

Article

Synthesis and Structure Characterization of Phenol-Urea-Formaldehyde Resins in the Presence of Magnesium Oxide as Catalyst

Dong-Bin Fan, Gai-Yun Li *, Te-Fu Qin and Fu-Xiang Chu *

Research Institute of Wood Industry, Chinese Academy of Forestry, Xiangshan Road, Beijing 100091, China; E-Mails: fandongbin8@163.com (D.-B.F.); qinteful@sina.com (T.-F.Q.)

* Authors to whom correspondence should be addressed;

E-Mails: ligy@caf.ac.cn (G.-Y.L.); chufuxiang@hotmail.com (F.-X.C.);

Tel.: +86-10-6288-9024 (G.-Y.L.); +86-10-6288-9435 (F.-X.C.);

Fax: +86-10-6288-1937 (G.-Y.L.); +86-10-6288-9300 (F.-X.C.).

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Abstract: The objective of this research was to provide a useful approach of polymer synthesis for accelerating the fast cure of phenol-urea-formaldehyde (PUF) resin as wood adhesive by optimizing its structure and composition. The PUF resins containing high contents of very reactive groups such as *para*-methylol groups were synthesized by reacting methylolurea, phenol, and formaldehyde in the presence of magnesium oxide (MgO) as catalyst. The effects of synthesis parameters including F/(P + U), OH/P, and MgO/P mole ratios on the structure, composition, curing characteristics, and their relationships of PUF resins were investigated. The results indicated that MgO seemed to be an efficacious catalyst for PUF resin synthesis and promote its faster cure. The increase in the F/(P + U) mole ratio or/and OH/P mole ratio appeared to be beneficial for the formation of *para*-methylol groups and cocondensed methylene linkages between phenolic methylol groups and urea units, and for the removal of unreacted urea. In case of Catalyst/P mole ratio, an appropriate dosage of added metal-ion was very important for synthesizing the high-content reactive groups of PUF resins, otherwise leading to the reverse effects.

Keywords: phenol-urea-formaldehyde resin; catalyst; synthesis; chemical structure; high-content reactive group; fast cure

1. Introduction

Phenol-formaldehyde (PF) resins are obtained in the reaction of phenol and formaldehyde in aqueous alkaline solutions. This type of resin has a wide range of commercial applications in industrial products such as molding compounds, coatings, flame retardants, and wood adhesives [1]. A well-known method to modify PF resin is the introduction of urea component during or after the resin preparation to synthesize phenol-urea-formaldehyde (PUF) resin, in order to reduce the production cost and accelerated cure process of PF resin [2–7]. In the past several years, many synthetic methods have been developed to prepare low-cost and high-performance PUF resins [5–12]. Resol-type PUF cocondensed resins can be prepared by alkaline treatments of the cocondensed resins once synthesized by reacting phenol with UF concentrate. Urea component addition in PUF resin has lead to additional reactions, additional structures and more complicated compositions. These variations in structures and compositions had profound influences on the cure characteristics of the resins. Although the synthesized PUF resins showed better cure properties especially in cure rate, as well as PF resin the *ortho*-methylol groups of PUF resin took up still the dominant proportion in all methylol groups' contents, which further restricted its cure reaction. Several reports also indicate that part of unreacted urea was still present in the PUF resin, which needed higher activation energy values to crosslink during the cure [9,10]. In general, *para*-methylol groups react more easily with other functional groups at higher rates than *ortho*-methylol groups during the resin cure. So if the proportion of *para*-methylol groups to *ortho*-methylol groups was increased and the residual amount of unreacted urea was reduced, the PUF resin would cure more rapidly in theory. The cure time significantly influences the productivity and cost for the manufacture of resin-based materials. Thus, an increasing cure rate can result in savings for manufacturers. Fraser *et al.* [13] and Huang *et al.* [14] reported that bivalent metal ions such as Mg^{2+} and Zn^{2+} can promote the polymerization of *ortho*-methylol groups to form the methylene linkages by *ortho*-directing effects and result in more *para*-methylol groups leave in PF resin. In 2009, our research found that Mg^{2+} can also accelerate the fast cure of PUF resin [8]. However, detailed studies on synthesis parameters and its influences on chemical structure, composition, and curing characteristics have not been reported in the literature. These are very important for the manufacture of resin-based composite products. Therefore, based on our earlier research [8,15], this study used magnesium oxide (MgO) as catalyst to synthesize PUF resins containing high contents of very reactive groups such as *para*-methylol groups and low residual amounts of unreacted urea, in order to make the resin fast cure by optimizing its structure and composition. The understanding of the chemistry, structure, and composition will give valuable information on reaction mechanism and product application of MgO-catalyzed PUF resins.

In this article, the series of PUF resins were synthesized by reacting methylolurea, phenol, and formaldehyde in the presence of MgO as catalyst. The effects of synthesis parameters including formaldehyde/(phenol + urea) [F/(P + U)] mole ratio, hydroxyl/phenol (OH/P) mole ratio, and catalyst/phenol (MgO/P) mole ratio on the structure, composition, curing characteristics, and their relationships of PUF resins were investigated by both liquid ^{13}C nuclear magnetic resonance (NMR) and cure time test.

2. Experimental Section

2.1. Materials

Phenol (>99%), formaldehyde aqueous solution (37%), sodium hydroxide (98%), and urea (>99%) were commercial products supplied by Beijing Yili Fine Chemical Co., Ltd. (Beijing, China). Magnesium Oxide (>99%) was nanopowder (particle size < 50 nm) was purchased from Aladdin industrial corporation (Los Angeles, CA, USA) and all the chemicals were used directly as raw materials without further purification.

2.2. Resins Synthesis

In this study, 10 PUF resins with a constant urea/phenol (U/P) mole ratio of 0.8 were synthesized in a 500-mL glass reactor fitted with a reflux condenser, a mechanical stirrer, and external heating units, according to our previous two-stage method [8]. Firstly, a mixture of methylolureas was prepared by the following procedure. About 97 g of formaldehyde was charged into a stirred reactor and adjusted at the target pH value between 7.0 and 8.0 with 30% sodium hydroxide solution. After stirring for 5 min, 48 g of urea was gradually added over a period of 10 min. Subsequently, the reaction mixture was heated to 90 °C within 40 min and maintained at this temperature for 30 min. The reaction product was then cooled to room temperature (20 °C) and mixture of methylolureas was obtained, named as MMU.

One of 10 resins (0, Table 1) was a reference with F/(P + U) mole ratio of 1.6 and OH/P mole ratio of 0.40 without addition of catalyst (MgO). Other resins (1–9, Table 1) were synthesized with F/(P + U) mole ratios of 1.4, 1.6, and 1.8 and with OH/P mole ratios of 0.25, 0.40, and 0.55 in the presence of MgO/P mole ratios of 0.02, 0.04, and 0.06, where the labeled PUF2, PUF5, and PUF8 were one resin synthesized at the same condition. Herewith is given the manufacturing procedure for PUF1 resin with F/(P + U) mole ratio of 1.4, OH/P mole ratio of 0.40, and MgO/P mole ratio of 0.04. About 94 g of phenol, 40 g of 40% sodium hydroxide solution, 89 g of formaldehyde, and 1.6 g of Magnesium oxide were charged into a stirred reactor. The reaction mixture was then heated to 70 °C over a period of 15 min and maintained for 20 min. Subsequently, the MMU was added into the reaction system, and the temperature was gradually increased to 90 °C within 15 min and then maintained for 30 min more. About 18 g of formaldehyde and some amount of distilled water were gradually added to the reactor and the reaction was continued at 85 °C until the resin reached a certain viscosity (measured at 25 °C) of 200–300 mPa·s.

2.3. Properties Characterization

The viscosity and pH values were obtained using a rotating viscometer (NDJ-5S, Shanghai Changyi Geological Instruments Co., Ltd., Shanghai, China) and pH meter (PHS-3B, Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) at 25 °C, respectively. The non-volatile solid content of resin was measured by heating about 4 g sample in a small aluminum pan (diameter: 60 mm) in an oven at 120 °C for 2 h. Cure time was measured according to a reported method [10]. This test method described the determination of the cure rate at any specified temperature for a PUF resin. The cure time test was done with about 1.2 g PUF resin sample at 140 °C and was recorded using a stopwatch.

Each value of cure time is an average of five test results. These properties of PUF resins are shown in Table 1.

Table 1. Properties of the control and MgO-catalyzed phenol-urea-formaldehyde (PUF) resins.

Resins	PUF0	PUF1	PUF2	PUF3	PUF4	PUF5	PUF6	PUF7	PUF8	PUF9
Nonvolatile solids (%)	49.1	49.1	49.2	48.7	48.9	49.0	48.6	48.8	48.9	48.5
pH	11.6	11.8	11.5	11.4	10.9	11.5	12.1	11.6	11.5	11.7
Viscosity (mPa·s)	282	276	257	264	268	251	282	274	260	249
Cure time (s)	304	285	266	257	293	266	243	289	266	275

2.4. Liquid ^{13}C -NMR Measurement

The chemical structures of all resins were characterized by high resolution ^{13}C -NMR spectroscopy on Agilent-400 (Santa Clara, CA, USA) spectrometer with a frequency of 100.74 MHz at 25 °C and using an inverse-gated ^1H decoupling technique. All the spectra were recorded with a delay time of 8 s and 8–10 h acquisition time. About 8000–9000 scans were accumulated for each spectrum and the chemical shifts were accurate to 0.1 ppm. All resin samples were directly used for ^{13}C -NMR measurement and residual methanol ($\delta = 50.1$ ppm) contained in the resins was used to reference the chemical shifts. Spectral peaks were integrated with the phenoxy carbon used as integral standard.

3. Results and Discussion

3.1. Chemical Structure

The synthesis of PUF resin is a complicated process that contains many kinds of individual reactions including addition and condensation reactions of phenol, urea, and formaldehyde. The addition reactions occur between phenol and formaldehyde, and urea and formaldehyde, respectively. The main reactions are condensation including self-condensation and co-condensation of methylolphenol, methylolurea, and urea, which contribute to the main structure and the increased polymer chain of PUF resin. These reactions are influenced by synthesis parameters such as mole ratio of reactants, pH value, and preparation methods. Figure 1 shows the condensation reactions of PUF resin.

To clearly identify the complicated relationships on the functional groups and synthesis parameters in the control and MgO-catalyzed PUF resins, ^{13}C -NMR spectrometer was used in this work for analyzing structure information of PUF resins with different synthesis conditions. The ^{13}C -NMR spectra of all PUF resins are presented in Figure 2. The assignments of the most characteristic chemical shifts are listed in Table 2 based on the former studies and literatures [7,8,14–19]. As can be seen, the spectral features of all PUF resin are qualitatively similar to each other. The peaks observed in ^{13}C -NMR spectrum can be divided in three main regions: high-field resonances between 46 and 85 ppm from the aliphatic methylene carbons in a variety of chemical environment, complex region between 116 and 159 ppm due to substituted and unsubstituted phenolic ring carbons, and low-field resonances of 160–164 ppm from urea carbonyl carbons. In the carbonyl signal group, the resonance of unreacted urea was found at the highest frequency of 163.3 ppm. Substitution of amide groups led to chemical shift toward lower frequencies, for example, the peaks at 160.3–162.1 ppm were assigned to

mono-, di-, and tri-substituted ureas. The chemical shifts of 151.6–158.1 ppm with the maximum centered at about 158 ppm were attributed to phenoxy carbons (C1–OH), which displayed an overlapping peak due to the reaction of urea units with phenolic ring. The peaks of *ortho* alkylated phenolic groups (C1) showed lower chemical shift values than the ones alkylated at *para* positions. Substituted aromatic carbons were superimposed in the range of 120–138 ppm, so that exact chemical shifts assignment of every group was also difficult as well as phenolic groups (C1). Relatively strong substituted peaks of all PUF resins confirmed that methylation was advanced, even if unreacted urea still existed in resin. Free *ortho* and *para* carbons, as important sites in the methylation reaction, occurred at 116–119 ppm with relatively minor signals, indicating that the amount of charged formaldehyde was sufficient to react with the majority of unsubstituted position. As expected, the characteristic signals of free formaldehyde and hemiformals were not detected in ^{13}C -NMR spectra for all PUF resins, which were confirmed by the absence of significant resonances in the 80–90 ppm region. This indicated that the charged formaldehyde was successfully transformed to either methylol groups or methylene bridges of PUF resin. Methanol is usually used as a stabilizer present in the Industrial formaldehyde solution. Thus, there was a very sharp peak of methanol appearing at around 49.6 ppm, which was used to reference the chemical shifts of all PUF resins in this work.

The chemical shift at 68.61–70.1 ppm was assigned to linear dimethylene ether linkage from self-condensation of urea units under alkaline condition. As is well known the dimethylene ether is susceptible to hydrolysis, but it can add elasticity to the cured resin and prevent shrinkage, which is why dimethylene ether as an important component is required in foam resins. It was noted that the methylol carbon of $-\text{N}(\text{CH}_2\text{OH})_2$ appeared at almost the same magnetic field as the methylene ether between phenol units (around 72.4–73.5 ppm). However, such resonance in the PUF resin spectrum was exclusively connected to methylol group of urea units. This can be justified by the fact that the condensation of two hydroxymethyl groups to form a dibenzylether bridges can occur near neutral or acid pH values, but it is rare in the alkaline environment used for these studied PUF resins [20]. Another type of methylol group ($-\text{N}(\text{CH}_2-)\text{CH}_2\text{OH}$) was observed in the chemical shifts of 70.8–72.1 ppm. Methylol groups are very important composition and make the polymeric molecules dissolved in the aqueous medium. In the range of 60–66 ppm, two significant peaks of phenolic methylol groups (*o*-Ph-CH₂OH and *p*-Ph-CH₂OH) were found. The most important chemical structure was the co-condensed methylene linkages between phenolic rings and urea units, which determined whether or co-polymerization took place successfully in PUF resin [21]. Methylene linkages were desirable in PUF resins used as wood adhesives because of its very stability to hydrolytic degradation [22]. The chemical shifts of the cocondensed methylene linkages were identified at 46.8–48.2 ppm (*o*-Ph-CH₂-Urea) and 54.7–55.8 ppm (*p*-Ph-CH₂-Urea), respectively, which resulted from two types of co-condensation reactions (Figure 1, Equations I and II). This result confirmed that the co-condensation reaction was indeed present, in agreement with the results from other reports elsewhere [9,23]. It is noted that there was no peak in the 29–42 ppm region, indicating that the self-condensation reaction of phenol methylols did not occur in the synthesis of PUF resin, which belonged to the equation III. This result further proved that urea units can be well converted into co-condensed methylene linkages by using urea replacement by methylolurea as reactant to synthesize PUF resins.

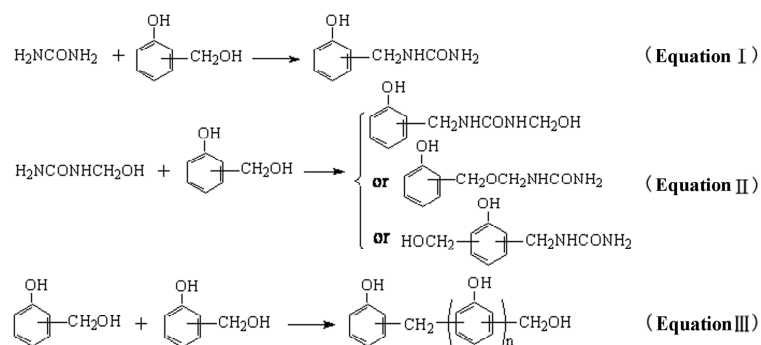
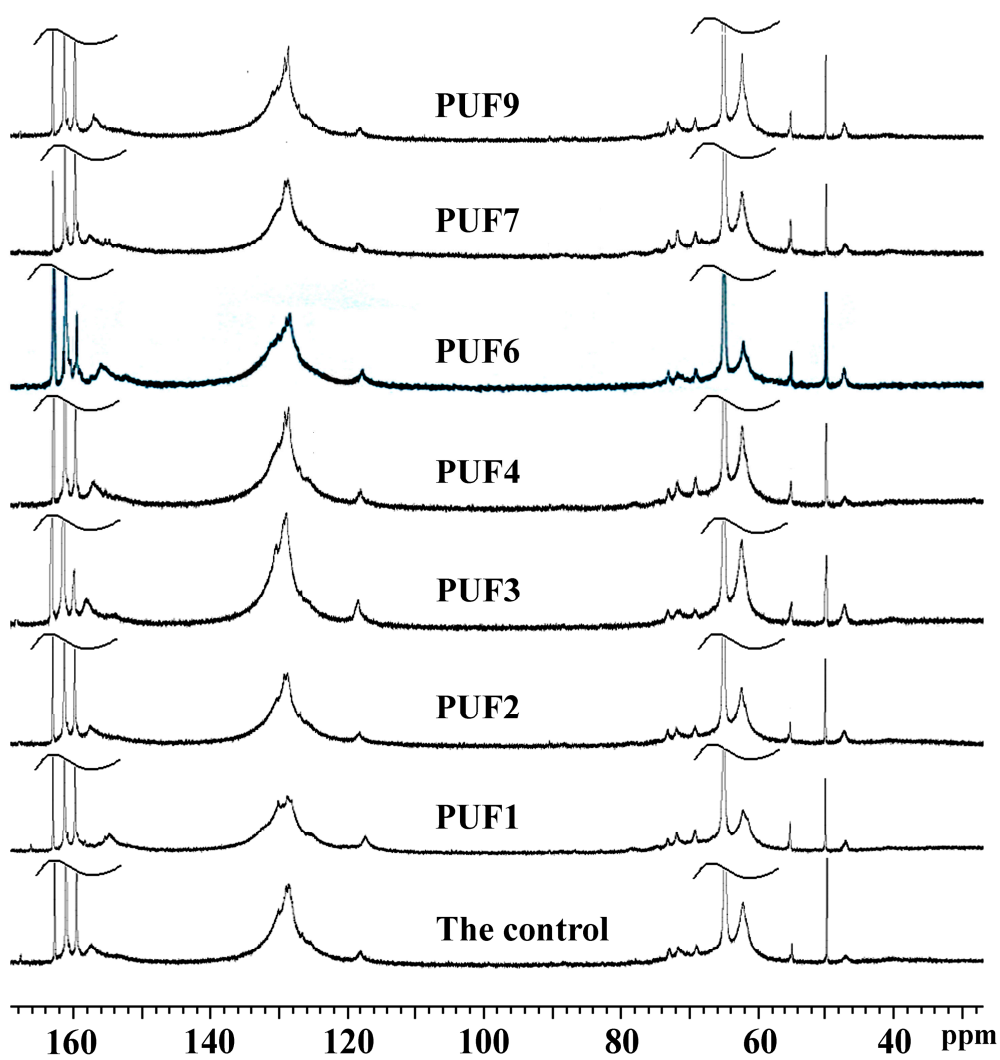
Figure 1. The condensation reactions during the synthesis of PUF resin.**Figure 2.** Liquid ^{13}C -NMR spectrum of PUF resins with different synthesis parameters.

Table 2. Liquid ^{13}C -NMR chemical shifts and group assignments of PUF resins.

Chemical Shifts (ppm)	Assignment of Groups
163.1–163.5	Unreacted urea
159.6–162.8	Mono-, di-, and tri-substituted ureas
152.9–159.1	Phenoxy region
125.6–137.1	Substituted aromatic carbons
116.1–123.5	Free aromatic carbons
80.0–91.0	Reactive formaldehyde adducts
69.7–73.6	Methylol groups of urea units
68.3–69.5	Methylene ether between ures units
63.5–66.3	Phenolic <i>para</i> methylol
60.3–63.0	Phenolic <i>ortho</i> methylol
54.6–55.4	Co-condensed methylene at phenolic <i>para</i> position
49.6	Methanol
46.1–48.2	Co-condensed methylene at phenolic <i>ortho</i> position
39–42	<i>para-para</i> methylene bridges
34–36	<i>ortho-para</i> methylene bridges
29–30	<i>ortho-ortho</i> methylene bridges

3.2. Synthesis

In order to study the effects of synthesis parameters including $\text{F}/(\text{P} + \text{U})$, OH/P and MgO/P mole ratios on the structure and compositions of PUF resins, the phenoxy carbon was used as integral standard. All integration of the function groups are expressed per phenolic unit and the quantitative results obtainable from ^{13}C -NMR spectra are summarized in Table 3. The $\text{F}_0/(\text{P}_0 + \text{U}_0)$ mole ratio calculated from integration values is a measure of the amount of formaldehyde units building into the chemical structure and also a useful check for accuracy of quantitative NMR analysis.

As shown in Table 3, $\text{F}_0/(\text{P}_0 + \text{U}_0)$ ratio were slightly lower than the actual materials charge ratios, which indicated that a satisfactory spectral integration data was obtained from ^{13}C -NMR analysis. In general, the *para* position of phenolic ring has higher reactivity with formaldehyde than the *ortho* position. It was obviously seen from Table 3, however, that more *ortho*-methylol groups were quantified than *para*-methylol groups for the control resin (PUF_0). The reasons were that there were twice as many *ortho* position of phenolic units available than *para* position; *para*-methylol groups reacted more easily with urea units to form methylene bridges, therefore, leading to the *para/ortho* ratio of methylols less than 1. A bivalent metal ion such as Mg^{2+} was reported to be beneficial for increasing the proportion of high-*ortho* linkage in PF resins due to its *ortho*-directing effect [14]. For our preparation methods of PUF resin, only co-condensed methylene between phenolic components and urea units were formed and none of self-condensation methylene of phenolic rings was present in all PUF resins. As a result, *ortho*-directing effect of MgO made more *ortho*-methylol groups react with urea units to form more *o*-Ph-CH₂-Urea linkages, further leading to the increase in *para/ortho* ratio of methylol groups and *ortho/para* ratio of Ph-CH₂-Urea linkages, and the decrease in methylol/methylene ($-\text{CH}_2\text{OH}/-\text{CH}_2-$) when comparing to the control resin. Higher $\text{F}/(\text{P} + \text{U})$ molar ratio accelerated this process. As previously investigated, unreacted urea in PUF resins increased the cure temperature and decreased the crosslinking strength of cured resins [7,15]. When the $\text{F}/(\text{P} + \text{U})$

ratio increased from 1.4 to 1.8 (PUF1, PUF2, and PUF3), more free aromatic groups were substituted and more unreacted urea was translated into substituted urea or co-condensed methylene bridges. Thus, free/substituted hydrogen ($-H/-CH_2OH-$) ratio of aromatic groups and unreacted urea units showed a decreasing and increasing trend, respectively.

Reaction pH has a significant influence on the succession of the addition and condensation reactions. The OH/P mole ratio as well as F/(P + U) mole ratio had a strong influence on the formation of the functional groups. As the OH/P mole ratio increased from 0.25 to 0.55 (shown in Table 3, PUF4, PUF5, and PUF6), both *para/ortho* ratio of methylols and *ortho/para* ratio of Ph-CH₂-Urea linkages gradually increased, whereas both the $-CH_2OH/-CH_2-$ ratio and unreacted urea units showed a significantly decrease. This was because higher alkali content promoted the formation of *o*-Ph-CH₂-Urea linkage mainly from the reaction of *o*-Ph-CH₂OH groups with urea units under the condition of MgO-catalyzed *ortho* effect, while *p*-Ph-CH₂OH groups have low reactivity to further co-condensation. It was also seen from Table 3 that the higher OH/P mole ratio, the higher was the $-H/-CH_2OH-$ ratio. The reason for this was that higher alkali content sped both the addition reaction of aromatic free hydrogen groups and the condensation reaction of methylol groups, however, the latter proceeded at a higher reaction rate in consuming methylol groups than the former; Another possibility might be that as the reaction proceeded, the main reactant, formaldehyde, was gradually consumed and resulted in decrease of the addition reaction rate, while the condensation reactions kept the high reaction rate in consuming methylol groups to form the methylene linkages, thus leading to the increase in the ratio.

Metallic ion concentration is also important parameter for the synthesis of MgO-accelerated PUF resins. The data in Table 3 shows that an increase in Catalyst/P mole ratio of PUF resins leads to the decrease in both the methylol/methylene ($-CH_2OH/-CH_2-$) ratios and the proportions of unreacted urea, and the increase in the $-H/-CH_2OH-$ ratio. Fraser *et al.* showed that the bivalent metallic salts accelerated both the reaction of phenolic nuclei with formaldehyde and the condensation of methylolphenol with other phenolic nuclei by forming the metallic ions/phenols/formaldehyde chelates [24,25]. As suggested by Pizzi, the accelerating reaction ability of bivalent metallic ions was directly proportional to the rate of metal exchange in solution or the instability of these chelates [25]. In case of a lower content of MgO (catalyst/P ratio less than 0.04), some phenol lacked metallic ions to form the chelate rings and made more *ortho*-methylol groups be consumed to form *o*-Ph-CH₂-Urea linkage, so that the ratio values of both *para/ortho* methylols and *ortho/para* Ph-CH₂-Urea linkages were increased with an increasing catalyst/P ratios from 0.02 of PUF7 to 0.04 of PUF8. When the catalyst/P ratio was greater than 0.04, the amount of MgO was relatively excessive and the superfluous metallic ions destroyed the formed chelate rings. Therefore, the increase in catalyst/P ratio (from 0.04 of PUF8 to 0.06 of PUF9) has an inverse effect on both *para/ortho* methylols ratio and *ortho/para* Ph-CH₂-Urea linkages ratio. When the catalyst/P ratio was 0.04, both *para/ortho* methylols ratio and *ortho/para* Ph-CH₂-Urea linkages ratio reach the highest values. These results indicated that the complex chelates formed by the bivalent metal, phenol, and formaldehyde demanded an appropriate range of metal-ion/phenol molar ratios. The results of cure time in Table 1 showed that MgO was remarkably effective in increasing the cure rate of PUF resins as compared to the control resin. Previous reports indicated that unreacted urea in PUF resins had retarded influence on the cure behavior and *para*-methylols of phenolic ring had higher relative reactivity during the resin

curing [10,26]. The cure time gradually decreased when increasing F/(P + U) mole ratio or OH/P mole ratio, which can be interpreted by the change tendency of both *para/ortho* methylols ratio and unreacted urea vs. F/(P + U) mole ratio or OH/P mole ratio (as seen in Table 3).

Table 3. Quantitative ^{13}C -NMR analysis results of PUF resins.

Resin No ^a	Synthesis Parameters				<i>Para/Ortho</i> ($-\text{CH}_2\text{OH}$) ^c	<i>Ortho/Para</i> ($\text{Ph}-\text{CH}_2-$ Urea) ^d	$-\text{CH}_2\text{OH}/-$ CH_2- ^e	$-\text{H}/-$ CHOH_2 ^f	Unreacted Urea
	F/(P + U) Mole Ratio		NaOH/P Mole Ratio	Catalyst/P Mole Ratio					
	Synthesis	Integration ^b							
PUF1	1.4	1.37			0.96	1.17	6.75	0.31	0.47
PUF2	1.6	1.55	0.40	0.04	1.13	1.62	5.42	0.26	0.38
PUF3	1.8	1.70			1.24	1.80	3.31	0.12	0.24
PUF4		1.49	0.25		1.06	1.15	6.55	0.21	0.50
PUF5	1.6	1.55	0.40	0.04	1.13	1.62	5.42	0.26	0.38
PUF6		1.58	0.55		1.28	1.68	3.17	0.33	0.33
PUF7		1.52		0.02	1.09	1.26	6.68	0.19	0.54
PUF8	1.6	1.55	0.40	0.04	1.13	1.62	5.42	0.26	0.38
PUF9		1.57		0.06	1.05	1.57	3.59	0.28	0.42
PUF0 (Control)	1.6	1.54	0.40	-	0.92	1.06	6.86	0.16	0.59

^a The PUF2, PUF5, and PUF8 resins are the same one; ^b (methylol groups + methylene + 2dimethylene ether)/phenolic carbons; ^c Ratio of methylol groups at *para* position to *ortho* position; ^d Ratio of co-condensed methylene linkages at *ortho* position to *para* position; ^e Ratio of methylol groups to methylene linkages; ^f Ratio of free aromatic hydrogen to methylol groups.

In conclusion, MgO as a catalyst was capable of increasing cure rate and *para*-methylols proportion of PUF resin, and decreasing the residual amounts of unreacted urea.

4. Conclusions

The MgO as catalyst seemed to enhance the formation of *para*-methylol groups and $\text{Ph}-\text{CH}_2$ -Urea linkages of PUF resins, and also capable of decreasing obviously the residual amounts of unreacted urea, eventually making the resins cure fast. Some synthesis parameters such as F/(P + U), OH/P, and MgO/P mole ratios showed significant effects on the proportion of specific function groups of PUF resins, despite for they possessing the similar chemical structure. When the F/(P + U) ratio increased from 1.4 to 1.8, more *ortho*-methylol groups reacted with urea units to form more *o*- $\text{Ph}-\text{CH}_2$ -Urea linkages, more free aromatic groups was substituted, and more unreacted urea was translated into co-condensed methylene bridges, thus leading to the change of different groups contents. As the OH/P mole ratio increased, both *para/ortho* ratio of methylols and *ortho/para* ratio of $\text{Ph}-\text{CH}_2$ -Urea linkages gradually increased, whereas both the $-\text{CH}_2\text{OH}/-\text{CH}_2-$ ratio and unreacted urea units showed a significantly decreasing tendency. The increase in Catalyst/P mole ratio of PUF resins from 0.02 to 0.06, led to the decrease in both the $-\text{CH}_2\text{OH}/-\text{CH}_2-$ ratios and the proportions of unreacted urea, and the increase in the $-\text{H}/-\text{CH}_2\text{OH}-$ ratio, respectively. In case of *para/ortho* methylols ratio and *ortho/para* ratio of $\text{Ph}-\text{CH}_2$ -Urea linkage, these ratios reached the highest values when the

catalyst/P ratio was 0.04, which indicated that the formation of beneficial chemical compositions in MgO-catalyzed PUF resins demanded an appropriate amount of metal ion.

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Author Contributions

Dong-Bin Fan contributed to the analysis of the test data and writing of the paper. Te-Fu Qin was in charge of the production of the specimens and carried out the tests. Gai-Yun Li and Fu-Xiang Chu coordinated the study, made the literature survey, interpreted the test results and performed analysis of the test data.

Conflicts of Interest

The authors declare no conflict of interest.

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