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Improving the accessibility of hemp fibres using caustic to swell the macrostructure for enzymatic enhancement

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ABSTRACT

The main aim of this study was to investigate the effect of mercerization prior to enzymatic treatments on the surface, on the thermal and morphological properties of hemp fibres. Hemp fibres were treated with sodium hydroxide (5%, w/v) and five different enzyme systems. The enzymes studied were xylanase, xylanase + 10% cellulase, pectinmethylesterase, polygalacturonase and laccase. A previous report utilizing enzymes alone (George et al., 2014) was used as a baseline to determine the impact of caustic swelling of the hemp fibres coupled to enzymatic treatment. Thermal gravimetric analysis (TGA) was used to study the effect of each system on thermal properties of the hemp fibres. Scanning electron microscopy (SEM) was used to monitor the changes in the morphological features of the hemp fibres, while X-ray photoelectron spectroscopy (XPS) was used to study the influence of each treatment of the surface chemical composition. Force tensiometry was used to investigate the effect of the different systems on the surface polarity of the treated fibres. The additional treatment with NaOH + hemicellulases was found to result in enhanced thermal properties when compared to previous systems. SEM micrographs confirmed greater fibre bundle rupture and increase in surface roughness of the base + enzyme treated samples. This work demonstrates that mercerization prior to enzymes, depending on the mode of action and arrangement of chemical components of the fibre, can be an effective method for improving the thermal and surface properties of fibres for composite applications.

1. Introduction

As a result of the growing environmental sensitivity, new legislations and regulations, industries are forced to develop and implement ecologically friendly materials. The engineering of materials that are sustainable, characterized by low carbon footprint and renewable content has been the focus of the past few decades. Specifically, the use of natural fibres instead of glass fibre for composite applications is a key focus. Natural fibres have many advantages compared to synthetic fibres, including decreased weight and they are most often recyclable and fully biodegradable (Bledzki et al., 1996). Additionally, natural fibres are obtained from renewable sources and cause decreased wear of processing equipment and yet have comparable strength and stiffness to synthetic fibres (Wambua et al., 2003; Mohanty et al., 2000). Nevertheless, natural fibres have a few inherent disadvantages in composite applications that have been the focus of much optimization research. These limitations include moisture uptake, low thermal stability and quality variations due to fibre processing (Oksman et al., 2003).

Many strategies have been investigated to improve the properties of natural fibres for composites applications. For example, chemical methods such as mercerization (Mwaikambo and Ansell, 2002), acetylation using acetic anhydride and propionic anhydride (Bledzki et al., 1996) and silane treatment using a number of quaternary functionalized silane groups (Xie et al., 2010) have been reported. The effect of compatabilizers such as maleic anhydride on the swelling properties (Naik and Mishra, 2007) and the mechanical properties of natural fibres have studied and thoroughly investigated (Mishra and Naik, 2005). Despite the success of these methods, environmental concerns associated with chemical waste disposal and exposure of processing workers to harmful chemicals have limited many of these technologies to the laboratory scale.

The use of biological methods such as enzymatic processing and microbial fermentation offer an answer to many of the limitations. Evidence for this is seen in the increase of publications in the area of biological agents for modifying natural fibres in the past decade. Pommet et al. (2008) successfully optimized a process for depositing bacterial cellulose onto the surface of loose hemp fibres and mates. They showed that the deposition of nanosized bacterial

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cellulose improved the surface and mechanical properties of the fibres. In an earlier study done by our research group, it was found that hemp and flax fibres treated with enzymes (hemicellulases, pectinases and oxidoreductase) were characterized with improved surface and thermal properties (George et al., 2014). White rot fungi was used to treat hemp fibres and the effect on the interfacial shear strength of polypropylene extruded and injected molded composites was reported by Li et al. (2009). They concluded that the use of the fungi specifically removed components of the fibres resulting in higher interfacial shear strength for composites when compared to untreated samples. In another work by Pickering et al. (2007a,b), the use of fungi coupled with a caustic treatment was shown to obtain the highest tensile strength for the composites produced. These studies showed that enzymatic and fungal methods can be used to impart the same changes characteristic of chemical methods used to modify these lignocellulosic materials. Generally, biological methods are advantageous because they often require lower energy input, the biological agents can be recycled and reused and their use results in less corrosion of processing equipment.

The scope of this study was to investigate the effect of mercerization prior to enzymatic treatment on the surface and thermal properties of hemp fibres. In a previous study from our group, hemp and flax fibres were treated with enzymes, and the surface and thermal properties were reported (George et al., 2014). As a result, the question was raised as to whether swelling of the macrostructure of hemp fibres would impart better enzymatic penetration and hence better enhancement of the hemp fibres and was thus investigated. It should be noted, this study was undertaken for two main reasons, one being the high cost of enzymes and the other the established know how about caustic being able to swell the fibres. The enzymes examined were xylanase, xylanase + 10% cellulase, pectinmethylesterase, polygalacturonase and laccase. The effect of mercerization + enzyme treatment was compared against untreated and enzyme treated hemp fibres. Properties studied included thermal, surface and morphological parameters. Also, of interest, was what percentage of the hemp fibres was degraded by each enzyme system, given that this has an implication in the overall effect when eventual life cycle assessment needs to be done. Based on the findings, it was concluded that mercerization prior to enzymatic treatment enhanced the effect of the hemicellulases on the thermal and surface properties of the hemp fibres. The swelling of the fibres had no significant effect on the pectinase activity on the hemp fibres.

In our previous study, the aim was to modify solely the surface of the hemp fibres, but in this case, the aim was to partially swell the cell walls of the fibres to allow the enzymes to percolate into the interior crevices of the fibres. To the best of our knowledge, this study is one of the first to highlight the improvement in hemp fibre properties especially the thermal properties and surface polarity as a result of the mercerization prior to enzymatic treatment. Removal of hemicellulosic materials from the primary and secondary cell walls resulted in improved thermal properties based on the thermal gravimetric analysis. The use of caustic to swell the structure, allowed for better removal of interstitial hemicellulosic and pectic material which effectively exposed lignin onto the surface. As a result, the there was an improvement in the surface polarity of the hemp fibres. The findings reported serves to provide an effective method for enhancement of hemp fibres for composite applications.

2. Experimental

2.1. Materials

Mechanically processed hemp fibre samples were provided by Alberta Biomaterials Development Center located in Vegreville, Alberta. Enzymes were provided by Novozymes (Bagsvaerd, Denmark). All material prior to experimental was stored at 4 °C. Sodium acetate (99%, mol. wt. 82.03 g/mol), glacial acetic acid (99.7%, mol. wt. 60.05 g/mol), sodium phosphate dibasic (99%, mol. wt. 141.96 g/mol) and sodium hydroxide (99%, mol. wt. 40.00 g/mol) were obtained from Fisher Scientific. Sodium citrate monohydrate (99%, mol. wt. 214.11 g/mol) was purchased from Sigma–Aldrich. Sodium phosphate monobasic (99%, mol. wt. 119.98 g/mol) was obtained from Acros Organics. Citric acid (99%, mol. wt. 192.13 g/mol) was sourced from EMD Chemicals. Sulfuric acid (98%, mol. wt. 98.075 g/mol) and calcium carbonate (99%, mol. wt. 100.09 g/mol) were also sourced from Fisher Scientific. D-(+)-Glucose (99.5%, mol. wt. 180.16 g/mol), D-(+) – galactose (99.5%, mol. wt. 180.16 g/mol), D-(+)-xylose (99%, mol. wt. 150.1 g/mol) were obtained from Sigma. Distilled water was used for all analyses.

Table 1
Characteristics of each enzyme system with corresponding activity at optimum conditions. For each system, pH was maintained using buffers (provided by Novozymes).

Enzyme	Optimum conditions		Activity
	pH	Temperature (°C)	
Xylanase	7	70	1000 AXU/g
Xylanase (10% cellulase)	6	50	2500 FXU-S/g
Polygalacturonase	4	45	3800 PGNU/ml
Laccase	7	50	1000 LAMU/g
Pectinmethylesterase	5	45	5 PEU/ml

2.2. Mercerization of hemp fibres

Approximately 1.0 g (done in triplicate) of hemp fibres was weighed into a 125 ml Erlenmeyer flask. 50 ml of 5% (w/v) NaOH was added to the fibre samples and kept at 80 °C for 90 min. The contents of the reaction flask were constantly stirred at 60 rpm. Samples were then removed, washed with distilled water containing 1% (w/v) acetic acid to neutralize excess NaOH. The samples were then oven dried at 80 °C for 5 h (Williams et al., 2011).

2.3. Enzymatic treatment of hemp fibres

For the enzyme treatments, approximately 1.0 g of fibre was weighed into a 125 ml Erlenmeyer flask. Each enzyme system required specific reaction conditions under which they function optimally. These conditions were provided by the enzyme supplier (Table 1). Concentration of 2 (% w/v) enzyme stock with corresponding enzyme activity as specified in Table 1 was used to treat the hemp fibres. For all experiments, the liquid (ml) to fibre (g) ratio was maintained at 50:1 to facilitate complete wetting of fibres. Enzymatic treatments were conducted for 90 min under constant agitation (80 rpm) at the optimum temperature in a standard water bath. Enzymes were deactivated by heating at 90 °C for 10 min. fibres were washed with excess warm water to remove traces of enzyme and buffer reagents. All samples were dried at 80 °C for 5 h and stored in polyethylene bags for subsequent analysis as outlined by George et al. (2014). All experiments were carried out in triplicate.

2.4. Mercerization prior to enzymatic treatment of hemp fibres

In order to investigate the effect of macrostructure swelling before enzymatic activity, hemp fibres were firstly treated with NaOH as outlined in Section 2.2. The fibres were completely dried and stored for enzyme treatment. The 1.0 g of mercerized hemp fibres was then exposed to each enzyme system as in Section 2.3.