

**BOND PERFORMANCE OF FORMALDEHYDE-
BASED RESINS SYNTHESIZED WITH CONDENSATE
GENERATED DURING KILN-DRYING STEP OF WOOD**

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ABSTRACT

This research investigated the potential use of condensate generated during vacuum drying with high frequency of wood in the synthesis of urea-formaldehyde (UF) and melamine-formaldehyde (MUF) resins. The liquid condensate (5 wt% of total resin composition) of walnut, beech or oak was replaced with deionized water used in the synthesis of UF and MUF resins. The condensate did not affect the properties of the UF and MUF resins in terms of density, solid content, viscosity, pH, and gel time as compared with the control resins. The control UF and MUF resins did not show a significant difference with the bond strength of UF and MUF resins at dry and wet conditions, except for the oak-UF resin. As for the dry condition, the control resin had the highest bond strength with a value of 12.9 N·mm⁻², followed by beech-UF resin (12.6 N·mm⁻²), walnut-UF resin (12.1 N·mm⁻²), and oak-UF resin (11.8 N·mm⁻²), respectively. A similar trend was observed for the wet condition. All the modified UF and MUF resins complied with the minimum requirements of EN 12765 standard at dry and wet conditions. The results of this research can be useful for environmentally friend solution of the waste condensate discarded to the ground water.

KEYWORDS: Condensate, resin, wood, extraction, bond performance, adhesive.

INTRODUCTION

A steam generated in a drying step of a lumber, sawdust or wood powder is usually discarded. The water movement in the cellular structure of wood, which is caused by the drying process, draws water soluble compounds extracted into solution (Rathke 2013). During drying of wood, both volatile and less volatile compounds can be emitted to air. The volatiles emitted by the wood, are primarily consists of monoterpene type of compounds. The less volatile compounds emitted by the wood, are composed of fatty acids, resin acids, diterpenes, and triterpenes (Granström 2005). During high temperature drying, thermal degradation of wood gives rise to formation of formic acid, acetic acid, alcohols, aldehydes and furfurals (Granström 2005, McDonald et al. 1999). In a previous study, Bucko et al. (1993) identified formic acid, acetic acid, levulinic acid, furfural, hydroxymethyl-furfural, formaldehyde, and acetaldehyde from the kiln-dried condensate of ash, beech, and oak wood.

Some of the wood species such as oak could not dried at high temperatures. Vacuum kilns which uses vacuum dryer with high frequency offers the possibility to avoid collapse and discoloration of the wood (Torres et al. 2011). One of the main advantages of vacuum dryers with high frequency is its ability to selectively heat water in the material rather than the surrounding material (Resch 2006). However, high amount of condensate is generated during drying process. Unfortunately, the liquid condensate produced in this process is discarded to ground water. When the condensate fluid is discharged to the ground water, it can be harmful for aquatic organisms (Dejmal and Zejda 2008). Recently, there have been many concerns about the environmental pollution with relating to the condensate generated by lumber companies. The impact of the increased consciousness about environment has also created a demand for environmentally-friendly solution of the discarded condensate. The condensate could play an important role in the manufacture of value-added materials and this could be the most efficient way to benefit from the condensate. The condensate obtained in the process contains valuable dissolved extractives which may be evaluated in the production high value added materials such as wood resins. Thus, the timber companies can obtain income from this waste as well as ensure an environmentally friendly production.

Based on the extensive literature search, there is no any study on the potential use of condensate fluid generated during kiln drying of lumber in the formaldehyde-based resins. The objective of the present study was to investigate potential use of condensate generated by cooling the steam obtained during high-frequency/vacuum drying step of a lumber. In this study, liquid condensate obtained from various lumbers of trees (oak, beech, and walnut species) during the drying in a vacuum dryer with high frequency were added into commercial urea-formaldehyde (UF) resin and melamine/urea formaldehyde (MUF) resin. The characteristics the modified resins were studied. The bond performance of the UF and MUF resins modified with the condensate fluid was determined using beech wood lamellas and compared with the results of the control UF and MUF resins.

MATERIALS AND METHODS

Liquid condensate

The liquid condensate samples were supplied from a commercial lumber mill in Adapazari, Turkey (Fig. 1). It was obtained from oak lumber (*Quercus petraea*), beech (*Fagus orientalis* Lipsky), and walnut (*Juglans regia* L.) lumbers during the drying in a vacuum dryer with high frequency.



Fig. 1: The condensate samples obtained from beech, walnut, and oak woods.

The average thickness of the lumbers were 10 mm. Drying time was between 9-14 days depending on the tree species. The frequency value of vacuum drying, environment temperature in dryer, and wood temperature were 7.8 Mhz, 50-60°C, and 30-40°C, respectively. The initial and final moisture contents of the lumbers were 40-60% and 8-14% depending on the tree species, respectively.

Resin

The UF and MUF resins were produced at the laboratory scale reactor of Polisan Chemical company. The liquid condensate (5 wt% of total resin composition) of walnut, beech or oak woods were replaced with deionized water used in the synthesis of UF and MUF resins.

Synthesis of UF resin

The preparation procedure of UF resin was as follows: the reactor having 5 L capacity was charged with 80 wt% concentration of urea-formaldehyde solution and then mixed with a mechanical stirrer. The formaldehyde solution (45 wt%) was added into the reactor. Deionized water was then added into the reactor to adjust solids concentration for the target level. The NaOH solution having 50% concentration was added into the reactor to adjust pH to 7.5-8.5. The urea was added into the mixture at a temperature of 80°C and pH 5.4-5.5. Due to the exothermic reaction, the temperature of the reactor was increased to 98°C and then viscosity is checked. As the viscosity reached to 300 cps at 45°C, the second part NaOH (50 wt%) solution was added into the reactor. The reaction temperature was decreased and then the reaction was completed. As the reactor temperature was decreased to 70°C, the urea was added into the reactor to set the molar ratio of formaldehyde: urea. Finally, the reactor was cooled to the room temperature (20°C) and then the sample was taken for the final properties of the UF resin given in Tab. 1.

Tab. 1: Technical specifications of the UF and MUF resins with the condensate.

Types of control and modified resins	Viscosity (cps, 20°C)	pH (20°C)	Gel time (s)	Solids content (wt%)	Density (g·cm ⁻³) 20°C)
Control UF	520	8.3	33	65.5	1.284
Beech_UF	480	8.2	36	65.9	1.285
Walnut_UF	420	8.3	36	65.6	1.285
Oak_UF	420	8.2	35	65.8	1.285
Limit values of UF resin	400-700	8.0-9.0	30-40	64-66	1.275-1.285
Control MUF	420	9.0	68	65.2	1.286
Beech_MUF	420	8.8	74	65.5	1.286
Walnut_MUF	480	9.0	75	65.8	1.287
Oak_MUF	430	8.8	75	65.8	1.288
Limit values of MUF resin	300-500	8.5-9.5	60-80	64-66	1.280-1.290

Synthesis of MUF resin

The preparation procedure of MUF resin was as follows: the reactor having 5 L capacity was charged with 45 wt% concentration of formaldehyde solution and then mixed with a mechanical stirrer. Deionized water was replaced with the reactor to adjust solids concentration for the target level. The NaOH solution having 50% concentration was added into the reactor to adjust pH to 7.5-8.5. The melamine was added to the mixture and temperature was increased to 70°C. The reaction continued until the mixture had clear color below pH 7.5. The urea was added to the mixture and the pH was adjusted to 7 by adding formic acid. The viscosity of the mixture was checked at 70°C and the reaction was continued. As the viscosity of the resin was reached 80 cps at 45°C reaction, the pH of the resin was increased to 8 by adding NaOH. Then the temperature of the reactor was decreased and urea was added into the reactor. Finally, the reactor was cooled to the room temperature (20°C) and then the sample was taken for the final properties of the MUF resin given in Tab. 1.

Characterization of control and modified UF and MUF resins

The pH of the resins was determined using a digital pH meter by inserting the pH meter into the resin solution. The viscosity (cps) and gel time (Brookfield RVT 20), density, and solids content of the modified UF and MUF resins were also measured.

Determination of bond strength of UF and MUF resins

The bond strength of the control and modified UF and MUF resins were determined according to EN 205 (2003) standard. Two beech wood lamellas with a thickness of 5 mm were bonded with each other using control or modified resins with the 5 wt% condensate. The resin was applied on one surface (180 g·m⁻²) of the lamella using a hand brush. The hot-press pressure, temperature, and pressing time were 1.5 N·mm⁻², 150°C, and 8 min, respectively.

The bonded lamellas were cut into specimens for the tensile shear test according to EN 205. The specimens were then conditioned in a climate room (20±2°C, relative moisture content 65±5%). The dimensions of the shear areas were measured for all of the specimens. The specimens from each group of resin were divided into two subgroups for the different pretreatments, prior to testing according to the standard EN 12765 (2001). The first subgroup of specimens (pre-treatment 1) was tested in the dry state after conditioning in a standard climate having 65% relative moisture content and 20 °C for 7 days. The second subgroup of the specimens (pre-treatment 2) was tested in the wet condition, which was the specimens were soaked in

water having of 23°C for 24 h. After the pre-treatments were completed, all the tensile shear specimens were immediately tested on a Lyod universal testing machine with a testing speed of 1 mm·min⁻¹. The loading was carried out until a break or separation occurred on the surface of the test specimens.

Statistical analysis

The analysis of variance (ANOVA, $p < 0.01$) was made to determine the effect of condensate content on the bond strength of the UF and MUF resins. Significant differences among the average values of the resin types were determined using Duncan's multiple range test.

RESULTS AND DISCUSSION

Bond strength of UF and MUF resins

The bond properties of control and modified UF and MUF resins are presented in Tab. 2. The condensate did not affect the technical properties of the UF and MUF resins in terms of density, solids content, viscosity, pH, and gel time as compared with the control resins. The gel time of the modified UF and MUF resins was longer than that of the control resins. All the properties of modified UF and MUF resins were complied with the technical specifications of control UF and MUF resins used in wood-based panel industry. The results of the bond strength of the UF and MUF resins modified with the condensate at dry and wet conditions are given in Table 2. As for the dry condition, the control resin had the highest bond strength with a value of 12.9 N·mm⁻², followed by beech-UF resin (12.6N·mm⁻²), walnut-UF resin (12.1 N·mm⁻² and oak-UF resin (11.8N·mm⁻²), respectively. A similar result was found in the MUF resins modified with the condensate.

Tab. 2: Bond strength of UF and MUF resins modified with condensate generated in a drying step of walnut, beech or oak wood.

The addition of condensate into the UF and MUF resins (wt%)	Bond strength (N·mm ⁻²)	
	Dry condition ¹ (N·mm ⁻²)	Wet condition ² (N·mm ⁻²)
Control_UF	12.9 (1.02) a ³	8.2 (0.95) ad
Beech_UF	12.6 (1.13) ab	8.1 (0.88) a
Walnut_UF	12.1 (1.32) ab	7.5 (0.74) ab
Oak_UF	11.8 (1.24) b	7.1 (0.69) b
Control_MUF	13.3 (1.17) a	9.4 (1.01) c
Beech_MUF	13.2 (1.45) a	9.2 (0.90) cd
Walnut_MUF	12.8 (0.95) a	8.8 (0.67) cd
Oak_MUF	12.5 (1.33) ab	8.5 (0.52) acd
Standard requirement(EN 12765)	≥ 10	≥ 7

¹ 7 days in standard atmosphere Interior, in which the moisture content of the wood does not exceed 15% (C1 durability class, EN 12765 (2001).

² 7 days in standard atmosphere and then 1 day in water (23°C). Interior, with frequent long term exposure to running or condensed water and/or to occasional high moisture content provided the moisture content of the wood does not exceed 18% (C2 durability class, EN 12765 (2001).

³ Groups with same letters in each column indicate that there is no statistical difference ($p < 0.01$) between the specimens according to Duncan's multiply range test. The values in the parentheses are standard deviations.

The bond strength of the UF and MUF resins at wet conditions were lower than that of the dry condition. The MUF resin had higher bond strength than that of the UF resin at dry and wet conditions. As for the wet condition, the control MUF resin had the highest bond strength with a value of 13.3 N·mm⁻², followed by beech-MUF resin (13.2 N·mm⁻²), walnut-MUF resin (12.8 N·mm⁻²), and oak-MUF resin (12.5 N·mm⁻²), respectively. The significant differences ($p < 0.01$) among the group averages for the bond strength are shown in Tab. 2. The control resins did not show significant differences with the modified UF and MUF resins at dry and wet conditions, except for the oak_UF resin. All the control and modified UF and MUF resins met the minimum requirements for durability classes C1 (dry condition: ≥ 10 N·mm⁻²) and C2 (≥ 7 N·mm⁻², indoor with frequent long term exposure to running or condensed water and/or to occasional high moisture content provided the moisture content of the wood does not exceed 18%) of EN 12765 (2001) standard.

In oak wood, hydrolysable tannins consist mainly of gallotannins and ellagitannins where the galloyl- and hexahydroxydiphenic acid (HHDP) moieties, respectively, are esterified to a core molecule, generally glucose (Dedic 2013). Common oak wood tannins consist of gallic acid and ellagic acid (Vivas et al. 1995). Among the modified UF and MUF resins, the highest performance in dry and wet conditions was found in the resins modified with the beech condensate. The lowest bond performance for the UF and MUF resins modified with the oak condensate could be explained by the incompatibility between the resin and extractives in the condensate. In a previous study, Garro Galvez et al. (1997) reported that thermal analysis of the reaction between tannins of *Caesalpinia spinosa* (Tara) and formaldehyde showed that tannins were not reactive enough towards formaldehyde and this could eventually be associated to weak mechanical board properties. In addition, they reported that probably the presence of sugars and the consumption of the base catalyst hydrolyzing the ester bonds of the extract reduced its reactivity. However, in other study Ozkaya et al. (2013) reported that bending strength and splitting strength of the laminated veneer lumber (LVL) increased by 8.2% and 13.9%, respectively, as 10 wt% extraction solution of ash tree leaves was incorporated into the UF resin. But, further increment in the extraction solution beyond 10 wt% decreased the mentioned properties.

CONCLUSIONS

The results of bond strength of the UF and MUF resins revealed that the condensate generated in a drying step of a wood could be efficiently used in the production of control UF and MUF resins. The control UF and MUF resins did not show significant difference with the bond strength of UF and MUF resins modified with 5 wt% condensate at dry and wet conditions, except for the oak-UF resin. In particular, the bond strength values of beech-UF and beech-MUF resins were very close to the values of the control resins. The dry and wet bond performance of all the modified UF and MUF resins were above the minimum requirements of EN 12765 (2001) standard. The condensate did not significantly change the technical characteristics of UF and MUF resins such as viscosity, gel time, density, solids content, and pH as compared to the control resins. Based on the findings obtained from the present study, it was concluded that the condensate obtained from the beech wood during vacuum drying was the most suitable constituent in the synthesis of UF or MUF resins, followed by the condensates obtained from walnut and oak woods, respectively. The results of this research can be useful for environmentally friendly solution of the waste condensate discarded to the ground water. The lumber companies can make money from collecting and selling the condensate to the resin industry.

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