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Improving the performance of hemp hurd/polypropylene composites using pectinase pre-treatments

Xiaoping Li[a,b], Rui Xiao[a,c], Jeffery J. Morrell[b,*], Xiaojian Zhou[a], Guanben Du[a,*]

[a] Yunnan Key Lab. of Wood Adhesives and Glue Products, Southwest Forestry University, Kunming, Yunnan, 650224, PR China
[b] Department of Wood Science and Engineering, Oregon State University, Corvallis, OR, 97331, USA
[c] Forestry Technology Promotion Department of Dashu Town, Chunan, Zhejiang, 311716, PR China

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ABSTRACT

The potential for using pectinase as a pretreatment to improve the properties of hemp hurd for use in a hemp/polypropylene composite was compared with the addition of a silane coupling agent. Pectinase pre-treatment reduced pectin levels in the hemp hurd ($p = 0.0014$) and this reduction was associated with improved tensile strength, modulus of rupture, modulus of elasticity and resistance to water uptake ($p < 0.0001$). Pre-treatment had no consistent effect on thickness swell. Addition of a coupling agent to non-modified hemp/polypropylene panels produced similar improvements to panel properties ($p < 0.0001$) and also markedly reduced thickness swell ($p = 0.01$). The results indicate that pectinase pretreatment can enhance panel strength properties but did not affect moisture behaviour.

1. Introduction

While natural wood products remain the dominant material for many siding and decking applications, wood plastic composites (WPC's) have seen increasing use, especially in North America (Ashori, 2008; Faruk et al., 2012). Wood is an abundant material in this region, but other cellulosic materials may be more readily available elsewhere. One alternative material for enhancing the stiffness and reducing the weight of a plastic composite is hemp (*Canabis sativa* L.). Hemp has long been grown for the bast fibers that are used to produce rope, canvas and a host of other materials; however, these fibers represent a small percentage of the overall biomass. Among the other hemp plant components is the xylem core; also called the hurd or shiv. Hurd has much weaker properties than the bast fibers (Duval et al., 2011; Li et al., 2013), but its low density makes it useful as an absorbent, a filler for bricks, or for insulation (0.24–0.26 g/cm^3) (Tang and Ma, 2010). Hurd may also be useful as a substitute for wood in wood/plastic composites. Hurd contains slightly higher levels of cellulose (~43%) and less lignin (~19–21 percent) than wood (Bag et al., 2011; Tang and Ma, 2010), making it a potentially more effective reinforcing material. The lower lignin levels in hurd also create the potential for using enzymatic pre-treatments to enhance properties of the resulting composite (George et al., 2014, 2015, 2016; Kalia et al., 2013; Li and Pickering, 2008; Mamun and Bledzki, 2013). Pectin is a relatively minor component in hemp (~3.5% mass/mass), but it is primarily located in the region between cells and is critical for retaining cellular cohesion (Palin and Geitmann, 2012). Altering pectin distribution could release individual hurd fibers allowing them to become more evenly distributed in a composite, resulting in a more uniform material with improved physical properties (Saleem et al., 2008). More even distribution might result in more complete encapsulation by the polypropylene that could also reduce water absorption. The effects would be analogous to the function of the coupling agents currently used to enhance fiber/plastic interactions.

The objective of this research was to compare the effects of pectinase pretreatments with those of coupling agents on the properties of a hemp hurd/polypropylene composite.

* Corresponding authors.
E-mail addresses: jeff.Morrell@oregonstate.edu (J.J. Morrell), gongben9@hotmail.com (G. Du).

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Table 1
Effect of water and pectinase pre-treatment on mass loss and cell wall polymer content of hemp hurd.[a]

Treatment	Time (min)	Mass Loss (%)	Component Content (%)				
			Pectin	Klason Lignin	Holocellulose	α-Cellulose	Hemicellulose
None	–	–	1.20 (0.1)	20.9 (0.1)	70.8 (0.1)	42.9 (0.1)	27.9 (0.2)
Water	30	6.04 (0.1)	1.36 (0.1)	21.5 (0.1)	71.1 (0.1)	43.1 (0.1)	28.0 (0.1)
	60	6.85 (0.1)	1.36 (0.1)	21.7(0.2)	71.5 (0.1)	43.4 (0.1)	28.1 (0.3)
	90	7.54 (0.1)	1.36 (0.1)	21.7 (0.1)	71.7 (0.1)	43.5 (0.1)	28.2 (0.1)
	120	7.73 (0.1)	1.36 (0.1)	22.0 (0.1)	71.9 (0.1)	43.6 (0.1)	28.3 (0.1)
Pectinase	30	8.94 (0.1)	1.04 (0.1)	22.3 (0.1)	71.4 (0.1)	43.3 (0.1)	28.1 (0.1)
	60	9.19 (0.4)	0.91 (0.1)	22.5 (0.2)	71.9 (0.1)	43.6 (0.4)	28.3 (0.3)
	90	9.90 (0.1)	0.82 (0.1)	22.8 (0.1)	72.2 (0.1)	43.9 (0.2)	28.4 (0.2)
	120	10.56 (0.1)	0.74 (0.1)	23.6 (0.1)	72.5 (0.1)	44.0 (0.1)	28.5 (0.1)

[a] Values represent means of 3 replicates per treatment while figures in parentheses represent one standard deviation.

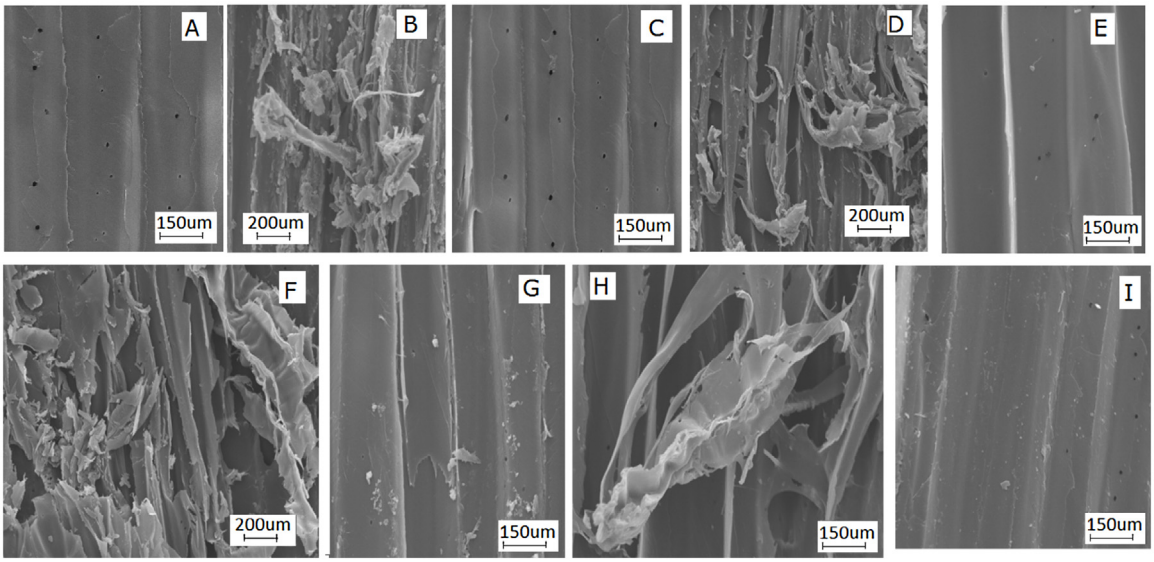

Fig. 1. Effect of pectinase pretreatment for 30, 60 90 or 120 min (B, D, F, H, respectively) on condition of hemp hurd samples compared with an non-exposed control or similar exposures with water alone (A, C, E, G or I, respectively).

2. Materials and methods

2.1. Hemp hurd

Hemp hurd was obtained from commercial sources and steamed at 100 °C for one hour before being disc refined between discs that were 0.5–0.8 mm apart to separate the fibers. The resulting fibers were oven dried at 104 °C then stored in plastic bags until used.

2.2. Polypropylene (PP)

PP pellets with a melting temperature of 165–170 °C, tensile strength of 500 MPa and modulus of elastic of 3850 MPa was purchased locally (Shanxi Tongshenghua Engineering Technology LTD, Xian, People's Republic of China). Although polypropylene was employed, polyethylene would also be suitable for this application.

2.3. Coupling agent

Silane coupling agent KH570 was purchased (Shanghai National Medicine Group Chemical Reagent Co, Shanghai, PRC).

2.4. Pectinase treatment

Pectinase enzyme was isolated from cultures of *Bacillus mojavensis* (Roberts et al., 1999) The resulting enzyme had a molecular weight of 39.3 kDa and optimum pH and temperature for activity of 5–5.5 and 45–50 °C, respectively. The resulting extract had an activity of 26.98 U/ml when tested according to previously described procedures (Albersheim, 1966). The enzyme was stored at 4 °C until needed.

1 kg of refined hurd fibers (1 kg) was weighed and placed into the enzyme solution at a ratio of 1:100 fiber to solution and incubated for 30, 60, 90 or 120 min at 50 °C. The enzyme solution was poured off at the end of a given time period, then the fibers were dried at 104 °C and weighed to determine mass loss associated with enzyme treatment. A comparison set of fibers was incubated at the same temperature and times using only water to delineate between the effects of heating in water with those of the enzyme.

2.5. Effects of pectinase treatment

The effects of pectinase treatment on the hurd fibers was determined by grinding the fibers to pass a 40 mesh screen but not a 60 mesh screen. The resulting powder was used to determine pectin, klason lignin, holocellulose, and alpha cellulose using previously described procedures (ASTM, 1985a,b, 2015b) (Table 1). Hemicellulose content was estimated by taking the difference between holocellulose and alpha cellulose content. Lignin and cellulose components were determined gravimetrically by sulfuric acid digestion. Pectin content was determined by sequential extraction of hemp hurd powder in 2:1 Benzene:ethanol, 1% ammonium