

Effect of Acetylation of Wood Flour and MAPP Content during Compounding on Physical Properties, Decay Resistance, Contact Angle, and Morphology of Polypropylene/Wood Flour Composites

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The effects of acetylation of wood flour with vinylacetate and the content of Maleic Anhydride Polypropylene (MAPP) coupling agent before compounding were evaluated relative to water absorption and thickness swelling. Hot water was used to extract materials of sawdust fir flour before acetylation. Fir flour was successfully acetylated using vinylacetate (VA) in the presence of potassium carbonate. The modification was confirmed by the weight percent gain (18.8%) and Fourier transform Infrared (FTIR) spectroscopy. The acetylated or control wood flour was mixed with MAPP coupling agent (0, 3, & 6 wt%) at 60 rpm and 160 °C, followed by extrusion. The wood plastic composite (WPC) was made by hot pressing at 200 °C and 25 MPa for 5 min. Specimens were exposed to white-rot decay for 16 weeks. In addition to the weight loss due to fungal treatment, water absorption, thickness swelling, and contact angle of the acetylated and decayed samples was investigated. Increasing the percentage of MAPP was found to decrease the percentage of weight loss, water absorption, and thickness swelling in all of the samples. In contrast, increasing the MAPP percentage increased the contact angle in all samples. The SEM micrographs revealed that the bonding between fibers and polymeric material was improved and strengthened by MAPP addition.

Keywords: Acetylation; Decay Resistance; Contact Angle; Morphology

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INTRODUCTION

During recent years, a great deal of work has been performed using wood to make wood-plastic composites (WPCs). Application of the wood flour for making the WPC has been increased due to its high strength to weight ratio, low density, low price, and simple processing and decomposability (Arbelaiz *et al.* 2005; Mechraoui *et al.* 2007). One of the main disadvantages of using the wood flour in WPC is the poor adherence between the two phases of fibers and polymer, which will decrease properties of the final product (Espert *et al.* 2004). Water absorption in WPC is a significant factor affecting the properties in the final applications. Increasing the moisture content in wood plastic simply leads to degradation of the mechanical properties. This is due to the absorption of moisture and the stabilization of their dimensions (Adhikary *et al.* 2008). Water absorption destroys the interface between the fibers and the polymer matrix, which may cause poor mechanical properties (Espert *et al.* 2004). Because most applications of WPCs are related to outdoor surfaces of buildings in direct contact with climatic

conditions and humid weather, considering the water absorption becomes important for these materials (Kazemi *et al.* 2007). The trend of water absorption and thickness swelling in the wood plastic has been studied by numerous researchers (Tajvidi *et al.* 2006; Shi and Gardner 2006). Moreover, much research has been done on chemical treatment of wood fibers in order to reduce the water absorption and thickness swelling; also, this research has shown improved dimensional stability of wood plastic (Tserki *et al.* 2005; Demir *et al.* 2006; Dominkovics *et al.* 2007). Polarity of the hydroxyl groups on the surface of the lignocellulose materials is an obstacle against the formation of a chemical bond with the polymer. Therefore, it is possible to reach a much stronger bond with the polymer by decreasing hydrogen bonding between the fibers. It is essential to improve the interface between the matrix and the hydrophilic lignocellulosic fibers, as well as the thermal stability of lignocellulosic fibers. The methods for improving the compatibility of lignocellulosic materials that are used as fillers are as follows: esterification, silane treatment, use of coupling agents, and treatment with other chemicals (Raj *et al.* 1989; Felix and Gatenholm 1991; Bledzki *et al.* 1996). In these studies it was reported that promoting the interfacial compatibility between hydrophobic matrix of the polymers and hydrophilic lignocellulosic fibers improves the physical and mechanical properties of the composites. Chemical modification can be observed by the chemical reaction between reactive parts of the lignocellulosic cell wall polymers (generally in hydroxyl groups) and a chemical reagent, with or without catalyst; as a result, a covalent bond forms between these two. All of the methods investigated to date have involved the chemical reaction of a reagent with the cell wall polymer hydroxyl groups. The chemical modification of lignocellulosic fibers with various reagents, including anhydrides (acetic, succinic, maleic, propionic, butyric, hexanoic, crotonic, and methacrylic anhydrides), isocyanates, formaldehyde, acetaldehyde, or epoxides (ethylene or propylene oxide, glycidyl methacrylate, allyl glycidyl ether, *etc.*) have been the subject of research for many decades (Banks and Lawther 1994; Hon 1996; Çetin 2000; Çetin and Özmen 2001; Rowell 2006; Hill 2006). For fabrication of wood plastic with proper physical and mechanical features, it is necessary to control hydrophilic properties of the lignocellulose materials by chemical modification methods using coupling agents. This, as a result, creates a good adherence between the two interfaces of polymer and lignocellulose fibers (Abdul Khalil *et al.* 2001). MAPP is a kind of compatibilizer commonly used in WPCs. MAPP has low surface energy; therefore, it is expected to give good compatibility between the wood and the polymer by the formation of stronger linkages in the interfaces and by reducing WPCs surface tension. Bonding between the wood and the polymer is weaker when a compatibilizer has not been applied. The hydrogen connections between the fibers weaken by the creation of connections by the coupling agents. The result of this is an easier dispersion of the fibers within the polymer matrix and also adherence enhancement (Chowdhury and Wolcott 2007).

Decay resistance of wood / heavy polypropylene composites were examined against white-rot and brown-rot fungus (Pendelton *et al.* 2002). The materials used in these composites were maple wood flour of mesh 40 and heavy polyethylene powder. They found out that almost no decay was apparent in most of the cases. The SEM micrographs were also only indicative of fungi development within the thermoplastic and wood, especially near surface of the samples. An increase in the heavy polyethylene content in the samples can prevent decay. This research was implemented with a purpose to investigate the effect of acetylation (new acetylation method using vinyl acetate) and content of MAPP coupling agent on physical properties (water absorption and thickness swelling). The extent of damages caused by the white-rot fungi was also studied using

examination of weight loss of the samples, contact angle, and morphology of acetylated wood / polypropylene composite.

MATERIALS AND METHODS

Polymer Matrix

The polypropylene (PP), with a melt flow index (MFI) of 9 g/10 min at 190 °C, was obtained from maroon Co., Iran, and was used as the matrix polymer.

Wood Flour

The fir sawdust flour was obtained from Moein Industry Co. (Iran). Particles passed through a 40 mesh screen and were retained on a 60 mesh screen.

Coupling Agent

Maleic anhydride grafted polypropylene (MAPP) with a density of 0.9 g cm⁻³ (MFI 15-30 g/10 min, grafted maleic anhydride 1 wt %) was provided by Javid Kimiya Sepahan Co. and was used as the coupling agent.

Chemical Modification of Fibers

Before acetylation, the extractive materials of wood flour were extracted using deionized hot water; then, these extracts were dried inside an oven at 103±2 °C for 24 hours. Afterwards, extracted wood flour was transferred to a desiccator and allowed to cool to room temperature. After cooling, it was then added to a glass balloon containing di-methyl formamide (DMF) and vinyl acetate. To accelerate the chemical reaction, potassium carbonate (K₂CO₃) was used as a catalyst. In the acetylating treatment, 0.02 mol of vinyl acetate and 50 ml of dimethyl formamide were used for each gram of the dry wood flour. This reaction was carried out at the temperature of 100±1 °C for 24 hours using a bath of hot water. After the treatment, the wood flour was rinsed again with hot water to remove the unreacted material, and then dried in an oven. The acetylated wood was dried once more at 105 °C for 24 hours. The percentage of weight percent gain (WPG) was calculated based on the following equation (1). The percentage of the WPG was obtained, resulting in 18.8%.

$$WPG(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

In Eq. 1, W_1 is the weight before acetylation, W_2 is the weight after acetylation, and WPG is the weight percent gain.

Infrared Spectroscopy

Infrared absorption spectra of acetylated and unmodified hemp fibers were obtained with the potassium bromide (KBr) technique. This was done using a Nexus 870 Thermo Nicolet FT-IR spectrometer USA, at a resolution of 4 cm (40 scans). In each case, 1% w/w of oven-dry hemp fibers was dispersed in a matrix of KBr and pressed to form pellets.

Sample Preparation

The sawdust was milled with a rotary mill prior to the sample preparation. It was then sieved to pass mesh +60/-40 and was oven dried at 103±2 °C for 24 hours. The PP,

oven dried wood flour flour, and MAPP were then weighted and bagged according to formulations given in Table 1. They then were properly mixed with the coupling agent and poured into the funnel of co-rotating twin-screw extruder (Collin T20 191-324 model) at the Iran Polymer and Petrochemical Research Institute. The screw speed was set at 60 rpm. The temperatures of its barrel zone (1-6) were adjusted at 170, 173, 175, 177, 179, and 180 °C. The compounded materials were subsequently ground using a pilot scale grinder (WIESER, WGLS 200/200 model). The resulting granules were dried at 105 °C for 24 hours. Test specimens were prepared with a laboratory press. The press was employed to press samples and cast them at 200 °C under a pressure of 25 MPa for 5 min. In order to avoid the creation of bubbles inside the samples, deaeration was repeated several times. Using a puncher, the samples were separated in order to avoid the formation of cracks. The specimens were stored under controlled conditions (50% relative humidity and 23 °C) for at least 14 days prior to testing.

Table 1. Composition of the Studied Formulations

Sample Code	PP Content (wt%)	Sawdust fir flour Content (wt%)	MAPP (wt%)
A1	50	50	0
A2	48.5	48.5	3
A3	47	47	6
U1	50	50	0
U2	48.5	48.5	3
U3	47	47	6
A1, A2, A3: Acetylated U1, U2, U3: Untreated			

Decay Test

After an exposure to *Trametes versicolor* for 16 weeks, the decay test was conducted in accordance with DIN EN113 standard and was performed by applying the Kolle flask method. Malt extract agar (48 g/L) was used as an agent for the fungus culture. The agar medium was sterilized in an autoclave at a temperature of 120 °C and pressure of 1.2 atm for 20 minutes. Subsequently, every Kolle flask was inoculated by a small plug of *T. versicolor* and allowed to stand at 25 °C for 7 days. During this time, its mycelium covered the entire surface of the agar. Each test was run in five replicates and the average values were reported. Next, acetylated and non-acetylated WPC specimens (60 mm x 20 mm x 2 mm) were dried at 103 ± 2 °C for 24 hours; from these results, the oven-dried weight was determined. In the following stage in order to avoid contact of specimens with fungal mycelia, the samples were placed on the top of two small glass legs in a Kolle flask. Both heartwood and sapwood samples were incubated at 25 °C and 70% relative humidity until they were acclimatized by the *T. versicolor*. Once acclimatization was done, the samples were then transferred to an incubator for 14 weeks (under the same conditions). Once the time period was expired, they were removed from the incubator and fungal mycelia were removed from the surface of the specimens. The samples were then placed in an oven at 103 ± 2 °C for 24 hours in order to reach to constant weight and determine weight loss for each individual sample, the equation (2) used is as follows,

$$\text{Weight loss} = [(W_1 - W_2) / W_1] \times 100 \quad (2)$$

where W_1 is the oven-dry weight of the sample prior to exposure and W_2 is the oven-dry weight of the sample after exposure to the fungus.

Measurements

Water absorption and thickness swelling tests were carried out according to ASTM D-7031-04. Six specimens of each formulation were selected and dried in an oven for 24 hours at 102 ± 3 °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, the specimens were removed from the water and the surface water was wiped off using blotting paper. Weight and thicknesses of the specimens were measured after 168 hours of immersion. The values of the water absorption in percentage were calculated using the following equation (3).

$$WA(t) = \frac{W(t) - W(o)}{W(o)} \times 100 \quad WA(t) = (W_t - W_0) / W_0 * 100 \quad (3)$$

In Eq. 3, $WA(t)$ 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 .

The values of the thickness swelling in percentage were calculated using Eq. 4.

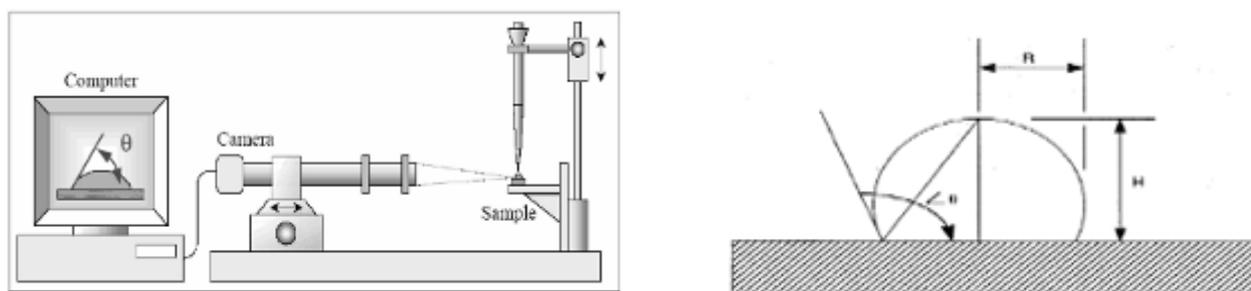
$$TS(t) = \frac{T(t) - T_0}{T_0} \times 100 \quad (4)$$

$$TS(t) = \frac{T(t) - T(o)}{T(o)} \times 100$$

In Eq. 4, $TS(t)$ is the thickness swelling at time t , T_0 is the initial thickness of specimens, and $T(t)$ is the thickness at time t .

Measurement of Contact Angle

The contact angle has a significant impact on the behavior of the droplet in collision with the solid surface. This can include deformation, scattering, or even disjoining of the droplet from the surface. One can assess hydrophobicity and hydrophilicity of the surface by means of the contact angle measurement system. Measurement of the contact angle was done only through water droplets of 4 μm in volume, and by using a system equipped with a camera capable to take picture and film from the droplet. A QCA14Plus device from the Dataphysic company (Germany) was used to carry out this work at Sharif University of Technology. Software from the same company was used for calculation of the contact angle of the droplet under examination. The contact angle of distilled water was measured on the surface of wood plastic composite samples by a dropping technique. Equation 5 was utilized to measure the contact angle between the droplet and the solid surface.



R = half width of droplet; H = height of water droplet; θ = contact angle

Fig. 1. Schematic view of the method used for contact angle measurement (Mohebbi *et al.* 2010)

The morphology of composites was characterized using scanning electron microscopy (SEM, Model LEO 440i, Oxford) at 25 kV accelerating voltage. The samples were first frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact. They were then coated with a gold layer to provide electrical conductivity.

Statistical Analysis

Data analysis was performed using SPSS Statistical Software (IBM Software, Armonk, New York) in terms of one-way analysis of variance. The average values were compared and classified at the 95% confidence level using the Duncan multiple range (DMRT) test.

RESULTS AND DISCUSSION

The reaction mechanism between wood hydroxyl groups and vinylacetate (VA) is shown in Fig. 2. As shown, a transesterification reaction is proposed. An approximate WPG level of 18.8% was achieved after 24 hours reaction with VA. The reaction between vinylacetate and wood flour was obtained by analyzing the samples with FTIR spectroscopy (Fig. 3). Acetylated samples were identified in the FTIR spectra. The emergence of a carbonyl stretching ($\nu\text{C}=\text{O}$) vibration at 1746 cm^{-1} in the spectra confirmed the presence of ester bonds after reactions with VA (Silverstein *et al.* 1991; Ozmen 2012). In addition, the intensity of the band about 1244 cm^{-1} also increased and was associated to the C-O stretching ($\nu\text{C}-\text{O}$) vibration of the acetyl moieties. The intensity of the bands located at 1378 cm^{-1} was also enhanced after the transesterification reaction. This band was attributed to the C-H bending ($\delta\text{s C-H}$) vibrations of the methyl groups introduced. The intensity of the band at 607 cm^{-1} also was increased and was associated to some vibrations of the grafted methyl groups (Ozmen 2012). The decrease in the absorbance around 3340 attributed to the O-H bending vibrations of the hydroxyl groups introduced.

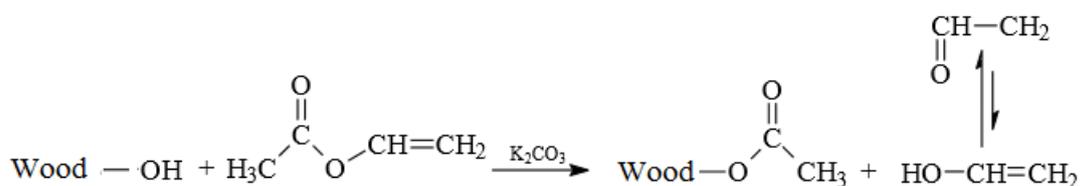


Fig. 2. The reaction of wood fir flour with vinyl acetate

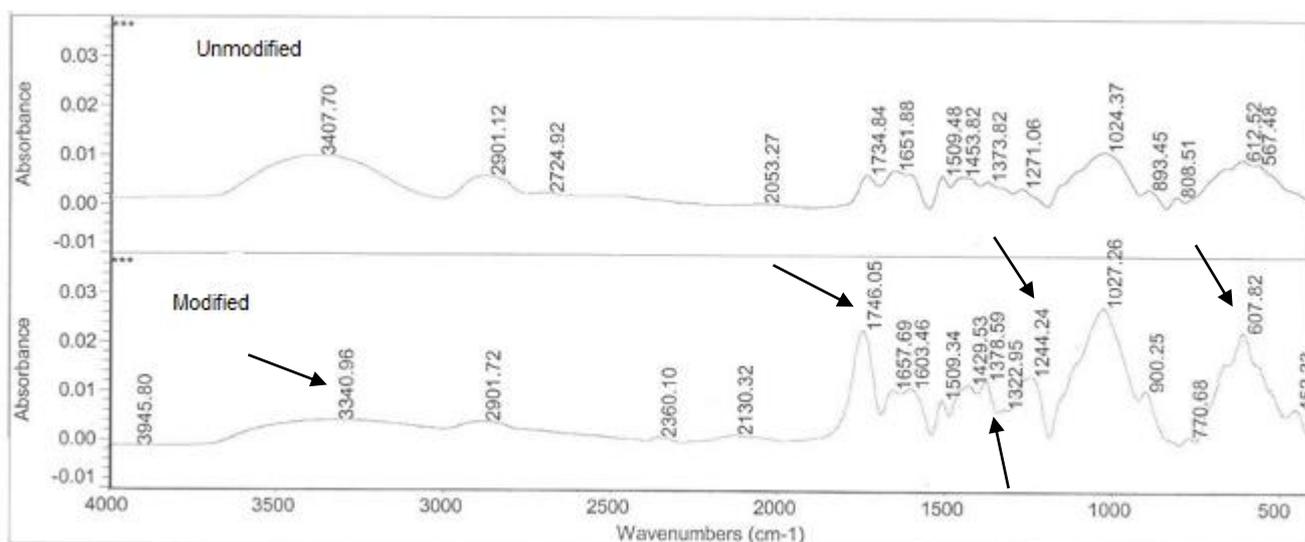


Fig. 3. FT-IR spectra of unmodified and modified (acetylated) wood flour

The F-value and significance level of coupling agent content in the composites are summarized in Table 2.

Table 2. Analysis of Variance (F-Value and Significance Level) of Coupling Agent Content in the Composites

Properties Variable	Water absorption (%)	Thickness swelling (%)	Weight loss (%)	Water absorption after decay (%)	Thickness swelling after decay (%)	Contact angle	Contact angle after decay
MAPP	179.587*	117.829*	154.027*	450.967*	53.402*	149.867*	63.658*

* 95% significance level
^{ns} no significance

Figures 4 through 10 illustrate the effects of MAPP and acetylation on physical properties (water absorption and thickness swelling of 168 h), weight loss of sample white-rot fungi exposure, physical properties 168 h after exposure to white-rot fungi, and contact angle of the composite samples. It can be observed that the acetylated samples had advantageous performance in comparison with the other treatments that did not include vinylacetate.

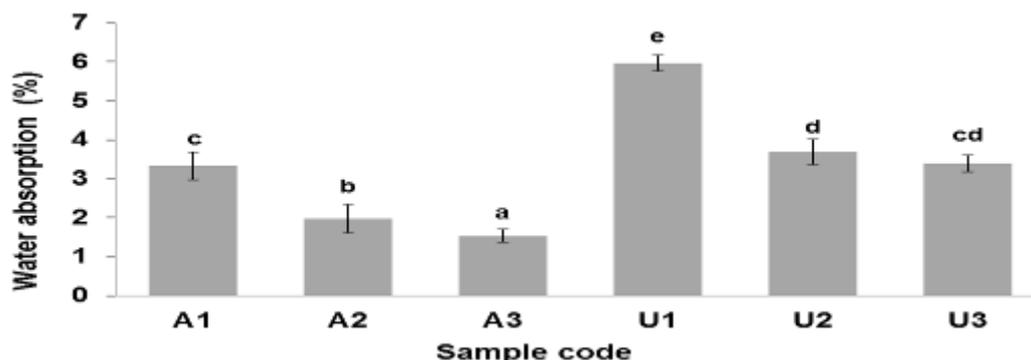


Fig. 4. Effect of acetylation and MAPP content on water absorption (Small letters indicate the Duncan of the averages at a 95% confidence interval, A1, A2, A3: is sample acetylated and U1, U2, U3: is sample untreated)

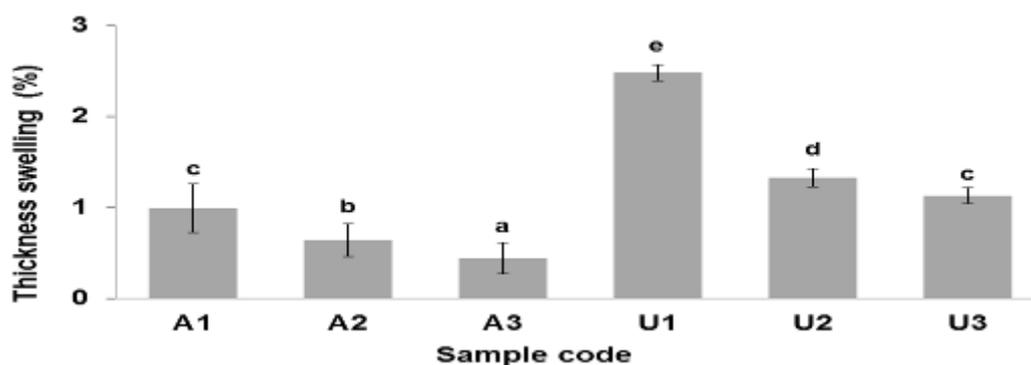


Fig. 5. Effect of acetylation and MAPP content on thickness swelling (Small letters indicate the Duncan of the averages at a 95% confidence interval.)

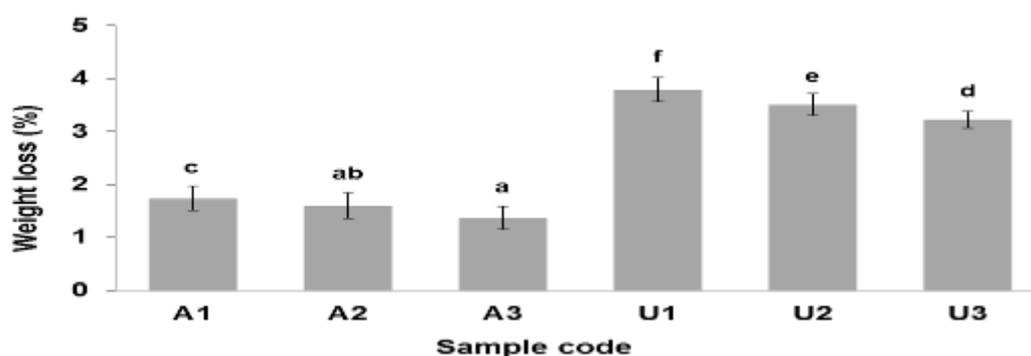


Fig. 6. Effect of acetylation and MAPP content on weight loss after fungal treatment (Small letters indicate statistical differences according to the Duncan test at a 95% confidence interval.)

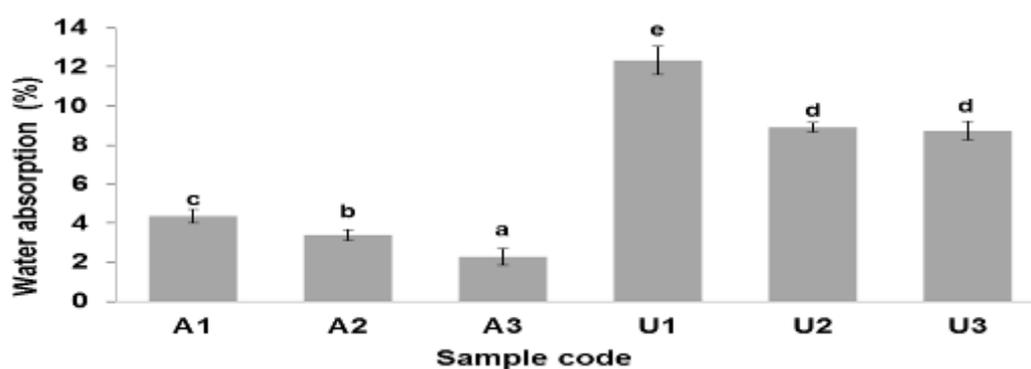


Fig. 7. Effect of acetylation and MAPP content on water absorption after fungal treatment. Small letters indicate statistical differences according to the Duncan test at a 95% confidence interval.

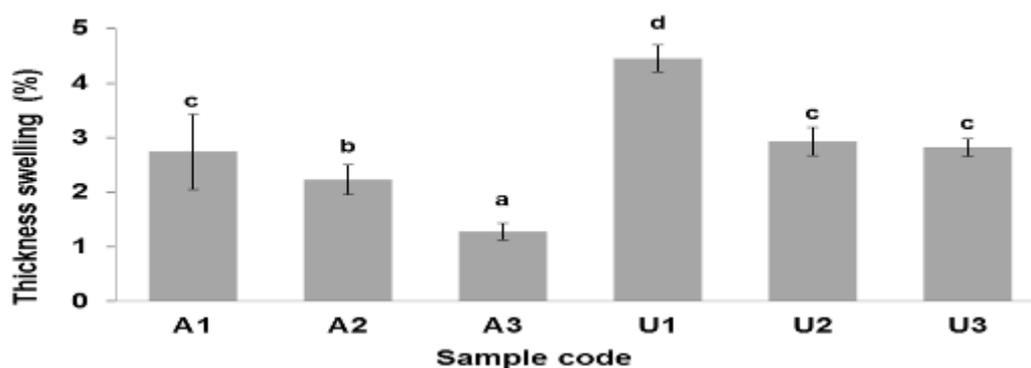


Fig. 8. Effect of acetylation and MAPP content on thickness swelling after fungal treatment. Small letters indicate statistical differences according to the Duncan test at a 95% confidence interval.

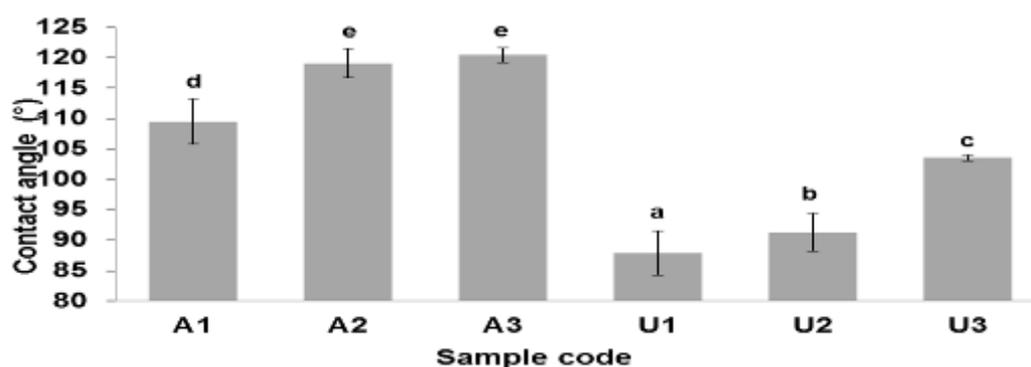


Fig. 9. Effect of acetylation and MAPP content on water contact angle. Small letters indicate statistical differences according to the Duncan test at a 95% confidence interval.

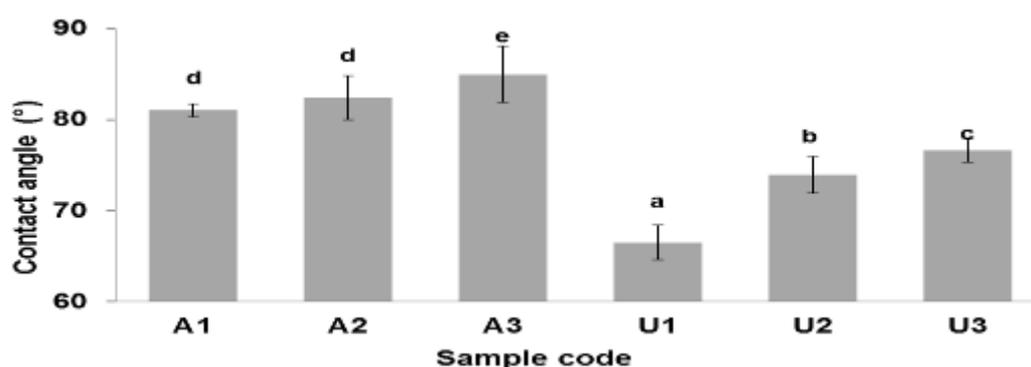


Fig. 10. Effect of acetylation and MAPP content on contact angle after fungal treatment. Small letters indicate statistical differences according to the Duncan test at a 95% confidence interval.

The effects of MAPP and acetylation on physical properties (water absorption and thickness swelling after 168 h soaking in water), weight loss due to white-rot fungi, physical properties after 168 h exposure to the white-rot fungi, and contact angle of the composite samples were significant at the 5% level (Table 2).

Water Absorption and Thickness Swelling

Taking into consideration the main applications of the wood plastic composites, which are usually placed in direct contact with climatic conditions and water, it seems necessary to investigate the water absorption of these materials.

Hydrophilic characteristics of wood fibers cause the water absorption to act as a limiting factor in the final application of the wood plastic composites. The obtained results show that the trend and amount of water absorption in the wood composites are affected by the following factors: type, content, and dimensions of the filler, polymer type, being manufactured from recycled or new material, and the use or lack of coupling agent.

The amount of water absorption is strongly dependent on the molecular structure formed in these materials, which becomes clearer over time. Most researchers who have worked with the wood plastic composites have found that increasing of the wood flour in the composites adds to the water absorption in these materials. This occurs because of the polar and hydrophilic nature of the lignocellulose fibers and also because of the presence of hydrophilic hydroxide groups accessible for the cellulose chains. This leads to formation of new hydrogen bonds with the water molecules, which contribute to the water absorption in these composites.

Effect of Coupling Agent on Water Absorption and Thickness Swelling

Generally speaking, the existing hydroxyl groups in the cellulose, hemicellulose, and lignin develop many hydrogen bonds among macromolecules of the wood composite. When the cellulose fibers are exposed to moisture, these bonds are broken and converted to new hydrogen bonds with the water molecules, leading to swelling of the material. As shown by the experimental results, adding to the percentage of the coupling agent decreases the water absorption and thickness swelling.

Moreover, increasing the amount of coupling agent to cause reduction of the water absorption and thickness swelling in the composite can be expected to result in a better connection in the intermediate phase of the reinforcement and polymer materials. This is because improvement of the connections in the intermediate phase, especially the one between wood flour and polypropylene, limits access of the water molecules to the free hydroxyl groups on the surface of the wood flour. It can also intensify the water absorption and thickness swelling in case the water enters the intermediate phase of the reinforcement and the polymer and destroys the connection between them.

Marcovich *et al.* (1998) studied the effect of MAPP coupling agent on the composites of polypropylene/wood fibers. Their results indicated that the MAPP at an addition level of 3% or smaller improves the magnitude of the water absorption of the composite.

Ziaei *et al.* (2009) studied the effect of a coupling agent material on physical properties of the polypropylene/wood flour and nano-clay composite. They reported that increasing the MAPP decreases the water absorption and thickness swelling.

Many polymeric materials, especially thermoplastic polymers, have hydrophobic characteristics due to their being nonpolar. Addition of the lignocellulose reinforcements causes greater water absorption and thickness swelling because they show hydrophilic and polar nature. The hydroxide groups with hydrophilic characteristics, which are accessible for the cellulose chains, contribute to formation of the new hydrogen bonds with the water molecules. This also results in water absorption and thickness swelling. The obtained results showed that an increase of the coupling agent from 3% to 6% decreases the water absorption and thickness swelling. For the coupling agent content of 6%, the MAPP forms ester bonding with hydroxyl groups of the cellulose materials,

which can finally limit the contact between water molecules and free hydroxyl groups of the cellulose materials. Thereby, the amount of free hydroxyl groups accessible for reaction with the water molecules will decrease, which will actually change the hydrophilic properties of the fibers to the hydrophobic features (Taib *et al.* 2006).

Effect of Acetylation on Water Absorption and Thickness Swelling

Polarity of the hydroxyl groups on the surface of the lignocellulose materials is a barrier against bond formation with a matrix polymer. Therefore, reduction of the hydrogen bonding between the fibers can contribute to reach a stronger bond with the matrix polymer. It is possible to improve wettability on the surface of the fibers to the matrix plastic. It is also possible to facilitate formation of a stronger bond between the wood and plastic and to eventually support the dimensional stability. Meanwhile, the acetylation effect can be compared against the efficiency of the MAPP coupling agent.

Based on the obtained results, it has been discovered that acetylation of the fibers has a positive effect in reduction of the water absorption and thickness swelling, which puts the same effect on the produced composite. In fact, it can be said that the water absorption is decreased by acetylation treatment. To explain the possible reason this happens, it can be said that during the acetylation reaction, the hydroxyl groups of the fibers are replaced with hydrophobic acetyl groups in vinyl acetate or acetic anhydride. Such fibers have limited water absorption due to their hydrophobic nature (Rowell 2006; Mohebbi and Hajihassani 2008).

In the acetylation reaction, the hydrophobic acetyl groups in the vinyl acetate gradually replace the hydroxyl groups of the fibers, which will decrease the water absorption due to their hydrophobic nature; therefore, the water absorption and thickness swelling decrease. At the same time, no matter how high the replacement level of the hydrophilic groups of hydroxide (OH) with the acetyl groups is, there will be fewer functional groups to establish bonds with the water molecules. Finally, the result is that the water absorption and thickness swelling will decrease. Thus, increasing the intensity of acetylation treatment will decrease the number of the hydroxyl groups, and significantly reduce the water absorption and thickness swelling (Rowell 2006; Mohebbi and Hajihassani 2008). Increasing the amount of MAPP coupling agent has also caused reduction of the water absorption. The effect of MAPP in reducing the water absorption of the non-acetylated samples is more significant than that of the acetylated samples. Although using MAPP decreased the water absorption in the acetylated samples, this reduction was not of much significance. The MAPP improves wettability of the fibers by polypropylene by reducing surface energy of the wood fibers and also by changing its surface energy to values that are close to that of the polypropylene. The result would be an increase of the adhesion in the intermediate phase of the filler material and polymer matrix material, as well as freeness degree of the polymer matrix material. These two factors increase adhesion of the wood plastic composites that have coupling agent by removing the voids and porosities (Arbelaiz *et al.* 2005). Using the MAPP makes the polar phase (wood fibers) and nonpolar phases (polypropylene) compatible with each other by removing the weak boundary layers. Therefore, adhesion is improved and the voids within the surface of these materials become smaller. This happens while the water absorption is decreased (Demir *et al.* 2006).

Generally, high swelling of the wood composites is attributed to scattering and weak adhesion of the wood particles in the polymer matrix. In the composites, the swelling is decreased by increasing the coupling agent content due to improvement of the compatibility between polymer and wood fibers (Adhikary *et al.* 2008). The thickness swelling will also decrease in the presence of the coupling agent. In fact, the coupling

agent enhances the adhesion between the two materials, and thus improves the dimensional stability (Tjong *et al.* 1999).

The MAPP coupling agent improves adhesion and connection between the fibers and the polymer matrix, while also facilitating the active and strong reactions of hydrogen bonds related to the fibers. The result would be improvement of the connection between nonpolar thermosoft polymer and polar cellulose fibers. This happens by reducing surface tension of the cellulose fibers and approaching to the values of surface tension for the molten polymer. Creation of the connections by the coupling agent agents lowers the frequency of hydrogen bonds between the fibers and facilitates scattering of the fibers within the thermosoft matrix, which improves the adhesion.

Effect of Fungi Treatment on Destruction of Wood Plastic

Having performed the white-rot fungi treatment on the polypropylene/wood composite, it was observed that the percentage of damage caused by the white-rot was much greater. The reason for this is that these fungi first use lignin and then attack cellulose and hemicellulose. Therefore, they provide a greater weight loss in comparison with the control sample.

Effect of Decay on Water Absorption and Thickness Swelling

Comparison of the results obtained from water absorption of the white-rot samples showed that in these samples, a greater water absorption might be seen in the remaining cellulose and hemicellulose, which comprise the greatest volume of the composite fibers after treatment. This is due to a longer exposure time and greater effect of the white-rot fungi, which affects the wood lignin as a hydrophobic material. Thereby, increasing the soaking will add to the water absorption. The interested reader in this regard is referred to the studies conducted by Zabihzadeh *et al.* (2010) and Hosseini hashemi *et al.* (2011), which report almost similar results.

Effect of Coupling Agent on Contact Angle

The results showed that the contact angle became larger with increasing content of the MAPP coupling agent. The contact angle implies surface tension of the samples. When the forces of surface tension in the sample overcome the adhesion forces between the water molecules, the molecules that are located on surface of the sample can absorb the water. The result of this absorption, considering distribution of the water droplets on the surface of the sample or absorption inside the sample, would be reduction of the contact angle (Mohebbi *et al.* 2010).

Once the forces of surface tension are not able to overcome the adhesion forces, the water droplet will keep its spherical shape, which will increase the contact angle. Therefore, in the first case the sample behaves as a hydrophilic material, and in the second case it behaves like a hydrophobic material (Mohebbi *et al.* 2010). The use of MAPP in the wood plastic composites results in a change from hydrophilic to hydrophobic. Therefore, it can be said that increasing of the contact angle in the wood plastic composite can be attributed to efficiency of the MAPP.

Based on these results, the use of the coupling agent intensifies hydrophobic characteristics of the composite and increases the contact angle. The composite is a combination of two different parts: one hydrophilic and one hydrophobic. The wood flour is the hydrophilic part, whereas the polypropylene acts as the hydrophobic part. The wood part has an important role in water absorption and surface tension. Therefore, using the MAPP reduces the number of microcracks in the composite and also the number of hydroxyl groups in the wood side (Lin *et al.* 2002). The hydroxyl groups will actually be

captured somewhere between the wood and the MAPP. Thus, confinement of the hydroxyl groups adds to hydrophobic features of the composite so that the water absorption will decrease and the contact angle will increase. This observation can be attributed to the presence of the free hydroxyl groups in the composite structure. Application of the MAPP reduces the microcracks, which will reduce permeability of the composite in turn and increasing of the contact angle. The results of this research are in agreement with those of Mohebbi *et al.* (2011).

Scanning Electron Microscope

Distribution and compatibility between the fibers and the matrix can be found based on the micrographs obtained from scanning electron microscope (SEM). This section examines fracture surfaces of the generated composite, while also evaluating the effect of coupling agent material on connection of the fibers with the matrix material.

Figures 11 and 12 below depict schematic views from fracture surface of the sample containing 0% and 3% of the MAPP coupling agent. It can be seen that the polypropylene matrix had surrounded the cellulose fibers to a large extent and created a proper adhesion. However, there was still some porosity in spite of the sufficient adhesion (Fig. 11), which tended to decrease as the coupling agent content increased (Fig. 12).

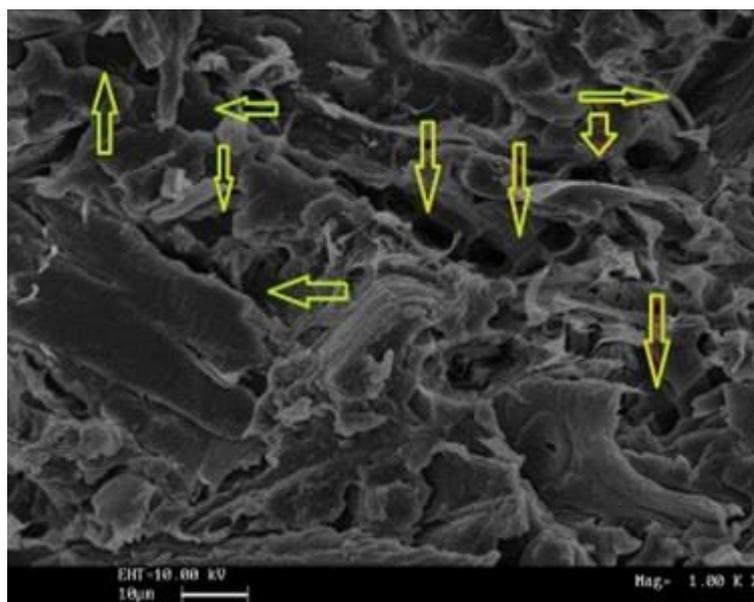


Fig. 11. SEM micrograph of the fracture surfaces in the composites with 0% coupling agent

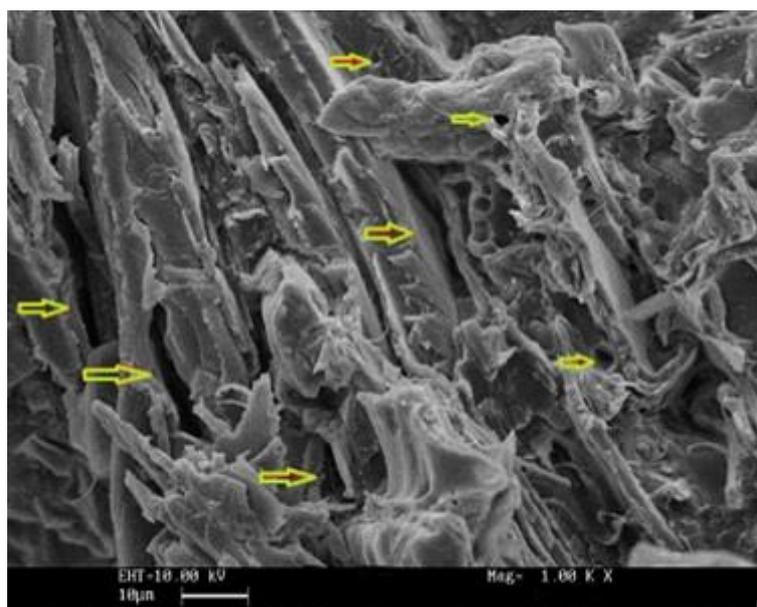


Fig. 12. SEM micrograph of the fracture surfaces in the composites with 3% coupling agent

Figure 13 shows schematic views from the fracture surface of a sample, which contains 6% of the coupling agent material. It can be inferred from this figure that the matrix material surrounds the cellulose fibers and makes a proper adhesion. However, there were some voids and porosity, which implies that a great connection has been established between the matrix and the fibers.

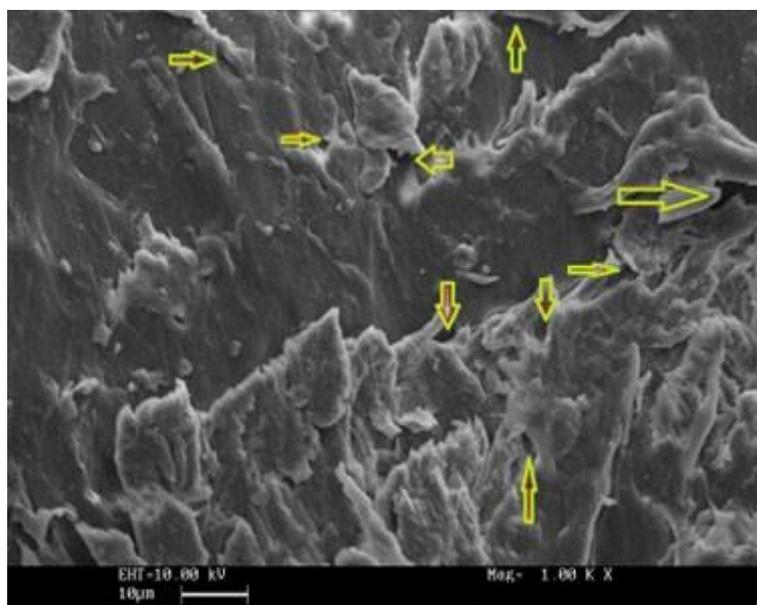


Fig. 13. SEM micrograph of the fracture surfaces in the composites with 6% coupling agent

The effect of the coupling agent material on the interface between cellulose fiber and polymer was studied based on the SEM images. The obtained micrographs implied that an increase of the coupling agent material will increase the connection surface between the cellulose material and the polymer matrix. Simultaneously, stronger connections between the matrix and the cellulose fibers are created, which can be understood from the existing voids and the uniform fracture surface in the composite.

Smaller voids are seen in the samples that contain 6% of the coupling agent, which indicates that the cellulose fibers do not detach the matrix because of the good connection they have.

CONCLUSIONS

1. By reaction of vinyl acetate with fir sawdust flour under experimental conditions of this study, a weight gain of 18.8% was observed.
2. The obtained results showed that increasing of the MAPP coupling agent content reduced the water absorption and thickness swelling in all samples, including decayed and non-decayed ones.
3. The results revealed that the acetylation reduced water absorption and thickness swelling in all the samples.
4. It was shown by the results that the increase of the coupling agent percentage reduced the percentage of weight loss, while the acetylation caused a smaller weight loss in the composite samples.
5. It was shown that an increase of the MAPP coupling agent led to greater contact angles of water. A similar effect on water contact angle resulting from acetylation of the wood flour.
6. The SEM micrographs showed that increasing the coupling agent improved the strength of the bond between the fibers and the polymer material.
7. The positive effect of acetylation was attributable to its role as a compatibilizer.

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Article submitted: Jan 3, 2015; Peer review completed: February 4, 2015; Revised version received and accepted: February 6, 2015; Published: February 10, 2015.