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The effect of diammonium phosphate and sodium silicate on the adhesion and fire properties of birch veneer

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Abstract: In built environments the combustibility of wood is a great concern, which limits the use of wood as a building material due to legislation. The reaction-to-fire properties of wood can be altered with the use of fire-retardant chemicals, and most of the commonly used fire retardants already have a long history of use. However, only limited information is available on the impact of different fire retardants on the adhesion properties of wood. Additionally, comparative studies between chemicals from different groups of fire retardants is scarce. The objective of this study was to investigate and compare the effects of two commonly used fire retardants, sodium silicate (SS) and diammonium phosphate (DAP), on veneer properties, the focus being especially on thermal behavior and adhesion. Thermal properties and combustibility were studied using thermogravimetric analysis (TGA), flame test and calorimetry. Glue bond strength was analyzed with an automated bonding evaluation system (ABES) and the leaching of chemicals was determined according to EN84. Additionally, the surface characteristics of modified veneers were imaged with scanning electron microscopy (SEM). Results revealed notable differences in the thermal properties of SS and DAP, with DAP having better fire-retardant performance in all thermal testing. SS also affected thermal properties and combustibility of modified veneers, but the effect was only moderate compared to DAP. Neither SS or

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Michael Altgen, Daniela Altgen, Tuomas Hänninen and Lauri Rautkari: Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Vuorimiehentie 1, Espoo 02150, Finland DAP had any significant resistance against leaching but ABES testing showed a notable increase in the glue bond strength of DAP modified veneers.

Keywords: adhesion, diammonium phosphate, fire retardant chemicals, sodium silicate, wood combustion

Introduction

Combustibility, which is often considered the greatest disadvantage of wood products in built environments, can be reduced effectively with the utilization of fire-retardant chemicals. The progress in the development of new fire retardants is relatively slow, especially in the field of wood technology, and the majority of the common fire retardants already have a long history of use (Kozlowski and Wladyka-Przybylak 2000; Rowell and Dietenberger 2012). Most of the recent studies on the subject have focused on the development of solutions with a lower environmental impact and more leaching resistant systems. Achieving a good fire performance is relatively easy, but leaching and migration within the material in moist conditions and humid environments is the main issue with many of the current fire retardants. This naturally limits their use in exterior applications (Rowell and Susott 1982; Östman et al. 2001; Obanda et al. 2008). However, the effects of fire retardants on other wood properties, especially adhesion, have received less attention.

In general, fire retardants do not improve the fire endurance of wood, but rather inhibit the flame spread and decelerate the ignition and heat release characteristics, which are the most important aspects considering real fire scenarios in built environments (Sweet 1993). Commercial fire-retardant formulations usually employ a wide mixture of different components to produce the best results. Ideally, the selected components should target different parts in the combustion process. Some fire retardants are more effective in delaying ignition, while others better inhibit smoke production or subdue glowing combustion (Kozlowski and Wladyka-Przybylak 2000;

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Winandy 2013). It is also important to acknowledge that commercial formulations also contain, for example, buffering agents; meanwhile laboratory research has traditionally focused on model compounds used as components of commercial mixtures. Buffers are used to eliminate the negative effect of low pH, which in combination with elongated exposure to elevated temperatures has been shown to decrease the mechanical properties of wood due to the degradation of hemicelluloses (Lebow and Winandy 1999; Winandy 2013).

The most common fire retardants used for wood and other lignocellulosic materials are inorganic compounds that can be further divided into the main groups of ammonium and alkali metal salts, borates and silicates, which all have been in commercial use already for decades (Kozlowski and Wladyka-Przybylak, 2000; Rowell and Dietenberger, 2012; Sharma et al. 2015). The differences between these subgroups and their mechanisms of action in reducing the combustibility are well known. However, only a few comparative studies of fire retardants from the different main groups are available. There is also great variation regarding the treatment dosages or concentrations used, as well as in the application methods themselves. Therefore, in this work a typical example of an ammonium salt and silicate were selected to be compared in their fire performance and their effects on veneer adhesion, using equal concentrations and treatment processes.

Diammonium phosphate (DAP) is one of the most used ammonium salt-based fire retardants. DAP decomposes to ammonia and phosphoric acid when exposed to heat. Phosphoric acid releases water, which together with ammonia dilutes the volatile pyrolysis gases. This type of combination of phosphorous and nitrogen presents effective synergism by enhancing the fire performance of the two individual components, when combined (Tyner 1941; Kozlowski and Wladyka-Przybylak 2000; Lowden and Hull 2013; Östman and Tsantaridis 2016b). The most explored forms of silicon-based fire retardants are those based on silicon dioxides, also known as silicates, which are also widely employed as additives (e.g. glue extenders). They are typically introduced to wood in an alkali form, the most common example being sodium silicate (SS; Na₂SiO₂), also known as water glass. In fire retardant formulations, SS functions by forming a heat barrier of accumulating inorganic silica residues on the wood surface. This residue functions as an insulating, porous barrier that prevents the release of the volatile pyrolysis products and also reduces the amount of heat that is transferred back to the wood substrate (Mai and Militz 2004; Lowden and Hull 2013; Lee and Thole 2018; Nguyen et al. 2019). Many fire retardants for lignocellulosic materials

work in a similar way by promoting char formation at lower temperatures, as char has a thermal conductivity several times lower than wood (Kozlowski and Wladyka-Przybylak 2000).

Impregnation is the most common method of incorporating fire retardant chemicals to veneers and veneer products. However, changes in the direct wood surface affect also the adhesion properties of the material. Adequate penetration of glue into the wood substrate is necessary in order for strong adhesion to take place (Jost and Sernek 2009; White and Dietenberger 2010). It is well acknowledged that modification with fire retardant chemicals may cause a disturbance with the adhesion of wood surfaces and especially in coating systems, as the chemicals interfere with the direct glue contact. This is likely to occur especially with silicate-based systems, as they tend to form a protective film on the wood material (Lowden and Hull 2013). Besides physically preventing the direct contact between the glue and wood substrate, fire retardants can also cause chemical interferences in the glue bond formation. Distinguishing these chemical effects of fire retardants on adhesion is more challenging because of the complexity of the polymerization reaction, as well as the generally high variability in the glue compositions (Black 1958). Fire retardants containing inorganic salts are known to release acid compounds in elevated temperature and moisture conditions, which are present in the hot-press curing. For example, the effectiveness of DAP as a fire-retardant chemical is based on its ability to release phosphoric acid and ammonia at elevated temperatures. Phosphoric acid and ammonia prevent the curing of phenolic resins, which are generally alkaline substances. Changes in the hygroscopicity of the wood material, which is a common side effect of many fire-retardant chemicals, also affects the glue bond formation, because water is a common carrier agent for most adhesives (Sernek 2002; White and Dietenberger 2010).

The aim of the present work was to compare two common fire retardants of different chemical groups, SS and DAP, in their thermal behavior and combustibility. Their effects on other veneer properties were also evaluated: the extent of leaching was determined, as well as their effect on veneer adhesion.

Materials and methods

Materials: The wood material used in all of the tests, except for mass loss calorimetry, was 0.8 mm thick rotary cut silver birch (*Betula pen-dula* Roth) veneer, cut to dimensions of 116×112.5 mm². Two different chemicals were used for modifications: SS (Merck KGaA, Darmstadt,

Germany, sodium silicate solution extra pure, CAS Number: 1344-09-8) and DAP (Merck KGaA, Darmstadt, Germany, ≥99%, CAS Number: 7783-28-0). From both, 30 w% and 15 w% aq. solutions were prepared and used to impregnate the wood material used in the thermogravimetric analysis (TGA), flame test, leaching test and scanning electron microscopy (SEM) and automated bonding evaluation system (ABES) analysis. Impregnation was carried out in a vacuum of 50 mbar absolute pressure for 1 h in room temperature. The treated veneers were then dried in 103°C for 24 h and conditioned in 25°C 30% relative humidity (RH) prior to testing. The weight percent gain (WPG) of samples was calculated from the difference of oven dry sample mass before and after the treatment, divided by the initial oven dry mass of the unmodified sample. For mass loss calorimeter (MLC) testing, separate laboratory plywood panels with dimensions of $10 \times 10 \times 1$ cm³ were prepared from 1.5-mm thick veneers, which is the typical thickness of birch veneer in plywood production. The thicker veneers were impregnated with 20% solutions of DAP and SS, with the impregnation carried out as previously described. Phenol-formaldehyde resin (14J025, Prefere Resins Ov, Hamina, Finland) without hardeners was used in the panel preparation, using glue spread of 160 g m⁻². After prepressing at room temperature for 8 min and hot-pressing at 130°C for 7 min, the panels were cooled down and stored at 20°C and 65% RH.

Thermal properties: The thermal behavior of the impregnated veneers and the pure chemical components themselves was characterized by TGA, using a Thermo Gravimetric Analyzer Q500 TGA (TA Instruments, New Castle, DE, USA) instrument. Samples were ground to a fine powder in a Wiley mill to pass through a 1-mm mesh and a sample mass of 10–15 mg was used in the analysis. The measurements were carried out under nitrogen gas a purge rate of 60 ml min⁻¹ and a heating rate of 10°C min⁻¹, ranging from room temperature to 600°C. The mass loss was recorded as a function of temperature and the onset point, the temperature at the maximum rate of decomposition and the final amount of residue were determined for each sample.

To assess combustibility characters such as flame spread and duration of flaming and glowing combustion stages, fire resistance was studied based on the procedure described by Pries and Mai (2013). The samples were clamped into a holder and placed on top of a balance, positioned at an angle of 45° to the vertical and ignited from the tip of the sample. The flame height, strength and distance from the sample during ignition were kept constant and mass loss against time was recorded for three samples per each treatment group. Durations of both flaming and glowing combustion were also determined visually.

Mass loss calorimeter testing was performed according to ISO 5660-1. The samples were wrapped in aluminum foil from their sides and bottom, leaving one face open. A heat flux of 50 kW m⁻² was used and the time to ignition (TTI), total heat release (THR) rate and mass loss were recorded for five samples per treatment group. The measured mass loss was compared with a calculated theoretical value, based on the known amount of fire retardant present in the wood by WPG. This was done in order to eliminate the effect of uncombustible plywood residues on the mass loss evaluation. The calculations were carried out according to Eq. 1, where $m_{plywood,0}$ is the plywood sample mass before calorimetry, $m_{plywood,a}$ is the plywood sample mass after calorimetry and m_{wood} the mass of dry wood present in the plywood panel without resin or fire retardants.

Corrected mass loss (%) =
$$\frac{m_{plywood,0} - m_{plywood,a}}{m_{wood}} \times 100$$
 (1)

Adhesion and leaching properties: Leaching of the chemicals was assessed applying the method EN 84:1997. The leaching test was performed separately from the other tests and was not applied as a pretreatment prior to testing of fire or adhesive properties. Ten oven-dry samples per each treatment group were vacuum impregnated with deionized water at 40 mbar for 20 min. After releasing the vacuum, the samples were left in the vessels for 2 h. The water was then replaced with 400 ml of fresh deionized water and the sample immersion was continued for 14 days at room temperature. During this time the water was changed in total 9 times: at the end of the first and second day of immersion and later at intervals of 1 to 3 days. Finally, the samples were dried at 103°C for 24 h and the amount of leachant was determined from the difference between the oven-dry sample mass before and after leaching, divided by the oven-dry mass of unmodified sample (Boonstra 1997; Baysal et al. 2006; Altun et al. 2010).

The surfaces of treated veneers were characterized using a SEM (Zeiss, Sigma VP, Jena, Germany). Veneer samples were coated with a 10-nm carbon layer and images were taken using a detector for back-scattered electrons (BSD) and a beam acceleration voltage of 5 kV.

Bonding of the veneers was evaluated with ABES (Adhesive Evaluation Systems Incorporated, Corvallis, OR, USA), using a phenol-formaldehyde resin (14J025, Prefere Resins Oy, Finland). A total of 8.6 μ l of the resin was dispensed on the sample, and using another sample spread evenly to an area of 20 × 5 mm², which corresponds to an adhesive load of 100 g m⁻². As soon as the spreading was finished, the glue line was pressed at 130°C and 2 MPa. Four different press times were used: 60, 100, 140 and 180 s. Shear strength in the grain direction was measured by the device immediately after pressing. A total of 11 specimen per treatment group was used in the analysis.

Results and discussion

Thermogravimetry

TGA revealed that both SS and DAP altered the veneer pyrolysis behavior. The TGA results of the reference veneer material and modified samples are presented in Figure 1 and summarized in Table 1. The effectiveness of a fire retardant can be evaluated from TGA data through a decrease in the pyrolysis onset point, T_{onset}, and the temperature of the maximum rate of decomposition, T_{max}. Additionally, an increase in the amount of produced charcoal is known as an indirect indicator of reduction in the amount of combustible gases produced in the process, which can be evaluated from the amount of residual mass (RM) after pyrolysis (Rowell and Dietenberger 2012). TGA revealed that the presence of SS had very little effect on the T_{onset}, which remained on the level of the reference with the 30% impregnated samples. For the 15% SS impregnated samples, T_{onset} rose by only 5°C. However, regardless of the treatment concentration, SS effectively lowered T_{max} compared to the reference and, therefore, shifted the pyrolysis pathway at least partially to lower temperatures by nearly



Figure 1: TGA curves of reference and 15% and 30% modified SS and DAP veneers.

60°C. An increase in the amount of RM was also observed for SS modified veneers, 27.3% for 15% SS and 33.5% for 30% SS, which is higher than that of the reference (13.1%). Additionally, the RM of modified samples was compared with the calculated theoretical RM based on the results from pure chemicals and reference. This was done in order to evaluate the impact of fire-retardant chemicals on the actual char yield after pyrolysis. For SS modified samples, a notable increase in the RM was indeed observed. The calculated theoretical RM values of 15% and 30% SS treatments did not compare with the actual test results: the theoretical RM was lower than the measured value (19.2% for 15% SS and 25.9% for 30% SS). This may indicate that increased char formation took place, which allowed protection of the wood substrate during pyrolysis. However, in a recent study Xiao et al. (2016) found alkaline silicate dispersions to have no effect on the char yield, so further study on the subject is needed.

Testing of pure aqueous SS in the TGA also revealed interesting aspects of its structure. White, hard and foamlike residue was formed, which expanded in volume during testing. Subasri and Näfe (2008) reported that this foaming of SS occurs at 400-750°C, which is later followed by the collapse of the porous structure. They also found that pure SS remains amorphous up to 300°C, which is close to the measured T_{max} values of 15% and 30% SS modified samples (305–308°C) in this work. The residues from 30% SS modified veneer samples showed a different structure than the DAP modified samples. The milled veneer remains of SS samples did not collapse to a powder-like form, which occurred with the DAP samples' residues. SS seemed to maintain the structure intact and form a protective layer on the wood material surface, as it is stated to function in the literature (Kozlowski and Wladyka-Przybylak 2000; Lowden and Hull 2013).

Modification with DAP effectively lowered both Tonset and T_{max} even more than SS, indicating an improved fire performance by shifting the overall pyrolysis to a lower temperature range. Modification with 30% DAP lowered on average the T_{onset} by 28°C, which was notably more than with SS. The WPG of the sample veneers affected the $\mathrm{T}_{\mathrm{onset}}$, which was lowered more with the 15% than with the 30% DAP concentration. This was unexpected, as stronger treatments and higher WPG values were assumed to be more effective and therefore lower the $\mathrm{T}_{_{\mathrm{onset}}}$ more compared to the reference. However, these differences were balanced out by the T_{max} values, which were within 4°C from each other for both treatment concentrations, independent of the differences in WPG values. DAP also increased the amount of RM by nearly 17% compared to the reference. The effect of DAP on the char yield was analyzed in the same way as with SS, and again the theoretical RM was lower than the actual measured value (19.4% for 15% DAP and 15.0% for 30% DAP). Indeed, Di Blasi et al. (2007) reported that DAP content of 20% in wood

Table 1: Results from TGA testing, listed together with the WPG values of modified samples.

	Treatment		TGA		
Sample	concentration (%)	WPG (%)	T _{onset} (°C)	T _{max} (°C)	RM (%)
Reference	-	_	257	362	13.1
SS	Pure component	-	116	129	36.4
	15	5.4 (0.7)	262	308	27.3
	30	11.5 (2.5)	257	305	33.5
DAP	Pure component	_	146	600	31.3
	15	7.8 (1.4)	201	274	30.4
	30	18.6 (2.7)	238	278	30.5

DAP, Diammonium phosphate; RM, residual mass; SS, sodium silicate; TGA, thermogravimetric analysis; WPG, weight percent gain.

strongly increased the char yield. This is also supported by the observation that RM of 15% and 30% DAP impregnated samples was within 0.1% from each other, which based on the different WPG values was unexpected. If the RM consisted mainly of the DAP salt itself, which was still at the stage of rapid decomposition in the TGA testing until 600°C, the RM should depend solely on the WPG of the samples. Therefore, the salt may have protected the wood substrate. Overall, it is evident from TGA results that SS and DAP affected the veneer pyrolysis differently, targeting different stages of the degradation process. DAP shifted the pyrolysis pathway to lower temperatures more effectively, which in the light of previous literature also indicates better performance in actual combustion.

Flame test

The mass loss results from flame test are presented in Figure 2a. The test revealed great differences in the combustibility of SS and DAP modified samples. Reference samples decomposed fully in the flame test, resulting in nearly 0% RM. Both SS and DAP provided at least partial fire protection to the modified veneer material, but the effect of the treatment concentration was clearly visible. With DAP this was the most prominent, as the 30% DAP impregnation inhibited the ignition almost completely and a mass loss of less than 1% occurred after the source of ignition was removed. The total RM was 92%, which was notably higher than with the other treatments. With 15% DAP impregnation, the amount of RM was only 33%, although this was still the second highest result of all samples. The durations of flaming and glowing combustion were also determined, and the results are presented in Figure 2b. With both 15% and 30% DAP samples, visible charring occurred close to where the source of ignition was placed, but no flaming or glowing combustion could be observed after the source was removed after 20 s.

In turn, SS modified veneers continued burning and the flames rapidly spread across the sample after the source of ignition was removed and the samples were thoroughly charred during the test. Fifteen percent of SS solution impregnated samples resulted in 14% of RM, but the 30% solution impregnated veneers improved the material protection so that the amount of RM was 28%. The amount of RM was clearly lower for SS than for DAP treated samples, but the SS samples remained physically intact after testing, instead of decomposing to powder-like ash as the reference. The observed duration of flaming combustion of the SS modified veneers was in the same range as that of the reference. However, the glowing combustion time of samples



Figure 2: Results from flame test, showing (a) mass loss of samples against time and (b) flaming and glowing combustion durations. Both treatments increased the amount of RM and SS also notably prolonged the glowing combustion time.

was clearly prolonged by SS modification, although the variation was also higher than with other samples. Similar behavior for cellulosic textile fibers was reported by Basak et al. (2014), who found that treatment with SS up to 6% WPG significantly prolonged the afterglow. In glowing combustion, CO and CO, are produced in the exothermic oxidation reactions of the highly active residual char, if sufficient oxygen is provided. Effective glow retardants are known to increase the ratio of CO to CO₂ formed, which minimizes the heat needed for the oxidative reactions to proceed. Cations, such as sodium, do the opposite and reduce the ratio of the two compounds. Therefore, the sodium component of SS may in fact promote glowing (Shafizadeh 1984). In turn, phosphoric salt compounds, such as DAP, are known to alter the CO to CO₂ ratio even in small amounts, which makes them highly effective in preventing glowing combustion (Browne 1958; Tyner 1941).

Mass loss calorimeter

Results from calorimeter testing verified the FR effect observed during the TGA and flame test for PF-bonded

Sample type	TTI (s)	THR (MJ m ⁻²)	Mass loss (%)
Birch	38 (6)	135 (5)	100 (1)
Plywood reference	38 (6)	143 (7)	97 (2)
SS plywood	38 (10)	110 (27)	79 (6)
DAP plywood	43 (29)	97 (6)	77 (1)

 Table 2: Results from MLC testing of modified plywood samples.

DAP, Diammonium phosphate; MLC, mass loss cone calorimetry; SS, sodium silicate; THR, total heat release; TTI, time to ignition.

veneer layers (plywood). Unmodified solid wood and plywood from unmodified veneers were compared with plywood prepared from veneers impregnated with 20% SS and DAP solutions, as is presented in Table 2. Unsurprisingly, SS and DAP both affected how the controlled combustion of samples proceeded, although clear differences were observed between the two treatments. Both resulted in a lowered THR, which is the total cumulative heat released over the total duration of the test. With DAP, a reduction in THR compared to reference solid wood and to unmodified plywood was observed, resulting in a decrease of 38 MJ m⁻² and 46 MJ m⁻² of THR, respectively. Similar findings regarding the effect of phosphate salts on the heat release of wood-based substrates during calorimetry have been reported in the literature (Grexa et al. 1999; Terzi et al. 2011; Ayrilmis et al. 2012). DAP was also found to be more effective against ignition, delaying the TTI by 5 s compared to the reference materials. High variation in the TTI of DAP samples is due to very weak burning of the samples during the test, with the fire self-extinguishing and re-igniting during the test. Similar effect did not occur with SS, which resulted in the same TTI of 38 s as the unmodified materials, although the data variation was high. Similar findings about silicate-based fire retardants not being able to delay the ignition of cellulosic substrates have been reported previously (Shabir Mahr et al. 2012; Grancaric et al. 2015).

Total mass loss of reference solid wood was 99.8%, which was higher than that of reference plywood with 97.1%. This is likely due to the amount of non-combustible residue from the phenol-formaldehyde resin present in the plywood panels, although the exact amount of residue could not be determined due to high data variation. The residual resin was excluded from the calculations, as it was considered to correspond to only to a small fraction in calculating the mass loss of modified plywood samples. Otherwise, the mass loss was evaluated similarly as the mass loss measured in the TGA. The mass loss was corrected for the WPG of the modified samples to ensure that the reduction in mass loss is not solely caused by the presence of a less-combustible material, and the calculations



Figure 3: Comparison of actual and calculated mass loss results from MLC.

were carried out according to Eq. 1. Thereby, the loss in mass was related to the pure wood material and the results are visualized in Figure 3. Even though the actual mass loss of 20% SS and DAP plywood were similar and seemingly low compared to the references, 79% and 77%, respectively, the corrected mass loss was higher. The corrected mass loss was 90.1% for SS and 86.2% for DAP plywood, taking into account the amount of remaining fire-retardant chemical. However, this is still lower than the reference mass loss, indicating that protective mechanisms have taken place to shield the wood substrate in the plywood samples. Mass loss for DAP was nearly 4% lower than for SS, signaling a slightly better performance, although the difference was so small that it would likely be negligible in real fire scenarios. It has been reported previously that elevated temperatures weaken the performance of fire retardants in an actual fire, which should be taken into account when considering these results (White and Dietenberger 2004). The treated veneers were briefly exposed to 130°C for 7 min during hot-pressing of the panels, which may have lowered their actual performance in calorimetry.

Leaching

Results from leaching tests are presented in Figure 4. The exact amount of leachant from each sample was calculated and compared with the original WPG value. The amount of leachant from the reference was 2.5%, which was likely due to the removal of extractives. In Figure 4, those showing resistance against leaching are the ones positioned under



Figure 4: Results from leaching tests.

the y = x line, marking the balance between leachant and original WPG values. The load of chemicals after leaching in 15% and 30% SS modified samples was -1.7 w% and 2.7 w%, respectively. This implies that from 15% SS samples, all of the modifying agent and some excess wood material were washed out in the process. However, 30% SS samples still held some chemicals after the leaching process, showing minimal resistance against leaching. As an alkaline substance, SS is highly soluble in water and readily forms anionic silanolate groups, where the silicon particles directly interact with hydroxyl groups (Pries and Mai 2013). With DAP, the difference between leachant and WPG was 0.2 w% for 15% samples and -0.1 w% for the 30% samples, indicating that nearly all of the salt was washed off. The low resistance of DAP against leaching was anticipated, because as an inorganic salt it is extremely susceptible to leaching (Holmes 1976; Östman et al. 2001; Östman and Tsantaridis 2016a). These results again highlight how additional chemical agents or multi-stage impregnation processes are need in in order to produce more leachresistant systems (Kozlowski and Wladyka-Przybylak 2000). Based on these results, SS and DAP as they are should only be used in interior applications, where severe leaching will not be an issue. The leaching tests in this work were performed separately from ABES testing or SEM imaging, not as a pre-treatment prior to any other tests.

SEM and ABES

SEM images of the surfaces of 30% DAP and SS modified veneers are shown in Figure 5. For 30% DAP modified veneers, large salt crystals could be found on the veneer surface and accumulation of salt especially near



Figure 5: SEM images taken from the surface of (a) 30% DAP veneer and (b) 30% SS veneer samples.

DAP salt crystals, as well as formation of a ceramic SS layer could be detected.

the pits was observed. This visible salt crystallization at the veneer surface indicates migration of the solute salt within the veneer material during drying, when the solvent has moved within the structures and evaporated from the surface (LeVan and Jerrold 1990; Östman et al. 2001). For SS, the well-known formation of a ceramic layer on the veneer surface was observed. Strong cracking of the layer was also detected, which is clearly visible on the right-hand side of Figure 5b. Similar behavior of the



Figure 6: Glue bond strength results from ABES testing.

cracking layer was previously reported with silicate nanoparticles and wood by Shabir Mahr et al. (2012), who concluded that this was likely due to the large solid content of the used silicate precursors. Interestingly, cracking of the silicate layer was also linked to a reduced fire performance during cone calorimetry.

Results from ABES testing are presented in Figure 6. The glue bond strength of unmodified reference birch veneers was in the range of 350-420 N, which was similar to strength values reported by Rohumaa et al. (2014). An abnormal decrease in the glue bond strength was observed after 140 s press time for the reference; however, the variation at this measurement point was also high. As expected, modification with SS decreased the glue bond strength, especially with the stronger 30% solution impregnation. This was likely due to the formation of a ceramic layer on the veneer surface that was observed with SEM, which prevents direct contact between the adhesive and the wood substrate. However, gradual improvement in the glue bond strength of SS veneers was observed over longer press times, and at 140 s the performance was already at the level of reference veneers. As was noticed in TGA, thermal degradation of pure SS begins already at a T_{onset} of 116°C. Therefore, the improvement of the glue bond strength over the longer press times at 130°C may be due to gradual degradation of the SS, which eventually allowed for better adhesion to take place. Interestingly, DAP in turn notably improved the glue bond strength of the veneers with both 15 and 30% concentrations. With 30% impregnated samples, the improvement in glue line strength was nearly linear with the longer press times. This was unexpected, as the gluing of DAP treated has veneers with phenol-formaldehyde has been reported to

produce only moderate adhesive strength at best (Selbo 1959). DAP releases phosphoric acid during heating, which due to the lowered pH prevents the setting of phenolic resins and overall weakens the wood material. This phosphoric acid formation takes place at 160-170°C, which is higher than the 130°C press temperature used in this work (Sam Williams 2010; Lowden and Hull 2013). The slightly alkaline pH-value of DAP solutions used in the treatments (8.5) may have promoted the glue bond formation during pressing, as the synthesis and curing reactions of phenol formaldehyde occur at basic conditions, and DAP had not vet decomposed into a product of lower pH-value at 130°C (Kline et al. 1946; Riedl and He 2004). The small difference between 15% and 30% DAP samples may be explained by the salt migration towards the surface, which would have evened out the differences in actual salt load at the bonded surface. The fact that DAP modification improved bonding could have practical relevance in developing plywood products, as the increased glue bond strength could potentially be used to compensate for the strength loss that ammonium salt-based fire retardants are known to have on plywood (Lebow and Winandy 1999). Further work is needed to determine the actual mechanism behind the phenomena and investigate the potential of DAP in improving the adhesion along with fire performance of veneer products. Also, the impact of cyclic humidity exposure should be investigated when considering veneers modified with fire retardants, as the moisture sensitive chemicals may cause weakening of the glue bond strength in varied moisture conditions (LeVan et al. 1996).

Conclusions

The effect of SS and DAP on veneer properties was evaluated. When comparing the two fire retardants regarding their thermal properties, DAP performed better than SS in all areas: in TGA it shifted the pyrolysis pathway most effectively to lower temperatures, indicating a superior fire performance. This was also demonstrated in a flame test and by mass loss calorimetry, where DAP was more efficient in reducing the flaming and glowing combustion, mass loss, TTI and THR. Compared to DAP, SS had only a moderate performance in TGA, flame test and mass loss calorimetry, although it did provide some fire retardancy to the modified veneers. The fire retardants were also compared regarding their resistance against leaching, but both SS and DAP performed poorly. Interestingly, DAP notably increased the glue bond strength in ABES testing, which was unexpected. This was likely due to the optimal pH-conditions during hot-pressing but further work is needed to determine the actual mechanism behind the finding.

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