EFFECT OF VENEER CURING PROCESS ON BONDING QUALITYOF MODIFIED PLYWOOD

Trinh Hien Mai

Vietnam National University of Forestry

SUMMARY

Beech (*Fagus sylvatica* L.) veneers were treated with: two formulations based on N-methylol-melamine (NMM): 1) NMM solution (NMM-1, 10% solid content), 2) fatty acid modified NMM dispersions containing paraffin (with an aluminum salt as catalyst, mNMM-2, 5% solid content); and 3) alkyl ketene dimer dispersions (AKD, 1% solid content). Five treated veneers were glued with a phenol formaldehyde adhesive to produce plywood in two different processes. In the first process, the impregnated veneers were cured before gluing and pressing. In the second process, the curing of the impregnated veneers and the pressing to make plywood were combined in one step. Plywood produced from water-treated veneers served as controls. Bonding quality of the plywood was performed following the standard EN 314-1 (2004) with three pre-treatments prior to the test. The results showed that regardless of the plywood production process and pre-treatment, the plywood treated with NMM-1 resulted in increased shear strength (up to 28.5%) in comparison to the controls, whereas the treatments with mNMM-2 and AKD diminished the shear strength of the plywood to different extents. The cohesive wood failure of the control plywood varied from 50 to 100%, while this percentage of the treated plywood was much lower, between 0 and 40% in both process 1 and process 2. Nevertheless, the plywood of both processes (except mNMM-2 treated plywood in process 1) reached the requirements for the plywood used in non-covered exterior conditions according to the EN 314-2 (1993). Statistical analyses indicated that plywood produced in process 2 induced comparable or higher shear strength than that in process 1, the curing before gluing application resulting in negative effects on bonding quality is also discussed. The number of delaminated plywood specimens after the soaking/drying cycles was in agreement with the bonding quality.

Keywords: AKD, Beech, bonding quality, N-methylol melamine, plywood, veneer.

I. INTRODUCTION

Many efforts have been undertaken in order to improve the dimensional stability of wood as well as its decay and weathering resistance and thereby to prolong the service life in outdoor application (Hill 2006). Various chemicals have been well established with regard to solid wood modification. Wood treated with melamine-based compounds brought about remarkable improvements for solid wood, such as enhanced water repellence and dimensional stability (Inoue *et al* 1993, Pittman *et al* 1994, Nguyen *et al* 2007), increased hardness, modulus of elasticity and bending strength (Inoue *et al* 1993, Deka and Saikia 2000, Gindl *et al* 2004). In addition, water-based melamine treated wood indicated the potential to increase resistance against wood destroying fungi (Rapp and Peek 1996, Lukowsky *et al* 1999) and photochemical wood degradation caused by weathering (Rapp and Peek 1999). Alkyl ketene dimer (AKD) is widely used in the paper industry as an internal sizing agent. The hydrophobic effect of AKD is attributed to an esterification with hydroxyl groups of wood fibers and subsequent orientation of hydrocarbon chains (Isogai and Taniguchi 1992, Hubbe 2006). Thus, the application of AKD to wood and wood-based panels is expected to result in an increased dimensional stability; however, there have been only few studies using AKD for wood modification.

Beech (*Fagus sylvatica* L.) is one of the most important wood species used in veneer industry in Europe. It is easily treatable; nevertheless, its low durability limits the area of application. Modification of plywood is supposed to improve many properties such as dimensional stability, resistance to biodegradation and UV radiation, and strength properties of the plywood.

Like with other wood-based panels, properties of plywood rely on the adhesive bond formed between the veneers. Hence, improving the bonding quality plays an important role in the development of higher performing materials (Rohumaa *et al* 2007). Adhesive properties, wood veneers, working conditions and process parameters are the main factors affecting the bonding quality and the performance of plywood (Dunky 2003, Scheikl and Walinder 2002). In this study, the factors related to the veneer material and adhesive properties were fixed; however, working conditions and process parameters (impregnation, pre-drying, curing, gluing, hot press) could affect the performance of plywood. Therefore, the objective of this work is to investigate the influence of two different processes (with and without curing before gluing) on bonding quality of the treated beech plywood.

II. MATERIALS AND METHODS

2.1. Chemicals

N-methylol-melamine (NMM-1) was Madurit MW 840/75 WA (Ineos Melamines, Frankfurt/Main, Germany). The dynamic viscosity of the formulation was 430 mPa s, the density 1,256 g $ml^{-1}$and the pH-value 9.3 (all values at 25°C). NMM-1 is partly methylolated (with residual amino groups of the melamine) and partly methylated; the behaviour of NMM-1, hence, is rather hydrophobic, but still with the possibility of hardening.

The fatty acid modified N-methylol melamine formulation containing paraffin (mNMM-2) was Phobotex VFN (Ciba, Basel, Switzerland). It is a white emulsion with a pH-value of 5.3 and a specific gravity of 0.991 g ml^{-1} at 25°C. Due to the modification with fatty acid and the addition of paraffin, the substance shows predominately hydrophobic character. An aluminum salt solution (Catalyst RB, Ciba, Basel, Switzerland) was used as a catalyst for the curing of Phobotex VFN.

Alkyl ketene dimer (AKD), a chemical of paper industry, was Basoplast 4118 MC (BASF, Germany). It is a white emulsionwith pH value of 3.5 – 4.5 and viscosity of max 100 mPas (20^0C).

Phenol formaldehyde resin Prefere 4976 and hardener Prefere 5909 (Dynea, Erkner, Germany) was used as shown in the technical data sheet (Dynea, 2003) for the bonding of veneers.

2.2. Plywood production

Rotary cut beech (*Fagus sylvatica* L.) veneers with the dimension of 1.5 × 400 × 400 mm^3 (thickness × width × length) were impregnated in an autoclave under vacuum (60mbar) for 30 min and subsequently under pressure (12 bar) for 2 h with the following solutions: 1) N-methylol-melamine (NMM) solution (NMM-1, 10% solid content), 2) fatty acid modified NMM dispersions containing paraffin (mNMM-2, 5% solid content) with an aluminium salt as catalyst (1.7%), and 3) alkyl ketene dimer dispersions (AKD, 1% solid content). Water impregnated veneers were used for control plywood. The impregnated veneers were pre-dried in an oven at 40°C for 24h to a moisture content of 3-8% prior to the following processes:

Process 1: Pre-dried veneers were cured in a hot press of 130°C, 5 min and pressure 1 N mm^{-2}. Moisture content of the veneers after curing in the hot press was too low for gluing application; therefore, the veneers were room-conditioned for 4 days until the moisture content of the veneers was between 3 and 8%. An amount of 160 g m^{-2} PF glue (Prefere 4976, Dynea, Norway) was applied per veneer using a roller. Afterwards, 5-layer-plywood was produced in a hot press (130°C) at 1.5 N mm^{-2} (10 min pressing time).

Process 2: The steps were the same as in process 1, but the curing of veneers and the hot pressing (to make plywood) were combined in one step.

The prepared plywood was room-conditioned for 3 days before cutting to different sizes for bonding quality tests.

2.3. Bonding quality test

The bonding quality of the plywood was determined according to the EN 314-1 (2004). Twelve plywood specimens of 7.5 × 25 × 100 mm^3 (thickness × width × length) from each treatment were prepared. Each specimen was cut so that the grain direction of the layer between the glue lines under test is perpendicular to the length of the specimen (Fig. 1).

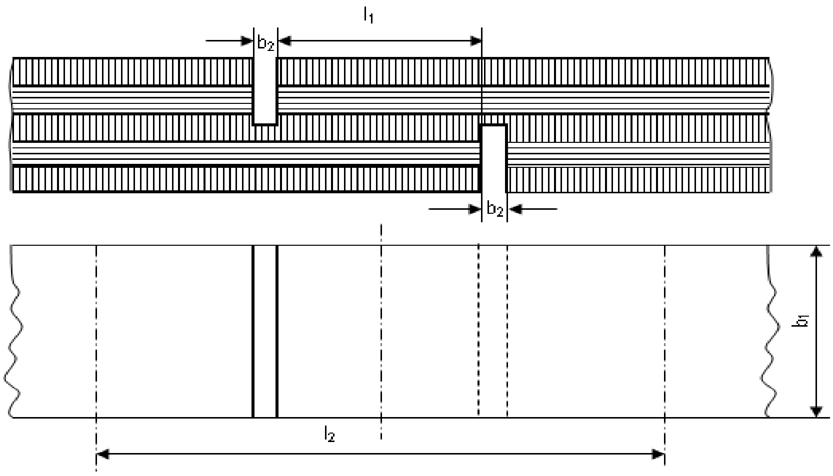

Figure 1. Bonding quality test specimen of 5 layer-plywood (Image based on the EN 314-1)

Where:

b_1: shear width of test specimen (25 ± 0.5) mm;

b_2: saw cut width from 2.5 to 4 mm;

l_1: shear length (25 ± 0.5) mm;

l_2: distance between two clamps 50 mm.

Prior to the test, the plywood specimens were pre-treated as follows: 1) immersion for 24h in water at 20°C, 2) immersion for 4h in boiling water, drying for 16-20h at 60°C, immersion for 4h in boiling water, and then cooling in water at 20°C for at least 1h, 3) immersion for 72h in boiling water, and cooling in water at 20°C for at least 1h.

As soon as the pre-treatments were fulfilled, the shear strength were determined using a universal testing machine Zwick/Z010 (Zwick, Ulm, Germany) and Equation 1:

$$f_v = \frac{F}{l_1 \times b_1} \qquad \textbf{(Equation 1)}$$

Where:

f_v: shear strength of each test specimen (N mm^{-2});

F: the failing force of the test specimen (N);

l_1: the length of the shear area (mm);

b_1: the width of the shear area (mm).

In addition, the cohesive wood failure of the separated plywood specimens was evaluated according to the reference illustrations in the standard EN 314-1 (2004) with an accuracy of 5%. Based on the mean values of shear strength and the mean values of cohesive wood failure, bonding quality of the plywood was classified as required in the EN 314-2 (1993).

2.4. Delamination test

The delamination test was conducted as

follows: ten plywood specimens of 7.5 × 50 × 50 mm^3 (thickness × width × length) from each treatment were oven-dried before the soaking/drying cycles. Each cycle consisted of 6 steps: 1) submersion in water 24 h; 2) water soaking under vacuum (60 mbar) 1 h , and storing under water 20 h; 3) air-drying 24h; 4) oven-drying 50°C, 24h; 5) oven-drying 80°C, 24h; 6) oven-drying 103°C, 24h and cooling to room temperature over silica gel in a desiccator. The cycle was repeated 6 times. The delaminated specimens were counted after each cycle.

2.5. Statistical analysis

Statistical analysis was applied to compare the shear strength of the plywood produced from process 1 (two step method) and process 2 (one step method). Since the data were not normally distributed, the results were analysed by a non-parametric method. The comparison between two means was conducted by Mann-Whitney-U test with the confident level of 95% (Hill and Lewicki 2007).

III. RESULTS AND DISCUSSION

3.1. Weight percent gain

The weight percent gain (WPG) of the veneers treated with 10% NMM-1 was 10.4 ± 1.0%; that of veneers treated with 5% mNMM-2 was 4.6 ± 0.2% and with 1% AKD was 1± 0.15%.

3.2. Bonding quality

A phenolic adhesive can produce better water and weathering resistant glue lines than the other synthetic adhesives because of the resistance to hydrolysis of the C-C bonds between the aromatic nuclei and the methylene bridges, therefore it is suitable for exterior products (Dunky, 2003). In this study, the phenolic glue had a recommended pressing time of 5.4 min for 5 layer-plywood with the veneer thickness of 1.5 mm and pressing temperature of 130°C (Dynea, 2003). However, a longer pressing time (10 min) for both processes was employed to avoid factors which could lessen the bonding quality and to ensure enough curing time for the veneers in process 2.

As observed in Fig. 2, regardless of the plywood production process and pre-treatment, the plywood treated with NMM-1 solution resulted in increasing of shear strength, whereas the plywood treated with mNMM-2 and AKD dispersions diminished shear strength of the plywood as compared to the control plywood. Nevertheless, the mean values of shear strength were higher than 1 N mm^{-2} in all cases (except mNMM-2 treated plywood in process 1).

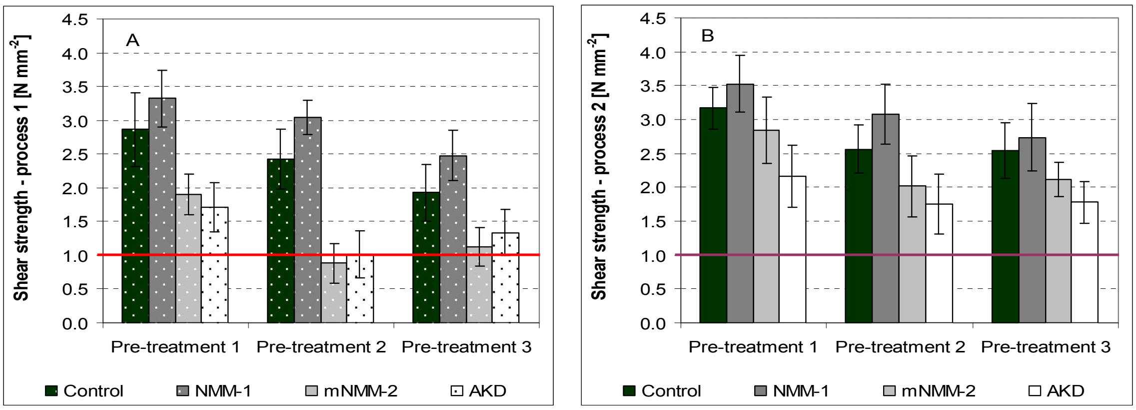

Figure 2. Shear strength of the control and treated plywood, process 1 (A) and process 2 (B)

The failure of the test plywood specimens occurred in the wood parts or in the glue lines between the saw cuts (within the shear test area) for both processes, hence the results of these shear tests were accepted according to the requirements of the standard EN 314-1.

The mean values of cohesive wood failure were shown in Table 1, in fact, the percentage of cohesive wood failure in the control plywood varied from 50 to 100%, while this percentage of the treated plywood was lower (0-40%) in both process 1 and process 2. According to the standard EN 314-2, the shear test of plywood-class 3 (for non-cover exterior use) needs to undergo the three pre-treatments. Each glue line of these three pre-treatments must satisfy two criteria about mean shear strength and mean cohesive wood failure; if the mean shear strength is higher than $1\ \mathrm{N\ mm^{-2}}$, there is no requirement of mean cohesive wood failure. As consequence, the plywood of both processes (except mNMM-2 treated plywood in process 1) passed the requirements of the plywood used in non-covered exterior condition.

Table 1. Mean values of cohesive wood failure of the control and treated plywood [%]

Treatment	**Mean values of cohesive wood failure [%]**		
	Pre-treatment 1	Pre-treatment 2	Pre-treatment 3
C_1	65.6	67.0	75.5
C_2	58.0	57.2	60.0
M_1	15.0	26.0	24.4
M_2	14.5	25.6	31.1
V_1	2.5	2.9	9.4
V_2	13.1	16.1	10.6
A_1	8.3	11.1	21.7
A_2	4.5	9.3	14.5

Where:

C_1: Control plywood–process 1

C_2: Control plywood–process 2

V_1: mNMM-2 treated plywood–process 1

V_2: mNMM-2 treated plywood–process 2

M_1: NMM-1 treated plywood–process 1

M_2: NMM-1 treated plywood–process 2

A_1: AKD treated plywood–process 1

A_2: AKD treated plywood–process 2

Mann-Whitney-U test indicated that plywood made in process 2 induced comparable or higher shear strength than in process 1 (Table 2), so the curing before gluing application could result in negative effects on bonding quality.

Table 2. Shear strength comparisons between process 1 and process 2 (Mann-Whitney-U test)

Pre-treatment 1	**Pre-treatment 2**	**Pre-treatment 3**
$C_1 = C_2$	$C_1 = C_2$	$C_1 < C_2$
$M_1 = M_2$	$M_1 = M_2$	$M_1 = M_2$
$V_1 < V_2$	$V_1 < V_2$	$V_1 < V_2$
$A_1 = A_2$	$A_1 < A_2$	$A_1 < A_2$

Chemical modification, which replaces polar hydroxyl groups of wood with more non-polar groups, is supposed to reduce adhesion by making the wood surface less polar and less porous, resulting in poorer adhesive wetting and less bonding possibilities (hydrogen bonding, van derWaals interactions) between the two surfaces (Hunt et al. 2007; Kamke and Lee 2007). In addition, the more polar the adhesive at the same molecular structure and molar masses, the better is the penetration into the untreated wood structure (Rowell 1995). The PF adhesive may penetrate into the cell lumens and cell walls of wood and thus enlarge the bonding interface.

Irrespective of the pre-treatment or plywood making process, NMM-1 treated plywood always displayed increasing mean values of shear strength and reduction of cohesive wood failure as compared to those of the control plywood. This implies that the veneers were strengthened due to the partial incorporation and polymerization of NMM-1 molecules into the wood structure whereas the surface energy and wettability of the veneer surface were reduced. Curing prior to gluing (in process 1) compared to gluing without pre-curing (in process 2) did not bring about any significant difference of bonding quality in case of NMM-1 treated plywood (Table 1&2). The treatment of wood with NMM-1 might reduce the surface energy and restrain the penetration of the PF adhesive into the wood pores. On the other hand, NMM-1 possesses *N*-methylol and amine groups which can potentially react with PF to form covalent bonds; NMM, however, is unlikely to be covalently bonded to the wood surface. NMM-1 might also dimensionally stabilise the wood surface under wet conditions as it was suggested for priming with hydroxymethylated resorcinol (Son and Gardner 2004; Gardner et al. 2006), and thus increase the wet shear strength.

In contrast to NMM-1 treatment, the treatments with mNMM-2 and AKD induced clear reduction in both shear strength and cohesive wood failure. Moreover, the shear strength of the treated plywood produced in process 2 was remarkably diminished as compared to that in process 1. The previous pressing (curing of veneers in process 1) was reported to cause loss of surface energy and reduce permeability (Christiansen 1990, Christiansen 1991), as a result the penetration of resin into the veneers was decreased. Therefore, the shear strength reduction can be explained by the fact that, after the curing in process 1, the veneers were more hydrophobic and displayed reduced permeability, less wettable surfaces, resulting in less efficiency in gluability of the treated veneers. mNMM-2 mostly acts as a hydrophobation agent because of its content of fatty acids and paraffin. It does not penetrate deeply into the wood and mainly concentrates at the surface due to relatively large diameters of the dispersion particles. It is assumed that it reduces both the surface energy and the adhesive penetration to a greater extent than NMM-1. The possibility of covalent bonding of the fatty acid modified NMM (mNMM-2) with the PF resin is also less than with NMM-1 because of the lower concentration and the substitution of the melamine component with fatty acid moieties.The weak bonding strength of cured veneers was confirmed in the study of Hundhausen (2009) who used AKD blended/impregnated wood chips for urea-formaldehyde bonded particleboards. The results revealed that AKD imparted more reduction in gluability when wood chips were cured prior to pressing.

The investigation into bonding quality of *N*-methylol melamine treated wood has not yet been reported in the literature. In a comparable work on beech plywood treated with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), the control plywood presented significantly higher shear strength (1.4 times) and higher percentage of cohesive wood failure than the treated plywood (Dieste et al. 2009). Vick and Rowell (1990) also found a reduction in bonding strength of acetylated yellow poplar veneers glued with a PF resin when compared to the controls. Lowering wettability and permeability due to the substitution of hydroxyl groups of cell wall polymers by acetyl groups was assumed to be the main reason for the poor performance of phenolic resins on acetylated wood. The treatments with N-methylol melamine compounds and AKD are not expected to reduce the number of hydroxyl groups in modified wood; however, the bonding quality was affected, especially the reduction in cohesive wood failure which is attributed to low wettabilty and low permeability of the treated veneers.

3.3. Delamination after soaking/drying cycles

Soaking and drying cycles caused swelling/shrinking stress for the plywood specimens. As a result, the bonding strength was reduced, and the specimens started delaminating during the cyclic test. The results showed that the quantity of delaminated plywood specimens during the cycles is in accordance with the bonding quality. There was insignificant change in bonding strength of NMM-1 treated plywood between process 1 and process 2. As a consequence, the numbers of delaminated specimens were similar in both processes; furthermore, the higher bonding strength of NMM-1 treated plywood in comparison to the controls, mNMM-2 and AKD treatments was confirmed by no delaminated specimens after 6 cycles of soaking and drying (Fig. 3).

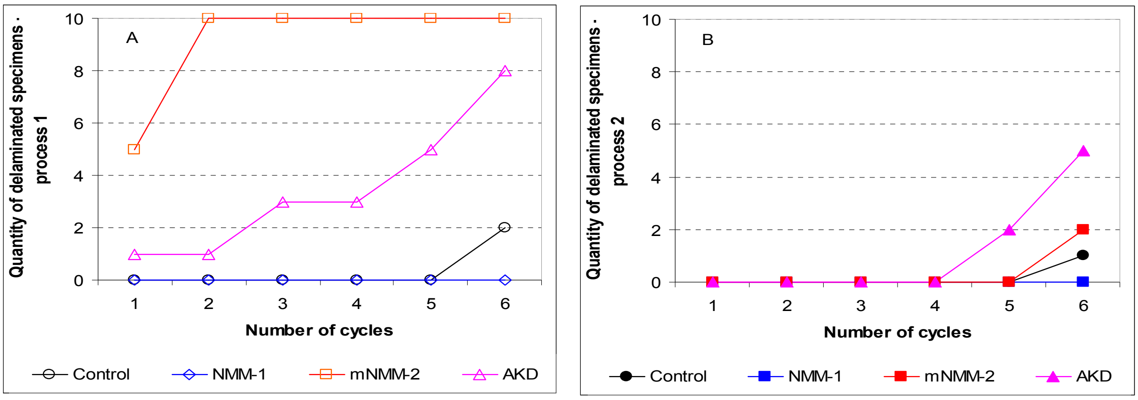

Figure 3. Quantity of delaminated specimens of the control and treated plywood, process 1 (A) and process 2 (B)

The mNMM-2 treated plywood specimens in process 1 were collapsed all after the cycle 2 because of the weak bonding strength, but in the process 2, only 2 of 10 specimens were delaminated after the last cycle. The same phenomenon occurred in the AKD treated plywood, 8 of 10 plywood specimens in process 1 were delaminated after 6 cycles whereas the delamination of the plywood specimens in process 2 proceeded in a later cycle (Fig. 3).

IV. CONCLUSIONS

The beech plywood treated with two N-methylol melamine formulations and AKD dispersions at different solid contents exhibited bonding quality above the requirements of plywood used in non-covered exterior conditions (except mNMM-2 in process 1). Due to hydrophobation and reduced permeability of the cured veneers in process 1, the plywood produced in process 2 (combined curing and pressing) showed higher bonding quality this was confirmed by higher shear strength and lower numbers of delaminated specimens over the soaking/drying cycles. Hence, process 2 did not only impart higher performance properties, but is also economically favourable due to lower energyinput.

REFERENCES

1. Christiansen, A.W., 1990, How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: a critical review of the literature, Part I. Physical responses, *Wood and Fiber Science*, Vol. 4, No. 22, pp. 441-459.

2. Christiansen, A.W. (1991) How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: a critical review of the literature. Part II. Chemical reactions, *Wood and Fiber Science*, Vol. 1, No. 23, pp. 69-84.

3. Deka, M. and Saikia, C.N., 2000, Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property, *Bioresource Technology*, Vol. 2, No. 73, pp. 179-181.

4. Dieste, A., Krause, A., Bollmus, S. and Militz, H., 2009, Gluing ability of plywood produced with DMDHEU-modified veneers of *Fagus sp., Betula sp.,* and *Picea sp.* I*nternational Journal of Adhesion and Adhesives*, No. 29, pp. 206-209.

5. Dunky, M., 2003, Adhesive in the wood industry. In: A. Pizz and K.L. Mittal (Editors), *Handbook of adhesive technology*, Marcel Dekker, New York, U.S.A, pp. 887-956.

6. Dynea (2003) Prefere 4976. Technical data sheet.

7. EN 314-1(2004) Plywood - Bonding quality – Part 1: Test methods.

8. EN 314-2 (1993) Plywood - Bonding quality – Part 2: Requirements.

ẢNH HƯỞNG CỦA QUÁ TRÌNH ĐÓNG RẮN SƠ BỘ CHẤT BIẾN TÍNHTRONG VÁN MỎNG ĐẾN CHẤT LƯỢNG DÁN DÍNH CỦA VÁN DÁN

Trịnh Hiền Mai

Trường Đại học Lâm nghiệp

TÓM TẮT

Ván mỏng gỗ Beech (*Fagus sylvatica* L.) được xử lý biến tính với: hai hỗn hợp của N-methylol-melamine (NMM): 1) dung dịch NMM (NMM-1, hàm lượng rắn 10%), 2) dung dịch NMM biến tính với axit béo, có chứa paraffin (mNMM-2, hàm lượng rắn 5%); và 3) dung dịch alkyl ketene dimer (AKD, hàm lượng rắn 1%). Ván mỏng sau khi xử lý biến tính được tráng keo phenol formaldehyde để sản xuất ván dán theo hai quy trình khác nhau. Trong quy trình thứ nhất, ván mỏng sau khi ngâm tẩm hóa chất biến tính được đóng rắn sơ bộ (curing) trước khi tráng keo và ép nhiệt. Trong quy trình thứ hai, quá trình "curing" ván mỏng sau khi ngâm tẩm với hóa chất được kết hợp với quá trình ép nhiệt. Ván dán sản xuất từ ván mỏng gỗ Beech ngâm trong nước (thay vì ngâm tẩm với dung dịch hóa chất) được sử dụng làm ván đối chứng. Chất lượng dán dính của ván dán biến tính và ván dán đối chứng được kiểm tra theo tiêu chuẩn châu Âu EN 314-1 (2004) với các bước tiền xử lý trước khi kiểm tra cường độ kéo trượt màng keo. Kết quả cho thấy, trong cả hai quy trình sản xuất ván dán và các bước tiền xử lý trước khi kiểm tra, ván dán biến tính với NMM-1 luôn có cường độ kéo trượt cao hơn ván dán đối chứng (đến 28.5%), trong khi biến tính với mNMM-2 and AKD làm giảm cường độ kéo trượt của ván dán tới các mức độ khác nhau. Tỷ lệ phá hủy sợi gỗ của ván dán đối chứng thay đổi từ 50 đến 100%, trong khi tỷ lệ này của ván dán biến tính thấp hơn nhiều, từ 0 đến 40%. Tuy nhiên, ván dán sản xuất theo cả hai quy trình (ngoại trừ ván dán biến tính với mNMM-2 trong quy trình 2) đều đáp ứng được các yêu cầu đối với ván dán sử dụng trong điều kiện ngoài trời không có mái che theo tiêu chuẩn EN 314-2 (1993). Phân tích thống kê đã chỉ ra rằng ván dán sản xuất theo quy trình thứ hai có cường độ kéo trượt màng keo tương đương hoặc cao hơn so với ván dán sản xuất theo quy trình thứ nhất, quá trình đóng rắn sơ bộ của hóa chất biến tính trước khi tráng keo có những ảnh hưởng không tốt tới chất lượng màng keo sẽ được thảo luận. Số lượng mẫu ván dán bị bong tách sau các chu kì ngâm nước/ sấy khô phù hợp với kết quả nghiên cứu về chất lượng dán dính theo EN 314.

Từ khóa: AKD, chất lượng dán dính, gỗ Beech, N-methylol melamine, ván dán, ván mỏng.

Reviewer : Prof.Dr. Tran Van Chu
Received : 23/3/2016
Revised : 08/4/2016
Accepted : 15/4/2016