Characterization and Performance of Melamine Enhanced Urea Formaldehyde Resin for Bonding Southern Pine Particleboard

Qi-Ning Sun,[1] Chung-Yun Hse,[2] Todd F. Shupe[1]

[1]*School of Renewable Natural Resources, Louisiana State University AgCenter, Baton Rouge, Louisiana 70803*
[2]*USDA Forest Service, Southern Research Station, Pineville, Louisiana 71360*

ABSTRACT: Urea-formaldehyde resins modified by melamine were synthesized by four catalysts (H_2SO_4, HCl, H_3PO_4, and $NaOH/NH_4OH$) with a F/U/M molar ratio of 1.38/1/0.074. Resin structure and thermal behavior were studied by ^{13}C-NMR and DSC techniques. For H_2SO_4, HCl, and H_3PO_4 catalysts, resins were prepared by two stage pH adjustment: the first pH stage was set at 1.25 (H_3PO_4 pH 1.60) and second pH stage was set at 5.0. For the $NaOH/NH_4OH$ catalyst, the resin was set at pH 5.0 from the start. Of the four catalysts, HCl catalyzed resins, with the highest free urea and lowest free formaldehyde, consistently yielded the lowest formaldehyde emission; $NaOH/NH_4OH$ catalyst resulted in the best IB strength tested at dry conditions and also after 24 h cold water soak and the lowest water absorption and thickness swell. The resins catalyzed with H_3PO_4 had the highest free formaldehyde and no free urea yielding the highest formaldehyde emission. Each DSC thermogram was proceeded by a weak exothermic peak and followed by an obvious endothermic peak. The exothermic peak temperatures were 125.0, 131.1, 111.4, and 125.2°C, and endothermic peak temperatures were 135.8, 147.6, 118.9, and 138.4°C, respectively, for H_2SO_4, HCl, H_3PO_4, and $NaOH/NH_4OH$ catalysts. The close proximity of the peak temperatures of the exothermic and endothermic reactions strongly suggests that there is potential interference of heat flow between the exothermic and endothermic reactions which may impact resin curing. © 2010 Wiley Periodicals, Inc.[†] J Appl Polym Sci 119: 3538–3543, 2011

Key words: ^{13}C-NMR; DSC; melamine-urea-formaldehyde resin; acid catalysts; southern pine particleboards; formaldehyde emission

INTRODUCTION

Low cost and proven performance have made urea-formaldehyde (UF) resins the most important wood adhesive for interior applications. However, concerns about formaldehyde emission from particleboard and compromised glue bonds caused by hydrolytic degradation of UF polymers have stimulated efforts to develop improved and/or new adhesives based on UF resins. Melamine is an ideal chemical to fortify UF resins primarily due to melamine's high functionality, stable molecular structure in comparison to urea, and its similar reaction mechanism as of urea with formaldehyde.[1–6] However, since melamine costs significantly more than urea, many of these amino resin adhesives are considered too costly to replace UF resin applications. Therefore, few studies have been published on gluing particleboard by melamine-urea-formaldehyde resins. Moreover, most of urea-formaldehyde resins modified by melamine (UMF) have been focused on various molar ratios of formaldehyde to urea to melamine reacting at different pH with H_2SO_4 and NaOH as catalysts. Few studies have been conducted on the effects of different catalyst species on resin synthesis and performance. Given an increased commercial importance of amino resins and the potential of melamine for improvements on durability, moisture resistance, and formaldehyde emission; four catalysts (i.e., H_2SO_4, HCl, and H_3PO_4, and $NaOH/NH_4OH$) representing a wide range of available catalysts were chosen to prepare the Urea-formaldehyde resins modified by low level melamine (UMF). Special emphasis was on reacting UF resin under strong acidic pH and reacting UF resin with low melamine content in weak acidic conditions. The effects of four catalysts on resin synthesis, chemical structure, and curing behavior of UMF resins were evaluated, and the performance of particleboard fabricated with the UMF resins were determined. The objective was to establish inter-relationships within/and among the resin synthesis, the chemical structure, resin curing, and bond performance to pave the way for developing of a new UMF resin with low cost and high performance.

Correspondence to: C.-Y. Hse (chse@fs.fed.us).

EXPERIMENTAL

Sources of chemicals

Formaldehyde solution: AR (ACS), 36.5–38.0%, Mallinckrodt; urea: USP Grade, >99.0%, AMRESCO; melamine: Usual industrial handling, 98% min. EASTMAN KODAK Company; sulfuric acid: Reagent (ACS) 95.0–98.0%, VWR Company; hydrochloric acid: GR 36.5–38.0%, EM SCIENCE; phosphoric acid: Analyzed reagent, 85.4%, J.T. Baker Chemical Co.; strong ammonia solution: ammonium hydroxide less than 40%, J.T. Baker Chemical Co.; sodium hydroxide: purum p.a. >97.0%, Fluka.

Preparation of UMF resins

Resins catalyzed by four catalysts H_2SO_4, HCl, H_3PO_4, and NaOH/NH_4OH (50/50 w: w, solid content) were prepared under the same F/U/M molar ratio of 1.38/1/0.074 in the laboratory. Each resin synthesis was replicated twice. To initiate the reaction, all formaldehyde (3 mol) and water were placed in a reaction kettle and pH was adjusted with four catalysts (pH 1.25 for H_2SO_4 and HCl; pH 1.60 for H_3PO_4 and pH 5.0 for NaOH/NH_4OH). Urea (1 mol) was added in three equal portions at 15-min intervals. The reaction kettle was heated and maintained at 70°C. Fifteen minutes after addition of the last portion of urea, the pH was adjusted to 5.0 and all melamine (0.16 mol) was slowly added in 15 min. The reaction was kept at 70°C till reached the cloudy point, and thereafter, the solution temperature was raised to 80°C, and the second urea (1.17 mol) was added in six equal parts in 60 min. No additional pH adjustment was made after adding melamine. Then the reaction was terminated by cooling to room temperature within 10 min.

Resins characterizations

Free formaldehyde determination

A slightly modified sodium sulfite method[4] was used for determination of free formaldehyde in the resins. Fifty mL of a 1-molar solution of sodium sulfite and three drops of thymophthalein indicator solution were placed in a 250 mL Erlenmeyer flask and carefully neutralized by titration within hydrochloric acid until the blue color of the indicator disappeared. An accurately measured, neutralized resin sample was then added to the sodium sulfite solution, and the temperature was kept at 4°C to minimize hydrolysis of the resin. The resulting mixture was titrated with 0.1 N HCl to complete decoloration. The percent of free formaldehyde was determined as:

$$\% \text{ HCHO} = \frac{(\text{acid titer}) \times (\text{normality of acid}) \times 3.003}{\text{weight of sample}}$$

Formaldehyde emission measurement

The determination of formaldehyde emission was conducted using ASTM D 6007-02 (ASTM 2008).[7] Gel times of resins were measured with a sunshine gel timer with temperature controlled at 100°C. The stability was evaluated by storing resins in a plastic container at room temperature (20°C) and measuring the viscosity. In addition, pH, solid content were determined.

^{13}C-NMR measurement

Fourier Transform ^{13}C-NMR spectra were obtained on a Varian Inova spectrometer at a relaxation delay of 5 sec with inverse proton decoupling. The chemical shifts were calculated by defining a ^{13}C chemical shift using capillary tube with a d-DMSO insert in a NMR tube for locking and chemical shift referencing.

DSC analysis

DSC data were obtained between 35 and 220°C using a TA Instrument Q20 differential scanning calorimeter (DSC). Freeze-dried samples in an aluminum pan without a lid were slowly cooled down to 35°C and then heated at 10°C min^{-1}. Nitrogen was used as the flushing gas.

Glue bond performance

All panels were manufactured with wood particles obtained from a local particleboard plant of Flakeboard Corp. (Ruston, La). The southern pine particles from the dry-end of the mill dryer were stored in polyethylene bags and used without additional preparation. The mean moisture content of particles was controlled at 3%. To prepare each panel, the wood particles were weighted and placed in a rotating drum-type blender. Each resin, 6% based on oven dry weight wood particles, was weighted and applied by an air-atomizing nozzle. After blending, the wood particles were felted into a 14 inch by 16.5 inch (35.56 cm by 41.91 cm) box to form the mat. And the mat was transferred to a single-opening hot-press with platen temperature of 370°F (188°C) and pressure 550 psi (3792 kPa) at 4 min so that the platen closed to 0.5 inch (1.27 cm)-thickness. Board manufacture replication was two boards for each condition.

All boards were conditioned in a chamber at 50% relative humidity and 77°F (25°C) before testing, ending with the moisture content that averaged 5.5%.

TABLE I
UMF Resin Properties Used in the Experiment

Catalyst	Viscosity after preparation (cp)	Solids content (%)	Free formaldehyde (%)	Gel time (min)	pH
H_2SO_4	73B[a]	46.55A	0.40A	62.89A	6.28A
HCL	57B	46.43A	0.34B	64.66A	6.29A
H_3PO_4	271A	46.83A	0.39A	21.92B	5.93AB
$NaOH/NH_4OH$	47B	47.93A	0.35B	64.15A	6.17B

[a] The same letter in the column indicates no significant difference at the 5% level.

The internal bond (IB) strength, thickness swelling (TS), water absorption, bending strength (MOR and MOE), and density were determined in accordance with ASTM D 1037-99 (ASTM 2009).[8] Results were statistically analyzed using analysis of Duncan's multiple range tests.

RESULTS AND DISCUSSION

Resin properties

Average physical and chemical properties of UMF resins as affected by reaction catalysts are summarized in Table I. The solid contents ranged from 46.43 to 47.93% with an average of 46.94%. As expected, the different catalysts had no significant effect on solids contents of the four resins.

Duncan's multiple range tests showed that the free formaldehyde content of resins catalyzed with H_2SO_4 and H_3PO_4 were significantly higher than that of the resins catalyzed with HCl and NaOH/NH$_4$OH. These results seemed to indicate that the HCl and NaOH/NH$_4$OH catalyst system resulted in a higher degree of addition reaction.

In regards to the catalytic effects of the four resins, the most interesting result was the one with the H_3PO_4 catalyst. As shown in Table I, the resin with the H_3PO_4 catalyst yielded significantly higher viscosity and free formaldehyde, substantially shorter gel time, and slightly lower pH. The strong catalytic action of H_3PO_4 was also shown in the determination of resin reaction end point which was obtained by the reaction time required to reach the same cloudy point during the resin preparation. The reaction end point H_3PO_4 catalyzed resin was ~ 30 min as compared to that of 50, 90, and 270 min, respectively, for H_2SO_4, HCl, and NaOH/NH$_4$OH catalyzed resins. Furthermore, it should be mentioned the adjustment of reaction pH to 1.25 by the addition of H_3PO_4 resulted in a resin which was extremely unstable after cooling. Thus, reaction pH for H_3PO_4 was slightly adjusted higher to 1.60 during the resin preparation. H_3PO_4 is recognized for its triprotic dissociation in solution with the presence of various ionic phosphate groups, e.g., as HPO_4^{2-} or $H_2PO_4^-$. The presence of both HPO_4^{2-} and $H_2PO_4^-$ moieties

implied that the transport of protons may involve an exchange of protons between a bronsted type acid ($H_2PO_4^-$) and bronsted type base (HPO_4^{2-}), which is closely related to H_3PO_4 concentrations. In general, in high H_3PO_4 concentrations, the dissociation of excess free H_3PO_4 is easier to yield solvated H_3O^+ ions and $H_2PO_4^-$ moieties, and hence greatly accelerate condensation reactions.

The stability of the resins under room temperature was determined by the change in resin viscosity. The viscosity of four resins increased over the 50-day period at room-temperature ($20^\circ C$) storage (Fig. 1). The resin catalyzed with H_3PO_4 gave the fastest increase in viscosity of the resins and gelled in about a week, which was closely associated to its shortest gel time and lower pH; however, resin with a NaOH/NH$_4$OH catalyst showed the best storage stability as compared to the other catalysts, which also was related to its longer gel time. Analysis above indicated H_3PO_4, comparing with other catalysts, highly affected the polymer interaction among melamine, urea, and formaldehyde during the resin preparation.
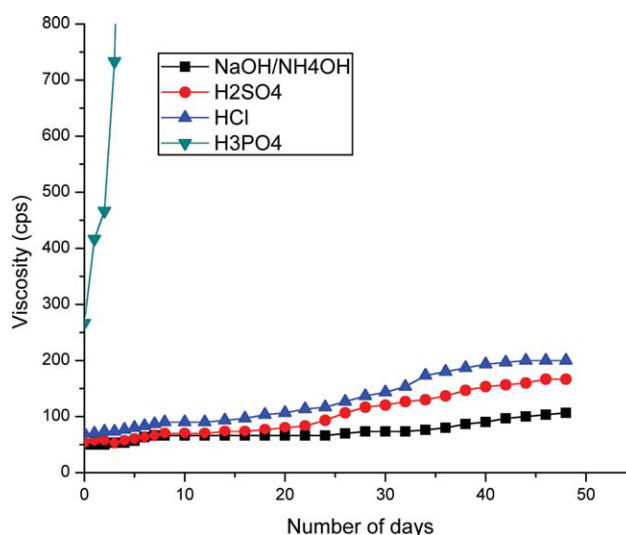

Figure 1 Storage life of UMF resins with four catalysts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
^{13}C-NMR Assignment of UMF Resins with Four Catalysts

Functional group	Chemical shift (ppm)	Relative peak area (%)			
		H_2SO_4	HCl	H_3PO_4	NaOH/NH$_4$OH
Total methylene linkages		32.89	33.12	45.89	36.14
HNC$\underline{H_2}$NH	45–47	21.19	20.12	32.82	18.75
HNC$\underline{H_2}$N(CH$_2$)	53–56	11.70	13.00	13.07	17.39
Total methylol groups		25.47	30.39	30.68	34.27
C$\underline{H_3}$OH	51–52	9.39	8.77	9.98	10.36
HNC$\underline{H_2}$OH	63	12.52	15.63	15.16	14.76
N(C$\underline{H_2}$)CH$_2$OH; N(C$\underline{H_2}$OH)$_2$	66–67	3.56	5.99	5.54	9.15
Total methylene-ether groups		41.64	36.5	23.43	29.58
HNCH$_2$OC$\underline{H_2}$NH	69–71	15.25	13.46	13.16	15.42
N(C$\underline{H_2}$) C$\underline{H_2}$OCH$_3$	76–77	12.40	7.87	0	0
CH$_3$OC$\underline{H_2}$NHCON(C$\underline{H_2}$OCH$_3$)$_2$	81	2.62	3.85	10.27	1.65
HOCH$_2$OC$\underline{H_2}$OH;NC$\underline{H_2}$OCH$_2$OH; HNCH$_2$OC$\underline{H_3}$;HOC$\underline{H_2}$OC$\underline{H_2}$OCH$_3$	88–92	11.37	11.32	0	12.51
Urea carbonyl region					
Tetra-sub or uron urea	156–158	31.80	32.69	38.31	29.19
Di-/trisubstituted urea	159–160	22.62	25.19	38.63	31.85
Monosubstituted urea	161	19.25	15.44	23.06	18.20
Free urea	164	26.33	36.39	0	20.77

Chemical structures

Table II summarizes the main ^{13}C-NMR signal assignments and integral values according to previous studies.[9–14] It can be seen from the integral intensities in ^{13}C-NMR spectra that H_2SO_4 yielded the most methylene–ether groups; HCl resulted in the highest amount of free urea; H_3PO_4 gave the most methylene linkages and monosubstituted di-tri- and tetra-substituted urea but the least amount of free urea. Moreover, the integration intensity order of methylene groups in the four resins was $H_3PO_4 >$ NaOH/NH$_4$OH $>$ HCl $> H_2SO_4$, which illustrates the different reaction degree of the amino group in urea with formaldehyde; the order of the methylol group was NaOH/NH$_4$OH $> H_3PO_4 >$ HCl $> H_2SO_4$; which indicates the high chemical reactivity of the NaOH/NH4OH catalyst system; the order of the methylene–ether groups was $H_2SO_4 >$ HCl $>$ NaOH/NH$_4$OH $> H_3PO_4$; the order of free urea was HCl $> H_2SO_4 >$ NaOH/NH$_4$OH $> H_3PO_4$.

Curing of UMF resins

Figure 2 depicts a typical DSC thermogram for UMF resins with four acid catalysts. It can be seen from Figure 2 that the UMF resins displayed different curing behaviors in the temperature range 30–220°C. In general, each DSC thermogram was proceeded by a weak exothermic peak and followed by an obvious endothermic peak. The exothermic peak temperatures were 125.0, 131.1, 111.4, and 125.2°C, and endothermic peak temperatures were 135.8, 147.6, 118.9, and 138.4°C, respectively, for H_2SO_4, HCl, H_3PO_4, and NaOH/NH$_4$OH catalysts. The exothermic heat of curing reactions included the bond for-

mations between urea and urea, melamine and urea, and melamine and melamine. The endothermic heat of reaction included the evaporation of condensation water, free formaldehyde, and part rearrangement of ether groups into methylene by splitting off formaldehyde. It should be noted that the close proximity of the peak temperatures of the exothermic and endothermic reactions strongly suggest that the potential interference of the heat flow between exothermic and endothermic reactions tend to interact to effect the measurement of the reaction thermogram.

Table III summarizes the results of four UMF resins from DSC analysis. Some interesting results can
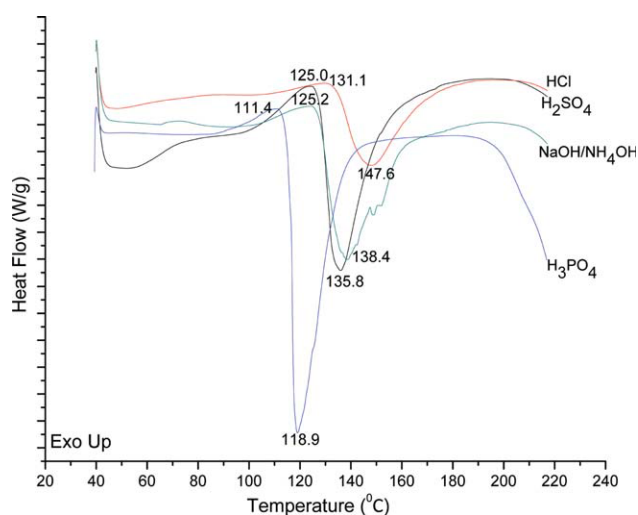

Figure 2 DSC curves of UMF resins with four catalysts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Results from DSC Analysis of UMF Resins with Four Catalysts

Catalyst	Exothermic peak (°C)	Exothermic ΔH (J/g)	Endothermic peak (°C)	Endothermic ΔH (J/g)	Peak temperature span (°C)[a]
H_2SO_4	125.0	11.8	135.8	68.3	10.8
HCl	131.1	5.3	147.6	54.0	16.5
H_3PO_4	111.4	8.5	118.9	84.7	7.5
NaON/NH_4OH	125.2	6.9	138.4	63.4	13.2

[a] Peak temperature span is the peak temperature difference between the endothermic and exothermic peaks.

be noted: (1) the resin catalyzed by HCl yielded the highest peak temperatures for both exothermic and endothermic reactions with the lowest reaction heat of exothermic and endothermic, (2) a similar trend (i.e., high peak temperature and low heat of reaction) was shown for the resin catalyzed with NaOH/NH_4OH but with values slightly lower than that of HCl, (3) the resin catalyzed with H_3PO_4 resulted in the lowest peak temperatures, the highest heat of endothermic reaction, and the smallest peak temperature span, (4) the significant values for resin catalyzed with H_2SO_4 was its highest heat of exothermic reaction.

Performance of UMF bonded particleboards

Average physical and mechanical properties and the formaldehyde emission from the particleboards fabricated from UMF resins are summarized in Table IV. According to Duncan's multiple range tests, the effects of catalysts on average MOR and MOE were not significant. This finding indicates that the resin variable was considered a minor factor affecting bending strength as compared to the physical characteristics of wood such as density.

It was interesting to note that the NaOH/NH_4OH catalyst resulted in the best overall panel properties with the exception of formaldehyde emission. With the lowest panel density, the NaOH/NH_4OH catalyst yielded the highest IB before and after 24-h water soaking, and the most stable panels with the lowest water absorption and thickness swelling. Apparently, the NaOH/NH_4OH catalyzed resins

consisted of several desirable resin properties, for instance: (1) adequate methylene linkages for high cohesive strength of cured resin, high resistance to hydrolytic degradation, and best dimensional stability, (2) the highest content of methylol groups for maximum chemical reactivity to enhance adhesive strength, (3) the highest content of branched-type methylene linkage (i.e., 17.39, Table II) and blanched methylol in the resin (i.e., 9.15, Table II) to facilitate the formation of a more branched structure during resin curing. Consequently, the water evaporation endotherm is shifted at a considerable higher temperature indicating the formation of a tighter network of cured resin which enhances resin performance, (4) relatively low exothermic heat of curing indicating less cross-linking formation but easy to attain the completion of resin cure, and (5) relatively low endothermic heat of evaporation indicating the relative ease for removal of moisture during resin curing.

The most significant effect of the HCl catalyst on resin performance was its substantially lowest formaldehyde emission. These results were likely related to the free formaldehyde content and free urea content of the resin. It is generally recognized that the free formaldehyde left in the panel can directly contribute to formaldehyde emission. Conversely, the free urea can react with formaldehyde as chemical compounds to tie-up the formaldehyde in situ. Therefore, with lower free formaldehyde and highest free urea, the HCl resins resulted in the lowest formaldehyde emission of the panels. It should be noted that the HCL catalyzed resin also yielded high IB

TABLE IV
Effect of Four Catalysts on UMF Resins for Selected Particleboard Properties

Catalyst	Density (g/cm³)	IB[a] (MPa)	IB[b] (MPa)	MOR (MPa)	MOE (MPa)	Formaldehyde emission (µg/mL)	Water absorption (%)	Thickness swelling (%)
H_2SO_4	0.830 A[c]	0.93 B	0.15 C	20.16 A	3409 A	2.34 A	74.68 A	40.20 A
HCL	0.834 A	1.08 A	0.23 B	21.88 A	3703 A	1.48 B	71.47 B	36.22 B
H_3PO_4	0.827 A	0.98 B	0.29 A	20.21 A	3462 A	2.90 A	70.41 B	34.91 B
NaOH/NH_4OH	0.818 A	1.13 A	0.31 A	21.34 A	3708 A	2.25 A	65.34 C	29.06 C

[a] IB tested in the dry condition at ambient room conditions.
[b] IB tested at 24 h cold water soak at ambient room conditions.
[c] The same letter in the column indicates no significant difference at the 5% level.

strength mainly because of its most favorable curing conditions (i.e., lowest exothermic heat of curing and endothermic heat of evaporation) and formation of tighter chemical bonds in the cured resin, which was similar to the NaOH/NH$_4$OH catalyzed resin.

Furthermore, the HCl catalyzed resin also has the largest peak temperature span (i.e., 16.5°C) which can minimize the potential interaction of heat flow between exothermic and endothermic reaction to adversely affect the resin cure.

Resin catalyzed by H$_3$PO$_4$ with the largest amount of methylene linkage, the greatest amounts of mono- di- tri- and tetra-substituted urea, and the lowest hydrophilic methylene-ether groups resulted in the higher viscosity, shortest gel time but excellent 24-h water soak IB strength. It should be noted that H$_3$PO$_4$ catalyzed resin had the highest formaldehyde emission likely because of little free urea and the highest free formaldehyde in the resin systems.

The H$_2$SO$_4$ catalyst in general yielded the least dimensionally stable and lowest strength panel of all. Since H$_2$SO$_4$ has been one of the most widely used catalysts for wood adhesives, its poor performance as shown in the study indicates the possibility of developing a better UMF resin for the future.

CONCLUSIONS

UMF resins were formulated with four catalysts (H$_2$SO$_4$, HCl, H$_3$PO$_4$, and NaOH/NH$_4$OH) under the same molar ratio. The characteristic of UMF resins and performance of particleboards were evaluated.

The NaOH/NH$_4$OH catalyst resulted in the best overall panel properties with the exception of formaldehyde emission. With the lowest panel density, the NaOH/NH$_4$OH catalyst yielded the highest IB before and after 24-h water soaking, and the most stable panels with the lowest water absorption and thickness swelling.

H$_3$PO$_4$ catalyst yielded significantly higher viscosity and fastest gel time, and slightly lower pH of the four catalysts. However, with the lowest exothermic

and endothermic peak temperatures and smallest peak temperature span, the close proximity of the peak temperatures span strongly suggest that the potential interference of the heat flow between exothermic and endothermic reactions which in turn affecting proper cure of the resin.

H$_2$SO$_4$ yielded the highest number of methylene-ether groups and the highest free formaldehyde. These were closely related to the highest formaldehyde emission of the resin. Furthermore, with the least amount of methylol groups and methylene linkages, the H$_2$SO$_4$ catalyst was considered to be chemically least active, lowest cohesive energy, and resulted in poor performance with the lowest IB and highest thickness swell and water absorption.

With the lowest free formaldehyde and the highest free urea, the HCl catalyzed resin resulted in the best performance in term of formaldehyde emission.

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