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TG-DTA STUDY OF MELAMINE–UREA–FORMALDEHYDE RESINS

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The thermal behaviour of MUF resins from different suppliers with different content of melamine was studied, along with the ^{13}C NMR spectroscopic analysis of resin structure and the testing of particleboards in current production at Estonian PB factory Pärnu Plaaditehas AS. The chemical structure of resins from DMSO-d_6 solutions was analysed by ^{13}C NMR spectroscopy on a Bruker AMX500 NMR spectrometer. The melamine level in different MUF resins is compared by the ratios of carbonyl carbon of urea and triazine carbon of melamine in ^{13}C NMR spectra. Curing behaviour of MUF resins was studied by simultaneous TG-DTA techniques on the Labsys™ instrument Setaram. The shape of DTA curves characterisises the resin synthesis procedure by the extent of polymerisation of UF and MF components and is in accordance with structural data.

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

Introduction

For the production of wood-based panels, diverse types of adhesives is used. Melamine–formaldehyde resins and their more economical variant, melamine–urea–formaldehyde (MUF) resins, are widely used today as thermosetting wood adhesives for the manufacture of exterior wood panels, such as particleboard (PB), medium density fiberboard and hardwood plywood [1, 2]. The presence of triazine ring in their structure provides improved hydrolytic and thermal stability, compared with urea–formaldehyde (UF) resins [3, 4]. Classical commercial MUF resins are synthesised with high level of melamine (>50%) [5] but considering the high price of melamine, it is attempted to reduce the content of melamine in MUF resins to as low as possible depending on the purposes of use [5, 6]. The synthesis of low-level melamine-modified urea–melamine–formaldehyde resins for binding PB has been elaborated [7]. Low levels of melamine added to UF resins in manufacturing MUF resins have improved the water resistance and/or decreased the formaldehyde emission to the required level. Several authors [e.g. 8, 9] have proposed methods for correlation of the molecular structure of a liquid MUF resins to the properties of PB bonded with them.

Several pathways have been proposed to synthesise MUF resins. Essentially, this synthesis is a two-step process consisting of the methylolation stage of amino groups and condensation of methylols to form polymeric chains [6]. The condensation may occur by the mechanism of the formation of methylene or dimethylene ether linkages in the resin structure. In synthesing of resins at relatively low levels of melamine usage, the urea components, present in large proportions, need to be preadvanced to appropriate extents before addition of melamine for increasing the cure rate of MUF resin [7].

MUF resins are of complicated structure due to the presence of two monomers reactive with formaldehyde in the polymer, and therefore, due to many reactive sites, a large variety of structural moieties are possible in the resins [10]. The principal structures are shown in Fig. 1.

The chemistry of melamine reacting with formaldehyde and of urea and formaldehyde condensations has been studied by many authors [1], but there are contradictory opinions about of cocondensation reactions of melamine and urea during resin synthesis. In [6] is asserted that in the MUF resin synthesis, condensation stage predominantly constitutes the self-condensation of melamine and urea rather than the cocondensation of melamine and urea. In [5] it is reported that due to overlapping peaks it is difficult to make conclusions about copolymerisation between urea and melamine units. As it has been shown in [11], under certain laboratory conditions copolymerisation can occur in an uncured MUF resin. By ^{15}N correlation spectroscopy cocondensation between melamine and urea has been established and the extent of copolymerisation in industrial preparations

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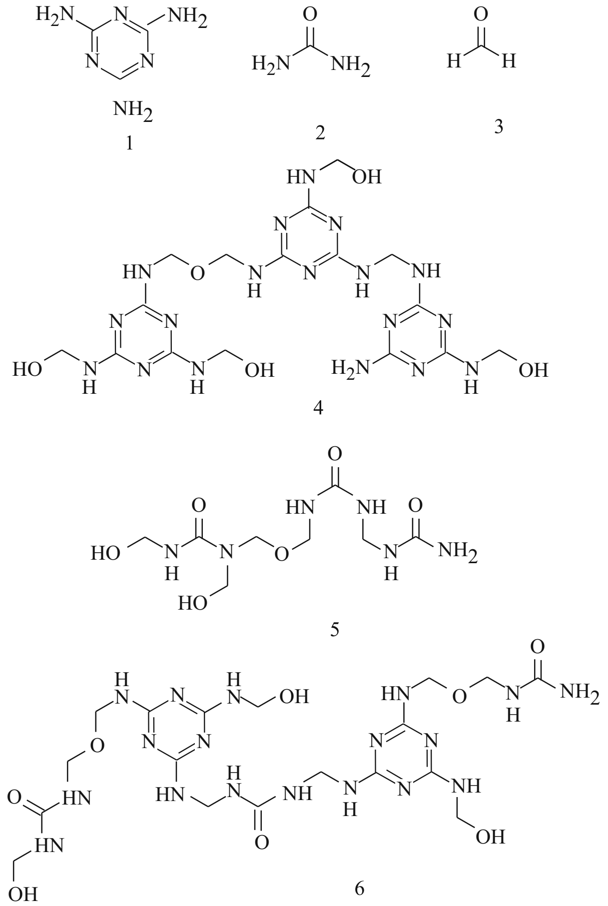

Fig. 1 1 – Melamine (M), 2 – urea (U), 3 – formaldehyde (F) and possible structures formed through reaction of 4 – M and F, 5 – U and F, 6 – M, U and F

of MUF resins was determined [10]. The authors [11–13] established that cocondensation certainly occurs in the resin curing process under acidic conditions where methylene or dimethylene ether linkages between melamine and melamine, melamine and urea, or urea and urea can be formed. The effect of the melamine content in MUF resins on the cured resin structure and formaldehyde emission has been studied [14]. It has been shown that melamine contributed to strong crosslinking linkages in the cured resin structures by increasing the branched-type methylene bond but the formation of methylene and dimethylene ether linkages between melamine and urea during curing is only supposed. So, it can be deduced that the formation of melamine-urea linkage is still unclear.

MUF resins made with different melamine levels and synthesis procedures reveal different curing parameters and rigidity values [4, 7, 15, 16]. The thermal stability and final rigidity of cured MUF resins are higher than those of cured UF resins and increase with increasing of melamine level [7]. It has been shown that F/U+M ratio would allow to be lowered to reduce F emission of PB compared to UF resins, without lowering the strength properties.

Compared to UF resins, the cure times of MUF resins are longer and increase with increasing melamine content, suggesting that higher temperatures or longer press times are needed to cure MUF resins in practice [5, 7]. The conclusion in [17] is that, because of the lower activation energy, the MUF resin cures faster than UF resin only during the early stages of the curing process.

Different methods have been proposed to study the curing mechanism of MUF resins. Curing behaviour of MUF resins have been studied by several authors using differential scanning calorimetry (DSC) [e.g. 13, 15, 17]. The curing effiency of UMF resins was investigated using the dynamic mechanical analysis method (DMA) [7]. Although the DMA method does not accurately simulate the hot-pressing conditions of boards, useful resin curing parameters have been obtained [7]. The commercial MUF resins with different content of melamine were compared by the gravimetric analysis to correlate the degree of hydrolytic decomposition of cured resins and formaldehyde liberation [18]. The technique of torsion braid analysis (TBA) was applied to analyse dynamic viscoelasticity and curing characteristics of modified by melamine UF resins [15]. Visco-elastic properties of melamine-modified UF resins were also studied by dynamic mechanical thermal analysis (DMTA) which is very sensitive method in the monitoring curing processes [17].

In our previous report [19], the curing behaviour of 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 ^{13}C NMR spectroscopy.

In the present work, the thermal behaviour of commercial MUF resins of different origin was studied together with the ^{13}C NMR spectroscopic analysis of resin structure and testing of PB in current production at Pärnu Plaaditehas AS. Also, curing behaviour of laboratory-synthesised MUF resins with low melamine level was studied, along with laboratory-made PB, and their curing was compared with a control MUF resin.

Experimental

For the present study, MUF resins were obtained from commercial sources, mainly from Finnish and Estonian factories. MUF resins of with different melamine content were selected and labelled as MUF1, MUF2, MUF3 and MUF4. Likely enough, used resins are manufactured by different technology but in the all modern commercial resins the mole ratio of F/M+U is lowered to narrow ranges of 1.0–1.15 for reducing

Table 1 Standard characteristics of commercial MUF resins

Characteristics	MUF1	MUF2 12.05	MUF3 15.08	MUF4 27.10
Dry solids 105°C 3 h/%	66.7	67.9	69.0	68.0
pH 25°C	9.1	9.2	9.2	9.0
Viscosity 25°C/cP, Rheotest	353	303	337	277
Density 25°C/g cm^{-3}	1.297	1.303	1.302	1.300
Gel time 100°C/s	73	106	121	102
Free formaldehyde/%	0.1	0.12	0.14	0.1
Water tolerance	1:3	1:4	1:5	1:4

formaldehyde emission. In Table 1, the standard characteristics of the commercial resins are presented.

As a comparison, the resins with low level of melamine was synthesised and tested in laboratory. Resins containing 6 mass% of melamine is labelled as UMF resins as in [5]. The synthesis was as a typical multistep procedure and proceeded in 20 L glass reactor. The synthesis was performed in the first stage of reaction with mole ratio of F/U=2.1, after acidic condensation melamine was added with formaldehyde in mole ratio of F/M=2.1, and the second part of urea was added to mole ratio of components as F/M+U=1.05.

The chemical structure of resins was analysed from DMSO-d_6 solutions by ^{13}C NMR spectroscopy on a Bruker AMX500 NMR spectrometer with ^{13}C frequency at 125.77 MHz by 5 mm ^{13}C–^{1}H dual probehead. Spectra were accumulated into 32 K data points and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. For the resulting spectra, 20000–25000 scans were accumulated. Chemical shifts were reported relatively to DMSO-d_6 central signal at 39.5 ppm. The assignments are 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. The melamine level in different MUF resins was estimated by the ratios of characteristic signal intensities of carbonyl carbon of urea and triazine carbon of melamine in ^{13}C NMR spectra.

TG-DTA measurements were carried out by the Labsys™ instrument Setaram with the heating rate of 5 K min^{-1} in dynamic nitrogen atmosphere, the mass of the samples 10–15 mg. Temperature of samples ranged from 20 to 450°C. Ammonium chloride as catalyst was used (20% solution) in the amount of 1 and 2%. As the TG-DTA test was carried out with an open crucible, the enthalpy of the curing reaction is not exactly determinable because of the characteristic exoeffect in DTA curve is partly overlapped by large water evaporation endotherm. The peak temperatures of thermal effects (T_p) and mass loss values are the main apparent indices to characterise the curing system. The shape of DTA curves characterise the resin synthesis procedure by the extent of polymerisation of UF or MF components and is in accordance with structural data.

Three-layer particleboards of 9700×2650 mm dimensions at Pärnu Plaaditehas AS (Estonian PB factory, production capacity of 48000 m^3 per year) are manufactured. In the present study, the board thicknesses of 12, 18 and 22 mm for load-bearing board P3 were selected. Wood raw material (pine, spruce) with moisture content of 1.7% consisted mainly of sawdust (85%) and cutter chips (15%). The catalyst NH_4Cl (25% solution) was added to core layer binder in the amount of 3.0%. Consumption of paraffin as hydrofobic agent was 0.9% from dry wood. The PB were manufactured at pressure of 210 bar and hot-press temperature of 210°C by pneumatic floating separation of wood particles. Hot-pressing time was 10.2–12.5 s mm^{-1} depending on the thickness of boards. Physical and mechanical parameters of PB were determined according to DIN 68763, and F emission was measured by the perforation method EN 120.

Laboratory-made single-layer particleboards with the dimensions of 30×30 cm×14 mm were prepared on the basis of the softwood cutter chips only at pressure of 1.6 MPa and temperature of 200°C. Hot-pressing time was 180 s. The consumption of resin was 11.3% of wood particles and the content of urea as scavenger was 7.5 and 2%. PB were made without paraffin.

Results and discussion

The relatively large range of chemical shifts in ^{13}C NMR spectra is a good probe for the analysis the chemical structure of resins because the integral values of structural groups would define the polymer structure type and substitution patterns [5, 6].

As it can be seen from Table 2, the integral values of structural fragments are presented in two main regions: high-field resonances (46–95 ppm) from methylene carbons and low-field resonances (153–168 ppm) from urea carbonyl carbons and melamine triazine carbons. The characteristic signals in the region of 153–168 ppm show that MUF resins from different suppliers are of different melamine levels. For the studied resins, the mole ratio of substituted and unsubstituted carbonyl carbons to melamine triazine carbons lies in the ranges of 27.6/72.4–45.5/54.5 which would correspond roughly to 10–20 mass% melamine in the resin. This content of melamine apparently has been optimised for producing load-bearing PB of P3 standard.

Table 2 Chemical structure of commercial MUF resins (mol%) by ^{13}C NMR analysis

Structural fragment	ppm	MUF1	MUF2	MUF3	MUF4
Distribution of bound F methylene linkages					
$HN\underline{C}H_2NH$	46–47	11.2	12.0	13.0	11.4
$HN\underline{C}H_2NH$	47–48	3.3	2.4	1.3	1.2
$HN\underline{C}H_2N(CH_2)$	52–54	10.7	13.5	11.4	11.6
$N(CH_2)\underline{C}H_2N(CH_2)$	59–60	–	1.3	0.5	0.4
methylol groups					
$HN\underline{C}H_2OH$	64	33.1	29.0	32.1	36.8
$HN\mathit{C}H_2OH$	65	22.3	20.3	17.7	15.0
$N(CH_2)\underline{C}H_2OH$ $N(\underline{C}H_2OH)_2$ }	70–71	3.5	3.9	3.2	4.6
dimethylene ether linkages					
$HN\underline{C}H_2O\underline{C}H_2NH$	67–69	15.8	10.6	12.7	13.7
$N(CH_2)\underline{C}H_2O\underline{C}H_2NH$	74–75	–	1.9	2.4	2.3
methylene methyl ethers					
$HN\underline{C}H_2OCH_3$	73	–	2.7	3.0	0.9
$N(CH_2)\underline{C}H_2OCH_3$	78–79	–	1.5	2.1	1.1
amino methylene $N(\underline{C}H_2)$	56–57	–	–	–	0.6
methylene glycols (free formaldehyde)	83–95	0.1	0.9	0.6	0.4
Carbonyl region					
free urea	161	12.8	17.4	14.3	26.1
monosubstituted urea	159–161	52.3	49.0	52.9	44.6
di- and trisubstituted urea	158–159	34.9	29.8	31.8	25.0
cyclic ureas	153–158	–	3.8	1.0	4.3
Triazine region					
free melamine	168	10.9	13.7	18.2	14.5
monosubstituted melamine	167.5	33.8	33.6	33.4	33.1
di- and trisubstituted melamine	166–167	55.3	52.7	48.4	52.4
Mole ratio					
triazine/carbonyl		45.5/54.5	40.7/59.3	38.3/61.7	27.6/72.4

From Table 2 it is seen that, comparing the resins shows that there are more condensation structures in the resin MUF1 with a higher triazine carbon/carbonyl carbon ratio. Regardless of the different melamine content in the resins, the relative content of the other structural fragments is not very different. Characteristic peaks in ^{13}C NMR spectra from melamine components and from urea components were not exactly differentiated, so it is not possible to make conclusions about cocondensation between melamine and urea. Also, on the basis of structural data we cannot assure the conclusion in [14] that the resins with a higher melamine content consisted of more highly branched crosslinkage structure and free melamine, compared to the resins with lower melamine contents. Distribution of the bound formaldehyde between the different structural fragments indicates that MUF resins contain in significant amounts of unstable dimethylene ether linkages which is formed in the condensation of methylolmelamines. Together with the weakly bonded >N-methylol groups they are the main sources of emittable formaldehyde. The content of unreacted formaldehyde species in studied resins differs, but the contribution of free formaldehyde in uncured resin to formaldehyde emission from PB is not so substantial. In resin MUF4, the content of unreacted urea is noticeable. According to [16], high amount of unreacted urea produces a resin of weaker strength but of lower formaldehyde emission from PB, and allows better performance in hardening. The content of the total methylol groups in the resins is close (~53–59% of bound formaldehyde), and by this characteristic alone it is difficult predict the cure rate of the resins.

Curing behaviour of MUF resins depends first of all on the content of reactive structural groups. Also, the content of catalyst has a very important role in the curing of aminoresins. 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. In our previous study [19], MUF resin cure was recorded both with 1 and 2% of NH_4Cl and without catalyst to compare the catalyst effect. It is known that the curing of MUF resins requires stronger catalysts and higher press temperatures, or longer press times, compared to UF resins because of the lower reactivity of the melamine methylol groups [5]. Although the cure time decreases with increased catalyst level [No-Kim, Proceed, lk 9], an optimal range of catalyst content used for the MUF resin cure must be selected. A higher catalyst content cause hydrolysis to occur during the latter stages of the curing process. Considering the technology on manufacturing PB, the amount of 2% of catalyst is added.

In Fig. 2 as example, the thermogram of resin MUF3 catalysed with 2% of NH_4Cl is presented. From the figure it can be seen that complicated DTA curve reveals the complex of exotherms with smooth transition to endotherms. The values of thermal effects are not determinable due to overlapping peaks.

In the earlier studies [13, 19], various possibilities of cross-linking reactions are assumed. From the Fig. 2, somewhat differing conclusions can be drawn: In the uncured resin MUF3, where the content of unreacted melamine is relatively high (Table 2), the exotherm with T_p=60°C should be correspond mainly to the reaction of the melamine with formaldehyde as the more preferred reaction and to the homocondensation of methylolmelamines. The exotherm with T_p=90°C expresses the reactions of urea-formaldehyde homocondensation. The thorough polycondensation reactions start only after water evaporation from system. The large endothermic peak of water evaporation with T_p=100°C is derived from initial resin water and that from condensation reactions. The band with T_p=140°C is dissipated because of the wide variations in resin functionality and are assumed to be different cocondensation reactions between urea and melamine derivatives. Exotherms at 180 and 202°C correspond to the various crosslinking reactions without noticeable water elimination Above 220°C, the beginning of the resin destruction takes place due to containing the hydrolysis-sensitive aminomethylene linkages involving urea (endotherm T_p=228°C) [19].

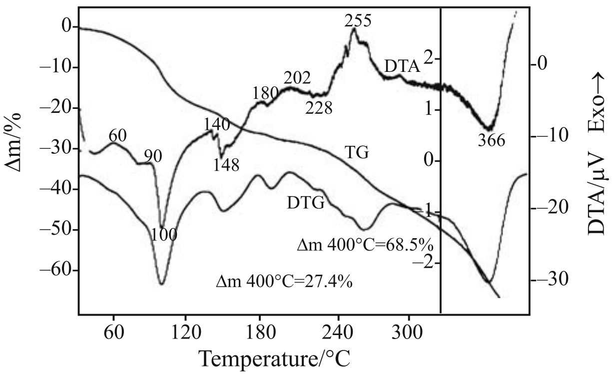

Fig. 2 TG/DTG-DTA curves of MUF curing

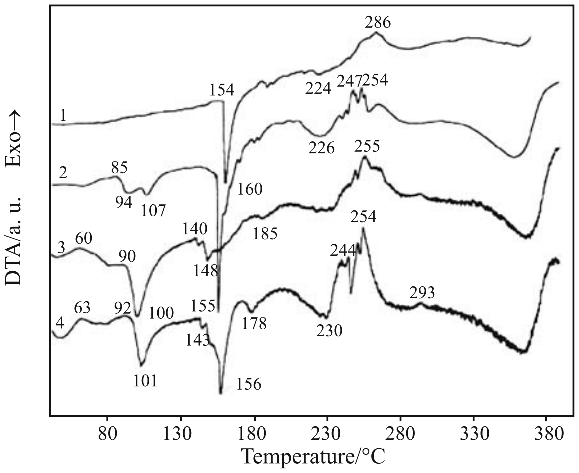

Fig. 3 DTA curves of commercial MUF resins of different melamine content: 1 – MUF1; 2 – MUF2; 3 – MUF3, 4 – MUF4

The resins with different formulation reveal differing curing curves. In Fig. 3, the DTA curves of four selected MUF resins are presented.

As it can be seen, some considerable differences in the shape of curves reveal. The DTA curve 1 of resin MUF1 does not reveal visible peaks in the exothermic region. This resin is of higher content of melamine and a great number of possible reactions may take place revealing the overlapping peaks in DTA curve. Therefore, it can be assumed that a higher melamine content in resin leads to more condensation and thus, higher molecular mass-resin compared to resins with a lower melamine content. Curve 2 of MUF2 shows the formation of ethers from condensation of methylol groups and is splitting to two parts. In case of resins of higher melamine content (curves 1 and 2), the tighter resin network structure is formed and the water evaporation endotherm, consisting both of resin initial water and that of reaction water, appears at higher temperatures (155–160°C). In case of looser networks of resins (curves 3 and 4), the water evaporation proceeds by steps beginning from lower temperatures. The shape of DTA curve 4 of MUF4 is analogous to curve 3 differing by the intensity of peak at 92°C. This is in accordance with structural data (Table 2) by which the content of methylolureas and unreacted urea is higher in resin MUF4.

In Fig. 4, the mass loss curves for the same resins are presented.

Mass loss curves show that in curing resins with higher content of melamine, tighter network is formed,

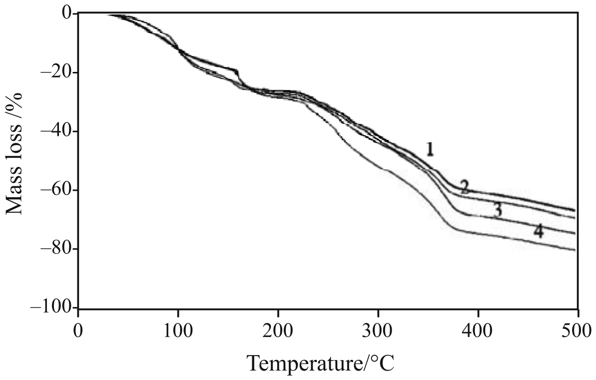

Fig. 4 Mass loss curves of MUF resins of different melamine content: 1 – MUF1; 2 – MUF2; 3 – MUF3, 4 – MUF4

therefore the water evaporation is restricted and mass loss of resins during curing is lower.

The real value of MUF resins under study becomes apparent in the manufacturing and testing PB (Table 3). Information from structural analysis and studies on curing behaviour of initial MUF resins and catalyst contents is useful in the establishment of optimal processing parameters in industrial line.

As it can be seen from the table, the mechanical properties, in general, satisfy the requirements for boards P3. IB strength (tensile strength perpendicular to the board surface) is the most sensitive physical characteristic, depending on the structure advancement of the resin during synthesis and on the crosslinking density of cured resin network. From the table it is seen that IB strength in all cases exceeds the value for industrial standard. Comparing the mechanical properties of boards bonded with resins of different melamine content shows that, contrary to [20], the bond quality deteriorates as the melamine content in resins decreases.

A higher melamine content in MUF resin (as in MUF1) leads to more condensation structures during hot-pressing compared to the resin with a lower melamine content (as in MUF4). As regards to bending strength, this value is not satisfied in case of resins MUF3 and MUF4 for thicknesses 12 and 18 mm.

Formaldehyde emission from finished boards is due to the residual formaldehyde present in the wood raw materials and mainly, from the hydrolysis of weakly bonded structures in resin. The content of unreacted formaldehyde in uncured resins is unimportant. The content of emittable formaldehyde in most cases corresponds to the requirements of E1 standard (a rotating half-year formaldehyde emission level less than 6.5 mg F/100 g PB). The perforator values show that there are significant differences in formaldehyde emission levels for PB bonded with studied resins. Remarkable lower emission is observed in case of resin MUF4 in which the melamine content is lower. On the other hand, the higher amount of unreacted urea in this resin gives the PB of weaker strength but of lower F emission.

According to some authors, at the same F/M+U mole ratio, formaldehyde emission from cured resin does not depend on melamine content or is unclear [9, 11], but our results in testing PB show that the emittable formaldehyde content by perforator value decreases significantly with decreasing the content of melamine in the resins.

In Table 4, the structure of three low-melamine (6%) content resin synthesised at different conditions is presented.

During the synthesis of UMF1 and UMF2, after stage of urea-formaldehyde reactions, melamine was added in alkaline medium together with formaldehyde in mole ratio of F/M=2.1. In the UMF1, the UF base resin

Table 3 Physical and mechanical properties of commercial MUF-bonded particleboards

Thickness of PB/mm	Resin	Dry resin/PB/ kg m^{-3}	Scavenger/% dry resin		Density/ kg m^{-3}	Bending strength/ MPa	IB strength/ MPa	Swelling 24 h 20°C/%	Free F/PB/ mg(100 g)$^{-1}$
			Face layer	Core layer					
12	P-3					15.0	0.40	14.0	6.5
	MUF1	74.5	4.0	8.0	722	18.5	0.77	3.8	7.4
	MUF2	66.2	0	7.5	648	16.8	0.63	6.2	7.2
	MUF3	66.7	0	5.5	640	13.5	0.54	7.6	7.1
	MUF4	67.1	0	5.5	642	12.0	0.45	7.7	5.3
18	P-3					14.0	0.35	14.0	6.5
	MUF1	74.5	3.5	8.0	736	17.8	0.64	2.6	7.3
	MUF2	66.2	0	7.0	647	15.9	0.50	5.0	6.9
	MUF3	66.5	0	6.0	641	14.4	0.47	6.4	5.9
	MUF4	67.4	0.6	6.0	634	10.8	0.41	7.4	4.4
22	P-3					12.0	0.30	13.0	6.5
	MUF1	74.5	4.0	8.0	693	19.5	0.68	2.6	5.8
	MUF2	66.2	0	7.0	651	18.2	0.47	6.3	6.5
	MUF3	66.5	0	5.0	634	14.7	0.41	8.0	5.4
	MUF4	67.4	0.6	5.0	649	12.1	0.38	7.1	4.0

Table 4 Chemical structure of laboratory-made UMF resins (mol%) by ^{13}C NMR analysis

Structural fragment	ppm	UMF1	UMF2	UMF3
Distribution of bound F methylene linkages				
$HN\underline{C}H_2NH$	46–47	13.1	10.9	15.6
$HN\underline{C}H_2NH$	47–48	0.6	0.5	2.3
$HN\underline{C}H_2N(CH_2)$	52–54	10.2	10.3	16.1
$N(CH_2)CH_2N(CH_2)$	59–60	0.6	0.6	1.2
methylol groups				
$HN\underline{C}H_2OH$	64	40.9	42.3	33.2
$HN\underline{C}H_2OH$	65	9.0	9.5	7.3
$N(CH_2)\underline{C}H_2OH$ $N(CH_2OH)_2$	70–71	3.9	4.3	5.5
dimethylene ether linkages				
$HN\underline{C}H_2O\underline{C}H_2NH$	67–69	12.1	11.8	9.8
$N(CH_2)\underline{C}H_2O\underline{C}H_2NH$	74–75	2.8	2.5	2.2
methylene methyl ethers				
$HN\underline{C}H_2OCH_3$	73	3.1	3.2	4.2
$N(CH_2)\underline{C}H_2OCH_3$	78–79	2.8	2.9	1.7
amino methylene $N(\underline{C}H_2)$	56–57	0.5	0.4	0.4
methylene glycols (free formaldehyde)	83–95	0.4	0.8	0.5
Carbonyl region				
free urea	161	24.9	28.9	25.6
monosubstituted urea	159–161	48.6	45.0	45.9
di- and trisubstituted urea	158–159	22.1	21.8	23.4
cyclic ureas	153–158	4.4	4.3	5.1
Triazine region				
free melamine	168	14.9	12.7	
monosubstituted melamine	167.5	27.6	29.4	27.1
di- and trisubstituted melamine	166–167	57.5	57.9	72.9
Mole ratio				
triazine/carbonyl		15.0/85.0	14.2/85.8	17.3/82.7

condensed in acidic media is more advanced. In case of UMF3, melamine was added without formaldehyde.

As it can be seen from Table 4, degree of condensation (content of methylene linkages) in UMF1 is higher and the content of methylolgroups is lower compared to UMF2. Due to the missing of second formaldehyde, the content of methylolgroups in UMF3 is lower than in the other resins.

In Fig. 5, DTA curves of laboratory-made UMF resins with 6 mass% of melamine are presented.

In all curves, the sharp exotherm with the peak maximum in the ranges of 90–93°C reveals. As the resins contain melamine only in the little amounts, the peak of melamine reaction with formaldehyde is only as inkling around ranges of 60°C, and the exotherm corresponds to urea-formaldehyde homocondensation reactions with following water evaporation, consisting both of resin initial water and that of reaction water. If during resin synthesis, melamine is condensed together with formaldehyde (curves 1 and 2), more functionalities are formed and the tighter resin network structure is build up due to this, the water evaporation endotherm appears at higher temperatures. Melamine, condensed with previously advanced UF resin functionalities without additional formaldehyde, forms a looser network, and the water evaporation proceeds at lower temperature.

Mass loss curves (Fig. 6) is presented for the temperature range up to 250°C where the apparent degradation of resins takes part. From the figure, it can be seen that mass loss value below this temperature at 200°C is higher in case of UMF3 synthesised without second formaldehyde.

Laboratory-made single-layer particleboards were dimensions of 30×30 cm×14 mm. The consumption

Table 5 Physical and mechanical properties of laboratory-made UMF-bonded particleboards

Resin	Moisture/%	Scavenger	Density/ kg m^{-3}	Bending strength/MPa	IB strength/MPa	Swelling 24 h 20°C/%	Free F/PB/ mg(100 g^{-1})
MUF-05VL	5.9	7.5	730	10.0	0.34	32.6	3.5
UMF1	5.7	7.5	745	10.2	0.39	40.2	2.8
UMF2	5.7	7.5	738	10.5	0.38	44.3	3.2
UMF3	5.9	7.5	741	10.0	0.36	41.8	2.3
UMF3	6.1	2.0	740	10.9	0.42	32.6	3.0

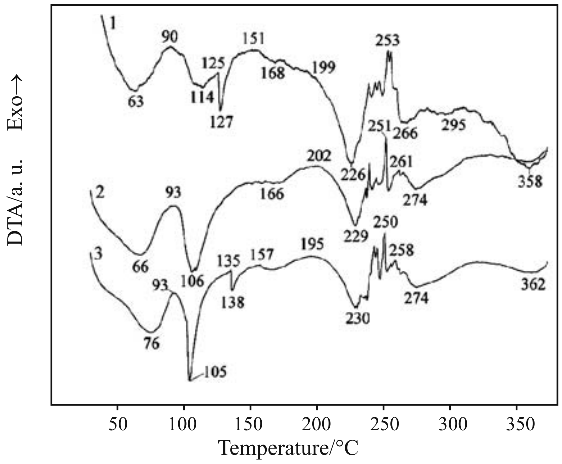

Fig. 5 DTA curves of laboratory-made UMF resins with melamine content of 6 mass%: 1, 2 – melamine is added with formaldehyde in mole ratio F/M=2.1/1, in UMF1 UF base resin is more advanced; 3 – without additional formaldehyde

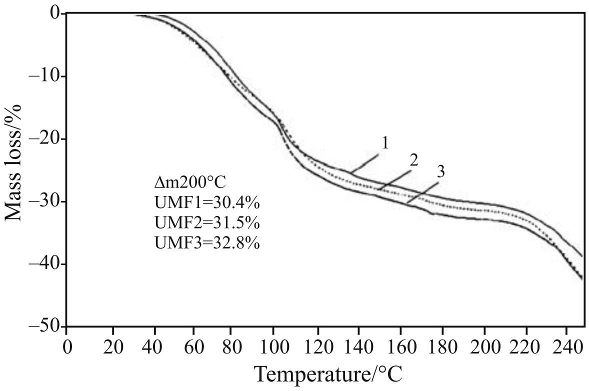

Fig. 6 Mass loss curves of laboratory-made UMF resins with melamine content of 6 mass%: 1, 2 – melamine is added with formaldehyde in mole ratio F/M= 2.1/1, in UMF1 UF base resin is more advanced; 3 – without additional formaldehyde

of resin was 11.3% of wood particles and the content of urea as scavenger 7.5%. For the comparison, a control MUF resin was tested (Table 5). The physical and mechanical properties of three UMF-bonded PB were compared to those of the control MUF-bonded PB. Panel water absorption and thickness swelling properties were observed after 24-h soaking test.

From the table it can be seen that formaldehyde emission from PB is lower in PB bonded with UMF resins compared to commercial resin MUF-05VL. All the low perforator values are due to wood component as PB are made in laboratory on the basis of cutter chips only. Industrial raw material consists of the mix of sawdust and cutter chips and, therefore, the level of free formaldehyde is higher (Table 3). The bending strength values are close in case of all resins if is used the same amount of scavenger, IB strength value is somewhat lower in case of UMF3 when melamine was condensed without additional formaldehyde. The lower amount of added urea as scavenger (2%) gives higher strength properties but the higher formaldehyde emission of PB. Boards bonded with the UMF resins show significantly higher thickness swell than that of bonded with the control MUF resin. The swelling data from laboratory-made PB is not comparable with those of industrial PB because of paraffin was not added. Due to the hydrophobic nature of paraffin, a small amount of paraffin added to wood material is exceedingly effective in reducing the short-term water absorption and thickness swell values [20].

Conclusions

TG-DTA analysis together with ^{13}C NMR structural analysis of MUF resins gives the useful information in the manufacturing of particleboards. The commercial resins from different suppliers are of different melamine levels, and consequently, of the different thermal behaviour. In case of resins of higher melamine content, the tighter resin network structure is formed and the water evaporation endotherm, consisting both of resin initial water and that of reaction water is restricted and appears at higher temperatures. In case of looser resin networks, the water evaporation proceeds by steps. Although the properties of industrial MUF-bonded particleboards depend on multitude of factors, our results in manufacturing and testing particleboards clearly show the favourable effect of melamine content in strength characteristics and formaldehyde emission.

References

1 A. Pizzi, Advanced Wood Adhesive Technology, Marcel Dekker, New York 1994, Chapters 2–3.
2 M. Dunky, Macromol. Symp., 217 (2004) 417.
3 M. Rammon, 31st International Particleboard/Composite Materials Symposium, (1997) 177.
4 R. Maylor, Proceed. Symp. Wood Adhesives, 1995, p. 115.
5 B. Y. No and M. G. Kim, J. Appl. Polym. Sci., 93 (2004) 2559.
6 A. S. Angelatos, M. I. Burgar, N. Dunlop and F. Separovic, J. Appl. Polym. Sci., 91 (2004) 3504.
7 B. Y. No and M. G. Kim, J. Appl. Polym. Sci., 97 (2005) 377.
8 M. G. Kim and L. W. Amos, Ind. Eng. Chem. Res., 29 (1990) 208.
9 A. T. Mercer and A. Pizzi, J. Appl. Polym. Sci., 61 (1996) 1687.
10 A. Philbrook, C. J. Blake, N. Dunlop, C. J. Easton, M. A. Keniry and J. S. Simpson, Polymer, 46 (2005) 2153.
11 B. Tomita and C. Hse, Mokuzai Gakkaishi, 41 (1995) 349.
12 M. Higuchi, S. Tajima, H. Irita J. Roh and I. Sakata, Mokuzai Gakkaishi, 37 (1991) 1050.
13 A. Pizzi and L. A. Panamgama, J. Appl. Polym. Sci., 58 (1995) 109.
14 S. Tohmura, A. Inoue and S. H. Sahari, Wood Sci., 47 (2001) 451.
15 J. Gu, L. Zhu and H. Ono, Linchan Huaxue Yu Gongye, 25 (2005) 11.
16 M. Zanetti and A. Pizzi, J. Appl. Polym. Sci., 91 (2004) 2690.
17 S. Kim, H.-J. Kim, H.-S. Kim, Y.-K. Lee and H.-S. Yang, J. Adhes. Sci. Technol., 20 (2006) 803.
18 O. Ringena, R. Janzon, G. Pfizenmayer, M. Schulte and R. Lehnen, Holz Roh Werkst., 64 (2006) 321.
19 K. Siimer, T. Kaljuvee, P. Christjanson and T. Pehk, J. Therm. Anal. Cal., 80 (2005) 123.
20 Y. S. Oh, Forest Prod. J., 49 (1999) 31.

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