

Response of *Shorea* Species to Drought Stress

Water Absorption Properties of Chemically Modified Sungkai

10

Water Absorption Properties of Chemically Modified Sungkai (*Peronema Canescens*) Wood Fibers in Medium Density Fiberboard

Kang Chiang Liew, Hui Ching Chong and Su Xin Ng

10.1 Getting Started

Chemical modification of wood began in the 1950s and interest in it has since grown. The aim of chemical modification is to increase the biological resistance and enhance the properties of wood, such as dimensional stability. This chemical modification process is non-toxic to humans compared with conventional wood preservatives and biocides (8Hon, 1996). Basically, chemical modification is the chemistry of cell wall polymers being altered, which can change important properties of wood including durability, hardness, dimensional stability, water repellency, thermal properties and UV-stability (13Peydecastaing, 2008). Controlling the moisture content in wood is an effective way to enhance wood durability by protecting it from biological attack, especially fungal attack.

Most fast-growing wood species such as Acacia (*A. mangium*) and Sungkai (*P. canescens*) are prone to deteriorate rapidly under physical and biological influence, especially fungi, due to high moisture sorption. To overcome this problem, the chemical modification of wood appears to be a multi-purpose method that can simultaneously improve wood durability. The chemical modification process involves the formation of covalent bonds with OH groups from cellulose, hemicellulose or lignin. Thus, the chemical nature of wood is changed and its properties can be enhanced. The modification of wood with anhydrides has proved to be efficient in improving dimensional stability.

Chemical modification is widely accepted as one of the effective methods to change wood's properties, including increasing dimension stability. The stability of modified wood brings great interest to environmental changes regarding commercial application of this technology. Chemical modification of wood in order to change its water absorption properties changes wood dimensions as well. 18Rowell (2005b) reported that this is because cell-wall polymers contain hydroxyl and other oxygen-containing groups that will attract water moisture through hydrogen bonding. This uptake of water moisture swells the cell wall and causes the wood to expand. Wood shrinkage occurs as

moisture is lost, and this process is reversible. The low water absorption of wood can decrease the chances of wood defects. Thus, this can decrease the loss of profit in the wood industry because of the wood's good stability.

Chemical modification can change other wood properties aside from water absorption. As well as Acacia, Sungkai was also chosen for this study because it is still a less well known species and more research is needed on it. Currently, there has still been no research carried out regarding the modification of Sungkai wood fiber by using anhydride-based chemicals.

This experiment aimed to investigate the effect of chemically modified wood fibers on the water absorption properties of Acacia and Sungkai Medium Density Fiberboard (MDF). The water absorption properties of wood fibers after chemical modification were investigated through this study to:

- 1) Determine the Weight Percent Gain (WPG) of wood fibers, moisture sorption properties (weight increase rate and thickness change rate) and pH of MDF for Acacia and Sungkai after reacting with 40%, 60%, and 80% (w/w) of Acetic anhydride (AA), Maleic anhydride (MA) and Succinic anhydride (SA);
- 2) Evaluate the relationship between the type and concentration of anhydrides and the water absorption properties of Acacia and Sungkai MDF.

10.2 Modification of Fiber and Testing

10.2.1 Wood Fiber Preparation

A. mangium and *P. canescens* obtained from Sabah Forestry Development Authority (SAFODA) Kinarut Station were used in this experiment. The trees chosen had a diameter at breast height (DBH) in the range of 20–25cm. Using a chainsaw, we cut the logs into billets and debarked them.

Wood fibers were extracted from the whole billet, excluding the bark. First, we reduced the billets to strips and chipped them. The knife flake ring mill was then used to produce the finer wood component of wood fibers by flaking the wood chips. Using a circular screening machine, we obtained <3 mm wood fibers (Figure 10.1) with a moisture content of 4%–8% approximately.

Based on ASTM D 4442-92 (direct moisture content measurement of wood), the wood fibers were stored in individual vapor-tight containers and weighed using a balance consistent with the desired

precision. Scoops of fibers were randomly weighed to get the moisture content, and approximately 60g of wood fiber was put into an oven for 24 hours at $103 \pm 2^\circ\text{C}$. Then, we put the dried fibers in a desiccator with fresh desiccant until they reached room temperature. The whole weighing process was carried out in closed weighing jars. By using Equation 10.1, we calculated the moisture content:

$$\text{MC\%} = (A - B) / B \times 100 \quad (10.1)$$

where

A = original mass, g,

B = oven-dry mass, g.

10.2.2 Chemical modification process

We carried out modifications with AA ($\text{C}_4\text{H}_6\text{O}_3$), MA ($\text{C}_4\text{H}_2\text{O}_3$) and SA ($\text{C}_4\text{H}_4\text{O}_3$) by mixing the anhydride with wood fibers in nine batches for each wood species.

The 60 g of oven-dried samples of wood fibers were oven-dried to a constant weight at $103 \pm 2^\circ\text{C}$. The concentration level of anhydride in the solution was established at 40%, 60% and 80% (w/w), respectively (23Teaca et al., 2014). Then, we refluxed the wood fibers with anhydride for 3 hours based on 3Azeh et al. (2013) with a cooking temperature of $120 \pm 5^\circ\text{C}$ (Figure 10.2).

The ratio amount of the anhydride added to the fiber was 1:5 based on the dry weight of the wood fibers. After the modification process (Figure 10.3), the residues were washed thoroughly with distilled water and then oven-dried for 3 hours (Figure 10.4). The best way to determine the effectiveness of modification was calculated as WPG and this was based on the difference between the oven-dried weight of the test pieces before and after modification (M_1) and after modification (M_2) according to Equation 10.2:

$$\text{WPG (\%)} = \frac{M_2 - M_1}{M_1} \times 100(\%) \quad (10.2)$$

where

M_1 = before modification

M_2 = after modification

10.2.3 Fabrication on Sample Manufacturing

The test piece for a water absorption test for wood-based fibers and particle panel material was 25.4 mm (width) \times 127 mm (length) \times 3 mm (thickness) in dimension, according to ASTM D 1037 – 99, with all four edges smoothly and squarely trimmed. 50g of wood fibers were coated with 72 g of the Urea formaldehyde (UF) (11Li et al., 2009). The coated fibers were manually loaded into a 25.4 mm (width) \times 127 mm (length) \times 3 mm (thickness) aluminum mold (fiber mat), which was then pre-pressed at 0.06 MPa for 10 minutes. Finally, it was pressed into fiberboard using a heat compressor at force 0.5 MPa applied at press temperature of 110°C for 20 minutes (Figure 10.5). The final thickness of the MDF was 3 ± 0.5 mm.

The targeted density was 0.70 g/cm³. The density for each fiberboard panel was obtained by dividing the fiberboard mass (wet basis) by its volume, and it was given as 0.70 g/cm³. The MDF was placed in an oven at 23°C for 2 days for further analysis. Each MDF panel was cut into three rectangular test pieces of 25.4 mm (width) \times 127 mm (length) for a water absorption test.

10.2.4 Water Absorption Test

From the different fiber batches, the test pieces underwent a 24-hour water absorption test. Measurement of the water absorption properties of the test pieces was carried out according to 2ASTM D1037-99 (2000). The 25.4mm \times 127mm test pieces (Figure 10.6) were soaked in water for 24 ± 1 hours at room temperature. Then, the test pieces were conditioned to a constant weight and a temperature of $20 \pm 3^\circ\text{C}$ for 2 days. After that, the test pieces were left to cool in a desiccator for 15 minutes and weighed to the nearest 0.001g. The test pieces were fully immersed in distilled water for 24 hours. Then, the test pieces were removed from the water one at a time, all the surface water on the test pieces was wiped off with a dry cloth, and they were immediately weighed to the nearest 0.001g (Figure 10.7).

Calculation of the percentage change in weight during immersion was carried out using Equation 3. Three replicates were produced for each variable, including the control. A total of 120 replicates with three samples for each concentration value and three non-treated samples for each tree species were produced.

Calculation of percentage changes in weight during immersion was calculated using Equation 10.3:

Weight Increase (WI) Rate (%):

$$\frac{\text{wet weight} - \text{conditioned weight} \times 100\%}{\text{conditioned weight}} \quad (10.3)$$

For water swelling tests, each fiberboard test pieces, each 51 mm × 51 mm, was placed in a container 10 cm × 10 cm square and 5 cm deep (Figure 10.8). Water was added to the container and the thickness recorded as a function of time. Measurements were taken every 5 minutes for the first hour, every hour for the next 6 hours, and then once a day for 5 days based on 14Rowell and Keany (1988). All of the water tests were done in duplicate. Water soaking tests were run on test pieces (51 × 51 mm) as previously described by 16Rowell and Ellis (1978). Each one of three cycles consisted of water soaking for 5 days followed by oven-drying at 103 ± 2°C for 2 days. Thickness of swelling was calculated as a percentage of the original oven-dried thickness. Reconditioning involved oven-drying for 24 hours at 60°C and then 2 weeks of conditioning at 20°C and 65% relative humidity (RH), based on 9Kojima and Suzuki (2010).

10.2.5 Data Collection and Analysis

The water absorption properties (Water Increase Rate, WIR), thickness change (TC) rate: Water Swelling Test and Water Soaking Test and pH of wood fibers were determined and analyzed using SPSS software. A total of 120 replicates were done for the whole experiment (2 species × 3 anhydrides × 3 concentration × 3 replicates × 2 tests + 12 controls). The average mean for each group of water absorption tests was calculated and recorded. The data was analyzed by using two-way ANOVA tests to evaluate the relationship between the anhydride and the concentration of anhydride and the water absorption properties of *A. mangium* and *P. canescens*.

10.3 Experimental Results

10.3.1 Weight Percent Gain (WPG)

The relationship between anhydride types and WPG of treated wood fibers were shown in Figures 10.9 and 10.10. It was found that the WPG values of wood fibers were dependent on wood species, anhydride and anhydride concentration.

It was noticed that the treatment parameter (anhydride: Acetic Anhydride [AA], Maleic Anhydride [MA] and Succinic Anhydride [SA]; anhydride concentration) that performed best in terms of WPG value was 60% of AA. It contributed the highest WPG value for both species: 13.79% for *A. mangium*

and 24.91% for *P. canescens*. The results also showed that 60% was the optimum concentration for both AA and MA. However, 80% was the optimum temperature for SA. The wood fibers of *P. canescens* modified with SA showed a significant increase when the anhydride concentration was increased.

Wood fibers of *P. canescens* showed a higher WPG value than *A. mangium*. The WPG value of wood fibers for *P. canescens* was 21.95% show two times higher than *A. mangium* that only 6.77% for using 80% of SA. The air-dried density range of *A. mangium* (650 kg/m³) is slightly higher than *P. canescens* (640 kg/m³). Of these two species, *A. mangium* has a higher density than *P. canescens*. With the same weight, the volume of *P. canescens* wood fibers was higher than that of *A. mangium*. Stamm (1964) had earlier found that higher density hardwood had greater activation energies. Thus, the wood fibers of *P. canescens* can absorb faster than the wood fibers of *A. mangium*.

MA exhibited a negative value of WPG on the wood fibers after modification. The negative WPG value of MA can be explained by the fact that the action of maleic acid at a high temperature can break down wood macromolecules. This process starts with hemicellulose followed by the amorphous part of cellulose and lignin (Bodirlau et al., 2008). The degradation of hemicellulose to xylose by maleic acid starts at 100°C and ends at 150°C (Lu and Mosier, 2008). Hemicellulose is the least thermally stable wood component due to the presence of the acetyl group (Bourgeois et al., 1989). Rowell (1984) also said that hemicellulose and cellulose polymers are degraded by heat well before lignin. However, there was a single positive value of WPG for the 60% MA for *P. canescens*, as shown in Figure 10.10. This is due to the bigger pores and pore arrangement types of wood fibers for *P. canescens*, which are able to absorb more anhydride and reach the level of WPG. Weight gain in fibers from absorbing chemicals is higher than weight loss, which can cause fiber degradation in the presence of high temperature (120 ± 5°C).

A. mangium wood is diffuse and porous (Krisnawati et al., 2011), *P. canescens* showed well-defined growth rings, featuring ring-porous porosity characteristics (Azim, 2014). Fibers of diffuse-porous for *A. mangium* has vessels and pores that are uniform in size across the entire growth ring. These vessels are usually small, uniform in size and are very difficult to see with the naked eye. However, *P. canescens* has ring-porous; the earlywood and latewood transition occurs abruptly and is

Comment [RC1]: AU: The text "...was 21.95% show two times higher....of SA" is not clear. Do you mean "The WPG value of wood fibres for P. Canescens was 21.95% which is two times higher than A. Mangium and shows that P. Canescens fibers absorb more chemical than A. Manguim fibers"?

Comment [RC2]: AU: We have edited the sentence "Weight gain in fibers..." based on your response to our query. Please check and let us know if we have retained your intended meaning.

very distinct, a band of large earlywood vessels is clearly visible to the naked eye within each growth ring.

10.3.2 Moisture Sorption Determination

Wood fiber is hygroscopic; the hydroxyl groups in the cell wall polymers are attracted and form hydrogen bonds with the moisture in the atmosphere. As water enters the cell wall, the wood volume increases nearly proportionally to the volume of said water (Stamm, 1964). Then, a swelling reaction occurs. Swelling of the wood fiber continues until the cell reaches the Fiber Saturation Point (FSP) and does not undergo any further swelling. Weight Increase Rate (WIR) and Thickness Change Rate (TCR) (water swelling test and water soaking test) were carried out to measure moisture sorption resulting from interaction with water.

10.3.2.1 Weight Increase Rate (WIR)

The obtained modified MDF test piece was subject to a weight increase test based on the examined weight before and after the water swelling test (24 hours' water immersion).

Based on Table 10.1, the analysis of variance for weight increase rate between anhydride types showed a significant difference in WIR at $p \leq 0.05$. The uses of AA to modify the *A. mangium* MDF test piece all showed significantly different values when different anhydride concentrations (40%, 60% and 80%) were used. These show that the concentration of AA has a significant effect on *A. mangium* MDF test pieces, with the lowest water absorption rate (16.28%) of the MDF test piece being reached at 60% (optimum concentration). However, it made no difference to the *P. canescens* MDF piece although the same anhydride (AA) is used. Analyzing the obtained results, it can be said that the treatment of *A. mangium* and *P. canescens* MDF test pieces with all anhydrides and concentrations had significant differences compared to the control (without chemical modification). However, the only result that did not have a significant effect in terms of lowering the weight increase rate was 80% MA. SA showed no difference with AA and MA with the same anhydride concentration, clearly showing in the WIR of 40% of AA, MA and SA for both *A. mangium* and *P. canescens* MDF test pieces.

Based on the obtained results, it has been discovered that acetylation of the fibers has a positive effect in reducing water absorption rates such as WIR. In fact, it can be said that the WIR is decreased by

acetylation treatment. To explain the possible reason why this happens during the acetylation reaction, Rowell (2006) said that the hydrophobic acetyl groups in AA replaced the hydroxyl groups of the wood fibers. So, the fibers have limited water absorption due to their hydrophobic nature. Also, moisture is presumed to be absorbed by MDF test pieces either as primary or secondary water. *Primary water* is water absorbed to primary sites such as the hydroxyl groups with high binding energy. *Secondary water* is water absorbed to sites with less binding energy, where water molecules are absorbed on top of the primary layer. Since some hydroxyl sites of wood cells are esterified with acetyl groups, there are lesser primary sites where water can be absorbed. Also, there may be fewer secondary binding sites since the fibers are more hydrophobic as a result of acetylation.

Figure 10.11 presented the results of the weight increases of chemically-modified MDF test pieces. When weight increase was measured after 24 hours, it was found that there was a progressive increase in weight for all types of anhydride. Chemical modification of an MDF test piece successfully brings down the WIR. The WIR of the non-modified *P. canescens* MDF test piece (control) was so high until it exceeded more than 50% and it was able to decrease to the average 23.18% by using 60% AA.

For wood, water repellency is a rate phenomenon and dimensional stability is an equilibrium phenomenon (Rowell and Banks, 1985). Chemical modification is one water repellent treatment, and it can prevent absorption or slow down the rate that moisture or liquid are taken up by the wood. Thus, the WIR of both *A. mangium* and *P. canescens* MDF pieces were reduced, and the water absorption rate was also slowed down.

10.3.3 Thickness Change Rate (TCR)

Two tests were carried out to determine the TCR of MDF test pieces: a water swelling test (cyclic water swelling test) and a water soaking test (cyclic water soaking and oven-drying test).

10.3.3.1 Water Swelling Test

The obtained modified MDF was subjected to water swelling test investigation. The rate and extent of thickness swelling of *A. mangium* and *P. canescens* MDF test pieces in water was shown in Figure 10.12 and 10.13.

During the first 60 minutes, MDF test pieces made from 80% MA modified fibers and the control swelled faster than others for *A. mangium* MDF test pieces, and both had almost the same TCR for the

first 6 hours. The observed lowest value of the TCR was 60% AA MDF for both species, which were 1.7%–2.31% for *A. mangium* MDF and 3.5%–4.07% for *P. canescens* MDF test pieces by the end of the first 60 minutes. This trend continued through 6 hours of water swelling, but at the end of 5 days, both control pieces of *A. mangium* and *P. canescens* MDF exhibited dramatic swelling compared to the other pieces with modified MDF. It shows that chemically modified MDF test pieces show an obvious decrease in TCR for both MDF pieces. The TRC of 80% MA MDF test pieces, which was almost same as control pieces during the first 6 hours, slowed down after 24 hours and in the rate and extend of 9%–11.5%.

The TCR data of the *A. mangium* and *P. canescens* MDF test pieces for various anhydrides (AA, MA and SA) and concentrations (40%, 60% and 80%) was analyzed. The analysis of the thickness change of the MDF test pieces revealed a significant lowering of TCR in the *A. mangium* and *P. canescens* MDF test pieces with various anhydrides and concentrations compared with the control test piece. However, there were still a few MDF test pieces that did not show a significant difference with control: the test piece of 40% MA at first 10 min, the piece of 80% MA at first 1–3 hours for *A. mangium* and the piece of 80% SA at first 40 min for *P. canescens*.

Overall, the TCR data of both non-chemically modified and chemically modified MDF test pieces of *P. canescens* was higher than *A. mangium*. Of these two species, *A. mangium* has higher density than *P. canescens*. The higher density hardwood had greater activation energies, as Stamm had found earlier in 1964. Thus, *P. canescens* swells faster than *A. mangium*. The rate of swelling of wood in water is dependent on several factors: hydrogen bonding ability, molecular size of the reagent, extractives content, temperature, and test piece size (5Banks and West, 1989). There is an initial induction period due to the diffusion of water into the cell wall structure, and water then penetrates the cell wall capillaries and moves from lumen to lumen in the direction of the fiber.

The swelling that occurs in wood composites is much greater than in wood itself. This is due to the release of compressive forces as well as normal wood swelling (17Rowell, 2005a). The compressive forces are a result of the physical compression of the wood elements during pressing of the board such as cold pressing and hot pressing. A dimensional stability treatment is one that reduces or prevents swelling in wood no matter how much time it is in contact with moisture or liquid water. Chemical

Comment [RC3]: AU: We changed “until” to “for” “...TRC for the first 6 hours.” Please confirm meaning retained.

Comment [RC4]: AU: We changed “at” to “by the end of the” in “...test pienes by the end of the fi 60 minutes.” Please confirm meaning retained.

Comment [RC5]: AU: We have edited the text “... at the end of 5 days...” based on your reponse to our query. Please confirm if intended meaning was retained.

Comment [RC6]: AU: Please review the sentence “The TRC of 80%.....”. We have edited based on y response to our query, however the second part the sentence “...slowered down after 24 hours...” unclear. Please clarify.

modification is also a dimensional stability treatment. Examples of other dimensional stability treatments are penetrating polymers, cross-linking cell wall polymers, bulking the cell wall with polyethylene glycol, or using bonded cell wall chemicals (20Rowell and Youngs, 1981).

10.3.3.2 Water Soaking Test (WST)

The thickness change analysis done for the *A. mangium* and *P. canescens* MDF test pieces showed significant differences for the control and the chemically modified MDF test pieces. The range of thickness change for the cyclic water soaking of *A. mangium* was 3–4% for the control MDF and reduced to less than 2% for modified MDF. However, the MDF test pieces of *P. Canescens* decreased from 4%–5% (control) to less than 3% (modified) for the thickness increase range. Anhydrides successfully controlled changes in thickness for the MDF test pieces; however, the trend still increased after oven drying. This means that it was not possible to bring MDF test pieces back to their original thickness even if they were re-dried in the oven for 2 days. Reversible swelling (cyclic water soaking test 2 [C2] – Oven-drying 1 [OD1] and C3 – OD2). which is normal wood cell-wall swelling, was much greater in the control MDF test pieces, being about 9.76%–12.8% for MDF made from *A. mangium* fibers and about 13.97–17.45% for MDF made from *P. canescens* fibers. It reduced to 3.71%–3.98% for 60% acetylated MDF made from *A. mangium* fibers and about 5% for 60% acetylated MDF made from *P. canescens* fibers.

The TCR of 60% acetylated MDF made from *A.mangium* fibers was 5.03% at a WPG of 13.79, and for MDF made from *P. canescens* fibers, it was 7.24% after a 5-day water soaking test. As a result of acetylation, the rate and extent of thickness swelling in the control MDF at the same level of acetylation is greatly reduced. At the end of 5 days of soaking, the control MDF test pieces for *A. mangium* fibers swelled by 13.51% and the control MDF test pieces for *P. canescens* fibers swelled by 19.83%, whereas MDF made from acetylated fibers swelled less than 8.48% percent for *A. mangium* MDF test pieces and reduced by 12.59% for *P. canescens* MDF test pieces. AA was the most efficient anhydride compared to MA and SA, shown by comparing the results of using the same concentration of all anhydrides. The control MDF test pieces exhibited a greater degree of irreversible swelling compared to the MDF test pieces made from acetylated fibers after drying at the end of the

test. Rowell (2006) said that the mechanism of dimensional stability or low TCR resulting from acetylation is a result of the bulking of the bonded acetyl groups in the cell wall polymer hydroxyl groups. Only a little swelling can occur when water enters wood because the volume of the cell wall is swollen to near the original green volume of the wood. Acetylated MDF test pieces can absorb water through capillary action and to some extent in the cell wall. Some swelling can occur in “completely acetylated wood” since water molecules are smaller than those of the acetyl group in wood cell wall, but swelling does not exceed the elastic limit of the cell wall.

Thickness changes in the cyclic water soaking/oven-drying test of *A. mangium* and *P. canescens* MDF test pieces with various anhydrides and concentrations are shown in Figures 10.14 and 10.15. There was increasing thickness in every subsequent cycle of both *A. mangium* and *P. canescens* MDF test pieces. Irreversible swelling caused by the release of residual compressive stresses imparted during board pressing during MDF production was greatest in the control MDF test pieces and lowest in the acetic-anhydride-reacted boards.

Both reversible and irreversible swelling took place (Rowell, 2005a). The release of compressive stresses imparted during board pressing and during the first wetting of composites is also known as *irreversible* swelling. It is known as irreversible swelling because it is not reversible upon re-drying. *Reversible* swelling also occurs during wetting and wood shrinks again as a result of re-drying. Irreversible swelling and reversible swelling were greatest in the control MDF pieces and lowest in the MDF test pieces treated with 60% of acetic anhydride. Rowell et al. (1991) also found that acetic-anhydride-reacted boards showed the lowest irreversible swelling and reversible swelling value. All the MDF test pieces showed an increase in permanent thickness swelling. Permanent swelling was probably caused by adhesive failures resulting from test conditions.

Drying (oven-drying) and rewetting (cyclic water soaking) causes an increase in both the rate of swelling and the extent of swelling (Rowell, 2005a). The degradation and extraction of hemicelluloses and extractives as well as some degradation of the cell wall structure during wetting, drying, rewetting and re-drying cycles results in the cell wall being more accessible to water. A significant amount of cell wall polymers can be lost when wood is exposed to high relative humidity

in repeated cycles. Although no cell wall polymers are extracted, repeated humidity cycles result in a slight increase in moisture content with each cycle.

10.3.4 pH

The MDF test pieces were immersed in water for 24 hours and the pH values are presented in Table 10.2. According to the analysis of variance for pH between anhydride types, there was a significant difference in pH value at $p \leq 0.05$. Acid anhydrides are molecules that form acidic solutions in water, and acid anhydrides are the oxides of non-metals that can react with water. Basically, the three acid anhydrides (“acids without water”) used for this study had acid properties and exerted an influence on *A.mangium*, changing the alkali (pH >7) properties of *A.mangium* to become acidic (pH <7). Significant differences were caused by using different concentrations of the same anhydride and also the same concentration but different anhydrides. The uses of higher concentrations of anhydride result in greater changes in pH scale. This clearly shows in the effect of MA on the *A.mangium* MDF test pieces, which had a pH of 6.37 for 40% concentration, which then decreased to a pH of 6.28 (60%) and then pH 6.12 (80%). These prove that MA had the highest acidic properties among the three anhydrides.

Comment [A7]: AU: The sentence “Basically, the three acid...” has been edited. Please confirm your intended meaning has been retained.

10.4 Conclusions

Modification of the wood fibers of Acacia and Sungka by using chemical anhydrides (AA, MA, and SA) has a significant effect on WPG. MDF pieces made from chemically modified fibers were slightly denser and have lower water absorption properties, lower weight increase rate (WIR) and lower thickness change rate (TCR) than MDF made from unmodified fibers.

The effectiveness degree of wood modified percentage was determined using WPG, and there was relationship between WPG and moisture sorption rate. Usually, a higher WPG of wood fibers results in lower moisture sorption uptake. However, this still depends on the type of anhydrides used. The treatment parameter (anhydride type, anhydride concentration) that performed best in terms of WPG value was 60% of AA. It contributed the highest WPG value for both Acacia and Sungkai wood species, with 13.79% for Acacia and 24.91% for Sungkai. The WIR of the non-modified Sungkai MDF test piece increased until it exceeded more than 50% of the weight for the test piece, but it decreased to an average 23.18% using 60% AA.

Comment [RC8]: AU: The sentence “The WIR of the...” has been edited. Please check if we have retained intended meaning.

The rate and extent of swelling in liquid water and water vapor were much greater in unmodified MDF test pieces than in chemically modified MDF test pieces. The observed lowest values of thickness change rate were in the 60% AA MDF test pieces for both species, which was 1.7%–2.31% for Acacia MDF test pieces and 3.5–4.07% for Sungkai MDF test pieces after the first 60 minutes. This trend continued through 6 hours of water swelling, but at the end of 5 days, the swelling of both unmodified Acacia and Sungkai MDF test pieces increased dramatically more than the modified MDF. The range of thickness change for the cyclic water soaking of Acacia was 3%–4% for unmodified MDF test pieces and reduced to less than 2% for modified MDF. However, MDF test pieces of Sungkai (unmodified) decreased from 4%–5% to less than 3% (modified) for the thickness increase range. AA is the best anhydride among the three anhydrides and it has significant effect in terms of slowing down or preventing moisture sorption. MDF modified by AA showed the lowest WIR and thickness change (TC).

References

2. ASTM D1037-99 2000. Standard test methods for evaluating properties of wood-base fiber and particle panel materials.
1. ASTM D 4442-92 2003. Standard test methods for direct moisture content measurement of wood and wood-base materials.
3. Azeh, Y., Olatunji, G. A., Mohammed, C., and Mamza, P. A. 2013. Acetylation of wood flour from four wood species grown in Nigeria using vinegar and acetic anhydride. *International Journal of Carbohydrate Chemistry*, 2013(141034): 6.
4. Azim, A. A. A. 2014. Growth ring formation of selected tropical rainforest trees in peninsular Malaysia. <https://doi.org/10.14989/doctor.k18338>
5. Banks, W. B., and West, H. 1989. A chemical kinetics approach to the process of wood swelling. In: Schuerch, C. (ed.), *Proc. Tenth Cellul Conf.*, John Wiley & Sons, New York.
6. Bodirlau, R., Teaca, C. A., Resmerita, A. M., and Spiridon, I. 2008. Chemical modification of beech wood: Effect on thermal stability. *Bioresource Technology*, 3(3): 789–800.
7. Bourgeois, J., Bartholin, M. C., and Guyonnet, R. 1989. Thermal treatment of wood: Analysis of the obtained product. *Wood Science and Technology*, 23(4): 303–310.
8. Hon, D. N. S. 1996. *Chemical Modification of Lignocellulosic Materials*, Marcel Dekker Inc, New York.
9. Kojima, Y., and Suzuki, S. 2010. Evaluating the durability of wood-based panels using internal bond strength results from accelerated aging treatments. *Journal of Wood Science*, 57(1): 7–13.

Comment [AR9]: AU: Please provide the complete details for reference 'ASTM D1037-99, 2000; ASTM D 4442-92, 2003'.

10. Krisnawati, H., Kallio, M. H., and Kanninen, M. 2011. *Acacia Mangium Willd.: Ecology, Silviculture and Productivity*, CIFOR.
11. Li, X., Li, Y., Zhong, Z., Wang, D., Ratto, J. A., Sheng, K., and Sun, X. S. 2009. Mechanical and water soaking properties of medium density fiberboard with wood fiber and soybean protein adhesive. *Bioresource Technology*, 100(14): 3556–3562.
12. Lu, Y., and Mosier, N. S. 2008. Kinetic modelling analysis of maleic acid-catalyzed hemicellulose in corn stover. *Biotechnology and Bioengineering*, 101(6): 1170–1181.
13. Peydecastaing, J. 2008. Chemical modification of wood by mixed anhydrides (Doctoral dissertation), Université de Toulouse.
21. Rowell, R. M. 1984. *The Chemistry of Solid Wood*, Advance in Chemistry Series No. 207, American Chemical Society, Washington, DC.
17. Rowell, R. M. 2005a. Moisture properties. In: Rowell, R. M. (ed.), *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Inc, Boca Raton, FL, Ch 4.
18. Rowell, R. M. 2005b. 14 chemical modification of wood. In: *Handbook of Wood Chemistry and Wood Composites*. p. 381.
19. Rowell, R. M. 2006. Acetylation of wood: Journey from analytical technique to commercial reality. *Forest Products Journal*, 56(9): 4–12.
15. Rowell, R. M., and Banks, W. B. 1985. Water repellency and dimensional stability of wood. USDA Forest Service General Technical Report FPL 50. Forest Products Laboratory, Madison, WI.
16. Rowell, R. M., and Ellis, W. D. 1978. Determination of the dimensional stability of wood using the water soak method. *Wood and Fiber Science*, 10(2): 104–111.
14. Rowell, R. M., and Keany, F. M. 1988. Fiberboards made from acetylated bagasse fiber. *Wood and Fiber Science*, 23(1): 15–22.
20. Rowell, R. M., and Youngs, R. L. 1981. Dimensional stabilization of wood in use. USDA Forest Serv. Res. Note. FPL-0243. Forest Products Laboratory, Madison, WI.
2525. Rowell, R.M., Youngquist, J.A., Rowell, J.S., and Hyatt, J.A. 1991. Dimensional stability of Aspen fiberboard made from acetylated fiber. *Wood and Fiber Science*, 23(4): 558–566.
22. Stamm, A. J. 1964. *Wood and Cellulose Science*. The Ronald Press Company, New York.
23. Teaca, C. A., Bodirlau, R., and Spiridon, I. 2014. Maleic anhydride treatment of softwood—effect on wood structure and properties. *Cellulose Chemistry and Technology*, 48(9–10): 863–868.
- 10.1 Figure 10.1 (a) Circular screening machine, (b) < 3mm screened wood fiber.
- 10.2 Figure 10.2 Set-up for chemical modification process.
- 10.3 Figure 10.3 Wood fibers were cooked with chemicals at $120 \pm 5^\circ\text{C}$ for 3 hours.
- 10.4 Figure 10.4 Dry look of three types of chemically modified wood fibers (a: *A. mangium*; b: *P. canescens*).

Comment [AR10]: AU: Please provide the editor names and publisher details for reference 'Rowell (2005b)'.

10.5Figure 10.5 Heat compressor machine: (a) the dimension required was marked by marker on the MDF; (b) (Left): Test piece for water swelling test and water soaking test, (Right): Test piece for water absorption test).

10.6Figure 10.6 Test pieces (a) of three chemical types for water absorption, thickness swelling and pH. Test pieces (b) ready for water swelling and soaking test.

10.7Figure 10.7 Test pieces were tied with iron wire to keep the gap or distance between another two test pieces (a). Then, the test pieces were fully immersed in distilled water for 24 hours (b).

10.8Figure 10.8 Test pieces for water swelling and water soaking test (a). Then, test pieces were fully immersed in the distilled water for 5 days (b).

10.9Figure 10.9 Weight percent gain (%) of wood fiber for *A. mangium*.

10.10Figure 10.10 Weight percent gain (%) of wood fiber for *P. canescens*.

10.11Figure 10.11 WIR of test piece for water absorption test of *A. mangium* and *P. canescens*.

10.12Figure 10.12 Thickness change rate (%) of *A. mangium* MDF test pieces for water swelling test.

10.13Figure 10.13 Thickness change rate (%) of *P. canescens* MDF test pieces (for water swelling test).

10.14Figure 10.14 Cyclic water soaking/oven-drying test of *A.mangium* MDF test pieces.

10.15Figure 10.15 Cyclic water soaking/oven-drying test of *P.canescens* MDF test pieces.

10.1Table 10.1 Weight Increase Rate of MDF Test Piece for Water Absorption Test of *A. mangium* and *P. canescens*

Different Concentration of Chemical	<i>A. mangium</i>	<i>P. canescens</i>
Control (without anhydride)	30.24 ^a _w ± 1.3668	54.21 ^a _w ± 6.0632
Acetic Anhydride	22.02 ^b _x ± 1.4683	27.20 ^{bc} _x ± 2.6493
40%		
60%	16.28 ^c _x ± 0.3176	23.18 ^{cd} _x ± 1.4367
80%	19.82 ^d _x ± 1.1389	29.39 ^{db} _x ± 0.4267
Maleic Anhydride	27.1 ^{bc} _{yw} ± 0.4073	37.2 ^{bc} _y ± 1.7246
40%		
60%	25.22 ^c _y ± 1.8196	35.18 ^{cd} _y ± 0.8901
80%	28.72 ^{ab} _y ± 2.1855	40.39 ^{db} _y ± 0.5050
Succinic Anhydride	24.58 ^{bc} _{zxy} ± 0.4073	33.16 ^{bc} _{zxy} ± 0.9933
40%		
60%	23.55 ^{cd} _{zy} ± 1.8196	32.01 ^{cd} _{zy} ± 2.0845
80%	23.02 ^{db} _{zw} ± 2.1855	29.79 ^{db} _{zx} ± 3.0260

*Note: Values are mean ± standard deviation.

Value in the same column with different letters (a, b, c, d) within a column (for each anhydride concentration) indicates a significant difference at $p \leq 0.05$ for each different weight increase rate of *A. mangium* and *P. canescens* MDF.

Value in the same column with different letters (w, x, y, z) within a column (for each anhydride) indicates a significant difference at $p \leq 0.05$ for each different weight increase rate of *A. mangium* and *P. canescens* MDF.

10.2Table 10.2 pH Value of *A. mangium* and *P. canescens* MDF after Immersion in Water for 24 hours

Different Concentration of Chemical	<i>A. mangium</i>	<i>P. canescens</i>
Control (without anhydride)	$8.14^a_w \pm 0.0100$	$7.13^a_w \pm 0.03606$
Acetic Anhydride	$6.87^b_x \pm 0.0264$	$6.50^{bc}_x \pm 0.0458$
40%		
60%	$6.71^c_x \pm 0.0360$	$6.44^{cd}_x \pm 0.0360$
80%	$6.48^d_x \pm 0.0458$	$6.41^d_x \pm 0.0173$
Maleic Anhydride	$6.37^{bc}_y \pm 1.7490$	$6.17^b_y \pm 0.0173$
40%		
60%	$6.28^{cd}_y \pm 0.0264$	$6.02^c_y \pm 0.0300$
80%	$6.12^{db}_y \pm 0.0458$	$5.91^d_y \pm 0.0100$
Succinic Anhydride	$6.85^b_{zx} \pm 0.0264$	$6.22^{bc}_{zy} \pm 0.0360$
40%		
60%	$6.72^c_{zx} \pm 0.0264$	$6.19^c_z \pm 0.0360$
80%	$5.91^d_z \pm 0.0200$	$6.03^d_z \pm 0.0264$

*Note: Values are mean \pm standard deviation.

Value in the same column with different letters (a, b, c, d) within a column (for each anhydrides concentration) indicates a significant difference at $p \leq 0.05$ for each different pH value of *A. mangium* and *P. canescens* MDF.

Value in the same column with different letters (w, x, y, z) within a column (for each anhydride) indicates a significant difference at $p \leq 0.05$ for each different pH value of *A. mangium* and *P. canescens* MDF.