WATER ABSORPTION AND CURING TIME PERFORMANCE OF UREA FORMALDEHYDE RESIN MIXED WITH DIFFERENT AMOUNT OF PHOSPHOROUS-BASED FIRE RETARANTS

[1]Izran Kamal, [2]Zaidon Ashaari, [1]Abdul Rashid Abdul Malek, [2]Faizah Abood, [1]Mohamad Jani Saad, [1]Suffian Misran, [1]Rafeadah Rusli & Mohd. Zharif Thirmizir

[1]Forest Research Institute Malaysia
Kepong, 52109, Selangor, Malaysia
[2]Faculty of Forestry
Universiti Putra Malaysia, 43400 Serdang Selangor, Malaysia

ABSTRACT. *The curing time and the properties of urea formaldehyde (UF) resin mixed with fire retardants, BP (mixture of boric acid, guanylurea phosphate and phosphoric acid), monoammonium phosphate (MAP) and diammonium phosphate (DAP) were studied. There were two amounts used, 8% w/w and 10% w/w. The curing time of the mixed resin was determined by using thermo oil at the temperature of 170ºC. Water absorption test and physical observations were done to evaluate the properties of the fire retardant-mixed resin. The non-fire retardant UF resin samples were used as controls. The solubility of MAP and DAP in the water at different weights also has been studied. The solubility test was done with and without the involvement of heat. The study showed that UF resin mixed with MAP and BP cured faster than DAP-mixed UF and control samples. The time taken for UF resin to mix with 10 % w/w and 8 % w/w MAP were 20 s and 28 s respectively. The time taken for UF resin mixed with 10 % and 8 % w/w DAP was slightly than the controls, which are 160 s and 150 s respectively. The time taken for UF resin mixed with 10 % w/w and 8 % w/w BP was 101 s and 92 s respectively.The curing time for control samples was 140 s respectively. MAP and DAP were shown to be highly soluble, as they took less than 1 minute to be dissolved in the water without heat, but BP took 30 minutes to be dissolved in the water without heat and less than 1 minute with heat. Water absorption test showed that the higher the amount of MAP, DAP and BP mixed into the resin, the higher would be the rate of water absorbed.*

KEYWORDS. *Monoammonium phosphate, diammonium phosphate, boron-phosphorous-based, solubility, gelation time*

INTRODUCTION

Fire retardants used in this research are BP® (mixture of 27-33 % boric acid, 67-73 % guanylurea phosphate and 0.0-4.2 % phosphoric acid), monoammonium phosphate (MAP) and DAP (diammonium phosphate). MAP and DAP are two of the most popular fire retardants which usually used in producing fire retardant-treated panels. Besides of being used as fire retardants, DAP is alkaline (pH 7.2-8.0) and MAP is acidic (pH 3.5-4.5) in nature and usually used as fertilisers to increase or reduce the pH of soils (Anon, 2009a;Anon,2009b). BP® is one of the latest fire retardants in the world (Anon, 1991). BP is known as a fire retardant with high molecular, very limited solubility and has a good stability in higher temperature (Anon, 1991). Based on previous research done by (Izran *et al.*, 2008), pH of BP is weak acid with pH 6. In producing panel products, the alkalinity and acidity of those fire retardants may cause problems, especially when the resins used are pH sensitive.

The use of urea formaldehyde resin as a major adhesive by the forest products is due to many advantages it has. The advantages are low cost, ease of use under a wide variety of curing conditions, low cure temperature, water solubility, and resistance to microorganisms and to abrasion, hardness, and excellent thermal properties (Anthony, 1999). However, DAP, MAP and BP may affect the curing time of the resin in manufacturing particleboard as UF resin is sensitive to either alkalinity or acidity (Zaidon *et al.*, 2004). Gelation time of the resin used for particleboard fabrication seemed very important to help researchers to calculate sufficient hot pressing time for particleboard that will be fabricated. The method of observing the gelation time was implemented by Zaidon et al (2004), Zaidon et al (2007) and Zaidon et al (2008). Calculation of sufficient hot pressing period through curing time is essential as insufficient hot pressing may cause adverse effects to the panels produced. It has been found that the increment of pH of urea formaldehyde, obviously affected the shear strength of wood. He also found that the glueline failure of UF increased with pH value (Freemen, 1959). In this study, the gelation time method was used to observe the effects of the phosphorous-based fire retardants to the gelation time of UF resin. It is expected that the study can provide useful information which can helps other researchers to do further research in order to overcome adverse effects that may happen when mixing urea formaldehyde resin with MAP, DAP and BP®.

MATERIALS AND METHODS

Curing time test

The curing test was done in order to determine the curing time of urea formaldehyde as it mix with fire retardants. This test is essential as it helps the researcher to calculate sufficient pressing time for panel product such as particle board mixed with fire retardant during hot pressing process. This method was implemented from Zaidon et al (2004), Zaidon et al (2007) and Zaidon et al (2008).

BP®, MAP and DAP were obtained from Fire Protection Laboratory, Forest Research Institute Malaysia and EuroScience Sdn Bhd. Urea formaldehyde resin was obtained from Malayan Adhesive Chemicals Sdn. Bhd. The mixtures of fire retardants and UF resin later will be used as a binder to produce fire retardant–treated particle board with density 700 kg/m^3. Based on the calculation made, 193 g of UF resin, 29 g hardener and 17 g are required to produce the 700 kg/m^3 particle board. The ingredients (urea formaldehyde, hardener (ammonium chloride) and wax were then mixed and divided into two portions, one portion was mixed with 10 % w/w fire retardant and another portion was mixed with 8 % w/ w fire retardant. The mixture was stirred using glass rod until they mixed well and the pH of each mixture was determined using Whatman Full Range PH Determination Paper. 10 ml of the mixtures was poured into the test tubes and at the same time, 600 ml thermo oil was heated in a beaker until it reached 170ºC. The temperature of the thermo oil was measured by soaking the tip of the Temperature Detector into the thermo oil.

Once the temperature of the resin reached 170ºC, the test tube filled with the mixture was soaked into the hot thermo oil and the time taken for the mixture to cure was recorded. After the mixture has cured, the mixture was taken out from the thermo oil and was left for 5 minutes at ambient temperature, so that the cured mixture can easily be taken out from the test tube. Before the properties of the mixture were observed, it was labelled. Then, the cured mixture was weighed to obtain the green weight and were kept in the oven at $^+$-105º C for a day / until it achieves constant oven-dry weight. The data of green and oven-dry weight is essential to know the moisture content of the samples. Ten replicates were produced for the test.

Solubility Test

A solubility test has been conducted to study the solubility of the fire retardants in the water with the involvement of heat or otherwise. The information on the solubility of the fire retardants will be really helpful to the readers, who have intention to use the chemical in liquid form. According to Anon (2009a), MAP and DAP are high soluble fire retardants with solubility 90% to 100 %. However, for BP®, the previous research revealed that BP® has a very limited solubility (Anon, 1991). The method was implemented and modified from Anon (2007)

Solubility with and without heat

Two hundred ml of water was heated in a beaker until it reaches 100ºC. The temperature was determined using Temperature Detector. Then, 20cm^3 of fire retardant (to establish 10% concentration solution) and 18 cm^3 (to establish 8% concentration solution) were poured into the hot water and stirred using glass rod. The time taken for the fire retardant to achieve ultimate solubility was determined by using stopwatch and the pH of the solution was obtained using Whatman Full Range PH Determination Paper. The same procedure was used as above for solubility test without heat, but the water was not heated before the fire retardant was poured in. The temperature of the water was 27ºC – 30 ºC.

Water Absorption Test

Water absorption test also was done to the cured fire retardant-mixed UF resin to determine the hygroscopicity of the mixture when exposed to the water. At the same time, the results of water absorption test will be used to evaluate the effect of chosen fire retardants to the strength of the cured resin. The samples from each mixture were placed into the oven at a temperature of ±105ºC for 24 hours or as they achieved constant oven dry weight. The samples used were the same samples produced from curing time test. The samples then were put into the dessicator for 30 minutes and re-weighed for oven dry weight. After that, the re-weighed samples were left soaked in a beaker of water for 24 hours. On the next day, the samples were taken out from the water; dabbed dry and re-weighed once again to get wet weight.

The percentage of water absorbed (WA) was calculated by using Eq. 1.1 (Anon, 2009):

$$WA\ (\%) = WW - OW / OW \times 100\ \% \qquad (1.1)$$

Where,

WA : Water absorbed (%)
WW : Wet weight (g)
OW : Oven dry weight (g)

RESULTS AND DISCUSSION

Curing Time Test

The average time taken for 8% w/w MAP-mixed resin and DAP-mixed resin to cure was 28 seconds and 92 seconds respectively. The pH of MAP-mixed resin was 5 and DAP-

mixed resin was 8. The average time taken for 10 % w/w MAP- mixed resin, BP®- mixed resin and DAP-mixed resin to cure was 20 seconds, 101 seconds and 160 seconds, with pH of the mixtures were 4, 6 and 9 respectively. As for control samples, the average curing time was 140 seconds and the pH was neutral. The results showed that as the amount of MAP and BP® added into the resin was increased, the curing time was shorter and the pH was lower. Longer curing time and higher pH value were recorded as the amount of DAP added into the resin was increased. This confirmed that the acid based resin, UF cure faster with the decrement of pH value and it shows that fire retardant added into the resin affected the curing time and pH of the resin (refer to table 1).

Table 1 Table shows the curing time and pH of BP®-mixed, MAP-mixed, DAP-mixed and control samples

Samples	pH	Water Absorption (%) ± S.D	Curing Time (s)
MAP 10 %	4	86.29 ± 5.00	20
MAP 8 %	5	162.22 ± 5.00	28
DAP 10 %	9	69.04 ± 6.00	160
DAP 8 %	8	31.86 ± 6.37	150
BP ®10%	6	21.89 ± 4.21	101
BP ®8%	6	21.41 ± 4.00	92
Control	7	202.77 ± 4.00	140

The alkalinity of DAP lengthen the curing time, the acidity of BP® and MAP shorten it. However, it was also expected that the curing time affected by the ammonium chloride added into the resin as a hardener during mixing process. It was well known that the effect of NH_4Cl on UF resin curing is to release H^+ by reacting with free formaldehyde, and then H^+ reacts with OH^- to forms water. The releases of H^+ reduced the pH of the resin; hence make it cure faster (Xing *et al.,* 2006). Therefore, further research can be done to investigate the curing time of DAP and MAP-mixed UF resin without the addition of ammonium chloride as a hardener.

Solubility Test

The average time recorded to dilute 8 % w/w MAP into a beaker of water without heat was 20 seconds. Longer dilution time was recorded as the amount of MAP added increased to 10 % w/w, which was 30 seconds. When heat was applied during the dilution process, the dilution was within 10 seconds for both amounts. For DAP, without application of heat, the chemical was so easily diluted for both amounts within 5 seconds. Different results were obtained for BP®. The chemical started to dilute at the temperature of 70º C and it took 14 seconds to be completely diluted for both amount when the temperature reached 100º C.

Water Absorption Test

The average percentage of water absorbed for the samples that have been mixed with 10% w/w MAP, BP® and DAP is 202.77%, 31.86% and 162.22% respectively. Average water absorption value recorded for resin mixed with 8 % w/w MAP, BP® and DAP is 86.29%, 21.89% and 69.04 %. For control samples lower average value was recorded, that is 21.41% (refer to Table. 1). Between the three fire retardants, DAP was found to be the most active fire retardant in increasing the moisture uptake of the resin, followed with MAP and BP®. Currently, there is still no research on water absorption of fire retardant-mixed UF resin can be found to be used as a comparison for this study.

It has been mentioned by Anthony (1996) that urea formaldehyde is a material which is highly hygroscopic. Therefore, the moisture absorption results summarized in the table

above were also affected by the hygroscopic property of the resin. However, based on comparisons made between mixed and control samples; it is clearly shown that MAP, BP and DAP triggered the moisture uptake of the resin. MAP and DAP themselves are naturally chemicals with high hygroscopicity. This was confirmed by Izran et al (2008) and Abdul Rashid et al (1990). They treated particle boards with both phosphorous-based fire retardants (MAP and DAP) and found out that those fire retardants increased the water absorption of the treated particle boards. The water absorption increased when higher amount of MAP, BP® and DAP was used. Bendtsen (1998) treated solid wood with MAP and DAP and it was also found that the fire retardants increased the water absorption of the solid wood.

The results of water absorption recorded for BP® above was contradicted with Izran et al (2008). In his research, he found that BP®-treated particle boards have the highest water absorption value compared to MAP and DAP-treated particle boards. This might be caused the amount of BP® existed in the particle boards is lower than the amount mixed into the resin. Boric acid exists in the formulation of BP® is the key factor in increasing the water absorption ability of the chemical. However, this component cans easily volatize to the surrounding from the sample together with water vapour. It was studied that, different amount of boric acid volatizes at different temperature (Zaidon, 1995). The temperature used for hot pressing BP®-treated particle boards was 180ºC, which is 10ºC higher than the temperature used during the curing time test. This might be the cause that increases the volatilisation of boric from the particle board, compared to the resin, thus created different water absorption rate of both mediums.

All three fire retardant-mixed resin and controls produced odour which minorly irritate the breathing system and cause skin itchiness. This might be caused by the existence of urea in the resin and also in the fire retardants (Anthony, 1996 and Anon,2009a). This is based on the 'pee-like' smell produced during the curing time test.

CONCLUSIONS

MAP, BP® and DAP affected the curing time and water absorption of UF resin. The higher the amount of fire retardant used the higher would be the amount of the water absorbed. However for the curing time test, MAP shortened the curing times but DAP lengthened it. Modification of the resin formulation is crucial to make the resin more stable, even after mixed with MAP, BP® and DAP, because shorter and longer curing time will not only affect the strength of the final products, but it also will affect the production cost and time. Modification can be made on the pH of the resin prior to the addition of fire retardants.

REFERENCES

Abdul Rashid, A. M & Chew, L. T. 1990. Fire retardant treated chipboards, In.*Preproceedings of Conference on Forestry and Forest Products Research CFFPR-90*, pp.37-44, Malaysia: FRIM

Anonymous. 2007. Determination of the solubility of unknown inorganic salts, *Picken Country School District report.*

Anonymous. 1991. Dricon® Fire Retardant Treated Wood, *Product Handbook,Hickson Corporation*

Anonymous. 1999. ASTM D750: Water Absorption 24 Hour / Equilibrium, *Inertek PlasticTechnology Laboratories*

Anonymous. 2009a. MAP 11-52-0 vs. DAP 18-46-0, Agronomic considerations (MAP vs DAP), *Intermountain farmers association report.*

Anonymous. 2009b.Comparisons of MAP and DAP.a review of literature, *Back-to-basic: Current fertility issues report. Soil fertility information.*

Anthony, H. C. 1996. Urea Formaldehyde Adhesives Resins. *Forest Product Laboratory, USDA Forest Service.*

Bendtsen, B. A. 1966. Sorption and swelling characteristics of salt treated wood, *Forest Products Laboratory, Forest Service, USDA*

Freemen, H. G. 1959. Relationship between physical and chemical properties of wood and adhesion, *J. of For. Prod.* **9 (12)**: 451-458

Izran, K, Zaidon, A, Abdul Rashid, A.M, Abood, F, Mohamad Jani, S., Nor Yuziah, M.Y, Suffian, M. & Zaihan, J. 2008a. Buffering capacity and gelation time of fire retardant treated kenaf particles and urea formaldehyde resin admixture, *Poster presented at National Symposium of Polymeric Materials 2008,*Universiti Sains Malaysia

Izran, K, Zaidon, A, Abdul Rashid, A.M, & Abood, F. 2008. ThicknessSwelling andWater Absorption, In. *Properties Evaluation of Particleboard treatedwith fire retardants*, Unpublished Report.

Xing, C., Zhang, X.Y., Deng, J. & Wang, S. 2006. Urea formaldehyde resin gel time as affected by the pH value, solid content and catalyst, *J. of Appl. Sci.,* **103**:1566-1569

Zaidon, A. 1995. A structure and properties of rattan in relation to treatment with boronpreservatives, *Ph. D thesis,* University of Aberdeen, Scotland, UK. p. 183

Zaidon, A., Abood, F., Norhairul Nizam, A.W., Mohd Nor, M.Y.,Paridah,M.T., Nor Yuziah, M.Y. & Jalaludin, H. 2008. Properties of pyrethoids-treated particleboards manufactured from rubberwood and oil palm empty fruit bunches (EFB), *Pertanika Journal of TropicalAgricultural Science*, 21:171-178

Zaidon, A., Abood, F., Norhairul Nizam, A.W., Mohd Nor, M.Y., Paridah, M. T., Nor Yuziah, M.Y. & Jalaludin, H. 2007. Efficacy of pyrethoid and boron preservatives in protecting particleboards against fungus and termites, *Journal of Tropical Forest Science*, 20(1):57-65

Zaidon, A., Paridah, M.T., Sari, C.K.M., Razak, W. & Yuziah M. Y. N. 2004. Bonding charactheristics of Gigantochloa scortechinii. J. *of Bamboo and Rattan* **3(1)**: 1-9