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Thermal behaviour of hydroxymethyl compounds as models for adhesive resins

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Abstract Urea–formaldehyde (UF) and phenol–formaldehyde (PF) resins are the most widely used wood adhesives. The first stage in resin manufacturing is the formation of methylol derivatives which polycondensation leads to building the tridimensional network. Understanding the behaviour of methylol compounds in curing provides useful information for developing appropriate resin structures. Thermal behaviour of *N,N′*-dihydroxymethylurea, 2- and 4-hydroxymethylphenols, urea and phenol as model compounds for UF, PF and phenol–urea–formaldehyde (PUF) resins was followed by TG-DTA method. The measurements were carried out by the *labsys* instrument Setaram at 30–450 °C in nitrogen flow. The characteristic signals for model compounds and for some reaction mixtures were measured by high resolution ^{13}C NMR spectroscopy.

Keywords Curing · ^{13}NMR spectroscopy ·
N, N′-dihydroxymethylurea ·
Monohydroxymethylphenols · TG-DTA analysis

Introduction

Urea–formaldehyde(UF) and phenol–formaldehyde(PF) resins have been the most widely used wood adhesives for many years [1]. UF resins convince by their high reactivity and good performance in the manufacturing of wood composites and by their low price, however they lack in water resistance of the hardened resin due to the reversibility of the aminomethylene link and hence the susceptibility to hydrolysis [2]. PF resins perform well in producing exterior-quality wood panels, but their main drawback is the lower curing rate than that of amino-type resins [3]. Many attempts have been made to accelerate the curing processes of PF resins, including different catalysts, additives, or modified resin formulas. Considerable attention [3–16] has been given to phenol–urea–formaldehyde (PUF) cocondensed resins to improve the curing behaviour, decrease the emittable formaldehyde, and reduce the resin cost significantly. It is shown in [4, 5] that by mechanical blending of UF resin and alkaline PF resin, the effective cocondensation cannot be expected. In order to develop practical uses it is necessary to introduce cocondensation between phenol and urea during resin synthesis [5].

In the numerous studies of Tomita and co-authors [4–13], the reactions of urea with methylolphenols under acidic conditions were investigated thoroughly. It was found that the cocondensation between *p*-methylol group and urea prevails against the self-condensation of methylolphenols in acidic conditions, and that *p*-methylol group has the stronger reactivity to urea than *o*-methylol group. Several new cocondensed compounds between urea and phenol through methylene linkage have been identified. In these works are established that the chemical cocondensation between resol and amino resins never occurs in alkaline media [13]. Contrary to this, in [14, 15] is

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suggested that, under alkaline conditions both self-condensation of *ortho*- and *para*-hydroxybenzyl alcohol and the condensation of the two hydroxybenzylalcohols with urea occurred at which the last reactions are more rapid than both the self-condensation reactions.

Curing behaviour of synthesised PUF resins has been studied by several authors using different analysis methods. Torsion braid analysis method (TBA) shows that the co-condensed resins displayed almost the same curing behaviour and heat-resistance as a commercial resol PF resin [6, 7, 10]. A great difference could be recognised in thermal properties between the cocondensed resins and the blended resins of UF resin and resol. The heat-resistances of the cocondensed resins were indicated to be superior to those of the mechanical blended resins. The alkaline curing concluded to be better than the acidic curing in attaining great heat-resistance from the cocondensed resins [10].

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used for studying curing behaviour of PUF resol resins with various F/U/P ratios [16]. The results indicated that the pH value played an important role in affecting the shape of the DSC curing curves, the activation energy, and the reaction rate constant. The curing kinetics and network properties of several PUF cocondensed resins were examined by DSC and dynamic mechanical thermal analysis (DMTA) [3]. A kinetic study indicated that the activation energy values of PUF resins are generally higher than those of PF resins during curing processes, but the curing rates of PUF resins are faster than those of PF resins. The rigidity of network for cured PUF resins was lower than that for cured PF resins. The relative performance of the different PF resins coreacted with urea was checked under different conditions by both thermomechanical analysis (TMA) and by preparation of wood particleboard [14].

In this study, thermal behaviour of dihydroxymethylurea and monohydroxymethylphenols as model compounds for UF, PF and PUF resins was followed by simultaneous TG-DTA technique. Curing tests were performed mainly in acid media because of UF resin cure only under acidic conditions while PF resin can cure both in acidic and alkaline conditions.

Experimental

A commercial grade 2-hydroxymethylphenol (*o*-MP) was used after recrystallisation from benzene/ethyl-alcohol mixture 20/1 (T_m 87 °C). 4-hydroxymethylphenol (*p*-MP) was synthesised by the reduction of *para*-hydroxybenzaldehyde with $NaBH_4$ aqueous alkaline solution by cooling. After neutralisation with H_2SO_4 and filtration, *p*-MP was recrystallised from ethyl acetate/hexane mixture 3/1 (T_m 120 °C). *N,N*′-dihydroxymethylurea (DMU) was prepared in the presence of Na_2HPO_4 from urea and formaldehyde 1/2 and recrystallised from ethanol (T_m 136 °C). Reagent-grade phenol (T_m 41 °C) and 5-methylresorcinol ($C_7H_8O_2{\cdot}H_2O$, T_m 58–61 °C) were used.

The characteristic signals for model compounds and for some reaction mixtures were measured by high resolution ^{13}C NMR spectroscopy. A Bruker AMX500 NMR spectrometer with ^{13}C frequency at 125.77 MHz at 25 °C from CD_3OD and DMSO-d_6 solutions by 5 mm ^{13}C–^1H dual probehead was used. Spectra were accumulated into 32 K data point and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. The ^{13}C signals were assigned according to earlier reported in the literature values. Quantitative data were based on integral intensities of the peaks.

TG-DTA measurements were carried out by *labsys*^{TM} instrument Setaram with the heating rate of 5 °C min^{-1} and measuring sensitivity 50 μV. The temperature range scanned was from 20 to 450 °C, and the measurements were recorded in nitrogen flow (40 mL min^{-1}), the mass of the samples being 10–15 mg. The TG-DTA test was carried out with an open standard platinum crucible (100 μL). Temperature calibration was performed with indium. The heat flow on DTA curves was expressed in μV s mg^{-1}.

The curing tests were carried out in a melt. It has been referred that curing conditions were best modelled using a melt reaction [17]. The endotherm characterises both the compound melting and water evaporation from condensation reactions. The use of powder mixtures causes some distortions in melting temperatures of components but is inevitable for avoiding the uncontrollable prepolymer formation. In this study, the peak temperatures and mass loss values are the main apparent indices to characterise the curing system.

Results and discussion

Thermal behaviour of *N,N*′-dihydroxymethylurea

In the manufacturing UF resins, the conditions of synthesis promote the formation of a maximum amount of *N,N*′-dihydroxymethylurea (DMU) in the first step [18]. So, the study of thermal behaviour of pure DMU in different catalytic conditions helps to understand the processes of polycondensation in resin synthesis and curing. In TG-DTA tests, the melting of DMU is revealed in the endotherm which area and peak temperature are influenced by the extent of condensation reactions occurred simultaneously with the melting (Fig. 1a, b).

Only possible route of polycondensation can be the formation of oligomers with dimethylene ether groups. Two

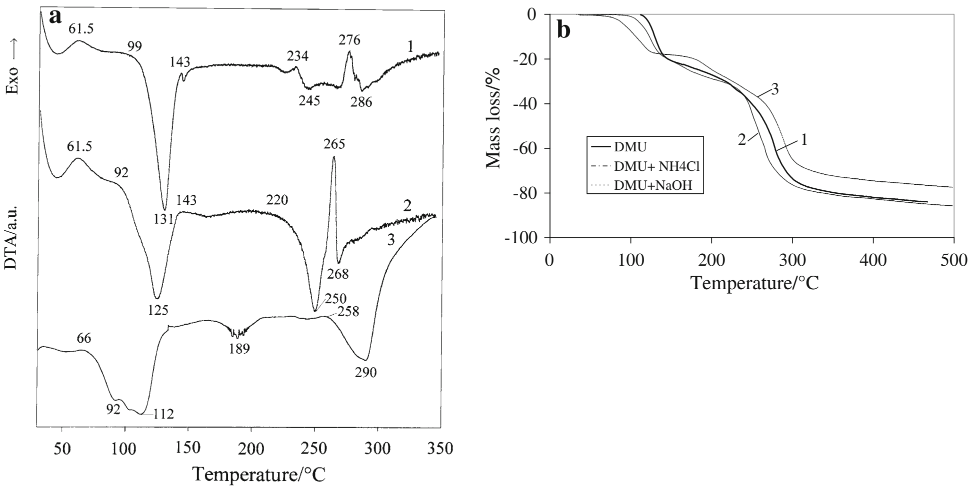
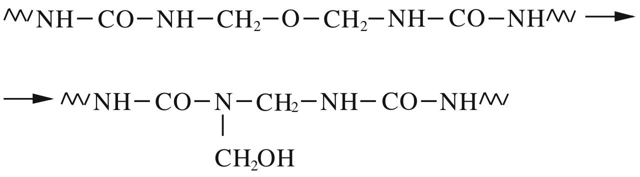


Fig. 1 **a** DTA curves of curing DMU: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH. **b** Mass loss curves of curing DMU: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH

opposite thermal effects influence the melting of DMU. The enthalpy of polycondensation with the liberation of reaction water causes the exothermal effect. The water evaporation from dimethylene ether formation reveals in mass loss during the melting and increases the endoeffect. The rate of mass loss after melting of DMU decreases because of formation of equilibrium mixture of DMU with dimethylene ethers. Temperature-promoted release of formaldehyde from dimethylene ether groups with the formation of methylene linked oligomers causes as the change in equilibrium of components as well a continuous slow mass loss due to evaporation of formaldehyde from the system.

Both, the acidic and alkaline catalyst as additional components favour the melting of DMU at lower temperature (Fig. 1a, in DTA curves 2 and 3, T_m 125 °C and T_m 112 °C, accordingly). At the same time, the extent of formation of dimethylene ethers increases in melting, causing the greater mass loss due to the evaporation of water formed. The extent of polycondensation in catalysed systems is higher, leading to smaller area of endotherm from the melting of DMU. The process of formation of methylene-linked oligomers by formaldehyde release from ethers is accelerated in the presence of catalyst. The endotherm due to the beginning of more intensive formation of methylenes is shifted to lower temperature. The mechanism of formaldehyde release from ethers is dependent on conditions. In process without catalyst, the higher activation energy is needed for temperature-promoted degradation. In presence of alkali, the intermediate isomerisation to hydroxymethyl methylene group before release of formaldehyde is more probable:



$$\sim NH-CO-NH-CH_2-O-CH_2-NH-CO-NH\sim \longrightarrow$$
$$\longrightarrow \sim NH-CO-\underset{\substack{|\\ CH_2OH}}{N}-CH_2-NH-CO-NH\sim$$

The absence of trisubstituted urea in alkali-treated product supports this mechanism [18]. The acid catalyst promotes an intermediate formation of azomethylene derivatives of the structure $–N=CH_2$, accompanied with higher mass loss due to the water evaporation and subsequent formation of structures with trisubstituted urea.

Thermal behaviour of monohydroxymethylphenols

Mechanism and kinetics of the self-condensation reactions of hydroxymethylphenols have been investigated by many authors [19–26]. The curing behaviour of mono- and dihydroxyphenols, also that of PF resol resins have been studied by DSC [22–24]. In the present study, thermal behaviour of *o*-MP and *p*-MP was followed in different media.

In uncatalytic conditions, the similar behaviour of *o*- and *p*-monohydroxymethylphenol (Fig. 2) was substantiated by

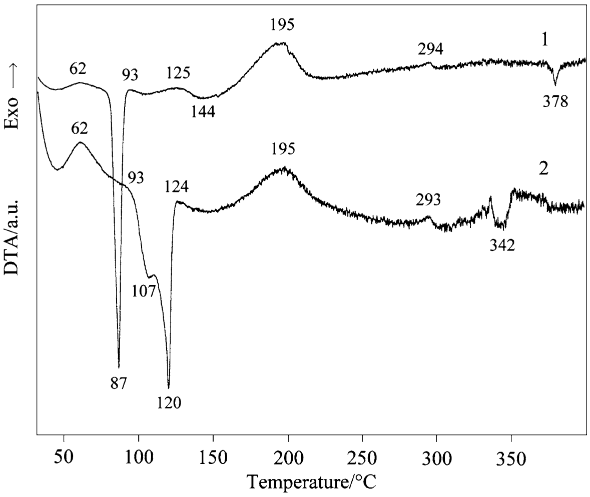


Fig. 2 DTA curves of curing methylolphenols without catalyst: 1—*o*-MP, 2—*p*-MP

the formation of dimethylene ether derivatives (T_p 62 °C) and their following splitting by free aromatic positions predominantly to *o,p′*-methylene linked phenolic polycondensates in both cases [26].

In the presence of catalysts, the polycondensation route changes considerably. From Fig. 3, it can be seen that after melting hydroxymethylphenols (T_m 87 °C for *o*-MP and T_m 120 °C for *p*-MP) the acid catalyst promotes the direct *o,p′*-methylene formation in reaction of formed carbanion with free aromatic position. Due to the higher reactivity of *p*-MP, the exotherm (curve 2) appears at lower temperature in very narrow range (T_p 101 °C) as compared to exotherm for the polycondensation of *o*-MP (T_p 117 °C). In the last case the partial formation of *o,o′*-methylenes broadens the exotherm to the higher temperature. High thermal stability of methylene-linked phenolics is consistent with the further insignificant changes in DTA curves.

The direct methylene formation proceeds also in alkaline catalysis by phenoxide ions [17] (Fig. 4). As compared to acid catalysis, the activation energy is higher, and methylene formation occurs consequently at higher temperature. The difference between two catalytic conditions is more pronounced in case of *o*-MP as compound of lower reactivity (Figs. 3 and 4; curves 1). The well-known more complicated oligomeric constitution in presence of alkaline catalyst broadens the temperature range of methylene formation. In case of *p*-MP (Fig. 4, curve 2) the melting endotherm is overlapped by the exotherm because of enthalpy of polycondensation. On the basis of exotherm shapes it can be supposed that the formation of *o,p*-methylene linked dimers from *p*-MP occurs with the highest rate.

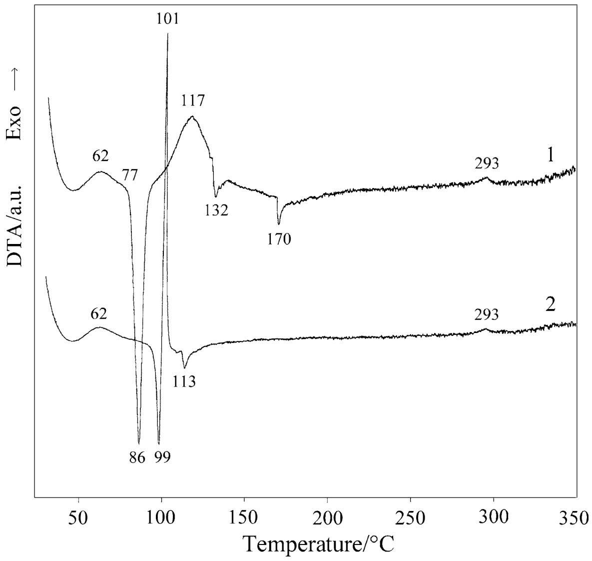


Fig. 3 DTA curves of curing methylolphenols with 2% NH_4Cl: 1—*o*-MP, 2—*p*-MP

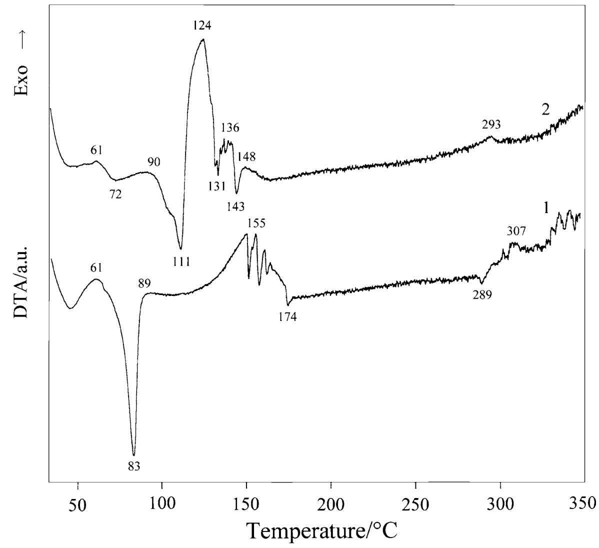


Fig. 4 DTA curves of curing methylolphenols with 2% NaOH: 1—*o*-MP, 2—*p*-MP

In all three catalytic conditions, the mass loss curves have similar shape for *o*-MP and *p*-MP but water elimination in case of *p*-MP is decelerated as compared to *o*-MP due to tighter network structure.

Thermal behaviour of the mixtures of *N,N′*-dihydroxymethylurea with phenols

An influence of phenolic compound depends on its reactivity with formaldehyde. In uncatalytic conditions, at 41 °C melted phenol favours the melting of DMU at lower temperature of T_m 122 °C (Fig. 5). The phenolic medium accelerates the formation of dimethylene ethers in melting of DMU and increases their equilibrium amount. It is revealed in substantially greater mass loss in melting of DMU because of evaporation of water. As well the enthalpy of ether formation leads to the diminished endothermal effect. No essential changes can be observed in the temperature promoted release of formaldehyde from dimethylene ethers as compared to that without phenol. It means that the conditions used do not increase the participation of phenol in polycondensation, and the evaporation of formaldehyde is preferred, as compared to water elimination.

High tendency to cocondensation reaction between DMU and phenol can be observed in the presence of acid catalyst (Fig. 6).

The melting endotherm with peak maximum at 68 °C is revealed weakly due to the overlapping with the great exothermal effect accompanied with the cocondensation at remarkably low and narrow temperature range (peak temperature of exotherm at 76 °C). An intensive formation of

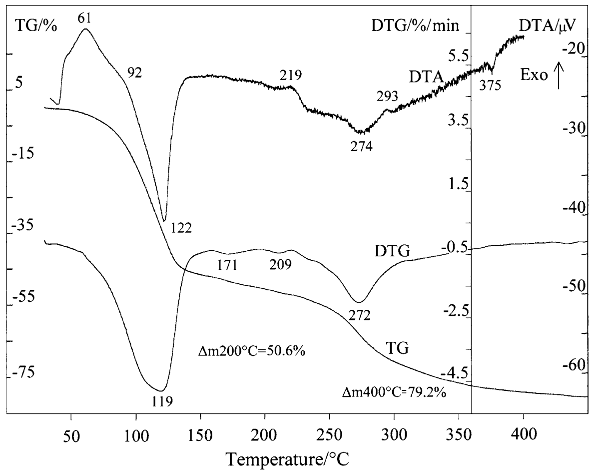


Fig. 5 TG-DTA curve of curing DMU with phenol without catalyst

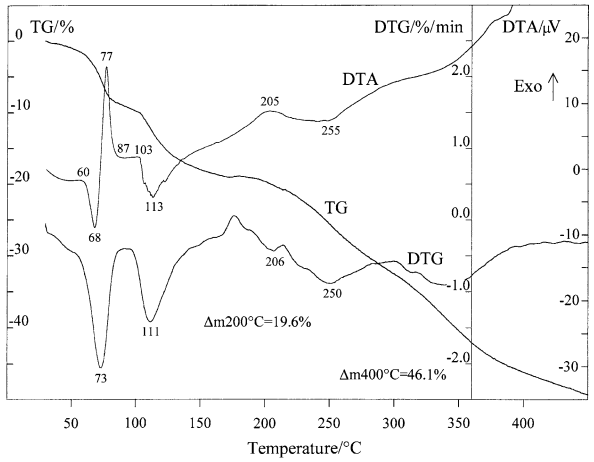
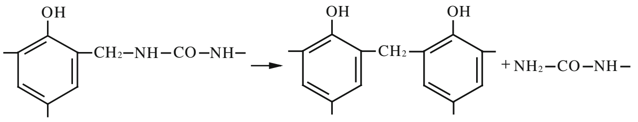


Fig. 6 TG-DTA curve of curing DMU with phenol (2% NH_4Cl)

water in cocondensation increases suddenly its amount and shifts the main mass loss due to evaporation of water to the following period. The endotherm with peak maximum at 113 °C appears mainly due to this process but the participation of cocondensates with unstable aminomethylene groups in following secondary reactions should be considered also:



DMU, which is not bonded in cocondensate, behaves as described previously.

Use of more reactive 5-methylresorcinol (5-MR) leads to the great difference in reaction route in uncatalytic conditions (Fig. 7).

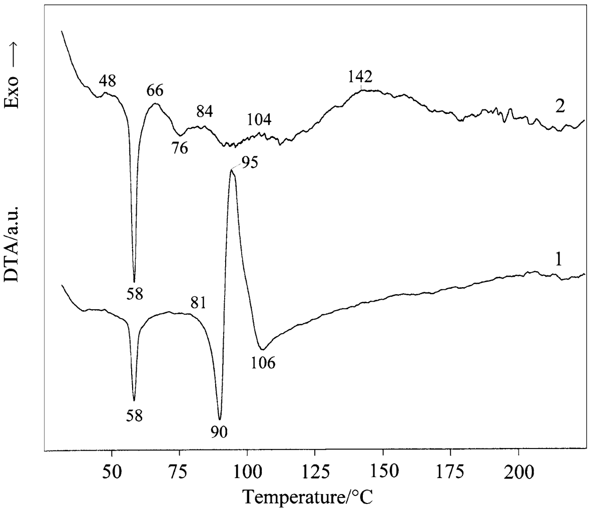


Fig. 7 DTA curves of curing DMU with 5-MR, 2 °C min^{-1}: 1—without catalyst, 2—2% NH_4Cl

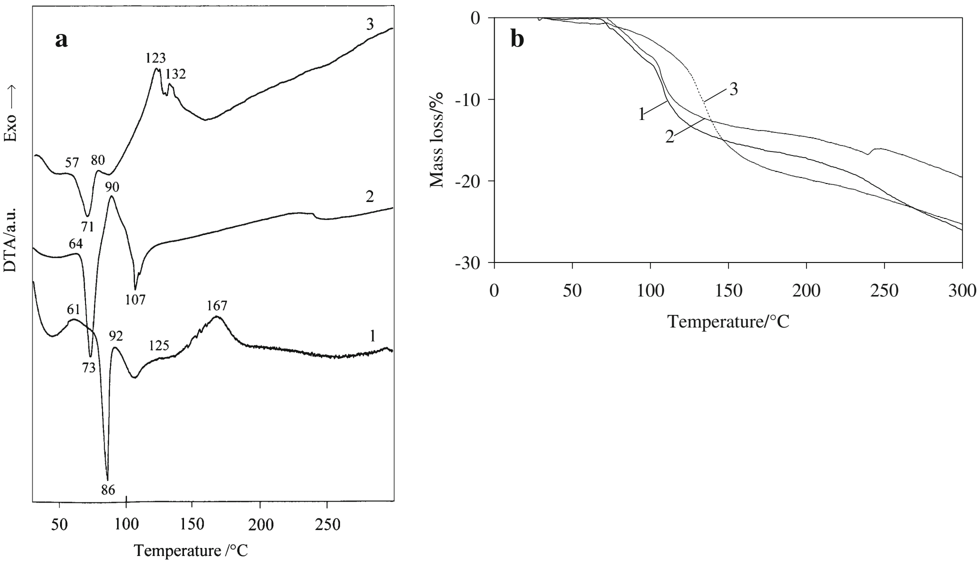
As it can be seen from Fig. 7 (curve 1), after melting of 5-MR H_2O (T_m 58 °C) the melting endotherm of DMU at lowered temperature (T_m 90 °C) is interrupted by the strong opposite exothermal effect due to intensive cocondensation reaction between DMU and 5-MR. The isomeric constitution of cocondensate is different due to multifunctionality of both reagents [27], but the narrow temperature range points to the similar activation energy of their formation. Mass loss in reaction system begins with the evaporation of water from 5-MR H_2O and accelerates after the strong exotherm due to the accumulation of water from cocondensation reaction. The acid catalyst diversifies the course of polycondensation reactions (Fig. 7, curve 2). After melting of 5-MR H_2O, the acid catalyst promotes the formation of dimethylene ether derivatives during the melting of DMU which are split by free aromatic positions to cocondensates and then to the most stable methylene-linked phenolic polycondensates. The high content of initial hydroxymethyl groups over final stable methylene groups causes the continual mass loss due to the evaporation of condensation water and released formaldehyde.

Thermal behaviour of the mixtures of *N,N′*-dihydroxymethylurea or urea with monohydroxymethylphenols

Uncatalytic conditions favour separate polycondensation of components. It can be seen from Fig. 8a (curve 1) that, because of intensive formation of both dimethylene ether derivatives at the same time, the melting endotherm of DMU is diminished.

The great mass loss during melting verifies this opinion (Fig. 8b, curve 1). The splitting of phenolic dimethylene

Fig. 8 **a** DTA curves of curing DMU with *o*-MP: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH. **b** Mass loss curves of curing DMU with *p*-MP: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH

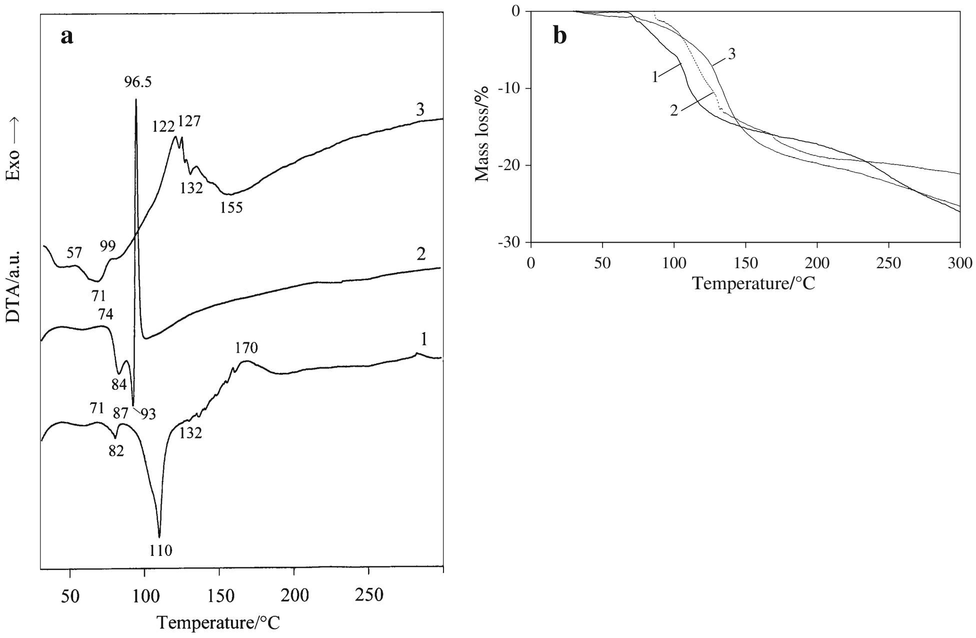


ethers by free aromatic positions leads to methylene-linked phenolics. The enthalpy of this polycondensation is expressed by the exotherm with the peak temperature at 168 °C. Some amount of formaldehyde released from dimethylene ether of urea reacts with *o*-MP, increasing the amount of phenolic methylene derivatives in mixture and consequently the enthalpy of polycondensation. The continuous fast mass loss is connected with evaporation of water of polycondensation of both components and released formaldehyde.

The thermal behaviour of mixture of *p*-MP with DMU in uncatalytic conditions is similar (Fig. 9a, b). Only the melting endotherm of DMU is not visible as the opposite exotherm from formation of *p,p′*-dimethylene ether is predominant (Fig. 9a, curve 1). The splitting of phenolic dimethylene ethers with aromatic positions in case of both methylolphenols mostly leads to *o,p′*-methylenes and consequently, occurs at the same temperature. It can be supposed that uncatalytic conditions do not favour the formation of unsymmetrical dimethylene ethers as intermediates.

In alkaline conditions the presence of DMU has insignificant influence on the direct methylene formation in polycondensation of both methylolphenols (Figs. 8a and 9a, curves 3). The polycondensation enthalpies reveal at the similar temperature ranges of 120-140 °C. It is not clear why DMU has some accelerating effect on the formation of methylene-linked phenolics only in case of polycondensation of *o*-MP.

Fig. 9 **a** DTA curves of curing DMU with *p*-MP: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH. **b** Mass loss curves of curing DMU with *p*-MP: 1—without catalyst, 2—2% NH_4Cl, 3—2% NaOH



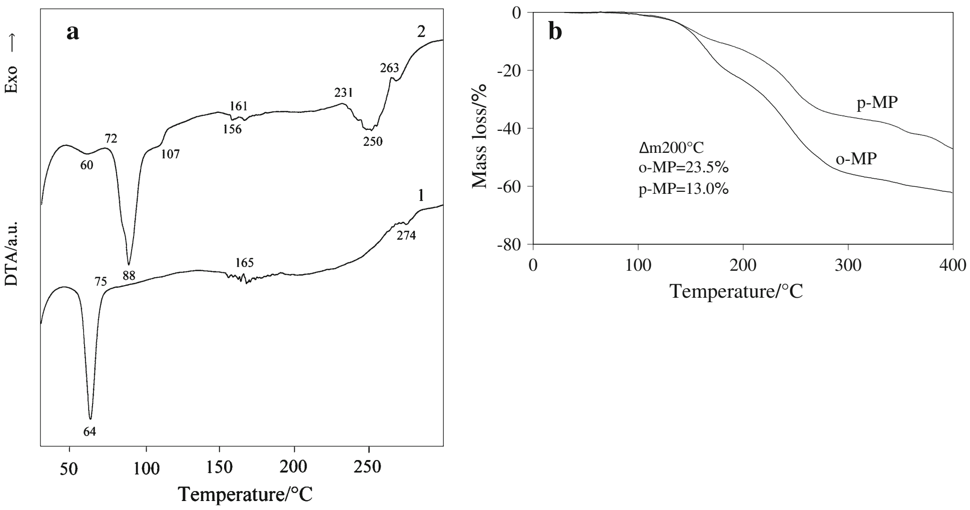


Fig. 10 **a** DTA curves and **b** Mass loss curves of curing urea with methylolphenols (2% NH_4Cl): 1—*o*-MP; 2—*p*-MP

The most favoured conditions for the formation of cocondensates are created in the presence of acid catalyst. As it was shown above (part 3), the previous binding of hydroxymethyl group in urea leads to the quantitative cocondensation (Fig. 6). The acid catalyst promotes the polycondensation of methylolphenols (Fig. 3) as well.

Otherwise, in the mixtures of urea and methylolphenols, the formation of cocondensate is preferred (Fig. 10).

As an example, in Fig. 11 the ^{13}C NMR spectrum of reaction system of urea and *p*-MP is presented which explains the reaction trend in DTA curve.

On the basis of the spectrum it can be concluded that, at half of conversion of *p*-MP, the content of cocondensate methylenes (signal at 44–45 ppm) exceeds the content of *o,p*-methylenes (35–36 ppm) more than nine times, due to homopolycondensation. Also, the intermediate *p,p′*-dimethylene ether (72–73 ppm) is preferably split by urea to cocondensate methylene as compared to release of formaldehyde. By reaching the quantitative reaction (5 h at 100 °C), about 94% of methylenes are bonded in cocondensate. The different cocondensate derivatives appear due to mono-, bis- and trisubstitution in urea with *p*-hydroxybenzyl groups. In case of *o*-MP, cocondensates of urea with *o*-hydroxybenzyl groups (signal at 40–41 ppm) arose mainly due to splitting the first-formed *o,o′*-dimethylene ether groups (69–70 ppm) by urea. Essentially lower reactivity of *o*-MP was ascertained. In case of 60% conversion of *o*-MP (12 h at 115 °C), the product contains predominantly cocondensates but the amount of phenolic methylene groups is also somewhat higher (the ratio of intensities of signals is about of 5.5). The shape of DTA curves (Fig. 10a) without remarkable thermal effects shows that the endoeffect of continuous water evaporation is compensated by the opposite enthalpy of splitting the intermediate phenolic dimethylene ethers by urea.

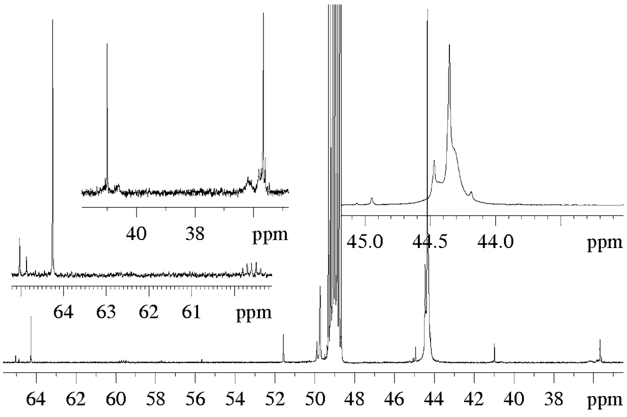
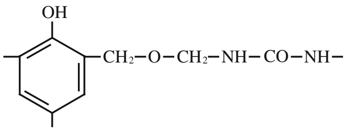


Fig. 11 ^{13}C NMR spectrum of reaction system of urea and *p*-MP in methylene region from CD_3OD solution, 17,500 scans

A different situation appears when both reagents are hydroxymethylated. After the melting of *o*-MP, (Fig. 8a) the great exotherm (T_p 90 °C) represents the enthalpy of formation of dimethylene ethers, predominantly of the unsymmetrically substituted structure:



The following changes include the recombinations in the equilibrium mixture of ethers as well as the slow release of formaldehyde with the formation of methylene-linked derivatives. *p*-MP in the same situation (Fig. 9a, curve 2) behaves differently. The melting of highly reactive *p*-MP occurs with the simultaneous formation of *p,p′*-dimethylene ether which is split immediately by *ortho* aromatic positions to *o,p′*-methylene linked phenolics. The fast mass loss due to evaporation of the formed water supports the proposed mechanism. The equilibrium formation of dimethylene ethers from DMU occurs as it was described above.

Conclusions

1. Thermal behaviour of hydroxymethyl compounds depends considerably on catalyst, and also on partial polycondensation occurred in some systems already during melting of components.
2. The polycondensation of *N,N′*-dihydroxymethylurea accelerates in presence of acid and alkaline catalysts and is dependent mainly on release of formed formaldehyde from equilibrium system.
3. In the polycondensation of monohydroxymethylphenols, *o,p′*-methylene formation occurs with highest rate immediately after melting in acidic conditions, and in uncatalytic conditions the reaction is retarded due the formation of dibenzylethers.
4. Only acid catalyst promotes the copolycondensation in systems *N,N′*-dihydroxymethylurea/phenol and monohydroxymethylphenol/urea with the considerably higher rate in the first case.
5. Substitution of phenol with high reactive 5-methylresorcinol leads to copolycondensation in uncatalytic conditions as well.
6. Acid catalyst fosters copolycondensation in mixtures of *N,N′*-dihydroxymethyurea/monohydroxymethylphenols with the formation of dimethylene ethers which are split subsequently with free *ortho*- and *para*-aromatic positions.

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