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Reinforcing efficiency of nanocellulose in polymers

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ABSTRACT

Nanocellulose extracted from renewable sources, is a promising reinforcement for many polymers and is a material where strong interfibre hydrogen bonds add effects not seen in microfiber composites. Presented is a tool for comparing different nanocellulose composites based on estimating the efficiency of nanocellulose reinforcement. A reinforcing efficiency factor is calculated from reported values of elastic modulus and strength from various nanocellulose composites using established micromechanical models. In addition, for the strength, a network model is derived based on fibre–fibre bond strength within nanocellulose networks. The strength results highlight the importance of the plastic deformation in the nanocellulose composites. Both modulus and strength efficiency show that the network strength and modulus has a greater effect than that of the individual constituents. In the best cases, nanocellulose reinforcement exceeds all model predictions.

1. Introduction

There is widespread interest in finding lightweight, sustainable materials that are efficient to produce as well as a drive to use bioresources as efficiently as possible. A positive development is the use of side streams from agricultural and forest industries as sources of nanocellulose and using it to good effect as reinforcements in polymers [1,2].

Nanocellulose is a general name for different types of cellulose structures where one of the dimensions is less than 100 nm. This includes material such as bacterial cellulose (BC) produced by certain strains of bacteria and nanofibres (CNF) and nanocrystals (CNC) isolated from plant sources. Nanocellulose based composites with a large number of combinations of polymers and nanocelluloses and widely varying concentrations have been reported in the literature. In a review by Hubbe et al. [3], there are 119 publications where the reinforcing effect of nanocellulose is used to motivate their investigations. Of this list, 49 publications reported an increase in the strength of the nanocellulose composite. The reinforcement effect of CNF isolated from wood pulp has also been demonstrated by the 28 studies reviewed by Siró and Plackett [4].

If nanocellulose based composites are to be used for lightweight construction solutions, good stiffness and strength are essential. It is then of interest for the development of these composites to gain a greater understanding of how the matrix and the nanocellulose combine to provide high composite modulus and strength. One method of doing this is to review nanocellulose based composites and evaluate the effectiveness of the material combinations, processes and fibre concentrations. Evaluating the efficiency of nanoparticles in composites can be done by applying a theoretical model. For example, Lui and Brinson [5] used the Mori–Tanaka model to compare the efficiency of different forms and arrangement of nanoparticles. The results showed that the efficiency of nanofibres is higher than platelets when the fibres are aligned. Also shown was that nanofibres generate a larger interphase that platelets that leads to higher stiffness in the bulk material. However, the models are aimed at carbon nanotubes and platelets and interfibre bonding is not considered.

In this work, existing parameters in micromechanical models are used to quantify efficiency and compare selected nanocellulose composites. Modulus efficiency uses the reinforcement factor in the Halpin–Tsai model [6] and the length efficiency in the Rule of Mixture (ROM) model [7]. Although these models are well established for composite materials, this method of using the efficiency factors for comparing nanocellulose composites has not previously been presented.

In the current comparison of nanocellulose composite strength, a ROM model for strength [8] is compared to a network strength model, which based on the fibre–fibre bonds as well as the strength of the matrix. This network model is founded on work reported by Kärenlampi [9]. Back-calculations from measured strength values together with this model are used to establish the fibre–fibre bond strength in different nanocellulose networks. These values of bond strength are used to obtain an average for nanocellulose and subsequently used to calculate theoretical

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network strength for different compositions of matrix and nanocellulose.

The developed tools are then used to compare modulus and strength efficiency of nanocellulose composites presented in various publications and to compare them to the efficiency of a typical natural fibre composite.

2. Methodology

2.1. Modulus efficiency

The modulus efficiency is calculated using composite laminate theory (CLT) [10] with the modulus of each layer calculated from Halpin–Tsai or ROM [6,8].

The modulus of the unidirectional ply, E_1, is calculated from Halpin–Tsai as

$$E_1 = E_m \frac{1+\zeta\eta V_f}{1-\eta V_f}, \tag{1}$$

where

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + \zeta}, \tag{2}$$

and E_m, is the elastic modulus of the matrix, V_f, is the fibre volume fraction, E_f is the elastic modulus of the fibre, and ζ is the efficiency of the reinforcement. E_1 is then used to calculate E_c, the modulus of the composite, using the CLT for a quasi-isotropic material with the layup [45/-45/0/90] as has been applied previously to nanocellulose composites [11]. The use of CLT is particular appropriate for nanocellulose with high fibre volume fractions because nanocelluloses self-organise to form layers with fibres oriented in the plane as is seen clearly in SEM images of nanocellulose networks and composite with high fibre volume fractions processed by filtration [12,13] and when solvent cast [14]. E_f was set to 138 GPa [11] and the other independent material constants required for the calculation are given in Appendix A. For comparison, ζ of a randomly oriented flax fibre composite was also calculated. For this calculation the flax fibre modulus was set as 65 GPa [15].

Rather than setting ζ as a shape factor as is done for short fibre composites, it is used here as an efficiency parameter. ζ is back-calculated from the experimentally measured stiffness of the composite by iterating value of ζ until E_c equals the experimental measured Young's modulus. A search algorithm, implemented in Matlab, is used to find ζ [16]. The material property values used for calculating the efficiencies from selected nanocellulose composites reported in the literature are shown in Table 1.

ζ gives a measure of efficiency of the fibres relative to a particular matrix. The efficiency of the fibres can also be expressed as a linear relationship as is done in ROM where the fibre efficiency η_f, is defined by [10]

$$E_1 = \eta_f E_f V_f + (1 - V_f)E_m. \tag{3}$$

High values of η_f and ζ have the same upper boundary in that a state of constant strain in the composite is being approached and the strain in the matrix is dominated by the fibres. In this limiting case, the modulus in the composite approximately equals the product of fibre volume concentration and fibre modulus. For these two reinforcing factors the lower boundary is different. $\eta_f \to 0$ reflects a very poor interface between the matrix and the fibres and in the worst case the fibres act as voids instead of reinforcing fibres. However $\zeta \to 0$ is when the fibres and matrix undergo equal stress and hence the strain is dominated by the matrix strain (Reuss model) [17].

The efficiency, η_f, is back-calculated using Eq. (3) and CLT in a similar procedure as for ζ for the selected nanocellulose composites and the results compared.

2.2. Strength efficiency

The strength efficiency is calculated by comparing the theoretical strength of nanocellulose composites to the reported measured strength. Two methods of calculating the theoretical strength are used; one is a commonly used micromechanical model based on the properties of the fibre and the matrix, the other is network model based on the strength of nanocellulose network without the presence of the matrix. The strength of the composite, σ_R, is calculated using ROM where [18]

$$\sigma_R = \eta_{os}\eta_{ls}\sigma_f V_f + (1 - V_f)\sigma_{mf}, \tag{4}$$

where

$$\eta_{ls} = \begin{cases} 1 - l_c/2l & l > l_c \\ l/2l_c & l < l_c \end{cases} \tag{5}$$

and where

$$\sigma_{mf} = \sigma_f \frac{E_m}{E_f}. \tag{6}$$

Here η_{os} is the orientation factor and it is assumed that the fibres are orientated in the 2D plane so $\eta_{os} = 3/8$. σ_f is the fibre strength and l_c is defined by

$$l_c = \frac{\sigma_f d}{2\tau}. \tag{7}$$

Here d is the diameter of the fibre and τ is the interface shear strength.

In nanocellulose composites, direct measurements of τ is very difficult and so it is assumed that there is a perfect interface

Table 1
Material properties from selection publication used in this study.

Ref	Matrix	Fibre type	E_m (GPa)	E_c (GPa)	V_f (%)
[34]	Epoxy	Flax	3.1	6.5	21
[22]	Starch	CNF	0.0016	6.2	61
[23]	Polyurethane (PU)	BC	0.2	11.6	43
[12]	Hydroxyethyl cellulose (HEC)	CNF	1.0	8.2	62
[35]	Cellulose acetate butyrate (CAB)	CNF	1.5	6.5	54
[24]	Epoxy	BC	3.0	7.1	49
[13]	Melamine formaldehyde (MF)	CNF	8.3	16.6	79
[31]	Chitosan (Ch)	CNF	1.4	2.1	17
[32]	Polylactic acid (PLA)	CNF	2.0	3.0	15
[33]	Starch	CNC	0.4	0.8	24
[29]	Cellulose acetate butyrate (CAB)	CNF	1.3	2.2	7
[30]	Polylactic acid (PLA)	CNF	2.9	3.6	4
[25]	Cellulose acetate butyrate (CAB)	CNF	0.8	3.2	4

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