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CHANGES IN CURING BEHAVIOUR OF AMINORESINS DURING STORAGE

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The curing behaviour of commercial UF and MUF resins, stored at room temperature nearly up to gelation, is studied by simultaneous TG-DTA technique and structural changes of resins are also followed during aging. On the basis of ^{13}C NMR spectra, the main chemical reaction during UF resin storage is the formation of methylenes and dimethylene ethers linked to secondary amino groups. Aging of resins results in a decrease of cure rate which is related to lower concentration of active functional groups and decrease in molecular mobility. On DTA curve, the resin with higher content of methylol groups reveals the curing exotherm earlier. With decreasing methylol content during storage, the peak maximum of exotherm is shifted to higher temperature value. Advanced polycondensation and sedimentation processes during storage produce partly locked in macromolecule structure water, and the water evaporation endotherm on DTA curve shifts to considerably higher temperature. The aged MUF resins are chemically less changed than UF resins and the aging process mainly involves non-covalent network formation due to complex molecular structure.

Keywords: *^{13}C NMR, curing, melamine-urea-formaldehyde resins, polycondensation, storage, TG-DTA technique, urea-formaldehyde resins*

Introduction

The wood-based composite panel industry is the major consumer of aminoresins. Among these, urea-formaldehyde (UF) resin is the most important type of adhesive in the manufacturing particleboard, medium density fibreboard, partly oriented strandboard, and plywood. Compared to other wood adhesives, UF resins possess advantages such as fast curing, good performance in the panel, water compatibility, and low price. Disadvantages of using UF adhesives are lower resistance to the influence of water, humidity, and weather. Melamine-urea-formaldehyde (MUF) resins are a feasible alternative to the use of high resistant, but also of higher price, melamine-formaldehyde resins. While a large variety of M/U ratios have been used in cocondensed resins, classical MUF resins are mostly as of 40/60 M/U molar ratio. The incorporation of melamine triazine ring in the resin structure improves the low resistance of UF bonds.

An important factor with respect to the technical use of aminoresins concerns their long-term storage stability. In general, resin consumers monitor resin stability by adhesive flow using viscosity measurements. During storage, aminoresins build up viscosity and this affects adhesive processability and performance properties. By the structural analysis of aminoresins and rheokinetic studies it has been concluded that resin storage consists of both physical and chemical interactions, and viscosity is not a real measure of the actual chemical changes occurring in the resin in storing [1, 2]. Network formation in aminoresins during storage and curing has been described by several authors but contradictory views are presented about shares of both influences [3–7]. For direct investigation of the network structure of the cured resins, the solid-state ^{13}C NMR, FTIR, XPS and ToF-SIMS spectroscopies provide the possibilities [8].

In our previous report [9], the curing behaviour of UF resins was studied in dependence on different technological cure parameters. It is of practical interest how the changes of chemical structure taking place during storage are reflected in the curing behaviour of aminoresins. In the present work, the curing behaviour of commercial aminoresins, long time stored at room temperature, was studied by simultaneous TG-DTA technique, also including the determination of the chemical structure of resins of the same age by high resolution ^{13}C NMR spectroscopy.

Experimental

The modern urea-formaldehyde resins are ordinarily synthesised with similar formaldehyde to urea molar ratio (1.03–1.08/1) and contain only small amounts of unreacted formaldehyde. For the present study, commercial resins of different origin, labelled as UF1,

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Table 1 Standard analysis of UF and MUF resins

Characteristics	UF1	UF2	UF3	UF4	MUF1	MUF2
dry solids, 105°C, 3 h/%	66.4	69.5	69.0	67.8	66.7	66.7
pH, 25°C	8.1	8.5	8.6	8.5	9.1	9.4
viscosity 25°C/mPa s	282	335	396	487	353	390
density 20°C/g cm^{-3}	1.270	1.285	1.290	1.273	1.297	1.295
gel time 100°C/s	61	52	54	66	73	75
free formaldehyde/%	0.12	0.14	0.13	0.15		
water tolerance	1:4	1:6	1:3	1:2	1:3	1:3

UF2, UF3 and UF4, were selected to compare the thermal behaviour of resins with close standard characteristics but of differing manufacturing technology. Also, two samples (MUF1 and MUF2) of commercial melamine-urea-formaldehyde resin were studied. In Table 1, the standard analysis of resins is presented.

Dynamic viscosity of resins was measured by rotational viscometer. It can be seen from the table that at a close solids content, resin viscosity is quite different and does not correlate with the gel time of catalysed (1% ammonium chloride) resin at 100°C. Lower gel time of UF2 and UF3 refers to higher reactivity of resins. In the synthesis of UF1 and UF4, formaldehyde aqueous solution with high methanol content was used which slow down the rate of gelation reactions. The slow structuration of resins during storage at 25°C does not depend on their initial viscosities but first of all on the content of methanol. The final gelation of UF2 and UF3 occurs during 30–35 days, gelation of UF4 during 50–60 days, and gelation of UF1 during 90–100 days. Considerably higher gel time in case of MUF resins can be explained by the buffering effect of melamine. The final gelation of studied MUF resins occurs during 70–75 days.

The chemical structure of resins was characterised by high resolution ^{13}C NMR spectroscopy 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 (25,000–35,000 scans) into 32 K data point and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. ^{13}C NMR spectra were recorded from fresh (1 day after manufacturing) and aged nearly up to gelation resins. The resins were stored at 25°C without mixing. The samples for analysis of aged UF2 and UF3 were taken after 30 days of storage, in case of UF4 after 40 days and UF1, after 60 days of storage. On the basis of integral intensities in ^{13}C 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 ^{13}C NMR spectra of UF1 during 60 days storage are shown below.

TG-DTA measurements were carried out by a labsys^{TM} instrument (Setaram) with the heating rate of 5 K min^{-1}, measuring sensitivity 50 μV. Temperature of samples ranged from 20 to 450°C, and the measurements were recorded in dynamic helium atmosphere (40 mL min^{-1}), the mass of the samples being 10 to 20 mg. The TG-DTA test was carried out with an open standard platinum crucible (100 μL). As a reference, an identical empty crucible was used. DTA, TG and DTG curves were registered considering reference runs at the same experimental conditions. The heat flow on DTA curves was expressed in μV. Enthalpy of the curing reaction is not exactly determined, as the characteristic exoeffect in DTA curve frequently is overlapped by water evaporation endotherm. The exothermic peak temperatures are the certain indices to characterise the curing system. Resin cure was catalysed with 1 and 2% of ammonium chloride, 20% solution of catalyst was used. Curing experiments were recorded at the same time with the structural analysis.

Results and discussion

Depending on different synthesis conditions and technology, the generally used multistep reaction of urea and formaldehyde produces resins with a broad variety of both linear and branched chains as well as tridimensional networks in the cured resin. The ^{13}C NMR analysis (Table 2) shows initial resins having higher content of total methylol groups included in UF2 and UF3, accordingly 53.3 and 54.4% of bound formaldehyde, and lower content in UF1 and UF4, accordingly 44.1 and 47.1%. This amount is correlated with the measured gel time (Table 1), indicating relationship between content of methylol groups and reactivity of resins. The content of methylene linkages which can be regarded as a measure of resin conversion degree, is considerably higher in UF4, at the same time the content of dimethylene ether linkages being lower. Deciding the content of

Table 2 Changes in chemical structure of urea-formaldehyde resins (mol%) during storage by ^{13}C NMR analysis

Assignment	ppm	UF1		UF2		UF3		UF4	
		fresh	aged	fresh	aged	fresh	aged	fresh	aged
methylene linkages									
$HNCH_2NH$	47–48	15.6	25.1	14.5	25.8	16.2	29.6	18.1	30.3
$HNCH_2N(CH_2)$	53–54	18.0	17.5	17.4	17.5	13.5	16.2	22.3	21.2
$N(CH_2)CH_2N(CH_2)$	60	0.9	0.8	–	–	–	–	–	–
methylol groups									
$HNCH_2OH$	65–66	33.0	26.9	44.2	30.6	47.7	28.8	39.0	25.8
$N(CH_2)CH_2OH$	71–72	11.1	4.8	9.1	5.7	6.7	4.3	8.1	4.4
$N(CH_2OH)_2$	71–72	11.1	4.8	9.1	5.7	6.7	4.3	8.1	4.4
dimethylene ether linkages									
$HNCH_2OCH_2NH$	69–70	9.6	13.4	8.7	14.6	10.2	15.3	6.5	10.7
$HNCH_2OCH_2N(CH_2)$	75–76	3.0	2.3	2.4	2.9	2.1	2.1	0.8	1.8
methylene methyl ethers									
$HNCH_2OCH_3$	73–74	8.6	8.9	3.1	2.7	3.3	4.3	5.2	5.8
$N(CH_2)CH_2OCH_3$	79–80	8.6	8.9	3.1	2.7	3.3	4.3	5.2	5.8
methylene glycols									
OCH_2OCH_2O	83–95	0.2	0.3	0.6	0.2	0.3	–	–	–
carbonyl region									
free urea	162	12.0	3.7	23.1	10.8	21.8	11.0	29.2	14.6
monosubstituted urea	150–161	47.5	46.4	47.2	51.9	51.1	53.5	45.6	53.0
di- and trisubstituted urea	159–160	33.9	43.6	28.4	35.3	27.1	35.5	25.2	32.4
cyclic ureas	152–158	6.6	6.3	1.3	2.0	–	–	–	–
distribution of linear	47	64.6	79.1	62.7	77.2	78.1	84.9	62.8	78.0
methylene	48–48	35.4	20.9	37.3	32.8	21.9	15.1	37.2	22.0

methylene methyl ether groups it should be considered that in the synthesis of UF1 and UF4 higher methanol content in formaldehyde solution was used in comparison with UF2 and UF3.

In general, it is proposed that the aging mechanism of UF resins involves chemical changes leading to a decrease in the methylol content, an increase in the methylene and dimethylene ether content. The extent of these changes depends on final molar ratio of formaldehyde and urea, content of free urea in the resin after manufacture, and pH during storage. From our earlier studies [10, 11] and from Table 2 it results that during storage, the main reaction is the formation of methylene linkages adjacent to secondary amino groups. This reaction occurs between methylolureas and urea in monomeric part, and also between free terminal methylol and amino groups of both monomeric and polymeric resin parts. Methylenes adjacent to secondary and tertiary amino groups form only during acid condensation, and their content does not change during long-temps storage. The extent of structural changes during storage depends on content of terminal methylol groups and free urea prior to storage. Beside the chemical reactions, in the network formation during storage of resin with various amounts of linear and branched chains, the formation of intermolecular hydrogen bonds between free NH and O=C groups should be considered. UF resin is the best example of the build-up of covalent network occurring in close connection with changes in physical network. Water should be regarded as active participant in formation of physical network on the basis of hydrogen bonds, as well the component, the changing amount and compatibility of which leads to different sedimentation conditions during formation of network of different density.

Thermal behaviour of UF resins during curing depends first of all on the content of reactive structural groups. As an example, in Fig. 1, a typical curing curve for UF2 catalysed with 1% of ammonium chloride is presented.

From the curve it can be seen that the exothermic reaction of UF2 cure with mass loss is characterised with a peak maximum at 83ºC and the large endotherm of water evaporation with a peak minimum at 108ºC.

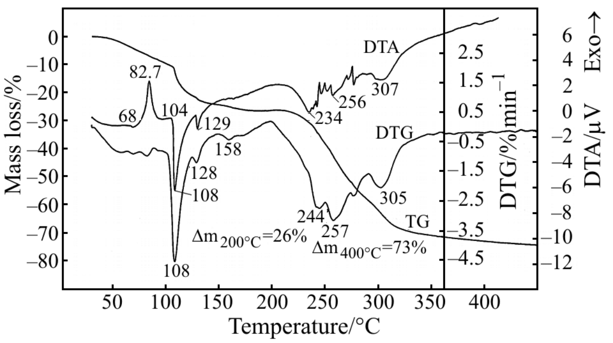

Fig. 1 TG-DTA curve of UF2 curing with 1% ammonium chloride

Noticeable degradation of cured resin begins above 230ºC. In Fig. 2, the DTA curves of four UF resins are compared. It appears that the resins of higher content of methylol groups reveal the first exothermic peak at lower temperature. The heat flow of the reaction for UF2, UF3 and UF4 is similar (in the range of 15.1–15.6 μV). In case of UF1, the run of thermal effects is quite different. The resin contains high amount of stable methylene methyl ether groups and remarkably higher amount of end methylol groups of branches (Table 2), which can form highly cross-linked structure of cured resin, constraining the molecular mobility. The first exotherm appears already at 82ºC, but the low value of the reaction heat flow (7.3 μV) indicates the possible other undetermined exoeffects in the region of 85–120ºC. The water evaporation from curing system begins only at 120ºC giving an endotherm minimum at 126ºC. This endotherm refers to the different states of water – that from resin synthesis and condensation water arising during cure. If the tight resin network is formed in the course of curing, the continuous processes of polycondensation and sedimentation produce partly locked water domains in macromolecular structure which elimination is more difficult. As the total content of ethers in UF1 is higher than in the other resins, the profound degradation of UF1 with splitting ether linkages begins at somewhat lower temperature showing an endotherm peak minimum at 228ºC.

In Fig. 3, DTA curves for the same but aged UF resins are presented. Aging of resins results in some loss of cure rate, expressed in higher cure temperatures in DTA curve. The shifts of peak temperatures depend on the extent of structuration during resin storage and correlate quite well with the methylol content. Due to low content of free urea and methylol groups in case of UF1, the first exothermic condensation reaction shows the shift of the peak maximum only by 1ºC but the broad shoulder on the exotherm refers to the another exoeffect. In comparison, in case of the other UF resins containing more reactive methylol groups, the shifts of the exothermic peak maximum are from 1.8 to 3.6ºC. The reaction heat flow of all these resins is decreased from 15 to 7–8 μV.

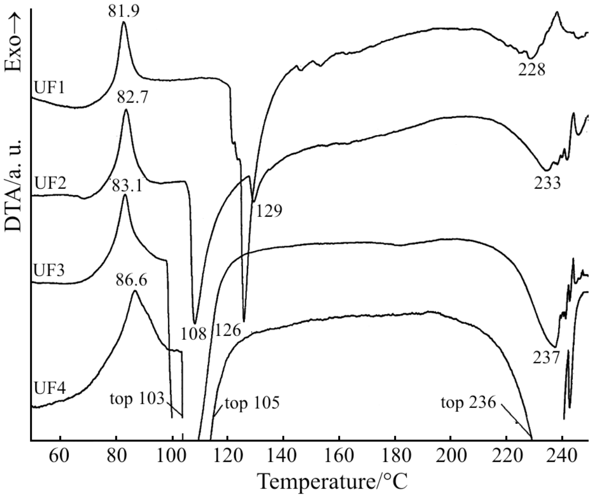

Fig. 2 DTA curves of fresh UF resin curing with 1% ammonium chloride

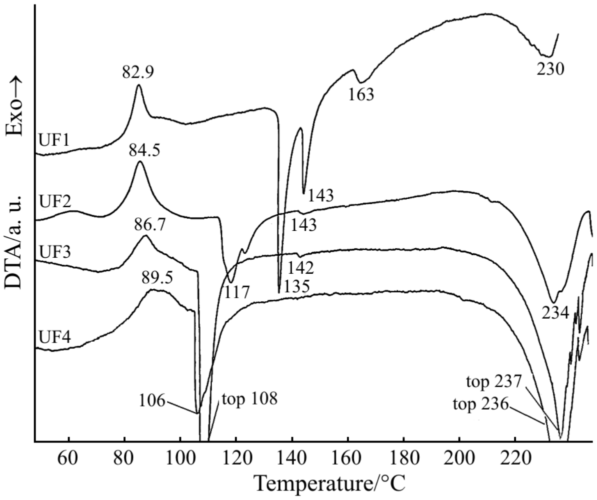

Fig. 3 DTA curves of aged UF resin curing with 1% ammonium chloride

In Fig. 4a, the differences of peak temperatures for fresh and aged UF1 are accentuated. As it was mentioned, a broad shoulder at 84ºC appeared which can be attributed to the reaction of the terminal dimethylol groups with urea. Due to high content of dimethylols in the initial resin, the tight network structure locking part of the water in the cavities is built up during long-time storage. Due to that, the water evaporation endotherms of UF1 are differentiated and appear at higher temperature with a peak minimum at 135ºC proving different states of water, the so-called free and bound water. As can be seen from Fig. 4b, there are great difference in mass loss rate of fresh and 60 days aged resins at the region of water evaporation during resin cure.

In case of other studied resins the mass loss difference between fresh and aged resins is less (Fig. 5), due to lower extent of cross-linking in network formation. As the initial resins contain less end methylol groups of branches (Table 2), the increase of methylene linkages in linear chains predominate during storage, and diffusional barrier for water evaporation is not so essential.

MUF resins are of more complicated structure due to the presence of two monomers reactive with formaldehyde in the polymer, and in hardening they can form methylene or dimethylene ether linkages between melamine and melamine, melamine and urea,

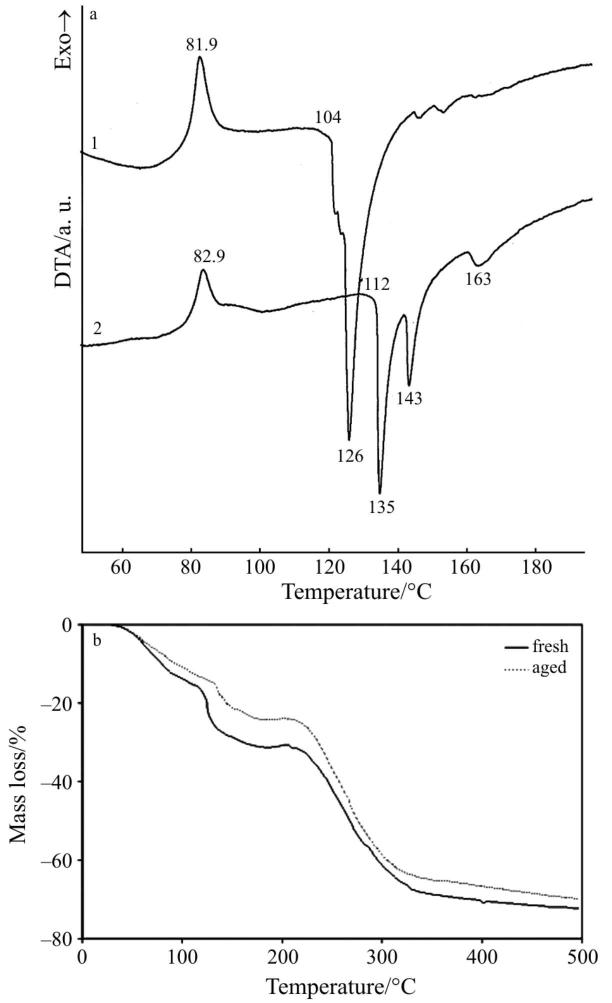

Fig. 4 UF1 curing with 1% ammonium chloride: a – DTA curves: 1 – fresh resin, 2 – aged resin; b – mass loss curves

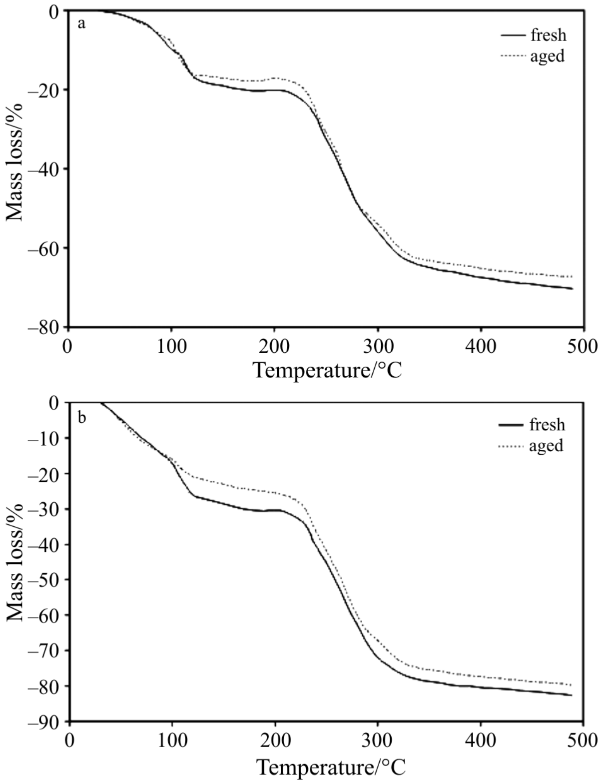

Fig. 5 Mass loss curves of UF resin curing with 1% ammonium chloride: a – UF3; b – UF4

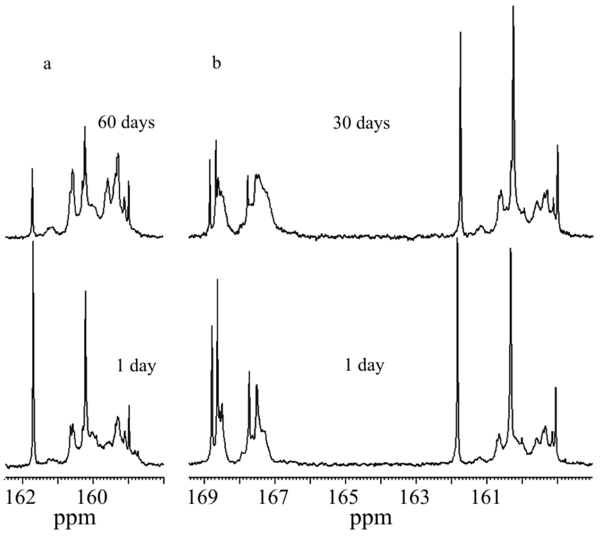

Fig. 6 Changes in chemical structure of aminoresins during storage by ^{13}C NMR analysis in DMSO-d_6: a – carbonyl region of UF1; b – carbonyl and triazine regions of MUF2

or urea and urea. In Table 3, the structural analysis for both fresh and aged up to 30 days MUF resins named as MUF1 and MUF2 is presented.

As appears from Table 3, the structural changes during MUF storage are not so extensive as compared to UF resins. More remarkable decrease in content of methylolmelamines and free melamine comparing to the decrease of methylolureas and free urea can be seen. Thus, it can be concluded that the preferred reaction during resin storage is the homocondensation of methylolmelamines with amino groups of melamine. Some changes can also be observed for branched methylols, methylenes and ether groups, but these changes are not so pronounced as those occurring with melamine triazine ring. In case of MUF2, the changes of chemical structure are more noticeable, therefore, further it will be focused on this resin. Figure 6 illustrates the structural changes in carbonyl and triazine carbon region for MUF resin during storage. Also, the structural changes in carbonyl carbon region for UF1 aging are shown. It can be seen that no considerable changes are observed in carbonyl region of MUF resin (158–162 ppm) as compared to the changes of UF resin which contain the remarkable decrease of free urea and different substitutions at nitrogen atom. In triazine region (167–169 ppm), the main

Table 3 Changes in chemical structure of melamine-urea-formaldehyde resins (mol%) during storage by ^{13}C NMR analysis

Assignment	ppm	MUF1		MUF2	
		fresh	aged	fresh	aged
methylene linkages					
$HNCH_2NH$	47–48	11.2	12.8	11.7	14.6
$HNCH_2NH$	48–49	3.3	3.7	1.8	4.4
$HNCH_2N(CH_2)$	53–55	10.7	11.1	11.6	11.6
methylol groups					
$HNCH_2OH$	65	33.1	30.7	31.4	29.0
$HNCH_2OH$	66	22.3	17.2	22.4	13.5
$N(CH_2)CH_2OH$	71–72	3.5	3.7	3.6	4.5
$N(CH_2OH)_2$	71–72	3.5	3.7	3.6	4.5
dimethylene ether linkages					
$HNCH_2OCH_2NH$	69–70	15.8	17.4	15.4	17.4
methylene methyl ethers					
$HNCH_2OCH_3$	73–74	–	1.1	–	
$N(CH_2)CH_2OCH_3$	79–80	–	0.7	–	
methylene glycols					
OCH_2OCH_2O	83–95	0.1	0.2	0.2	0.4
carbonyl region					
free urea	162	12.8	10.7	15.2	11.7
monosubstituted urea	160–161	52.3	53.5	52.0	53.2
di- and trisubstituted urea	159–160	34.9	35.8	32.8	35.1
triazine region					
free melamine	169	10.9	7.5	13.3	6.0
monosubstituted melamine	168–169	33.8	31.3	33.4	28.3
di- and trisubstituted melamine	166–168	55.3	61.2	53.3	65.7

changes are the decrease in the content of ring carbons bearing primary amino groups and the increase in the relative content of ring carbons linked to secondary amino groups. Condensation reactions during resin storage are accompanied by the appearance of additional peaks in this region.

The aged MUF resins are chemically less changed than UF resins, thus excluding only chemical cross-linking during room temperature storage. According to [12], the aging process of MF resins mainly involves physical gelation due to complex molecular interactions. In case of MUF resin, chemical reactions also contributed to the network formation in storing.

MUF resins are attractive systems for studying the cure process as they can harden with acid catalyst and also without adding catalyst in mildly alkaline environment. MUF resin cure was recorded both with 1 and 2% ammonium chloride to compare the effect of catalyst. In Fig. 7, the curing curve for MUF2 with 2% of catalyst is presented.

From Fig. 7 it appears that TG-DTA curve for catalysed MUF curing is more undetermined as compared to UF resin curve and only weak peaks in the exothermic region are visible. Although it is not possible to ascertain the exact location of exothermic peak maximums, the expressive endothermic peak with a minimum at 153°C and mass loss values indicate the proceeding of complicated polycondensation reactions which are represented by several overlapping exothermic peaks with water evaporation endotherms. In the case of the acidic catalyst added, the formation of methylene linkages already starts before water evaporation from the system. Three amino groups in MUF triazine ring assure a three-dimensional cross-linked molecular structure in curing and proceed to a much tighter, highly cross-linked final network, hence, a higher strength of the joints compared with UF resins. Beyond the endothermic water evaporation, a further tightening of the network due to further curing occurs. However, the visible degradation of resin begins at the same temperature region

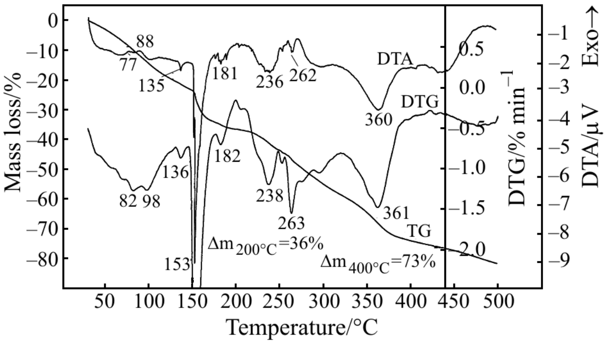

Fig. 7 TG-DTA curve of MUF2 curing with 2% ammonium chloride

as in the case of UF resins (230–235°C), due to containing the hydrolysis-sensitive aminomethylene linkages involving urea.

According to general opinion, in case of MF resin curing in alkaline conditions more dimethylene ether linkages between triazine rings are formed [e.g. 13] the majority of which are converted to thermodynamically more stable methylene linkages. Without adding the acidic catalyst, the final MUF resin hardening only occurs after water evaporation from the system [14]. It causes diffusional problems in the resin, limiting the extent of the reaction and leading to looser final network even in higher curing temperatures. Because of the wide variation in functionality of resin structure and reactivity of intermediates, the exothermic peaks are dissipated by many simultaneous reactions.

In Fig. 8, the comparison of DTA curves for fresh and aged MUF curing catalysed with 2% ammonium chloride is presented. Also, the DTA curve for fresh MUF curing without catalyst is shown (curve 3). In this curve, the poorly observed exotherms are revealed as well the complicated water evaporation endotherm refers to occurring plurality of condensation reactions. A noticeable water evaporation begins from 98°C, and large endotherm consists of several sharp peaks with a minimum at 114°C. It appears to be an imperfect and undesirable curing mechanism, resulting in poor physico-mechanical properties of final cured resin. The water evaporation at lower temperature refers to thinner structure of MUF resin.

From Fig. 8 it appears that there are no remarkable differences between curing temperatures of fresh and aged resin (curves 1 and 2). Water evaporation endotherm in case of aged resins is shifted to higher temperatures and divided to several peaks. As mentioned above, it can be explained by different states of water in the resin network and, therefore, by different rate of elimination from system.

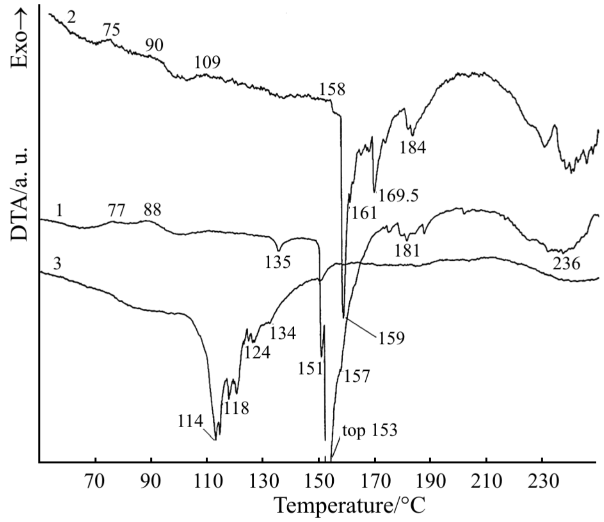

Fig. 8 DTA curves of MUF2 curing with 2% ammonium chloride: 1 – fresh resin; 2 – aged resin; 3 – fresh resin cured without catalyst

The expanded DTA curves for fresh and aged resin make it possible to distinguish between the exothermic peak temperatures. In case of 1% as compared to 2% of catalyst, the peaks are better differentiated (Fig. 9).

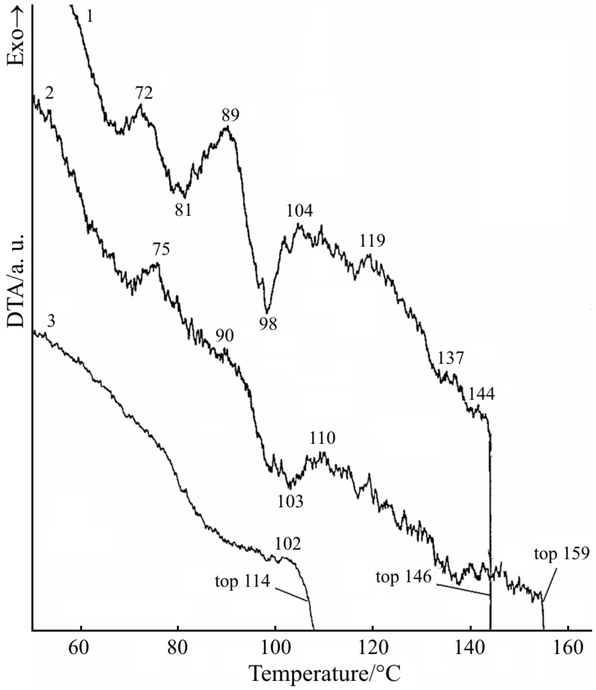

Fig. 9 Expanded DTA curves in exothermic region of MUF2 curing with 1% ammonium chloride: 1 – fresh resin; 2 – aged resin, 3 – fresh resin cured without catalyst

On the basis of our earlier studies and [15], the following variants of cross-linking reactions for MUF resin should be assumed. The first exotherm in the region of 74–76°C should be attributed to melamine-methylolmelamine homocondensation as the more preferred reaction. Exothermic peak of urea-formaldehyde homocondensation, as compared to UF resin alone, is shifted to higher temperatures and reveals with a peak maximum at 89°C. The broad band at the region of 104–120°C are assumed to be the different condensation reactions between urea and melamine derivatives. A minimum of water evaporation endotherm for fresh resin in case of 1% catalyst is located at somewhat lower temperature (146°C) as compared to 2% catalyst (153°C). Comparing the temperatures of water evaporation endotherms for aged resins catalysed with 1 and 2% it appears that they are similar with a peak minimum at 159°C.

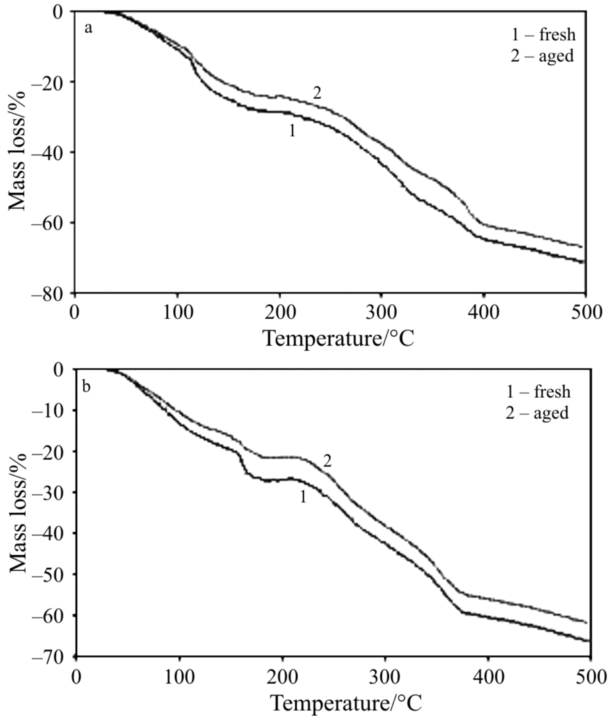

Fig. 10 Differences in mass loss values of fresh and aged MUF2 curing: a – without catalyst; b – with 2% ammonium chloride

If compared the mass loss curves of fresh and aged MUF resin (Fig. 10) the conclusion can be drawn that in curing without catalyst as well as with 2% of catalyst, mass loss level of aged resin in both cases is lower than that of fresh resin. It can be explained by diffusional barriers for water evaporation in aged resin network.

Due to the compositional complexity of MUF resin it is difficult to interprete in detail the connection between the aging process and the thermal behaviour of resin. Differently from UF resins, physical effects predominate during storage, and the determining effect is the locking of water in cured resin network which surpasses the influences of the chemical cross-linking.

Conclusions

The aging of UF resins generally involves chemical changes leading to a decrease in the methylol content and an increase in the methylene and methylene ether content. The main reaction during resin storage is the formation of methylene linkages adjacent to secondary amino groups. The extent of structural changes depends on the content of free urea and methylol groups prior to storage. As compared to fresh resin, a decrease in cure rate is observed during curing of aged resin, expressed by higher exothermic peak temperatures on DTA curve. The decrease in cure rate upon aging appears to be related to the decrease in methylol content. Resins stored nearly up to gelation reveal decreased rate of water evaporation due to probable locking water in network structure.

In case of MUF resins, the changes in the chemical structure during resin storage are not so extensive as compared to UF resins, and the increase in viscosity does not provide a measure of resin chemical change. For the formation of the gel, the specific intermolecular interactions probably perform an important role. Due to complex physical effects, in curing of aged MUF resin decreased molecular mobility slows down the evaporation of water and, consequently, causes the shift of endothermic peak to higher temperature.

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