

THE EFFECT OF HARDENER ON ADHESIVE AND FIBERBOARD PROPERTIES

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ABSTRACT

Ureaformaldehyde adhesive requires hardener and about 4-6.5 pH to be cured. In this study, boric acid, boron oxide, borax, sodium perborate tetrahydrate, sodium chloride, sodium chlorite and control samples containing ammonium chloride was used as an hardener to investigate cureability of urea formaldehyde adhesive. Chemicals used as an hardener tested to demonstrate the effect on gelation time, swelling properties, MOR and MOE. Ammonium chloride, boric acid and boron oxide improved to properties when used as an hardener in single use or in mixture.

KEYWORDS: Hardener, gel time, physical and mechanical properties, fiberboard.

INTRODUCTION

Medium density fiberboard (MDF) is an engineered wood products made of fiber glue, wax and different additives. Desired properties can be imparted to the board with a variety of adhesives and chemical additives. MDF mechanical properties depend on the adhesion between the fiber to fiber bonding ability (Halvarsson et al. 2008). Therefore, the properties of adhesives and the chemicals used in MDF production is important.

Ureaformaldehyde is one of the most important and most commonly used amino-formaldehyde resin in board panel industries. There are some advantageous to use urea formaldehyde resins. It is cheap, water soluble, stable, fire resistant, has good thermal properties,

when cured, it is colorless and easily adapted to different curing conditions (Pizzi 2005b). Ureaformaldehyde resin requires acidic condition and pH usually set around 4 to be cured. Therefore, ureaformaldehyde resin either at ambient temperature or at elevated temperatures needs the addition of a hardener to be cured. The most common hardener is ammonium sulfate and ammonium chloride to be used to control pH and cure adhesive. In addition to these chemicals, boric acid, phosphoric acid, hydrochlorite, phthalic anhydride was used to control pH and harden adhesive (Pizzi 2003a). The type of hardener, concentration, the ratio of hardener adhesive are an important factor to provide relevant stiffness. The effect of hardener and extenders was studied on 3 different urea formaldehyde resin (Eom et al. 2008). Ammonium chloride was used as a hardener. Increasing ammonium chloride concentration decreased pH to 2. In addition to that, increased concentration changed the gelation period and decreased curing temperature. Viscosity of adhesive also decreased.

Hashim et al. (2009) investigated the addition of zinc borate, sodium aluminate and aluminum trihydrate on MDF properties. These chemicals usually used for the fire retardancy. It was concluded that the addition of those chemicals decreased mechanical properties due to interference with binding groups on fiber and gel time was increased.

The mixture of boric acid, guanidylurea phosphate and phosphoric acid, monoammonium phosphate and diammonium phosphate were used to determine the effect on ureaformaldehyde adhesive (Kamal et al. 2008). Concentration was set to 8 and 10 % (w/w). Test was carried out at 170°C due to fire retardant chemicals. All the chemicals improved gel time except for diammonium phosphate.

Ustaomer and Usta (2012) treated wood fiber with 10 to 15 % concentration of boric acid, borax, sodium perborate tetrahydrate, zinc borate, boric acid-borax and boric acid-sodium perborate. Melamine formaldehyde resin was used. Mechanical and physical properties of the board were tested. Bor compound increased the swelling ability of the materials, at the same time mechanical properties were also deteriorated. Xing et al. conducted a research (2004) and searched the effect of the wood pH on urea formaldehyde resin curing period. It was concluded that the wood pH and hardener were affecting gelation period.

The objective of this project was to determine the effect of sodium chloride (NaCl), sodium chlorite (NaClO₂), borax (Na₂B₄O₇·10H₂O), sodium perborate tetrahydrate (SPT) (NaBO₃·4H₂O) on the ureaformaldehyde resin. Each molecule contains Na and other ions. The size of the molecules different to each other when they were compared. The particle size of the reactant affects the speed of the reaction.

MATERIAL AND METHODS

Material

Commercially produced wood fiber (contained 60 pine and 40 % fir fiber obtained from Kastamonu Entegre A.Ş. Kastamonu OSB plant and manufactured with TMP pulping method) and urea formaldehyde adhesive (E1 type and obtained from Kastamonu Entegre A.Ş. Kastamonu OSB plant) were used. Materials were dried under room temperature to reach 7-8 % moisture content.

The panels were manufactured at a target density of 0.70 g·cm⁻³ with 10 % resin content using urea formaldehyde based on the oven dry (o.d.) weight of the materials and the panels were prepared at the thickness of 11 mm. The panels comprised of furnishes at varying degrees (20 %) of biomass (okra and tobacco stalks, hazelnut and walnut shell, and pine cone) and pine, beech

and oak fiber mixtures. The properties of the urea-formaldehyde resin used in this study were given in Tab. 1. As a hardener ammonium chloride, sodium chloride (NaCl), sodium chlorite (NaClO_2), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium perborate tetrahydrate solution was added in all the board production, respectively.

Tab. 1: The properties of urea-formaldehyde (UF) adhesive.

Properties	UF
Solid (%)	55±1
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.20
pH	8.4
Viscosity (cps)	160
Free formaldehyde (%)	0.15
Urea : Formaldehyde ratio	1:1.17
Storage time (25°C, max day)	90
Flowing point (25°C, sec.)	20-40

Gelation time and pH

Gel time was measured through the addition of 5 g of the prepared samples to a test tube (15 x 150 mm) and heating in a 100°C water and 175°C oil bath. Three replicate measurements for each sample were made. Test samples were prepared according to (TS 12009 1996) standart test methods. Ureafomaldehyde resin (50 g) was mixed with hardener. Hardener was prepared with NH_4Cl solution as 25-75, 50-50, 75-25 and 100 % (w/w) mixture, respectively. Hardener solution was added to resin as 10 % (w/w). Samples expected to unobservable, gelation time was set to continue for 600 seconds.

Board production

The panels were produced at a target density of $0.70 \text{ g}\cdot\text{cm}^{-3}$ with 10 % panel resin content using urea formaldehyde based on the oven dry (o.d.) weight of the materials and the panels were prepared at the thickness of 11 mm. All panels were consolidated using the heated press in the laboratory of Kastamonu University. The panels were pressed to $20 \text{ kg}\cdot\text{cm}^{-2}$ at 175°C for 10 min. Test panels having dimensions of 31 x 36 x 1.1 cm was conditioned at $20\pm 2^\circ\text{C}$, and 65 ± 5 % of relative humidity to reach the moisture content of 12 %. Finally, the edges of the boards were trimmed to the final dimension of 30 x 30 x 1.1 cm. Fiberboard production parameters were summarized in Tab. 2.

Tab. 2: Production parameters of fiberboards.

Parameter	Value
Press temp. ($^\circ\text{C}$)	175
Pressing time (min)	10
Press pressure ($\text{N}\cdot\text{mm}^{-2}$)	2.0-2.1
Thickness (mm)	11
Dimensions (mm)	310×360
Specific gravity ($\text{g}\cdot\text{cm}^{-3}$)	0.70
Number of board for each type	3

Mechanical and physical properties

Mechanical and physical properties were tested according to (ASTM D 1037, 1999) test standard methods. Modulus of elasticity (MOE), modulus of rupture (MOR), tensile strength perpendicular to the surface, thickness swelling were obtained.

RESULTS AND DISCUSSION

Ureaformaldehyde resin is commonly employed to bind a wide range of wood products. Condensation and addition reactions, which are the main reaction in reacting urea and formaldehyde resins. As a result of that, polymerization reactions take place and polymer grows. This growth is influenced by the buffer solutions. Buffer salts accelerate the addition reaction between urea and formaldehyde to form methylolureas (Jong and Jonge 1952). Buffer salts control the pH and affect the gelation time of adhesive in MDF production. Therefore, it is important to control pH. In order to react and cure ureaformaldehyde adhesive, adhesive hardener mixture pH should be lower than 7. Since the pH of the hardener adhesive mixture sufficiently low, it will cure faster with the temperature. Sodium chlorite is the salt of a weak acid. So, it is slightly basic. Sodium chlorite is a strong oxidant forms chlorine dioxide and chlorous acid and lower pH. Borate ion conjugate base of boric acid generally used as a primary or adjunct pH buffer system. SPT serves as a source of active oxygen (Su et al. 1995). Sodium perborate undergoes hydrolysis in contact with water producing hydrogen peroxide and borate. Therefore, these chemicals demonstrate acidic character in aqueous solutions due to conjugate ion.

The pH of the aqueous solution was given in Tab. 3 having different mixture ratios with urea formaldehyde adhesive, which has an average pH of 8.4. Borax and sodium perborate tetrahydrate (SPT) mixed with ureaformaldehyde resin reached greater than pH 7. Tab. 3 shows also gelation time increased with increasing pH. Increasing the level of the catalyst reduces the pH and gel time of UF resins (Xing et al. 2007). However, increased acidic character in a reaction medium may cause to degrade cured UF resin and reduce the strength. In addition to that, some chemicals have similar pH, but different gel time. Chemicals used singly as 10 % hardener solution did not change the gel time (600 s). It could be two reasons for this. First one, inability to obtain an adequate pH value to cure resin. The second reason, it is likely to prevent the hardening of the glue in the respective temperature due to conjugate ion difference. According to Weinstabl et al. (2001) the reason of this situation will be based on high viscosity of the glue and hardener mixture. These chemicals are commonly used as fire retardants. Therefore, they require high temperature to cure. When they heated in oil bath at 175°C and measured gel time, they give lower gelation period. It can be said that increasing temperature accelerate the curing reactions of urea formaldehyde. The curing period significantly influences the productivity and the cost for the manufacture of resin-used products. During the curing process, some individual reactions take place. However, the most important reaction is the condensation reaction. These reactions influenced by the polymer properties in addition, the pH value of the medium, and temperature. Increased temperature forces the fraction of molecules whose kinetic energy exceeds the activation energy, as a result increases the reaction rate.

Tab. 3: Adhesive pH value, gel time at 100°C in water and 175°C in oil bath.

Chemicals	Mixture ratio (%w/w)	pH	Gel time at 100° C (second)	Gel time at 175° C (second)
Amonium Chlorite (Control)	25	6.1	64.33 (2.62)***	40.67 (1.25)
	50	6.0	54.40 (1.20)	40.33 (0.47)
	75	5.9	46.67 (0.94)	38.67 (0.47)
	100	5.8	44.60 (0.49)	33.67 (0.47)
Boric acid	25+ 75°C	6.1	44.00 (1.63)	38.33 (0.47)
	50 + 50°C	5.9	45.00 (1.41)	38.67 (0.47)
	75 + 25°C	5.8	51.33 (0.47)	43.33 (1.25)
	100	6.9	- *	132.00 (2.83)**
Boron oxide	25+ 75°C	6.0	42.00 (0.82)	37.33 (0.47)
	50 + 50°C	5.9	44.33 (0.47)	38.67 (0.94)
	75 + 25°C	5.8	57.00 (0.82)	43.00 (0.82)
	100	6.7	- *	127.33 (2.62)**
Borax	25+ 75°C	7.3	50.33 (0.94)	41.67 (0.47)
	50 + 50°C	7.9	69.67 (1.25)	48.67 (1.25)
	75 + 25°C	8.2	104.00 (7.04)	61.67 (0.94)
	100	8.9	- *	137.33 (2.05)**
SPT	25+ 75°C	7.2	54.33 (1.70)	40.00 (0.82)
	50 + 50°C	8.4	66.67 (1.25)	40.67 (1.70)
	75 + 25°C	8.6	94.67 (1.70)	51.67 (0.47)
	100	9.5	- *	128.33 (4.99)**
NaCl	25+ 75°C	6.1	45.33 (0.47)	35.33 (0.47)
	50 + 50°C	6.2	46.67 (0.94)	38.00 (1.63)
	75 + 25°C	6.3	55.00 (0.00)	40.33 (0.47)
	100	7.8	- *	138.33 (0.47)**
NaClO ₂	25+ 75°C	6.8	55.67 (1.25)	47.67 (1.25)
	50 + 50°C	6.8	60.00 (3.74)	51.00 (2.16)
	75 + 25°C	7.1	82.67 (2.49)	65.00 (1.41)
	100	9.6	99.33 (0.47)	95.67 (1.70)**

* Unchanged during 600 second

** Gel

***Standard deviation (number in paranthesis).

Experiments conducted at 175°C in oil bath was important to be seen how long the glue would harden in the press condition. Based on these values, sufficient pressing time can be determined and used in real time process. Urea-formaldehyde adhesive curing period was accelerated and shortened by raising temperature of 175°C when these chemicals were used.

Mechanical and physical properties of the board produced with those chemicals were given in Tab. 4. The change in percentage of chemicals in mixtures was investigated with testing physical and mechanical properties and variance analysis were performed to determine significance. Duncan test was applied for determining statistically significant results. Homogeneous groups based on the test results were compared. In general, tensile strength was affected at most with the chemical addition. Acidic condition may degrade the cured urea formaldehyde resin to reduce the strength. In contrast, the strength of the catalyst was not high and the pH of the reaction

medium was not low and the reaction was not taking place under appropriate conditions in some cases. Formaldehyde content can not react appropriately with the chemicals. Therefore, they are giving low strength values like in literature studies (Akbulut et al. 2004; Ayrılımsı 2007; Hashim et al. 2009).

Tab. 4: Board physical and mechanical properties with standard deviation.

Chemicals	Mixture	Thickness swelling (%)	Water absorption (%)	Tensile strength (MPa)	MOE (MPa)	MOR (MPa)
Amonium Chlorite (Control)	25	36.61 (4.11)	125.52 (8.39)	0.06 (0.01)	1577.20 (71.04)	8.80 (1.69)
	50	38.31 (4.16)	122.92 (1.45)	0.07 (0.01)	1129.72 (265.77)	6.44 (2.01)
	75	66.06 (9.09)	137.74 (12.27)	0.03 (0.00)	1180.12 (206.81)	4.63 (0.53)
	100	54.00 (5.44)	141.01 (7.16)	0.05 (0.01)	1355.08 (186.71)	7.14 (1.46)
Boric acid	25+ 75°C	38.21 (9.89)	98.31 (11.32)	0.10 (0.01)	1500.69 (130.17)	9.17 (1.07)
	50 +50°C	36.70 (3.37)	115.28 (6.12)	0.06 (0.01)	1140.11 (112.08)	7.29 (1.29)
	75 +25°C	34.33 (4.47)	115.94 (12.97)	0.06 (0.01)	1739.98 (334.47)	10.14 (2.14)
	100	44.90 (9.38)	129.01 (10.82)	0.05 (0.00)	1011.32 (197.01)	5.37 (1.13)
Boron oxide	25+ 75°C	37.46 (3.97)	116.73 (7.59)	0.08 (0.02)	1595.21 (213.56)	9.60 (2.14)
	50 +50°C	36.33 (6.61)	109.47 (6.71)	0.07 (0.01)	1749.85(75.70)	10.82 (1.03)
	75 +25°C	35.57 (7.96)	112.08 (3.69)	0.05 (0.00)	1758.13 (273.55)	9.23 (1.098)
	100	42.02 (6.80)	104.81 (8.72)	0.07 (0.02)	955.70 (250.79)	5.85 (1.83)
Borax	25+ 75°C	29.00 (3.29)	113.00 (12.75)	0.06 (0.01)	1473.38 (333.371)	8.07 (1.73)
	50 +50°C	32.46 (7.43)	120.77 (26.71)	0.09 (0.01)	1819.59 (125.85)	10.17 (1.11)
	75 +25°C	38.48 (3.04)	129.18 (0.92)	0.04 (0.01)	1153.72 (167.81)	5.61 (1.46)
	100	46.74 (2.07)	156.96 (8.18)	0.06 (0.01)	1665.91 (994.011)	6.67(1.58)
SPT	25+ 75°C	41.64 (4.30)	142.31 (11.10)	0.05 (0.01)	1280.80 (242.16)	8.63 (1.39)
	50 +50°C	32.12 (22.30)	138.08 (26.60)	0.05 (0.01)	2121.29 (1033.36)	10.57 (4.26)
	75 +25°C	39.20 (2.97)	123.91 (7.01)	0.05 (0.02)	1287.93 (138.93)	7.46(0.66)
	100	36.72 (6.16)	94.31 (13.61)	0.04 (0.01)	1130.73 (272.41)	4.80 (1.67)
NaCl	25+ 75°C	52.20 (4.46)	130.77 (18.11)	0.07 (0.00)	1050.05 (165.32)	4.93 (0.76)
	50 +50°C	73.49 (5.97)	138.08 (39.98)	0.04 (0.01)	693.0 (60.43)	4.484 (1.89)
	75 +25°C	34.74 (4.87)	123.56 (15.72)	0.04 (0.00)	594.40 (133.01)	3.56 (0.99)
	100	40.38 (5.15)	121.21 (1.84)	0.09 (0.03)	1624.94 (119.88)	7.89 (1.03)
NaClO ₂	25+ 75°C	62.19 (9.84)	170.83 (17.64)	0.07 (0.01)	1426.01 (548.14)	5.54(2.22)
	50 +50°C	51.54 (11.32)	153.25 (29.21)	0.01 (0.01)	878.35 (125.96)	3.39 (0.37)
	75 +25°C	52.77 (8.36)	127.02 (2.57)	0.04 (0.02)	918.78 (254.88)	3.73 (1.20)
	100	36.63 (2.15)	117.26 (10.63)	0.09 (0.03)	2130.82 (130.94)	11.43 (0.67)

Standard deviation (number in paranthesis).

Tab. 5: Duncan test results.

Chemicals	Thickness swelling (%)	Water absorption (%)	Tensile strength	MOE	MOR
Control	48.82 B	131.80 BC	0.0507 BC	1310.53 A	5.45 B
Boric acid	3.54 A	114.64 AB	0.0675 A	1348.02 A	7.99 A
Boron oxide	37.85A	110.77 A	0.0650 AB	1514.72 A	8.88 A
Borax	36.67 B	129.98 BC	0.0642 AB	1528.15 A	7.64 A
SPT	37.42 A	124.65 ABC	0.0458 C	1455.18 A	8.59 A
NaCl	50.20 B	128.38 BC	0.0608 ABC	990.61 B	5.22 B
NaClO ₂	50.78 B	140.57 C	0.0533 ABC	1338.49 A	6.03B

In the production of panels from fiber, the less water absorption is desired. According to Tab. 5, boron oxide and SPT contributed positively to water absorption and thickness swelling properties when compared to the control groups ($p \leq 0.05$). Although ureformaldehyde resin water soluble, sodium perborate tetrahydrate (SPT) solution gave the best average value among all the hardener solution by 94.31 % with 10 % concentration (Tab. 2). In comparison, this group gave 33.12 % less moisture content than the control group. In addition to that, boron oxide and boric acid were also given better results in thickness swelling compared to control group ($p \leq 0.05$) (Tab. 3). According to the Tab. 4 tensile strength values when used in a mixture of ammonium chloride, the chemical used has the negative effects on tensile strength when increase the percentage of chemicals in ammonium chlorite solution ($p \leq 0.05$). The chemicals used in mixture should not be more than 50 % for optimum tensile strength values.

Tab. 6: Duncan test result for tensile test with different chemical mixture.

Concentration	Tensile strength (MPa)
25+ 75 K	0.0689 A
50 + 50K	0.0552 B
75 + 25 K	0.0442 C
100	0.0645 AB

Mechanical properties provide information about the material behavior under load in the areas where it is used. Boric acid, boron oxide, borax, sodium perborate were contributed positively to the bending strength compared to the control group. There is no statistical difference on sodium chloride, sodium chlorite used group compared to the control group ($p \leq 0.05$) (Tab. 6).

CONCLUSIONS

Aqueous solutions of chemicals used or the mixture with ammonium chlorite has the qualities to be used as a hardening agent in the fibreboard industry. The only ammonium chloride solution formed from this chemical. In particular, it was observed that the boric acid and boron oxide improve board properties when used in alone or mixed with ammonium chlorite solution. Similarly, the use of these solutions did not create a significant difference compared to the control group in the properties of board. Therefore, chemicals can be considered as an alternative to the use of ammonium chlorite solution.

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