Figures 2 and 3, SEM image showing the surface morphology of curaua fibre bundle before and after rupture. The rupturing process is found to be effective in

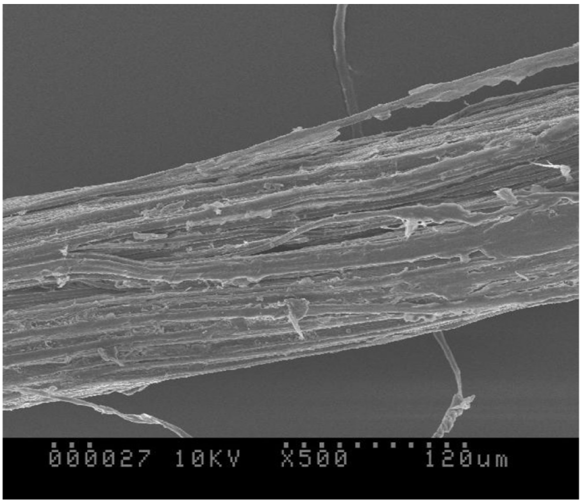

**Figure 2.** Curaua fibre before rupture.

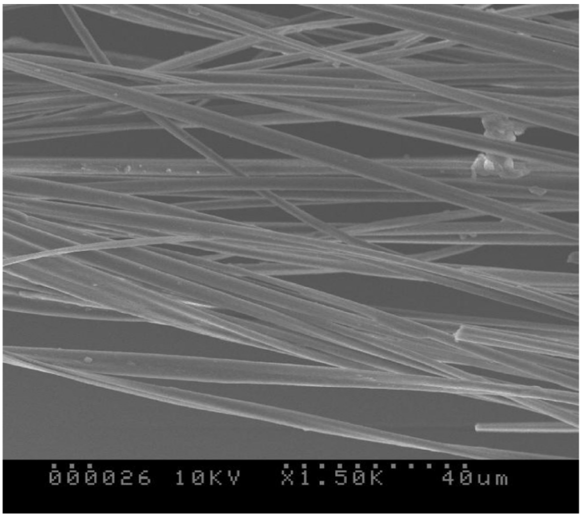

**Figure 3.** Curaua fibre after rupture.

breaking the fibre bundle and individualizing the cellulose fibre present in the bundles. From the micrograph, the individualized cellulose fibre seems to have a diameter distribution between 3–4 μm. In Figure 3, after the bleaching and disintegration processes the elementary fibre split, showing a diameter of approximately 20 μm, from an original fibre bundle diameter of 100 μm.

Tensile strength of single fibres was measured using 30 samples. The average result obtained was 795.78 MPa for tensile test and the Young modulus was 10.7 GPa with 3.9 mm of elongation at break.

Chemical characterization was conducted and showed that these fibres have an excellent quantity of cellulose that is important for this study. The cellulose content was 70.4%, and the rest 30% was distributed in lignin, hemicelluloses extractives and ashes (Table 2). Table 2 proves the high percentage content of cellulose fibres embedded in the raw curaua fibre which confirms the efficiency of these fibres to be used for high strain composite applications.

**Table 1.** Comparison of curaua and other crop fibers

| Fibre | Specific stress (MPa) | Young's modulus (GPa) | Elongation at break (%) | References |
|---|---|---|---|---|
| Curaua | 796 | 10.7 | 3.9 | Souza *et al.* |
| Curaua | 900 ± 200 | 36 ± 10 | 3 ± 1 | Spinacé *et al.* |
| Curaua | 150–300 | 48.7 | 4.57 | Tomczak *et al.* |
| Curaua | 913 | 30 | 3.9 | Gomes *et al.* |
| Banana | 764 | 30 | 3.1 | Kulkarni *et al.* |
| Pineapple | 126.6 | 4.4 | 2.2 | Arib *et al.* |
| Abaca | 980 | 23.4 ± 6.4 | 3.0 | Tomczak *et al.* |
| Sisal | 600 | 17.4 | 3.5 | Symington *et al.* |

**Table 2.** Composition of curaua fibre

| Components | Quantity (%) |
|---|---|
| Extractives | 5.5 |
| Lignin Klason | 11.1 |
| Hemicellulose | 10.8 |
| Cellulose | 70.4 |
| Ashes | 2.2 |

### *Characterization of Nanofibres*

SEM images showed that nanofibres were obtained from curaua fibres after a series of processes (Fig. 5). The morphology of the fibres proves to have an interconnected web-like structure with nano ordered chains, which elevate the high reinforcing capability of the developed nanofibrils in the composite matrix. Over 75% of these nanofibres have a diameter smaller than 50 nm (Fig. 6).

Yano *et al.* [18] reported the utilization of bacterial cellulose having width 50 nm as a significant reinforcer in resin composites. Iwamoto *et al.* [13] were also successful in the developmement of high strength optical transparent composites from wood fibres having diameter width of 50 nm. The cellulose fibres produced from curaua fibres by high mechanical defibrilation (cryocrushing and high pressure) having width range 50 nm, also finds promising application in composite systems.

The aspect ratio of the nanofibrils were determined from the SEM image. The total fibre length which seems to be visible is counted for calculation of the aspect ratio. In some cases total fibril length was not visible, therefore only the visible portion was considered for the calculation in TEM graphs (provide statistical significance of this assumption). The fibres depicts an aspect ratio of 55 approximately.

It can be also observed from Figure 6 that there was a gauss distribution, and with its peak toward the small particle's size, the nanofibres extraction became more efficient with very few fibres above the upper limit for nanoscale.

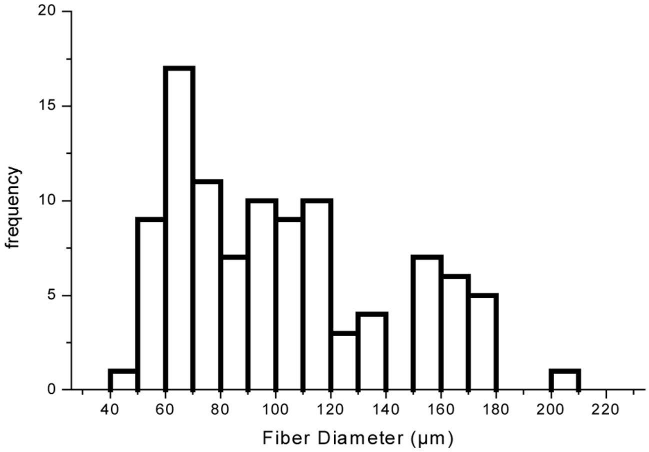

**Figure 4.** Distribution of curaua fibres diameters.

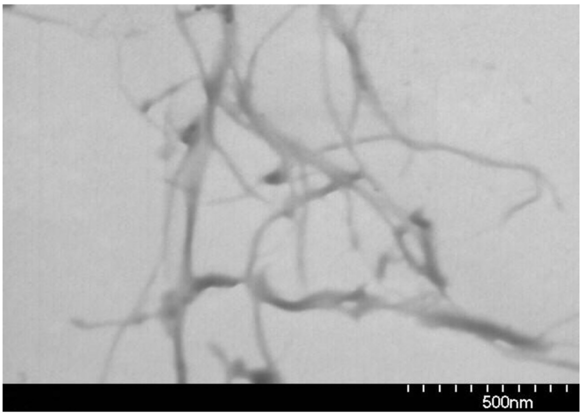

**Figure 5.** Nanofibres from curaua fibres.

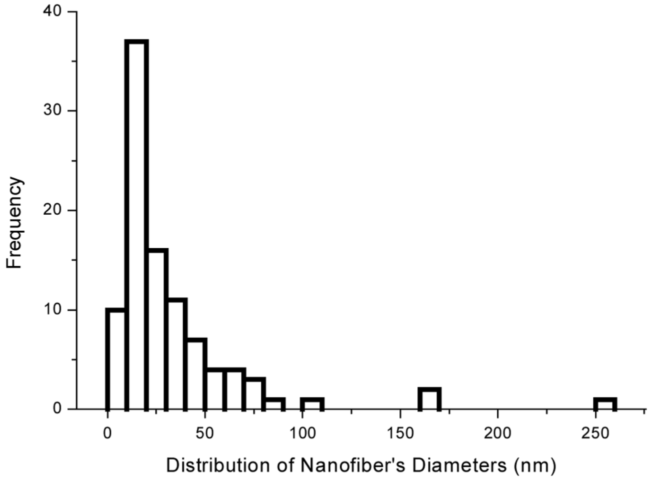

**Figure 6.** Diameter distribution of the extracted nanofibres.

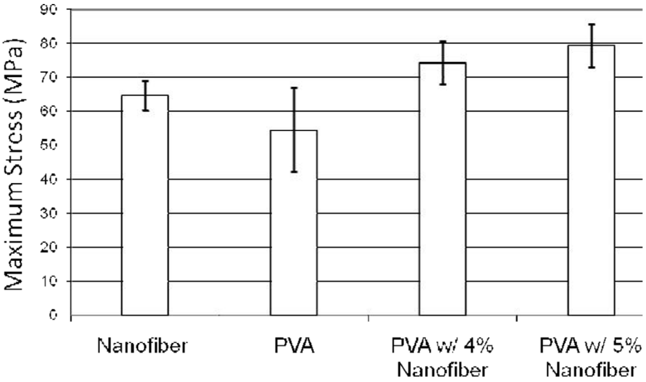

**Figure 7.** Tensile strength of the films produced.

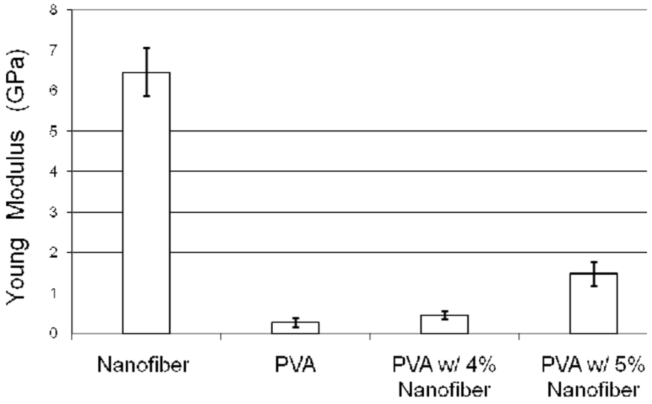

**Figure 8.** Young modulus of the obtained films.

### *Mechanical Properties of Nanocomposites*

The incorporation of nanofibrils in the PVA matrix shows a profound increase in the tensile stress of the composite. A significant increase was observed in the maximum stress of 36 and 44% with the addition of 4% and 5% nanofibres, respectively (Fig. 7). This proves the effective reinforcement of the fibres in the matrix offering good interfacial adherence between fibre and matrix with diminished tendency of agglomeration in the hydrophilic matrix. The higher loading of nanofibres could add positively towards the increase in the mechanical properties of the composites.

Comparing to the pure PVA resin, the pure nanofibre film showed a very high modulus. With the addition of nanofibres at 4% wt, the modulus was 67% higher than that of pure PVA film, and with 5% of fibre loading the increase was up to 450% (Fig. 8). More studies will be carried out in order to identify the optimal concentration of nanofillers in the PVA matrix. Moreover, the presence of trace amount of microfibre in the film mixed with nanofibre may lower mechanical properties of the composites.

## Conclusions

It was found that with 4% of fibre loading, the maximum stress and modulus of the composite increased by 36% and 67%, respectively. With 5% of fibre loading, the increase became more significant, particularly in the Young modulus (448%). The results revealed the strong reinforcing ability of curaua nanofibres and their compatibility with PVA and could be much more improve by the absence of microfibres. New applications are possible with the property enhancement, including packaging, biomedical, optical devices among others that should be further studied.

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