WOOD-PLASTIC COMPOSITES USING THERMOMECHANICAL PULP MADE FROM OXALIC ACID-PRETREATED RED PINE CHIPS

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Abstract

The characteristics and properties of wood fiber is one of many factors of critical importance to the performance of wood-plastic composites. In commercial thermo-mechanical pulping (TMP) of wood chips to produce fibers, high temperatures (≥100°C) are used to separate the fibers during TMP refining. These mechanical pressures and temperatures are usually modulated to achieve the desired fiber characteristics and properties. However, relatively high total electric energy is required to produce these TMP pulps. Recently, an oxalic-acid pretreatment of wood chips prior to TMP refining has been developed. Previous, experiments have found that the energy required in refining after such pretreatment can be dramatically reduced. In addition, other work with medium-density fiberboard made using TMP fiber from oxalic acid-pretreated chips was shown to have enhanced moisture resistance when compared to fiberboard made with non-treated fiber. In the experiments reported in this paper, wood chips were first pre-treated using either oxalic acid- or dialkyl ester oxalic acid-derivatives, then refined into fiber using traditional TMP refining processes. These variously treated fiber groupings were then compounded with high-density polyethylene and injected molded into flexural test specimens (ASTM D790). Wood-plastic composites made using fibers from these oxalic acid- and diethyloxalate-pretreatments were shown to produce wood-plastic composites with similar mechanical performance to that of composites made using untreated control fibers. With further work, oxalic acid- and diethyloxalate-pretreatments may result in a modified wood fiber that has potential to enhance physical properties such as dimensional stability, has virtually no effect on mechanical performance, but greatly diminishes the energy required to refine pine chips into fiber.

Introduction

The typical process for making thermomechanical wood fiber involves three steps. First the wood is passed through a chipper to produce wood chips. Then the chips are soaked using a hot-water cook of heat and soften, rather than remove, the lignin from the chips. Finally, the softened chips are refined into fiber using a pressurized steam refiner. This process is effective, but it requires significant inputs of energy for heat and steam. Recent work has developed a pretreatment process to improve the energy efficiency of thermomechanical refining that involves soaking the chips in an mild oxalic-acid (OA) or diethyloxalate (DEO) solution instead of the hot-water extraction prior to pressurized refining (Kenealy et al 2007a). This soaking is done in a separate batch-type vessel just prior to introducing the pre-treated chips into the pressurized refiner. In this study we used a 300-liter or 50 kilogram (dry weight basis) laboratory-capacity digester to pre-treat red pine (*Pinus resinosa*) with the OA or DEO solutions (Figure 1). This larger batch-type digester was used to produce enough fermentable extraction liquid and treated wood chips prior to processing into thermomechanical pulp (TMP) using a 300-mm pressurized refiner (Figure 2).

Our objectives were to identify if the pretreatment process detracted or enhanced the performance properties of wood-polyethylene composites made using this energy-efficient fiber processing method.

Materials and Methods

Red pine logs were obtained from a paper mill in northern Wisconsin. The logs were frozen. Nine days later they were thawed, cut, pealed and chipped. Solids content of chips was 42% (wet-weight basis). The chips were then bagged and frozen.

The wood chips were then thawed and pretreated by one of four methods, the direct oxalic acid pretreatment method, the indirect DEO pretreatment method, the pretreatment control which used the same thermal/pressure conditions as the DEO pretreatment (but no chemicals were used), or the traditional autohydrolysis method of hot-water-cooking currently used in commercial practice in North

America. The first two methods, using oxalic acid and DEO, have been reported to result in similar fiber characteristics and energy savings at the refiner when compared to the commercial autohydrolysis method (Kenealy et al 2007a). However, the first two methods differ in the manner in which the oxalic acid chemistry is ultimately delivered to the wood chips for the pretreatment reaction. In all cases, the wood chips were added to a 300-liter or 50 kilogram (dry weight basis) capacity digester and atmospherically steamed for approximately 10 minutes. This process prepares the wood chips for chemical loading by removing the air from the wood chips and from the surrounding interior reaction chamber. The third method represents a control to evaluate the effects of the OA- and DEO-pretreatment process without the addition of the OA- or DEO-chemicals. The fourth autohydrolysis method represents a control with a common commercial method used to produce TMP fiber.

For the direct oxalic acid pretreatment method, 50 kg (dry weight basis) of wood chips were then impregnated with a dilute solution of oxalic acid liquor at 70°C from the bottom to the top of digester with a vacuum assist. The excess oxalic acid was drained after impregnation and the chips were then subjected to direct steam injection to pressurize the reaction vessel to quickly achieve 130°C and held at that temperature for 10 minutes.

For the indirect or DEO pretreatment delivery method, the wood chips, after the 10-minute pre-steam, were brought up to pressure with direct steam injection to about 240 MPa or 140°C. At this temperature and pressure, a solution of 500 milliliters of DEO was introduced by an injector pipe attached to the top of the digester and forced into the digester using nitrogen gas pressure. Wood chips were held at that temperature for 30 minutes for the reaction to go to completion. The DEO delivery method is unique in the fact that it is delivered via liquid and due to the vapor pressure in the reaction chamber will gasify once entering the digester. Once in this gaseous form, the chemical will then locate water molecules within the wood chips where oxalic acid is produced in situ.

For the controls, the wood chips experienced the same 140°C heating conditions for 30 minutes as the DEO pretreatment, but no chemicals were added to the hot water. These wood chips will serve as the positive controls for the three pretreatments.

For the autohydrolysis or hot water pretreatment method, which represents the traditional commercial process, we used hot water cooking only at 170°C for 60 minutes at a ratio of 4 parts water and 1-part wood chips.

After the oxalic acid and DEO pretreatments, the pressure was relieved and the wood chips were flooded with 90°C hot water, which was circulated for 1 hour to rinse the wood chips of hemicellulosic sugars. After the hot water pretreatment, the pressure was relieved and the wood chips were removed after the collection of the hemicellulosic sugars, which consisted of simply collecting the cooking water after the pretreatment. For both the oxalic acid and DEO pretreatments, the hemicellulose extracts were removed at an approximate solids content of 1% and approximately 10% solids content for the hot water pretreatment. The extracts for all pretreatments were then separately concentrated to a fermentable solids content for subsequent conversion to biofuels (i.e., ethanol) or other biochemical feedstocks (Kenealy et al 2007b).

The wood chips were then collected and processed through the thermomechanical refiner to produce wood fiber of the type commonly used for medium-density fiberboard (ANSI A208.2 2002). The TMP refiner was a Sprout-Bauer, model #1210P, using 300-mm diameter plates, a D2B505 plate pattern, and refiner gap settings of 0.075-0.125 mm. Energy consumption was measured using an Ohio Semitronic Model WH 30-11195 integrating wattmeter attached to the power supply side of the 44.8 kW electric motor. During TMP, the wood chips were placed into the presteaming tube and pressurized with steam to 690 MPa for 10 minutes prior to defibration. The refining feed rate was approximately 1 kilogram per minute on the dry weight basis. The wood chips were refined at a consistency of approximately 32% solids. Energy was calculated for each control and treatment sample. Once the wood chips passed through the refining zone, the resulting fibers were released immediately into atmospheric conditions via cyclone and collected. These fibers were later dried and used in both MDF and composite board preparations.

Commercially available wood flour is the most common filler for wood-plastic composites (WPC). Laboratory WPC were manufactured using mixed western pines (*Pinus* spp.) wood flour (AWF 4020, 40 mesh) supplied by *American Wood Fibers* (Schofield, WI, USA). Wood flour filled WPC were compared with WPC containing untreated and treated TMP fiber, manufactured as described above. The wood flour and various types of TMP wood fiber were oven-dried at 105 °C for 24 hours. Wood flour and various types of TMP wood fiber were individually compounded at 30% by weight with purchased high-density polyethylene (HDPE) (*ExxonMobil* HD 6733, 33mfi, 0.950 g/cm^3, Houston, TX) in a 1-L high-intensity thermokinetic mixer (K-Mixer, *Synergistics, Inc,* St. Remi de Napierville, Quebec) in 120 g batch sizes. The thermokinetic mixer was run at 5000 rpm. An IR sensor monitored temperature, and the discharge temperature was set at 196°C. The discharged, molten composite was pressed into a patty and allowed to cool at room temperature. The wood-plastic mixture was then granulated using a *Ball and Jewell* granulator outfitted with a 7.9 mm screen (*Sterlin*g, North Uxbridge, MA).

Granulates were again oven-dried dried before being injection molded. Composites were injection molded into flexural samples using a 33-ton *Cincinnati Milacron* (Batavia, OH) injection molder. The mold temperatures ranged from 179°C at the feed throat to187°C at the nozzle. The American Society for Testing and Materials (ASTM) mold cavity used for the flexural samples was 127 × 3.2 × 12.7 mm (ASTM 2004).

Flexural tests of WPC specimens were carried out according to ASTM D790 (ASTM 2004) on an *Instron* Universal Testing machine. The three point loading system was utilized with a crosshead speed of 1.3 mm/min. Five replicate specimens were tested for each formulation. Maximum strength and tangent modulus of elasticity (MOE) were calculated according to the standard.

Results and Discussion

It is common behavior for stiffness of polymeric materials to increase (i.e. increase in MOE) when a filler is added (Osswald and Menges 1995). In WPC, stiffness generally increases with increasing wood content. To a lesser degree, stiffness also increases with increasing aspect ratio (length/diameter ratio) of the wood particle (Stark and Rowlands 2003). The effect of aspect ratio on MOE is more pronounced as the wood content of the WPC increases. Wood flour produced using a similar mesh screen tends to have a lower aspect than wood fiber passing through that same screen (Figure 3). However, to gain this advantage in MOE related to the aspect ratio of the filler, it is also critically important to obtain uniform and ordered bonding along the filler-matrix boundary.

The mechanical test results for MOE and MOR are shown in Figures 4 and 5, respectively. In these two figures, each bar represents the mean of that data set and the error bars at the top of the bars represent one standard deviation. To determine significant differences between the fiber treatments, Student’s two-tailed *t*-tests, assuming unequal variance, were carried out at $\alpha = 0.05$. Superscript letters were used to denote significance. If the letters are the same, the hypothesis that the means were the same was accepted. In other words the two means are not significantly different. The converse is that if the letters are different, the means are significantly different.

As expected, adding either wood flour or TMP wood fiber significantly increased the MOE of the composite compared with unfilled HDPE (Figure 4). The largest MOE was observed for WPC containing untreated TMP wood fiber. Because wood flour is the most common filler for WPC in the building products industry, it is useful to compare performance between wood flour and TMP wood fiber. The MOE of WPC containing untreated TMP wood fiber was 7% higher than the MOE of WPC containing wood flour. The TMP wood fiber has a larger aspect ratio than wood flour. WPC containing variously pretreated TMP wood fiber experienced an MOE of 3-8% less than WPC containing wood flour. The reason for these significant decreases when these pretreatments are used is not yet entirely understood, but it could be a result of physical changes such as fiber length degradation, or chemical changes resulting from the extraction of hemicelluloses that might make the pretreated wood fiber and HDPE less compatible, or some combination of the two.

The strength of polymeric materials is enhanced when stress transfer occurs between the polymeric matrix and the filler. As the aspect ratio of the filler increases, the stress transfer increases until the critical fiber length is reached (Osswald and Menges 1995). This effect has been demonstrated for WPC. Comparison between polypropylene based WPC containing either wood flour or refined wood fiber demonstrated that increased WPC strength was a result of the larger aspect ratio of wood fiber compared with wood flour (Stark and Rowlands 2003).

Adding either wood flour or untreated TMP wood fiber to HDPE significantly increased the strength compared with the unfilled HDPE (Figure 5). This suggests that stress was effectively transferred from the HDPE to the wood component. Compared with WPC containing wood flour, the strength of WPC containing untreated TMP wood fiber significantly increased 21%. We believe that this effect was primarily due to the geometry (i.e., high aspect ratio) of the red pine wood fiber. A significant loss in WPC strength occurred when the TMP wood fiber underwent subsequent pretreatment, but the strength of WPC with variously pretreated TMP wood fiber was significantly higher by 2-11% than the strength of the WPC containing wood flour.

The four types of red pine fiber were analyzed for carbohydrate and Klason lignin content using the methods of Davis (1998) and Effland (1977), respectively. Recall that the primary objective of commercial hot-water autohydrolysis is to soften wood chips for refining and that additional critical objectives of the various DEO or OA pretreatments are to decrease energy consumption in TMP refining and to reclaim carbohydrate extracts for subsequent processing into biofuel or bio-based chemicals. Thus, as expected the results clearly indicate that 140°C red pine control pretreatment of the wood chips tended to result in higher carbohydrate contents and lower Klason lignin contents when compared to the other three pretreatments (Table 1). Again, as expected, the more thermally severe 170°C autohydrolysis pretreatment had the greatest effect on minimizing carbohydrate content. The DEO and OA pretreatments, performed at 140°C and 130°C respectively, were generally intermediate in their effects. Decreased hemicellulose contents and increased lignin contents in fiber could suggest improved moisture resistance in wood fiber and wood-based fiberboard made using such (Winandy and Krzysik 2007). These changes in fiber and surface chemistries might also alter wood-to-plastic bonding, though this idea needs further study.

Table 1: Chemical analysis of red pine fiber after refining and before being processed into fiberboard.

Material	**Klason lignin (%)**	**Arabinan (%)**	**Galactan (%)**	**Glucan (%)**	**Xylan (%)**	**Mannan (%)**
Red pine Control (140°C)	29.5	1.03	1.74	41.07	6.37	10.80
Red pine Autohydrolysis (170°C)	33.0	0.17	1.01	45.98	5.03	7.56
DEO (140°C)	32.3	0.49	1.22	43.71	5.39	8.50
Oxalic Acid (130°C)	31.7	0.33	1.19	43.63	5.47	8.65

Summary and Conclusions

As alternative treatments are sought to reduce the energy requirements of manufacturing TMP wood fiber, care must be taken to ensure that the treatments do not adversely affect the properties of products made with these wood fibers. In the best-case scenario, the treatments will change the characteristics of the wood fibers in such a way as to enhance the properties of resulting products.

In this paper, the mechanical properties of HDPE-based wood-plastic composites containing pine wood flour were compared with WPC containing both untreated and treated red pine TMP fiber. Both flexural MOE and strength of WPC increased when red pine TMP fiber was used compared with pine wood flour. Each treatment of the red pine TMP fiber slightly decreased the mechanical performance. However, the MOE and strength properties of WPC containing TMP fiber were similar to the MOE and strength properties of WPC containing wood flour.

Further work to fully evaluate fiber surface chemistries and physical properties needs to be completed to fully understand how treatments affect the TMP fibers, and the mechanisms behind the loss in mechanical properties. In addition, there may be other properties, such as moisture absorption, for which treatment increases WPC performance. The work here suggests that WPC are a promising outlet for treated TMP fibers.

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Figure 1: The 300-liter or 50 kilogram (dry weight basis) laboratory-capacity digester used to pre-treat red pine (*Pinus resinosa*) with the OA and DEO solutions or with a hot-water (control) cook prior to pressurized steam refining.

Figure 2: The pressurized 300-mm thermomechanical refiner used in this study to make wood fiber

Figure 3: Comparison of commercial 40-mesh mixed pine wood flour (left) and processed and refined pine fiber passed through a 40-mesh screen (right).

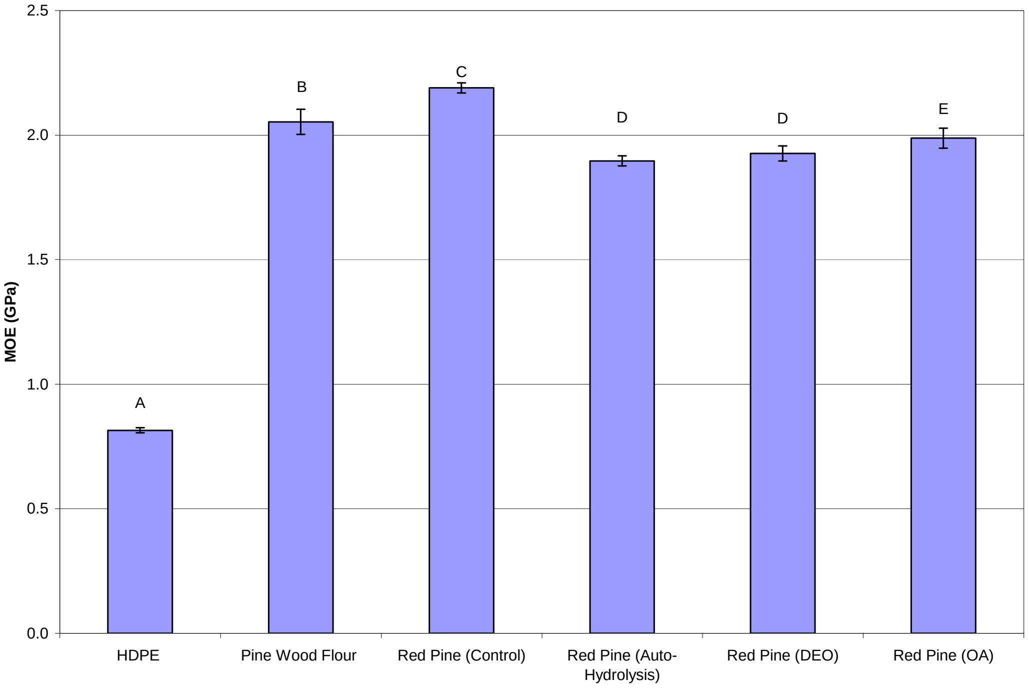

Figure 4: Influence on tangent Modulus of Elasticity of wood-plastic composites made from wood fiber obtained after various organic acid pretreatments of wood chips prior to thermomechanical refining to fiber.

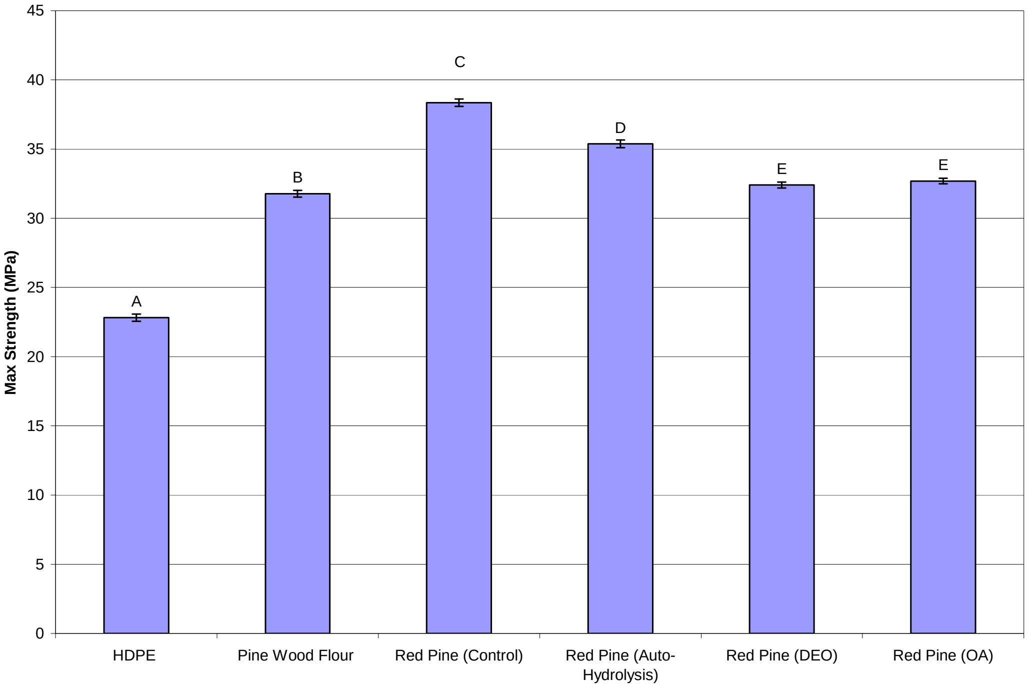

Figure 5: Influence on flexural strength of wood-plastic composites made from wood fiber obtained after various organic acid pretreatments of wood chips prior to thermomechanical refining to fiber.

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