

Structural changes in urea-formaldehyde resins during storage

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The changes in structure of fresh and stored commercial UF resins were characterised by high resolution ^{13}C NMR spectroscopy. The three-step synthesis produces the resin consisting of two parts: the polymeric part from condensation of formaldehyde with first amount of urea, and monomeric part formed after addition of second part of urea. Some differences in structure depending on details of synthesis are of temporary character and level mainly in transhydroxymethylation from polymeric to monomeric part of resin. The reactions occurring after addition of second urea and following during storage are considered as one continuous process. Methylenes adjacent to secondary and tertiary amino groups form only during acid condensation. The main reaction during storage is the formation of methylenes adjacent to secondary amino groups. This reaction occurs between free terminal hydroxymethyl and amino groups of both resin parts. The physical and mechanical properties of particleboards confirm the close performance characteristics of studied resins. Particleboards satisfy requirements for general purpose boards P2 and emission standard E1.

Die Strukturänderung bei der Alterung der Harnstoff-Formaldehydharze

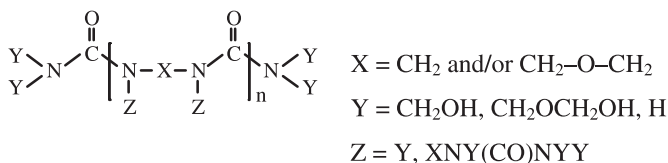
Die in den frischen und veralteten UF Handelsharzen stattfindenden Strukturänderungen sind vermittels des ^{13}C NMR Spektroskopie von hohen Auflösung gekennzeichnet. Die dreistufige Synthese liefert ein aus zwei Teile bestehendes Harz: ein polymerer Teil, der bei der Kondensation des Formaldehydes mit der ersten Portion des Harnstoffes entsteht, und ein monomerer Teil, der bei der Zugabe der zweiten Portion von Harnstoff sich bildet. Die einzelnen Unterschiede in den Struktur, die von den Synthesedetails abhängen, sind zeitweilig und nivellieren hauptsächlich im Lauf der Transhydroxymethylierung aus dem polymeren in den monomeren Teil. Man kann die Reaktionen, die nach der zweiten Zugabe von Harnstoff und nachfolgen-

den Alterung statt finden, als einen einheitlichen Prozeß betrachten. Die Methylenes, die an die sekundären und tertiären Aminogruppen gebunden sind, entstehen nur bei der sauren Kondensation. Die wesentliche Reaktion bei der Alterung ist die Bildung von Methylenbrücken zwischen den sekundären Aminogruppen. Diese Reaktion findet statt zwischen den freien Hydroxymethyl- und Aminogruppen in den beiden Teilen des Harzes. Die physikalischen und mechanischen Eigenschaften der Spanplatten bestätigen den ähnlichen Charakter der Umwandlung der zu untersuchenden Harze. Die Spanplatten werden Anforderungen gerecht, die an die P2-Platten und E1 Emissionsstandard gestellt sind.

1 Introduction

Urea-formaldehyde (UF) resins are the most important type of binders for the production of particleboards and other wood-based panels. Despite the fact that UF resins consist of only two main components, the broad variety of possible reactions in synthesis, storage and curing continues to make this object a needful area for research and development (Dunky 1998). The lability of aminomethylene linkage is an inherent feature of this polycondensate, causing the subsequent formaldehyde (F) emission and low resistance of hardened resins against hydrolysis. The structures in oligomer formation during synthesis can be modified with technological means, however the final performance characteristics of modern resins remain low because of insufficient crosslinking. At the same time, the earlier problem of F emission can now be regarded as solved. Most of producers have stopped on the final F/U ratio between 1.03–1.08/1, compromising between the strength and emission requirements. By the different approach (Pizzi 1994), there are additional possibilities to reduce this ratio to 0.96/1 by changing the F distribution in the synthesis between polymeric and monomeric part (free urea, hydroxymethylureas, methylenediurea).

The structure of polymeric part can be visualised by the next formula:



Great success in the analysis of UF resins was attained by use of ^{13}C NMR spectroscopy (Tomita 1978, Kim 1990).

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This method has been regarded by many researchers as the best for quantitative determination of structural groups in UF resins at various stages of synthesis and curing. Relative content of hydroxymethyl, methylene and dimethylene ether groups, and the ratio of branched and linear structural units can be determined.

A three-step procedure is used to obtain the desired structure of UF resins:

- Hydroxymethylation step in aqueous alkaline solution ($F/U \sim 2$) produces the mixture of mono-, di- and tri-hydroxymethylureas ($-NH-CH_2OH$ 45–60%, $-N(CH_2OH)_2$ 10–15%) with the partial polycondensation to dimethylene ethers (15–20%), leaving 10–15% of unreacted F (Kim 1990, Siimer 1999);
- In acid condensation step, because of great saturation with hydroxymethyl groups, prevailing formation of methylenes of type $-N(CH_2OH)CH_2-NH-$ occurs ($\sim 20\%$), formation of $-NH-CH_2-NH-$ is limited ($< 10\%$). Due to trifunctionality of urea in this reaction, the probability of formation of $>N-CH_2-N<$ units is low ($< 5\%$). Some of F liberates from dimethylene ethers and by dehydroxymethylation (Siimer 1999), raising the amount of free F to 15–25%;
- In the third step, after reestablishment weak alkaline conditions, subsequent reactions with secondary added urea are responsible for the formation of monomeric part of resin. The reaction between free F and excess of urea should produce mainly monohydroxymethylurea (MMU). Uneven distribution of hydroxymethyl groups between first and second added ureas promotes dehydroxymethylation, displacing hydroxymethyl groups ($\sim 5\%$) to monomeric part (Kim 1999).

The storage stability of UF resins as well as the performance characteristics (including degradation) arise from the processes starting with the addition of second amount of urea. The reaction of free F with urea is very fast and the structure of product cannot essentially be changed with the conditions for these process (Kim 2000). Only the extent of the reaction may be different, depending on the content of F after the condensation step. Useful information has been obtained by following the reactions occurring in the product in case of temperature treatment at 40–70 °C and at room temperature after quick cooling (Kim 2000). In both cases, the extensive migration of hydroxymethyls bonded to tertiary amino groups of resin proceeds; these groups can be chain end-groups or side-groups. The increase in content of hydroxymethyls of type $-NH-CH_2OH$ and methylenes of type $-NH-CH_2-NH-$ is caused by transhydroxymethylation from polymeric to monomeric part. Different from heating at higher temperatures, the replacement of hydroxymethyls stops in the later room-temperature storage period, giving way to condensation in monomeric part between MMU and free urea. This change in the structure of product is reflected in the decrease of content of $-NH-CH_2OH$ by the equivalent increase of $-NH-CH_2-NH-$ units. In the carbonyl carbon region of ^{13}C NMR spectrum, free urea signal decreases and carbonyls from the monosubstituted urea appear. That type methylene formation in weak alkaline conditions can also be followed by 1H NMR (Suurpere 1999).

This change reflects in the decrease of signal intensity for primary amino groups of free urea at the constant level of signal intensity for monosubstituted urea.

The comparison of different data (Siimer 1999, Kim 2000, Root 2000) shows that the properties of UF resins depend dramatically on chemical reactions which proceed after second urea addition. Cooling conditions can cause the changes in the amount of different structural groups. No essential decrease in content of hydroxymethyl groups occurs before the end of synthesis (Siimer 1999). Transhydroxymethylation is the only source in changing the ratio of two types of hydroxymethyls in favour of $-NH-CH_2OH$, belonging mainly to MMU and less to chain end-groups. In aged, as compared with fresh resin, the content of hydroxymethyl groups and free urea is much lower (Root 2000, Siimer 1999). Main reaction should be the condensation to methylenediurea (MDU), as the increase in the content of $-NH-CH_2-NH-$ quite accurately agrees with the other changes in contents of structural elements. The number of chain end hydroxymethyl groups is significant because of good correlation with curing rate of resin (Root 2000). The other important change is the decrease in content of hydroxymethyls of type $>N-CH_2OH$ (Root 2000, Siimer 1999). Considering the constant level of methylenes $-NH-CH_2-N<$, the main model of this change should be transhydroxymethylation.

In this study, commercial UF resins of particleboard binder type, synthesised by quite different technologies, were chosen as the object for investigation of their storage and performance behaviour. The changes in structure of fresh and stored resins were characterised by high resolution ^{13}C NMR spectroscopy. The process of ageing of resins is discussed in dependence on treatment with second urea in synthesis. The standard mechanical properties and content of free F were determined for particleboards manufactured with resins studied.

2 Experimental

2.1 Technical characteristics of resins

For detailed study, three commercial urea–formaldehyde resins from different producers were selected, labelled as UF1, UF2 and UF3. The modern resins in the present investigation are synthesised with low F to urea ratio (1.03–1.08/1) and contain small amounts of free F (0.1–0.15%). A typical three-step procedure was used in case of all syntheses. In the synthesis of UF1 and UF3, 37% F aqueous solution with 6.5% of methanol content, and in case of UF2 methanol-free F solution of higher concentration was used. The synthesis of UF3 occurred with the same final F/U ratio as the synthesis of UF1, but this ratio was achieved by gradual addition of urea in smaller portions. In Table 1, the standard analysis of resins is presented. Dynamic viscosity was measured by rotational viscometer. It appears that viscosity of resins is different at a close solid content and does not correlate with the gelation time of catalysed (1% NH_4Cl) resins at 100 °C, indicating a more complicated relation between resin structure and curing

Table 1. Standard characteristics of commercial UF resins
Tabelle 1. Standardgemäße Charakteristiken der kommerziellen UF Harze

Characteristics	UF1	UF2	UF3
Dry solids 105°C, 3 hours, %	68.7	69.0	67.8
pH, 25°C	8.2	8.1	8.5
Viscosity 25°C, mPa·s	288	383	487
Density 20°C, g/cm ³	1.275	1.295	1.273
Gel time 100°C, s	56	51	66
Free formaldehyde, %	0.13	0.1	0.15

behaviour. The initial viscosity determine the rate of slow structuration of resins during storage at 25 °C. The final gelation of UF1, UF2 and UF3 occurs during 53, 39, and 27 days according to their initial viscosities.

2.2 ¹³C NMR spectroscopy

¹³C NMR spectra were obtained on a Bruker AMX500 NMR spectrometer with ¹³C frequency at 125.77 MHz at 25 °C from DMSO-d₆ solutions by 5 mm ¹³C -¹H dual probehead. Spectra were accumulated into 32 K data points and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. 25000–35000 scans were accumulated for the resulting spectra. All spectra were accumulated at identical conditions using power gated Waltz decoupling with 25 degree measurement pulse and 1 s prepulse delay. Quantitative information on changes of different structural elements was obtained by the manual integration routine of XWINNMR 2.1 software. ¹³C NMR spectra were recorded from fresh resins (1–2 days after manufacturing) and aged resins up to 20, 40 and 60 days. Some spectra have been registered for gelatinised state of resins in DMSO-d₆ solution. On the basis of integral intensities in ¹³C NMR spectra, the

distribution of bound F between different chemical groups in the region of 40–100 ppm was determined (Table 2). Carbonyl region from UF resins (150–165 ppm) gives the possibility to calculate the content of free urea, mono- and di(tri)substituted urea. The changes in carbonyl region of ¹³C NMR spectra for the UF1 of different age are shown in Fig. 1.

2.3 Manufacturing and testing particleboards

Three selected resins were used at Pärnu Plaaditehas AS in current particleboard manufacturing. Wooden raw material consisted mainly of sawdust and cutter chips (pine, spruce). Three-layer particleboards of 9700×2650 mm dimensions were manufactured at 210 °C from resinated particles after pneumatic spreading. Hot-pressing rate was 8.0–9.5 s/mm. Depending on the density of the particleboards, the pressures of 210 bar (<700 kg/m³) and 230 bar (>700 kg/m³) were used. Particleboards of thicknesses in the range of 6–28 mm at Pärnu Plaaditehas AS are produced. In the present work, the thicknesses of 11, 18 and 22 mm for general-purpose boards P2 were selected. Physico-mechanical parameters were determined according to DIN 68763, formaldehyde emission was measured by the perforation method (EN 120). General-purpose boards should correspond to the requirements of EN 312–2 for use in dry conditions, and the content of free F to the requirements of emission class E1. If necessary, to fulfil the E1 requirements, urea (40% solution) as scavenger was added to adhesive mixture up to 4% of dry resin, as usual to core layer. Consumption of paraffin wax as hydrofobic agent was 0.4% of dry wood. The amount of hardener NH₄Cl (25% solution) on the average 2% of dry resin was used. In Table 3, physical and mechanical properties of particleboards made with UF1, UF2 and UF3 resins are presented.

Table 2. Changes in the relative content (in %) of structural elements of UF resins during storage at 25°C
Tabelle 2. Die Änderung in dem relativen Gehalt (in %) der Strukturelemente in den UF Harzen während der Aufbewahrung bei 25°C

Assignment	ppm	Storage time, days											
		UF1				UF2				UF3			
		0	20	40	60	0	20	40	60	0	20	40	60
–HNCH ₂ NH–	47–48	16.3	26.2	32.1	34.2	21.0	24.8	30.5	32.7	18.1	25.3	30.3	36.8
–HNCH ₂ N(CH ₂ –)	53–54	18.4	19.3	20.6	20.2	16.8	16.9	15.7	17.7	22.3	21.5	21.2	20.6
–HNCH ₂ OH	65–66	41.3	32.3	25.1	23.3	43.4	38.9	33.7	29.0	39.0	32.1	25.8	22.9
–N(CH ₂ –)CH ₂ O } > N(CH ₂ OH) ₂ }	71–72	9.0	6.9	5.0	4.6	5.0	3.6	3.3	3.1	8.1	5.9	4.4	4.1
–HNCH ₂ OCH ₂ NH–	69–70	7.9	9.7	10.2	10.4	12.3	14.0	15.4	16.3	6.5	8.3	9.7	8.9
–N(CH ₂ –)CH ₂ OCH ₂ N(CH ₂ –)–	75–76	0.2	0.4	0.4	0.3	1.2	1.4	1.2	1.0	0.8	1.0	1.8	0.9
–HNCH ₂ OCH ₃ } –N(CH ₂ –)CH ₂ OCH ₃ }	73–74 79–80	6.9	5.2	6.6	7.0	0.3	0.4	0.2	0.2	5.2	5.9	6.8	5.8
Carbonyl region													
Free urea	162	27.0	20.4	16.2	12.2	24.7	17.6	14.4	12.6	29.2	20.7	14.6	13.1
Monosubstituted urea	160–161	49.0	53.7	54.3	54.3	49.1	52.9	54.1	54.0	45.6	51.3	53.0	54.6
Di- and trisubstituted urea	159–160	24.0	25.9	29.5	33.5	26.2	29.5	31.5	33.4	25.2	28.0	32.4	32.3
Distribution of linear methylenes (in %)	47	73.7	76.6	82.6	83.5	77.3	77.9	82.7	83.6	62.8	75.8	78.0	81.0
	48	27.3	23.4	17.4	16.5	22.7	22.1	17.3	16.4	37.2	24.2	22.0	19.0

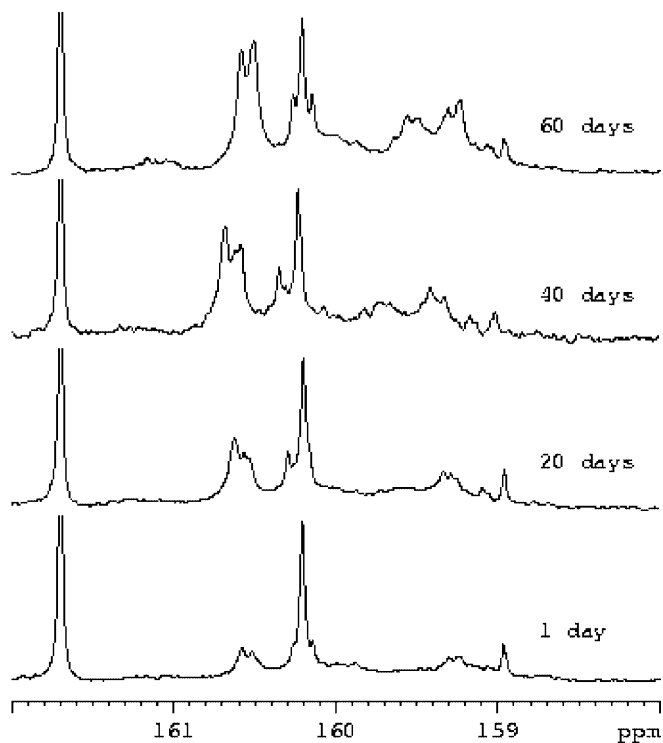


Fig. 1. Changes in carbonyl region of ^{13}C NMR spectra of UF2 resin during storage at 25 °C

Bild 1. Die Änderung in der Karbonylregion der ^{13}C NMR Spektrum von dem UF2 Harz Während der Aufbewahrung bei 25 °C

3 Discussion

The data in Table 2 show that there are some distinct differences in content of structural groups derived from F. In case of UF1 and UF3, methanol in F solution produces stable methoxymethylene derivatives of urea surviving all changes in synthesis and ageing, and can participate only in the further resin curing processes. It means that about 6% of F cannot actively take part in preceding reactions. This amount can be estimated as quite remarkable, considering that a slight decrease of F/U ratio leads to essential differences in resin structure. It also appears that the gradual addition of urea has not caused great differences in the content of structural groups of UF3 compared with UF1. Comparing the initial viscosities of resins (Table 1), it should be concluded that the condensation degree of UF3 is substantially higher. However, the content of free urea (Table 2) shows that the conversion degree of urea is rather low. It means that the gradual addition of urea during synthesis does not increase its binding. In UF3, as compared to UF1, the ratio of methylenes to bound urea is about 1.2 times higher. A similar structure of resins follows from the similar ratio of methylene linkages in linear and substituted chains. The difference between contents of hydroxymethyl groups in UF3 and UF1 is significantly lower.

In the structure of UF2, some differences appear because of the absence of methanol. The determinative factor is equilibrium between ether groups, including dimethylene ethers or methoxymethylenes and other structural

groups. In resins with methanol, the release of F from dimethylene ethers during condensation is more extensive to obtain the regular content of ether groups (12–15% from F). Consequently, the higher content of dimethylene ethers in UF2 is not surprising. The formation of methylenes from ethers only by F release is accepted as a well-known route, avoiding other possibilities, e.g. cleavage by primary amino groups. Greater amount of available F and milder technological conditions in treatment with second urea result in another structure of UF2 to some extent. On the basis of methylene content, the formal condensation degree in UF2 is higher, compared to UF1. At the same time, the whole substitution degree in UF2 is lower. This result is in accordance with the lower content of hydroxymethyl groups, occurring as chain side-groups or dihydroxymethyl end-groups.

Although the initial reaction mixture consists only of two main components, the final resin structure is formed after complicated combination of reactions. ^{13}C NMR analysis determines the relative content of structural groups, but does not subdivide these groups into fractions belonging to two parts of resin. As an exception, the methylene carbons adjacent to secondary amino groups revealing two well-separated peaks at 47–48 ppm with difference of 0.7 ppm, are assigned by Tomita (1995) to MDU and to longer chains (Table 2).

The most characteristic constituents of polymeric part are methylene linkages adjacent to secondary and tertiary amino groups (at 53–54 ppm). Their content is quite similar in UF1 and UF2. Methylenes of this type are forming in the step of acid condensation and their amount does not change substantially in further steps of synthesis. The higher content of these methylenes in UF3 shows the deeper condensation in polymeric part. A quite stable amount of hydroxymethyl groups adjacent to tertiary amino groups (at 71–72 ppm) in the course of condensation shows the predominant formation of amino groups substituted with hydroxymethyl and methylene groups. There are several routes for their formation (Siimer 1999). The substitution of urea is limited by the trisubstitution. It means that only every second amino group can be disubstituted. The real condensation in different resins first of all is determined by the extent of reaction between side hydroxymethyl groups and free amino groups of urea fragments, resulting branched structures.

The reactions occurring after addition of second urea and following during storage can be considered as one continuous process of quite complicated mechanism. The ratio between polymeric and monomeric parts is practically the same in all resins, as the urea is divided to the first and second parts according to the most-used twofold F excess in the hydroxymethylation and condensation steps. The five to six time molar excess of urea to free F produces mainly MMU. About 15–20% of free F has disappeared by this reaction. In UF1 and UF3, greater amount (~5%) of F has reacted, as these resins contain more free F after condensation step due to additional release from dimethylene ethers.

After second urea treatment, the content of monosubstituted urea is substantially higher as what can be pre-

Table 3. Physical and mechanical properties of industrial UF-bonded particleboards
Tabelle 3. Physikalische und mechanische Eigenschaften der industriellen UF-gebundenen Spanplatten

Thickness of particle-board (mm)	Resin	Dry resin/particle board (kg/m ³)	Scavenger (%/dry resin)		Density (kg/m ³)	Bending strength (MPa)	IB strength (MPa)	Swelling (%; 20°C 2 h)	Free F/(mg/100 g particle board)
			Surface layer	Core layer					
11	UF1	64.7	2.5	2.5	679	14.3	0.33	6.3	5.2
	UF2	65.1	0	2.5	695	14.2	0.44		5.4
	UF2*	65.1	0	2.5	686	13.1	0.45		5.8
	UF2	70.4	0	2	717	15.3	0.53	5.5	6.1
	UF3	66.0	0	0	698	14.9	0.45	7.1	6.3
18	UF1	68.9	0	0	715	18.6	0.32	4.5	6.0
	UF1	68.9	2	2	688	14.2	0.30	6.8	5.2
	UF2	63.2	0	1	692	14.8	0.46	5.5	5.8
	UF3	62.8	0	1	683	16.6	0.39	5.0	5.8
22	UF1	65.0	1.7	1.7	671	15.0	0.31		5.9
	UF1	70.7	1.7	1.7	688	16.8	0.44	2.8	4.9
	UF2	62.7	0	1	673	14.8	0.38	5.0	5.4
	UF2	62.7	0	3.6	687	13.6	0.40	5.6	4.6
	UF2	70.0	0	2	672	14.0	0.45		6.5
	UF3	62.8	0	0.5	667	14.8	0.39	5.4	5.9

* stored 21 days

sumed. The slow condensation between free urea and MMU, producing methylenes adjacent to secondary amino groups occurs partly already after adding second urea, and is also one of the main reactions during storage of resins. From Table 2, it appears that the extent of this reaction depends on the initial amount of methylenes of this type. In UF2, the initial amount of methylenes is higher and their content does not increase so much during the same time as in case of UF1 and UF3. The decrease in content of free urea quite well correlates with the increase in content of methylenes.

The total content of hydroxymethyl groups before storage is quite similar in all resins (about 50%). These groups are derived from two sources. The first one includes hydroxymethylureas from the reaction of urea with free F (about 15–20%) in monomeric part. The other part exists in polymeric part before addition of second urea. The changes in content of various structural groups are in good accordance only in case of transhydroxymethylation from polymeric part of resin to monomeric part. This is not surprising, as the most favoured hydroxy-methylation of urea in alkaline conditions is the equilibrium process, and the second urea is not satisfied with the amount of hydroxymethyl groups obtained from free F. The migration of hydroxymethyl side-groups should be accompanied with decrease in the amount of methylenes between secondary and tertiary amino groups. The content of methylenes of this type does not change in treatment with second urea and at the following storage of resins. Hence, the extensive migration of terminal mono- and dihydroxymethyl groups from polymeric part to monomeric occurs. This transition is notable as it causes the twofold change in content of monosubstituted urea. Simultaneously, free terminal amino groups appear in polymeric part and MMU in monomeric part. The migration does not change the total content of hydroxymethyl groups. In case of single mi-

gration from dihydroxymethyl derivatives, the equivalent amounts of monohydroxymethyl terminal groups and MMU in monomeric part are formed. It can be supposed that the migration is the fast process and occurs mainly before storage of resins. The content of various structural groups shows that about one half of hydroxymethyl groups migrate from polymeric part to monomeric part. It can be calculated that the content of methylenes adjacent to secondary amino groups is quite similar in polymeric parts of resins (4–6%). The difference in methylene content of UF1 and UF2 levels in polymeric part after greater migration of hydroxymethyl groups in case of UF2, having less free F for reaction with second urea.

In case of urea excess, the other possible condensation mechanism in alkaline conditions over dimethylene ether formation is not so extensive as compared to methylene formation. During storage, this reaction also occurs to some degree in monomeric part of resins (Table 2), but can be regarded as side-reaction. In case of UF2, the role of dimethylene ether groups is more essential in comparison with other resins, but the total content of ether groups is similar in all resins.

During room-temperature storage for an extended period, the essential increase of viscosity occurs with final gelation of resins (Fig. 2). The resin network formation can be explained by the increase in content of di(tri)substituted urea (Table 2) due to subsequent reactions in monomeric part. The constant value of methylenes adjacent to secondary and tertiary amino groups allows to assume that some methylene formation during storage occurs in reaction between free terminal amino groups and hydroxymethyl groups. These groups exist both in polymeric and monomeric parts of resin. The reaction between terminal hydroxymethyl groups of polymeric part and free urea or MDU can be one of the possibilities. UF3 with higher condensation degree shows smaller tendency

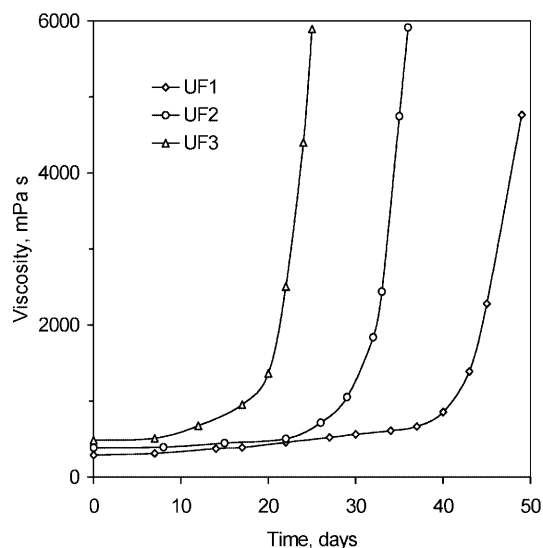


Fig. 2. Changes in viscosity during storage of UF1, UF2 and UF3 resins

Bild 2. Die Änderung in der Viskosität während Aufbewahrung der UF1, UF2 und UF3 Harze

to further condensation in polymeric part, at the same time promoting the reaction of urea in monomeric part.

The real value of UF resins under discussion becomes apparent in manufacturing particleboards. Comparing the mechanical properties of boards bonded with these resins (Table 3), it is seen that IB strength (tensile strength perpendicular to the board surface) shows the lowest values in case of resin UF1. IB strength is the most sensitive physical characteristic, depending on crosslinking of cured resin network. As UF1 has lower condensation degree (Table 2), more time to attain the same crosslinking is necessary. At the same time, smaller viscosity promotes impregnation of resin, causing insufficient adhesive bond. The mechanical properties in all cases satisfy the requirements for general purpose boards P2 (IB strength 0.28 MPa, bending strength 12.5 MPa). The content of free F was regulated with additional scavenger if necessary, but in all cases it corresponds to the requirements of E1 standard (a rotating half-year F emission level is less than 6.5 mg F/100 g particleboard). Storage of UF2 resin for 3 weeks in technological acceptable level of viscosity does not decrease the physical and mechanical properties of particleboards.

4

Conclusions

- The most important factor in synthesis of UF resins is the F/U ratio. As UF resins were manufactured with close F/U ratio, they have a quite similar structure and show quite similar performance characteristics. Some differences in initial content of structural groups

depending on details of synthesis are of temporary character and level during further reactions, mainly by transhydroxymethylation. Migration of hydroxymethyl groups from polymeric part of resins to second urea evens the structure of resins and promotes obtaining homogenous crosslinking density of cured resins.

- The total content of ether groups including dimethylene ethers and methoxymethylenes is quite similar in different resins. Methoxymethylenes are the most stable groups, and can participate only in further acid catalysed crosslinking in resin processing.
- The methylenes adjacent to secondary and tertiary amino groups are formed only during acid condensation and their content remains unchanged during resin storage till to next acid condensation in curing.
- The differences in content of structural groups after condensation in the most part disappear during second urea treatment and subsequent storage of resins.
- The main reaction during resins storage is the formation of methylene linkages adjacent to secondary amino groups. This reaction occurs between hydroxymethylureas and urea in monomeric part, and also between free terminal hydroxymethyl and amino groups of both resin parts.

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