FIBER-REINFORCED POLYPROPYLENE COMPOSITES FROM SMALL-DIAMETER SOUTHERN PINE TREES BY WET PROCESS
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Abstract: Wood-plastic composites are being expanded rapidly in these years. To take advantage of the unique characteristics of the wood fiber by combining them with plastic in conventional panel pressing methods, a new wet process was developed to make fiber-reinforced plastic composites using PP and steam-exploded flour from small-diameter loblolly pine. Wet-laid wood fiber/polymer composites were fabricated using a standard TAPPI handsheet method followed by compression molding to consolidate the mixed mats into panels. MAPW was used as a coupling agent to enhance the strength of PP composites. DMA and DSC measurement led some insights into the structure of composites and SEM was used to observe the interfacial adhesion. The variables that may affect the product properties were investigated as well, which include mat layer number, wood fiber content, MAPP content, fiber dimension, and molding temperature.

Keywords: pine, small-diameter, steam-exploded, composite, PP, plastic

1. INTRODUCTION

Wood plastic composites (WPC) are utilized worldwide, particularly in North America as durable outdoor materials and automotive interior substrates (English and Fahl, 1995). Extrusion and injection molding are the typical methods to manufacture WPC using wood flour/small particles or fibers and polymers (Kiltough, 1995). Many factors of materials used for WPC may affect the end-product properties. First, moisture content is one of the most important factors. Second, wood is sensitive to temperature change. At higher temperature wood can become volatile and partly burn. Third, wood can affect the product properties as the bulk density material. The flexural strength of extruded WPC was increased by different wood flour species. The flexural MOE was increased in a linear relationship with the increasing of wood flour content. The maximum flexural strength was occurred in the range of 30 to 40% percent filler for different wood species (Berger and Stark, 1997). The flexural and tensile modulus and strength were increased with increasing wood particle size (Stark and Berger, 1997). Maleic anhydride polypropylene (MAPW) is a graft copolymer widely used as modifier to improve the properties of lignocellulose-filled polypropylenes. The maleic anhydride content can graft to each polymeric polypropylene chain and increased the strength of WPC (Snijder and Bos, 1999). MAPW dramatically altered the crystal structure around the wood fiber (Yin et al., 1999).

Typically, the wood flour/fibers are from wood wastes or prepared by cutting or chipping wood from logs, chips, and dried before extruded or injection molded. Steam explosion (SF) treatment is an effective method to produce wood flour/fibers. After pressuring and penetrating saturated steam into wood chips or fiber bundle, they are split by the explosive expansion to a mixture of wood elements of different sizes, which includes small and big particles, single fibers, and fiber fragments. The nonfibrous byproducts are dissolved and remove from this process. Single fibers have higher specific surface than fiber bundles (Kohler and Kessler, 1999). The steam-exploded wood flour can increase the fracture strength and water resistance of the polymer

The MOE of SE wood flour and PP composites by dry process was increased remarkably by using 50% flour without compatibilizer. After adding 2.5% of MAPP, the flexural properties of the composites were improved significantly (Yin et al., 2005). In this study, a wet processing was investigated to make WPC using SE wood flourfibers and PP. Compared with traditional intensive mixing processes, the wet forming process can be used to make in-plane randomly oriented composite mats with little fiber damage and a more uniform fiber distribution in polymer matrix.

2. EXPERIMENTAL

2.1 Materials
Small-diameter loblolly pine (Pinus taeda L.) chips were converted to wood flours by a steam explosion process. It is a mixture of wood elements of different sizes. To make a homogeneous distribution in the plastic matrix, the flour must be sufficiently fine and oversized particles eliminated by screen filtering. The big particles were refined using a mill chopper in order to use the whole materials after steam explosion and #20 and #16 screens were used to separate the oversized particles. Polypropylene was provided by FiberVisions Inc. (Covington, GA) in the form of fiber bundles. MAPP was provided by Eastman Chemicals.

2.2 Wet Process Development and Composite Processing
Generally speaking, the wet-laid wood fiber/polymer composites were fabricated using a standard TAPPI handsheet method followed by a hot compression molding process. The wood flour and polymer fiber were suspended in water, and after sheet formation using a standard 159mm sheet machine and drying, the mats were compression molded into round sheets with a diameter of 159 mm and a thickness of 1, 2 or 3 mm. The target density of the composites was 1 and 0.91 g/cm³ for neat PP panels. A typical hot press profile was used for compression molding. After the temperature was raised to 175°C, the pressure was then increased gradually to 4 MPa from less than 0.5 MPa in about 5 minutes until the temperature of 195°C or expected levels and held at this pressure for another 4 min to 5 min. Then cold water was used to cool down the mold temperature to around 50°C.

2.3 Experimental Design
At least two panels were made for each condition. Neat PP panels were made as control tests. To observe the effects of different forming and molding, single and multiple layers were used to mold the composites. The wood flour was passed through #16 screen. The ratio of PP/wood was 1:1. The top-top in core and bottom-bottom in core combinations were used to combine two layers into a single mat. To investigate the effects of different factors on the mechanical properties of the composite, seek a better technical procedure and save experiment numbers, an orthogonal test (L9(3⁴)) was chosen to design the experiment. Nine samples were made and consolidated using 2 layers and 2 mm in thickness. Four factors and three levels were chosen: (1) wood fiber contents (35%, 50%, and 65%), (2) MAPP contents (0, 2.5%, 5%), (3) fiber sizes (screen size: <16#, 16#-20#, and <20#), and (4) molding temperature (195, 210, 225°C).

2.4 Material Characterization
Flexural properties were chosen to evaluate the composites according to ASTM D 790 by an Instron testing machine. The nominal width of specimens was 12.5mm. The specimens were tested until rupture occurred in
the outer surface of the composite specimens or until a maximum load was obtained for neat PP panels. A strain rate of 0.89 mm/min for 2mm panel and 1.27 mm/min for 3mm panel was employed. At least five specimens were tested for each sample.

A Perkin-Elmer Diamond dynamic mechanical analyzer (DMA) was used to determine the storage modulus $E'$ and the loss tangent $\tan \delta$. The specimens were heated at a rate of 2°C min from -60°C to 130°C in a nitrogen atmosphere and applied oscillating stress at a frequency of 1 Hz. Differential scanning calorimetry (DSC, Perkin-Elmer Diamond) was performed to observe the melting properties of the composites under a nitrogen atmosphere from -50 to 220 °C with a heating rate of 10 °C/min. The mass of specimens was 5-6 mg. The morphology of fractured surfaces was examined using a Hitachi S-800 Scanning electron microscope (SEM). Fresh fractured surfaces were coated with gold on an ion sputter coater. SEM microscope was operated at 10 kV and various magnification levels.

3. RESULTS AND DISCUSSIONS

3.1 The Effects of Single and Multiple Layers
Although the wood flours distributed quite well in the mats, it was not thick enough for 1mm composite. For 2mm and 3mm panels, the results indicated that there were not significant differences in flexural properties between single and multiple layers. The standard deviations of multiple layers were slightly smaller and this means that they were more uniform. For two layers combinations, there was not a big difference of the flexural properties between top-top and bottom-bottom in core combinations, but the surfaces of bottom-bottom in core combinations appear more homogeneous. So two layers for 2mm panels with bottom-bottom in core combinations were used for further experiments.

3.2Orthogonal Tests
To analyze the effects of the different factors on the mechanical properties, maximum difference was used to compare the properties. The results indicate that the effects of factors for MOE rank as: Wood content > MAPP content > Fiber size > Temperature. There were not too much different among MAPP content, fiber size, and temperature. The MOE increased with the wood flour content and MAPP content increasing, but not linear increasing. These are the similar results as reported by Stark and Berger (1997). The flexural MOE decreased with the temperature increasing at higher temperatures and longer times could degrade the wood flour. For MOR, the effects of factors rank as: Wood content > MAPP content > Temperature > Fiber size. The best factor group may be Wood (50%) + MAPP (5%) + Fiber size (#16-#20) + Temperature (195°C) for both of MOR and MOE. The MOR decreased linearly with the wood flour content increasing, increased with MAPP content increasing and decreased with the temperature increasing. The larger particles were a benefit to both of MOR and MOE.

Generally, the modulus of the composites could be increased by adding fillers with higher modulus than that of the matrix, and the strength may be decreased because there is not enough or no adhesion between the filler and the matrix. The results indicated that the flexural MOE of composites made with PP and SE wood flour was much higher than that of neat PP (Figure 1). Apparently, the addition of wood fiber decreased the flexural strength (Figure 2). Addition of MAPP improved the flexural and tensile strength, impact strength and strain at break by increasing the interface adhesion of PP and wood. The results revealed that both flexural
MOE and MOR of composites made with PP and SE wood flour had increasing trends by the MAPP content increasing. The increasing trends were not very clear. This may be because there were some interactions among the factors.

Figure 1. The effect of wood content on flexural MOE in groups of MAPP contents

Figure 2. The effect of wood content on flexural MOR in groups of MAPP contents

### 3.4 Dynamic mechanical analysis (DMA)

For composites, the responses to a dynamic load are very specific to its compositions and the history prior to the test, so specific test conditions are needed. Figure 3 shows the temperature dependence of tanδ in the range of -50 to 120°C for PP, PP/DP and PP/MAPP/DP composites, respectively. Neat PP displayed two rubbery transitions in the vicinity of 10°C and 85°C. The low temperature one corresponded to the β-transition and the higher peak is α-transition. The E' value decreased with the temperature increasing. The composites exhibited a distinct β-transition peak with reduced magnitude, but did not have clear α-transition peak. The location of the Tg was shifted to lower temperatures by the SE flour loading because of the role of SE flour in the
3.5. Morphology of the fractured surfaces of the composites

For the composites without MAPP, some fibers or fiber fragments were pulled out and there were some gaps between fiber and matrix (Figure 5a), indicating that the interfacial failure was the main mechanism causing the rupture. The addition of MAPP produced better compatibility between the SE flour and the PP, and hence stronger interfacial adhesion, as illustrated by the rougher surface, less gaps between fiber and matrix, and the fiber breakage in the longitudinal direction (Figure 5b). These observations imply the interfacial adhesion around some of the fibers was stronger than the individual components so that matrix cracking and fiber breakage after adding MAPP, but the weak interphase regions still existed because the gaps between the PP matrix and some fibers can be observed.

![SEM micrographs of the fractured surface: a) (left): Without MAPP, b) (right): With MAPP](image)

**Figure 5.** SEM micrographs of the fractured surface: a) (left): Without MAPP, b) (right): With MAPP

4. CONCLUSIONS

A wet process was developed to form mats using SE wood flours and PP fibers and followed by a compressive molding process to make wood plastic composites. This method produced less damage to the wood fibers than those by dry process but may have lost some very fine wood flours and water resolvable components during wet forming. The whole materials after SE treatment can be used to manufacture WPC. The MOE increased, while MOR decreased with the SE wood flour content increasing. After MAPP was added, both MOE and MOR of the composites were increased. The larger particles were better for reinforcing the properties and higher temperature could decrease the mechanical properties of the composites. DMA and DSC measurements revealed that the SE wood flours increased the crystallinity of PP. SEM observations also demonstrated the better interfacial adhesion produced by the interactions among the filler, MAPP and PP.

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