NANOFIBRILLATED CELLULOSE AS A COMPOSITE FILLER

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NANOFIBRILLATED CELLULOSE (NFC)

Nanofibrillated cellulose (NFC) are long entangled cellulose fibrils that consist of both amorphous and crystalline regions. This is unlike CNCs that are almost perfectly crystalline (Cao *et al.*, 2016). They also have extremely high aspect ratio

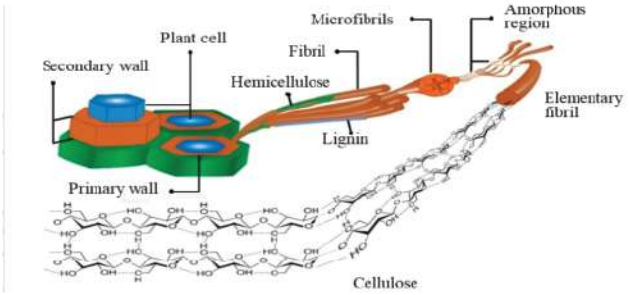

Fig. 1. Structural hierarchy of cellulose.

with lengths up to 2000nm and widths of 4-20nm making them fall within the nanoscale range (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). The long structures of NFC allow them to form colloidal dispersions in water even when in low concentrations below 1wt% due to the entanglement of the fibers (Cao et al., 2016). Therefore, besides microscopy techniques, the viscosity of the cellulose suspension can be a good indication of the aspect ratio of NFC (Henriksson & Berglund, 2007). In order to extract NFC from plant biomass, the hierarchical structure of cellulosic fibers must be known (Figure 1). NFC is produced by breaking down microfibrillated cellulose or the larger cellulose fibrils by means of mechanical shearing with optional enzymatic pre-treatments (Vilarinho, Sanches Silva, Vaz, & Farinha, 2018). In contrast to the aggressive acid hydrolysis method used to develop CNC, production of NFC employs a milder approach using cellulase enzymes which modify the cellulose without degrading it (Siró & Plackett, 2010). There is another reason as to why enzymatic pre-treatments are used in conjunction with mechanical shearing and this is due to the high amounts of energy consumed when producing NFC. Spence et al., reported that up to 4,000kJ of energy was needed per pass to make 1kg of NFC when using homogenization as a shearing method. Subsequently, microfluidization was also pointed out by the author to consume roughly 630kJ/kg/pass at 30kpsi. Micro-grinding, another shearing technique, uses up about 620kJ/pass/kg of NFC (Nakagaito & Yano, 2004). The high energy consumption is also accompanied by a problem of entanglement of the plant fibers on the equipment, causing plugging and potential damage. Enzymatic pre-treatments have the advantage of loosening up the fibers by decreasing their length and reducing the total energy consumption of the shearing process (Spence *et al.*, 2011).

NFC AS A COMPOSITE MATERIAL

When it comes to choosing a suitable material to be used as a filler, many parameters have to be considered. Mechanical properties such as tensile strength, elastic modulus and flexibility have to be assessed. The thermal properties of the materials are also vital information that contributes to the overall durability of these composites. Research has shown that nanocellulose-based films have potentially high tensile strengths. Qing et al. and Yano and Nakahara have found that NFC has the ability to withstand over 230 MPa of tensile stress when formed properly.

The tensile strength of a material is the amount of tension the material can withstand before breaking. Flexural strength, on the other hand, is the tensile strength of a material when subjected to force across its depth. According to the compilation of mechanical test results in Table 1, it seems that the addition of NFC to thermoplastic polymers would generally increase their tensile strengths. This has been attributed to the extremely high aspect ratios of NFC which allow them to form strong interactions with the polymer matrices (Farahbakhsh et al., 2017; Perić et al., 2019).

Another important parameter to consider when observing material properties is the elongation at break. The elongation at break of a material is the percentage of length the polymer stretches before breaking. It is an indication of the ductility of the polymer. According to Yasim-Anuar et al., a decrease in the elongation at break of the polymers is due to the rigid nature of the CNF fillers. That being said, Zimmermann *et al.*, mentions that is is possible to improve both the tensile properties of a polymer without sacrificing its ductility through proper interfacial interaction and crosslinking between the CNF and the polymer matrix.

Polymers with high elastic moduli or Young's moduli have many uses and applications. The Young's modulus of a polymer or composite is directly related to the tensile strength and the strain of the polymer. In fact, it is the ability of the polymer to resist a change in length when under tension. Fortunately, as shown in Table 1, there are evidence that nanocellulose has the potential to increase the Young's modulus when added to polymer blends as a filler (Zimmermann *et al.*, 2004; Tomé *et al.*, 2013; Kurihara and Isogai, 2014; Farahbakhsh et al., 2017; Igarashi *et al.*, 2018; Norrrahim *et al.*, 2018; Samarasekara *et al.*, 2018; Perić *et al.*, 2019; Yasim-Anuar *et al.*, 2019)

Table 1: Effectof NFC on the properties of various polymers. PE, polyethylene; PLA, polylactic acid; PP, polypropylene; HDPE, high density polyethylene; LDPE, low density polyethylene; PVA, polyvinylacetate

Polymer matrix	Properties Improved	Properties Worsened	Source
PE	Young's modulus, tensile strength, flexural strength, flexural modulus crystallinity, hydrophilicity	Thermal stability, elongation at break, toughness	(Yasim-Anuar et al. , 2019)
PLA	Young's modulus, impact strength, elongation at break, crystallinity		(Perić et al., 2019)
PP	Tensile strength, Young's modulus, flexural modulus, crystallinity, thermal stability	Elongation at break	(Norrrahim et al. , 2019)
PP	Tensile strength, impact strength, hardness, water absorption		(Samarasekaraet al. , 2018)
HDPE	Tensile strength, Young's modulus, coefficient of thermal expansion	Elongation at break	(Igarashi et al. , 2018)
LDPE	Thermal stability, crystallinity, Young's modulus, tensile strength	Transparency, elongation at break	(Farahbakhsh et al. , 2017)
Poly(acrylamide)	Young's modulus, tensile strength, yield stress	Elongation at break	(Kurihara and Isogai, 2014)
Corn starch/chitosan	Thermal stability, Young's modulus, tensile strength	Elongation at break	(Tomé et al. , 2013)
PVA	Tensile strength, Young's modulus	Elongation at break	(Zimmermann et al., 2004)
Hydroxypropyl cellulose	Tensile strength, Young's modulus, elongation at break		(Zimmermann et al., 2004)

When it comes to the toughness of a material, it is a balancing act. When a material is subjected to a force that exceeds the limit of its strength, one of two things will happen, it will either undergo deformation or fracture. A tough material is able to absorb high amounts of energy and undergo plastic deformation without fracturing. By calculating the area under the stress-strain curve, one can determine the toughness of a polymer or composite. Zimmermann, *et al.*, 2004, found that composites that incorporated cellulose showed a higher degree of toughness. The changes in the thermal stability of the composites depend on the thermal stability of NFC relative to the polymer matrix. For example, in the case of polyethylene (PE), NFC has a relatively lower thermal decomposition temperature as compared to PE.

Therefore, the decrease in thermal stability in the PE/NFC can be attributed to the degradation of NFC at a lower temperature which then triggers the decomposition of the PE matrix (Yasim-Anuar et al., 2019). Improvements to the thermal stability of the composites are suggested to be due to the compatibility of the polymer matrix with the NFC filler and also the interfacial interaction between the two (Farahbakhsh et al., 2017). In fact, for such cases, an additional degradation step appears which is assumed to be due to the degradation of the NFC fractions of the composites (Farahbakhsh et al., 2017; Tomé et al., 2013).

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