



## Physical Properties of Lignin Added Wood Flour-Polypropylene Composites: A Comparison of Direct and Solvent Mixing Techniques

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(Received: 30 November 2010;

Accepted: 12 September 2011)

AJC-10390

In this study, lignin addition (by two mixing techniques) and its influence on the long-term water absorption and thickness swelling of wood-plastic composites (WPCs) were investigated. Lignin powder extracted from Kraft black liquor mixed with the wood flour with ratios of 0, 2, 5 and 10 % (based on wood dry weight) by direct and solvent techniques. The composites were manufactured by hot press method after mixing of the wood flour, lignin compound with polypropylene including maleated polypropylene (0 and 2 %) in an internal mixer. The results indicated that water absorption and associated thickness swelling were decreased by increasing of lignin content in all of the studied composites. Also the results showed that the composites were produced by solvent mixing exhibit less water absorption and associated thickness swelling rather those were produced by direct mixing method. Application of maleated polypropylene in the composites decreased water absorption and thickness swelling as well as water absorption coefficients. The result also indicated that the lignin can be used as co-compatibilizer of maleated polypropylene in the wood-plastic composites. Water absorption of the studied composites was proved to follow the kinetics of Fickian diffusion process.

**Key Words:** Wood plastic composites, Lignin, Solvent mixing technique, Direct mixing technique, Water absorption, Thickness swelling.

### INTRODUCTION

Natural fiber thermoplastic composites are a family of reinforced plastic composites which are becoming more and more common place by the development of new production techniques and processing equipment<sup>1</sup>. Lignocellulosic materials, which have polar hydroxyl groups on the surface contributed predominantly by cellulose and lignin, have difficulty in forming well-bonded interface with a non-polar polymer matrix such as polyethylene and polypropylene. It is well known that compatibility between lignocellulosic material and the polymer matrix plays a crucial role in determining the properties of wood-plastic composites (WPCs). Hence so far various chemical reagents such as silane, isocyanate and anhydride (maleated polypropylene, maleated polyethylene) have been employed to enhance the compatibility between the constituent materials<sup>2</sup>.

Wood is made up mainly of three macromolecular species *i.e.*, cellulose, hemicelluloses and lignin. Lignin is an amorphous polyphenolic polymer and its content varies between 15 and

40 % in woody plants. As result of wood cooking in chemical pulping process, black liquor is obtained which mainly containing degraded lignin in a soluble form. The lignin can be extracted as a by-product of the pulping and is considered as a waste product. The majority of this waste is used as a fuel and only about 2 wt % is utilized in higher value application<sup>3</sup>. Lignin production is expected to rise significantly with the current shift toward biorefineries. The utilization of lignin as a specialty chemical is thus limited by the physical and chemical properties it exhibits after the pulping process. Most of the isolated lignin is lignosulfanates. Lignosulfanates are used as additive to concrete for water reduction, strength development, oil well drilling products, mud thinners, rheology modifier, dispersant and binder, *etc.*

The use of Kraft lignin as a copolymer or polymer additive has also received a considerable amount of attention<sup>3,4</sup>. The most straightforward application is the use of lignin as a filler material in polymers, with limited positive and negative effects on physical and mechanical properties. Since lignin contains both polar hydroxyl groups and non-polar hydrocarbon and

benzene rings, it is believed that it can play a role in enhancing the compatibility between polar and non-polar surfaces<sup>2</sup>. Wood-plastic composites are often subjected to the outdoor use where the moisture conditions change rapidly<sup>5</sup>. It is well known that water environment can affect the polymeric matrix, fibers and even the interface causing interaction loss between matrix and fiber and disturbing the mechanical integrity of the composites<sup>6</sup>. Hence, the aim of this study is to investigate the effect of lignin addition by two mixing techniques (solvent and direct) and its role as a modifier on the long-term water absorption and thickness swelling of wood-plastic composites.

## EXPERIMENTAL

**Polymer:** The thermoplastic homopolymer polypropylene (grade PI0800) in the form of pellets with a melt flow index (MFI) of 9 g/10 min was supplied by Bandar Imam Petrochemical Industries (BBIC).

**Wood flour:** The wood flour prepared of *Fagus orientalis* wood with +60/-40 mesh size.

**Maleated polypropylene:** Maleated polypropylene (MAPP) with melt flow index 100 g/10 min ( $T = 230\text{ }^{\circ}\text{C}$ , load = 2.16 kg) and 1.1 % maleic anhydride coupled used as compatibilizer.

**Lignin:** Black liquor was prepared from a local Kraft pulp mill and the lignin powder was extracted by sulfuric acid method<sup>7</sup>.

**Lignin-wood flour mixing:** Lignin and wood flour were mixed by two separate techniques, solvent and direct mixing. In solvent mixing the extracted powdered lignin was dissolved in a solvent solution ethanol:DMSO (3:1 v/v) and then mixed with the wood flour for 5 min. After the treatment time, the solvent was removed by rotary evaporation and in direct mixing the lignin powder was mixed just physically with the wood flour. The degree of lignin loading was: 0, 2, 5 and 10 % (based on the dry weight of wood flour).

**Composite preparation:** Polypropylene and treated wood flour were mixed in a internal mixer at 30 rpm and at  $190\text{ }^{\circ}\text{C}$  in presence and absence of maleated polypropylene according to Table-1. The wood flour was added to the mixer after the polymers had reached to its melting point. The amorphous composites removed from the mixer were then pressed into sheets with 2 mm thickness and 15 cm  $\times$  15 cm dimensions using a laboratory hydraulic hot press at  $190\text{ }^{\circ}\text{C}$ . Specimens for water absorption were cut out of these sheets.

TABLE-1  
COMPOSITION OF STUDIED COMPOSITES

Code	PP (%)	MAPP (%)	Lignin (%)*	(Lignin + Wood flour) = g/100 g
PW	40	0	0	(0+60)
PWL2	40	0	2	(1.2+58.8)
PWL5	40	0	5	(3+57)
PWL10	40	0	10	(6+54)
PWM	38	2	0	(0+60)
PWL2M	38	2	2	(1.2+58.8)
PWL5M	38	2	5	(3+57)
PWL10M	38	2	10	(6+54)

\*Based on wood flour dry weight.

PP = Polypropylene; MAPP = Maleated polypropylene.

**Water absorption:** Water absorption tests were carried out according to ASTM D-7031-04<sup>8</sup>. Five specimens of each formulation were selected and oven dried for 24 h at  $102 \pm 3\text{ }^{\circ}\text{C}$ . The weight and thickness of dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weight and thicknesses of the specimens were measured at different time intervals during the long-time immersion. The measurements were terminated after the equilibrium thicknesses of the specimens were reached. Water absorption percentage was calculated using the following equation:

$$WA(t) = \frac{W(t) - W_0}{W_0} \times 100 \quad (1)$$

where, WA(t) is the water absorption (%) at time t,  $W_0$  is the oven dried weight and W(t) is the weight of specimen at a given immersion time t.

Also the values of the thickness swelling in percentage were calculated using the eqn. 2.

$$TS(t) = \frac{T(t) - T_0}{T_0} \times 100 \quad (2)$$

where TS(t) is the thickness swelling (%) at time t,  $T_0$  is the initial thickness of specimens and T(t) is the thickness at time t.

## RESULTS AND DISCUSSION

Figs. 1 and 2 indicates the long-term water absorption behaviour of different composites which were produced by solvent and direct mixing techniques, respectively. As it is clearly seen, in both figures water absorption increases with extension of immersion time and reaches to a certain value at saturation point. The figures also show regular change in water absorption of wood-plastic composites by increasing lignin content. It can be observe that increasing lignin to 10 % and adding maleated polypropylene to the composites decreased water absorption content of studied composites produced by direct and solvent mixing techniques. Also the results show that the composites were produced by solvent mixing technique exhibit less water absorption than those produced by direct mixing technique (Fig. 3). Wood flour is containing *ca.* 70 % carbohydrates (cellulose and hemicellulose) hence it has hydrophilic nature whereas lignin contains phenylpropane unit

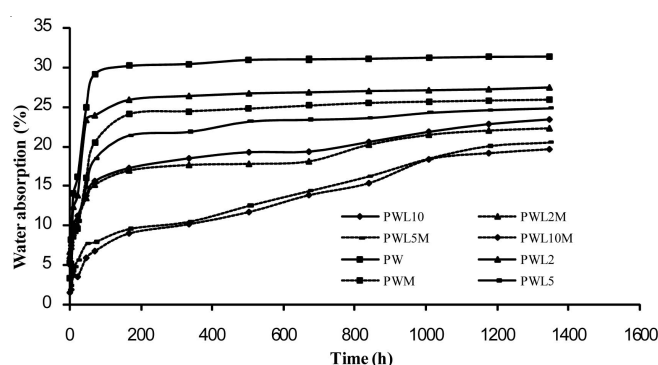


Fig. 1. Long-term water absorption behaviour of studied composites: solvent mixing

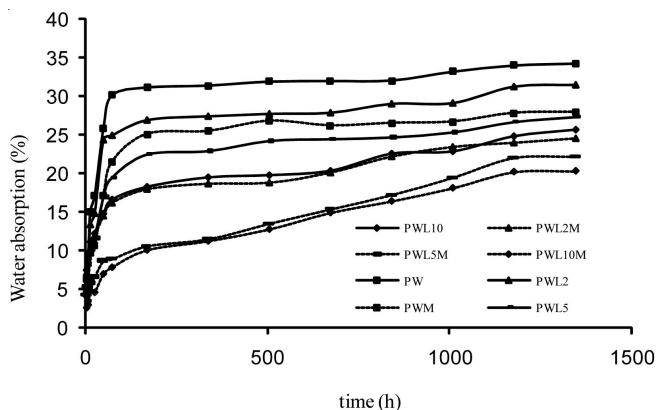


Fig. 2. Long-term water absorption behaviour of studied composites: direct mixing

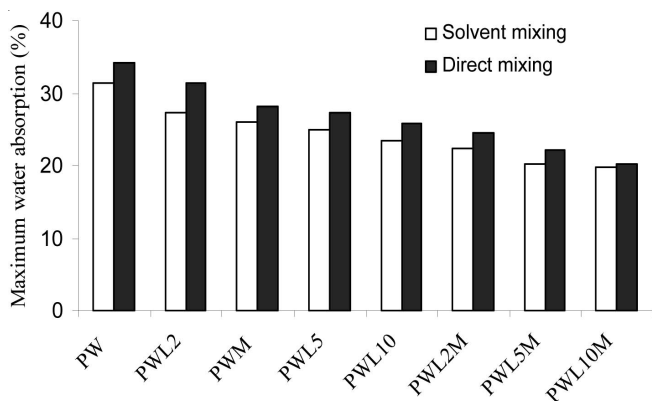


Fig. 3. Comparison of maximum water absorption of composites in two mixing methods

which has a hydrophobic nature. In solvent mixing technique lignin solvate in solvent that caused coating wood flour, completely. But in dry mixing technique the lignin powder was mixed just physically with the wood flour.

The analysis of diffusion mechanism and kinetics was performed based on the Fick's theory and fitting the experimental values to the eqn. 3 according the method described by Espert *et al.*<sup>9</sup>.

$$\log\left(\frac{M_t}{M_\infty}\right) = \log(k) + n \log(t) \quad (3)$$

where,  $M_t$  is the water absorption at time  $t$ ;  $M_\infty$  is the water absorption at the saturation point;  $k$  and  $n$  are constants.

The  $n$  values are similar for all formulations and close to the value of  $n = 0.5$  (Tables 2 and 3). Therefore, it can be concluded that the water absorption of all formulations approach the Fickian diffusion case. The diffusion coefficient is the most important parameter of the Fick's model and shows the ability of water molecules to penetrate inside the composite structures.

Tables 2 and 3 show the water diffusion coefficients for all formulations. It is evident that the water diffusion coefficients decrease with applying maleated polypropylene and lignin. The composites containing both maleated polypropylene and lignin exhibited the lowest diffusion coefficients. Also the composites produced by solvent mixing method exhibited less maximum water absorption and water diffusion coefficients rather those made produced by direct mixing method.

Code	k (h <sup>2</sup> )	n	Maximum water absorption (%)	Water absorption coefficients (× 10 <sup>-12</sup> m <sup>2</sup> s <sup>-1</sup> )
PW	0.045	0.45	31.30	4.22
PWL2	0.048	0.47	27.40	3.47
PWM	0.021	0.44	26.01	3.26
PWL5	0.057	0.49	24.88	2.97
PWL10	0.031	0.48	23.40	2.75
PWL2M	0.046	0.46	22.30	2.62
PWL5M	0.048	0.49	20.20	2.43
PWL10M	0.056	0.46	19.70	2.07

Code	k (h <sup>2</sup> )	n	Maximum water absorption (%)	Water absorption coefficients (× 10 <sup>-12</sup> m <sup>2</sup> s <sup>-1</sup> )
PW	0.051	0.49	34.2	5.12
PWL2	0.047	0.49	31.4	5.03
PWM	0.046	0.42	28.1	4.78
PWL5	0.043	0.47	27.3	4.37
PWL10	0.041	0.48	25.7	4.15
PWL2M	0.040	0.47	24.6	3.82
PWL5M	0.038	0.49	22.2	3.53
PWL10M	0.037	0.48	20.3	3.17

Figs. 4 and 5 indicates the long-term thickness swelling behaviour of different composites which were produced with direct and solvent mixing technique, respectively. Similarly to water absorption, thickness swelling increases with extension of immersion time to a certain value at saturation point. It is clearly seen that the thickness swelling decreased in the composites with higher content of lignin. In Figs. 4 and 5, it can be observe that using both lignin and maleated polypropylene decreased thickness swelling regularly in the composites produced by both mixing techniques.

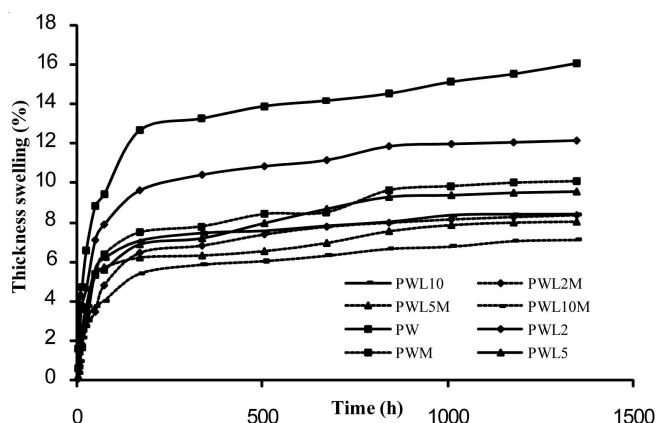


Fig. 4. Long-term thickness swelling behaviour of studied composites: solvent mixing

Moisture absorption depended upon void contents in the composites and any increase in the void content, led to increase in the water absorption<sup>10</sup>. Using compatibilizing agents such as maleated polypropylene improve the interfacial bonding

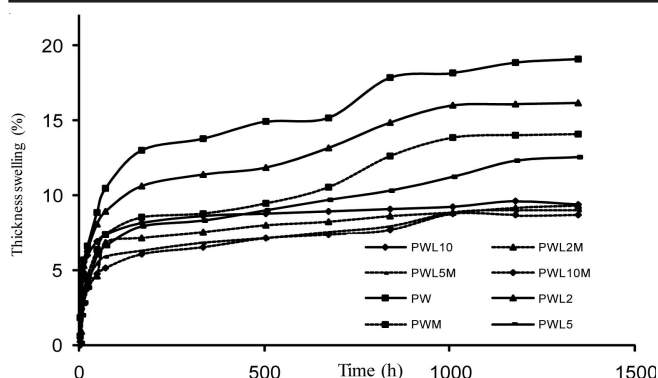


Fig. 5. Long-term thickness swelling behaviour of studied composites: direct mixing

between the filler and polymer matrix. The maleated polypropylene can chemically bond to the OH groups of the lignocellulosic materials which lead to limits the water absorption of the composites. It seems necessary to use the coupling agents to improve the quality of adhesion between plastics and fibers to reduce the gaps in interfacial region and to block the hydrophilic groups<sup>11</sup>. Najafi *et al.*<sup>12</sup> showed that maleic anhydride polypropylene decreased void content and water absorption in wood-polypropylene composites. Decreasing water absorption by using maleated polypropylene is due to the formation of ester bonds between the anhydride carbonyl groups of maleated polypropylene and hydroxyl groups of the wood flours<sup>13</sup>. This hypothesis is confirmed by previous studies<sup>14,15</sup> that show anhydride moieties of functionalized polyolefin coupling agents entered into an esterification reaction with the surface hydroxyl groups of wood. Upon esterification, the exposed polyolefin chains diffuse into the polymer matrix phase and entangle with polymer chains during hot pressing. These changes improve the compatibility between the wood and polymer matrix.

On the other hand, Rozman *et al.*<sup>2</sup> indicated that lignin enhanced the adhesion at the interfacial region between the coconut fiber and polypropylene and decreased void content and water absorption as well. This may be attributed to the non polar hydrocarbon chains and aromatic rings in the lignin. According to Rozman *et al.*<sup>2</sup>, there are two possibilities of how the lignin could reduce the absorption of water; bulking the cell wall, plugging the lumen of the cell wall by entering through bordered pits. If the cell wall is bulked by lignin and together with its hydrophobic characteristics, water could not enter and bulk the cell wall further. The second possibility is more likely, since, the lignin molecule is considered too big to enter into the cell wall<sup>2</sup>. As the carbohydrates have more hydrophilic nature than lignin, hence water absorption decrease when a part of carbohydrates replaced by lignin. Also in the composites produced by solvent mixing technique wood-flour coated by lignin helps to decreased water absorption content than those produced by direct mixing method. Klason *et al.*<sup>16</sup> observed that the presence of lignin in the filler influences the

adhesion to the matrix. The results of Toriz *et al.*<sup>17</sup> indicated that lignin can be increased adhesion between filler and matrix too. It is obvious the lignin incorporated is able to reduce the extent of swelling of wood-plastic composites since the swelling reduced with the increased level of lignin. Generally the result shows that lignin is able to reduce the amount of water going into and swelling the cell wall and caused decreasing thickness swelling of wood plastic composites. As the results have shown, application both maleated polypropylene with lignin caused reduction in water absorption of the composites.

## Conclusion

In this study, physical properties of lignin added wood flour-polypropylene composites was investigated. Also effect of direct and solvent mixing techniques on the physical properties of the composites were studied and the following conclusions could be made from the experimental results:

- Kraft lignin modified the physical properties of wood-plastic composites.
- Lignin can be used as co-compatibilizer of maleated polypropylene in wood-plastic composites.
- The composites produced by solvent mixing technique exhibited less water absorption and thickness swelling rather those made with direct mixing.
- Water absorption of the studied composites was proved to follow the kinetics of a Fickian diffusion process.

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