

First/second generation of dendritic ester-co-aldehyde-terminated poly(amidoamine) as modifying components of melamine urea formaldehyde (MUF) adhesives: subsequent use in particleboards production

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Abstract Particleboards production, which depends mainly on thermoset resins, e.g., such as melamine urea formaldehyde (MUF) and urea formaldehyde (UF), can result in subsequent liberation of the carcinogenic formaldehyde of the panel in service. This situation needs the substitution of formaldehyde with less active aldehydes. However, to date, the resins prepared from less active aldehydes suffer from markedly lower reactivity, difficult processing, short shelf-life and inferior performance after application to particleboards manufacture. The current work addresses such an issue, which is of both health and environmental concern while keeping in mind the economic aspect. It depends upon two routes of modification of MUF resins: first by using different generations of a hyperbranched ester-terminated-co-aldehyde-terminated poly(amidoamine)s, HB(PAMAM-(COOCH₃)_n(CHO)_m), after their preparation and characterization using fourier

transform infrared (FTIR), ¹³C nuclear magnetic resonance (NMR), and matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS), as reactive additives and property enhancers in the first reaction step without altering the usual ratios of the reactants as in the basic recipe. Second, the use of the additives in the first step involved a parallel systematic substitution of formaldehyde, without seriously influencing resin properties or their relevant particleboards. The upgrading of either some resins or particleboards properties was confirmed by contact angle measurements, mechanical properties as well as thermomechanical analysis (TMA). It could be suggested that HB(PAMAM-(COOCH₃)_n(CHO)_m) worked in the second case as a co-condensing agent rather than a bridging agent as in the first case.

Keywords Poly(amidoamine)s dendrimers · MUF adhesives · Particleboard · Additives

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Introduction

Urea-formaldehyde (UF) resin [1] is one of the most important binding agents used for wood based composites, e.g., particleboard (PB), medium density fibreboard (MDF) and hard plywood [1]. However, they have some drawbacks which entitle low resistance to hydrolytic conditions and high formaldehyde emission [2]. Final formaldehyde/urea (F/U) ratio of UF resins is the key factor to lower the formaldehyde emission. On the industrial level, it is currently at a level of 1.15 or lower. Further decrease of F/U ratio to control the formaldehyde emission may encounter a remarkable fall in the bond strength and water resistance of their based particleboards. This can be mainly ascribed to the associated limitation of cross-linking level. Melamine which has a higher functionality (3 or

higher) can also be used with minor amounts of urea in manufacturing melamine-urea-formaldehyde (MUF) resins.

These resins are broadly applied in bonding of wood composites. Small amounts of melamine can be added to UF resins for manufacturing of melamine- urea-formaldehyde (MUF) resins which have the advantage of improved resistance to water beside a lower level of the emitted formaldehyde [3]. The chemistry of melamine-formaldehyde (MF) resins is generally analogous to UF resins but with a few major variations [4]. Melamine is significantly more expensive than urea and consequently the synthesis of MUF resins has received more attention [4]. Urea is added mostly in two steps (U1 and U2) during the production of MUF resins [5]. The first urea (U1) reacts with the formaldehyde under weak alkaline conditions at F/U1 ratio of 2.1 and this step gives rise to mono-, di-, and tri- hydroxymethylurea. Then, the reaction is continued at 95 °C after the pH being adjusted to 4–5. At this step, the hydroxymethylureas polcondense to form urea-based oligomers linked together by methylene bridges (almost 80 %) and methylene ether bonds (about 20 %). Also, in this step a portion of the formaldehyde is splitted off from the formed species due to reverse hydroxymethylation. The polycondensation reaction is typically progressing until a solid content of 60–65 % is accomplished. The reaction is ceased by raising the pH to 8. At this stage the resulting resin is a mixture of polymeric methylene/methylene-ether hydroxymethylureas. The reaction mixture is subsequently cooled to 60 °C and the third step commences by the addition of a second urea (U2) that switches the final F/(U1 + U2) ratio to 1.15. At last, the system entitles cooling to room temperature. It may be noted that a part of the second urea addition reacts with the free formaldehyde of the reaction mixture which results in the formation of monomeric hydroxymethylureas and this leaves behind a level of free formaldehyde in the resin in the range of about 0.5 %. It is worthy to mention that the added urea exists mainly in the medium as monomeric and polymeric species of hydroxymethylated methylene ureas [1] whereas a minor part (25 % in average) remains as free urea.

A prior report [6] showed that property improvement and formaldehyde emission of systems based on MUF resins can fall within a wide range of values by using variable levels of melamine ranging from 4 to 35 %. It was observed that the resin performance did not essentially improve with increasing the content of melamine. However, it was also found that MUF resins prepared using melamine loadings of 50 % or above require stronger acid catalysts [7] while otherwise may need stronger acid catalysts and/or higher press temperatures or longer press times in comparison with UF resins. The solubility of the melamine-formaldehyde (MF) resin components formed during MUF resin synthesis decreases rapidly with molecular weight. Thus, these resins may contain insoluble MF components in the form of suspended particles hence their thermosetting quality becomes problematic.

Modification of the MUF resin with low levels of hyperbranched polymers (HBPs) proved to be a very efficient way to overcome precure or overcure problems in addition to many property enhancements, which is attributed to the high reactivity of this class of polymers as a result of the high number of terminal reactive functional groups.

In the current study, we continue our previous efforts on the modification of UF/MUF resins [8–12] but with ester-terminated poly(amidoamine)s possessing a number of aldehyde terminals. To the best of our knowledge it is the first time for a hyperbranched polymer, containing some aldehyde terminals in addition to the main ester ones, to be employed as modifier for polycondensation resin such as MUF. This is thought to help the use of these species not only as co-condensing agents but also as bridging agents.

Materials and methods

Materials

Paraformaldehyde, aminoacetaldehyde dimethylacetal (AADA), trifluoroacetic acid (TFA), urea and methanol were purchased from Merck-Germany. Melamine was a product of DSM, Netherlands. Methyl acrylate (MA) and ethylenediamine (EDA) were provided by Sigma-Aldrich, France. All other chemicals were of laboratory grade and used without further purification. Industrial mixture of core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*), with moisture content around 4 % were used for particleboards production.

Synthesis of ester-terminated dendritic poly(amidoamine)s

Ester-terminated poly(amidoamine)s dendrimers were prepared according to the procedure of Tomalia and co-workers [13] which depends on consecutive addition of methyl acrylate (MA) and ethylenediamine (EDA) to produce a tetra-functional ester-terminated half generation (G0.5). Employment of ethylenediamine as a nucleophilic core to the obtained G0.5 yields a full-generation amine-terminated poly(amidoamine) (G1). The repeat of methyl acrylate addition on G1 gives rise to another higher half generation with 8 ester terminals (G1.5).

Modification of ester-terminated dendritic poly(amidoamine) s using aminoacetaldehyde dimethylacetal

Some aldehyde-terminals were inserted into the poly(amidoamine)s dendrimers beside the main ester terminals, for activation purpose, according to a novel short synthetic sequence [14]. This sequence involves the activation of the produced ester-terminated half generations (G0.5 & G1.5)

using calculated little amounts of aminoacetaldehyde dimethylacetal (AADA) by stirring a methanol/dichloromethane solution of the components at room temperature for 3–5 days. The solvent was removed under vacuum (2 mmHg, 40 °C, 14 h) to produce viscous ester-terminated counterparts with some acetal groups in a reasonable yield. Subsequent hydrolysis of these acetal terminals on the poly(amidoamine)s main structure with trifluoroacetic acid in methanol/dichloromethane under continuous stirring for 48 h at room temperature eventually leads to ester-terminated dendrimers containing some aldehyde-terminated groups, after removal of the solvent under vacuum (10 mmHg, 40 °C, 8 h). The products will be symbolized as **G1** & **G2**.

Preparation of Gn modified MUF resins

A commercially well-established procedure was described before for the preparation of MUF resin [15, 16]. 62.64 g paraformaldehyde, 39.68 g urea and 56.68 g water were added under continuous stirring to a glass reactor equipped with a reflux condenser and thermometer. Different proportions of Gn with aldehyde-terminated species were added individually based on the employed solid material at this step [11, 12] (route 1). Then, the pH was set at 10–10.5. The temperature was increased to 92 °C while the continuous mechanical stirring was maintained and the reaction continued for additional 30 min. The pH was then adjusted to 5–5.5 by addition of 10 % formic acid solution. After 1 h, the pH was brought to 9.5 or higher using 33 % NaOH solutions. 41 g melamine and 19 g water were additionally added to the reaction mixture. The water tolerance of the resin was checked every 10 min. while the pH was allowed to decrease spontaneously. When the water tolerance of the resin reached 300 %, a second urea (6.5 g) was charged to the mixture and the pH was adjusted again to 9.5 using 33 % NaOH solution. The reaction continued for 10–15 min. until the water tolerance reached 170–180 %. The pH was again adjusted to 9.5. The resin was cooled and stored at room temperature. An another series of experiments was conducted where the dendritic structures (Gn) were added initially at different ratios on the expense of some formaldehyde for F:(M + U) ratios in a range covers 1.9–1.3 (route 2). Thus, MUF + 4%G1:(F/(U + M) = 1.7) means that 4%G1 was added as a co-reactant together with formaldehyde, melamine and urea whereas the molar ratio of F/(U + M) was 1.7. Likewise, MUF + 2%G2:(F/(U + M) = 1.5) means that 2%G2 was added while the molar ratio of F/(U + M) was 1.5.

Fourier transform infrared spectroscopy and nuclear magnetic resonance investigations

Fourier transform infrared (FTIR) spectra of the aldehyde-terminated hyperbranched polymers were collected with a JASCO FTIR-6100E spectrometer, Japan. Bruker DRX-400

Nuclear Magnetic Resonance (NMR-100 MHz) spectrometer was utilized for recording the spectra of the dendritic polymers at 25 °C in APT mode using acetone-d₆ as a solvent. The pulse program was performed in jmod sequence and comprised acquisition time of 1.3631 s and a sweep width of 24,037 Hz.

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry measurements

The MALDI-TOF spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The duration of a single laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), and 100–150 pulses per spectrum. The delayed extraction technique was used by applying delay times of 200–800 ns. The samples were mixed with acetone solution (5 mg/mL acetone) of the matrix (2,5-dihydroxy benzoic acid). NaCl was added to the matrix (0.1 mol/ml in methanol/water solution, 2/1 methanol/water by volume) for enhancement of ion formation. The solutions of the sample and the matrix were mixed in the following proportions; 3 parts matrix solution + 3 parts sample solution + 1 part NaCl solution then 0.5–1 µL of the resulting mixture was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

Thermomechanical analysis (TMA)

The hardening reactions of the different resin systems were evaluated by studying the rigidity of a wood-resin joint for each system as a function of temperature using Mettler TMA SDTA 840 thermomechanical analyzer with STARe software for data treatment. All experiments were conducted under the same conditions: 25 mg of resin, heating rate 10 °C/min. in the temperature range 25–250 °C. Deflection curves which allows to determine the modulus of elasticity (MOE), have been obtained in three point flexion mode on two beech wood veneers of dimensions 18×5×0.5 mm³ for each specimen while the liquid resin layer was spread between the two specimens. The MOE of a wood-resin system gives a good indication of the end rigidity. This is enough to predict the final application of the glued system. The measurements of the thermomechanical properties were made in triplicates on three similar specimens and the average value was taken.

Contact angle measurements and gel times

The contact angle measurements for the liquid resins on a solid substrate (beech piece) before and after modifications were recorded using KRÜSS optical drop shape analysis instrument (DSA), Germany. The gel times were measured

in triplicates by registering the elapsed times until gelation when a glass test tube containing 4 g of each resin was immersed in boiling water in absence and presence of 2 % wt/wt of 25 % ammonium chloride solution.

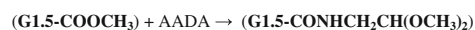
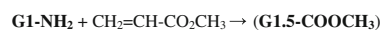
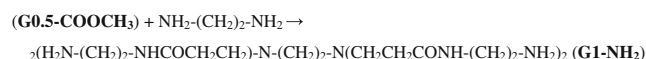
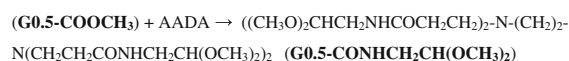
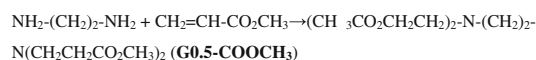
Wood particleboards preparation and testing

Triplicates of one-layer particleboard of $350 \times 300 \times 14 \text{ mm}^3$ dimensions, pressed at a temperature of 195°C for 7.5 min total press time under maximum pressure of 28 kg/cm^2 were carried out. The resin solids content was 10 % based on dry wood particles. All particleboard panels were tested for dry internal bond (IB) strength, as well as wet IB strength after 2 h immersion in boiling water followed by drying at 103°C for 16 h, using Instron 4467 universal testing machine at a speed of 2 mm/min. The modulus of rupture (MOR) was also registered with the same machine.

Results and discussion

Few studies [17, 18] suggested strategies for the modification of polycondensation resins, namely UF using low molecular weight aldehydic components (succinaldehyde and glutaraldehyde) at the condensation steps. The main purpose of these studies was to increase the water resistance of these resins while their limitation in invoking other improvements was correlated with the poor solubility in water. The rich literature on poly(amidoamine)s (PAMAM) preparation with different terminal groups was encouraging for the authors to use these forms as modifiers for UF/MUF resins [8, 9, 11, 12]. We intend this modification mainly for verifying environmental/health requirements initiating from concerns related to the use of the carcinogenic formaldehyde. Extendedly, we are wishing to obtain other properties enhancements considering the unique features of this class of materials (better solubility and reduced viscosity) which allows a lot of desired properties at least due to their high functionality. For realizing all possibilities of involvement of the ester-co-aldehyde-terminated dendrimers (Scheme 1) in the resin structure of MUF, some suggested steps are listed in Scheme 2.

The synthesis starts with ethylenediamine (EDA) as a core initiator which reacts via Michael addition in the presence of excess methyl acrylate (MA) to yield a tetrafunction half generation ester-terminated poly(amidoamine) (PAMAM) (**G0.5**). Two parallel subsequent reactions can take place starting from **G0.5** as a precursor. The first involves partial acetalization of **G0.5** dendrimer in the presence of aminoacetaldehyde dimethylacetal (AADA) which can be subjected to hydrolysis in the presence of trifluoroacetic acid (TFA). In this step, the acetalized ester terminals will be converted to aldehyde-terminated poly(amidoamine) (PAMAM) (**G1-CHO**) (Scheme 1).

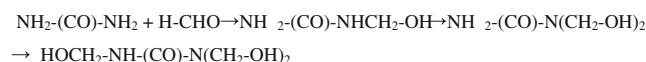


Scheme 1 Steps sequence for the synthesis of PAMAM dendrimers with some aldehyde terminal units

The second one entitles amidation on the ester groups of **G0.5** using EDA thus gives rise to a full generation with 4 amine terminals (**G1-NH₂**). The reaction of excess MA with **G1-NH₂** produces **G1.5** dendrimer terminated with 8 - COOCH₃ end groups. Exposure of **G1.5** to consecutive controlled acetalization and following hydrolysis reactions leads to **G2-CHO** with equivalent number of -CHO groups too (Scheme 1). Figure 1 displays the chemical structures of first generation (G1-CHO) as well as second generation (G2-CHO) of the dendritic poly(amidoaldehyde) supposing complete conversion of the terminal ester groups into the aldehyde ones. However, it should be stressed that our products from these steps are ester-terminated dendritic structures partially converted to aldehydic ones.

In continuation to our previous work on this topic, we employ different generations of dendritic poly(amidoester-co-aldehyde) in a variety of proportions during the first step of condensation on the expense of some (para)formaldehyde. The synthesis of MUF involves mutual simultaneous

Urea with formaldehyde



Melamine with formaldehyde



Urea with aldehyde-terminated dendrimer

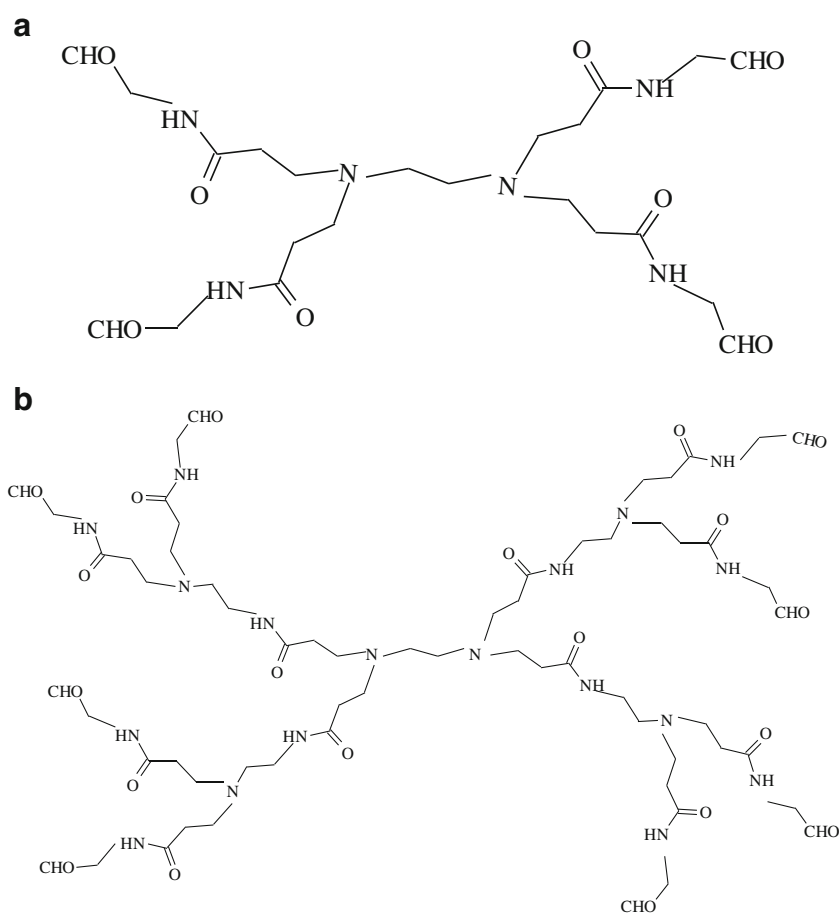


Melamine with aldehyde-terminated dendrimer



Scheme 2 Hydroxymethylation reactions of urea and melamine in the presence of aldehyde-terminated PAMAM as monomeric species for the synthesis of MUF

Fig. 1 Chemical structures of dendritic poly(amidoaldehyde) supposing complete conversion of the ester groups **a**) G1-CHO, **b**) G2-CHO



reactions of melamine (M) and urea (U) with formaldehyde (HCHO) to form monomeric species that constitute the seed for further condensation (Scheme 2).

The aldehyde-terminated dendritic species are also able to be involved similarly in reactions with both urea and melamine to reason successive hydroxymethylation steps on their amine sites (Scheme 2). Further, straightforward polycondensation reactions between these species can be undergone to yield the modified MUF resin.

As the terminal groups of dendrimers affect very much their reactivity [18] and this broadens also to viscosity and solubility [19, 20] thus their incorporation into any system is usually expected to invoke toughening effects [21–23], provide control over rheological properties [24] or promote the adhesion [25]. The impact of this modification on the resin properties and their based particleboards will be investigated in this work especially the resistance to water and formaldehyde emission. It should be kept in mind that the main ester terminals can participate as well in the involved reactions during particleboard production with the cellulosic hydroxyl groups via methanol removal and formation of new ester linkages.

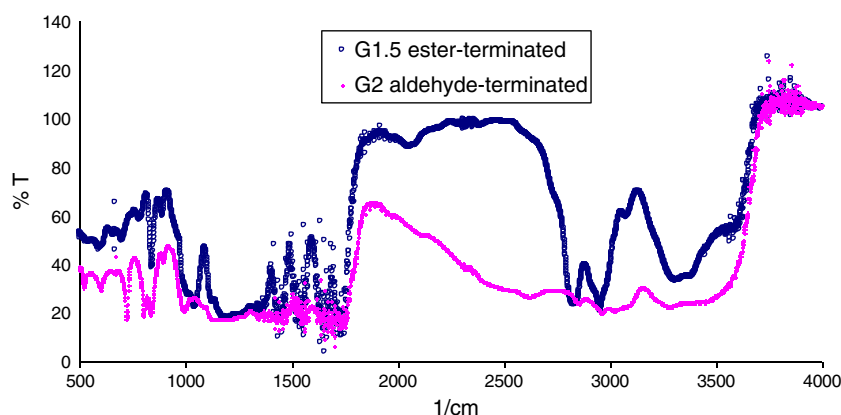
The conversion of some ester groups of the precursor to the aldehyde ones was confirmed at first using FTIR spectroscopy (Fig. 2). Comparing the related spectra of the precursor with

the counterpart of the expected partially aldehyde-terminated product gives rise to a decrease in the peaks intensity of the -CH_3 groups of the precursor, which are assigned at $2,940$ and $2,845\text{ cm}^{-1}$. The appearance of additional carbonyl peak at $1,725\text{ cm}^{-1}$, associated with reshaping/broadening and perturbation of the original one (appears at $1,750\text{ cm}^{-1}$), supports the formation of a new carbonyl environment. This is thought to originate from the emergence of some aldehyde groups within the main ester-terminated PAMAM.

Figure 3a, b displays the APT ^{13}C NMR spectra of the targets G1-CHO and G2-CHO, which are almost identical in the sense of the peaks positions for a given carbon. Most important, the -CHO appears obvious at 207 ppm [14] and became more intense in case of G2-CHO possibly because of the doubling of terminal groups content. The -C=O(NH) moieties can be recognized at 172 ppm while the signals around $29/30\text{ ppm}$ are related to the solvent. On the other hand, some signals appear in the range $50\text{--}52\text{ ppm}$ and are ascribed to different methylenic carbons ($\text{-N-CH}_2\text{-CH}_2\text{-N-}$, NH-CH_2 , $\text{CH}_2\text{-C=O}$). Based on these spectra, it could be inferred that the targets are successfully obtained.

Further investigation of possible G1-CHO and G2-CHO formation was undertaken using MALDI-TOF analysis (Figs. 4 and 5). In G1 spectra, the masses are low and it seems there is no

Fig. 2 FTIR spectra of precursor ester-terminated PAMAM as well as its successor with some aldehyde-terminated species



Na^+ enhancement. First of all, the 513 Da fragments are pertaining doubtless to the G1-CHO traces without Na^+ enhancement while the main product is the ester-terminated species (405 Da). A mass of 114 Da appears to represent an arm with a chemical formula of $-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO}$. As the molecular weight of G1-CHO is 512 Da thus the 403 Da fragment seems to characterize the G1 after a loss of one arm with 114 Da while the 427 Da species signify the G1 after losing two -

CH_2CHO . On the other hand, 443 Da species are thought to be formed after the 427 Da fragment received somehow one -OH whereas the 627 Da is a result of G1 plus one 114 Da arm. The suggested fragments are depicted in Scheme 3.

For understanding the fragments appearing in the G2-CHO (Fig. 5) it is also useful to look at the suggested fragments in Scheme 3. It is evident here that a series of peaks are separate by a 200 Da increment:

$$\begin{aligned}
 &405 \text{ Da} - 604 \text{ Da} - 805 \text{ Da} + 16 \text{ Da} = 821 \text{ Da}; \\
 &\quad 805 \text{ Da} - 1005 \text{ Da} \text{ and } 1005 - 16 \text{ Da} = 991 \text{ Da} - 1191 \text{ Da} \\
 &1005 \text{ Da} - 1205 \text{ Da} - 1405 \text{ Da} + 16 \text{ Da} = 1421 \text{ Da} - 1623 \text{ Da} - 1827 (1821 \text{ protonated}) \text{ Da} - 2027 - 16 \text{ Da} \\
 &\quad = 2012 - 2027 \text{ Da}.
 \end{aligned}$$

The 200 Da period can be composed of two combinations: either (i) 114 Da + 86 Da, or (ii) 114 Da + 2×43 Da.

The fragments corresponding to 114 Da has been already described in G1 spectrum. The 86 Da

fragment is likely $-\text{CO}-\text{NH}-\text{CH}_2\text{CHO}$ while the 43 Da fragment corresponds to the structure $-\text{CH}_2\text{CHO}$.

Additional fragments can be assigned as follows:

$$\begin{aligned}
 602 - 604 \text{ Da} & \quad 404 \text{ Da} + (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 627 \text{ Da} & \quad 427 \text{ Da} + (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO}) + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO} \\
 802 / 805 \text{ Da} & \quad 404 \text{ Da} + 2 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 823 \text{ Da} & \quad 805 + 16 \text{ Da} (-\text{OH}) \\
 991 \text{ Da} & \quad (404 - 16) \text{ Da} + 3 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 1005 \text{ Da} & \quad 404 \text{ Da} + 3 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 1191 \text{ Da} & \quad (404 - 16) \text{ Da} + 4 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 1205 \text{ Da} & \quad 404 \text{ Da} + 4 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 1213 \text{ Da} & \quad \text{G2} - 2 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO}) \\
 1227 \text{ Da} & \quad 1229 \text{ Da deprotonated} \\
 1229 \text{ Da} & \quad \text{G2} - 2 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO}) - 1 \times -\text{OH} \\
 1405 \text{ Da} & \quad 404 \text{ Da} + 5 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 1427 \text{ Da} & \quad \text{G2} - 1 \times -\text{OH}
 \end{aligned}$$

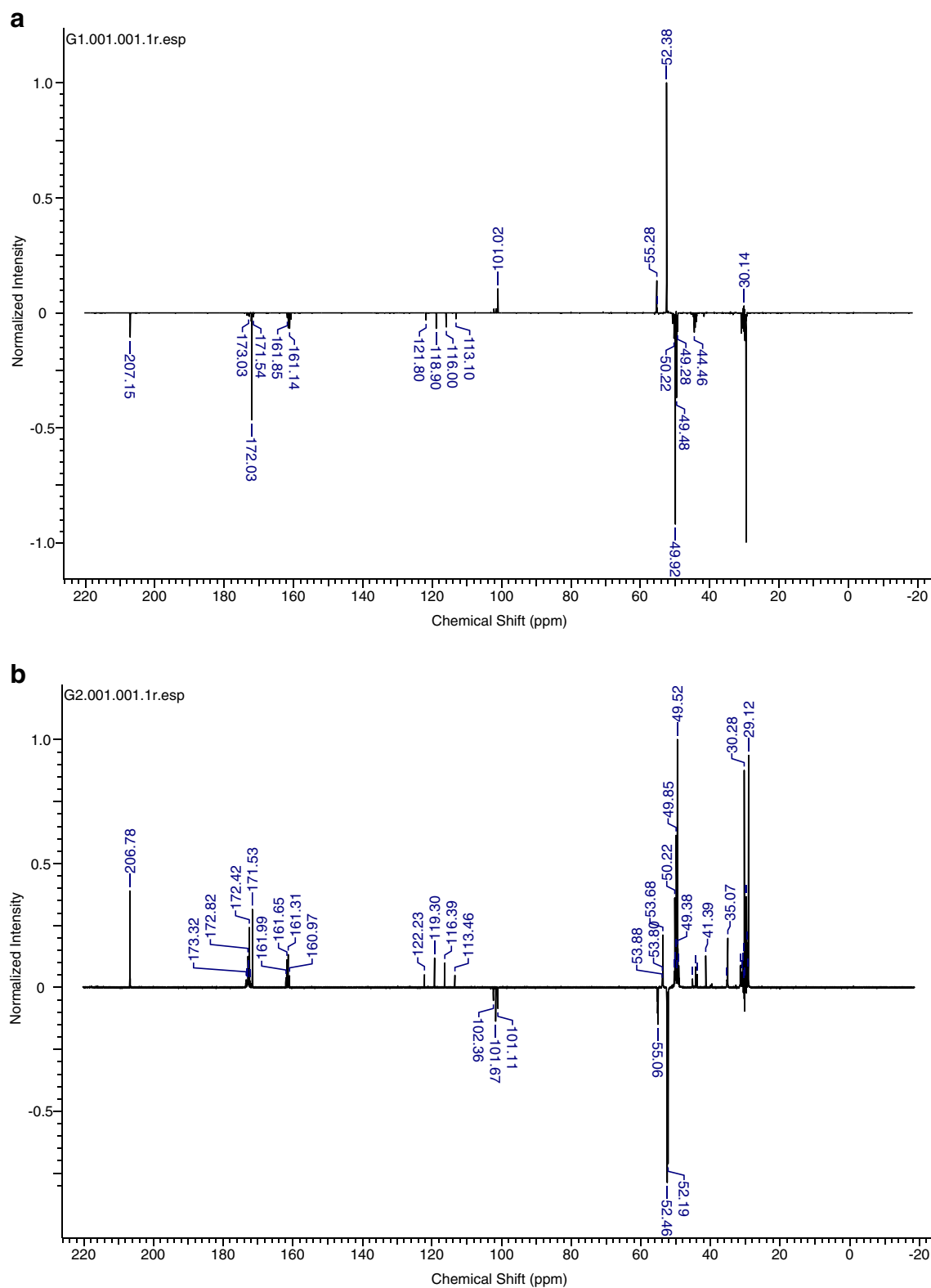


Fig. 3 APT ^{13}C NMR spectra of ester-terminated PAMAM with some aldehyde terminals (**a**) G1- $\text{COOCH}_3\text{-co-CHO}$ and (**b**) G2- $\text{COOCH}_3\text{-co-CHO}$

Performance
Data: <Untitled>.J8[c] 12 Sep 2013 17:08 Cal: 26 Mar 2013 11:25
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 82, Blanked, P.Ext. © 2094 (bin 74)

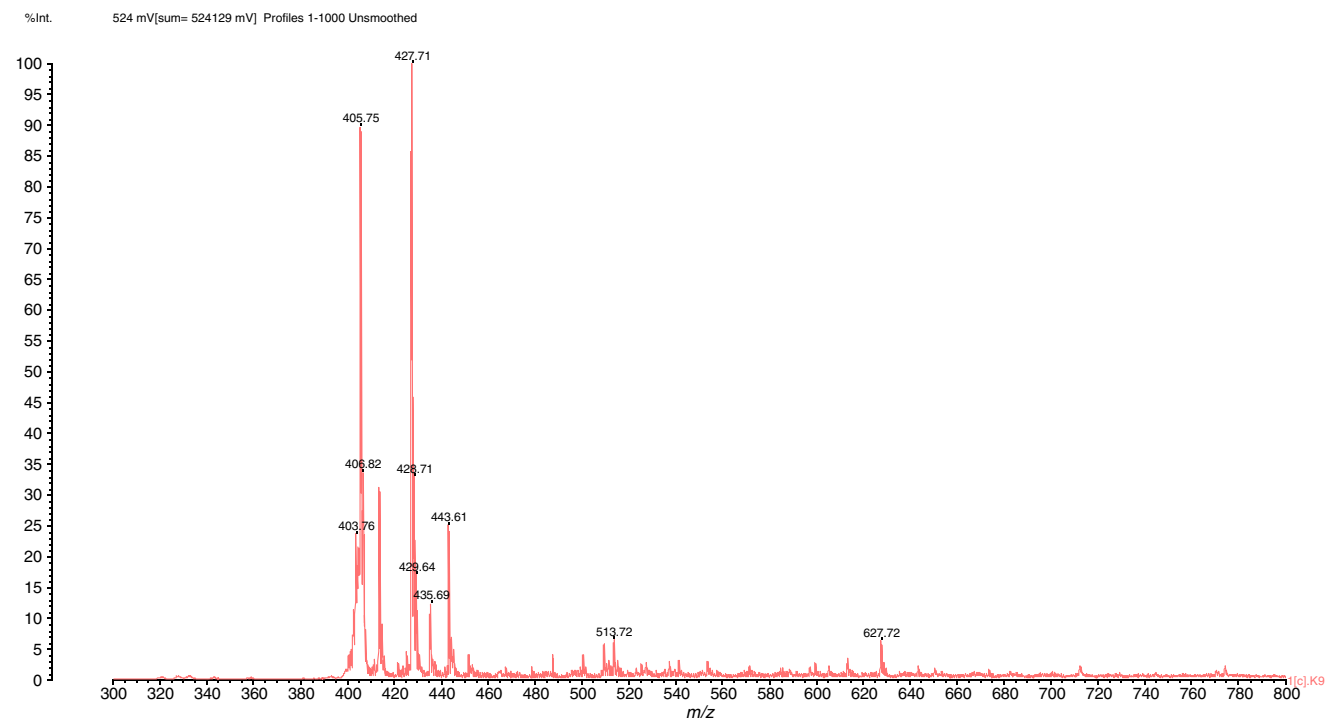


Fig. 4 MALDI-TOF spectra of G1-COOCH₃-co-CHO

Performance
Data: <Untitled>.J9[c] 12 Sep 2013 17:16 Cal: 26 Mar 2013 11:25
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 86, Blanked, P.Ext. © 2094 (bin 74)

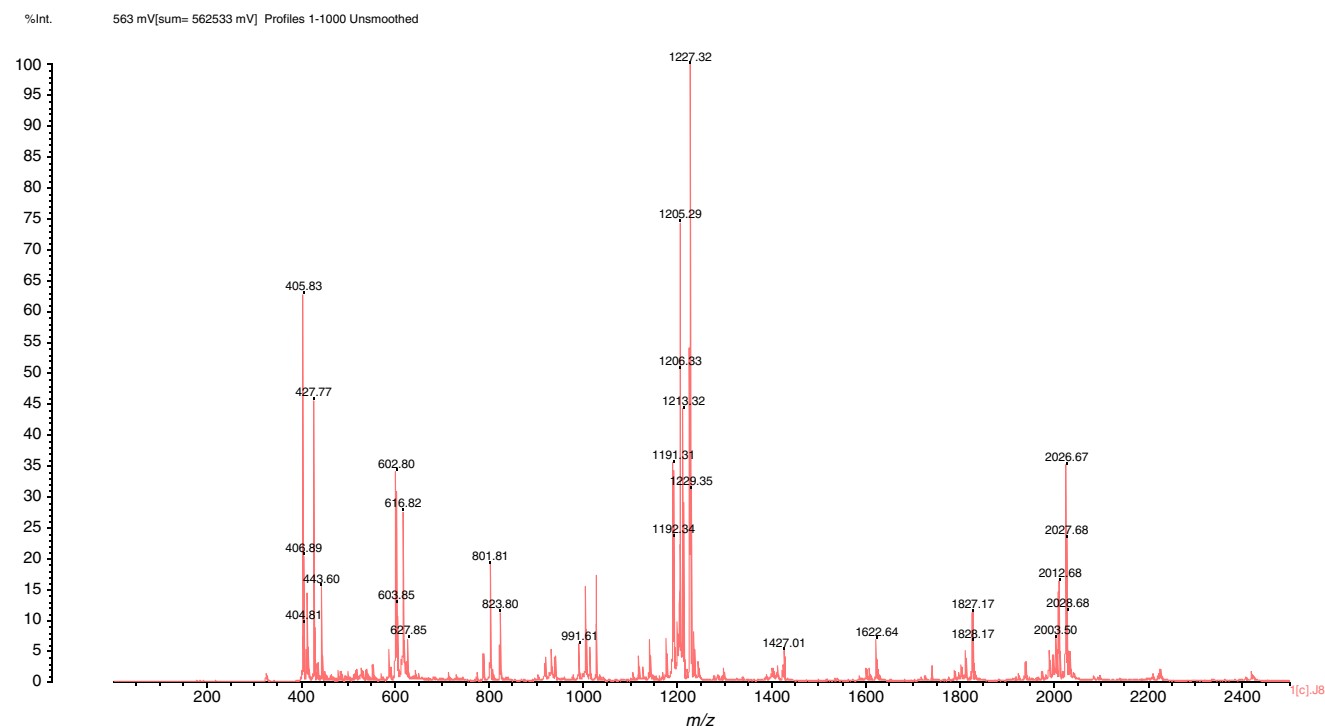
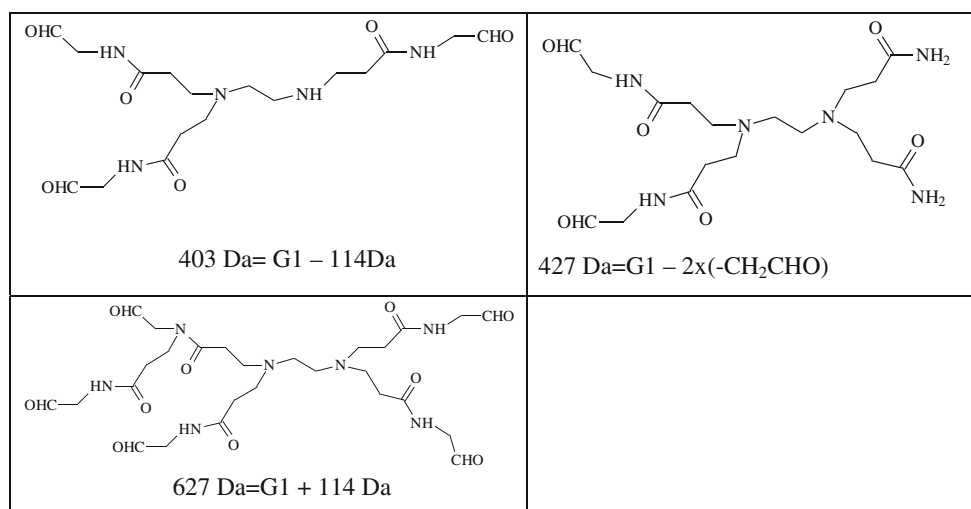


Fig. 5 MALDI-TOF spectra of G2-COOCH₃-co-CHO

Scheme 3 The major detected fragments of G1 during the MALDI-TOF analysis

terminated species of G1.5, there are other fragments that belong to grown species in a non-controlled manner, perhaps by bridging, or may be related to other complicated species

containing some aldehyde terminals. Thus, these fragments represent the broad distribution of molecular weights and can be signified as follows:

$$\begin{aligned}
 1623 \text{ Da} &= 404 \text{ Da} + 6x(-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) + -\text{OH} \\
 1821 \text{ Da protonated} &= 1827 \text{ Da} = \\
 404 \text{ Da} + 7 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) + -\text{OH} \\
 2013 \text{ Da} &= 404 \text{ Da} + 8 \times (-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) \\
 2028 \text{ Da} &= 404 \text{ Da} + 8x(-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{CHO} + -\text{CO}-\text{NH}-\text{CH}_2\text{CHO} + -\text{CH}_2\text{CHO}) + -\text{OH}
 \end{aligned}$$

It was then necessary at the beginning to find out the best way to modify the melamine urea formaldehyde (MUF) resin using the hyperbranched polyamidoamine ending partially with aldehyde groups. Two series of experiments were conducted. In the first series, the reaction conditions were set constant and after that the hyperbranched polymer was charged as an additive in different proportions to the prepared MUF resin (Tables 1, 2, 3, and 4).

The impacts of G1 and G2 as additives in different ratios for the prepared MUF resin on the characteristics of the produced resins are summarized collectively in Tables 1 and

2. The pH of the resin at the end of the preparation process remained unchanged which was also the case for the solid content. For either G1 or G2 based systems, the viscosity decreased in a systematic way with the increase in their proportions but the effect was surprisingly more in case of G1. The changes in gel times, as measures of the resins reactivity in the presence of the additives or may be liability of these additives to interact with the reacting species, were statistically insignificant in both cases while the contact angles were considerably lowered in both cases but with more effectiveness in case of G1 that provoked faster drop in the contact angles.

Table 1 Characteristics of modified MUF resin with different proportions of G1 during the resin synthesis in the first step

Resins	pH	Solid content (%)	Viscosity (mPa·s)	Gel time (s)	Contact angle (°)
MUF	9.5	57	100	55	70
MUF + 1%G1	9.5	57	80	55	45
MUF + 2%G1	9.5	57	70	56	42
MUF + 3%G1	9.5	57	55	56	45
MUF + 4%G1	9.5	57	55	54	48

Table 2 Characteristics of modified MUF resin with different proportions of G2 during the resin synthesis in the first step

Resins	pH	Solid content (%)	Viscosity (mPa·s)	Gel time (s)	Contact angle (°)
MUF	9.5	57	100	55	70
MUF + 1%G2	9.5	57	80	54	50
MUF + 2%G2	9.5	56	85	54	55
MUF + 3%G2	9.5	56	80	53	55
MUF + 4%G2	9.5	56	75	56	52

Table 3 Characteristics of laboratory-made particleboards fabricated with conventional MUF resin as well as modified ones with different proportions of G1 at the first step during the resin synthesis

Resins	Density (g/cm ³)	Dry IB strength (MPa)	IB strength after 2 h in boiling water (MPa)	MOR (MPa)	MOE (MPa)
MUF	0.72	1.03	0.17	18	3056
MUF + 1%G1	0.72	1.03	0.20	19.38	3452
MUF + 2%G1	0.72	0.96	0.25	20.31	3342
MUF + 3%G1	0.72	1.07	0.28	19.85	3510
MUF + 4%G1	0.72	0.94	0.29	24	3805

This translates into a reasonable surface activity exhibited by the additives which likely mean their main accumulation on the surface of the resin colloidal particles that grow with the advancement of the co-polycondensation reaction. Additionally, this may mean either reaction with the hydroxyl groups at the boundaries of the already formed resin network, which accounts for the acquired surface activity, or the additives played the role of crosslinkers bridging 2 of the hydroxy-functionalized MUF growing species by splitting off water molecules (one oxygen from the aldehyde group with hydrogens from 2 condensating MUF species, Scheme 4). The scheme makes it also obvious the consequent possibility for further successive reaction with cellulosic -OH groups to produce particleboards through intensive co-condensation and removal of the splitted off water. This can additionally occur by reaction of one ester group from the dendritic modifier moieties with a hydroxyl group from the cellulosic material through a removal of methanol.

Overall, the practical importance of this lies in their effect to increase spreadability of the resin over the wood substrates or at least keep it unchanged in case of resin advancement and/or during relatively long storage times (Tables 1 and 2). Tables 3 and 4 show the characteristics of the corresponding particleboards fabricated with the conventional as well as modified MUF resins. The density of the particleboards remained in the same level in all cases while the dry internal bond strength was scattering either upward or downward in most of the cases except for the formulation based on 1 % addition of G2 which exhibited 15 % elevation of the bond strength. Interestingly, the real advantage of using such additives was the augmentation of the wet internal bond strength of the particleboards, after soaking for 2 h in boiling water, with respect to the based particleboards on the pristine MUF.

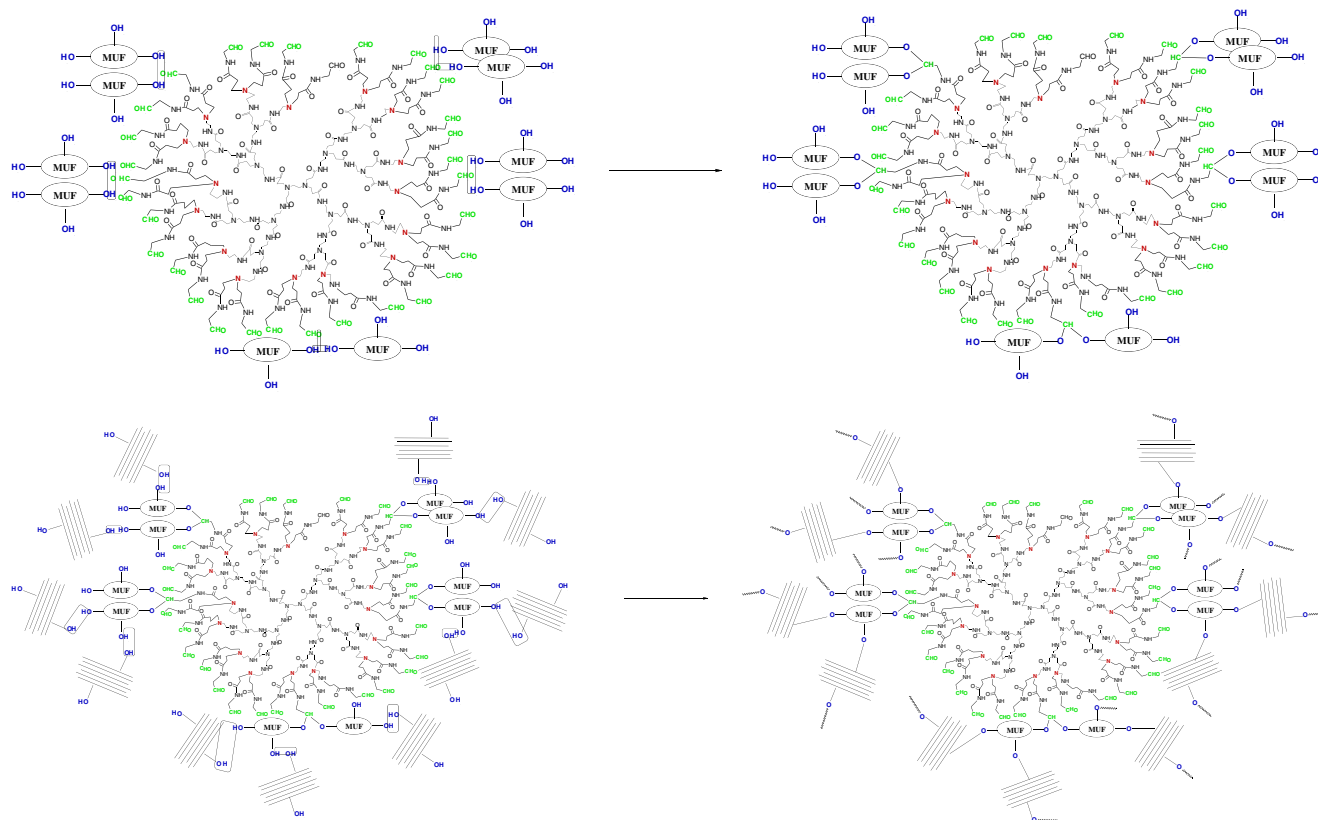
As the bond strength in this case is a measure of the extent of resistance to hydrolytic degradation encountered during exposure to humid atmospheres especially in summer time therefore both G1 and G2 incorporation led to improvement of this resistance. This parameter varies directly proportional to the level of addition but with more effectiveness in case of G1, which may be ascribed somehow to a more loose network structure in case of G2 addition. Thus, the augmentation in the wet internal bond strength reached 18 % for 1 % addition, 47 % for 2 % addition, 64 % for 3 % addition and 70 % for 4 % addition of G1, respectively. Further, the modulus of rigidity (MOR) elevates satisfactorily with the addition, reaching maximum for the G2 based composition at 1 % addition (increased about 7.5 %, Table 4) while the maximum increase was in the level of 33 % in case of G1 at 4 % addition (Table 3).

To deal with the modulus of elasticity (MOE), it was necessary to check the relevant thermomechanical curves in both cases (Figs. 6 and 7). First of all, the resinification process was accelerated in the presence of the additives in the sense of the earlier onset of the gelation step along with the higher rate of curing until reaching peak maximum (MOE) before turning downward again as a result of the vitrification process. The maximum attained peak intensity values for the G1 based compositions can be arranged in the sequence: 3,805 MPa (4 %) > 3,510 MPa (3 %) > 3,452 MPa (1 %) > 3,342 MPa (2 %) > 3,056 MPa (0 %).

On the other hand, the attained peak intensity values in case of G2 based compositions can be sequenced in the following order according to the intensification level: 3,492 MPa (1 %) > 3,383 MPa (2 %) > 3,179 MPa (3 %) > 3,056 MPa (0 %). These data reveal the superior performance of G1 in general as a function of the increase in the level of addition as compared

Table 4 Characteristics of laboratory-made particleboards fabricated with conventional MUF resin as well as modified ones with different proportions of G2 at the first step during the resin synthesis

Resins	Density (g/cm ³)	Dry IB strength (MPa)	IB strength after 2 h in boiling water (MPa)	MOR (MPa)	MOE (MPa)
MUF	0.72	1.03	0.17	18	3056
MUF + 1%G2	0.72	1.18	0.25	19.38	3492
MUF + 2%G2	0.71	1.06	0.25	19.38	3383
MUF + 3%G2	0.71	1.07	0.20	18.46	3179
MUF + 4%G2	0.69	0.90	0.18	17.08	3083



Scheme 4 Possibility for reaction of Gn-COOCH₃-co-CHO with MUF when employed as an additive and consequent participation in particleboard fabrication

to G2. Furthermore, the action of the additive is intensified at higher levels in case of G1 while the action is reversed when increasing the G2 proportion which signifies the compromise and competition between the factors of degree of branching and content of terminal function groups in governing the different characteristics of the produced particleboards. That is to say that, the formed network in case of G2 was looser despite the higher number of interacting terminal function groups as a result of the predominance of the higher degree of branching in this particular case, as compared to G1, in

governing the mechanical behavior and this is a limitation of the use of such materials as modifiers when acquire a high degree of branching. This was deduced supposing that, since there is a competition between the Gn-CHO and formaldehyde, at the first reaction step, to react with urea and melamine. Therefore, this competition dictates preponderance of the formaldehyde, which is more active, over Gn-CHO. This factor together with the low -CHO functionality especially in case of G1-COOCH₃-CO-CHO may suggest its action mostly as bridging/crosslinking agent more than a co-condensing agent in case of route 1.

Fig. 6 Thermomechanical curves of modified MUF with different proportions of G1-CHO

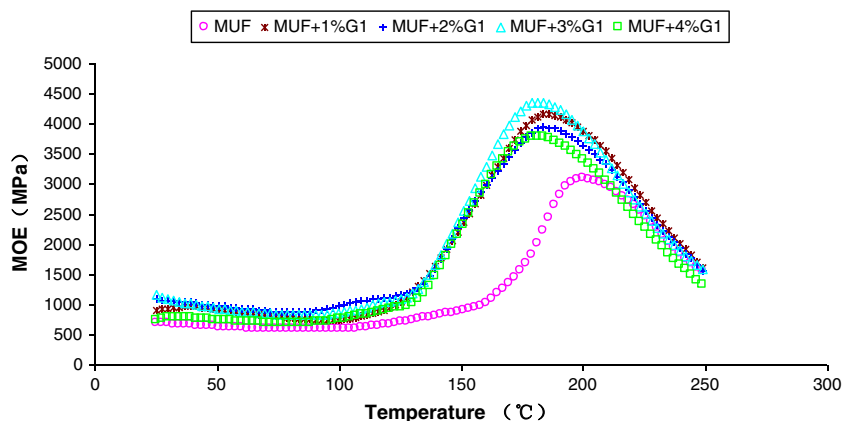
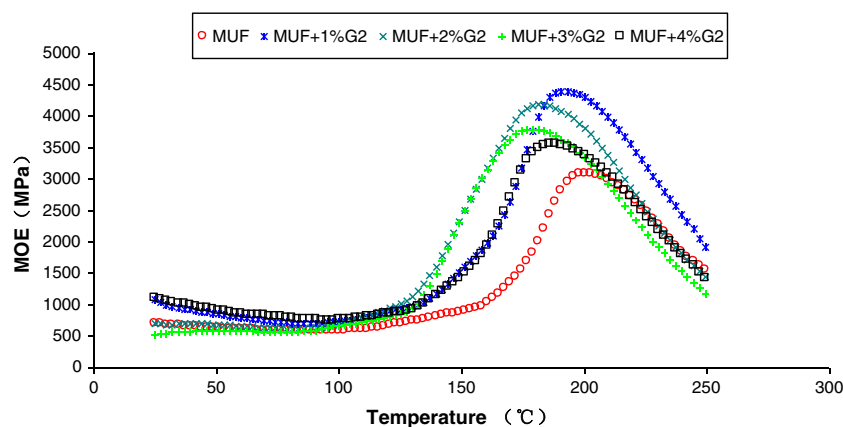


Fig. 7 Thermomechanical curves of modified MUF with different proportions of G2-CHO



In all, the toughening role that could be acquired by such modifiers is now clearly evident from the heightening of MOE. Usually, the MUF is likewise to the other thermoset resins, e.g., UF, PF, turn into a hard brittle highly crosslinked mass during curing or after overcuring leading to premature failure and decrease in strength. The increase in MOE indicates enhanced load bearing capability of the wood joints glued with the modified adhesives as a result of the easier and faster relieve of either the imposed/developed stress on the network structure of the resin through imparting sufficient flexibility to the network structure. This can be compiled into a dilution of the crosslinking density in a positive way thereby the usually encountered premature failure could be avoided.

Principally, it is now doubtless that the dendritic poly(aminoester-co-aldehyde)s are polycondensatable with the MUF and this assumes again their compatibility together. Therefore, the extent of effective incorporation within the network skeleton of the resin is subject to reaction conditions

and addition sequence. However, the shape of the TMA profile along with the significant enhancement in the MOE up to the vitrification point (note the intensification of the initial shoulder in the range 150–200 °C) generally suggests their co-reaction and ability not only to react with the hydroxyl groups at the boundaries but this extends also to bridge the condensing MUF species.

Formaldehyde, as a very toxic material, represents one of the main components of many polycondensating resins, thus there has been always desires to replace it with other less active aldehydes. As this causes severe drop in the reactivity of the resulting resins and extends to the corresponding particleboards, accordingly most of the successful trials were dedicated with emphasis on partial substitution of the carcinogenic formaldehyde. Therefore, in a second series of experiments the ratio of the formaldehyde was reduced systematically with respect to total (melamine + urea) and different additions of

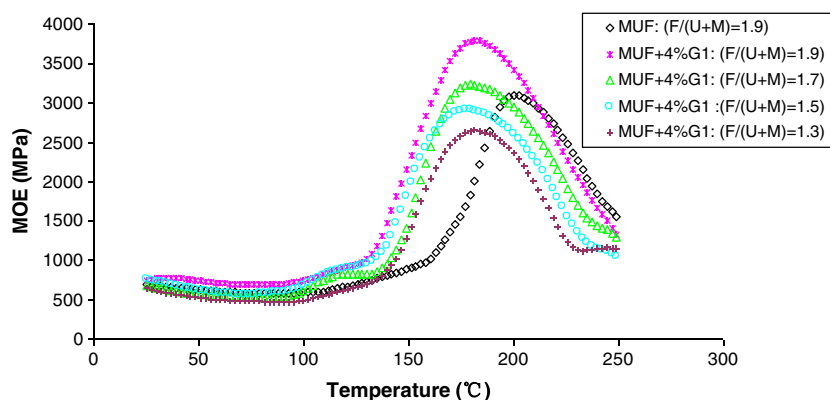
Table 5 Characteristics of MUF resins modified with 4%G1 and 2%G2 on the expense of some formaldehyde at the first stage of resin synthesis as a function of the molar ratio of F/(M + U)

Resins	Viscosity (mPa.s)	Gel time (s)	Contact angle (°)
MUF + 4%G1			
Molar ratio F/(M + U) = 1.9	55	54	48
Molar ratio F/(M + U) = 1.7	72	65	53
Molar ratio F/(M + U) = 1.5	80	80	60
Molar ratio F/(M + U) = 1.3	92	65	65
MUF + 2%G2			
Molar ratio F/(M + U) = 1.9	85	54	55
Molar ratio F/(M + U) = 1.7	89	70	59
Molar ratio F/(M + U) = 1.5	92	80	60
Molar ratio F/(M + U) = 1.3	95	90	65

Table 6 Dry and wet IB strength values of particleboards formulated with different MUF resins modified with 4%G1 and 2%G2 as a function of the molar ratio of F/(M + U)

Resins	Density (g/cm ³)	Dry IB strength (MPa)	IB strength after 2 h in boiling water (MPa)
MUF + 4%G1			
Molar ratio F/(M + U) = 1.9	0.72	0.94	0.29
Molar ratio F/(M + U) = 1.7	0.72	1.02	0.22
Molar ratio F/(M + U) = 1.5	0.71	1.02	0.19
Molar ratio F/(M + U) = 1.3	0.72	0.96	0.12
MUF + 2%G2			
Molar ratio F/(M + U) = 1.9	0.72	1.06	0.25
Molar ratio F/(M + U) = 1.7	0.72	1.05	0.25
Molar ratio F/(M + U) = 1.5	0.72	1.00	0.24
Molar ratio F/(M + U) = 1.3	0.72	0.95	0.13
European standard NF EN 312 type P5		≥0.35	≥0.15

Fig. 8 Thermomechanical curves of modified MUF with 4%G1 as a function of F/(M + U) molar ratio



G1/G2-CHO (aldehyde-terminated hyperbranched copolyesters) were charged during the first synthesis step (Tables 5 and 6).

For the modified resins with 4 % G1, the viscosity increased linearly with the decrease in the formaldehyde ratio in the resins which definitely means unease of processing/application of these resins. Additionally, there was also a parallel increase in the gel time indicating that the formaldehyde is supposedly more active in imparting higher reactivity to the resin as compared to the aldehyde-terminated HBP and that this dendritic structure may not compensate completely the absence of formaldehyde hence this point will be more studied with TMA. The latter case was exactly the same on dealing with the contact angle of the resins over the substrate which translates into inferior spreadability as far as the formaldehyde is reduced. Shifting the modification to 2 % G2 produced identical impacts on the resin properties (Table 5).

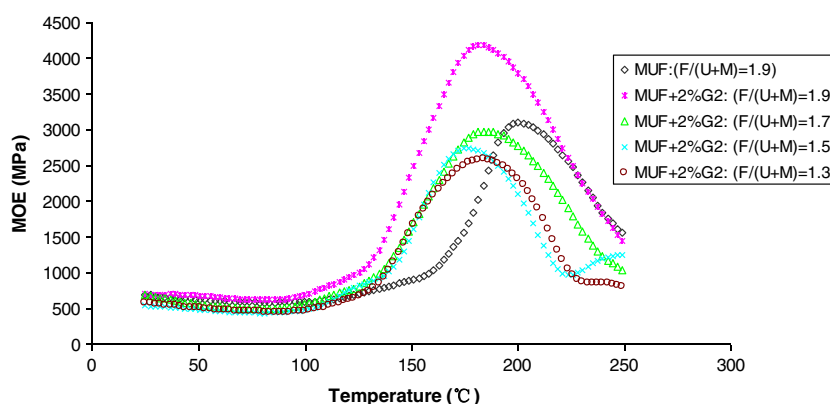
The characteristics of the corresponding particleboards are collected in Table 6 which shows a comparable density in all cases. The dry internal bond strength remained all the time in a same satisfying level while, after inducing hydrolytic degradation, the wet internal bond strength was adversely affected and there was a gradual loss that reached 58 % for the F/M + U molar ratio of 1.3 in case of 4 % of G1, which was the only case that could not adhere to the European standard (Table 6). 2 % of G2 worked better at least in case of the wet internal

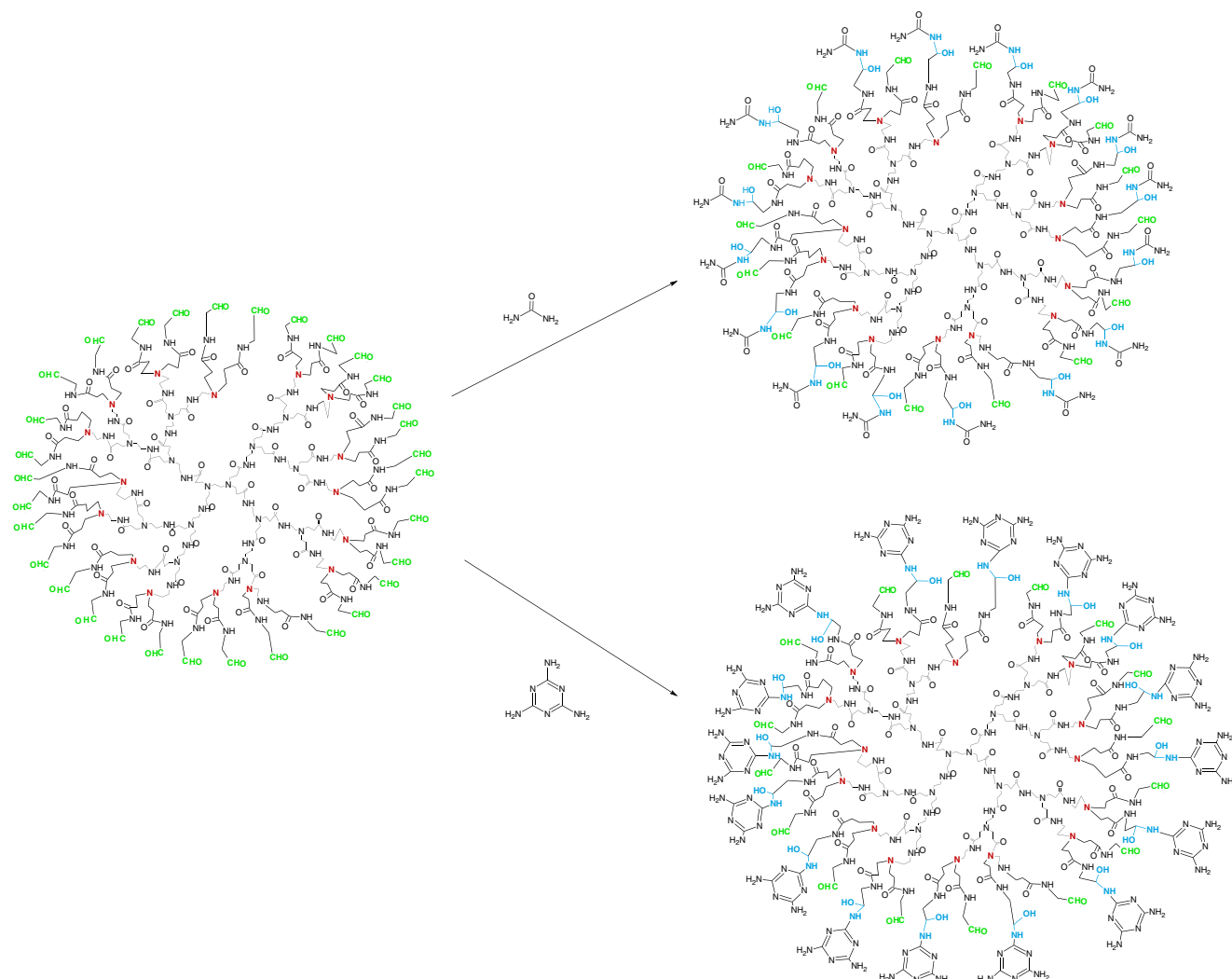
bond strength, except for the F/M + U molar ratio of 1.3, which was again beyond the minimum level specified in the European standard. These results ensure the potential of these modifiers to practically compensate the absence of the formaldehyde which would help to broaden the applicability of the based particleboards for indoor use considering the very much less harmful effect of the carcinogenic formaldehyde.

For better evaluation of the resin reactivity after replacing some portions of the formaldehyde with comparable amounts of the HBPs, thermomechanical runs were recorded for these resins (Figs 8 and 9). It was evidenced from the recorded runs in case of 4 % G1 that, under dynamic cure conditions, the gelation times are shortened obviously along with higher rate of curing was noticed. Further, the attained maximum MOE levels could be amplified with respect to the unmodified MUF in case of F/M + U ratio of 1.9 and up to 1.7. It is worthy to note that the curing shoulder, starts immediately after gelation and up to the maximum MOE, is more upright as compared to the modification of MUF by the HBPs in case of route 1 of modification. This may be an evidence of the more efficient participation in the network structure and that their role in this case entitled principally co-reaction of Gn-CHO with melamine and urea to form methylol groups, that condense further to yield the modified resins (Scheme 5).

The same attributes were found for the G2 in the sense of sharper curing peaks and higher curing rate. However, as the

Fig. 9 Thermomechanical curves of modified MUF with 2%G2 as a function of F/(M + U) molar ratio





Scheme 5 Possibility for condensation reactions taking place between Gn-CHO with urea and melamine when employed from the beginning as a co-reactant

G2 encounters a higher degree of branching it may work against the strength. Therefore, it was used in half amount with respect to G1 and the TMA profile (Fig. 9) confirmed that it was actually the case and the maximum MOE could only be elevated for the F/M + U molar ratio of 1.9 as compared to the conventional MUF.

Conclusions

Hyperbranched poly(aminoester-co-aldehyde)s of different generations can be exploited as modifiers for MUF resins via two different routes. They proved to be good candidates to substitute the carcinogenic formaldehyde component in the resins without causing detrimental effect either on the resin properties or the attributes of the produced particleboards thereof. The real added value in case of utilization as additives (route 1) is the improvement of the particleboards properties

particularly the resistance to hydrolytic degradation. Moreover, when used at the expense of some formaldehyde portions (route 2) these additives are beneficial because of health and environmental considerations. This helps to broaden the applicability of the relevant particleboards for indoor use.

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