

Thermal behaviour of melamine-modified urea–formaldehyde resins

Kadri Siimer · Tiit Kaljuvee · Tõnis Pehk · Ilmar Lasn

MEDICTA2009 Special Issue
© Akadémiai Kiadó, Budapest, Hungary 2009

Abstract Thermal behaviour of industrial UF resins modified by low level of melamine was followed by TG-DTA technique on the *labsys*TM instrument Setaram together with the ¹³C NMR analysis of resin structure and testing boards in current production at Estonian particleboard factory Pärnu Plaaditehas AS. DTA curve of UF resin which has been cocondensed during synthesis with even low level of melamine shows the shift of condensation exotherm and water evaporation endotherm to considerable higher temperatures. The effect of melamine monomer introduced to UF resin just before curing was compared. The effect of addition of urea as formaldehyde scavenger was studied.

Keywords Curing · ¹³C NMR · Particleboards · TG-DTA analysis · Urea–formaldehyde modified resins

Introduction

Formaldehyde emission from urea–formaldehyde(UF) resin-bonded wood products is a major problem in the particleboard and plywood industry [e.g. 1–9]. In the studies of many authors it has been pointed out that

formaldehyde is mainly emitted from the following sources: residual formaldehyde in the resin; formaldehyde generated by condensation reactions between hydroxymethyl groups and formaldehyde released by hydrolytic degradation of weakly bonded structures in cured resins. The reversibility of the aminomethylene linkage in UF resins explains the susceptibility to hydrolysis [4].

During recent years, a lot of work has been done in Europe to reduce the value of the emittable F from wood-based boards to the world's toughest emission standard—the Japanese F standard, applicable to fixed interiors and building materials [5]. This limit for F of 0.3 mg L⁻¹ (by desiccator method) for particleboards was found to be equivalent to 0.04 mg m⁻³ in the European chamber test and 2.8 mg/100 g board by the perforator test. Today, particleboards of E1 emission class in Europe is still dominating and the present level is of about 5 mg/100 g board [8]. Demand for UF resin of reduced emission has grown recently, therefore the synthesis of low-emittable formaldehyde resins has been studied by several authors using various modifiers, e.g. melamine, phenol, resorcinol and borax [10–18].

The release of formaldehyde is predominantly determined by the mole ratio of formaldehyde to urea (F/U) in the adhesive system. The lower the mole ratio, the lower the post-production formaldehyde emission out of the produced board. However, the reduction of the F/U ratio has great impact on the properties of the adhesive. Free formaldehyde in the resin is necessary to induce the hardening reaction through the reaction with the hardener; hence, this reduces the reactivity of the resin resulting in a prolonged curing time. Also, because formaldehyde serves as a crosslinker of the chains, the degree of crosslinking decreases in the cured network causing lower mechanical properties. An alternative for overcoming the undesired

K. Siimer (✉) · T. Kaljuvee
Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
e-mail: ksiimer@staff.ttu.ee

T. Pehk
National Institute of Chemical and Biological Physics, Akadeemia tee 23, 12618 Tallinn, Estonia

I. Lasn
Pärnu Plaaditehas AS, 12 Savi, 80041 Pärnu, Estonia

reduction of the ratio F/U is the addition of scavengers binding free formaldehyde that is released during resin curing. This is attained mainly by the addition of substances containing NH or NH₂ groups [8, 15]. In general, known and used in particleboard manufacturing practice is the method of binding free formaldehyde with urea [e.g. 16, 19, 20]. The incorporation of a low content of melamine during the synthesis of UF resin is described by several authors [e.g. 6, 11, 12, 15]. Considering the high price of melamine, the content of melamine in resins is reduced to as low as possible depending on recommended emission level.

Curing behaviour of regular UF and modified UF resins has been studied by many different methods mainly using DSC [13, 18, 21], DMTA [18], DMA [12] and gravimetric analysis [7]. In the present study, the curing process of melamine-modified UF resins was followed by the TG-DTA technique which makes it possible to simultaneously reveal the heat of curing process and the thermal stability of cured resin. Thermal behaviour of modified UF resins was studied together with the ¹³C NMR spectroscopic analysis of resin structure and testing particleboards in current production at Estonian particleboard factory Pärnu Plaaditehas AS.

The objective of the study was to evaluate thermal behaviour of selected industrial resins and to compare the properties of particleboards bonded by these resins. The final result of the investigation is expected to contribute the production of low formaldehyde-emittable particleboards. The study of the curing process of modified UF resins and thermal stability is of great importance both from theoretical and practical point of view.

Experimental

For the present study, three modified UF resins were obtained from commercial sources and derived from the current production line of Pärnu Plaaditehas AS. UF resins of with low melamine content were selected and labelled as UFM1, UFM2 and UFM3. Thermal behaviour of these resins was studied and compared with that of regular UF resins of the same enterprises UF1 and UF2. Likely enough, used modified resins are manufactured by different technology but for the all modern commercial resins is common the low F/(NH₂)₂ mole ratio in the narrow ranges of 0.85–1.1 for reducing formaldehyde emission. In Table 1, the standard characteristics of the studied resins are presented.

Industrial resins from different enterprises, presumably of different synthesis procedures may reveal different curing parameters.

Earlier, the laboratory resins with low level of melamine of 2–6 mass% were synthesised and tested [16]. The

Table 1 Standard analysis of industrial UF resins

Characteristics	UF1	UF2	UFM1	UFM2	UFM3
Dry solids 105 °C, 3 h/%	69.0	68.0	69.1	68.2	67.0
pH 25 °C	8.6	8.0	8.5	7.9	8.5
Viscosity 25 °C/mPa s	305	361	305	345	306
Density 25 °C/g cm ⁻³	1.280	1.288	1.285	1.297	1.290
Gel time 100 °C/s	54	49	104	92	80
Free formaldehyde/%	0.12	<0.2	0.15	<0.2	0.15
Water tolerance	1:3	1:6	1:5	1:4	1:3
Mole ratio F/U + M	1.06	1.065	1.00	0.95	0.90

synthesis was as a typical multistep procedure with the first reaction stage of F/U = 2.1, after acidic condensation followed by the reaction of melamine in alkaline media, and the second part of urea was added to mole ratio of components as F/U + M = 1.05. In [11], laboratory resins were synthesised with melamine levels up to 10 mass%.

The chemical structure of resins was analysed by high resolution ¹³C NMR spectroscopy 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 point and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra, 25,000–30,000 scans were accumulated. Chemical shifts were reported respectively to DMSO-d₆ central signal at 39.5 ppm. The peak assignment is according to our previous studies [e.g. 19] and those of the other authors [e.g. 6]. The integral values of main structural groups define the resin structure. 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 of 150–165 ppm gives the content of free urea, mono- and di(tri)substituted urea and triazine region of 166–168 shows the substitutions of melamine. Based on the ratios of characteristic signal intensities of triazine carbon of melamine and carbonyl carbon of urea in ¹³C NMR spectra, the melamine/urea mole ratio in the resins was estimated.

TG-DTA measurements were carried out as in our earlier studies [e.g. 22, 23] 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 nitrogen flow (40 mL min⁻¹), the mass of the samples being 10–15 mg. The TG-DTA analysis was carried out using 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. Enthalpy of the curing

Table 2 ^{13}C NMR analysis of UF resins modified with low melamine content

Structural fragment	ppm	UF1	UF2	UFM1	UFM2	UFM3
Distribution of bound formaldehyde						
Methylenes						
$\text{HN}\underline{\text{C}}\text{H}_2\text{NH}$	45–48	16.8	12.4	12.7	14.3	14.5
$\text{HN}\underline{\text{C}}\text{H}_2\text{N}(\text{CH}_2)$	52–54	14.4	17.3	14.9	14.8	14.3
$\text{N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{N}(\text{CH}_2)$	59–60	1.0	1.2	1.1	1.2	0.5
Methylols						
$\text{HN}\underline{\text{C}}\text{H}_2\text{OH}$	64–65	47.4	35.8	41.1	31.9	42.7
$\text{N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{OH}$	70–71	4.3	15.2	8.2	14.9	8.4
$\text{N}(\underline{\text{C}}\text{H}_2\text{OH})_2$	67–68					
Dimethylene ethers						
$\text{HN}\underline{\text{C}}\text{H}_2\text{O}\underline{\text{C}}\text{H}_2\text{NH}$	68–70	9.6	0.7	9.3	12.9	11.1
$\text{N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{O}\underline{\text{C}}\text{H}_2\text{NH}$	74–75	2.0	4.7	3.7	5.3	3.0
Methylene methylethers						
$\text{HN}\underline{\text{C}}\text{H}_2\text{OCH}_3$	73–74	3.0	0.6	3.2	1.5	3.5
$\text{N}(\text{CH}_2)\underline{\text{C}}\text{H}_2\text{OCH}_3$	77–79	0.7	0.5	2.6	1.3	0.9
Amine $\text{N}(\underline{\text{C}}\text{H}_2)$	57–58	0.2	0.2	0.4	0.6	0.4
Methylene glycols (formaldehyde)	83–95	0.6	1.4	2.8	1.3	0.7
Carbonyl region						
Free urea	161	21.2	30.8	27.4	32.8	33.7
Monosubstituted urea	159–161	46.6	35.8	50.5	34.4	38.2
Di- and trisubst. ureas	158–159	28.3	31.4	19.4	29.3	26.2
Cyclic ureas		3.9	2.0	2.7	3.5	1.9
Triazine region						
Free melamine	168	-	-		Unresolved	
Monosubstituted melamine	167–168			27.9		32.5
Di- and trisubstituted melamine	166–167			72.1		67.5
Triazine/carbonyl mole ratio		-	-	5.2/94.8	3.2/96.8	4.6/95.4

reaction is not exactly determined, as the characteristic exoeffect in DTA curve frequently is overlapped by water evaporation endotherm. The exothermic peak temperatures (T_p) and mass loss values are the certain indices to characterise the curing system. Resin cure was catalysed with 2% of ammonium chloride (20% solution). The interpretation of DTA curves is based on our earlier investigations in the field of UF and MUF resins [19, 22].

Results and discussion

In Table 2, the data from ^{13}C NMR spectroscopic analysis of melamine-modified commercial resins are presented in comparison with regular UF resins.

As it can be seen from table, the total content of main structural groups (methylenes, methylols and dimethylene ethers) is quite similar. The greatest difference lies in the content of unreacted urea in resins which appears to be substantial in mixing adhesive for particleboard

manufacture. The condensation degree (content of methylene groups) is to some extent lower in case of melamine-modified resin as compared to regular UF resin. The value of molar ratio triazine/carbonyl refers to the content of melamine in resins approximately of 1.5–2.5 mass%. The specific for UF2 and UFM2 is the high content of branched methylols which condensation leads to the tighter resin network.

In Figs. 1 and 2, typical thermograms of the industrial UF1 and UF2 resins cured with 2% of NH_4Cl are presented. Both thermograms reveal the similar shape of DTA and mass loss curves. The exothermic peak temperatures (T_p) of U–F condensation are situated at 81 and 83 °C and water evaporation endotherms at 103 and 111 °C, accordingly. Although UF2 show a lower gel time at 100 °C (Table 1), the remarkable higher content of branched structures as compared to UF1 (Table 2) causes differences in the peak temperatures, particularly differs rate of water evaporation during condensation ($T_p = 103$ and 111 °C). Noticeable degradation of cured resins begins above 230 °C with $T_p = 230$ and 231 °C. For comparison

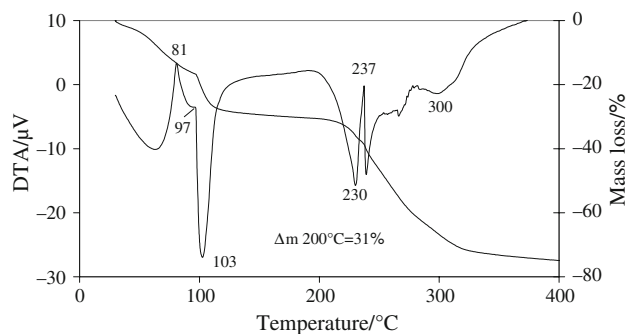


Fig. 1 TG-DTA thermogram of regular UF1 curing with 2% of NH_4Cl

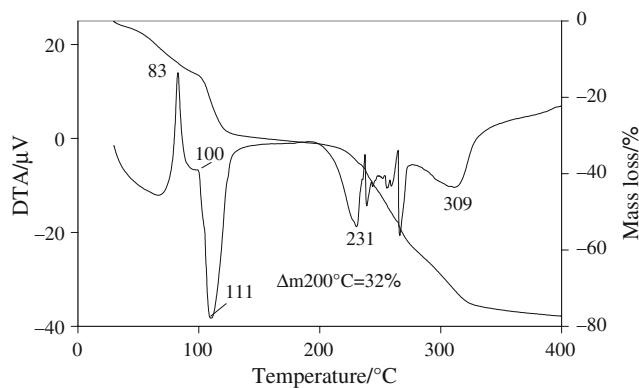


Fig. 2 TG-DTA thermogram of regular UF2 curing with 2% of NH_4Cl

of the resins' mass loss in all experiments, these values are pointed out at the same temperature of 200 °C, that is after proceeding curing and before resin degradation. In Figs. 1 and 2, these values are similar for both resins, 31–32 mass%.

The situation is different if even a little amount of melamine is incorporated in UF resin structure during synthesis. As it was mentioned above, the synthesis of modified resin is usually realised as a multi-step procedure [11, 16]. The melamine content influenced the resin structure during curing by increasing the branched-type methylene bond, curing process proceeds in larger temperature ranges than that of regular UF resin and the shape of the curing curve for melamine-modified resin is different. The more cross-linked structure in the cured resin contributes to greater bond strength.

In Fig. 3, the thermogram of melamine-modified resin UFM1, estimatedly containing 2 mass% of melamine (Table 2) is presented. As compared to UF1, DTA curve of cocondensed with melamine resin shows the shift of U–F condensation exotherm by 6 °C ($T_p = 87$ °C), the broad peak at 107 °C is revealed and water evaporation endotherm is shifted ($T_p = 117$ °C). The peak at 107 °C can be attributed to the reaction of melamine amino groups with

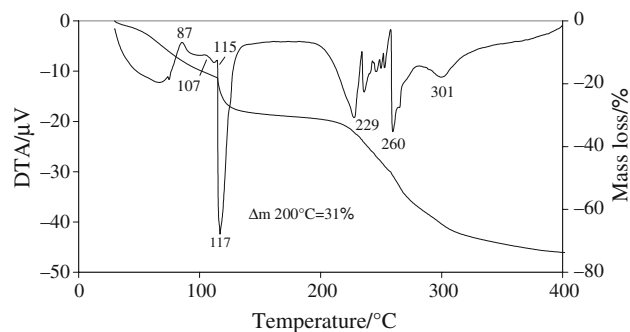


Fig. 3 TG-DTA thermogram of modified UFM1 curing with 2% of NH_4Cl

urea methylol groups. Noticeable higher curing temperature in case of cocondensed with even small amount of melamine is explained by the buffering capacity of triazine ring. The mass loss value is the same as in case of UF1 (31 mass%).

The thermogram of UFM2 (Fig. 4) also shows the shift of peaks to considerable higher temperatures. As the content of melamine in this resin is lower (Table 2), the peak of urea–melamine cocondensation on DTA curve is not revealed but the shift of shoulder from 100 to 121 °C gives evidence about of formation of additional linkages. UFM2 reveal water evaporation at $T_p = 122$ °C. High content of branched methylols in resin (Table 2) causes the formation of more branched structure during curing. Mass loss of UFM2 up to 200 °C is low as compared to UFM1 due to hindered water evaporation from tighter network of cured resin.

In Fig. 5, TG-DTA thermogram of resin UFM3 is shown. A little exotherm ($T_p = 100$ °C) may be attributed to urea–melamine reaction [22]. The exotherm shows smooth transition to endotherm with $T_p = 108$ °C. The evaporation of water at considerable lower temperature compared to the other resins refers to insufficient cross-linking of network structure depending on the low mole

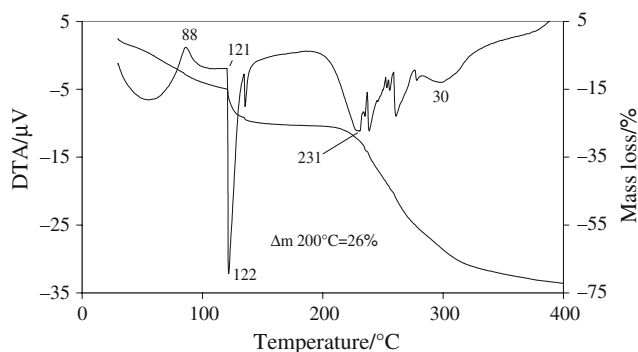


Fig. 4 TG-DTA thermogram of modified UFM2 curing with 2% of NH_4Cl

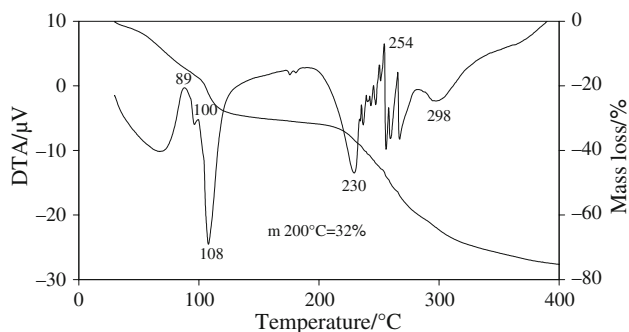


Fig. 5 TG-DTA thermogram of modified UFM3 curing with 2% of NH_4Cl

ratio of F/U + M and high content of unreacted urea in UFM3 (Fig. 5).

In regards to reducing formaldehyde emission from particleboards, several authors have noticed that more effective than the incorporation of melamine into resin structure during synthesis is the addition of melamine monomer into adhesive mix just before curing [e.g. 15]. Considering the sufficient content of reactive methylol groups in all UF resins ($\sim 50\%$ of bound formaldehyde), cocondensation reaction should take place readily between methylols and melamine amino groups during curing.

The experiments were performed to follow thermal behaviour of UF1 resin with melamine monomer added directly before curing in amount approximately corresponding to quantity in cocondensed resin (2 mass%). In Fig. 6, the enlarged curing peaks of regular UF1, UF1 with 2 mass% of added melamine and cocondensed with assumably 2% of melamine UFM1 are compared. DTA curves 2 and 3 show that U–F homocondensation reaction takes place at similar temperatures in both state of melamine ($T_p = 86$ and 87 °C) but water evaporation begins earlier in case of directly added melamine ($T_p = 113$ and 117 °C). It can be seen from Fig. 7 that, although the rate

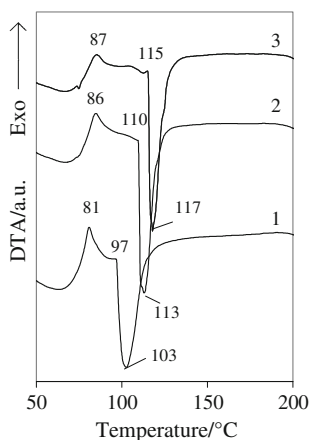


Fig. 6 DTA curves of curing: 1 regular UF1, 2 UF1 with 2% of added melamine, 3 cocondensed with 2% of melamine UFM1

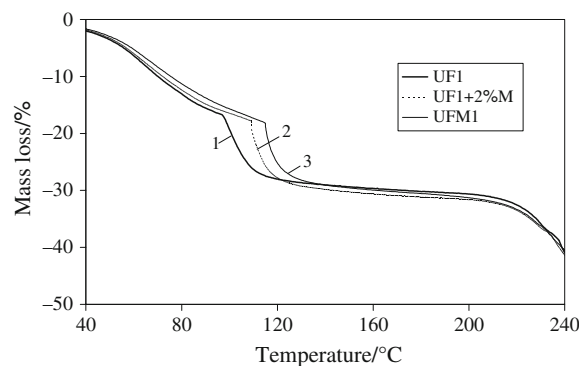


Fig. 7 Mass loss curves of: 1 regular UF1, 2 UF1 with 2% of added melamine, 3 cocondensed with 2% of melamine UFM1

of water evaporation during condensation reactions is different in all cases, the total of mass loss at 200 °C is similar, approximately 31–32 mass%.

A higher melamine amount (5 mass%) introduced to resin just before TG-DTA test should lead to more condensed structure compared to resin with lower melamine content and the cure temperature should increase with increasing melamine levels. The experiment shows that the location of both exothermic and endothermic peaks T_p are not shifted. The mass loss value in case of 5 mass% of melamine is somewhat higher (33 mass%) than that of in case 2 mass% melamine due to greater extent of cocondensation. The results in [10] show that a reduction in formaldehyde emission by increasing the melamine content has limitations. The reason may be in the high content of unstable dimethylene ether structures in melamine-containing resins [23] especially under high humidity and high temperature circumstances.

TG-DTA analysis of selected resins confirms the fact proved also in particleboard manufacture that higher temperature or increased time are needed to cure melamine-modified resins in practice.

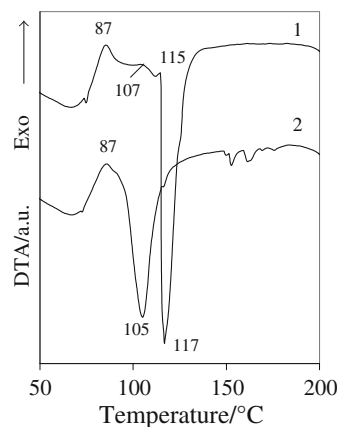


Fig. 8 DTA curing curves of: 1 UFM1, 2 UFM1 with 7% of added urea

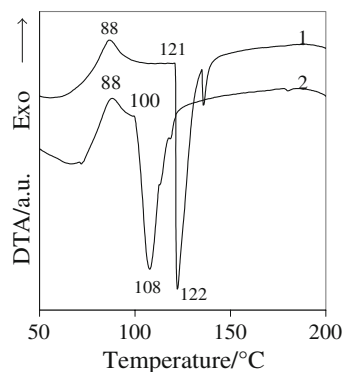


Fig. 9 DTA curing curves of: 1 UFM2, 2 UFM2 with 7% of added urea

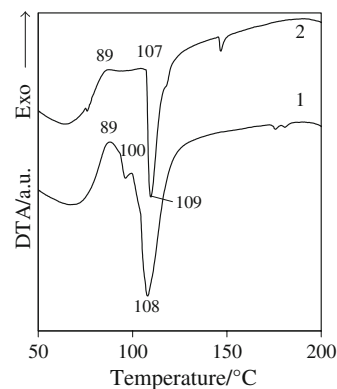


Fig. 10 DTA curing curves of: 1 UFM3, 2 UFM3 with 7% of added urea

Table 3 Physical and mechanical properties of melamine-modified UF resins-bonded particleboards

PB/mm	Wood material		Dry resin/ PB/kg/m ³	Urea/% dry resin/core layer	Press time factor T ₂ /s	Density/kg/m ³	Bending strength/MPa	IB strength/Mpa	Free F/PB/ mg/100 g
	Chips	Sawdust							
<i>UF1</i>									
10	20	80	68.8	6.5	110	671	13.0	0.43	5.8
18	20	80	63.7	5.5	180	669	14.0	0.37	5.7
22	20	80	55.8	6.0	205	625	12.5	0.31	5.5
<i>UFM1</i>									
15	23	77	65.4	8.5	140	620	12.0	0.32	3.9
15	23	77	65.4	8.5	140	623	11.5	0.32	3.8
15	23	77	65.4	8.5	150	650	12.4	0.39	3.6
22	23	77	63.3	8.5	230	629	12.4	0.35	3.3
22	23	77	63.3	8.5	230	620	11.7	0.31	3.4
<i>UFM2</i>									
15	42	58	67.2	0	140	615	11.9	0.14	4.3
15	42	58	67.2	0	150	620	12.7	0.20	4.1
15	42	58	67.2	0	160	630	13.1	0.21	4.0
15	14	86	67.2	2.0	160	637	13.7	0.24	3.6
15	14	86	67.2	4.0	160	626	12.6	0.23	3.1
15	14	86	67.2	6.0	160	637	13.5	0.20	2.9
15	14	86	67.2	8.0	160	628	12.8	0.18	2.7
18	14	86	66.2	4.0	190	607	13.2	0.20	3.0
18	14	86	66.2	8.0	200	636	13.2	0.18	2.9
22	14	86	62.8	4.0	240	588	11.0	0.14	2.7
22	14	86	62.8	8.0	240	570	10.6	0.15	2.6
<i>UFM3</i>									
15	42	58	66.5	-	170	645	12.5	0.14	3.9
15	42	58	66.5	-	170	619	13.0	0.12	3.8
18	42	58	66.2	-	205	610	13.9	0.19	3.8
18	42	58	66.2	-	205	613	13.1	0.18	3.6
22	42	58	63.7	-	240	623	12.7	0.12	4.4
22	42	58	63.7	-	240	626	13.0	0.11	4.2

The industrial experience of manufacturing particleboards is proved that, for producing boards of E1 emission class, formaldehyde scavengers are needed. In Pärnu

Plaaditehas AS, the addition of urea as formaldehyde catcher up to 7–8.5 mass% has been used depending on the properties of initial resin and wood materials. All the more,

this point is essential for reducing formaldehyde emission below 4 mg/100 g. Thermal behaviour of the focused melamine-modified resins with 7 mass% of urea is studied. In Figs. 8–10, the enlarged peaks of UFM resins in the curing ranges up to 200 °C are illustrated.

DTA curves of resins UFM1 and UMF2 (Figs. 8, 9) show that the addition of 7 mass% of urea before curing accelerates the condensation reactions which takes place between free amino groups of added urea and resin methylol groups while U–F homocondensation temperatures at 87 or 88 °C being as the same. Water evaporation endotherms of both resins is shifted to considerable lower temperatures. TG curves showed that the mass loss values before degradation of cured resin at 200 °C. In the case of UFM1 was approximately the same if cured the resin without additive and with 7% of urea being ca 31%. In the case of UFM2 these values are 26 and 28.7% accordingly. Depending on the higher content of branched structures in UFM2, the evaporation of water from resin network is restricted. Due to higher content of unreacted urea in initial resin, cocondensation reaction proceeds deeper.

Different situation reveals in the case of UFM3 in which due to the low mole ratio of $F/(NH_2)_2$ and high content of unreacted urea deficiency of formaldehyde for additional urea is revealed. This changes the shape of DTA curve and broadens the condensation region to the higher temperature (Fig. 10).

In Table 3, physical and mechanical properties of particleboards bonded with melamine-modified resins UFM1, UFM2 and UFM3 for selected thicknesses are presented. In regards to the main goal of the factory which is getting prepared for the production of particleboards of formaldehyde emission down to 4 mg/100 g board (between E1 and E0 emission class) it can be judged that it can be attained by suitable manufacturing technology. The amount of added urea as scavenger depends on the content of formaldehyde in the used resin. The value of formaldehyde emitted decreases with increasing the content of added urea. In the case of UFM3 containing high level of unreacted urea, the boards were manufactured with additional urea.

Comparing the mechanical properties of boards bonded with these resins, it should be noted that all boards correspond to the standard for P1 boards. The internal bond (IB) is the most sensitive physical characteristic depending on the crosslinking density of cured resin network. IB strength shows the highest values in the case of resin UFM1 (mole ratio of $F/U + M = 1.0$, Table 1) with more advanced structure. UFM3 shows lower IB values compared to the other resins due to the low mole ratio of $F/U + M$. It can be seen from Table 3 that melamine-modified resins need longer press time as compared to UF1 resin to attain the needful crosslinking degree. Alongside with other

parameters, the pressing rate is dependent on the reactivity of the resin-catalyst combination.

Conclusions

Thermal analysis of low-level melamine-modified resins using TG-DTA technique confirm the fact that higher temperature or increased time are needed to cure melamine-modified resins in practice. Incorporation of low amount of melamine monomer (2–5 mass%) into UF resin just before curing shows curing exotherm at lower temperature as that of cocondensed with melamine during synthesis of UF resin. TG-DTA measurements together with ^{13}C NMR structural analysis of resins provide useful information for the manufacturing of particleboards. The effect of addition of urea as formaldehyde scavenger on thermal behaviour of studied systems was followed. 7 mass% of urea, added before curing, accelerates the condensation reactions, shifting exothermic and endothermic peaks to lower temperatures. By comparing the thermal behaviour of selected resins, reasonable processing parameters for manufacturing boards were recommended. The content of even low level of melamine in resin contributed to the improved formaldehyde emission. As compared to regular UF1, perforator value below 4 mg/100 g board can be attained at corresponding to P1 board standard mechanical properties.

References

- Sundin EB. The formaldehyde problem. Publications 1976–1992, Stockholm, Sweden, p. 1–360.
- Pizzi A. Urea-formaldehyde adhesives. In: Pizzi A. Advanced wood adhesives technology. New York: Marcel Dekker; 1994. p. 19–66.
- Dunky M. Adhesives based on formaldehyde condensation resins. *Macromol Symp.* 2004;217:417–29. doi:10.1002/masy.200451338.
- Park BD, Kim YS, Singh AP, Lim KP. Reactivity, chemical structure, and molecular mobility of urea-formaldehyde adhesives synthesized under different conditions using FTIR and solid-state ^{13}C CP/MAS NMR spectroscopy. *J Appl Polym Sci.* 2003;88:2677–87. doi:10.1002/app.12115.
- Risholm-Sundman M, Larsen A, Vestin E, Weibull A. Formaldehyde emission-comparison of different standard methods. *Atmos Environ.* 2007;41:3193–202. doi:10.1016/j.atmosenv.2006.10.079.
- Oh YS. Evaluation of melamine-modified urea-formaldehyde resin binders for particleboard. *For Prod J.* 1999;49:31–4.
- Ringena O, Janzon R, Pfizenmayer G, Schulte M, Lehnen R. Estimating the hydrolytic durability of cured wood adhesives by measuring formaldehyde liberation and structural stability. *Holz als Roh- und Werkstoff.* 2006;64:321–6. doi:10.1007/s00107-005-0087-3.

8. Dunky M. Resins for ultra-low formaldehyde emission according to the Japanese F**** quality. In: Proceedings of the wood adhesives 2005, San Diego, California, USA, p. 343–49.
9. Zorba T, Papadopoulou E, Hatjiissak A, Paraskevopoulos KM, Chrissafis K. Urea-formaldehyde resins characterized by thermal analysis and FTIR method. *J Therm Anal Calorim.* 2008;92: 29–33. doi:10.1007/s10973-007-8731-2.
10. Tohmura S, Inoue A, Sahari SH. Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure. *J Wood Sci.* 2001;47:451–7. doi:10.1007/BF00767897.
11. No BY, Kim MG. Syntheses and properties of low-level melamine-modified urea-melamine-formaldehyde resins. *J Appl Polym Sci.* 2004;93:2559–69. doi:10.1002/app.20778.
12. No BY, Kim MG. Curing of low level melamine-modified urea-formaldehyde particleboard binder resins studied with dynamic mechanical analysis (DMA). *J Appl Polym Sci.* 2005;97:377–89. doi:10.1002/app.21759.
13. Gu J, Zhu L, Ono H. Curing mechanism of low-formaldehyde emission urea-formaldehyde resins. *Linchan Huaxue Yu Gongye.* 2005;25:11–6.
14. Pedersen A, Sandbakken PO. Low emission adhesive system. WO 2007040410 (A1).
15. Dunky M, Durkic K, Andersen G. Adhesive system and wood based panels comprising the adhesive system with low subsequent formaldehyde emission and suitable production procedure. WO 2008/026058 (A2).
16. Siimer K, Kaljuvee T, Christjanson P, Pehk T, Lasn I, Saks I. Urea-formaldehyde resins for low formaldehyde emission particleboards. In: Proceedings of the polymer processing society 24th annual meeting 2008, Salerno, Italy.
17. Çolakoğlu G, Demirkir C. Characteristics of plywood panels produced with urea formaldehyde resin (UF) containing borax. *Holz als Roh- und Werkstoff.* 2006;64:250–1. doi:10.1007/s00107-005-0077-5.
18. Kim S, Kim HJ, Kim HS, Lee YK, Yang HS. Thermal analysis study of viscoelastic properties and activation energy of melamine-modified urea-formaldehyde resins. *J Adhesion Sci Technol.* 2006;20:803–16. doi:10.1163/156856106777638671.
19. Siimer K, Kaljuvee T, Christjanson P, Lasn I. Curing of urea-formaldehyde resins on a wood substrate. *J Therm Anal Calorim.* 2006;84:71–7. doi:10.1007/s10973-005-7185-7.
20. Rammon RM. Melamine-modified urea formaldehyde resin for bonding particleboards. In: 31st International particleboard/composite materials symposium, 1997, p. 177–81.
21. Pizzi A, Panamgama LA. Diffusion hindrance vs. wood-induced catalytic activation of MUF adhesive polycondensation. *J Appl Polym Sci.* 1995;58:109–15. doi:10.1002/app.1995.070580112.
22. Siimer K, Kaljuvee T, Christjanson P, Pehk T. Changes in curing behaviour of aminoresins during storage. *J Therm Anal Calorim.* 2005;80:123–30. doi:10.1007/s10973-005-0623-8.
23. Siimer K, Christjanson P, Kaljuvee T, Pehk T, Lasn I, Saks I. TG-DTA study of melamine-urea-formaldehyde resins. *J Therm Anal Calorim.* 2008;92:19–27. doi:10.1007/s10973-007-8721-4.