

IS HIERARCHY USEFUL IN NATURAL FIBRE COMPOSITES?

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ABSTRACT

Natural fibre composites have gained attention during the last years. As a result, research on how to improve their performance has been continuously conducted. Several routes have been explored, such as chemical or physical modifications of the fibres/matrices. However, can these composites improve their performance by utilizing hierarchy? By using a green nanosize additional reinforcement, nanocellulose, the properties of the composites could be enhanced. But, is the use of a nanosize additional reinforcement always improving the mechanical performance of natural fibre composites? This work aims to respond this question.

1 INTRODUCTION

Natural fibre composites have found many applications during the last years due to an emerging trend of eco-awareness and the need to reduce the use of polymers and waste while increasing the performance of the resulting materials. The low price of natural fibres, renewability, low density and high specific stiffness and strength [1] has become an incentive to use them.

Extensive investigations on enhancing the mechanical performance of natural fibre composites have been carried out, for example by modifying the surface of the fibres or by adding compatibilizers to improve the interface of the fibres [2, 3]. However, there is an unexplored route to improve the performance of natural fibre composites: utilize hierarchy. This can be done by including another reinforcement within the composites, from vastly different size (nanosize) compared to the main reinforcing fibres, to create hierarchical natural fibre composites. The chosen nanosize reinforcement in this study was nanocellulose.

There are two main approaches to obtain nanocellulose. In the top-down approach, the nanocellulose is obtained by applying a mechanical or chemical treatment to lignocellulosic materials [4, 5]. The nanocellulose fibrils obtained by this approach also contain other constituents, such as lignin and hemicellulose, naturally present in the natural fibre structure. In the bottom-up approach, some bacteria, such as *Gluconoacetobacter xylinus* produce pure cellulose fibrils, known as bacteria cellulose (BC), as an extracellular product under certain culture conditions [6]. Nanocellulose is known for its high surface area, which leads to strong interactions with its surroundings [7]. Furthermore, nanocellulose can form a dense 3D network structure, by irreversible hydrogen bonding between the individual nanocellulose fibrils upon drying [8]. This structure can be further utilize as a binder, for example, to create nonwovens [9, 10]. Nanocellulose has been used as only binder for loose flax or sisal fibres, where no additional binder or entanglement method was used to produce nonwovens. The mechanical performance of the nonwovens

containing 30 wt.% BC as binder was comparable to other nonwovens or even natural fibre composites with polymeric matrices [9]! Furthermore, nanocellulose has also been used as reinforcement (not binder) for polymeric matrices [11-13]. So, what happens when everything is combined together?

Lee et. al [10] reported the use of BC as additional binder for sisal/polyAESO composites, by creating a sisal/BC nonwoven preform which was later infused with AESO. The addition of just 10 wt. % BC doubled the tensile and flexural properties of the composites. But, is the addition of nanocellulose always improving the mechanical performance of natural fibre composites? Does the nature of the polymeric matrix (thermoset or thermoplastic) influence the effect of the nanocellulose additional reinforcement?

In this work, we aim to discover if the use of a nanosize additional reinforcement, nanocellulose, is always improving the mechanical performance of natural fibre composites. To do so, we have mainly produced hierarchical composites combining flax fibres with different thermoplastic matrixes: maleic anhydride grafted polypropylene (PP/MAH-g-PP) and polylactic acid (PLA); and flax and sisal fibres with different thermosetting polymers: polyacrylated soybean oil (polyAESO) and epoxy resin.

2 EXPERIMENTAL

2.1 Materials

Flax fibres were kindly supplied by S.A.R.L. Novalin (France) and sisal fibres by Wigglesworth & Co. Ltd. (London, UK). The nanocellulose used as reinforcement, bacterial cellulose, was obtained from commercially available nata de coco (CHAOKOH coconut gel in syrup, Ampol Food Processing Ltd., Nakorn Pathom, Thailand) and extracted following [14]. The sodium hydroxide used for the bacterial cellulose purification was purchased from Sigma- Aldrich. Polypropylene fibres were kindly supplied by Schwarzwälder Textil-Werke (STW) and polylactic acid fibres by MiniFIBERS Inc. Epoxy resin Araldite ® LY556 and hardener XB 3473 were purchased from Huntsman Advanced Materials Ltd. (Cambridge, UK). Acrylated epoxidised soybean oil (AESO) containing 4,000 ppm monomethyl ether hydroquinone as inhibitor and Luperox P (*tert*-butyl peroxybenzoate), used as initiator for AESO, were both purchased from Sigma Aldrich.

2.2 Manufacturing methods of composites and nonwovens

Two different manufacturing methods were used, one for thermoplastic and another for thermoset natural fibre composites. Thermoplastic composites were manufactured using a filtration process followed by compression moulding. Mainly, the natural and polymer fibres were commingled and soak in a dispersion containing nanocellulose. These dispersion was the vacuum filtrated emulating a paper making process. Then the wet cake was hot compress at 120°C, to enable the formation of the nanocellulose network, and at 175°C, to enable the melting of the polymer fibres [12].

The thermoset composites were produced by vacuum assisted resin infusion (VARI) of a nonwoven preform, which used nanocellulose as a binder [9]. These procedure has already been reported [10, 15]. The infusion conditions for each thermosetting polymer can be found in table 1.

Matrix	Mixing ratio [wt.%]	Degassing Conditions	Temperature during Infusion [°C]	Curing Cycle
AESO/Luperox	100/5	80 °C 30 min	80	2 h at 110 °C 2 h at 130°C
Araldite/Hardener	100/23	80 °C 30 min	80	2h at 120 °C 4h 180 °C

Table 1. Mixing ratios, degassing conditions, infusion and curing conditions for epoxy and AESO resins.

2.3 Characterization of polymers and composites

The rheology of PP and PLA melts was characterized using a rheometer (Physica MCR 301, Anton Paar, Graz, Austria). Prior to the measurement, the PP and PLA polymer fibres were moulded at 175°C into 1 mm thick sheets. The test specimens were obtained by cutting 25 mm diameter discs from the sheets. The specimens were then subjected to a frequency sweep from 628 to 0.01 rad·s⁻¹ at 5% strain. A gap of 1 mm was used as the distance between the plates during the measurement.

The tensile properties of the (hierarchical) composites were obtained using an Instron universal testing machine (Instron 5969, Instron GmbH, Germany). The tests were carried out with a 1kN or 50kN load cell (depending on the strength of the specimens) and at a speed of 1mm·min⁻¹. A minimum of 5 specimens were tested for each set of samples. The dimensions of the testing specimens for the thermoplastic composites were around 80×15×2 mm³ (the thickness varied with the different matrices used). The distance between the clamps was set to 50 mm. In the case of the thermoset composites, the specimens possessed dimensions of 100×15×1.5 mm³ (the thickness varied with the fibre/matrix type), and the distance between the clamps used was 60 mm. For all the tests, the strain of the samples was measured with a video extensometer (iMetrum Ltd, UK) and the gauge length was set to 30 mm.

3 RESULTS AND DISCUSSION

The aim of this work was to discover if the hierarchy produced by the addition of a nanoreinforcement into natural fibre composites improved the mechanical performance of the resulting composites. It is important to be noted that the nanoreinforcement is not only acting as a nanofiller, but as a binder for the natural fibres (and the thermoplastic fibres, when used), enhancing the stress transfer between them [9].

The first part of the work focused on the effect of nanocellulose in natural fibre composites using thermoplastic matrices [12]. The investigation was carried out with two different thermoplastic matrices: a mixture of PP and MAH-g-PP, and PLA. Due to the difference on the behavior of these two matrices during the compression moulding process, the volume fraction of the natural fibres used varied in both matrices. For the composites using PP/MAH-g-PP as matrix, 40 wt.% flax fibres were used. On the other hand, when PLA was used as matrix, the weight fraction of flax fibres was 60 wt.% (overflow of the polymer matrix when more PLA was used). To see the effect of the addition of nanocellulose (10 wt.% of the amount of fibres used) on the natural fibre composites, the mechanical properties of the hierarchical composites were tested. In Figure 1, the tensile strength of the (hierarchical) natural fibre composites using PP/MAH-g-PP and PLA as matrices can be observed. It can be observed that the composites containing PP/MAH-g-PP as matrix outperformed the composites containing PLA (it has to be taken into account that they possessed different fibre volume fractions, so no further conclusions could be obtained from this fact). However, when the nanocellulose additional reinforcement was added, the behavior of the hierarchical composites was completely different.

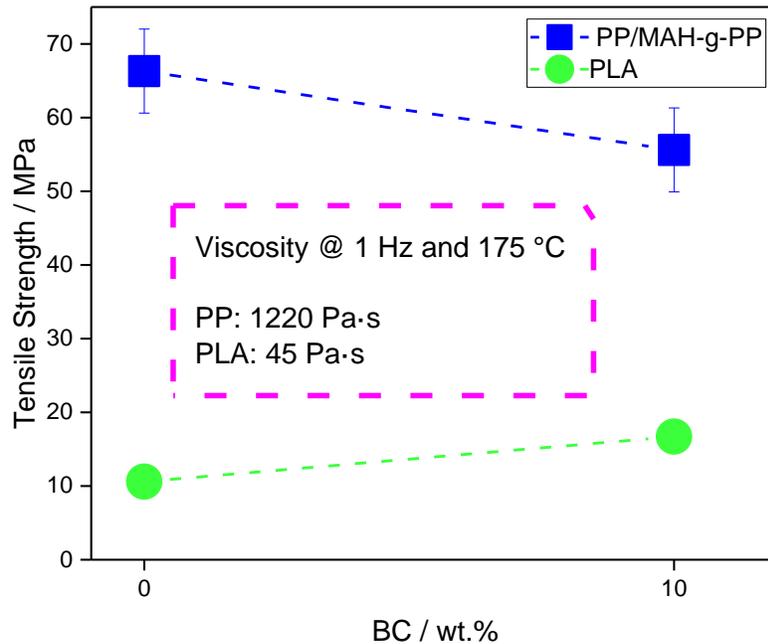


Fig.1 Tensile strength of thermoplastic composites

The addition of nanocellulose as additional binder in flax/MAH-g-PP composites slightly decreased the tensile strength of the resulting hierarchical composites, but the addition of the BC reinforcement to the flax/PLA composites nearly doubled the tensile strength of the resulting hierarchical composites! In Figure 1, the viscosity of both polymers is also reported. It was observed that the viscosity was a key parameter to explain the behavior of these composites. The viscosity would determine if the polymer melt can permeate the nanocellulose network, and thus, influence the interface with the flax fibres. It was observed that the viscosity of PP was nearly two orders of magnitude higher than the viscosity of the PLA.

On the other hand, the use of nanocellulose as additional reinforcement in thermoset natural fibre composites [16] can be observed in table 2. In table 2, the tensile properties of natural fibre composites with 2 different matrices: polyAESO and epoxy resin, using two different reinforcing fibres: flax and sisal fibres, can be observed. It can be seen that when BC was added to the flax/polyAESO composites, the mechanical performance of the composites decreased. The same trend was observed for sisal/epoxy composites. However, when the sisal fibres were reinforcing polyAESO, the tensile modulus of the composite more than doubled with the addition of nanocellulose. It can be concluded that the use of nanocellulose to create hierarchical natural fibre composites increased the mechanical performance of the composites when the main reinforcing fibres and the matrix to be reinforced were low or medium performance. If the main reinforcing fibres or the matrix used in the hierarchical composites were high performance, the mechanical properties of the nanocellulose network were not utilized within the composites.

Fibres	Matrix	BC [wt.%]	σ_T [MPa]	E_T [GPa]
Flax	polyAESO	0	50.2 ± 2.9	11.3 ± 2.8
Flax	polyAESO	10	48.1 ± 4.4	8.9 ± 1.4
Sisal	polyAESO	0	27.0 ± 3.5	4.3 ± 2.6
Sisal	polyAESO	10	29.9 ± 3.3	11.1 ± 3.7
Sisal	Epoxy	0	33.7 ± 2.9	10.6 ± 2.7
Sisal	Epoxy	10	22.9 ± 5.9	7.6 ± 1.2

Table 2. Tensile strength (σ_T) and modulus (E_T) of natural fibre thermoset composites.

4 CONCLUSIONS

It has been observed that the use of a nanosize additional reinforcement is not always improving the mechanical performance of natural fibre composites. It depends on the matrix and fibres used. For instance, when a thermoplastic polymer was used as matrix, the improvement of the composite properties upon the addition of nanocellulose strongly depended on the viscosity of the thermoplastic melt (at the consolidation temperature of the composite), which determined if the melt permeated the nanocellulose network. On the other hand, the use of nanocellulose as additional reinforcement for thermoset natural fibre composites increased the mechanical performance of the composites when the main reinforcing fibres and matrix to be reinforced were low or medium performance.

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