

Influence of Different Mixing Ratios of Adhesives for Wood Bondline Quality

Jan Vanerek, Anna Benesova, and Pavel Rovnanik

Abstract—The research study was based on an evaluation of the ability of glued test samples to pass the criterion of sufficient bondline adhesion under the exposure conditions defined in EN 302-1. Additionally, an infrared spectroscopic analysis of the evaluated adhesives (phenol-resorcinol-formaldehyde PRF and melamine-urea-formaldehyde MUF) with different mix ratios was carried out to evaluate the possible effects of a faulty technological process.

Keywords—Adhesives, bondline, durability, timber.

I. INTRODUCTION

GLUED timber products are becoming increasingly popular, especially for structures where they achieve satisfactory load-bearing parameters with relatively low bulk density. Other advantages include the possibilities for creating structures with atypical shapes and aesthetics, as well as higher volume stability compared to solid wood. For the purposes of surface gluing, the most frequently used glues are certified products based on phenol-formaldehyde, melamine-urea-formaldehyde, resorcinol-formaldehyde or polymeric diphenylmethane diisocyanate (pMDI). For glulam products, which are made with finger joints, the greatest advantages include fast hardening and sufficient durability upon the application of polyurethane glue. Glues used for wooden adherends must be considered in terms of how a sufficiently durable bond is made between the glue and adherend with the main factor of the bond's consistence being the creation of a mechanical interlocking of adhesives to sound wood structures, two to six cells deep [1].

A. Technology of Gluing Wooden Parts

The production aspect of wooden parts includes the preparation of plate segments which must have a guaranteed moisture content depending on the particular type of glue. The glue is then applied on the surface of the individual lamella using mainly the ribbon spreader in the amount required by the producer of the glue; afterwards, the lamella are assembled into the final profile and put under pressure for the prescribed length of time. In products of non-rectangular shape, the glue is usually applied by hand and the final set is loaded with threaded rods. The final quality of a glued product results from fulfilling the main technical requirements, such as the mixing

ratio of multi-component glues, the assembly time, the time and size of load for the given set of building features, and the temperature during the gluing.

B. Objective of the Study

In terms of the influence of the technological process, the main factors that should be controlled are the moisture of the lumber and the temperature of surroundings. Additionally, variable moisture content lumber can be a problem for the gluing process. Another factor that may substantially influence insufficient glue hardening for two-component glues is the failure to meet the conditions of the mixing ratio. Machine-aided application eliminates this effect by its very nature, but in on-site application or during additional reinforcing this factor can significantly affect the final quality of the glued joint. This study was conducted in order to investigate the effects of possible failures in mixing a 2-compound adhesive system.

II. MATERIALS AND METHODS

A. Materials

This study compared the characteristics of commercially available adhesives on beechwood (*Fagus sylvatica* L.). The adhesives used were phenol-resorcinol-formaldehyde (PRF) and melamine-urea-formaldehyde (MUF) from the AkzoNobel Company. These are structural adhesives for load-bearing structures suitable for long-term external exposure (adhesive type I according to EN 302), and generally their durability is confirmed by many studies. The chemistry of both the adhesives used and detailed discussions of their reactions have been published [2], [3].

The adhesives were studied in terms of the influence of deviation from the mixing ratio of the adhesive/hardener on the resulting integrity of the bondlines. Three mixes of MUF and PRF glues were prepared. The first mix was made in a reference ratio according to the manufacturer's recommendation, while the other mixes contained a lower volume of hardener – 20% and 50% less than recommended. All mixed adhesives were applied in the amount of 350 g/m² on the surface of prepared 5 mm thick beech boards, which were then used to form the conglomerate. Such conglomerates were loaded under pressure of 0.8 MPa for the prescribed time as indicated for the relevant type of glue. These boards were allowed to cure and were then cut into samples for testing tensile shear strength. In terms of wood gluing, these were tested as samples with a thin layer of adhesive, defined by the maximum thickness of 0.1 mm.

Jan Vanerek, Anna Benesova, Pavel Rovnanik. All authors are permanent employees of the Brno University of Technology, Faculty of Civil Engineering, Brno, 602 00 Czech Republic (corresponding author's phone: +420 541 147 514; fax: +420 541 147 502; e-mail: vanerek.j@fce.vutbr.cz).

B. Exposure Conditions

The test samples were then split into five groups, which were exposed to different moisture classes. One group was held as a control set and was tested after acclimatization to the equilibrium moisture content in conditions 20°C/65%. The other four groups were subjected to moisture classes according to EN 302-1. Two groups (A2, A3) of testing samples were exposed to conditions of soaking in water with a temperature of (20±5)°C for four days; one was tested wet (A2) and the other was tested after achieving equilibrium moisture content in conditions of 20°C/65% (A3). The other two groups (A4, A5) of testing samples were exposed to a boiling test specified as soaking in boiling water for six hours and soaking in water with a temperature of (20±5)°C for two hours; one group was tested wet (A4), the other was tested after achieving equilibrium moisture content in conditions 20°C/65% (A5).

C. Tensile Shear Strength

The load-bearing capacity of the joints is standardly defined as the tensile shear strength of one lap joint sample of 20/150 mm dimensions. The average shear strength was determined from a set of 15 testing objects. The shear area was created by notches 3 mm wide in the tensile shear strength specimens. The tensile shear strength of the glued testing samples was measured by Testometric M350-20CT at a crosshead speed of 2 mm/min. To define the exact method of joint failure, the wood failure characteristics after the tensile shear strength test was determined in each disturbed sample on the shear area. This value was estimated visually on each testing object and rounded up to the nearest 10%.

D. Infrared Absorption Spectroscopy

Infrared absorption spectroscopy is an analytical method used for finding and identifying the structural characteristics of organic and inorganic compounds. It is a molecular spectroscopy technique, providing information on bonds in a molecule from vibration and rotation movements. Absorption of infrared radiation of a certain frequency occurs only when some of the components of the dipole moment of the molecule change during the vibration or rotation with the same frequency.

The output of the measurement is a spectrogram. A spectrogram can be divided into two parts. The first part, at wavelengths of 4000–1400 cm⁻¹, is a characteristic area of predominantly stretching vibrations, especially of organic functional groups. Bending vibrations mostly occur at wavelengths lower than 1400 cm⁻¹, i.e. in the so-called fingerprint area.

Testing samples were prepared for IR spectroscopy from the tested adhesives in the reference mixing ratio and 50% lower volume of hardener. Hardened samples were ground into fine powder and pressed into tablets containing potassium bromide. Analyses of the adhesives were performed on a Thermo Nicolet 380 FT infrared spectroscope with Fourier transformation, using the extension for the transmission method of measurement.

III. RESULTS AND DISCUSSION

A. Tensile Shear Strength

The results of the tensile shear strength tests were defined for all the stated adhesives and are shown in the graphs below. The influence of different mixing ratios on the shear strength value was also recorded in binary adhesives.

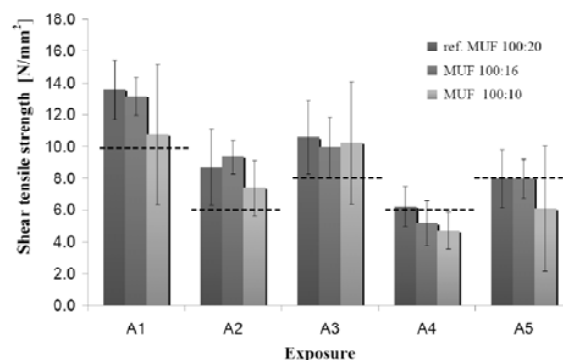


Fig. 1 Comparison of the achieved average strengths in individual exposures determined by standard EN 302-1 for MUF-type glue with different mixing ratios

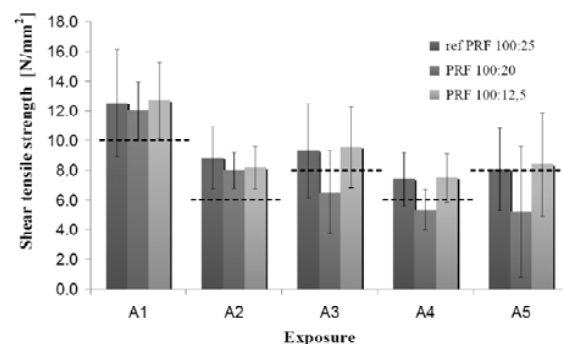


Fig. 2 Comparison of the achieved average strengths in individual exposures determined by standard EN 302-1 for PRF-type glue with different mixing ratios

The comparison of the results of the selected adhesives by the values achieved through shear tests showed that with reference mixing, PRF and MUF adhesives show minimum values of shear strength in all the exposures guaranteeing their placing as type I adhesives, i.e. adhesives recommended for external exposure. Both of the adhesive types showed a decreasing strength trend in relation to moisture load in classes A2 to A5. In terms of different mixing ratios of the glue and hardener, the failure to meet the minimum shear strength requirement for exposure in A4 and A5 was proved in the case of MUF, with the same applying to exposure in moisture conditions A3, A4, and A5 in the case of PRF (see Fig. 1, Fig. 2). This drop in strength was observed from a 20% reduction of hardener content from the reference mixing ratio.

B. Wood Failure

Within the strength testing, the wood failure parameter of the shear area of testing samples was also evaluated. The achieved values are shown in the table below.

TABLE I
VALUES OF WOOD FAILURE FOR THE TESTED TYPES OF ADHESIVES

Adhesive	Exposure				
	A1	A2	A3	A4	A5
ref MUF 100:20	63	25	37	20	45
MUF 100:16	40	40	40	10	37
MUF 100:10	37	20	11	35	25
ref PRF 100:25	62	26	64	20	42
PRF 100:20	57	25	61	35	22
PRF 100:12.5	63	36	53	33	22

As predicted, the lower percentage of wood (substrate) failure under wet conditions with all the adhesives indicated that bond properties weakened due to the volume changes in wood adherend; therefore more interfacial failures were indicated. Proper penetration of adhesives into the wood structure can stabilize the interfacial wood cell walls and force air bubbles out from wooden lumens. This allows for the distribution of the expansion differences further into the stabilized wood structure. But the difference seems to be influenced only by the moisture content of the wood. As the study showed for epoxy adhesive [4], testing objects tested wet and in the re-dried state after this wet exposure again showed an increase in their shear strength as well as an increase in wood failure values. This recovery of bond properties upon re-drying indicates that the effect of water was not a permanent change in the bond, but a temporary effect of the water on the bond (an influence of increasing internal bond line strain deriving from differences in swelling between the wooden adherend and adhesives) [5]. The lower viscosity of both formaldehyde resins ensured complete penetration of adhesives into the wood, the most important issue for gaining optimal surface interaction between adhesive and wood substrate.

C. Infrared Absorption Spectroscopy

Fig. 3 and 4 show the infrared spectra of adhesives in absorption mode. The images contain spectrograms of different mixing ratios of adhesive/hardener in the prescribed mixing ratio and with a 50% reduction of hardener content. In both cases, the main chemical component of the hardener is formic acid. Formic acid absorbs at approximately these wavelengths: 3600 cm^{-1} , 2940 cm^{-1} , 1770 cm^{-1} , 1390 cm^{-1} , 1230 cm^{-1} , 1110 cm^{-1} , and 1033 cm^{-1} .

As some of these spectral bands in the adhesive/hardener mixes are overlapped or combined with adhesive bands, the reduced hardener ratio can be determined only if a new spectral band or a band with significantly increased intensity appears in the spectrogram of a mix with a higher content of hardener. Spectral bands determining a higher concentration of hardener are shown in green rings; the bands are 2940 cm^{-1} and 1770 cm^{-1} for MUF and 1033 cm^{-1} for PRF.

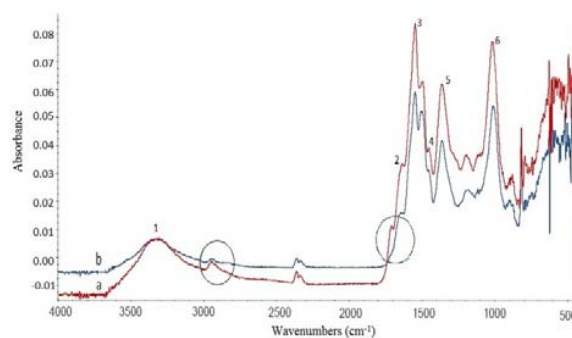


Fig. 3 Comparison of the FTIR spectra of the reference MUF adhesive (a) and the same adhesive with 50% vol. less hardener (b)

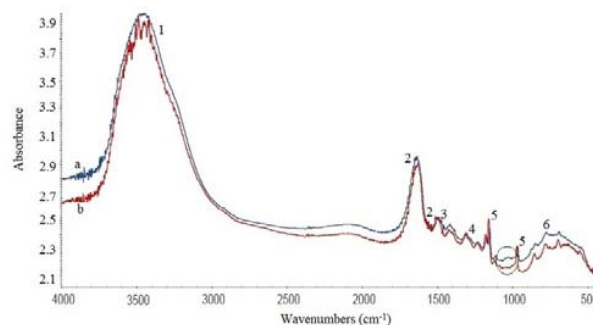


Fig. 4 Comparison of the FTIR spectra of the reference PRF adhesive (a) and same adhesive with 50% vol. less hardener (b)

TABLE II
OVERVIEW OF CHEMICAL BONDS IN FORMALDEHYDE ADHESIVE
SPECTROGRAMS [6] – [11]

No.	MUF adhesive			PRF adhesive		
	Area [cm ⁻¹]	Chemical bond	Vibration type	Area [cm ⁻¹]	Chemical bond	Vibration type
1.	3500 – 3200	NH	amine, methylol	3340	OH	phenolic valence
2.	1660	C=O	valence	1610 and 1510	Ar	aromatic valence
3.	1540	NH	amine – deformation	1474	CH ₂	deformation
4.	1440-1465	CH	deformation	1222	C-O-C	valence
5.	1360	C-N	aromatic valence	1140 and 960	Ar	resorcinol
6.	1360	C-N, N-C-N	aliphatic valence	757	Ar	phenolic

Adhesive spectrograms serve as reference spectra for assessing the degradation of adhesive during long-term durability tests; spectrograms will be further monitored during the adhesive aging process. It is assumed that the curves will change mainly in terms of the intensity of the individual bands relative to the opening of macromolecular bonds. It can be assumed that some bands will show a higher intensity at the end of the test or that bands with completely different wavelengths will occur. This phenomenon is probably caused by the vibration of macromolecular end bonds and a change of position of partial molecules, i.e. by gaining new degrees of

freedom. A new degree of freedom will probably demonstrate itself by a new type of stretching, but especially by a bending vibration.

IV. CONCLUSION

The objective of the study was to test traditional adhesives used for wooden products (PRF, MUF) and to verify the listing of the glue type under class I or II according to the minimum shear strength value upon the requirements of the relevant EN standard. The testing proved that the tested adhesives meet the requirements for external exposure classification (class I) even after being exposed to moisture and hygrothermal exposure. These two-component adhesives were also studied in terms of the influence of varying adhesive/hardener mixing ratios, when a significant strength decrease of the bondline was observed from a 20% lower hardener content. Testing samples with different mixing ratios confirmed the presumption of a significant quality decrease in the glued bond, especially in exposure categories with hygrothermal exposure on the bondline.

In terms of IR spectroscopy assessment, the spectrograms showed the influence of different hardener ratios through formic acid spectral bands with clearly increased intensity, which shows IR spectroscopy to be a suitable tool for determining the quality of bondline in wooden glued products. However, for this application it is necessary to further develop the methodology of taking samples of the adhesive from the bondlines to eliminate the influence of the wooden adherend.

ACKNOWLEDGMENT

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REFERENCES

- [1] Vick C. B. Adhesive Bonding of Wood Materials, Wood handbook, Wood as an engineering material, Forest Products Laboratory. 1999. Gen. Tech. Rep. FPL-GTR-113. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 463 p.
- [2] Pizzi, A. Melamine-formaldehyde adhesives. In Pizzi, A. and Mittal, K.L. (Eds), Handbook of Adhesive Technology (2nd ed.), Marcel Dekker, New York, chap. 32
- [3] Pizzi, A. Resorcinol adhesives. In Pizzi, A. and Mittal, K.L. (Eds), Handbook of Adhesive Technology (2nd ed.), Marcel Dekker, New York, chap. 29
- [4] Vick, C. B., Okkonen, E.A. Structural durable epoxy bonds to aircraft woods. Forest Prod. J. 1997:47 (3), p. 71-71
- [5] Frihart, Ch. R. Are epoxy-wood bonds durable enough? In: Frihart, CH. R. Proc. Of Wood Adhesives 2005 Conference, Madison, Forest Products Society, p. 241 – 246
- [6] SVEHLA, G.: Comprehensive analytical chemistry VI, Amsterdam, Elsevier scientific publishing company 1976, p. 1-555, ISBN 0-444-41165-8.
- [7] Chow, S., Steiner, P.R. Determination of Resorcinol Content in Phenol-Resorcinol-Formaldehyde Resins by Infrared Spectrometry, *Holzforschung – International Journal of the Biology, Chemistry, Physics and Technology of Wood*. Volume 32, Issue 4, Pages 120–122, ISSN (Online) 1437-434X, ISSN (Print) 0018-3830, DOI: 10.1515/hfsg.1978.32.4.120, July 2009
- [8] Silverstein, R.M., Webster, F.X. Spectrometric Identification of Organic Compounds, 6th edition, John Wiley & Sons, 1997, ISBN 0-471-13457-0
- [9] Kemp, W. Organic Spectroscopy, 3rd edition, W.H.Freeman and Co., 1991, ISBN 0-716-72227-4
- [10] Spectroscopic Techniques for Organic Chemists; J.W.Cooper, John Wiley & Sons, 1980. ISBN 0-471-05166-4
- [11] Spectroscopic methods in organic chemistry; D.H.Williams, I.Fleming, 4th edition, McGraw Hill, 1987, ISBN 0-077-07212-X