Modification of Melamine-Formaldehyde Resins by Substances from Renewable Resources

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ABSTRACT: In the present contribution, investigations on the chemical modification of thermosetting melamine formaldehyde resins by natural polyol compounds are presented. As representative agents soluble starch, sucrose, and glycerol were chosen to cover three different classes of polyols. The major aim was to use substances produced from natural bio-renewable feedstock that are available in large quantities and may serve as environmentally innocuous and bio-renewable substitutes for petro-chemically derived and potentially hazardous materials. Different reaction conditions lead to resins with varying technical performance. For soluble starch no reaction conditions could be found that allow the adoption of this substitute for the laminate industry due to insufficient technological performance. Sucrose and glycerol on the other hand yielded impregnation resins with suitable performance. Chemical linkage of the modifying agent into the chain propagation by poly-condensation however, was only found with glycerol. The covalent incorporation of glycerol in the network was observed with addition of glycerol at different stages during synthesis. The technological performance of the various modified thermosetting resins was assessed by determining flow viscosity, molar mass distribution, the storage stability, and in a second step laminating impregnated paper to particle boards and testing the resulting surfaces according to standardized quality tests. Spectroscopic evidence of chemical incorporation of glycerol was found by applying by ^{1}H, ^{13}C, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, and ^{1}H DOSY methods. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4416–4423, 2012

Key words: modification; thermosets; melamine formaldehyde resin; DOSY NMR; renewable resources

INTRODUCTION

During the last decade the interest in using raw materials based on bio-renewable resources for synthetic polymers and composite materials[1] increased largely in the context of a trend towards greener production technologies,[2] sustainability,[3] and bio-refinery.[4] This trend also affects the engineered wood products and decorative laminates industries. Recent developments in eco-efficient bio-based adhesives for wood bonding include the use of tannin, lignin, protein, and carbohydrate derived natural binder systems as well as chemically modified natural unsaturated oils like for instance, epoxidized linseed oil.[5] Although in special cases, like in wood welding[6] or in the manufacturing of fiberboards in the wet process,[7] natural binders like lignin may be used as the sole adhesive, bio-based binders are most often used as supplements to existing glues to make them more environmentally friendly, more cost effective, and better performing.[5] In this context, kraft lignin has only recently been studied for its potential to substitute portions of synthetic phenolic (PF) resin in impregnation resins for the manufacturing of decorative laminates.[8] While such phenol-based laminates consist of stacks of PF impregnated papers, their surface finish consists of a cover sheet made of melamine formaldehyde (MF) impregnated paper. For such surfaces MF resins are used because of their unique surface properties in terms of hardness, chemical stability and transparency which allow brilliant visual appearance of the surface decors and good performance in use at reasonable prizes. In contrast to PF, natural modification agents may not be based on lignin or the like aromatic structures because the color of such compounds interferes strongly with the transparency required to obtain a good optical impression of the decor.
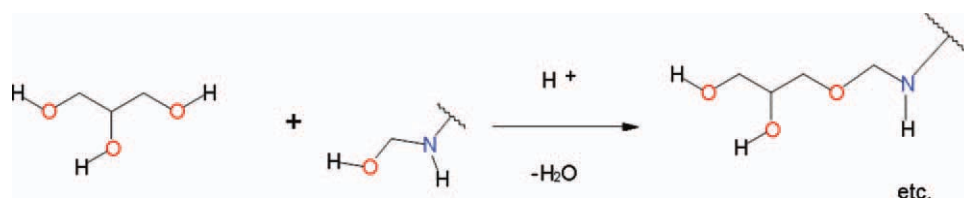
Figure 1 Schematically depicts the proposed reaction taking place during glycerol modification of the melamine formaldehyde impregnation resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Instead, other modification agents need to be employed. Many research groups found possibilities of modifying MF and also urea formaldehyde (UF) resins by various alcohols, sulfonamides, lactames, acrylates, etc. for special applications.[9–12] Only recently, the copolymerization of urea with melamine and formaldehyde was described that yielded an impregnation resin of technologically sufficient performance for special interior applications.[13–15] However, one major drawback of the urea modified MF surface film is its slightly lower performance in terms of chemical resistance and hydrolysis under wet conditions (in bathrooms or exterior applications).

Because of the potential chemical accessibility via multiple hydroxyl groups, the present work focused on the incorporation of starch, sugar and polyhydric alcohols. As representative compounds for these substance classes soluble potato starch, sucrose, and 1,2,3-propantriol (glycerol) were selected as natural modifiers for MF-based impregnation resins. Glycerol has some advantages over other potential polyol-type modifying agents like starch or conventional sugars such as sucrose due to its liquid form at room temperature and its excellent water solubility. Glycerol is an interesting compound also because of its trivalent chemical structure and the fact that it is produced in large quantities as a cheap and sufficiently purified byproduct from the biodiesel industry which renders it readily available in an environmentally sustainable way. Because of its lack of toxicity glycerol decreases the overall content of potentially harmful compounds making up traditional MF impregnation resins by substituting significant portions of melamine. Furthermore, glycerol has also been described in the literature as an effective plasticizing agent[16,17] which in turn might lead to better technological performance of glycerol-modified MF films. For laminate application, the formation of a three-dimensionally cross-linked copolymeric network of MF and glycerol is a crucial point. Insufficiently cured resins are prone to chemical attack and yield minor surface quality. Homogeneity in terms of good copolymerization and integration of the bio-based modifying agent in the polymeric network is required for good performance of the modified resin. Moreover, the chemically modified impregnation resin needs to fulfill the specifications required by the laminate industry such as good paper impregnation speed, low volatile emission, rapid curing speed and overall good processability.

In the present contribution, the preparation of a novel, covalently glycerol-modified melamine formaldehyde resin intended for use in impregnated paper based decorative laminates is described and the chemical analysis demonstrating the successful copolymerization is presented.

BACKGROUND

Synthesis

The synthesis of MF prepolymers is well understood[18] and consists of two major steps: (1) methylolation and (2) condensation. The initial nucleophilic attack of the amino group to the formaldehyde molecule under slightly acidic or alkaline conditions[19] yields hydroxymethylene[12–22] compounds and depends on the molar ratio of melamine and formaldehyde. The progress of the reaction is associated with the solubility of the complex mixture of mono-, di-, tri- up to hexamethylene melamine compounds in water. In the second step oligo-condensation takes place by acid catalysis. In principle, during this second step, polyhydroxy molecules can be incorporated as comonomers and be inserted into the growing network as an etherification agent (Fig. 1).

The etherification is competing with the cross linking reaction and has therefore to be carried out under close to pH neutral conditions. The obtained prepolymer can be stored under alkaline conditions up to several weeks accompanied by a slow progress of the condensation reaction. The final formation of the three dimensional network by poly-condensation is achieved by acid catalysis at elevated temperatures and pressure. What degree of cross-linking is finally adjusted by selecting appropriate pressing conditions depends strongly on the desired application[23] and can be modelled and correlated with the final surface properties by appropriate thermochemical analysis methods.[24,25]

DOSY NMR

The translational motion of molecules in solution is termed diffusion or self-diffusion. Diffusion of a

spherical molecule is described by the Stokes-Einstein eq. (1):

$$D = \frac{kT}{6\pi\eta r_s} \qquad (1)$$

Here, D is the self-diffusion coefficient, k is the Boltzmann constant, T is the temperature, η is the viscosity of the liquid, and r_s is the hydrodynamic radius of the molecule. Diffusion Ordered SpectroscopY (DOSY)[26] allows for the measurement of self-diffusion coefficients in solution. This method relies on the temporary introduction of linear deviations to the homogeneous magnetic field inside an NMR magnet. Field gradients of limited duration can spatially encode a spin's position within the NMR sample tube at a certain time, by introducing a phase shift to its NMR signal.[27] After a given diffusion time the displacement of an ensemble of spins can be measured by a second gradient. Analysis of the movement during the diffusion time yields the (apparent) self-diffusion coefficient D. From the Stokes-Einstein equation we then obtain a value for the hydrodynamic radius of the analyte. Hydrodynamic radii can finally be transformed into molecular masses using assumptions for shape and density of the molecule.

EXPERIMENTAL

Chemicals

Melamine (99%), Formaldehyde 36.8 wt. % in H_2O, HCl 10%, NaOH 20%, Formic acid (88%) Glycerol (99%), soluble starch from potato and sucrose (99,5%) was used as received by Sigma Aldrich. Acid catalyst, release agent and surfactant for the paper impregnation were a gift from Impress Decór Austria GmbH and used as received.

Prepolymer synthesis

The conventional melamine formaldehyde (MF) precondensate was synthesized as described elsewhere[28] with the following modifications. The M : F ratio was 1 : 1.9. The reaction temperature was kept between 92 and 94°C. The condensation lasts approximately 90 min. To determine the degree of oligomerisation, the water tolerance was measured.[14] The resin was condensed until a water tolerance (20°C) of 250% was observed, and then cooled to room temperature. For assaying water tolerance, 5 mL aliquots of the resin were transferred into a test tube and metered amounts of distilled water were added using an automatic titration system until the resin dispersion became cloudy. The amount of water first causing a permanently white dispersion

(due to the precipitated resin) equalled the water tolerance. Moreover, the methylolation reaction of melamine was also followed by thin layer chromatography[29] on cellulose plates with $DMF/H_2O/CHCl_3$/isopropanol (1 : 1 : 1 : 3) eluent. The prepolymer had a solid content of around 52%. After preparation, the resin was kept at controlled temperature (20°C) and was kept in a dark vessel to avoid exposition to irradiation by sunlight.[30]

Modified resin was synthesized by substitution of 7.5–25 wt. % of the melamine content by either starch, sucrose, and 1,2,3-propantriol (glycerol). Because of that substitution of melamine by the modifying agent the M:F ratio steadily increased with increasing amounts of polyol. The synthesis had to be adapted in order to efficiently modify the resin with glycerol or carbohydrate compound. To find out the best time point to add the modifying agent, the substances were added at three different stages of the synthesis: stage A, addition of the modifying agent right after the addition of formaldehyde in the initial phase of the reaction; stage B, addition after complete solubilization of melamine due to the reaction with formaldehyde and the respective formation of hydroxymethyl groups (methylolation), and, Stage C, addition after the condensation process was practically finished at a water tolerance of 300%. Free formaldehyde content was determined according to a method published earlier.[31]

Gel permeations chromatography

GPC analysis was based on the procedures described earlier.[14,32] Molar mass distributions were measured on an Agilent 1100 Series HPLC equipped with a GPC-Precolumn MZ-Gel SDplus 100 Å 5 μm at 50×8.0 mm² and a MZ-Gel SDplus 100 Å 5 μm 300×8.0 mm² operated at a flow rate of 1 mL/min. For detection of the eluted compounds, the instrument was equipped with a refractive index (RI) and a diode array detector (DAD) system. Prior to the GPC analysis, the instrument was calibrated for molar mass distribution using standard polyethylene glycol reference materials. DMF was used as an eluent.

NMR measurements

NMR measurements were conducted on a Bruker Avance DPX300 NMR spectrometer at a magnetic field strength of 7.05 T (300.13 MHz for ^1H, 75.46 MHz for ^{13}C) and at room temperature ($T = 26$°C). Quantitative ^1H-NMR and ^1H Diffusion Ordered SpectroscopY (DOSY)[26] NMR measurements were recorded using a Bruker 5 mm ^1H/BB inverse probe equipped with z-gradient accessory. ^1H-NMR measurements typically involved the following

acquisition parameters: acquisition time: 4.19 s, 128 accumulations, relaxation delay 5 s, 90° pulse: 7.9 μs. DOSY NMR experiments were recorded using a stimulated echo pulse sequence with one spoil gradient and as supplied by the instrument manufacturer, 32,768 real data points in the directly acquired ^{1}H dimension, 16 gradient increments (2–95% of the maximum available gradient strength), 2.7 s acquisition time, 3-s relaxation delay, 150 ms diffusion time, 2.5 ms diffusion gradient length, and 16 accumulations per increment. All acquired ^{1}H FIDs in one- and two-dimensional datasets were multiplied with an exponential window function using a line broadening of 0.3 Hz prior to Fourier transform. Manual zero- and first-order phase correction, as well as automatic polynomial baseline correction yielded the final ^{1}H-NMR spectra and spectral dimensions, respectively. ^{1}H-NMR and ^{1}H DOSY NMR data were analyzed using the dedicated tools available in Bruker TopSpin 1.3 and 3.0.

Viscosity

The apparent viscosity was determined with a flow cup viscosimeter according to the DIN EN ISO 2431 standard at 20°C. In this method, the time (s) required for a sample of liquid resin to flow from a cup of defined volume is measured and used as an estimate of the viscous behavior of the tested liquid.

Preparation of b-stage paper samples

Paper sheets of 30 × 30 cm^2 were manually impregnated with the obtained MF and with the glycerol-modified resins containing also minor amounts of curing catalyst, which was a 0.5M aqueous hydroxyl amine hydrochloride solution, and additives: acid catalyst <0,5%; release agent <2%; surfactant <1.5%.; the used release agent and the surfactant both were aqueous tenside mixtures. In contrast to industrially manufactured papers which are typically impregnated in a two-step process, all laboratory papers prepared for this study were impregnated and coated in a single step using the same (modified) MF formulation for core impregnation and surface film formation. Impregnation was performed using a laboratory impregnation device with accurate rollers and an electric propulsion control. After completing core impregnation the paper was impregnated once again in order to simulate more closely the industrial process. Wet paper sheets were oven-dried for 90 s at 130°C. After drying, paper weight and humidity were controlled. All papers were coated with 100 g m^{-2} of resin to a final dry weight of ca. 170 g cm^{-2}. Final moisture content after drying was 6 ± 0.5%. After preparation, the paper sheets were wrapped in thermoplastic foil to prevent moisture equilibration with the environment and they were kept in a conditioning room at 25°C and 50% relative humidity until pressing. Papers were never stored longer than two days.

Preparation of boards

All sheets were pressed onto 7-mm-thick particleboards in a short-cycle laboratory press (Robert Bürkle GmbH, Freudenstadt, Germany) at 25 N cm^{-2} for 25 s at a press plate temperature of 185°C.

Testing of boards

Standardized surface quality tests were used to characterize the technological performance of manufactured boards. Surface gloss was determined from specular reflectance measurements at an incident angle of 60° as the average of ten measurements per board. Surface porosity was visually judged under a microscope after tinting an area of 25 cm^2 with soft pencil, rubbing the pencil marks out with an eraser, and counting the remaining dark dots. The surface was classified on an arbitrary scale from very good or "1" (no remaining stains of pencil) to very bad, or "5" (large areas of remaining pencil) at 0.5 unit intervals. The resistance of the boards towards chemical attack was similarly evaluated under the microscope by using the so-called "acid value". The acid value was determined by treating a defined surface spot with concentrated hydrochloric acid for 15 min. Afterwards the surface was microscopically classified according to an arbitrary scale from very good or "1" (no attack of the surface by the acid) to very bad, or "5" (surface completely destroyed) in 0.5 unit intervals.

RESULTS AND DISCUSSION

Technological suitability of surface finished laminates based on glycerol-modified MF

Overall aim of the study was to obtain technologically flawless laminates by using modified melamine formaldehyde impregnation resins as the basis for a surface finish. A major problem with novel resin formulations is the comprehensive compliance of the surface film properties with the numerous requirements of the decorative laminates industry.

Table I shows representative technological data and material parameters for the conventionally synthesized MF prepolymer and the laminates produced there from (Table I, entry 1) in comparison to the laminates derived from the modified resins (Table I, entries 2-10). Different glycerol-modified impregnation resins were tested for their suitability, the difference between them being (a) the stage of addition of glycerol to the reaction mixture and (b)

TABLE I
Characteristic Properties of Melamine Formaldehyde Impregnation Resins Containing Different Amounts of Modifying Polyols and the Corresponding Surface Properties of a Decorative Surface After Hot Pressing of the Impregnated Paper to a Particleboard

		Resin characteristics					Board properties		
	Modifying agent[a]	Molar ratio[d] M : F	Free Formaldehyde[e] [%]	$M_n{}^{\text{f}}$ [g mol^{-1}]	$M_w{}^{\text{f}}$ [g mol^{-1}]	ΔH^{g} J g^{-1}	Gloss	Porosity	Chemical resistance
1	None	1:1.90	0.340	300	400	64.51	84	4	4
2	Glycerol, 7.5 %[b]	1:2.05	0.207	330	420	n. d.	85	4	4
3	Glycerol, 7.5 %[c]	1:2.05	0.230	320	430	52.47	85	4	4
4	Glycerol, 10.0 %[c]	1:2.11	0.382	322	431	52.32	79	4	3
5	Glycerol, 13.0 %[c]	1:2.18	0.512	320	426	38.05	77	4	3
6	Glycerol, 15.0 %[c]	1:2.24	0.228	312	410	n. d.	76	3	2
7	Glycerol, 18.0 %[c]	1:2.32	0.189	322	431	23.04	77	2	2
8	Glycerol, 25.0 %[c]	1:2.53	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
9	Sucrose, 7.5 %[c]	1:2.04	0.220	320	430	n. d.	80	3	3.5
10	Potato starch, 7.5 %[c]	1:2.04	0.290	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.

[a] Amounts of modifying agent are given in wt. % relative to the portion of melamine substituted.
[b] Addition of glycerol in this case was performed directly at the beginning of the reaction right after the addition of formaldehyde (Stage A).
[c] Addition of glycerol, sucrose and potato starch after solubilization of melamine (Stage B). At this stage methylolation of melamine is completed and the solutions were transparent.
[d] M ... Melamine; F ... Formaldehyde.
[e] Free Formaldehyde content as determined by the sulfite method.[27]
[f] M_n, M_w ... Molar masses as determined by GPC experiments.[14,28]
[g] ΔH ... Peak integral obtained from differential scanning calorimetry (DSC) analysis of the cross-linking of the synthesized resins. Thermograms were recorded on a Mettler-Toledo (Greifensee, Switzerland) 822e differential scanning calorimeter at a temperature range from 25 to 250°C, and a heating rate of 10°C min^{-1}.

the amount of melamine substituted by glycerol which was varied from 7 to 25%. Some technological data for sucrose (Entry 9) and soluble potato starch modified resins (Entry 10) are also given in Table I.

To find a suitable reaction stage at which addition of modifier is preferable, several time points for modifier addition were tried out. In a first experiment, 7.5% of melamine were substituted by the respective polyols by addition at the very beginning of resin synthesis just before heating up the dispersed melamine solution (Stage A). In a second experiment, in order to not to interfere with the rate-determining step, the same amounts of modifying agent were added after the point of complete solubility of the methylolated triazine rings (Stage B). In a third experiment, 7.5% of the polyols were added after completed resin condensation (Stage C).

All selected reaction stages turned out to be suitable addition points for glycerol at the low loading. In case of sucrose however, only addition at Stage B (Table I Entry 9) lead to a transparent resin that was suitable for further impregnation tests. Trials at the other stages did not give promising results (data not shown). Potato starch on the other hand had a negative influence on the reaction pathway in all applied tested synthetic procedures, even when added at Stage B. Because of the high molar mass compared to the MF molecules the viscosity of the solution increased after addition and no modified product

suitable for paper impregnation could be obtained (Table I Entry 10).

The experimental data for the glycerol modified MF resin showed no negative effects on the processability immediately after paper impregnation. This fact is very important for the treatment of decorative paper with amino-plastic resins in order to maintain proper penetration, distribution and filling of the resin in the paper matrix.

By direct comparison of the glycerol modified resins to the glycerol-free standard MF system, the time dependent flow viscosity showed a slightly different performance during storage periods of several days. Figure 2 shows that the glycerol-modified resins display slightly higher starting viscosities immediately after synthesis compared to the pure MF resin. Depending on the reaction stage at which glycerol was added the resins behaved differently in terms of storage stability, that is, in the changes in flow viscosity with time over a period of one week storage at room temperature. One week is a typical period of time during which an impregnation resin that does not contain any further stabilization agents should remain processable which is indicated by its flow viscosity remaining below a threshold of 25 s flow time (as measured by the DIN cup). The resin prepared by supplementing glycerol during the final formation of oligomers (addition at Stage C) at low pH and high temperatures showed (1) significantly reduced storage stability of the resin
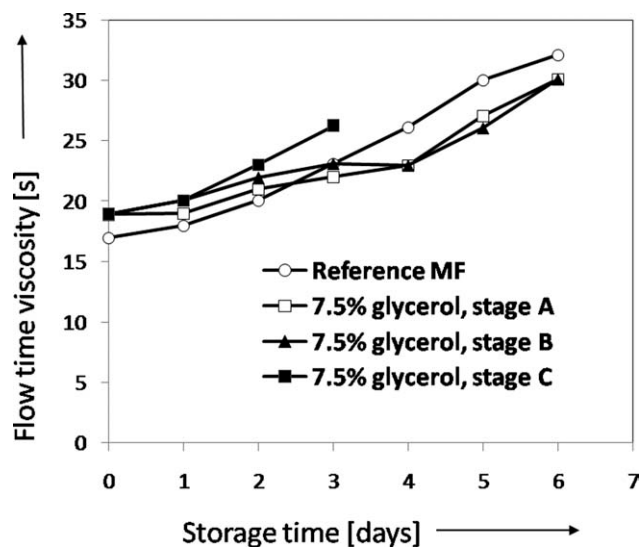
Figure 2 Influence of the reaction stage at which glycerol is incorporated during melamine formaldehyde resin synthesis on the resulting impregnation resin flow time viscosity as measured using the DIN flow cup method in dependence of the storage time at room temperature. Stage A: addition of glycerol right after addition of formaldehyde prior to initiating the reaction by heating. Stage B: addition of glycerol after solubilization of melamine (after completion of methylolation). Stage C: addition of glycerol at a late stage of MF synthesis after reaching 300% water tolerance of the reaction mixture.

which was evident from comparatively strong increase in flow viscosity, and (2) a significant loss of performance due to gelation after a period of 72 h after synthesis. Adding the glycerol at the stage of complete solubility (Stage B) of the reaction intermediate also lead to an increased viscosity as compared to the standard MF resin. Because of the slightly lower reactivity in the ongoing condensation reaction, however, the viscosity still remained below the critical value of 25 s after four days of storage. The resin showed a more linear increase in viscosity. Adding the resin right at the start of the synthesis at Stage A also lead to a performance sufficiently well in terms of both storability and flow viscosity.

Because of the promising performance of glycerol-modified resins, further tests were performed on this system using the addition of varying amounts of glycerol at reaction Stage B for further experiments (Entries 3–8, Table I). The resulting storage time-dependent flow viscosities for a series of MF resins containing 7.5–18% of glycerol are summarized in Figure 3. It is deduced that modified resins containing up to 13% glycerol can be prepared that behave very similar to unmodified MF resin and display still good processabilities after three days of storage. Only when higher amounts of melamine are substituted (15 or 18%) the resins show a very steep increase in viscosity so that these resins cannot be used anymore for the impregnation process. Increas-

ing the glycerol content even further by substituting 25% of the melamine did not anymore yield a useful condensation product; the condensation proceeded much faster and did not yield transparent resins at all. Increasing the amount of glycerol, however, lead to slightly worse performance of the surface finish in terms of chemical resistance, porosity and gloss (see Table I). Thermal analysis of the glycerol modified MF resins by DSC showed a slightly decreasing trend for the obtained reaction enthalpies with an increasing amount of glycerol. This illustrates that the network formed between melamine and formaldehyde is less developed and strong due to fewer available triazine cross-linking centers. This is also evident from the increased melamine-to-formaldehyde ratio of these resin mixtures. This comparatively worse degree of MF cross-linking is reflected by the observed deterioration in surface performance of the corresponding laminated particleboards.

Ideally, after hot pressing the curing of the resin should be near to complete because, since the industry is dealing with poly-condensates, only high degrees of conversion lead to high molar masses and the resistance against chemical hydrolysis. The test impregnations revealed no negative influence on board surface properties as seen in Table I. Crucial properties like surface porosity and the acid test showed no drawbacks in comparison to the MF system. It is safely assumed that the modification is not having any adverse effects on the curing behavior and hence, the technological performance of the boards.

The main requirement for the modified resin was the ability to form a stable and lasting thermosetting
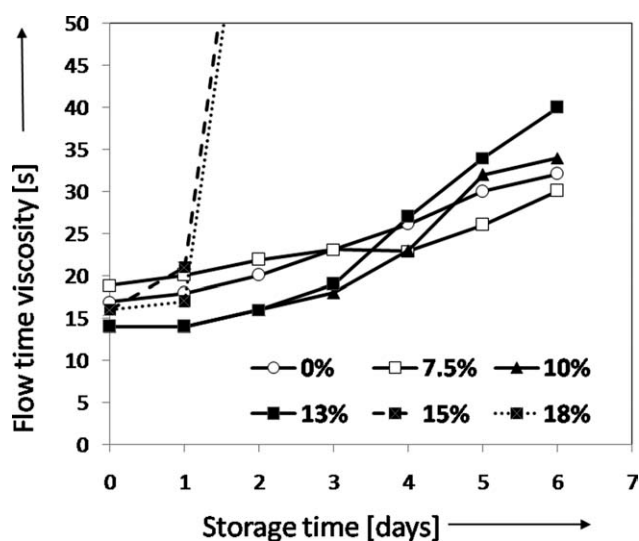
Figure 3 Influence of the amount of glycerol incorporated into melamine formaldehyde resin at reaction Stage B on the processing properties of the resulting impregnation resin expressed as flow time viscosity as measured using the DIN flow cup method in dependence of the storage time at room temperature.
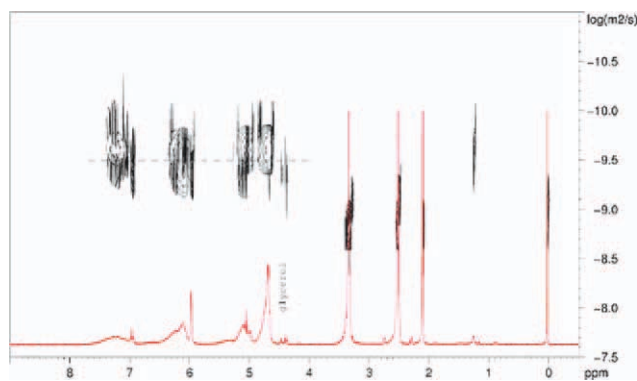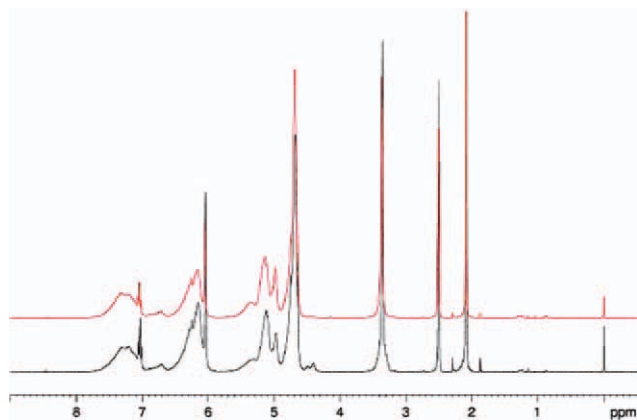
Figure 4 ^{1}H DOSY NMR of a modified MF resin with 7.5% wt of glycerol (1,2,3 propantriol) addition Stage B; The DOSY NMR measurement has been conducted on a dilute sample of the analyte in DMSO-d$_6$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

network, along with good resin storability at viscosities suitable for further processing The chemical incorporation of the polyolic groups was targeted at in order to have a predictable system without free low molecular weight compounds, which would possibly cause difficulties with other additives during the wetting or the lamination process. Diffusion-Ordered NMR was used as a tool to characterize the modified oligomers in terms of chemical structures.

Copolymerisation of glycerol, melamine, and formaldehyde

Melamine-formaldehyde (MF) resins containing glycerol and sucrose have been investigated by high resolution ^{1}H, ^{13}C, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, and ^{1}H DOSY (*Diffusion Ordered SpectroscopY*) NMR spectroscopy.[29] The incorporation of polyol residues into the MF structure was assessed. Figure 4 shows a 1H DOSY NMR spectrum of a MF resin modified with 7.5% of glycerol at stage B during

Figure 5 ^{1}H-NMR of melamine formaldehyde resin with 1/1.9 ratio and modified MF resin with 7.5% of glycerol ratio M/F/G 1/1,9/0,07. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Peak Assignment of Chemical Shifts Observed in
^{1}H-NMR Spectra of Modified Melamine
Formaldehyde Resin

[1]H Chemical shift [ppm]	Peak assignment [functional group]
0	Tetramethyl silane (reference)
1.23	Traces of detergent (SDS)
2.08	Acetone, H$_3$C-CO-CH$_3$
2.50	DMSO (signal of deuterated solvent)
3.32	Water, H$_2$O
3.35	Glycerol, C-H
3.43	Glycerol, CH$_2$
4.37 and 4.45	Glycerol, O-H
4.68	Mainly methylole: Triazine-NH-(CH$_2$-OH)
4.74–5.09	Mainly methylole: Triazine-N-(CH$_2$-OH)$_2$
6.0–6.4	Methylole: Triazine-N-(CH$_2$-OH)$_2$ and Methylole: Triazine-NH-(CH$_2$-OH)
7.0–7.6	Methylole: Triazine-NH-(CH$_2$-OH)

resins synthesis. In Figure 5, the results from 1H NMR spectroscopic analysis of this modified MF resin and the unmodified MF reference resin are compared. Table II summarizes the peak assignment of the chemical shifts observed with the modified and unmodified resins. Multidimensional heteronuclear NMR spectroscopy yielded, however, no indication of covalent bonding between modifying agents and the MF resin. All detected ^{1}H and ^{13}C chemical shifts correspond to that of free substance, and the pure MF resin. Instead, diffusion (DOSY) NMR results suggest the formation of chemical bonds between the resin and the monomeric polyalcohol.[33] The apparent self diffusion coefficient determined for glycerol within a MF-glycerol mixture is much smaller than expected. Accordingly, its apparent molecular weight seems much larger than for the free glycerol. The self diffusion rates determined for the polyalcohol signal largely conform to those found for the MF resin even at massive dilution. Additionally, the spectral lines of the polyalcohol are broadened similarly to that of the resin at increasing NMR sample concentrations (Fig. 4), which is another indication of chemical bond formation. To rule out self-aggregation of the polyalcohol during MF condensation, we have also investigated the diffusion properties of a glycerol in water (1 g/10 mL) sample treated for 30 min at pH = 9.3 and 90°C. Under these conditions glycerol showed no signs of self aggregation, i.e. narrow line widths and expected apparent self diffusion coefficients.

CONCLUSION

Three different polyols (soluble starch, sucrose, and glycerol) were tested for their potential in the chemical modification of MF resins for impregnated paper based laminates. These polyols were selected

because they are nontoxic, commercially available from renewable resources and their multiple hydroxyl groups were hypothesized to be readily covalently linked to the melamine-formaldehyde resin framework. However, with soluble starch and sucrose, there was no covalent binding to the MF oligomers observed and, even more importantly, substitution of melamine by these polyols lead to severe losses in technological performance of the modified MF resins. On the other hand, the results with glycerol as modifier indicate that successful incorporation into a conventional MF resin matrix can be achieved without any loss in performance as long as the amount of polyol added is not chosen too high. However, for successful chemical modification, the stage of the synthesis at which the glycerol is added to the reaction mixture is crucial. Addition at an early reaction stage was found to be best to instigate reaction of glycerol with the growing oligomers, as was demonstrated by DOSY NMR measurements. However, the results were worse, when the glycerol was added immediately at the start of the synthesis or after resin formation was basically finished. Rheological and standard technological tests revealed no negative influence on the cocondensation of prepolymers with respect to the technological requirements of the decorative laminates industry. It was possible to prepare highly transparent films with satisfactory technical performance comparable to standard MF films. Glycerol has several advantages in terms of chemical reactivity, accessibility, purity, environmental, and cost benefits. Since glycerol is available in industrial quantities from natural feedstock in high purity and at reasonable cost it is a highly promising molecule as a bio-based modifier from bio-refinery material streams. Our findings demonstrate the possibility to replace several percent of the petrol-based product melamine by compounds obtained from renewable resources.

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