



Surface and thermal characterization of natural fibres treated with enzymes



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ABSTRACT

Natural fibres are a potential replacement for glass fibre in composite materials. Inherent advantages such as low density, biodegradability and comparable specific mechanical properties (relative to glass fibre composites) make natural fibres an attractive option. However, limitations such as poor thermal stability, moisture absorption and poor compatibility with polymeric matrices are challenges that need to be resolved. The primary objective of this research was to study the effect of five enzymatic systems on the surface chemical, morphological and thermal properties of natural fibres. Flax and hemp fibres were treated with hemicellulases, pectinases and oxidoreductase. Surface and thermal properties were measured using X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and force tensiometry. Each treatment rendered the surface topography of both fibres free of contaminants and exposed the individual fibre bundles. Treatment with hemicellulase and pectinase improved the thermal properties for both fibres. XPS measurements confirmed reduction of the hemicellulosic content of both fibres for xylanase and pectinases (polygalacturonase and pectin-methylesterase). Removal of amorphous hemicellulosic material from the fibre surface and consequent exposure of the crystalline cellulose network resulted in a lower contact angle for all the treated samples. This work demonstrated that enzymes offer an inexpensive and environmentally attractive option to improve the surfaces of natural fibres for composite applications.

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1. Introduction

High-performance composite materials require a dispersed phase with elevated surface wettability and elevated cohesion with the polymeric matrix in order to attain efficient transfer of stress within the structure. While natural fibres constitute an attractive alternative to glass fibres owing, their limited thermal stability and incompatibility with synthetic polymer matrices constitute a significant challenge toward industrial implementation of these materials platforms (Mohanty et al., 2002; Milanese et al., 2012; Fei et al., 2009). Several strategies have been investigated to address these deficiencies. For examples, mercerization (Mwaikambo and Ansell, 2002), acetylation (Bledzki et al., 2008) and silane treatment (Anyakora and Abubakre, 2011) are known either to reduce hydrogen bonding within the complex structure or by reacting with the many hydroxyl groups on the surface (Gonzalez et al., 1999; Tserki et al., 2005). Physical methods have also been

studied and a comprehensive review was compiled by Mukhopadhyay and Figueiro (2009). Methods such as steam explosion (Kalia et al., 2009), plasma treatment (Yuan et al., 2004) and corona discharge (Gassan and Gutowski, 2000) promote separation of fibre bundles into more homogenous structures that can be evenly deposited in one direction in the matrix materials.

An alternative to chemical and physical methods is represented by the rapidly expanding use of biological agents such as fungi (Pickering et al., 2007; Gulati and Sain, 2006) and enzymes (Gustavsson et al., 2005; Kharazipour et al., 1997 and Pietak et al., 2007). Biological modifications offer several advantages over chemical and physical methods. They can selectively remove hydrophilic pectic and hemicellulosic material and require lower energy input. Enzymatic systems, in addition, can be recycled after each use (Li and Pickering, 2008). Li and Pickering (2008) used chelators and enzymes to separate hemp fibres into individual bundles. They found that the crystallinity (X-ray diffraction) and thermal properties (thermal gravimetric analysis) improved after separating the bundles. In another study, Pietak et al. (2007) investigated the surface wettability of natural fibres using atomic force microscopy and contact angle measurements. They measured an increase in adhesion force for treated samples because enzymatic and chemical

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treatments (steam explosion) removed the primary cell wall exposing the secondary wall. The same study provides clear evidence of hemicellulose removal from hemp fibres.

Enzymatic treatments have also been used to modify the physical network of natural fibres. Kardas et al. (2009) investigated the effect of four enzyme treatments (Lipase A, Lipase AK, Lipozyme and Esterase) on the micro-topography of polyester fabric. They found that the esterase preparation was the most effective method for producing a more uniform and homogenous texture of the fabric material. Saleem et al. (2007) treated bast fibres with pectinase and then reported the mechanical characteristics of the reinforced thermoplastic composites. According to their study, hemp fibres treated with 8% of the enzyme in maleic anhydride medium, were characterized by increased tensile strength, flexural strength and moduli of elasticity. These improvements were attributed to higher aspect ratio of the fibre bundles which resulted in better dispersion within the polymeric matrix (polypropylene). A recent study conducted on bamboo fibres using a number of enzymes (xylanase, cellulase, pectin lyase and laccase) revealed that the different systems were effective in improving fibre fineness (Liu et al., 2012), presumably as a result of the removal of the more polar hemicellulosic fraction.

The scope of this study was to investigate the effect of five commercially available enzyme systems (xylanase, pectin-methylesterase, polygalacturonase, laccase and a xylanase with cellulase background) on the surface of two different sources of bast fibres, hemp and flax. It should be noted that each of these enzyme system may have accessory enzymes such α -glycosidase and arabinosidase. Fundamental surface chemistry and thermal information collected in this work provided the basis for better understanding the properties of natural fibres and how these may influence the fibre-matrix interface. Enzymes enable the modification of the fibre surface properties with limited or no effect on the bulk properties because, owing their size percolation into the inner structure is impeded. For example, Boisset et al. (2001) while studying the action of a recombinant cellulase on the cross section of cottons fibre for applications in the textile industry found that there was no indication of enzyme penetration or damage to the interior of the fibres.

To the best of our knowledge, this study is one of the first that examines the influence of solely enzymes in the absence of any mediator (chemicals) on thermal properties of natural fibres specifically for composites applications. Removal of pectic and hemicellulosic materials resulted in improved thermal properties based on thermal gravimetric analysis. X-ray photoelectron spectroscopy and contact angles indicated the removal of the hygroscopic primary cell wall. The findings reported serves to link enzymes as a pretreatment method for natural fibres to be used in composite applications.

2. Experimental

2.1. Materials

Mechanically processed hemp and flax samples were provided by the Alberta Biomaterials Development Centre located in Vegreville, Alberta. The samples were placed in air tight bags and stored at 4 °C. All enzymes were provided by Novozymes (Bagsvaerd, Denmark) and 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.

2.2. Washing of natural fibres

Fibres were washed using 2% (w/v) Sparkleen (No. 1) industrial detergent for 1 h at 70 °C to ensure removal of dirt and any surface contaminant that may affect the enzymes activity. Samples were filtered and washed several times with distilled water. Fibres were dried in a convection oven at 80 °C for 5 h and stored in a desiccator (Bismarck et al., 2001).

2.3. Natural fibre composition

The methods outlined by Ramadevi et al. (2012) were adopted to estimate the lignin, hemicellulose and cellulose content. Briefly, the lignin content was measured by placing 2 g of sample in a 500 ml beaker and 15 ml of 72% sulfuric acid was added and agitated at 100 rpm for three hours at 25 °C. 200 ml of water was then added to the mixture and boiled for two hours. Once cooled, after 24 h, lignin was transferred to a crucible and washed with hot water. The crucible with its content was dried at 105 °C and weighed every hour until a constant weight was reached.

The holocellulose content was measured by placing 160 ml of water, 0.5 ml of acetic acid, 1.5 g of sodium chloride and 3 g of fibre in a beaker. The beaker was placed in a water bath maintained at 75 °C for an hour, after which 0.5 ml of acetic acid was added with 2.5 g of sodium chloride. This was repeated for another two hours. Once completed, the beaker was then placed in an ice bath and cooled. The isolated holocellulose was sequentially washed with acetone, ethanol and water. The sample was finally dried at 105 °C until constant weight was reached.

The content of α -cellulose was measured by adding 10 ml of 18% (w/v) sodium hydroxide to 2 g of the isolated holocellulose. The fibres were continuously agitated at 120 rpm and kept at 20 °C. Every 5 min, 10 ml of the sodium hydroxide solution was added for another half hour. 35 ml of water was added to the beaker and kept for another hour. The holocellulose residue was isolated by washing with 100 ml of 8.5% sodium hydroxide, 200 ml of water, 15 ml of 10% (w/v) acetic acid and water. The contents of the crucible were dried at 105 °C until constant weight was reached.

The hemicellulose content was calculated by subtracting the holocellulose from the α -cellulose content (Kalia et al., 2009).

ASTM Method D4442-07 was followed to determine the moisture content of the flax and hemp samples. Approximately 0.5 g (done in triplicate) of sample was weighed in a pre-weighed and dried tin pan. The pan was placed in a convection oven at 105 °C \pm 5 °C for 5 h. The sample pan was removed, cooled in a desiccator and then weighed. The sample was heated, cooled and re-weighed until constant mass. The moisture content was calculated based on percentage mass lost.

ASTM Method E1755-01 was used to estimate the ash content of the different fibre samples. The method involved weighting approximately 0.5 g (done in triplicate) of fibre sample into a pre-weighed crucible. The crucibles were heated to 575 °C \pm 25 °C for 3 h or until all the carbon was eliminated. To avoid causing flames, the sample was heated to 250 °C and gradually increased to 575 °C. The residue left after 3 h was cooled in a desiccator and weighed. The contents were heated in a convection oven at 105 °C until constant weight. The ash content was calculated as a mass percentage.

The Dumas method or Combustion Nitrogen Analysis (CNA) method was used to determine the total organic and inorganic

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