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RETENTION OF COPPER AZOLE AND ALKALINE COPPER QUAT IN WOOD-BASED COMPOSITES POST - TREATED BY VACUUM IMPREGNATION

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ABSTRACT

Inductively coupled plasma (ICP) analyses were conducted to determine the amounts of elemental copper in wood-based composites that had been post-treated with alkaline copper quat (ACQ) or copper azole (CA) by vacuum impregnation. Specimens prepared from 5 commercially available, structural-use, wood-based composites softwood plywood (SWP), hardwood plywood (HWP), medium density fiberboard (MDF), oriented strand board (OSB) and particleboard (PB) were treated with ACQ and CA at different retentions. The analytical results demonstrated that there was a remarkable retention gradient between surface and core sections of SWP and HWP: there was greater retention in the surface than in the core. However, there was less or equal amounts of both preservatives in the surface compared to the core for MDF, OSB and PB. This prominent difference may have been due to the homogeneity of the composites as a result of the shape and thickness of the raw materials. While the current ICP analyses could not fully explain the difference in biological resistance among the tested composites and softwood sapwood, they clearly support a profile of biocidal gradients in various composites. The combined effects of retention gradients, selective absorption and a possible non-uniform distribution of active ingredients in the microstructure of the composites should also be to gain a better understanding of the biological performance of composites.

KEYWORDS: ICP, wood-based composites, retention, CA, ACQ, post-treatment.

INTRODUCTION

As documented elsewhere (Laks 2002, Kirkpatrick and Barnes 2006), wood-based composites have recently become widely substituted for lumber as structural and non-structural

components in houses. With the increased use of wood-based composites under conditions conducive to biodegradation and biodeterioration, the protection of these products has become an important issue (Gardner et al. 2003). There are a few options for obtaining composites that are resistant to against biological attack: use of highly durable raw materials (e.g. materials prepared from naturally durable tree species or from preservative pretreated- and chemically modified wood), in-process treatment with glueline additives or mixing of biocides with the constituents, and post-manufacture treatment with preservatives. Although in-process treatment is commonly used with MDF, OSB and PB, post-manufacture treatment can be applied to any type of composite.

Preservative chemicals are generally thought to provide wood-based composites with long-term protection against biological agents, if sufficient amounts of the biocides are introduced to an adequate depth of the treated substrate. Liquid preservative systems have been used to treat wood and wood-based materials over the past few decades using pressure/vacuum phases (Van Acker and Stevens 1993). Retention and penetration levels are closely related not only to the physical characteristics of the biocide used, but also to the wood or wood-based materials to be treated. Variations in these physical properties will affect biocide retention, which in turn alters biological performance. Since retention, as calculated from the uptake and strength of the treatment solution, does not consider the selective absorption or uneven distribution of active ingredients, it does not seem to be very accurate for precisely determining the amount of biocide within the treated material. Therefore, a method is needed to chemically determine biocide retention in wood and wood-based composites (Schultz et al. 2004). There have been some early studies on biocidal gradients in wood-based composites (Ruddick and Walsh 1982, Van Acker and Stevens 1989, Khouadja et al. 1991), and it was found that a glueline was important for inhibiting the even distribution of a preservative and that no treated plywood could meet the performance requirements for biological attack even at retentions appropriate for ground-contact conditions, although the presence of lathe checks, core gaps and incomplete gluelines rendered plywood treatable (Mitchoff and Morrell 1991).

The aim of the current study was to determine the retention of ACQ and CA in the surface and core sections of treated wood-based composites to discuss the preservative distribution in relation to the biological resistance of treated composites.

MATERIAL AND METHODS

Wood-based composites

Five commercially available, structural-use, wood-based composites softwood plywood, hardwood plywood, medium density fiberboard, oriented strandboard and particleboard were used for ACQ and CA treatments. These composites had a density range from 0.59 to 0.71 $g.cm^{-3}$ and thickness range from 11.7 to 12.7 mm. The details of these wood-based composites have been presented in Tab. 1. The specimens (210 x 30 mm x composite thickness) were double-coated with a two-component epoxy resin on each cut end to simulate penetration of the preservative into a full-size composite product. All specimens were conditioned at 60 ± 2°C for 72 hours prior to treatment.

Preservatives

The preservatives used in this study were alkaline copper quaternary (ACQ; JIS K 1570, 2004) and copper azole (CA; JIS K 1570, 2004). These were supplied by Koshii Preserving Co.

Ltd. (Osaka, Japan) and Xyence (Isezaki, Gunma, Japan), respectively. The treatment solutions were prepared by dilution with distilled water to achieve the target retentions in the treated materials. The target retentions were selected according to the requirements for lumber described in the Japanese Agricultural Standard JAS 1083 (2007), and were 0.65, 1.30 and 2.60 $kg.m^{-3}$ as ACQ and 0.25, 0.50 and 1.0 $kg.m^{-3}$ as CA, respectively, in the 5 composites. The pH values were around 9.6 and 8.8 for ACQ and CA solutions, respectively.

Tab.1: Manufacturing details of wood-based composites tested (from Tascioglu and Tsunoda 2010 a).

Composite	Details of material
SWP (Softwood plywood)	Larch (*Larix* spp.), 5 ply construction (2+2+3+2+2 mm), bonded boiled-water resistant grade phenol-formaldehyde adhesive.
HWP (Hardwood plywood)	*Dipterocarpaceae* spp., 5 ply construction (2+3+2+3+2 mm), bonded boiled-water resistant grade phenol-formaldehyde adhesive.
MDF (Medium density fiberboard)	Unknown hardwood fibers, 3 layered construction (2+8+2 mm), bonded melamine-urea-formaldehyde adhesive.
OSB (Oriented strand board)	Aspen, 3 layered construction (3+6+3 mm), bonded phenol-formaldehyde adhesive.
Particleboard (PB)	Hard-/softwood mixed strands, 3 layered construction (3+6+3 mm), bonded melamine-urea-formaldehyde adhesive.

Treatment

A vacuum-soak treatment was used to deliver the ACQ and CA solutions into wood-based composites. Composite specimens were placed in a cylindrical glass chamber and the air inside the chamber was evacuated without treatment solution down to an absolute pressure of 6 kPa. The solution was then introduced into the chamber under vacuum. At the end of treatment, the pressure inside the chamber was returned to ambient atmospheric pressure before the specimens were removed from the treatment chamber. Details of treatment schedules were given in Tab. 2. Based on the treatment schedules mentioned on Tab. 2, mean water retentions of composites were recorded as 153, 193, 398, 339 and 364 $kg.m^{-3}$ for SWP, HWP, MDF, OSB and PB specimens, respectively (Tascioglu and Tsunoda 2010a). Post-conditioning and handling of the treated specimens were performed as described in the previous paper (Tascioglu and Tsunoda 2010a, b).

Chemical analysis of copper retention

Three specimens were randomly selected from the same treatment group for further preparation. Analytical samples measuring 80 x 28 mm x panel thickness were cut from the middle part of each treated specimen after the epoxy coating was removed. Each sample was divided into three equally thick parts consisting of two surface sections and one core section. The surface and core sections were separately milled to pass through a 60-mesh screen for chemical analysis. A wet ashing procedure designated in American Wood Protection Association standard AWPA A7-04 (2009) was used to digest the milled materials prior to chemical analysis. Half a gram of milled material was placed in a 50-ml Erlenmeyer flask with three glass beads. Ten milliliters of concentrated nitric acid were added to each flask. The mixture was boiled on a hot plate at 130°C until the solution became clear. After the heat was reduced, 3 ml of hydrogen peroxide was added dropwise to clarify the digest further.

Tab. 2: Details of treatment schedules used to impregnate wood-based composites (from Tascioglu and Tsunoda 2010).

Composites	Treatment Schedules (wet vacuum time + dry vacuum time)
SWP	30 min + 60 min
HWP	30 min + 20 min
MDF, OSB and PB	10 min + 1 min

The digest was quantitatively transferred into a 50-ml volumetric flask for dilution with deionized water. The diluted digest was then passed through a 25-mm polypropylene disposable syringe filter with 0.45-micron nylon membrane for further analysis by inductively coupled plasma (ICP) atomic emission spectroscopy (Seiko Instruments Inc. SPS 7800, Chiba, Japan). Since preliminary analyses did not reveal any variation in the amount of ACQ or CA among the three specimens, a single analysis was conducted with a mixture of the milled materials from the same treatment group. Elemental copper concentrations determined by ICP were converted into retentions ($kg.m^{-3}$) of ACQ or CA in the treated composites.

RESULTS AND DISCUSSION

Retention gradient

Since ICPAE is believed to give analytical values close to the target retentions of metal elements in wood (Miyauchi et al. 2008) and composites (Tsunoda et al. 2002), the recovery rate was not examined with a known amount of ACQ or CA in wood and composites.

Overall, the analytical retentions were generally lower than the calculated retentions (Tabs. 3 and 4). However, these data should be interpreted with caution because retentions determined from solution uptake tended to be over estimated, as recognized in plywoods. This inconsistency might be explained by the selected absorption of treatment solutions in composites and a difference in permeability among composites. In addition, very low pressure and the lack of a pressurization period in the current treatment schedules may also contribute to these phenomena.

Although the retention gradient varied with the type of wood-based composite, the two preservatives showed similar distribution characteristics, as shown in Tabs. 3 and 4. A greater quantity of preservative was always found in the surface section than in the core section of SWP and HWP. Surface/core ratios ranged from 1.52 to 3.72 and from 1.05 to 2.32 for SWP and HWP, respectively. A similar retention gradient was documented in an early study on CCA-treated southern pine plywood (Khouadja et al. 1991), although their ratios were between 1.21 and 1.30. This large difference in the range of surface/core ratios might be explained by the treatment schedule used in the previous study: a 3-hour pressure period (at 1034 kPa), which could force more preservative to penetrate deeper. This would be consistent with the notion that retention gradients are greatly reduced in practical pressure/vacuum impregnation processes using higher pressures (Barnes 1988). It has been reported that impermeable gluelines prevented the adequate penetration of preservatives into core veneers (Ruddick and Walsh 1982, Van Acker and Stevens 1989). Ruddick and Walsh (1982) stated that glueline blockage could be less important when the preservative was quickly carried into the inner veneers through artifacts such as lathe checks and gaps between adjacent veneers, whereas it was hard to effectively protect plywoods

from biological agents (Mitchoff and Morrell 1991). The permeability of raw materials is another factor that may affect the preservative distribution in treated composites. For example, a preliminary treatment showed that SWP was relatively impermeable, with very low water uptake: 153 kg.m^{-3} (unpublished data).

On the other hand, MDF, OSB and PB showed differences in their biocidal gradients. In most cases, a greater amount of preservatives was present in core sections. The surface/core retention ratios ranged from 0.70 to 1.26 for MDF, 0.54 to 0.92 for OSB and 0.76 to 1.17 for PB (Tabs. 3 and 4). These results seemed to support the idea that the preservative distribution was remarkably affected by the permeability of the test composites. It is thought that permeability reflects the porosity of composites, and these three composites (MDF, OSB and PB) exhibit substantial and systematic variations in their porosity in cross-sections. In general, core sections with relatively higher porosity absorbed more treatment solution than less-porous surface sections.

Tab. 3: Calculated and analytical retentions (kg.m^{-3}) and surface/core ratios of ACQ in post-treated wood-based composites.

Composite	Target retention	Calculated	Analytical			Surface/core ratio
			Overall	Surface	Core	
SWP	0.65	0.63	0.51	0.67	0.18	3.72
	1.30	1.28	0.88	0.99	0.65	1.52
	2.60	2.58	1.63	2.02	0.85	2.38
HWP	0.65	0.65	0.47	0.58	0.25	2.32
	1.30	1.33	0.83	0.95	0.59	1.61
	2.60	2.58	1.24	1.26	1.20	1.05
MDF	0.65	0.76	0.42	0.37	0.53	0.70
	1.30	1.50	0.84	0.76	1.02	0.75
	2.60	2.95	1.71	1.59	1.94	0.82
OSB	0.65	0.64	0.39	0.34	0.48	0.71
	1.30	1.31	0.67	0.52	0.97	0.54
	2.60	2.62	1.48	1.44	1.57	0.92
PB	0.65	0.65	0.36	0.32	0.42	0.76
	1.30	1.30	0.75	0.68	0.91	0.75
	2.60	2.61	1.22	1.28	1.09	1.17

Relation between preservative gradients and biological resistance of treated wood-based composites

Since there was no clear effect of preservative treatment on untreated MDF and PB due to their high resistance to decay fungi and termites, these composites were excluded from further discussion. This difference in biological resistance might be due to unavoidable variations in density and the natural durability of the raw materials (Behr 1972, Okoro et al. 1984, Kamden and Sean 1994). The type of adhesive is also a factor that may affect the biological resistance of composites (Laks and Manning 1995).

Tab. 4: Calculated and analytical retentions (kg.m^{-3}) and surface/core ratios of CA in post-treated wood-based composites.

Composite	Target retention	Calculated	Analytical			Surface/core ratio
			Overall	Surface	Core	
SWP	0.65	0.63	0.51	0.67	0.18	3.72
	1.30	1.28	0.88	0.99	0.65	1.52
	2.60	2.58	1.63	2.02	0.85	2.38
HWP	0.65	0.65	0.47	0.58	0.25	2.32
	1.30	1.33	0.83	0.95	0.59	1.61
	2.60	2.58	1.24	1.26	1.20	1.05
MDF	0.65	0.76	0.42	0.37	0.53	0.70
	1.30	1.50	0.84	0.76	1.02	0.75
	2.60	2.95	1.71	1.59	1.94	0.82
OSB	0.65	0.64	0.39	0.34	0.48	0.71
	1.30	1.31	0.67	0.52	0.97	0.54
	2.60	2.62	1.48	1.44	1.57	0.92
PB	0.65	0.65	0.36	0.32	0.42	0.76
	1.30	1.30	0.75	0.68	0.91	0.75
	2.60	2.61	1.22	1.28	1.09	1.17

Both ACQ and CA were shown to be highly effective at controlling biological attack, based on thresholds for *C. japonica* sapwood (Tab. 5), while they were ineffective with SWP, HWP and OSB. The performance of treated SWP against the white-rot fungus *T. versicolor* was satisfactory at retentions higher than the threshold values with *C. japonica* sapwood. This was within the range of our expectation and suggested the possible selective absorption of preservatives. Surprisingly, similar results were not seen with the brown-rot fungus *F. palustris*. These results could not be explained by preservative gradients as determined by ICP analysis, since both surface and core sections contained a sufficient amount of preservatives. Larch generally sustains greater mass loss with *F. palustris* than with *T. versicolor* in the laboratory JIS K 1571 (2004) test (unpublished data). The combined effects of remarkable retention gradients, selective absorption and possible non-uniform distribution in the microstructure of the plywood might help the fungus to degrade core sections. These factors should be considered to examine the difference in decay- and termite-resistance between SWP and solid wood. The performance of HWP against fungal exposure was opposite to that of SWP. Treatments with ACQ and CA were effective against F. palustris, but ineffective against *T. versicolor*. However, as with SWP, the analytical results suggest that HWP would show high performance against the two test fungi. Therefore, it was impossible to further discuss the factors involved.

The results with OSB were far beyond our thoughts and expectations. Although the analytical results demonstrated that both surface and core sections contained sufficient amounts of both test preservatives to suppress the activities of the biological agents regardless of selective absorption, biological resistance was not improved. However, ICP analysis did not provide

Tab. 5: Threshold values (kg.m^{-3}) against two decay fungi and termites, with overall retentions and surface/core ratios in parenthesis [1].

Composite	*Trametes versicolor*		*Fomitopsis palustris*		*Coptotermes formosanus*	
	ACQ_	CA	ACQ_	CA	ACQ_	CA
SWP	0.63-1.28 (0.51/3.72-0.88/1.52)	0.47-1.00 (0.33/2.56-0.77/1.68)	>2.58 (1.63/2.38)	>1.00 (0.77/1.68)	>2.58 (1.63/2.38)	>1.00 (0.77/1.68)
HWP	>2.58 (1.24/1.05)	>1.22 (0.77/1.13)	1.33-2.58 (0.83/1.61-1.24/1.05)	0.57-1.22 (0.50/1.32-0.77/1.13)	>2.58 (1.24/1.05)	>1.22 (0.77/1.13)
OSB	>2.62 (1.48/0.92)	>1.01 (0.67/0.66)	>2.62 (1.48/0.92)	>1.01 (0.67/0.66)	>2.62 (1.48/0.92)	>1.01 (0.67/0.66)
Cryptomeria japonica sapwood*	<0.67	<0.27	0.67-1.37	0.27-0.50	<0.67	0.27-0.50

[1] This table was compiled from data in two previous papers Tascioglu and Tsunoda (2010a, b). Data with MDF and PB were excluded from the table because of the high resistance of the untreated materials.
* Data for *C. japonica* are calculated retentions.

a clear picture of the micro-distribution of active ingredients. It was thought that this micro-distribution could be changed due to swelling caused by solution uptake, and re-distribution may have occurred during post-treatment shrinkage. The homogeneous micro-distribution of preservatives should be seriously considered, especially in OSB. This was supported by the successful results in zinc borate-incorporated MDF made of pine fibers, aspen OSB and PB made of hardwood particles. These composites were produced by an in-manufacture process and it was supposed that zinc borate was evenly distributed (Laks and Manning 1995, Tsunoda et al. 2002, Tascioglu et al. 2009).

CONCLUSIONS

The ICP assay clearly demonstrated that retention gradients were unavoidable in all types and that in SWP and HWP surface sections always held a greater amount of preservatives than core sections. A sharp biocidal gradient was seen between surface and core sections, with ratios ranging from 1.05 to 3.72. These preservative retention gradients meant that core sections were generally more susceptible to biological agents. However, the difference in biological performance between solid softwood *C. japonica* sapwood and plywoods was not attributed solely to retention gradients, but likely also to the selective absorption and micro-distribution of the active ingredients. The latter two factors seemed to be more important in OSB, which did not show improved biological resistance after treatment with ACQ or CA.

The calculated retentions after vacuum/pressure impregnation are not particularly meaningful in plywoods, and the natural durability and permeability of the raw materials, the adhesives used and the macro/micro-distribution of active ingredients in the composites play a more important role in enhancing protection against biological attacks. The treatment schedules at commercial plants are much different from those in the current study. Since much higher pressure is

applied to lumber and composite boards for a longer period at such plants, and this enables the treatment solution to more deeply penetrate the substratum, it is expected that composites treated commercially should perform better than those tested in this study.

REFERENCES

1. AWPA 7-04, 2009: Standard for wet ashing procedures for preparing wood for chemical analysis.
2. Barnes, M., 1988: A review of treatment cycles and application method in wood preservation. In: Wood protection techniques and the use of treated wood in construction (Ed. by Hamel, M.P.). FPS Proceedings No. 47358, Forest Prod. Soc., Madison, WI. Pp 35-41.
3. Behr, E.A., 1972: Decay and termite resistance of medium-density fiberboards made from wood residue. Forest Prod. J. 22(12): 48-51.
4. Gardner, D.J., Tascioglu, C., Wålinder, M.E.P., 2003: Wood composite production. In: Wood deterioration and preservation: Advances in our changing world. (Ed. by Goodell, B., Nicholas, D.D. and Schultz). Am. Chem. Soc., Washington, D.C. Pp 399-419.
5. JAS 1083, 2007: Lumber (Sawn timber).
6. JIS K 1570, 2004: Wood preservatives.
7. JIS K 1571, 2004: Test methods for determining the effectiveness of wood preservatives and their performance requirements.
8. Kamden, D.P., Sean, S.T., 1994: The durability of phenolic-bonded particleboards made of decay-resistant black locust and nondurable aspen. Forest Prod. J. 44(2): 65-68.
9. Khouadja, A., Barnes, H.M., Lyon, D.E., 1991: Properties of CCA-treated southern pine plywood after redrying. Proceedings of American Wood Preservers' Association (AWPA) 91: 82-99.
10. Kirkpatrick, J.W., Barnes, H.M., 2006: Biocide treatment for wood composites – A review. 37th Annual meeting - The int. res. group on wood protection. Document No. IRG/WP 06-40323, Tromso, Norway.
11. Laks, P.E., 2002: Biodegradation susceptibility of untreated engineered wood products. In: Enhancing the durability of lumber and engineered wood products. FPS Symposium Proceedings No. 7249. Forest Prod. Soc., Madison, WI. Pp 125-130.
12. Laks, P.E., Manning, M.L., 1995: Preservation of wood composites with zinc borate. The Int. Res. Group on Wood Preserv. Document No. IRG/WP 95-30074, Stockholm, Sweden.
13. Mitchoff, M.E., Morrell, J.J., 1991: Preservative treatment of plywood panels from the Pacific Northwest. Forest Prod. J. 41(9): 11-18.
14. Miyauchi, T., Mori, M., Imamura, Y., 2008: Leaching characteristics of benzalkonium chloride from wood treated with ammoniacal copper quaternary wood preservative. J. Wood. Sci. 54(3): 225-232.
15. Okoro, S.P.A., Gertjejansen, R.O., French, D.W., 1984: Influence of natural durability, laboratory weathering, resin content, and ammonical copper arsenate treatment on the decay resistance of African hardwood particleboards. Forest Prod. J. 34(9): 41-48.
16. Ruddick, J.N.R., Walsh, A., 1982: Treatability of plywood containing intermountain Douglas fir v veneers. The Int. Res. Group on Wood Preserv. Document No. IRG/WP/3203, Stockholm, Sweden.

17. Schultz, T.P., Nicholas, D.D., Dalton, T.J., Keefe, D., 2004: Biocide retention variation of southern yellow pine products treated with waterborne preservatives in commercial, pilot plant, or laboratory cylinders. Forest Prod. J. 54(3): 85-90.
18. Tascioglu, C., Tsunoda, K., 2010a: Biological performance of copper-azole treated wood and wood-based composites. Holzforschung 64(3): 399-406.
19. Tascioglu, C., Tsunoda, K., 2010b: Laboratory evaluation of wood-based composites treated with alkaline copper quat against fungal and termite attacks. International Biodeterioration and Biodegradation 64(8): 683-687.
20. Tascioglu, C., Umemura, K., Tsunoda, K., 2009: Termiticidal performance of zinc borate-incorporated particleboard. Proc. of the 6th Conference of the Pacific Rim Termite 21. Research Group, Kyoto, Japan, 2-3 March 2009. Pp 114-116.
21. Tsunoda, K., Watanabe, H., Fukuda, K., Hagio, K., 2002: Effects of zinc borate on the properties of medium density fiberboard. Forest Prod. J. 52(11/12): 62-65.
22. Van Acker, J., Stevens, M., 1989: Treatment of poplar plywood with solvent and waterborne preservatives. The Int. Res. Group on Wood Preserv. Document No. IRG/WP/3538, Stockholm, Sweden.
23. Van Acker, J., Stevens, M., 1993: Improvement in decay resistance of some commercial plywoods by waterborne and solvent-borne preservative treatments. In: IUFRO Sym. on the protection of wood-based composites (Ed. by Preston, A.F.), Forest Prod. Soc., Madison, WI. Pp 88-89.

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