PAPER-BASED COMPOSITES FOR PACKAGING APPLICATIONS

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Abstract

There is a waste problem with plastics used for packaging and used biopolymers, i.e. PLA, could be the solution. Unfortunately, they have some drawbacks compared to commonly used plastics for packaging applications. Could the performance of bioplastics be improved by implementing an interconnected network as reinforcement? Hybrid papers from nanocellulose and pulp fibres derived from bagasse were used in this work to produce hierarchical PLA composites suitable for packaging applications, due to their high tensile strength and low oxygen transmission rate, derived from the network structure fromed by the cellulosic fibres. The composites were manufactured by compression moulding of the PLA film in between hybrid papers. This could offer a biobased and biodegradable solution for the waste problem we are currently facing.

1. Introduction

The use of plastics and other non-biodegradable materials for single-use food packaging applications, either as sealant or as containers, is creating a waste problem. The raw materials, their processing and manufacturing, and the fact that after one use they need to be recycled (not easily performed) or disposed implies that a lot of energy as well as money is consumed. There is a real need for substituting these materials with renewable ones, whose biodegradability and composability are assured.

One example of bio-based and renewable material is polylactic acid (PLA). PLA can be produced from lactic acid, which is produced by fermentation of agricultural sources and it can be recycled back to lactic acid by hydrolysis or alcoholysis [1]. It is recyclable and compostable [2], and it possesses good stiffness [3]. Nevertheless, it has some drawbacks compared to the petrol-based polymers, such as moisture sensitivity, low deformation at break and relatively high price [4]. It is used in biomedical applications [5] and it is promising as packaging material [6]. The performance of PLA (and thermoplastic biopolymers) is limited and it can be improved by reinforcing them. Cellulose is the most abundant polymer on earth [7]. Furthermore, cellulose fibres are fully biodegradable and cheap, as compared to other reinforcements such as carbon fibres or glass fibres [8], they are a CO_2 neutral resource and they possess high specific properties [7]. Cellulose can be used as fibre reinforcement in several forms: in the form of loose natural fibres or fabrics, in the form of paper and in the form of nanopaper (produced from naocellulose). The appealing of nanocellulose is that it has a high surface area, which enables the formation of strong 3D network structures by irreversible self-hydrogen bonding upon drying. This process is known as hornification [9]. The increased surface area of the nanocellulose leads to strong interactions with the surroundings, which enables the embedding of considerably large amounts of water and allows for strong interactions with other biomaterials or polymers, and with itself [10], which can lead to a reduction in the permability of materials, a key issue for packaging applications.

Natural fibre composites have been extensively studied [11, 12], and in a smaller extent have been paper based composites (using pulp fibres) with thermoplastic matrices [13, 14]. The use of nanocellulose as further reinforcement in natural fibre composites with PLA as matrix has also been studied [15, 16] and so has the use of nanocellulose as reinforcement for PLA [17]. However, a combination of paper (from pulp fibres) and nanocellulose has not been yet used to reinforce PLA (or other thermoplastic matrices) and improve its barrier and mechanical properties.

In this work, we report paper based-composites combining pulp fibres and nanocellulose as reinforcement for PLA to improve some of the most important packaging properties, such as the tensile strength, which is connected to the mechanical stability and the oxygen transmission rate, one of the most important barrier properties for packaging materials.

2. Experimental part

2.1. Materials

Bleached bagasse pulp paper (Lot 1201, Environment Pulp and Paper Co.Ldt, China) was kindly supplied by City University of Hong Kong. The PLA films were manufactured using an extruder (Plastik maschinenbau PM 30, Kelburg, Germany) with a tapered screw (30 mm diameter and 102 mm length) and a flat film die. The working temperatures were 180°C, 190°C and 210°C at zones 1,2 and 3, respectively. The temperature in the die was 230°C. The melt pressure was 120 bar. The take-off speed was 5.1 m/min. Nanocellulose was obtained by grinding the bagasse pulp paper following an optimized procedure (MKCA6-23, Granomat JP 150, Fuchs Machinen AG, Switzerland).

2.2. Manufacturing

The composites were manufactured by sandwiching a layer of PLA film between two hybrid papers (same composition) by compression molding at 175°C under 2 t weight for 15 min (25-12-2HC, Carver Inc., Wabash In, USA). The hybrid papers from bagasse pulp and nanocellulose were manufactured by blending (Braun Multiquick 5 Jug Blender, Braun GmbH, Germany) the two components separately in water for 2 min, and then together for another 2 min. The suspension was then vacuum filtered onto a filter paper (Qualitative filter paper 431, Particle Retention: 5-13 µm, VWR, Austria) in a büchner funnel. Once the water was removed by filtration, the wet paper was sandwiched between blotting paper (Qualitative filter paper, Grade 520A, Whatman, GE Healthcare Europe GmbH, Austria) and compressed at 2 t to remove the excess water. This procedure was repeated 3 times exchanging the blotting papers. The hybrid papers were then compressed at 120°C and 2 t, for 15 min to hornify the cellulosic fibres.

2.3 Characterization

2.3.1Tensile strength

The samples were cut into dog-bone shaped specimens according to EN ISO 527-2 type 1BA using a zwick cutting device (BZCP 020 Schneidevorrichtung 87181, Zwick Roell Group, Germany). Before each measurement, the thickness and weight of the specimens was recorded. To prevent any damage in the specimens, cardboard endtabs were glued to the part in contact with the clamps. Prior to the tensile measurements, all the specimens were conditioned at 24°C and a RH of 35%. The tensile tests were carried out in a Universal testing machine (5869 dual column universal testing system, instron GmbH, Buckingshire, UK) equipped with a 1 kN load cell at a speed of 1mm/min. The gap length used was 57 mm (in accordance with the used dog-bone shape dimensions).

2.3.2 Oxygen transmission rate

The oxygen transmission rate (OTR) was measured in a gas permeability tester (VAC-VBS, Labthink Instruments Co. Ltd., China). The tested area was a circular shaped with a diameter of 80 mm. The test was performed at ambient conditions. The test was performed using a proportional mode with a 10% pressure difference. Prior to the test, the specimens were conditioned in the machine for 4h under vacuum, to ensure that no particle remains in the films. The Oxygen transmission rate was calculated according to the standard GB/T1038-2000.

3. Results and discussion

In order to investigate the effect of the addition of nanocellulose to pulp paper based PLA composites, different hybrid papers were manufacture as reinforcement for PLA. The hybrid papers contained 0, 20, 40, 50 and 100 wt.% nanocellulose content. It was observed that the laminated composites with only nanocellulose as reinforcement (100 wt.% NFC) could not be further processesed (cut into specimens) due to a severe delamination. In figure 1 it can be observed the delamination, which occurred while cutting a specimen for a permeability test. The layers of the composite; a NFC layer, the PLA film in between and another NFC layer; can be clearly observed.

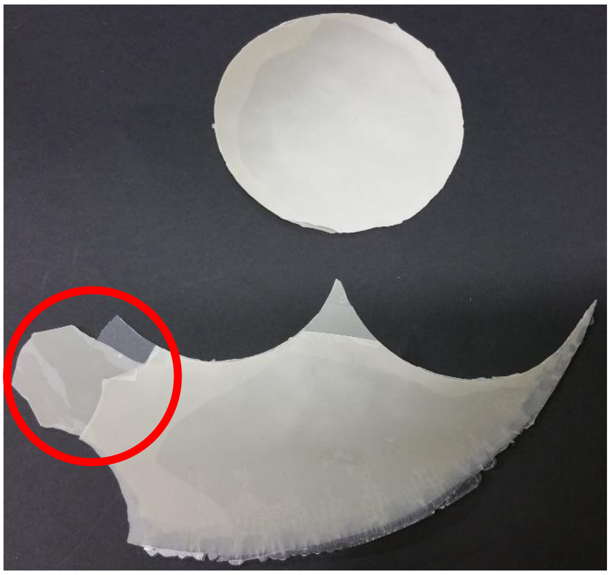

Figure 1. Image of the delamination of the PLA laminated composites containg 100 wt.% NFC papers as reinforcement.

Nevertheless, the addition of nanocellulose to the hybrid papers in more moderated contents, i.e. 20-50 wt.%, improved both the mechanical and the oxygen barrier properties of the hierarchical composites (table 1). The use of 50 wt.% nanosized cellulose in the hybrid papers increased the tensile strength of the composites up to 96 MPa, due to the fact that the nanocellulose paper possessed a tensile strength more than 5 times higher than paper made from pulp fibres. The increase of the mechanical properties evidences the utilization of the nanocellulose network. A similar trend was observed with the oxygen transmission rate of the samples. The addition of the nanocellulose increases the tortuosity of the path that the gas requires to pass, reducing the amount of oxygen that can go through the samples. Furthermore, the use of nanocellulose in the composite decreased the oxygen transmission down to 100 $cm^3/(m^2 \cdot 24h \cdot atm)$, a value suitable for packaging applications.

Table 1. Tensile strength and oxygen transmission rate (OTR) of the paper-based PLA composites

Pulp/NFC ratio (wt.%)	*Tensile strength* (MPa)	*OTR* ($cm^3/[m^2 \cdot 24h \cdot atm]$)
100/0	53.2 ± 1.7	>900000
80/20	77.1 ± 2.8	43901 ± 61923
60/40	88.3 ± 13.4	26 ± 9
50/50	96.0 ± 9.6	94 ± 73
0/100	Delamination	Delamination
PLA	46.6 ± 2.6	1943 ± 70

4. Conclusion

Hierarchical paper based composites were successfully manufactured and characterized to be used as packaging materials due to their biobased origin and biodegradability. A combination of pulp and nanocellulose, both from bagasse, was used to create hybrid papers and to produce hierarchical composites with PLA. It was observed that the use of only nanocellulose lead to delamination of the composites. However, an increase on the nanocellulose content in the hybridized papers (up to 50 wt.%) lead to an increase of the tensile strength up to 96 MPa and a decrease of the oxygen transmission rate below 100 $cm^3/[m^2 \cdot 24h \cdot atm]$.

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