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THERMAL BEHAVIOUR OF UREA-FORMALDEHYDE RESINS DURING CURING

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Abstract

Urea-formaldehyde (UF) resins are the most widely used polycondensation resins today in manufacturing particleboards. The performance of UF resins in their processing is greatly influenced by curing characteristics. The cure process has been monitored by TG-DTA technique on a Setaram labsys^{TM} instrument in dynamic heating conditions at different heating rates. Commercial UF resins from different suppliers used in Estonian particleboard factories were selected for TG-DTA measurements. Experiments were carried out without and with catalysts. Ammonium chloride and ammonium sulphate were used. Curing characteristics were evaluated both for fresh and aged resins.

Keywords: curing, polycondensation, storage, TG-DTA technique, urea-formaldehyde resins

Introduction

Urea-formaldehyde resins are the most widely used adhesives for bonding wood products today, in particular, for manufacturing particleboards. Their processing is greatly influenced by curing conditions, especially by the degree of cure, therefore it is very important to study the curing characteristics of the resins. Various methods for evaluating curing characteristics of UF resins have been proposed and used in practice. The thermal behaviour of the resins during curing has been followed by thermogravimetric analysis [1], differential thermal analysis [2], differential scanning calorimetry [3–6], supported by data from IR spectroscopy [2] and ^{13}NMR spectroscopy [5]. The generation of bonding strength during curing was directly monitored by dynamic mechanical analysis [7–8], more modern thermomechanical analysis [9], and automatic bonding evaluation system [10]. Direct investigation of formaldehyde emission during curing has given valuable information concerning the crosslinking and decomposition processes [4, 11].

In the present work, the curing process of UF resins was followed by the TG-DTA method which makes it possible to simultaneously characterise the heat of curing process and the thermal stability of cured resin. Commercial UF resins from different suppliers, and presumably of different synthesis procedures in Estonian particleboard factories have been used. Consequently, it is interesting to compare their curing behaviour and thermal stability both from theoretical and practical point of view. In this study, four commercial resins were selected for TG-DTA measurements.

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Experimental

TG-DTA measurements were carried out by a labsys^{TM} instrument (Setaram) with the heating rates of 3, 5 and 10 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 s mg^{-1}. Enthalphy of the curing reaction is not exactly determined, as the characteristic exoeffect in DTA curve is overlapped by water evaporation endotherm. In this study, the peak temperatures are the main apparent indices to characterise the curing system.

Commercial UF resins from different suppliers, and presumably of different synthesis procedures have been used, which are labelled as UF1, UF2, UF3 and UF4. In Table 1, the standard analysis of these resins is presented.

Table 1 Standard analysis of commercial UF resins

Characteristics	UF1	UF2	UF3	UF4
Dry solids (treated at 105°C, 3 h)/%	68.7	69.0	67.8	68.2
pH	8.2	8.1	8.5	8.4
Viscosity 25°C/ cP	307	380	490	480
Density 20°C/ g cm^{-3}	1.275	1.295	1.273	1.286
Gel time at 100°C/ s	56	51	66	81
Free formaldehyde/ %	0.13	0.1	0.15	0.1

From the table it appears that standard properties of all resins studied are quite similar regardless of different sources of resins. It is explained by the fact that modern UF resins are synthesised by a typical three-step procedure with close formaldehyde to urea ratio (1.03–1.08/1). This final ratio may be achieved by gradual addition of urea in small portions during synthesis. Due to the nearly equal molar ratio of components, UF resins contain only small amounts of free formaldehyde (0.1–0.15%). In the synthesis of resins, formaldehyde aqueous solution with 5–8% of methanol content was used, only in case of UF2 the methanol-free formaldehyde solution of higher concentration was applied. It is seen from the table that dynamic viscosity of resins is different at a close solid content, and it does not correlate with the gelation time of catalysed (1% NH_4Cl) resin at 100°C, thus indicating a complicated relation between resin structure and curing behaviour. Otherwise, the initial viscosity of resins determines the rate of slow structuration at room temperature. The final gelation of UF1, UF2, UF3 and UF4 occurred during 53, 39, 27 and 31 days according to their initial viscosities. Curing characteristics were evaluated both for fresh resins and aged up to gelation resins.

Curing experiments were carried out without and with ammonium chloride and ammonium sulphate as catalysts. 20% solutions of catalysts were used.

Results and discussion

The curing mechanism of UF resins depends on curing conditions, whether reactions are carried out with or without catalyst, hence, in acid or alkaline media. To make more obvious the differences between the various resins, curves of UF resins with different reactivity are compared as an example. UF1 is the resin of high content of hydroxymethyl groups (over 50% of bound formaldehyde), therefore, with high reactivity [12]. On the contrary, the resin UF4 has the highest condensation degree as compared to other resins studied, and contains only 37% of hydroxymethyl groups. UF4 was well-proved in industrial PB manufacturing and therefore, greater attention was paid to this resin in this work.

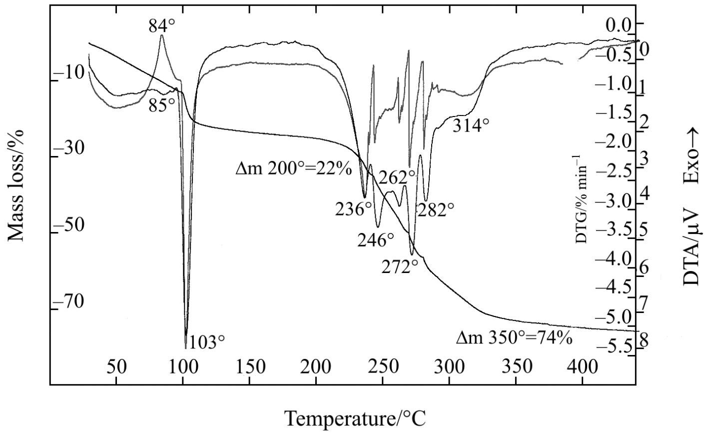

Fig. 1 TG-DTA curves of UF1 curing with 1% ammonium chloride (5 K min^{-1})

In Fig. 1, curing curve of UF1 with 1% of ammonium chloride is shown.

It is generally believed that in presence of acid catalyst, the first exotherm arises from polycondensation reaction of primary amino groups of unreacted urea with hydroxymethyl groups of resin. Exothermic reaction of UF1 cure with mass loss takes place with a peak maximum at 84°C. The large endothermic peak of water evaporation with a minimum at 103°C is derived from the initial resin water and that from condensation reaction. In temperature region up to 200°C no obvious thermic effects take place, the slight mass loss in this region is contributed to slow formaldehyde emission [6].

In Fig. 2, curing curve of UF1 obtained without ammonium chloride is presented. In curing without catalyst, in mildly alkaline medium (resin pH 8.2), polycondensation takes place preferably over formation of methylene linkages between linear resin fragments [12]. The resin curing process proceeds in extended temperature region and the exothermic effects are overlapped by endothermic effects of water evaporation. A slight exotherm can be observed in the range of 95–100°C, and the endoeffect with a minimum at 114°C in DTA curve refers to water evaporation. The other slight exotherms are visible at 130 and 162°C. Characteristic temperatures of resin decomposition begin in the same temperature region as in the case of UF1 catalytic curing. Resin destruction endotherm with a minimum at 233–236°C has been attributed to degradation of methylene ether linkages by many authors. The proved endotherm with a minimum at 314°C belongs to decomposition of the most stable unit in the UF resin – methylenediurea [1].

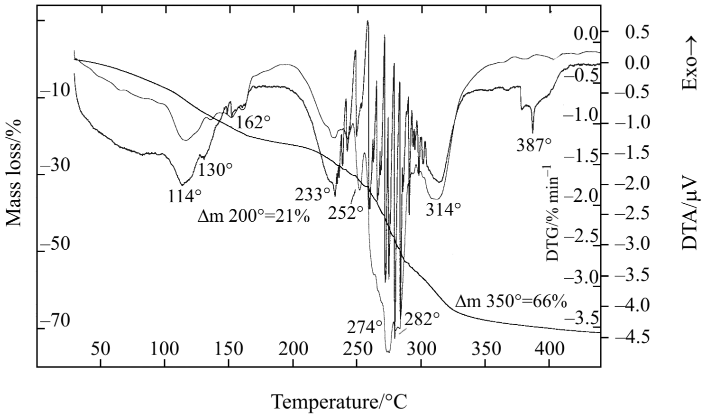

Fig. 2 TG-DTA curves of UF1 curing without catalyst (5 K min^{-1})

For comparison, curves for UF4 curing with and without ammonium chloride are presented. This resin, as compared to UF1, contains smaller amount of reactive hydroxymethyl groups. Lower reactivity of resin also reveals in considerably higher gel time (Table 1). In Fig. 3, curve of UF4 curing with 1% ammonium chloride is shown.

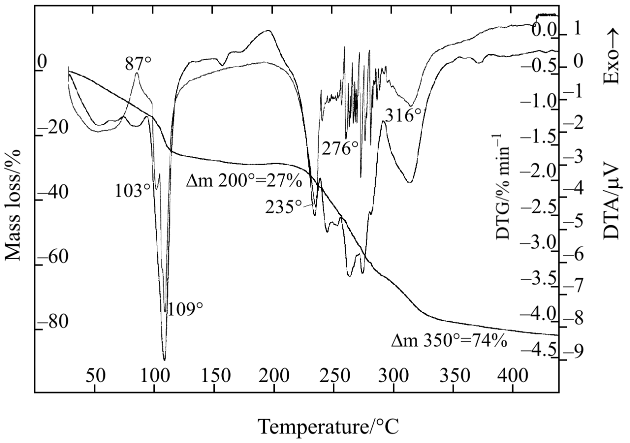

Fig. 3 TG-DTA curves of UF4 curing with 1% ammonium chloride (5 K min^{-1})

From the figure it can be seen that curing exotherm is shifted to higher temperature than in case of UF1. The exothermic peak maximum reveals at 87°C and the water evaporation endotherm at 109°C.

In Fig. 4, curing UF4 without catalyst is illustrated. The same observations as in case of UF1 can be brought out: water evaporation from initial resin begins earlier as polycondensation reaction, and curing takes place in extended temperature region. As compared to curing UF1 without catalyst (Fig. 2), the characteristic temperatures are shifted to higher values.

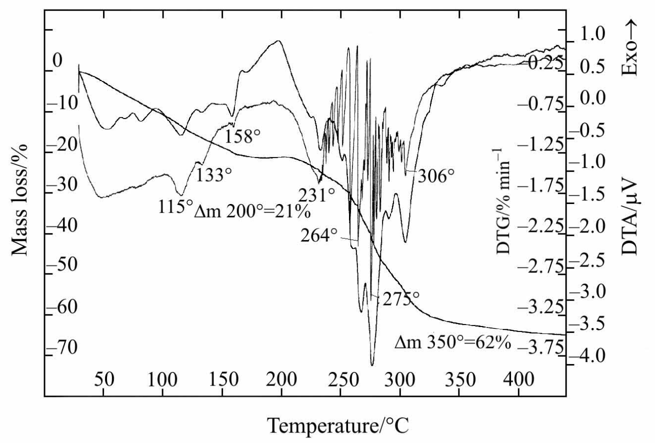

Fig. 4 TG-DTA curves of UF4 curing without catalyst (5 K min^{-1})

In Fig. 5, the mass loss of all studied resins cured without and with 1% ammonium chloride is shown. As can be seen from Fig. 5a, in case of curing without catalyst, the structural differences appear more clearly because of slower polycondensation processes. The degradation is higher in case of methanol-free UF2 which does not contain the more stable methyl ether groups. In curing with catalyst (Fig. 5b), because of a more profound structuration of resins, the mass loss in all cases is quite similar.

The temperatures of exotherms and endotherms depend strongly on heating rate with which the curing experiments are recorded. In Fig. 6, crosslinking exotherms and water evaporation endotherms for resin UF2 at various heating rates are compared. The peak maximum of exotherm shifts from 80 to 91°C with raising heating rate. The use of higher heating rate (10 K min^{-1}) generally reduces the resolution between different events. The lower heating rate (3 K min^{-1}) is much more sensitive to variations. From Fig. 6 it appears that in this case, two endothermic peaks of water evaporation with minimums at 107 and 115°C, derived from two different sources, are revealed. In the present work, mainly the rate of 5 K min^{-1} was used.

For commercial applications, the combination of high reaction heat and fast curing rate is desirable. Observed effects differ with resin type. In Fig. 7, the curing curves of more reactive resin UF1 with 1 and 1.5% ammonium chloride (the amounts commonly used in practice) are compared. Increasing the catalyst content only in this narrow range produces a more reactive system which reveals in somewhat lower temperatures of exotherm and endotherm. Also, the exothermic reaction heat has risen a little. Curing the resin with higher content of catalyst, total mass loss is more extensive due to resin hydrolysis.

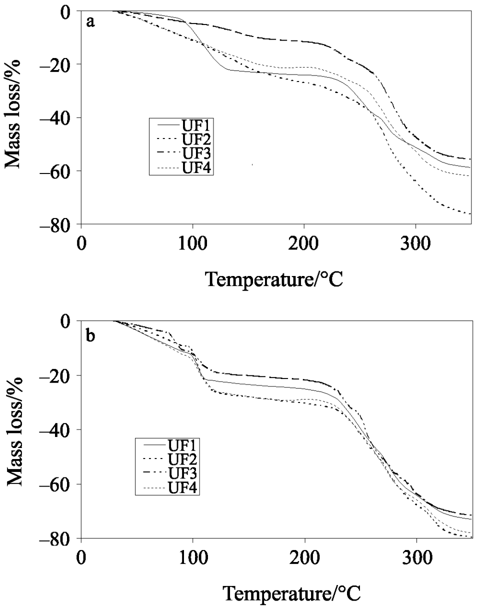

Fig. 5 Mass loss of four UF resins during curing (5 K min^{-1}), a – without catalyst, b – with 1% ammonium chloride

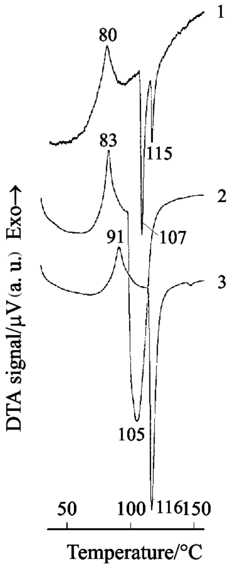

Fig. 6 DTA curves of UF2 curing: 1 – 3 K min^{-1}; 2 – 5 K min^{-1}; 3 – 10 K min^{-1}

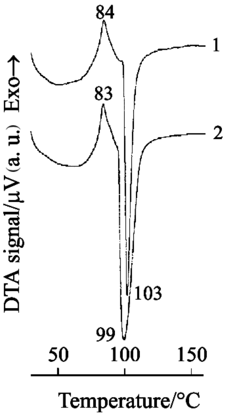

Fig. 7 DTA curves of UF1 curing: 1 – 1.0% and 2 – 1.5% ammonium chloride

When comparing the less reactive resin UF4 with UF1, the changes in peak temperature values depending on catalyst content are less noticeable. Only minor changes occur, increasing the catalyst content in relatively large limits. In Fig. 8, curing exotherms for UF4 depending on catalyst content in the range of 1 to 4% are presented. For more detailed examination of the formation of curing exotherm, in Fig. 8b the peak maximums are shown in expanded scale. It can be seen from the figure that the twofold increase in catalyst content from 1 to 2% diminishes the exothermic peak maximum temperature only 0.4°C. The total shift of exothermic peak maximum in this range is 1.4°C.

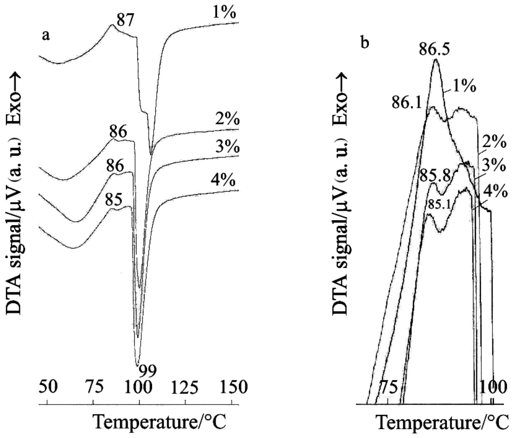

Fig. 8 Dependence of UF4 curing on ammonium chloride content

In the presence of acid catalyst and excess of amino functionalities, resin curing occurs mainly by the formation of methylene groups [12]. From Fig. 8 it is seen that the exothermic behaviour during curing depends on the amount of catalyst. Increase in catalyst content only promotes one part of curing reactions, shifting the exothermic peak to lower temperature. At the same time, higher amount of catalyst approximates the rate of different reactions, giving the other exothermic peak with a maximum in the region of 93–94°C. The possibilities for such kind of behaviour are evident, considering the presence of amino groups and hydroxymethyl groups of different functionality and reactivity in polymeric and monomeric parts of resin, and of very different chain length and branching rate [13]. Also, higher amount of catalyst promotes deeper curing of resin, which results in crosslinking of the most complicated structures giving exothermic effect at higher temperature.

Degradation of cured resins begins with the liberation of formaldehyde from dimethylene ether groups [11]. Clear dependence of peak temperature of endothermic decomposition on acid catalyst content (Fig. 9) is caused by poor resistance of ether structures to acid.

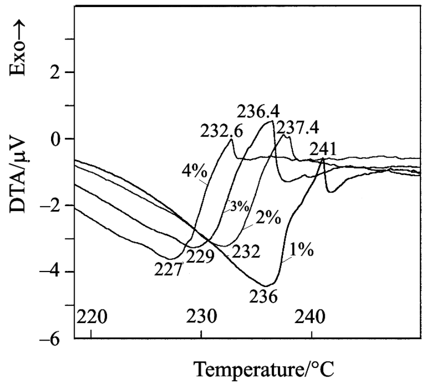

Fig. 9 UF4 decomposition endotherms in the region of 230–240°C depending on ammonium chloride content

In fact, this kind of destruction can be regarded as postcuring of resin, as released formaldehyde participates in further reactions, finally giving more stable methylene groups. Otherwise, dimethylene ether groups in cured resin can be the source of free formaldehyde due to preferred hydrolysis in presence of moisture. At the same time, the conditions favour formaldehyde release from particleboards as compared to further curing reactions.

In several particleboard factories, ammonium chloride is not used as catalyst because of the generation of hydrochloric acid causing corrosion problems. The other commonly used curing catalyst is ammonium sulphate. A set of experiments was performed with UF4 using ammonium sulphate as catalyst. In Fig. 10a, DTA curves up to 350°C depending on catalyst content are presented. In Fig. 10b, the precise structure of curing exotherm is illustrated. Comparing the exothermic peak temperatures with those in Fig. 8, it can be concluded that the same amount of ammonium sulphate promotes the curing process more than ammonium chloride, shifting curing reactions to lower temperature (e.g., in case of 2% catalyst the first exothermic peak maximums are 84.5 and 86.1°C, respectively).

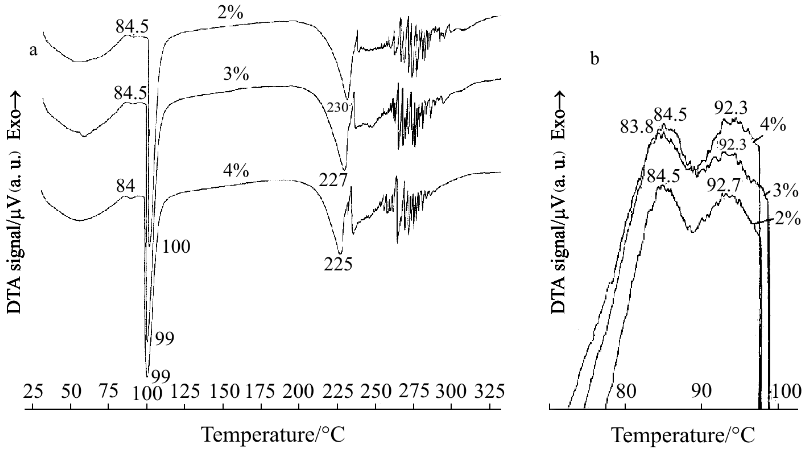

Fig. 10 Dependence of UF4 curing on ammonium sulphate content

From the technological standpoint, it is important to know the behaviour of long-time stored resins in curing process. During resin storage, the structural changes in resin take place. The main reaction during storage is the formation of methylene linkages adjacent to secondary amino groups [12]. This reaction occurs not only between hydroxymethylureas and urea in monomeric part but also between free terminal hydroxymethyl and amino groups in polymeric part of resins. Storage period also involves the migration of hydroxymethyl groups from the polymeric to monomeric resin components [12, 14]. In connection with the decrease of the content of hydroxymethyl groups during storage, the higher temperature values in exothermic curing reaction are revealed. In Fig. 11, curing curves of fresh and aged resins for UF1, UF2 and UF3 are presented.

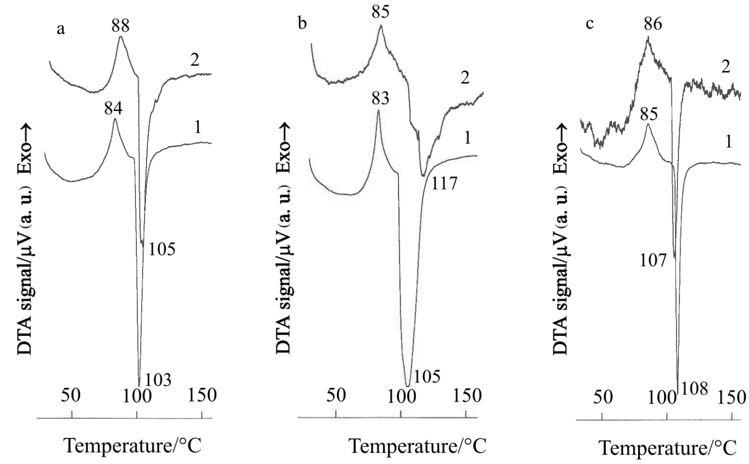

Fig. 11 DTA curves of 1 – fresh and 2 – aged resins curing with 1% ammonium chloride: a – UF1, b – UF2 and c – UF3

From Fig. 11 it appears that the shift of the exothermic peak maximum of aged resin is greater in case of more reactive UF1 reaching to 4°C. In case of UF2 this shift is 2°C and in case of UF3 only 1°C. The last resin is of higher conversion degree as compared with the others [12]. In Fig. 12, DTA curves of cure process for aged (30 days at 25°C) UF4 with ammonium chloride and in alkaline medium without adding catalyst are compared with those of fresh resin.

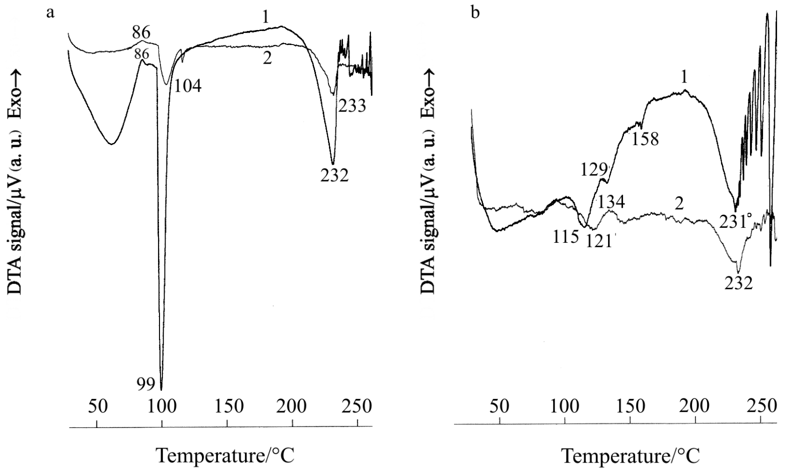

Fig. 12 DTA curves of 1 – fresh and 2 – aged UF4 curing: a – with ammonium chloride; b – without catalyst

In case of aged UF4, no differences in curing exotherm temperatures compared to fresh resin are revealed (Fig. 12a) but as a result of structuration processes during resin storage, exothermic heat of crosslinking is decreased about four times. The shift of the minimum of water evaporation endotherm is 5°C. DTA curve of aged resin in decomposition region (over 200°C) shows only somewhat higher temperature of endotherm (1°C). In curing without catalyst, aged resin reveals very slight peaks in extended temperature region (Fig. 12b).

Conclusions

Curves for commercial UF resins from different suppliers cured with 1 to 4% ammonium chloride show that exothermic reaction of crosslinking with mass loss takes place in all cases at 83–86°C, and the reaction heat evolved is close. Water evaporation from curing system exhibits by large endothermic peak in DTA curve with a minimum at 103–109°C. Common to all resins is that in further heating up to 200°C, no changes in the reaction heat values with simultaneous slight mass loss are observed, explained by the formation of extended polymer chains. At temperatures over 200°C the resins begin to decompose showing series of endothermic and exothermic effects in similar temperature regions. The curing mechanism depends strongly on pH value of the system. Increasing the catalyst content, a more acidic system is produced and the resin crosslinking takes place at lower temperature with somewhat higher reaction heat evolved. The same content of ammonium sulphate, as compared to ammonium chloride, promotes the curing process noticeably more.

UF resins without catalyst, hence in alkaline medium, cure in extended temperature region, and DTA curves have no sharp exothermic peaks. Total resin mass loss during curing is lower in this case.

Aged nearly up to gelation, UF resins reveal higher crosslinking temperatures, and essentially lower reaction heat is evolved. The shift of the exothermic peak temperature as a result of resin storage is higher in case of UF1, which has a lower initial degree of conversion.

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