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Increasing inorganic nanoparticle impregnation efficiency by external pressure for natural fibers

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ABSTRACT

The effect of external pressure during the inorganic nanoparticle impregnation (INI) process on the content of impregnated calcium carbonate nanoparticles in kenaf fibers was investigated. The in situ INI process was used to introduce the calcium carbonate nanoparticles into the fibers. The retted kenaf fibers were immersed into calcium chloride solution with various pressures and then treated by sodium carbonate solution to produce calcium carbonate nanoparticles impregnated kenaf fibers. It was found that the calcium carbonate content increased by 76.7% when a 13.8 MPa external pressure was applied during the calcium chloride immersing process. The impregnation efficiency for reducing the fiber porosity was increased by 70.1%. The mechanical properties, including modulus of elasticity, modulus of rupture and tensile strength of the INI-treated fiber/polyester composites were enhanced by 43%, 79% and 86% compared with the un-treated fiber/polyester composites.

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1. Introduction

Lignocellulosic fibers are widely used in textile, pulp and paper, fiber-reinforced composites, etc. Kenaf (*Hibiscus cannabinus* L.) and allied fibers are abundant natural fibers with an estimated production of 288,000 tons/year averaged over 2007–2012 in the report of Food and Agriculture Organization of the United Nations (FAO) (Anon, 2013). Kenaf fibers and their polymer composites are known to have excellent mechanical properties and be similar to glass fiber (Akil et al., 2011; Roger et al., 1999). Dr. Tahir's team carried out a comprehensive approach regarding the characterization of nanofibers from kenaf, such as, the characteristics of nanofibers extracted from kenaf core (Joonobi et al., 2010), the physico-chemical characterization of pulp and nanofibers from kenaf stem (Jonoobi et al., 2011), the isolation/characterization of cellulose whiskers from kenaf bast fibers (Zaini et al., 2013), the effect of fiber extraction methods on some properties of kenaf bast fiber (Amel et al., 2013) and an investigation of the kenaf bast cellulosic fibers hierarchy from micro to nano sizes (Karimi et al., 2014).

Natural fiber reinforced polymers may have some concerns, e.g., matrix-fiber interfacial adhesion, fiber dispersion, and porosity of the fibers (Bledzki et al., 2005). Different types of surface treatment procedures have been suggested to enhance the interaction between natural fibers and matrix. As a promising surface treatment method, calcium carbonate nanoparticles probably could be used to address these concerns (Shi et al., 2011b). It can be employed as an adhesive between the kenaf fibers and polymer matrix, as well as the fillers for the voids of the fibers. In the previous studies, the mechanical properties of both kenaf fibers and kenaf fiber/polymer composites were increased by impregnating calcium carbonate nanoparticles into kenaf fibers (Liang et al., 2014).

The inorganic nanoparticle impregnation (INI) is an effective method to improve the compatibility between natural fibers and polymer matrices (Shi et al., 2011b). The tensile strength of the kenaf fibers was increased by more than 20% after the INI treatments. The INI treatments improved the compatibility between kenaf fibers and polypropylene matrix, resulting in the increased tensile modulus and strength of the composites reinforced with INI-treated fibers. Cheng et al. (2014b) also reported that the compatibility between bamboo fibers and polypropylene matrix materials was increased by the $CaCO_3$ treatment of the filled bamboo fibers. The tensile strength and modulus of composites reinforced with treated fibers increased by 14.58 and 19.66%, respectively. In their later work (Cheng et al., 2014a), $CaCO_3$ particles were successfully deposited in situ to bamboo fibers by means of ionic reaction of Na_2CO_3 and $CaCl_2$ aqueous solution at various temperatures. The crystallinity of inorganic materials was significantly affected by the reagent's concentration. A 10.4% increase

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in tensile strength and a 16.7% increase in tensile modulus were observed after fiber treatment with $CaCO_3$ at a concentration of 0.2 mol L^{-1}. As the loading of $CaCO_3$ increased, an increased trend of the panel tensile strength and modulus was also observed. However, the pressures applied for increasing the $CaCO_3$ loading efficiency were caused by the internal pressures that were produced due to the heating temperatures.

There is a limit for the loading amount of $CaCO_3$ because the nanoparticles need to penetrate into the cell walls of the fibers. Thus, the pressure in the reactor plays an important role in the INI process. In the previous studies, the treatment pressures were created by the heating temperature because no external pressure was introduced to the reactor, which limited the use of high pressures and high $CaCO_3$ loading amount (Cheng et al., 2014a). For instance, the saturated water vapor pressure is only 0.60 MPa at 160 °C (Shi et al., 2011a,b), which may not be high enough to have a sufficient impregnation pressure for the nanoparticles. For these reasons, external pressures are expected to be introduced for improving the loading efficiency.

Historically, pressure treating is the most effective method of applying preservatives to wood for protection (Loferski, 2001). In this process, the wood is placed in a treating cylinder, flooded with preservative, and subjected to extremely high pressure to force the chemical deep into the cell walls of the wood. The amount of chemicals retained by the wood determines the preservation results and is regulated by the manufacturer's treating schedule (i.e., pressure, and time). As a successful method used in the wood protection practice, the external pressures would be introduced in the nanoparticle loading for natural fibers.

In this study, it was aimed at applying external pressure during the impregnation process in order to improve the performance of nanoparticle loading and the distribution. The effect of the applied pressures in the primary salt immersing process on the final loaded calcium carbonate contents would be explored.

2. Materials and methods

Kenaf bast fibers were obtained from the Kengro Corporation (MS, USA). The fibers were chopped into approximately 50.8 mm in length. Sodium hydroxide (NaOH) solution (5%, w/v) was prepared using NaOH beads (≥97%, Acros Organics) and distilled water from Millipore Milli-Q Integral Water Purification System. The 0.1 mol/L calcium chloride ($CaCl_2$, ≥96%, Fisher Scientific) and sodium carbonate (Na_2CO_3, ≥99.5%, Fisher Scientific) solutions were prepared. The unsaturated polyester AROPOL Q 6585 (30% styrene, Ashland Chemicals) and *tert*-butyl peroxybenzoate (*t*-BP, 98%, Acros Organics) were used to fabricate the fiber/polymer composites.

2.1. $CaCO_3$ loading through INI processes

(1) A mixture of 120 g kenaf bast fibers (9.11% moisture content measured by Mettler–Toledo HB43-S Moisture Analyzer) and 1.8 L NaOH solution were added into a hermetical reactor (Parr Instrument Co., 251 M). This alkali retting process was carried out at 160 °C for 1 h with the mechanical stirring. The saturated vapor pressure remained at 0.60 MPa in the hermetical reactor. After cooling, the retted fibers were washed using running water and then dried. The fiber yield was measured as 38.5 ± 1.0%.

(2) The retted fibers and 1.8 L $CaCl_2$ solution were added into the hermetical reactor. The reactor was then heated to 100 °C and maintained for 0.5 h. During the process, nitrogen gas was injected into the reactor through a high-pressure cylinder to obtain pressures of 0.69 MPa (100 psi), 3.45 MPa (500 psi), 6.89 MPa (1000 psi) and 13.8 MPa (2000 psi). The saturated vapor pressure was 0.10 MPa without external pressure applied. After cooling, the excessive ionic solution was removed from kenaf fibers first by gravity, and then by hand-squeezing.

(3) The retted fibers obtained from step 2 were mixed into the 1.8 L Na_2CO_3 solution in the hermetical reactor. After the reaction at 100 °C for 0.5 h, the mixture was cooled down to a room temperature, filtered, washed with running water, and then dried.

Table 1
The effect of immersing pressures on the $CaCO_3$ loading.

Sample #	Immersing pressure (MPa)	$CaCO_3$ content (%)	Increase (%)
1	0.10	2.18	–
2	0.69	2.41	10.4
3	3.45	2.56	17.5
4	6.89	3.59	64.9
5	13.8	3.85	76.7

2.2. $CaCO_3$ content determination

The $CaCO_3$ contents were calculated based on the difference in ash contents between the retted kenaf fibers and $CaCO_3$ impregnated kenaf fibers. The ash contents were determined by burning the samples in a muffle furnace first at 400 °C for 30 min, and then at 850 °C for 45 min (Shi et al., 2011b).

2.3. Porosity determination

Mercury porosimetry is a traditional technique to determine the porosity of samples. A Micromeritics AutoPore IV 9500 was employed for the porosity measurements of the fibers in this study. The procedure for the measurement of the porosity was described as follows: the samples were dried overnight at 105 °C before the measurements. The penetrometer for powdered samples was used, which had 3 cm^3 capacity and 0.412 cm^3 steam volume.

2.4. Microtopography analysis

A Quanta 200 environmental scanning electron microscope (SEM) with an accelerating voltage of 20 kV and a magnification of 500× and 1000× was used to observe the fiber surfaces. The size distributions of $CaCO_3$ particles on the fiber surfaces were examined using the software Digimizer with a counting of 300 for each sample.

Table 2
Mercury intrusion porosimetry results of fibers.

Sample	Mercury intrusion porosity		Average pore diameter	
	Mean (SD[1]) (%)	Decrease (%)	Mean (SD) (μm)	Decrease (%)
Un-treated fiber	22.3 (2.2)	–	10.0 (0.8)	–
INI (2.18%) treated fiber	17.8 (1.8)	20.1	5.2 (0.5)	48.0
INI (3.85%) treated fiber	8.8 (0.8)	60.4	5.1 (0.4)	48.6

Note: [1]SD: standard deviation.