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Pulp fiber-reinforced thermoset polymer composites: Effects of the pulp fibers and polymer

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ABSTRACT

In this study, composites were fabricated with four types of pulp fibers and two types of thermoset polymers. Four pulp fibers included hardwood and softwood high-yield pulp (HYP), Kraft pulp, and Whatman cellulose fibers and two polymers included unsaturated polyester (UPE) and vinyl ester (VE). FTIR and TGA results showed the chemical differences among the four pulp fibers and confirmed the existence of lignin on the HYP pulp fibers. The two HYP fibers were more compatible to the UPE resin, while the Kraft and Whatman cellulose fibers were more compatible to the VE resin as indicated by the tensile properties. Lignin on the two HYP fibers acted as a natural coupling agent for the natural fiber and the more hydrophobic UPE resin. The two cellulose-rich pulp fibers performed better when the VE resin was used. Composite storage moduli were significantly improved as compared with those of the neat UPE and VE resins. Only a slight increase in glass transition temperature was noted for the composites.

1. Introduction

Driven by increasing environmental awareness, natural fiber has been emerging as a desirable reinforcement for fiber-reinforced composites. Among various types of the natural fibers, wood pulp fibers have been studied as reinforcement for thermoset polymers since the 1940s [1,2]. In recent years, pulp fibers are still being used as a prevailing reinforcement material as it offers the possibility for fabricating green composites [3–7]. There are different types of pulp fibers depending on the process for obtaining the fibers from wood. Kraft pulp is one of the most commonly used pulp fibers in the pulp and paper industry. It is converted from wood into pulp fiber by a sulfate pulping process. As a result, Kraft fiber consists of almost pure cellulose as most of the lignin has been removed during the pulping process. The Kraft pulp yield is normally within 45–65% [8]. The high-yield pulp (HYP) is produced by a chemithermomechanical pulping process, through which lignin is only partially removed. This process gives a high yield of fibers from the wood (with 91–95% in yield for softwoods, 88–95% in yield for hardwoods) [9]. Residual lignin content is one of the major differences between the two pulps.

In recent years, studies have shown that lignin acted more than as fillers in natural fiber-reinforced polymer composites. It was found to react with the resin and improve fiber–matrix interfacial bonding. Paauw and Pizzi [10] investigated the effect of five types of fillers on the degree of cross-linking of the UPE resin. As measured by the differential scanning calorimeter (DSC), the neat polyester resin only showed one exothermic peak at 115 °C. Two additional peaks were observed at 56 °C and 70 °C if two percent by weight (wt%) of lignin was added. Lignin co-reacted with the UPE resin. Thielemans et al. [11] treated hemp fibers with lignin. Composites were made using the lignin-treated hemp fibers and a commercial vinyl ester (VE) resin. The composite tensile and flexural properties were improved if a low amount of lignin was added on the hemp fiber surface (0.2 wt% of the composite). Addition of a higher amount of lignin (6.3 wt% of the composite) on the hemp fiber surface resulted in a decrease in the mechanical properties. Mwaikambo and Ansell [12] fabricated hemp fiber-reinforced cashew nut shell liquid/formaldehyde resin composites. The interface was more coherent for the untreated than the alkali treated fibers. They proposed that the presence of lignin in untreated hemp fibers offered additional cross-linking sites and the untreated fiber surface was more compatible with cashew nut shell liquid resin than the alkali treated fiber surface. Thielemans and Wool [13] found that butyrated Kraft lignin improved the interface between the natural fibers and a thermoset acrylated and expoxidized soybean oil resin. An increase of 40% in flexural strength for short wheat straw fiber-reinforced soybean oil composites was observed if a 5 wt% butyrated lignin was added.

Above-mentioned studies suggested that lignin on the natural fiber surface would play an important role on the natural fiber-reinforced polymer composite interface. There were a few studies focused on the contributions of different pulps to the mechanical

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properties of thermoset polymer composites. Zadorecki and Flodin [14] made composites with UPE and three pulps fibers: filter paper, thermomechanical pulp, and bleached Kraft sulfate pulp. The composite tensile moduli and strengths were nearly linearly in proportional to the fiber volume fractions. The pulp variety seemed to have no effect on the tensile properties. A later publication by Zadorecki and coworkers [15] proposed an indirect method to back-calculate cellulose fiber's Young's modulus from the composite's modulus using the Halpin–Tsai and Tsai–Pagano equations and Young's moduli of the four pulp fibers from different pulping processes were determined. The deviation in composite's tensile moduli was ascribed to the fiber's Young's modulus itself rather than to the fiber–matrix interfacial bonding. Neagu et al. [16] expanded the research to a large variety of pulp fibers and evaluated the effects of hornification, prehydrolysis, and sulfite processing on the fiber's Young's modulus. They estimated the contribution of a variety of pulp fibers to the elastic properties of the composites with an epoxy VE matrix. An optimal kappa number, which is an indirect indication of the residual lignin contents, was obtained to be 30–50. They claimed that, instead of affecting the fiber–matrix interfacial bonding, the lignin affected the fiber's Young's moduli and the fiber's Young's moduli in turn influenced the composite's Young's modulus.

There were no studies investigated the interactions between different pulp fibers and two widely-used thermoset resins (UPE and VE) and their impact on the composites' mechanical properties. As reinforcing materials, pulp fibers vary in mechanical properties and they may also have different interfacial bonding strengths with these two resins. So, these pulps may contribute diversely to composites' mechanical properties. Besides, pulp prices vary significantly and the selection of the pulp fibers may have to consider cost. Therefore, it is necessary to study the effect of the pulp fibers and polymers and their potential interactions on the resultant composite properties. If the residue lignin on the fiber promotes fiber–polymer interfacial bonding, low-cost HYP fibers would perform better as reinforcement. The objectives of this paper are to fabricate composites with four types of pulp fibers (two lignin-containing HYP fibers and two cellulose-rich fibers) and two commercial polymer matrices using the newly-developed optimum process [17] and to investigate how the difference in pulp and resin variety interacts to influence the composite performance.

2. Materials and methods

2.1. Materials

Hardwood HYP (HW), softwood HYP (SW), and commercial bleached Kraft softwood pulp fibers (Kraft) were supplied by Tembec (Montréal, QC). Whatman (WM) cellulose pulp was purchased from Cole-Parmer Canada Inc. (Montréal, QC).

The UPE (#77) and VE (#1110) resins, purchased from Fibre Glast Development Corp (Brookville, OH), were used as matrices. The viscosities of UPE and VE resins are 475 and 275 cP, respectively. Both polymers contain 40–50 wt% of styrene as a diluent and are pre-promoted with cobalt naphthenate. Methyl ethyl ketone peroxide (MEKP) was used as a hardener.

2.2. FTIR and TGA

Fourier Transfer Infrared Spectroscopy (FTIR) absorption spectra of these four pulp fibers were recorded on a FTIR TENSOR 27 spectrometer with a FTIR attachment (Bruker Optics) over a spectral range of 4000–400 cm^{-1}. Thermal stability of the four fibers was measured with a TGA-Q500 thermal gravimetric analyzer (TGA) (TA instruments). Four samples (20–30 mg) were heated from the ambient temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen purging gas (40 mL/min).

2.3. Composite fabrication

The composites were fabricated as previously described [17]. HW, SW, and Kraft pulp fibers were preformatted into sheets at a nominal grammage of 120 g/m^2. The dry fiber weight per unit composite area was 360 g/m^2. The WM fibers were used in the sheet form as received and the dry fiber weight per unit composite area was 420 g/m^2. The resins were prepared using 100 parts of resin and one part (for UPE) or 1.25 parts (for VE) of MEKP by weight. These sheets were dried to moisture-free and were impregnated with the resin to be assembled into prepregs immediately after they were removed from the oven. The prepregs were pressed in a Carver standard hydraulic bench press at the room temperature under a pressure of 2 MPa for 24 h followed by postcuring at 60 °C for 1 h.

2.4. Composite tensile property testing

Composite – Six Type 1 tensile specimens from each of eight samples were tested on an Instron 3367 (Instron Corporation) universal testing machine in accordance with ASTM Standard D638-10. Tensile strains were recorded with an Instron 2630 extensometer.

2.5. Fiber morphology and composite fracture surface

The morphology of four pulp fibers before processing and the fracture surfaces of eight selected tensile specimens were examined by scanning electron microscopy (SEM). Specimens were mounted on aluminum stubs and were coated with gold in a sputter coater (Quorum SC7620) for 60 s before examination. SEM images of the specimens were collected on A JEOL (JSM-6610LV) SEM.

2.6. Dynamic mechanical properties

Dynamic mechanical properties of the composites were measured on a DMA Q800 model dynamical mechanical analyzer (TA Instruments). Samples were cut into small strips (5 × 15 mm). Measurements were performed at a constant frequency of 1 Hz, and strain amplitude of 0.1%. The temperature scanning range was set from room temperature to 150 °C at a heating rate of 2 °C/min. The samples were tested twice under the same conditions and the data collect in the second run were recorded to assure the resin was fully cured.

3. Results and discussion

3.1. Fiber morphology

Differing from some prevailing natural fibers, pulp fibers have less lignin content as some amount of the lignin is removed during the pulping process. In the Kraft process, the lignin, which binds the cellulose fibers together, is broken down by heat and chemicals. HYP fibers are produced by a chemithermomechanical pulping process, in which wood chips are pretreated chemically and followed by refining similar to a mechanical pulping. Therefore, there are more mechanical damages on the HYP fibers than on the Kraft fibers.

Morphological features of the four pulp fibers are shown in Fig. 1. Different morphological structures were observed for these