

Plywood Treated with Didecyl Dimethyl Ammonium Tetrafluoroborate (DBF) and Didecyl Dimethyl Ammonium Chloride (DDAC): Mechanical Properties and Biological Resistance

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Abstract

This study evaluated decay and termite resistance of plywood panels treated with didecyl dimethyl ammonium tetrafluoroborate (DBF) and didecyl dimethyl ammonium chloride (DDAC) as quaternary ammonia compounds. Mechanical properties and bonding quality of treated plywood specimens were also tested. The modulus of rupture (MOR) values of both DBF- and DDAC-treated plywood specimens fulfilled minimum requirements for plywood F25-F30 (38-45 N/mm²) set by the EN standards. The modulus of elasticity (MOE) of DDAC-treated plywood specimens decreased when compared with DBF-treated and untreated plywood specimens. The bonding quality values of all specimens did not meet the requirements set by the TS standards.

The results suggest that DBF and DDAC may decrease mechanical properties by possible interaction with the glue and wood components depending on both chemical structure and retention levels in treated plywood specimens. Decay resistance tests showed that DBF-treated plywood specimens were more resistant against the fungi tested when compared with those of DDAC treated; however, both DBF and DDAC had no protective effect against termite attack.

Keywords: Didecyl dimethyl ammonium tetrafluoroborate, didecyl dimethyl ammonium chloride, quaternary ammonia compounds, plywood, biological resistance, mechanical properties.

1. Introduction

Wood based composites as building materials have received considerable attention in recent years. Although wood based composites are generally accepted to show a greater resistance to biodegradation than solid wood, these products are still susceptible to biological attack in exterior applications (Curling and Murphy, 1999; Kartal and Green, 2003). Compatibility of commercial wood preservatives with adhesives and manufacture parameters such as temperature and pressure is one of the most important concerns in protection of wood-based composites. Inorganic copper-based preservatives, boron compounds such as boric acid, borax and borates, vapor boron and organic biocides have been proposed for inhibition of fungal and termite attack (Kamdem et al., 2002). Some protective chemicals to be used for wood-based panels may interfere with the resin and manufacturing conditions, resulting in poor bonding, in turn, low mechanical strength and poor durability (Barnes and Amburgey, 1993).

Quaternary ammonia compounds (QACs) first synthesized in the late 1800s are well known for their bactericidal, germicidal, fungicidal, and termiticidal properties. The fungicidal activity of QACs and their surface-activity properties have been described in detail and considerable attention has been focused on QACs and development of novel types of such compounds due to health, environmental, and cost factors (Gosselin et al., 1984; Preston et al., 1987; Matejuk et al., 2004). A novel quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF), with boric tetra fluoride (BF_4^-) ion has recently been developed in the laboratories of Pharmaceutical and Cosmetic Materials Research Department, Sanyo Chemical Industries, Ltd., Kyoto, Japan (Kartal et al., 2005; Hwang et al., 2005). Since cations and anions in the formulation of wood preservatives play a significant role in determining their melting temperature, density, viscosity, solubility in water, and protective characteristics (Pernak et al., 2004), the chemical formulation of commercially available DDAC (didecyl dimethyl ammonium chloride) has been changed to develop DBF compound (Figure 1).

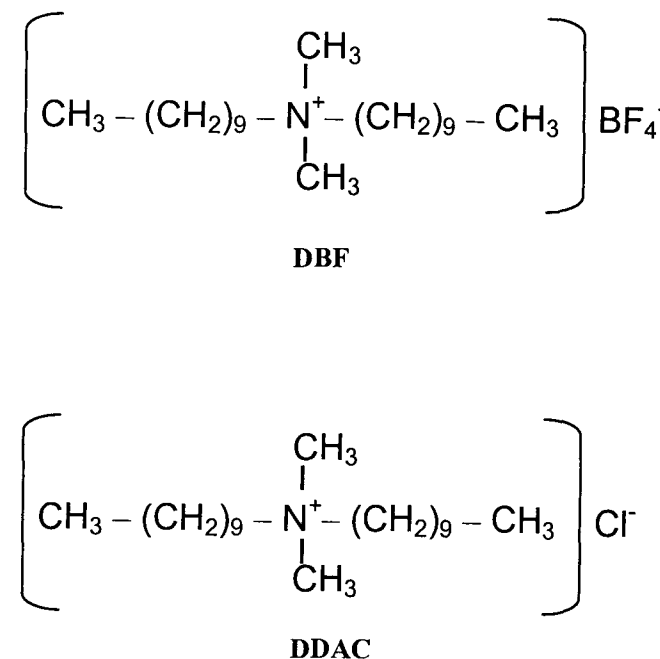


Figure 1. Chemical structure of didecyl dimethyl ammonium tetrafluoroborate (DBF) in comparison with didecyl dimethyl ammonium chloride (DDAC).

Şekil 1. Didecyl dimethyl ammonium tetrafluoroborate (DBF) ve didecyl dimethyl ammonium chloride (DDAC) bileşiklerinin kimyasal yapıları

Our previous laboratory studies on decay and termite resistance of wood treated with DBF showed that wood specimens treated with 0.5 and 1% DBF solutions at retention levels of 4 and 8 kg/m^3 , respectively, inhibited the brown-rot fungus, *Fomitopsis (Tyromyces) palustris* and white-rot fungus, *Coriolus (Trametes) versicolor* attack even after a 10-day severe weathering process, suggesting that adequate fixation of DBF in wood had occurred. DBF treatment with 0.1% concentration at 0.8 kg/m^3 retention level was, however, effective against subterranean termites, *Coptotermes formosanus* (Kartal et al., 2005). In another study by Hwang et al. (2005), the ability of DBF and DDAC to inhibit discolorations by selected mold and stain fungi was screened under laboratory conditions. On the one hand, both DBF and DDAC at 1% concentration provided protection against the fungi tested. DBF and DDAC at lower solution strengths were also capable of protecting wood against the fungi for 2 weeks.

The objective of this study was to determine the applicability of DBF wood preservative in the formulation of phenol formaldehyde industrial plywood resin. Modulus of rupture (MOR), modulus of elasticity (MOE) and bonding quality of the produced plywood panels treated with DBF were evaluated in comparison with commercial DDAC wood preservative. In addition, resistance of the plywood panels treated with either DBF or DDAC was tested against white- and brown-rot fungi and subterranean termites under laboratory conditions.

2. Material and Methods

2.1. Plywood manufacture

Commercially manufactured rotary cut veneers (300 mm by 300 mm by 1.18 mm for top and bottom layers, 300 mm by 300 mm by 3.20 mm for inner layer) of Radiata pine were used to manufacture structural plywood panels. Veneer specimens were kept in a conditioning chamber until they equilibrated at 7% moisture content.

A commercial phenol formaldehyde (PF) resin (C-4S037-B) was used for the glue mix to manufacture the plywood. The ingredients of the glue mix and the amount of didecyl dimethyl ammonium tetrafluoroborate (DBF) and didecyl dimethyl ammonium chloride (DDAC) wood preservatives are listed in Table 1. All ingredients were weighed and the ready glue was mixed with target concentrations of 3, 6, and 9% DBF or DDAC wood preservatives.

Each treated veneer was re-conditioned to 7% moisture content before plywood panels were manufactured. The glue was applied to the veneers at a rate of 200 - 225 g/m² using a commercial glue spreader. The glue spread rate was kept constant by adjusting and using the same speed and glue thickness on the glue spreader. The veneers were weighed before and after spreading to determine the exact amount of adhesive actually applied. The 3-ply panel was assembled immediately after the veneers were spread with adhesive and pre-pressed at 10 kg/cm² for 30 min. The veneers were then laid-up into a plywood billet and hot pressed using a pressure of 10 kg/cm² at 145°C for 8 min in a press. Plywood panels were conditioned at 20°C and 65% relative humidity for three weeks before any tests were carried out.

Table 1. The properties of glue mixture used in plywood manufacture

Tablo 1. Kontrplak üretiminde kullanılan tutkal karışımın özellikleri

Component	Phenol resin glue (Untreated control)	Phenol resin glue (DBF-2)	Phenol resin glue (DBF-4)	Phenol resin glue (DBF-6)	Phenol resin glue (DDAC-2)	Phenol resin glue (DDAC-4)	Phenol resin glue (DDAC-6)
Original Phenol resin (g)	234.4	234.4	234.4	234.4	234.4	234.4	234.4
Soybean powder (g)	11.7	11.7	11.7	11.7	11.7	11.7	11.7
Flour (g)	18.8	18.8	18.8	18.8	18.8	18.8	18.8
Na ₂ CO ₃ (g)	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Water (g)	33.4	33.4	33.4	33.4	33.4	33.4	33.4
Total glue (g)	300.1	300.1	300.1	300.1	300.1	300.1	300.1
DBF (g)	0.0	9.6	19.2	28.8	0.0	0.0	0.0
DDAC (g)	0.0	0.0	0.0	0.0	12.0	24.0	36.0
Total (g)	300.1	309.7	319.3	328.9	312.1	324.1	336.1
DBF or DDAC	0.0%	3.1%	6.0%	8.8%	3.1%	5.9%	8.6%
Plywood treatment							
DBF or DDAC (kg/m ³)	0.0	2.0	4.0	6.0	2.0	4.0	6.0

2.2. Mechanical properties

Tests of mechanical properties were conducted on specimens cut from the plywood panels. Prior to mechanical property tests, specimens were conditioned for at least 3 weeks at 20°C and 65% relative humidity. Modulus of rupture (MOR) and modulus of elasticity (MOE) were measured according to EN 310 (1993) and evaluated based on EN 636 (1996) by using Zwick Z010 Universal Test Machine (Germany) with a loading capacity of 10 tons. Twenty specimens with dimensions of 76 mm by 290 mm by panel thickness were prepared from each panel. Ten specimens were cut with their long dimension parallel to longitudinal direction of the outer layer and 10 specimens with their long dimension perpendicular to longitudinal direction of the outer layer.

2.3. Bonding quality

Bonding quality tests were performed in accordance with EN 314-1 (1993) immersing the specimens in boiling water for 4 h, drying in the ventilated drying oven for 16 h to 20 h at 60°C then re-immersing the specimens in boiling water for 4 h, followed by cooling in water at 20°C for at least 1 h to decrease temperature of the specimens to 20°C. Bonding quality was a measurement of the bond strength in shear by a mechanical test by using Losenhausen Test Machine with a static loading capacity of 1000 kg.

2.4. Decay resistance tests

Plywood specimens with the dimension of 20 mm by 20 mm by plywood thickness were then cut from the plywood panels for decay resistance tests. A monoculture decay test was conducted according to Japanese Industrial Standards (JIS) JIS K 1571 (JIS, 2004) using the brown-rot fungus, *Tyromyces palustris* (Berkeley et Curtis) Murrill (FFPRI – Forestry and Forest Products Research Institute- 0507) and the white-rot fungus, *Trametes versicolor* (L. ex Fr.) Quel. (FFPRI 1030). After measuring oven-dried weight, specimens were sterilized with gaseous ethylene oxide. Three specimens per treatment were placed in a glass jar on the surface of 250 g quartz sand wetted with 80 ml nutrient solution and inoculated with liquid fungal cultures. Liquid fungal cultures were prepared inoculating 1000 ml liquid medium which contained 40 g glucose, 3 g peptone, 15 g malt extract and 1000 ml distilled water. The medium was shaken at 26°C for 10 days at 100 rpm. The nutrient solution used for wetting the quartz sand contained 40 g glucose, 3 g peptone, 15 g malt extract and 1000 ml distilled water for the white-rot fungus and 20 g glucose, 1.5 g peptone, 7.5 g malt extract, and 1000 ml distilled water for the brown-rot fungus.

The test jars were then incubated at 27°C for 12 weeks. Nine replicates were tested for each decay fungus. The extent of the fungal attack was expressed as the percentage of weight loss.

2.5. Termite resistance tests

Specimens with the dimension of 20 mm by 20 mm by plywood thickness were cut from the plywood panels for termite resistance tests. Specimens were exposed to the subterranean termite *Coptotermes formosanus* Shiraki according to Japanese Industrial Standards (JIS) JIS K 1571 (JIS, 2004). A test specimen was placed at the centre of the plaster bottom of a cylindrical test container (80 mm diameter). A total of 150 worker termites was introduced into each test container together with 15 soldiers. Five solid wood and five plywood specimens per treatment were assayed against termites. The assembled containers were set on damp cotton pads to supply water to the specimens and kept at 27°C and >80% RH in darkness for three weeks. Termite mortalities were determined every week during the tests and the weight loss of specimens due to termite attack was calculated based on the differences in the initial and final dry weight of specimens after cleaning off the debris of termite attack.

3. Results and Discussion

Figures 2, 3, and 4 show MOR, MOE, and bonding quality for each type of plywood specimens, respectively. There is no any statistically significant decrease in MOR values of DBF- and DDAC-treated plywood panels when compared with untreated specimens. Parallel and perpendicular-to-plane MOR values of the plywood specimens treated with DBF and DDAC and control specimens fulfilled the minimum requirements for plywood F25-F30 (38-45 N/mm²) (EN 636, 1996). The MOE of DDAC-treated plywood specimens decreased when compared with DBF-treated and untreated plywood specimens. Perpendicular-to-plane MOE values of the plywood specimens treated with DBF and DDAC and control specimens fulfilled minimum requirements for plywood E20 (2000 N/mm²) (EN 636, 1996). Parallel-to-plane MOE values of the plywood specimens treated with DBF and DDAC and control specimens also fulfilled minimum requirements for plywood E60 (6000 N/mm²) (EN 636, 1996). Unexpectedly, the bonding quality values of all specimens did not meet the requirements (0.8 N/mm²) set by the TS 4520 (1985). DDAC-treated plywood specimens showed better performance in comparison with untreated and DBF-treated ones. The results also showed that as the amount of DBF and DDAC in the specimens increased, bonding quality decreased. This was much clearer in 4 and 6 kg/m³ DBF-treated specimens.

The mechanical properties of plywood specimens treated with DDAC and DBF may suggest that these preservatives did not adversely influence bending values however, bonding quality decreased in DBF-treated specimens when compared with control and DDAC-treated plywood specimens. Bonding quality values in untreated control specimens were much lower than the requirements set by TS 4520 (1985), suggesting that the glue used in the study is not compatible with the manufacturing process or wood species. This observation was also seen in the DBF-treated specimens, suggesting that the PF resin, heat and pressure in manufacturing process were not compatible with DBF wood preservative. It is clear that DBF has a considerable effect

on bonding performance of PF resin. However, DDAC had little effect on bonding quality of plywood specimens when compared with untreated control specimens; however, these specimens' bonding quality was still lower than the standard values. Several researchers have stated that water-soluble preservatives may generally have little or no effect on the bonding performance of urea-formaldehyde resin; however, these chemicals may have a negative effect on the bonding performance of phenol formaldehyde resin (Laks and Manning, 1995, 1997; Tsunoda et al., 2002; Akbulut et al., 2004). This is most likely due to gelling of phenolic adhesive by such chemicals before the adhesive can penetrate wood structure (Barnes and Amburgey, 1993).

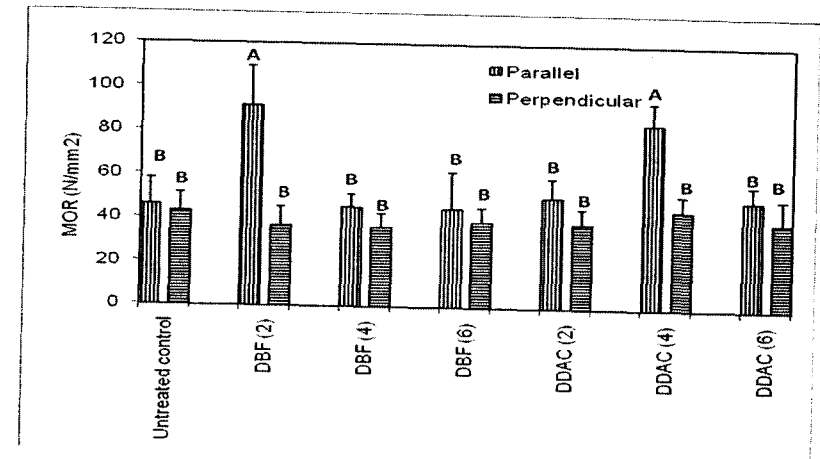


Figure 2. MOR values in plywood specimens (2, 4, or 6 kg/m³ DBF or DDAC retention in the plywood specimens; the same letters on each bar indicates that there is no statistical difference between the specimens according to the Duncan's multiply range test ($P \leq 0.05$)).

Şekil 2. Kontrplak örneklerinde MOR değerleri (2, 4, ve 6 kg/m³ DBF ve DDAC retensiyon değerleri; barlardaki aynı harfler istatistiksel bakımdan (Duncan's multiply range test ($P \leq 0.05$)) farklılık olmadığını göstermektedir).

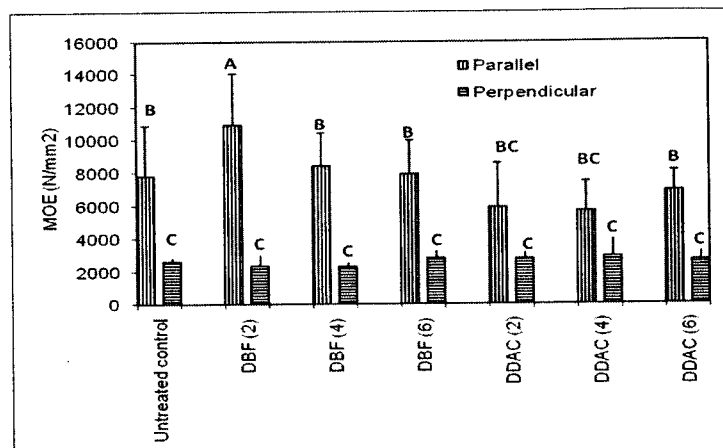


Figure 3. MOE values in plywood specimens (2, 4, or 6 kg/m³ DBF or DDAC retention in the plywood specimens; the same letters on each bar indicates that there is no statistical difference between the specimens according to the Duncan's multiply range test ($P \leq 0.05$)).

Şekil 3. Kontrplak örneklerinde MOE değerleri (2, 4, ve 6 kg/m³ DBF ve DDAC retensiyon değerleri; barlardaki aynı harfler istatistiksel bakımdan (Duncan's multiply range test ($P \leq 0.05$)) farklılık olmadığını göstermektedir).

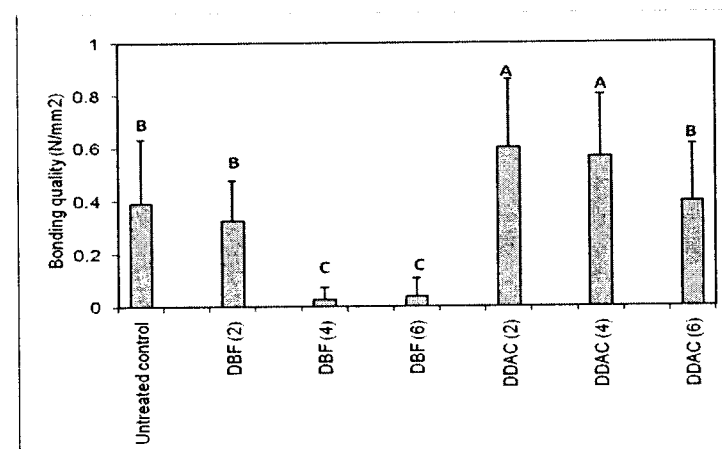


Figure 4. Bonding quality in plywood specimens (2, 4, or 6 kg/m³ DBF or DDAC retention in the plywood specimens; the same letters on each bar indicates that there is no statistical difference between the specimens according to the Duncan's multiply range test ($P \leq 0.05$)).

Şekil 4. Kontrplak örneklerinde bağlanma kalitesi değerleri (2, 4, ve 6 kg/m³ DBF ve DDAC retensiyon değerleri; barlardaki aynı harfler istatistiksel bakımdan (Duncan's multiply range test ($P \leq 0.05$)) farklılık olmadığını göstermektedir).

Average weight losses in untreated plywood specimens exposed to *T. palustris* and *T. versicolor* were 31.9 and 29.4%, respectively. DBF had a significant effect on the susceptibility of plywood specimens to the brown-rot fungus, *T. palustris*. Higher weight losses were found in the plywood specimens treated with DBF and exposed to the white-rot fungus, *T. versicolor* compared with those exposed to *T. palustris* (Table 2). However, the weight losses in DDAC-treated plywood specimens were considerably higher than those in DBF-treated ones for both fungi.

Table 2 shows the weight losses and termite mortalities in plywood specimens after 3-week termite exposure. Average weight loss in untreated plywood specimens was 17.9%. Plywood specimens with DBF- and DDAC-treated veneers resulted in weight losses, which are either lower or slightly higher than untreated plywood specimens. All plywood specimens with treated veneers showed slightly higher termite mortalities than untreated plywood specimens. In general, termite mortality conformed to specimen weight loss. These results suggest that DBF and DDAC have no protective effect against termite attack in the plywood specimens.

Table 2. Weight loss in decay and termite resistance tests and termite mortalities

Tablo 2. Çürüme ve termit testlerinde elde edilen ağırlık kayıpları ve termit ölüm yüzdeleri

	Decay resistance tests		Termite resistance tests		
	Weight loss (%)		Weight loss (%)	Termite mortality (%)	
	<i>T. palustris</i>	<i>T. versicolor</i>		Soldier	Worker
Untreated control	31.89 A <i>7.30</i>	29.40 A <i>3.60</i>	17.88 AB <i>1.61</i>	0.00 <i>0.00</i>	10.00 <i>2.00</i>
DBF (2 kg/m ³)	2.44 D <i>0.30</i>	16.23 C <i>5.96</i>	15.10 B <i>0.66</i>	2.22 <i>3.85</i>	12.00 <i>0.67</i>
DBF (4 kg/m ³)	2.11 D <i>0.54</i>	16.57 C <i>8.56</i>	14.82 B <i>1.95</i>	8.89 <i>7.70</i>	22.00 <i>4.16</i>
DBF (6 kg/m ³)	2.45 D <i>0.64</i>	19.29 B <i>8.79</i>	10.66 BC <i>1.33</i>	8.89 <i>7.70</i>	24.22 <i>3.67</i>
DDAC (2 kg/m ³)	21.19 B <i>4.98</i>	32.72 A <i>4.35</i>	17.70 AB <i>1.31</i>	8.89 <i>3.85</i>	11.56 <i>1.68</i>
DDAC (4 kg/m ³)	27.98 AB <i>6.31</i>	27.37 AB <i>7.59</i>	20.08 A <i>2.36</i>	4.44 <i>7.70</i>	12.89 <i>0.38</i>
DDAC (6 kg/m ³)	21.75 B <i>5.07</i>	14.68 C <i>4.79</i>	15.29 B <i>1.87</i>	4.44 <i>3.85</i>	23.11 <i>9.10</i>
Radiata pine solid wood	-	-	19.17 A <i>0.48</i>	22.22 <i>16.78</i>	18.00 <i>1.76</i>

Figures in italics are standard deviations. The same letters in each column indicates that there is no statistical difference between the specimens according to the Duncan's multiply range test ($P \leq 0.05$). 2, 4, or 6 kg/m³ DBF or DDAC retention in the plywood specimens.

Our previous studies showed that both DBF- and DDAC-treated solid wood specimens were effective against the same fungi in the same decay tests and the subterranean termites in the same termite resistance tests (Kartal et al., 2005; Hwang et al., 2006; Kartal et al., 2006; Hwang et al., 2007a; Hwang et al., 2007b). A study using alkyl ammonium compounds by Acker and Stevens (1993) showed that little protection against fungal resistance under laboratory conditions was conferred on poplar plywood at a retention level of 3 kg/m³, and only at higher retention levels of such compounds, full protection could be achieved. The results from our present study may suggest that DBF and DDAC interfered with the glue used in the plywood manufacture. It might also be concluded that the temperature of 145°C during plywood manufacture had an effect on DDAC wood preservative. Our previous laboratory thermal analyses revealed that DBF was degraded at the temperatures as high as 250°C; however, DDAC was degraded at a temperature of 150°C (unpublished data). Incorporation of either DBF or DDAC into adhesive before plywood manufacture may have also resulted in weak penetration of the preservatives to wood surfaces, decreasing chemical retention levels in the veneers used in the plywood manufacture.

4. Conclusions

No considerable change was seen in mechanical properties of plywood specimens treated with DBF and DDAC wood preservatives in comparison with untreated control specimens. Decay-resistance tests revealed that DBF wood preservative was much more effective against the fungi tested than DDAC. Plywood specimens treated with either DBF or DDAC was not resistant to the termites under laboratory conditions. The results suggested that the PF resin used under the study and manufacturing conditions were not compatible with DBF and DDAC wood preservatives. In such plywood panels, more retention levels of DBF and DDAC are needed to obtain complete protection against biodegradation by wood-degrading fungi and termites. Since mixing either DDAC or DBF with PF resins can cause bonding and biocide efficacy problems, treatment of veneers with the preservatives before plywood manufacture may result in higher composite performance and better durability against biodeterioration. Likewise, modifications in manufacture process such as lower pressure time might limit any possible changes in the glue and preservative matrix.

Didecyl Dimethyl Ammonium Tetrafluoroborate (DBF) ve Didecyl Dimethyl Ammonium Chloride (DDAC) ile Emprenye Edilmiş Kontrplaklar: Mekanik Özellikler ve Biyolojik Direnç

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Kısa Özet

Bu çalışma didecyl dimethyl ammonium tetrafluoroborate (DBF) ve didecyl dimethyl ammonium chloride (DDAC) ile emprenye edilmiş kontrplak levhaların mekanik özellikleri ile mantar ve termitlere karşı dayanıklılığını incelemektedir. Levha örneklerinin yarılma dirençlerinin (MOR) EN standartları tarafından belirlenen F25-F30 (38-45 N/mm²) limitlerden düşük olmadığı fakat elastikiyet modülü (MOE) değerlerinin DDAC ile emprenye edilen örneklerde DBF ve kontrol levhalarına karşılık azaldığı belirlenmiştir. Yapışma direnci değerlerinin ise TS standartları tarafından belirlenen limit değerlerinden düşük olduğu bulunmuştur. Böylece DBF ve DDAC emprenye maddelerinin, tutkal ve odun komponentleri arasında olası etkileşimlerden dolayı mekanik özellikleri olumsuz etkileyeceği belirlenmiştir. Ayrıca, DBF ile emprenye edilen levhaların DDAC ile korunanlara karşılık test edilen mantarlara karşı daha dayanıklı olduğu fakat her iki maddenin de termitlere karşı levhaları koruyamayacağı bulunmuştur.

Anahtar Kelimeler: Didecyl dimethyl ammonium tetrafluoroborate, didecyl dimethyl ammonium chloride, kontrplak, biyolojik dayanıklılık, mekanik özellikler.

1. Giriş

Odun esaslı kompozitler son yıllarda yapı malzemesi olarak önemli bir ilgi görmektedir. Odun esaslı kompozitler masif oduna göre biyolojik degradasyona karşı daha fazla dayanıklılık göstermesine rağmen bu ürünler dış ortam uygulamalarında biyolojik saldırılara karşı halen hassastırlar (Curling and Murphy, 1999; Kartal and Green, 2003). Odun esaslı kompozitlerin korunmasında emprenye maddelerinin tutkallar ile sıcaklık ve basınç gibi üretim parametreleri arasındaki uyumluluk en önemli konulardan birisidir. Bakır esaslı emprenye maddeleri, borik asit, boraks ve boratlar gibi bor bileşikleri ve organik biyosidler mantar ve termit saldırılarının engellenmesi amacı ile önerilmektedir (Kamdem et al., 2002).

İlk olarak 1800'lerin sonlarında sentezlenen dörtlü amonyum bileşiklerinin (QAC) bakterisit, fungusit ve termisit etkileri iyi bilinmektedir. Yeni bir dörtlü amonyum bileşiği olan didecyl dimethyl ammonium tetrafluoroborate (DBF) Eczacılık ve Kozmetik Malzemeler Araştırma Birimi, Sanyo Kimya Endüstrileri, Ltd., Kyoto, Japan laboratuvarlarında geliştirilmiştir (Kartal et al., 2005; Hwang et al., 2005). Emprenye maddelerinin formülasyonlarında anyonlar ve katyonlar bu maddelerin erime sıcaklığı, yoğunluk, vizkozite, suda çözünürlük ve koruyucu özelliklerini belirlemede önemli bir rol oynadığından (Pernak et al., 2004), ticari olarak elde edilebilen didecyl dimethyl ammonium chloride (DDAC)'in kimyasal formülasyonu DBF bileşiğini elde etmek amacı ile değiştirilmiştir.

Bu çalışmanın amacı endüstriyel kontrplak tutkalı olan fenol formaldehidin formülasyonuna odun koruyucu olarak DBF'in uygulanabilirliğini ortaya koymaktır. DBF ile emprenye edilerek üretilmiş kontrplak panellerin yarıma direnci (MOR), elastikiyet modülü (MOE) ve yapışma kalitesi ticari bir emprenye maddesi olan DDAC ile karşılaştırmalı olarak değerlendirilmiştir. Ayrıca, DBF ve DDAC ile emprenye edilmiş kontrplakların beyaz ve esmer çürüklük mantarları ile toprak altı termitlerine karşı dayanıklılık özellikleri belirlenmiştir.

2. Malzeme ve Yöntem

Kontrplak üretiminde radiata çamından ticari olarak üretilmiş soyma kaplamalar kullanılmıştır. Kaplama örnekleri kondisyonlama kabiniinde %7 denge rutubetine ulaşmaya kadar tutulmuştur.

Kontrplak üretimi için tutkal karışımında ticari bir fenol formaldehit (PF) reçinesi (C-4S037-B) kullanılmıştır. Bütün tutkal bileşenleri tartılmış ve hazırlanan tutkala % 3, 6 ve 9 konsantrasyonundaki DBF ya da DDAC emprenye maddeleri karıştırılmıştır.

Kontrplak panellerinin üretimi öncesinde emprenye edilmiş her kaplama % 7 rutubete ulaşak şekilde tekrar kondisyonlanmıştır. Tutkal kaplama yüzeyine 200-225 g/m² oranında uygulanmıştır. Tutkal püskürtülmüş 3 kaplama hemen birleştirilmiş ve 10 kg/cm² basınç altında 30 dakika ön basınç uygulanmıştır. Daha sonra 10 kg/cm² basınç altında 145°C'de 8 saat sıcak pres uygulanmıştır. Testler öncesinde kontrplak paneller 20°C sıcaklık ve % 65 bağıl nemde 3 hafta boyunca kondisyonlanmıştır.

Kontrplak panellerden kesilen örnekler üzerinde yarıma direnci (MOR) ve elastikiyet modülü (MOE) EN 310 (1993) standardına göre yapılmış ve EN 636 (1996) standardına göre değerlendirilmiştir. Yapışma kalitesi denemeleri EN 314-1 (1993) standardına göre gerçekleştirilmiştir.

Çürüme testleri Japonya Endüstriyel Standartı (JIS) JIS K 1571 (JIS, 2004)'e göre esmer çürüklük mantarı *Tyromyces palustris* (Berkeley et Curtis) Murrill (FFPRI – Forestry and Forest Products Research Institute- 0507) ve beyaz çürüklük mantarı *Trametes versicolor* (L. ex Fr.) Quel. (FFPRI 1030) kullanılarak yapılmıştır. Termit denemeleri ise JIS K 1571 (JIS, 2004) standardına göre *Coptotermes formosanus* Shiraki toprak altı termiti kullanılarak gerçekleştirilmiştir.

3. Sonuç ve Tartışma

DBF ve DDAC ile emprenye edilmiş kontrplak örneklerinin MOR değerlerinde emprenyesiz örneklerle karşılaştırıldığında istatistiksel anlamda önemli bir azalma olmadığı tespit edilmiştir. DBF ve DDAC ile emprenye edilmiş kontrplak örnekleri ve kontrol örneklerinin paralel ve dikey yöndeki MOR değerleri kontrplak için gerekli minimum şartları sağlamıştır F25-F30 (38-45 N/mm²) (EN 636, 1996). DDAC ile emprenye edilmiş örneklerin MOE değeri DBF ile emprenye edilmiş örneklere ve kontrol örneklerine göre daha düşük olarak tespit edilmiştir. Beklenmedik bir şekilde hiçbir örnekte TS 4520 (1985) standardında belirlenen yapışma kalitesi değeri (0.8 N/mm²) sağlanmamıştır. DBF ve DDAC emprenye maddeleri ile emprenye edilmiş kontrplak örnekleri ile emprenye edilmemiş kontrol örnekleri karşılaştırıldığında mekanik özelliklerde önemli bir değişiklik görülmemiştir.

T. palustris ve *T. versicolor* mantarlarına maruz bırakılan emprenye edilmemiş kontrplak örneklerinde meydana gelen ortalama ağırlık kayıpları sırası ile % 31.9 ve % 29.4 olmuştur. DDAC ile emprenye edilen kontrplak örneklerinde DBF ile emprenye edilenlere göre her iki mantar türünde de önemli derecede daha yüksek ağırlık kayıpları meydana gelmiştir.

Termit denemeleri sonucunda emprenye edilmemiş kontrplak örneklerinde % 17.9 ağırlık kaybı meydana gelmiştir. Emprenye edilmiş bütün kontrplak örneklerinde emprenye edilememiş kontrplak örneklerine göre hafif derecede daha yüksek termit ölümleri görülmüştür. Bu sonuçlar DBF ve DDAC emprenye maddelerinin kontrplak örnekleri üzerinde termit saldırılarına karşı koruyucu bir etkiye sahip olmadığını göstermektedir.

Elde edilen sonuçlar çalışma ve üretim koşullarında kullanılan PF reçinesinin DBF ve DDAC emprenye maddeleri ile uyum göstermediğini ortaya koymaktadır.

References

- Van Acker, J.C.R. and M.K.M. Stevens, 1993.** Improvement in decay resistance of some commercial plywoods by waterborne and solvent-borne preservative treatments. *In: Proceedings of IUFRO Symposium on the Protection of Wood-Based Composite Products.* May 1993, Orlando, Florida, USA, pp. 88-92.
- Akbulut, T., S.N. Kartal and F. Green III, 2004.** Properties of medium density fiberboard (MDF) treated with N'-N-(1, 8-Naphthyl) hydroxylamine (NHA-Na), borax and boric acid. *Forest Products Journal.* 54 (10): 59-64.
- Barnes, H.M. and T.L. Amburgey, 1993.** Technologies for the protection of wood composites. *In: Proceedings of IUFRO Symposium on the Protection of Wood-Based Composite Products.* May 1993, Orlando, Florida, USA, pp. 7-11.
- Curling, S.F. and R.J. Murphy, 1999.** The effect of artificial ageing on the durability of wood-based boards materials against basidiomycete decay fungi. *Wood Science and Technology.* 33: 245-257.
- EN 310., 1993.** Wood-based panels. EN 310: Determination of bending strength and modulus of elasticity. European Committee for Standardization.
- EN 636., 1996.** Plywood-Specifications-Part 1: Requirements for plywood for use in dry conditions. European Committee for Standardization.
- EN 314., 1993.** Plywood-Bonding quality-Part 1: Test methods. European Committee for Standardization.
- Gosselin RE, R.P. Smith, H.C. Hodge and J.E. Braddock, 1984.** Clinical Toxicology for Commercial Products. 5th Edition. Williams and Williams: Baltimore, MD.
- Hwang, W.J., S.N. Kartal, K. Shinoda, and Y. Imamura, 2005.** Surface treatment for preventing decay and termite attack in wood using didecyl dimethyl ammonium tetrafluoroborate (DBF) incorporated with acryl-silicon type resin. *Holz als Roh und Werkstoff.* 63: 204-208.
- Hwang, W.J., S.N. Kartal, Y. Imamura, K. Tsunoda and, K. Shinoda, 2007.** Comparative effectiveness of two alkylammonium compounds as wood preservatives. *Journal of Wood Science.* 53: 332-338.
- Hwang, W.J., S.N. Kartal, T. Yoshimura and Y. Imamura, 2007.** Synergistic effect of heartwood extractives and quaternary ammonium compounds on termite resistance of treated wood. *J of Pest Management Science.* 63: 90-95.
- Hwang, W.J., S.N. Kartal and Y. Imamura, 2006.** Evaluation of new quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) in comparison with DDAC: Leachability and termite resistance tests. *Holz als Roh und Werkstoff.* 64: 111-116.
- JIS K 1571., 2004.** Test methods for determining the effectiveness of wood preservatives and their performance requirements (in Japanese). Japanese Standard Association.
- Kamdem, D.P., A. Pizzi and A. Jermennaud, 2002.** Durability of heat-treated wood. *Holz als Roh und Werkstoff.* 60:1-6.
- Kartal, S.N. and F. Green III, 2003.** Leachability of boron from wood treated with natural and semi-synthetic polymers and calcium precipitating agent. *Holz als Roh und Werkstoff.* 61 (5): 388-389.

- Kartal, S.N., K. Shinoda and Y. Imamura, 2005.** Laboratory evaluation of boron-containing quaternary ammonia compound, didecyl dimethyl ammonium tetrafluoroborate (DBF) for inhibition of mold and stain fungi. *Holz als Roh und Werkstoff.* 63: 73-77.
- Kartal, S.N., W.J. Hwang, K. Shinoda and Y. Imamura, 2006.** Laboratory evaluation of boron-containing quaternary ammonia compound didecyl dimethyl ammonium tetrafluoroborate (DBF) for control of decay and termite attack and fungal staining of wood. *Holz als Roh und Werkstoff.* 64 (1): 62-67.
- Laks, P.E. and M.J. Manning, 1995.** Preservation of wood composites with zinc borate. Doc. No. IRG/WP 95-30074. The Inter. Res. Group on Wood Preservation, Stockholm, Sweden.
- Laks, P.E. and M.J. Manning, 1997.** Mobility of zinc borate wood composite preservative. IRG/WP 97-30153. International Research Group on Wood Preservation, Stockholm, Sweden.
- Matejuk J.Z., E. Urbanik and J. Pernak, 2004.** New bis-quaternary ammonium and bis-imidazolium chloride wood preservatives. *Holzforschung.* 58: 292-299.
- Pernak J, J.Z. Matejuk, A. Kropacz and F. Flaczyk, 2004.** Ionic liquids in wood preservation. *Holzforschung.* 58: 286-291.
- Preston A.F., P.J. Walcheski, P.A. McKaig and D.D. Nicholas, 1987.** Recent research on alkylammonium compounds in the U.S. *In: Proceedings, American Wood Preservers' Association (AWPA)* 83: 331-34.
- TS 4520., 1985.** Kontrplak - Yapıda Kullanılan. Turk Standardlar Enstitüsü, Ankara.
- Tsunoda, K., H. Watanabe, K. Fukuda and K. Hagio, 2002.** Effects of zinc borate on the properties of medium density fiberboard. *Fores Prod. J.* 52 (11/12): 62-65.