

# Properties and Curing Behavior of Urea-Modified Phenolic Resins

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**Abstract** : The influence of adding urea to phenol-formaldehyde (PF) resins as a co-polymer component were investigated aiming at synthesizing useful phenol-urea-formaldehyde resins. Urea was added at 10% by total resin weight. Several methods for the addition of urea to the PF resins during synthesizing resins to see the co-polymerization occurs between urea and PF resins. The urea was added at the beginning, at three different middle stages, and at the end of PF resin synthesis. The copolymerized methylene bridges between phenol and urea molecules were not observed by <sup>13</sup>C-NMR; no signal around 50ppm. The curing of urea-modified PF resins, evaluated by dynamic mechanical analysis(DMA), showed some differences among the resins. DMA gel times ranged from 2.75 min to 3.25 min and the resins made with earlier urea additions showed slightly shorter gel times. The longest cure time and gelation time was observed for the resin PFU. Catalyst effects on the DMA cure time values of resins were not significant with different amounts of catalyst or different types of catalyst for all resins tested. Gel times of urea-modified PF resins shortened the most by triacetin catalyst.

**Keywords** : phenol-formaldehyde resins, urea, catalysts, co-polymerization, <sup>13</sup>C-NMR, urea-modified PF resins, dynamic mechanical analysis

## 1. Introduction

Water resistant PF resol resins are by far the most widely used binders for structural panels, such as exterior-grade OSB and softwood plywood. OSB industry uses highly polymerized PF resins that sometimes has had some urea added after PF resin synthesis. This urea addition has been known to reduce the viscosity of PF resins without affecting the cure rate of PF resins. This

urea also lowers the cost of resins due to its lower cost compare to phenol. However, the effects of the urea have not been clearly elucidated [6]. In addition, the post-addition of urea does not perform any further copolymerization reaction with PF resin.

In efforts to elucidate the effect of urea and to react urea with PF resin polymers, several approaches have been investigated. Tomita and Hse [8,9] reacted urea under an acidic condition with 2- and 4-hydroxybenzyl alcohol and 2,4,6-trimethylolphenol. Compounds co-condensed through methylene linkages were obtained and identified by

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$^{13}\text{C}$ -NMR spectroscopy and gel permeation chromatography (GPC). The reaction products also contained small amounts of self-condensed components of phenol through methylene or methylene ether linkages. Similar reaction products were also made by reacting urea and a mixture of various methylphenols. Tomita et al. [10] also studied a resin synthesis method to obtain co-polymerized phenol-urea-formaldehyde (PUF) resins by reacting phenol with UF-concentrate (F/U = 2.5) under an acidic condition. The products were analyzed by  $^{13}\text{C}$ -NMR spectroscopy and GPC. The extent of co-condensation increased up to 20% when the UF-concentrate prepared under alkaline condition was used. It was also found that the resol-type PUF resins were obtained under the acidic condition but it showed phase separation and thus it was not suitable as wood binders. Ohyama et al. [5] synthesized resol-type PUF resins under acid conditions and studied the curing and adhesive performance behavior by the torsional braid analysis method (TBA). The co-condensed resins cured almost the same way as pure PF resol resins except when curing at a low temperature.

Due to the instability of acid prepared PUF type resins, during the past several decades most researches are focused on the co-condensation of PF resins with urea under alkaline conditions. Kim and Watt [2] studied the effects of urea addition to PF resin binders for OSB. They synthesized PF resins and added urea up to 26% based on the resin solids weight. Analysis results of the synthesized resins indicated that the urea lowered the free formaldehyde content and increased the degree of polymerization, but slightly decreased the curing rates. Zhao et al. [11] co-reacted PF resin with urea under alkaline condition. They added urea up to 42 mole % of phenol during resin preparation. At the higher urea levels (24 mole % or higher), unreacted urea remained in the resin.

Increasing the F/P mole ratio decreased the unreacted urea and increased PUF resin formation. Increasing the amount of urea and increasing the F/P mole ratio gave faster hardening times. They claimed that co-polymerization between phenol and urea reached about 18 mole % of phenol.

Although PUF resins are used commercially, minimum research effort has been directed thus far toward the resin system and research results have been conflicting with regard to the co-polymerization of urea and phenol. Thus, more detailed research in this area is needed.

## 2. Materials and methods

### 2.1. Materials

Reagent grade 99% phenol (Aldrich Co.) was diluted to 90% aqueous solution with deionized water, and 50% formaldehyde aqueous solution and a commercial PF resin (CON) were provided by Georgia-Pacific Resins. Reagent grade 50% sodium hydroxide aqueous solution and reagent grade 98% urea (Aldrich Co.) were used.

### 2.2. Methods

#### 2.2.1. Resins preparation

Resins were synthesized at F/P mole ratio of 2.1 with a 5.76% sodium hydroxide content and 51%±1% nonvolatile content. Urea was added at 10% level on total resin weight basis. Urea addition points and resin codes are summarized in Table 1. Detailed synthetic method for resin PUA is illustrated as follows:

Resin PUA: The flask was initially charged with 245 g of 90% phenol, 100 g of 50% NaOH solution, 137.5 g of distilled water, and then 197.5 g of 50% formaldehyde solution was added dropwise over 20 min. The temperature was held at 45°C for 10 min for methylation reaction. Urea, 88.9 g, was

added and the temperature raised to 90°C over 30 min and held for 30 min. Then, 98.8 g of 50% formaldehyde solution were added. The temperature was held at 90°C until the resin viscosity reached "KL" by the Gardner-Holdt viscosity scale. The resin was then cooled to room temperature. The final viscosity of the resin was "MN".

Table 1. Summary of resin codes and urea addition points

Resin Code	Point of Urea Addition
PUA	In the beginning
PUB	At PF resin viscosity of B
PUE	At PF resin viscosity of E
PUI	At PF resin viscosity of I
PFU	At the end of PF resin cook

### 2.2.2. Catalyst addition for gel time and DMA cure tests

All resins were used with and without catalysts to measure gel times and DMA curing properties. Catalysts used were 50% potassium carbonate aqueous solution, 50% sodium carbonate aqueous solution, and 100% triacetin. Catalysts addition levels were 0, 2.5, 5 and 10% based on resin solids content. The resin sample (10 g) was measured and 0 g (for 0% catalyst level), 0.26 g (for 2.5% catalyst level), 0.52 g (for 5% catalyst level) and 1.04 g (for 10% catalyst level) of 50% potassium carbonate or 50% sodium carbonate was added, respectively. Triacetin amounts added were 0 g (for 0% catalyst level), 0.13 g (for 2.5% catalyst level), 0.26 g (for 5% catalyst level) and 0.52 g (for 10% catalyst level).

### 2.2.3. Analyses of resins

Gardner-Holdt viscometer, Brookfield viscometer, pH meter, specific gravity meter, gel timer, hot plate, and convection oven were used to measure resin physical

properties. Selected synthesized resins were examined by  $^{13}\text{C}$ -NMR and DMA.

Viscosity of all resins was measured with a Brookfield viscometer at 25°C, using a number 2 spindle with a turning rate of 5.2 rad/s (50 rpm). Non-volatile solids contents were measured with an analytical balance as follows. About 1.00 g of resin was placed in an aluminum pan and the pan heated in an oven at 125°C for 2 h, cooled to room temperature, and reweighed. Stroke cure times were measured on a hot-plate at 125°C using about 1.00 g of resin. Specific gravity of resins was measured with a Troemner density balance at 25°C. The pH of the resins was measured with a pH meter at 25°C. Gel times at 100°C were measured with a Sunshine Gel Timer.

### 2.2.4. Dynamic mechanical analysis

The curing properties of urea-modified PF resins were measured by DMA using Du Pont TA 983 DMA. The results were recorded and analyzed by DMA standard data analysis program [7]. Each resin sample (approximately 1.00 g) was mixed with 0, 2.5, 5, 10 (wt %) potassium carbonate, sodium carbonate, and triacetin as catalysts. Approximately 20 mg of resin sample was uniformly spread on a fiberglass braid (18.5× 11.2×0.12-mm dimensions) held by a lab-made holding tool. The resin spreaded braid was then clamped horizontally between the two sample holding arms.

DMA were performed in the fixed displacement mode with an amplitude of 0.8 mm and oscillation frequency of 1.0 Hz. The DMA runs were made isothermally, starting with an initial equilibration at 30°C, increasing the temperature at a rate of 25°C/min to 180°C, and holding at 180°C for 20 min.

The storage modulus ( $G'$ , the energy stored by the elastic component of the sample, which relates to the rigidity), the loss modulus ( $G''$ , the energy lost through

the viscous component of the sample, referred to as the damping signal), and  $\tan \delta$  ( $G''/G'$ ) curves were obtained. According to measurement methods used by earlier workers [1,4], cure time was recorded as the time to the intersecting point of the maximum storage modulus rise and the plateau line. Gel time was recorded as the time to the initial starting point of the slope of the storage modulus curve. Cure rate was recorded as the slope of the storage modulus curve of the maximum storage modulus rising region

### 2.2.5. $^{13}\text{C}$ -NMR spectroscopy

$^{13}\text{C}$ -NMR spectroscopy of resin samples (PUA, PUB, PUE, PUI, PFU and CON) were obtained using a Bruker AMX-300 spectrometer at ambient temperature. NMR spectra were obtained using a 12-s pulse width and a 5-s delay time, and the sample concentration was 1000 mg/mL. The solvent was deuterium oxide ( $\text{D}_2\text{O}$ ).

## 3. Results and discussion

All measured resin properties are summarized in Table 2. Most resin properties were close to the aimed values predetermined through comparison with the commercial PF resin control. The urea addition level was set at 10%, viscosity was

set to "MN", and solids content ranged from 50–52%. Specific gravity, pH, stroke cure time and gel time were determined after resin syntheses.

Final viscosity values of the synthesized resins ranged from "MN" to "N", specific gravity ranged from 1.192 to 1.220, pH ranged from 10.70 to 11.68, stroke cure time ranged from 2.25 min to 3.15 min, and gel time ranged from 18.92 min to 43.30 min.

The gel times increased as the urea addition point was delayed but decreased as the F/P mole ratio was increased (Figure 1). The decrease in gel time due to the increase in F/P mole ratio can be attributed to the higher degree of branching and higher functionality.

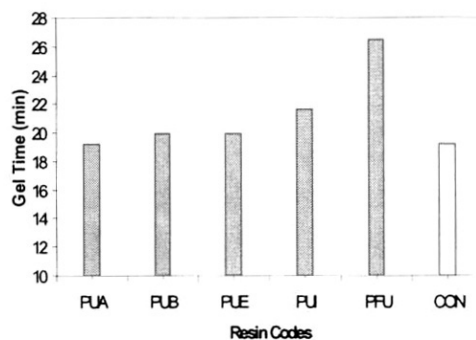


Fig. 1. Gel times of urea-modified PF resins with different urea addition points.

Table 2. Properties of resins

Resin Code	Viscosity	Specific Gravity	pH	Stroke Cure (min)	Gel Time (min)	Solids Content (%)
PUA	MN	1.200	11.65	2.50	19.20	50.4
PUB	N	1.192	11.62	2.50	19.90	51.8
PUE	N	1.217	11.58	2.45	19.90	52.0
PUI	MN	1.194	11.61	2.25	21.65	52.1
PFU	MN	1.212	11.68	2.40	26.45	52.2
CON	N	1.220	11.51	3.15	19.20	51.2

Gel times of resins were further studied to determine the effect of catalysts. Potassium carbonate, sodium carbonate and triacetin were chosen as catalysts. The results are shown in Figure 2. Increasing the amount of catalysts decreased the gel time. Of all three catalysts, triacetin produced the fastest gel time, whereas potassium carbonate and sodium carbonate only slightly reduced the gel time compared to uncatalyzed resins.

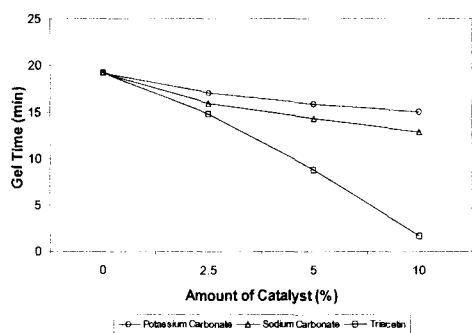


Fig. 2. Gel times of urea-modified PUA resin with 3 different catalysts.

The DMA gelation time differences of resins are shown in Figure 3. There are only small differences in gelation time between the resins, ranging from 2.75 min to 3.25 min. Urea-modified PF resins made with earlier urea additions showed lower cure rate values than resins made with later additions Figure 4. The DMA cure time values of urea-modified PF resins (Figure 5) were longer for resins made with earlier urea additions and for the resin made with a urea addition at the end of synthesis. But the differences are small although all synthesized resins showed longer cure times than the commercial control. Cure time values are combined results of gelation time and cure rate values.

Triacetin decreased the DMA cure rate values with increasing extents of catalyst level for resins made with later urea additions, but the resins made with early

urea additions were not affected very much. Potassium carbonate and sodium carbonate produced increased cure rates for resins made with early urea additions (PUA and PUB) to a range comparable to those of other resins. However, potassium carbonate and sodium carbonate decreased the DMA cure rate values on resins made with later urea additions. Catalyst effects on the DMA cure time values of resins were not significant with different amounts of catalyst or different types of catalyst for all resins tested (Figure 6). Of all three catalysts, triacetin produced the greatest reduction, followed by sodium carbonate and potassium carbonate.

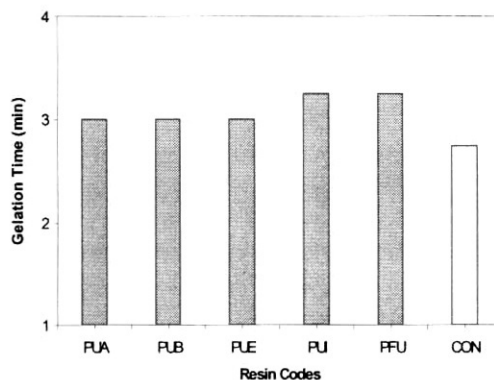


Fig. 3. Gelation times from DMA test results of urea-modified PF resins (no catalyst).

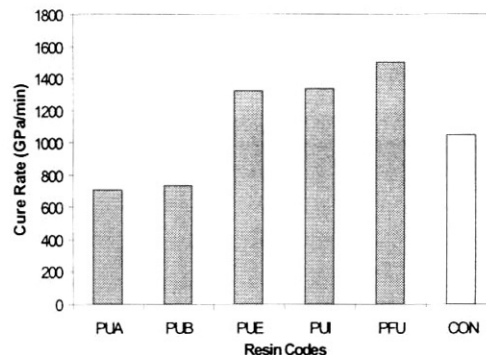


Fig. 4. Cure rate from DMA test results of urea-modified PF resins (no catalyst).

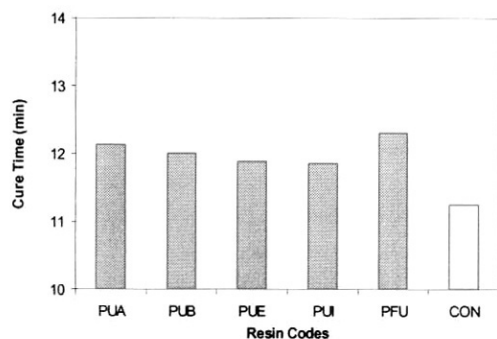


Fig. 5. Cure Time from DMA test results of urea-modified PF resins (no catalyst).

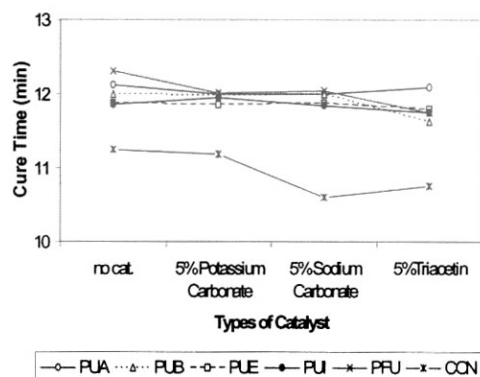


Fig. 6. Catalysts effects on the cure times of urea-modified PF resins.

The chemical shift of the  $^{13}\text{C}$ -NMR spectrum generally agreed with reported data [11], except the peak at around 50 ppm that was claimed to represent methylene groups between phenol and urea group. The relative percentages of various linkages in the urea-modified PF resins were calculated from the integrals representing each peak, and are shown in Table 3.

### 3.1. Methylene bridges

The presence of methylene bridges in the resins was confirmed by  $^{13}\text{C}$ -NMR. The *ortho-para* phenolic methylene bridges occurred at 34.8–37.6 ppm and *para-para* phenolic methylene bridges at 39.6–40.3 ppm, while *ortho-ortho* phenolic methylene bridges were absent in all resins tested. The percentages of methylene bridges between two phenol molecules were between 29.3% and 42.2%. There was no signal representing methylene groups between two urea molecules. Under alkaline pH, both phenol and urea react with formaldehyde to form methylolphenol and methylolurea. Methylolphenol does condense to form oligomers linked by methylene bridges, but methylolurea did not condense at alkaline pH.

Table 3. Percentages of different types of carbon present in urea-modified PF resins determined from  $^{13}\text{C}$ -NMR spectra

Resin Code	% methylene C -CH <sub>2</sub> - <sup>1)</sup>	% methanol CH <sub>3</sub> OH <sup>2)</sup>	% methylol C -CH <sub>2</sub> OH <sup>3)</sup>	F/P molar ratio <sup>4)</sup>
PUA	29.3	1.7	69.0	2.60
PUB	42.2	-	57.8	2.93
PUE	33.8	2.4	63.8	2.42
PUI	35.1	2.7	62.2	2.89
PFU	34.3	2.9	62.9	2.92

- 1) Calculated from the integral representing methylene linkages between 2 phenolic carbons divide by total integral of formaldehyde related peaks.
- 2) Calculated from the integral representing methanol peak at around 50 ppm divided by total integral of formaldehyde related peaks.
- 3) Calculated from the integral representing all methylol carbons divided by total integral of formaldehyde related peaks.
- 4) Calculated from the integral representing all formaldehyde related peaks divided by the integral representing all phenolic carbon related peaks.

Methylolureas were reported to react with phenol or methylolphenol, resulting in copolymerization, to form methylene bridges between phenol and urea. However, in this research the copolymerization through methylene bridges between phenol and urea molecules was not observed and the signal at around 50 ppm observed were all due to methanol. This peak appeared in all resins. Therefore, under the strong alkaline condition used in this research the copolymerization between phenol and urea does not appear to occur. The percentages of methanol carbon were 1.7 to 2.9%.

### 3.2. Methylol groups and methylene ether groups

The methylol group carbons of resins appeared at 60.0–61.7 ppm for *ortho*-methylolphenol and at 64.2–64.8 ppm for *para*-methylolphenol and methylolurea. The *para*-methylolphenol carbon chemical shift values of resins were almost superimposed on those of the methylolurea. The percentages of total methylol groups per total integrals of formaldehyde related peaks are shown in Table 3. The methylol group values ranged between 57.8% and 69.0%.

The methylol groups are reactive groups and change to methylene or methylene ether linkages in resin curing. *Ortho*-methylolphenol groups are more abundant than *para*-methylolphenol groups due to reactivity difference between two reactive groups. In the  $^{13}\text{C}$ -NMR spectra, methylene ether groups were absent as no signals were observed between 69.0 ppm and 95.0 ppm.

### 3.3. Phenolic carbons

Chemical shift assignments of phenolic ring carbons were based on earlier studies [2,3,11]: *meta* unreacted (C3, C5) sites on phenolic ring at 127.2–133.2 ppm, *ortho* unreacted (C2, C6) sites on phenolic ring carbons at 116.4–120.9 ppm, *para* unreacted (C4) sites on phenolic ring carbons at

118.9–127.8 ppm, substituted (C2, C3, C4, C5 and C6) phenolic ring carbons at 117.9–133.2 ppm, *ortho*, *para*substituted (C2, C4) carbons at 128.8–135.5 ppm, and C1 phenolic ring carbons at 156.5–158.7 ppm. All of the above mentioned chemical shifts were found in all resins examined in this study.

### 3.4. Urea carbonyl carbons

The carbonyl signals of urea derivatives occurred at 159.3–165.4 ppm. Unreacted free urea carbonyl carbons occurred at 162.9–165.4 ppm for all resins tested, mono-substituted urea carbonyl carbons occurred at 160.4–163.6 ppm, di-substituted urea carbonyl carbons occurred at 160.0–161.5 ppm, and tri-substituted urea carbonyl carbons occurred at 159.0–159.2 ppm. Mono- and di-substituted urea carbonyl carbons occurred in all resins. Tri-substituted urea carbonyl carbons occurred only in resins PUA and PUB, but tetra-substituted urea carbonyl carbons chemical shift did not occur in all resins. Most urea remained unreacted and only small amounts of mono-, di-, and tri-substituted ureas were observed.

### 3.5. Other species

Formate or formic acid carbonyl carbons, which occurs at 168–173 ppm, were observed in all resins. The absence of free formaldehyde and presence of formate signals indicate that all formaldehyde reacted and some formaldehyde was transformed to formate forms. In resins PUB, PUE, PUI, and PFU small quinonoid signals were seen at 173.8–188 ppm.

## 4. Conclusions

The effects of adding urea to PF resin were investigated to find the optimum procedure of urea incorporation and also to determine if any co-polymerization occurs between urea and phenol. The urea was

added at various points in a typical strand board binder PF resin synthesis procedure. The co-polymerization through the formation of methylene bridges among phenol and urea was not observed in this research. Small differences in gelation time between the resins, ranging from 2.75 min to 3.25 min. Urea-modified PF resins made with earlier urea additions showed lower cure rate values than resins made with later additions. The DMA cure time values of urea-modified PF resins were longer for resins made with earlier urea additions. Triacetin decreased the DMA cure rate values with increasing extents of catalyst level for resins made with later urea additions, but the resins made with early urea additions were not affected very much. The curing rates of early urea added urea-modified PF resins were generally slower than those of later urea added resins. Only an addition of auxiliary catalysts increased the cure rate of early urea added resins to the comparable range of later urea added resins.

## References

1. Kim, M. G., W. L. S. Nieh and R. M. Meacham. Study on the Curing of Phenol-Formaldehyde Resol Resins by Dynamic Mechanical Analysis. *Ind. Eng. Chem. Res.*, **30(4)**, 798 (1991).
2. Kim, M. G. and C. Watt. Effects of Urea Addition to Phenol-Formaldehyde Resin Binders for Oriented Strandboard. *J. of Wood Chemistry and Technology*. **16(1)**, 21 (1996).
3. Kim, M. G., Y. Wu and L. W. Amos. Polymer Structure of Cured Alkaline Phenol-Formaldehyde Resol Resins with Respect to Resin Synthesis Mole Ratio and Oxidative Side Reactions. *J. of Polym. Sci.: Part A: Polymer Chemistry*. **35**, 3275 (1997).
4. Nieh, W. L. S. The Chemical Structure, Molecular Weight and Dynamic Mechanical Properties of Phenol-Formaldehyde Resin. Ph.D. Dissertation, Mississippi State University, Starkville, MS. 63 (1990).
5. Ohyama, M., B. Tomita and C. Y. Hse. Curing Property and Plywood Adhesive Performance of Resol-Type Phenol-Urea-Formaldehyde Cocondensed Resins. *Holzforschung* **49(1)**, 87 (1995).
6. Sellers, T. Jr. Plywood and Adhesive Technology. Marcel Dekker, Inc. New York, NY. 30 (1985)
7. TA Instruments Inc. TA DMA 983 Instructional Manual; DMA Standard Data Analysis Program Operator's Manual. New Castle, DE. (1995).
8. Tomita, B. and C. Y. Hse. 1992. Cocondensation of Urea with Methylolphenols in Acidic Conditions. *J. Polym. Sci.*, **30**, 1615 (1992).
9. Tomita, B. and C. Y. Hse. 1993. Syntheses and Structural Analyses of Cocondensed Resins from Urea and Methylolphenols. *Mokuzai Gakkaishi* **39(11)**, 1276 (1993).
10. Tomita, B., M. Ohyama and C. Y. Hse. Synthesis of Phenol-Urea-Formaldehyde Cocondensed Resins from UF-concentrate and Phenol. *Holzforschung* **48**, 522 (1994).
11. Zhao, C., A. Pizzi and S. Garnier. Fast Advancement and Hardening Acceleration of Low-Condensation Alkaline PF Resins by Esters and Copolymerized Urea. *J. Appl. Polym. Sci.*, **74**, 359 (1999).