Study of the Structural Changes in Urea-Formaldehyde Condensates During Synthesis

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SUMMARY: Chemical constitution of urea-formaldehyde resins in synthesis and in storage was determined using ^{13}C NMR spectroscopy. Methylolation, methylene and dimethylene ether bond-forming reactions were discussed. The changes in the content of structural elements with secondary and tertiary amino groups of urea at various stages were followed. The resin synthesis technology was used, which considers the requirement in low free formaldehyde content, connected with somewhat smaller storage stability of resins.

Introduction

Urea-formaldehyde (UF) resins are the most important type of adhesive resins for the production of wood composites. When particleboards were first manufactured, resins of formaldehyde/urea (F/U) molar ratio 1.8/1 to 1.6/1 were used as binders. Nowadays, clean indoor air requirement has promoted the development resins with F/U ratios between 1.2/1 and 1.05/1, or even less. Decreasing the F/U molar ratio is an efficient method of reducing F emission from wood-polymer composites. However, it results in the decrease of the reactivity of UF resins and bond strength of particleboards due to lower degree of crosslinking. These resins are characterized by higher sensitivity to synthesis process parameters and lower storage stability.

Great success in the chemistry of UF resins was achieved by the use of ^{13}C NMR spectroscopy for the determination of various structural units [1,2]. Quantitative studies gave the extent of branched structures [3] and molar contents of structural elements at various stages in the synthesis, using different F/U molar ratios [4]. In the last case, the essential increase of

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methylene amount after second urea addition at pH 7.5 was explained by analytical faults. ^{13}C CP/MAS NMR study of F/U reaction clearly showed that high pH (about 12) directs the condensation very selectively to the formation of secondary dimethylene ethers of urea [5]. At the same time, it was proposed [6] to reduce the polycondensation stage pH to 4 for the preferred formation of methylene linkages in comparison with dimethylene ethers not considering their formation already in methylolation step. Three different procedures for UF resins synthesis were thouroughly investigated [7,8]. The most used technology with the methylolation stage at pH 8-8.5 seems not to be the best, as the content of dimethylene ethers is twice as large as compared to that of direct acidic condensation at pH 4.5-5. It should be the main reason of lower F emission from particleboards bonded with these resins. At the same time, starting the reaction under acidic conditions gives insoluble cyclic methylene linked ureas [9]. The increase in molar mass of resin during polycondensation was monitored by gel permeation chromatography.

Under strong acidic conditions (pH 1) the high content of tertiary urea and especially of uron derivatives leads to great disproportion of methylene linkages with tertiary amino groups in the structure. In spite of low F emission, the strong acid catalyzed resin cannot form highly developed network in curing [8]. The wellknown two-step technology (pH 8.5 and pH 5.2) was modified by the stepwise urea addition after acid condensation [10]. No changes in internal bond strength of particleboards were obtained, but the F emission decreased about 30%. Correlations between the mentioned characteristics and ^{13}C NMR peak ratios for resins appear to have some practical value. In addition, the method allows to reduce the F/U ratio in resin to 0.96 at the same level of internal bond strength of particleboards [11]. The F emission depends on the hydrolytic stability of cured resin and first of all are attacked unstable dimethylene ether groups. It was shown that quite a small change in acidity of cured resin due to catalyst type causes the remarkable difference in released F amount [12]. The comparison of UF resins of various producers (17 examples) showed that at the quite constant level of methylol content (39-45%) the F emission (6-14 mg/100 g) is highly dependent on dimethylene ether and methylene content of resins (14-27 and 18-36 molar % of F, accordingly) [13].

The main objective of this work was the ^{13}C NMR study of the chemical structure of UF resins during industrial batch-wise synthesis and of the storage stability of resins obtained by this technology.

Experimental

Commercial formalin containing 37% formaldehyde and 5 or 7% methanol, and urea of industrial quality were used as starting materials. Two-step technology of synthesis was used including alkaline methylolation followed by acid condensation. 25% NaOH and formic acid were used as catalysts. After condensation with additional urea and vacuum treatment, the final UF resins with solids content of 67-68% and viscosity of 400-500 mPa·s were obtained. The samples from three resins in different stages of synthesis were taken for ^{13}C NMR analysis. Four commercial resin examples were used for storage stability study.

^{13}C NMR spectra were obtained on a Bruker AMX500 NMR spectrometer with ^{13}C frequency at 125.77 MHz at 25°C from DMSO-d_6 solutions by 5 mm ^{13}C-^{1}H dual probehead. Spectra were accumulated into 32K data points and processed using exponential multiplication with 2 Hz line broadening into 128K spectra. About 10000 scans were accumulated for the resulting spectra. Chemical shifts in tables 1 to 3 are grouped to the wellknown assigned absorbtion bands [2,13]. In many cases additional fine sructure in these bands is observed at 125.77 MHz (Fig.1). As the aim of present study was the measurement of changes within individual functionalities, all spectra were accumulated at identical conditions using power gated Waltz decoupling with 25 degree measurement pulse and 1 sec prepulse delay. Used method results in much higher S/N ratio as compared with the gated decoupling method with unavoidable long delays without proton decoupling to avoid NOE buildup. Quantitative information on changes of different structural elements was obtained by the manual integration routine of XWINNMR 2.1 software.

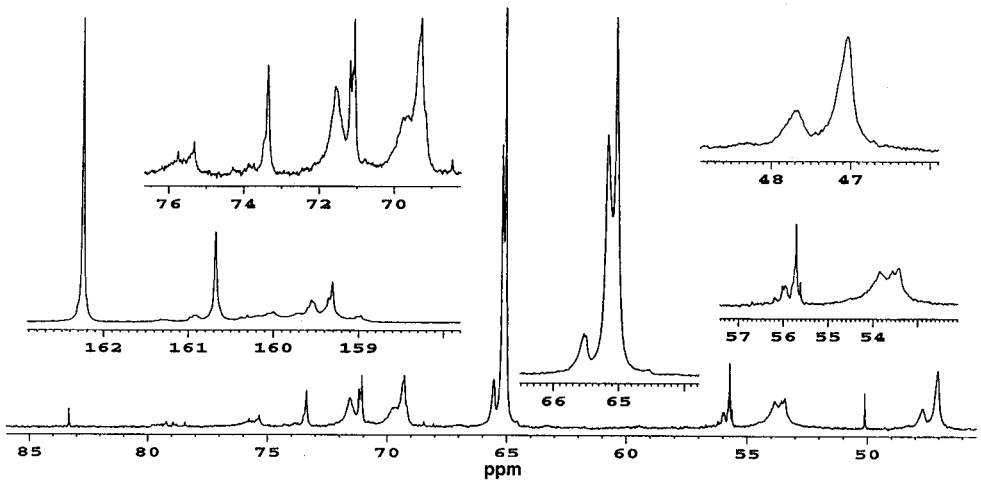

Fig.1: A typical ^{13}C NMR spectrum of low F/U molar ratio resin in DMSO-d_6, 12000 scans.

Results and discussion

In ideal the methylolation step in urea-formaldehyde reaction with F/U = 2/1 should result in the quantitative formation of 1,3-dimethylolurea (DMU). However, various competitive reactions lead to complicated reaction mixture (Table 1).

By the heating from 25 to 85°C the equilibrium is reached and additional heating at 85-90°C causes no changes in the composition of reaction product. Otherwise, the final value of pH is important. The amount of unlinked F remains at the same level. At the same time, the maximum amount of methylols (67.5% of total F) is obtained at final pH 7.0. The decrease of pH to 6.7 to the end of this step causes the additional condensation, resulting in methylols content not more than 60%. The alkaline condensation is not desirable as it proceeds mainly by ether formation mechanism. From the amounts of combined F (84%) and tertiary amino groups (11-16%) the calculated part of unreacted amino groups makes up about 26% (22-32%). As tertiary amino groups are not included essentially in the condensated structures (< 2.5%), the 1,1- dimethylol derivatives of urea are the remarkable constituents in the product of methylolation stage (6-11%). Carbonyl carbon region (159-163 ppm) of NMR spectra (Fig.2) reveals that the amount of unreacted urea is not more than 1-2% from its initial amount and free amino groups are included mainly in monosubstituted urea derivatives at 161 ppm (28-31%).

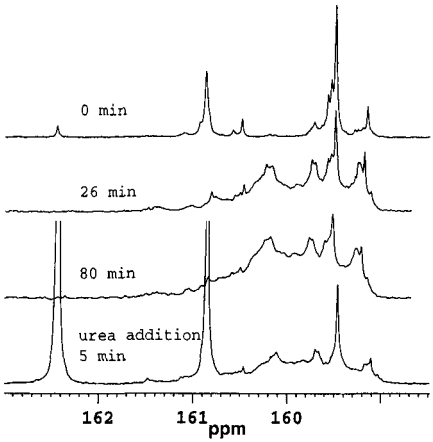

Fig. 2: Changes in carbonyl region during synthesis.

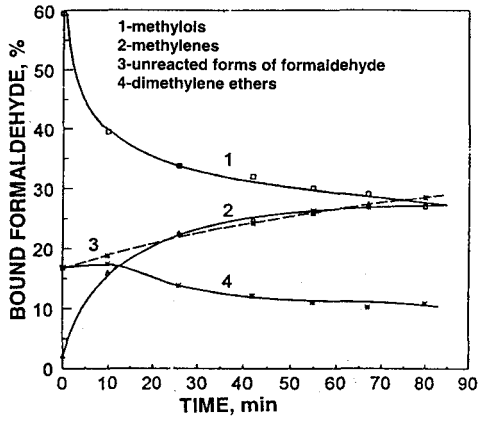

Fig. 3: Changes in the content of structural elements during acidic condensation.

Acid condensation step initiated by the addition of formic acid resulted in constant rise of temperature (5°C) in different resin synthesis reactions. The pH was held at the same level

(about 4.6). The condensation to the same degree of conversion took significantly different time (after acid addition from 20 to 70 min). The evident difference of the slowest synthesis (Table 2, Fig.3) from others studied is in the content of methanol in formaldehyde solution used. The increase in methanol content to 7% in this case in comparison with 5% in other studied syntheses gives the remarkable decrease in condensation rate.

The following features of condensation step were noted:

– An extremely rapid decrease in content of –NH–CH_2OH methylols at 65 ppm (Table 2). Main condensation of methylols occurs immediately on the addition of acid. During the condensation step the content of >N–CH_2OH groups at 72 ppm remains constant. Simultaneous increase in intensity of signals from the methylene groups at 54 ppm refers to the formation of structural elements with tertiary amino groups predominantly with methylol and methylene substituents. Several routes for this condensation are possible. The reaction of one methylol in 1,1-dimethylol derivative with free amino group appears to be one of possibilities. Another one includes the reaction between two methylol derivatives by the mechanism of repeated substitution in amino group. And finally, the methylene derivative with secondary amino groups at 47 ppm can be itself methylolated.

– Two-fold amount of F in comparison with that for linear polycondensate leads to the structural elements with tertiary amino groups. At the same time, the content of methylene groups between two tertiary amino groups around 60 ppm remains quite low during condensation in spite of great free F level in the mixture. It is not very clear whether the methylolation hindrances or polycondensate structure peculiarities are responsible for this phenomenon.

– In the early stage of condensation to some extent occurs the reaction between methylol and one of secondary amino groups of dimethylene ether linkage (69 ppm), giving the ether derivative with different substitution pattern (76 ppm). The formation of ethers in addition to that of methylolation stage is not probable. The slow decrease in ethers occurs with the release of F (Table 2), but not less than a half of them remain in the resin after the condensation step. Rapid formation of methanol ethers occurs during the acidification process. In the further stage they are quite stable and the release of methanol can only occur from the hydrolysis in the particleboards.

– The changes in carbonyl region of NMR spectra cannot be quantitatively interpretated. Main reason for this is very strong overlap of signals from different environments (Fig.2). The condensation causes the decrease of ^{13}C signals intensities of carbonyls of methylol ureas (161 and 159 ppm). Advancing of condensation leads to complicated structures with different substitution models. It is evident from the relative increase of signals in the region of 159-161 ppm due to continuing growth in substitution extent in urea amino groups.

Table 1. Average values of bound formaldehyde distribution (in %) from different syntheses

Reaction stages	$-CH_2-$			$-CH_2OH$		$-CH_2-O-CH_2-$		$-CH_2OCH_3$		$-OCH_2O-$
	47 ppm	54 ppm	60 ppm	65 ppm	72 ppm	69 ppm	76 ppm	73 ppm	80 ppm	83–95 ppm
Methylolation	1–2.7	0–1.0	–	45.8–56.4	8.8–13.7	12.1–16.7	0.9–1.9	2.5–4.5	0–0.2	14.6–16.7
Acidic condensation	7.8–9.0	17.1–19.8	2.2–3.5	13.0–16.2	14.0–16.5	6.0–6.5	3.5–4.4	3.2–3.9	2.1–3.0	19.1–28.5
Second urea condensation	9.2–11.8	17.4–19.4	2.0–2.6	37.3–37.9	12.4–13.1	5.0–6.1	1.9–3.0	3.5–4.7	2.1–3.8	2.4–3.4
Vacuum treatment	12.2–12.6	18.3–18.5	1.4–2.0	40.0–41.7	9.4–10.5	5.9–6.2	1.9–2.4	3.8–5.2	2.0–2.6	1.2–2.2

Table 2. Changes in bound formaldehyde distribution (in %) during acidic condensation stage

		$-CH_2-$			$-CH_2OH$		$-CH_2-O-CH_2-$		$-CH_2OCH_3$		$-OCH_2O-$
No.	Time	47 ppm	54 ppm	60 ppm	65 ppm	72 ppm	69 ppm	76 ppm	73 ppm	80 ppm	83–95 ppm
1	0	1.6	0.6	–	45.8	13.7	15.0	1.9	4.5	0.2	16.7
2	10 min	6.5	8.9	0.6	24.4	15.1	12.5	4.9	6.3	2.1	18.8
3	26 min	7.3	13.6	1.6	18.0	15.7	8.8	5.0	4.8	3.0	22.2
4	42 min	7.4	15.7	1.7	16.0	15.9	7.5	4.5	4.3	2.9	24.1
5	55 min	7.5	16.4	2.0	14.7	15.3	6.6	4.4	4.0	2.9	26.2
6	67 min	7.7	17.6	2.1	14.1	15.0	6.2	4.0	3.7	2.8	26.8
7	80 min	7.8	17.1	2.2	13.0	14.0	6.4	4.4	3.6	3.0	28.5

Condensation with the additional urea and subsequent vacuum treatment after alkali addition do not give any essential changes in resin structural units (Table 1). The great excess of urea predominantly causes its monomethylolation reaction. This is confirmed by the increased methylol signal at 65 ppm with the simultaneous appearance of carbonyl signal of mono-substituted urea at 161 ppm. The intensity increase of both these bands can be estimated to about 25%. Following condensation of monomethylolurea with free urea, which should be reflected in the increase of methylene intensity at 47 ppm (–NH–CH_2–NH–) is of slight importance. Due to methylol deficiency with respect to amino groups no ether increase at 69 ppm is observed.

Storage stability

Lower stability of modern UF resins is an inevitable phenomenon in obtaining environment friendly products. Two-fold viscosity rise during 45-60 days limits the real shelf life to one month. The following changes in the content of main structural elements can be mentioned (Table 3) during the storage:

Table 3. Changes in the relative content (in %) of structural elements of UF resins during storage

Assignment	ppm	Storage time, months										
		Resin A				Resin B			Resin C		Resin D	
		0	1	2	3	0	4	6	0	2	0	1
Methylenes	47	13	15	20	21	16	20	22	16	24	15	18
	54	18	16	17	17	18	16	17	16	19	18	16
	60	2	2	2	2	–	–	2	2	2	2	2
Methylols	65	40	39	35	35	43	38	35	38	26	41	37
	72	10	8	4	4	6	3	3	9	5	7	6
Dimethylene ethers	69	6	7	10	10	7	10	10	8	10	7	9
	76	2	3	2	2	2	1	2	3	3	2	3
Methylene methyl	73	5	5	6	5	5	6	6	5	6	4	4
ethers	80	3	3	2	3	2	3	2	3	3	2	3
Methylene glycols	83–95	1	2	2	1	1	3	1	2	2	2	2
Carbonyl region												
a) Free urea	163	32	29	19	18	28	20	17	27	18	28	22
b) Monosubstituted	161–162	27	32	38	39	33	41	40	32	39	32	37
c) Disubstituted	159–161	40	38	42	42	39	39	42	40	42	39	40
d) Cyclic ureas	155–158	1	1	1	1	–	–	< 1	< 1	< 1	1	1

– Continuous decrease in methylol content (signals at 65 and 72 ppm).

– Increase in the content of –NH–CH_2–NH– methylene units due to the reaction between methylol urea and free urea.

– The different molar ratio of F/U in final resin as compared to that of acid condensation promotes the increase of ratio of secondary and tertiary amino groups of urea.

– The changes in carbonyl region show the continous decrease in content of free urea at 163 ppm and the increase of monosubstituted urea at 161 – 162 ppm.

– The signal intensity rise at 69 ppm refers to the slight condensation by the undesired ether formation mechanism.

Conclusions

Despite the undesired dimethylene ether bridged urea formation under alkaline conditions, the synthesis of UF resins without methylolation step can not be regarded as an effective practical technology. The maximum amount of methylols can be obtained at pH values not under 7 in this stage. Acid condensation leads to great percentage of structural elements with tertiary amino groups of urea. At the same time, the content of methylenes in >N–CH_2–N< units is quite low. The additional formation of dimethylene ethers during acid condensation is not very probable. The release of F from ethers is quite slow, and about a half of ethers remains in resin after acid condensation. The monomethylolation of urea is the main reaction responsible for the decrease of F content in the next alkaline step of condensation and vacuum treatment. The great content of methylols is the reason of low storage stability of resin. Their condensation with amino groups of free urea is the main reaction in storing.

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