Composites Science and Technology 68 (2008) 3293–3298

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Hemp fibre reinforced composites using chelator and enzyme treatments

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ARTICLE INFO

Article history:
Received 1 May 2008
Received in revised form 20 August 2008
Accepted 21 August 2008
Available online 2 September 2008

Keywords:
A. Short-fibre composites
B. Fibre/matrix bond
Chelator
Enzyme
Treatment

ABSTRACT

The main objective of the current work was to investigate using chelator treatment, and combined chelator and enzyme treatments, to separate hemp fibre from its bundles, as well as remove non-cellulosic compounds, and thus therefore improve the interfacial bonding in the composite. Wet chemical analysis, FTIR, X-ray diffraction (XRD), thermal analysis and single fibre tensile testing were used to characterise the effect of treatment on hemp fibres. The higher chelator concentration treated hemp fibre composites had the highest tensile strength of 42 MPa, an increase of 19% compared to composites with untreated hemp fibre.

1. Introduction

Industrial hemp fibre is one of the strongest and stiffest available natural fibres [1] and therefore has great potential in composite materials. However, improving interfacial bonding between fibres and matrix is an important issue in using fibre as reinforcement in composites. The most successful approach has been to use maleated polypropylene as an addition to polypropylene which increases its hydrophilicity, thus making it more compatible, and also enables covalent and hydroxyl bonding with the natural fibre [2]. In addition, to improve interfacial bonding, modifications can also be made to the fibres to separate hemp fibres from their bundles, remove non-cellulosic compounds and modify the fibre surface morphology. Commonly used alkali treatment is now losing popularity on environmental grounds. A more promising method regarding environmental impact involving the use of the chelator/enzyme methods to treat hemp fibres has been investigated in this study.

Chelating agents are organic compounds capable of forming covalent bonds with metals through two or more of their atoms. It has been reported that some chelators such as EDTA (ethylene diamine tetra-acetic acid) can remove calcium ions from pectin in plant cell walls such as in hemp fibres [3], resulting in the pectin becoming soluble in many liquids. This allows the hemp fibres to separate from their bundles. However, EDTA persists in the environment and due to its strong metal chelating properties, enhances the mobility and bioavailability of contaminant heavy metals. An alternative is EDTMPA (ethylene diamine tetra methylene phosphonic acid), a phosphonated analogue of EDTA. EDTMPA has a very strong interaction with all mineral surfaces [4], so it is easily removed from technical and natural systems. Due to this strong adsorption, little or no remobilization of metals occurs. Therefore, compared to EDTA, EDTMP has less impact on the environment.

Some published reports have described the effect of enzymatic degradation of non-cellulosic compounds on hemp fibres [5]. Pectinases degrade pectin and laccases modify lignin. However, waxes and other non-cellulosic compounds can be a barrier to these enzymes. In order to achieve good results, these enzyme treatments have been preceded by pre-treatments such as chelator treatments with EDTA [3]. Pectinases can be broadly classified into acidic and alkaline pectinases based on their pH requirement for optimum enzymatic activity. Alkaline pectinases, which come mostly from bacterial sources, are capable of degrading pectin in the middle lamella of a fibre cell wall. They are widely used in the separation of bundles in crops such as flax, hemp and jute to obtain fibres [5].

Laccases are one of most important lignin degrading enzymes. It has been reported that laccase alone cannot depolymerise lignin [6], but, when HBT (1-hydroxybenzotrlazole hydrate) is used as a mediator, a degree of delignification up to 40% has been obtained. The mechanism of laccase-mediator systems, involves the oxidation of the mediator by laccase, followed by the oxidation of lignin by the low-molecular weight oxidized mediator, which can diffuse into the structure to oxidise the lignin molecule.

The purpose of the current project is to use EDTMP, as well as the combined EDTMP and enzymes treatments, to separate hemp fibre from its bundles, remove non-cellulosic compounds as much as possible, and therefore, increase the access to cellulose hydroxyl groups which can take part in bonding.

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doi:10.1016/j.compscitech.2008.08.022

2. Materials

Industrial hemp (*Cannabis sativa* L.) grown in Hamilton, New Zealand was used in this investigation. After harvesting in 2007, green non-retted hemp fibres were separated by hand and allowed to dry during storage on shelves. EDTMP.Na5 (ethylene diamine tetra methylene phosphonic acid pentasodium salt), a sodium salt of EDTMP was kindly supplied by Taian Waste Water Treatment Factory in China. Pectinase (P2401) from Rhizopus, and laccase (53739) from Trametes versicolor, were purchased from Sigma. HBT (1-hydroxybenzotrlazole hydrate), a mediator, was also purchased from Sigma. Polypropylene (Icorene® PP CO14RM) with a density of 0.9 g/cm3, supplied by Aldrich Chemical was used as the composite matrix. A-C 950P, a high molecular weight MAPP, supplied by Honeywell International Inc., USA, was used as the coupling agent.

3. Experimental

3.1. Fibre treatment

Treatment of the green non-retted fibres was achieved by immersing the fibres in solution (fibre: solution = 10 g: 200 ml) consisting of either EDTMP.Na5 or enzyme (see Table 1). Fibres were then washed for 10 min in water and dried in an oven at 80 °C until an equilibrium moisture content was achieved.

3.2. Fibre chemical analysis

The chemical analysis of the untreated and treated hemp fibres was carried out according to GB 5881-86 (National Standard of China for Ramie Chemical Analysis). This gravimetrical method involved the degradation and extraction of wax, water-soluble components, pectin and hemicellulose from the hemp fibres. The wax was extracted in a benzene/ethanol (2:1) solution, water-soluble components in water, pectin in 5 g/l ammonium oxalate solution and hemicellulose in 20 g/l NaOH (sodium hydroxide) solution, consecutively. The loss of dry matter was assumed equal to weight reduction in the sample. Lignin analysis was carried out with sulphuric acid treatment; the residue after wax extraction was treated with 72% sulphuric acid for 24 h, and then boiled in water, washed, filtered and dried. The remaining compound was assumed to be lignin.

3.3. FTIR spectra

Prior to FTIR testing, sample discs were prepared by first mixing 2 mg of dried sample with 150 mg of KBr in an agate mortar and then pressing the resulting mixture successively at 8 tonnes/cm^2 for 5 min. FTIR spectra for the untreated and treated fibres were then recorded between 4000 and 400 cm^{-1}.

Table 1
Description of treatments

Treatment	Description
Raw	Green non-retted hemp fibres separated by hand after harvesting and dried on the shelf
P	Pectinase (100 U) adjusted to a pH of 8 with NaOH at 50 °C for 6 h at shake rate of 50 U/min
L	Laccase (100 U) with mediator HBT (300 μM) adjusted to a pH of 4.5 with acetic acid at 50 °C for 6 h at shake rate of 50 U/min
E	EDTMP.Na5 (5 g/l) adjusted to a pH of 11 with NaOH at 60 °C for 6 h
E2	EDTMP.Na5 (10 g/l) adjusted to a pH of 11 with NaOH at 60 °C for 6 h
E + P	Treatment E, washed, air-dried and then treatment P
E + L	Treatment E, washed, air-dried and then treatment L

3.4. Scanning electron microscopy (SEM)

Prior to SEM evaluation, the sample was coated using plasma sputtering to avoid the sample becoming charged under the electron beam. SEM micrographs of treated and untreated fibre surfaces were then taken using a scanning electron microscope.

3.5. X-ray diffraction

Fibre was cut finely to produce a powder, pressed into a disk and analysed using a Phillips X'Pert-MPD system over a range of 2θ values from 10° to 50° at a scanning speed of 0.03 mm/s.

3.6. Thermal analysis

Untreated and treated fibre samples weighing between 6 and 13 mg were analysed using an Instruments SDT 2910 thermal analyzer operated in a dynamic mode, heating from ambient temperature to 773 K at 10 K/min in air purged at 150 ml/min with an empty pan used as a reference. Differential thermal analysis (DTA) curves and thermal gravimetric analysis (TGA) curves were obtained.

3.7. Single fibre tensile testing

Single fibres were tensile tested in accordance with ASTM D 3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials at a rate of 0.5 mm/min, testing 20 samples at each treatment level. Fibre diameters were measured (average of six readings equally spaced along fibre) using an optical microscope at 200× magnification.

3.8. Composite fabrication

Fibre was guillotined into 10 mm lengths. Fibre, polypropylene and maleated polypropylene (MAPP) coupling agent were dried at 70 °C for 48 h, then compounded at 3 wt.% MAPP and 40 wt.% fibre content using a ThermoPrism TSE-16-TC twin-screw extruder, pelletised, dried at 70 °C for a further 48 h and then injection moulded using a BOY 15-S injection moulder into composite tensile test specimens. Tensile test specimens were conditioned at 20 °C and 50% relative humidity for 48 h prior to tensile testing using an Instron-4204 tensile testing machine with a 5 kN load cell, operated at a rate of 5 mm/min. An Instron 2630-112 extensometer was used to measure the strain with 12 specimens of each composite type.

4. Results and discussion

4.1. Fibre chemical analysis

Table 2 shows the results of chemical analysis carried out on untreated and treated hemp fibres. Treatments with E and E2 were found to reduce the amount of wax, pectin hemicellulose and lignin in the fibre compared to the amounts in the untreated fibre. It was noted that E2 with higher EDTMP concentration removed more pectin than E. The combined EDTMP and enzyme treatments (E + P and E + L) reduced a little more of the non-cellulosic compounds than the EDTMP treatment only (E, E2). Evidence of pectin and lignin removal was also obtained by a change in fibre colour; fibres with E, E2, E + P and E + L treatments were lighter in colour than the untreated fibre (see Table 2).

4.2. Hemp fibre separation

Visual inspection highlighted that the untreated fibre existed in fibre bundles. The enzyme-only treated fibres (P and L) remained