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Investigations on the Crosslinking Reactions of Melamine Resins in the Presence of Wood

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Summary. The crosslinking behavior of MFRs (melamine formaldehyde resins) in the presence of wood was investigated. The influence of various factors (wood content, resin structure, *etc.*) on the crosslinking temperature of the resins was examined using DMTA and DSC/TGA. Fully methylated MFRs turned out to be more stable in the presence of wood than partially methylated MFRs. A dependence of the crosslinking temperature on the wood content was found. Model reactions with wood components demonstrated, that cellulose, hemicelluloses, and lignin affect the crosslinking temperature to different extends, whereas hemicelluloses (xylan) showed the strongest effect. Solvents, especially water, led to a further decrease of the crosslinking temperature of wood/MFR compounds.

Keywords. Melamine resin; Polycondensation; Wood; Acidity; Catalysts.

Introduction

The stability of melamine formaldehyde resins (MFRs) in wood is of great importance for the creation of wood/MFR compounds. MFRs can react in many ways, but the two major reactions are crosslinking and hydrolysis [1]. A survey of the reactions of MFRs is shown in Table 1.

The crosslinking reaction of MFRs depends on the *pH* and is catalyzed by acids. Hemicelluloses and lignin, two of the major wood components, possess acidic groups [2] (*e.g.* 4-*O*-methylglucuronic acid side chains of hemicelluloses or phenolic hydroxyl groups of lignin), so wood is supposed to influence the crosslinking reaction of MFRs. *Pizzi* [3] discussed the crosslinking of resins in the presence of cellulose. He posited a catalytic activation of the crosslinking reaction of MFRs by cellulose.

Correlations between resin properties (resin structure, resin content, solvent type, solvent content, *etc.*) and the crosslinking temperature were not published

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Table 1. Reactions of melamine formaldehyde resins according to *Bauer* [1]

1 $-NCH_2OCH_3 + ROH \rightarrow NCH_2OR + CH_3OH$
2 $2\text{-}NCH_2OCH_3 + H_2O \rightarrow -NCH_2N- + H_2C{=}O + 2CH_3OH$
3 $-NCH_2OCH_3 + -NH \rightarrow -NCH_2N- + CH_3OH$
4 $2\text{-}NCH_2OCH_3 \rightarrow -NCH_2N- + CH_3OCH_2OCH_3$
5 $-NCH_2OCH_3 + -NCH_2OH \rightarrow -NCH_2OCH_2N- + CH_3OH$
6 $-NCH_2OCH_3 + H_2O \rightarrow -NCH_2OH + CH_3OH$
7 $-NCH_2OH \rightarrow -NH + H_2C{=}O$
8 $-NCH_2OH + -NH \rightarrow -NCH_2N- + H_2O$
9 $2\text{-}NCH_2OH \rightarrow -NCH_2N- + H_2C{=}O + H_2O$
10 $-NCH_2OH + ROH \rightarrow NCH_2OR + H_2O$
11 $2\text{-}NCH_2OH \rightarrow -NCH_2OCH_2N- + H_2O$

until now. Therefore we determined the crosslinking temperatures of different MFRs and wood/MFR blends using DMTA (dynamic mechanical thermo analysis) and DSC (differential scanning calorimetry)/TGA (thermo gravimetric analysis).

Results and Discussion

Dependence on the Wood Content

The crosslinking temperatures of all investigated wood/resin blends are summarized in Table 2. The crosslinking reactions of all wood/resin blends show a dependence on the wood content. Wood, as acidic material, catalyses the crosslinking reaction of the resins when resin and wood are intimately mixed. Depending on their structure, some resins were influenced stronger than others.

Resin A and resin B, two partially methylated MFRs, show the strongest influence. The addition of 5% wood diminishes the crosslinking temperature from 212°C to 195°C, resp. 185°C. A wood content of 50% leads to crosslinking temperatures of 145°C, resp. 155°C. The crosslinking of resin D, a fully methylated MFR, was influenced to a lesser extent under these conditions. Addition of 5% wood leads to a decrease of the crosslinking temperature of 3°C, the addition of

Table 2. Properties of the used resins and crosslinking temperatures of the resins in dependence of the MFR/wood ratio

properties	Resin A	Resin B	Resin C[a]	Resin D	Resin E
M:F	1:3	1:3.5	1:4	1:3.5	1:3
M_W (g/mol)	<1000	<1000	<1000	<1000	2000
ratio OH/OCH_3	~1	~1	~0	~0	~0
ratio resin:wood	crosslinking temperature (°C)				
100:0	212	212	210	215	205
95:5	195	185	208	212	200
80:20	165	170	208	210	190
50:50	145	155	195	200	180

[a] Urea resin, ratio U:F

Table 3. Crosslinking temperatures of resin A/wood blends

ratio	TGA	TGA	DSC	DMA
Resin/wood	onset temp. (°C)	inflection point (°C)	peak (°C)	onset temp. (°C)
100:0	188	211	203	212
95:5	170	200	185	195
80:20	133	170	155	165
50:50	123	155	137	145

50% wood reduces the crosslinking temperature from 215°C to 200°C only. Out of these results fully methylated resins seem to be less influenced by wood catalysis than partially methylated resins.

These experimental results are also confirmed by the crosslinking behaviors of resins C and E. Resin C is a highly methylated urea formaldehyde resin. The crosslinking behavior of this resin was found to be analogous to the crosslinking behavior of resin D. The crosslinking temperature decreased from 210°C (0% wood) to 195°C (50% wood), similar to resin D. Resin E, also fully methylated MFR with higher molecular weight, shows a decrease in the crosslinking temperature (from 0 to 50% wood content) of 25°C, what is also in the same range as found for resins C and D.

Additionally, the crosslinking of resin A and resin A/wood blends was also investigated using DSC/TGA measurements. The results are listed in Table 3. The inflection points of the TGA curves correspond to the onset temperatures of the DMTA measurements. The onset temperatures obtained in TGA are 20 to 40°C lower than obtained in DMTA because TGA is much more sensitive than DMTA. These results show that the crosslinking starts at lower temperatures than detectable with mechanical methods (DMTA). Nevertheless, DMTA results have greater technical relevance, because the viscosity of the compound is the parameter of interest for the processing of a wood/MFR compound.

Dependence on the Wood Components

Further the influence of the three main wood components cellulose, lignin, and hemicelluloses (xylan) on the crosslinking reaction of a MFR (resin A) was investigated. The results are listed in Table 4. The descending order of crosslinking temperatures of the resin/wood component blends is: resin/cellulose > resin/wood > resin/lignin > resin/xylan.

Table 4. Crosslinking temperature of resin A in dependence of wood and wood components

	crosslinking temp. (°C)	*pH*
no additive	212	
20% wood	165	5.1
20% cellulose	178	6.7
20% lignin	140	3.6
20% xylan (hemicelluloses)	123	2.9

Table 5. Dependence of the crosslinking temperature of resin E on the moisture content of the wood/MFR blend ($w/w = 80/20$)

moisture content (%)	crosslinking temperature (°C)
0	190
6	190
18	185
25	180
50	168
100	163

Table 4 shows that the order of the crosslinking temperatures correlates with the *pH* of the added wood component. This indicates, that the *pH* of the wood components is the criteria for the decrease of the crosslinking temperature.

Dependence on the Moisture and Alcohol Content

Investigations on the influence of the moisture content on the crosslinking temperature of wood/MFR compounds show, that a significant influence is noticeable from 25% moisture content on (Table 5). Water as protic solvent with a high dielectric constant ($D = 78.5$) enhances the dissociation of the carboxylic acids and phenolic groups of wood and facilitates the transport of the resin to the acidic sites of the wood components. Further the wood components (especially hemicelluloses) are degraded at higher temperatures in the presence of water and the degradation products contain additional acidic groups.

Interestingly, an amount of 25% water or alcohols (listed in Table 6) does not show an influence on the crosslinking temperature of the pure resin. This result indicates that free acidic components of wood have the main influence on the crosslinking temperature of the composites. Higher alcohols, which are often used as solvents for resins, show significantly weaker effects on the crosslinking temperature of wood/MFR blends than water. Table 6 demonstrates, that the decrease in the crosslinking temperature of wood/resin/solvent mixtures correlates with the dielectric constants of the solvents. Those with higher dielectric constants lead to a more distinctive decrease of the crosslinking temperature.

Table 6. Crosslinking temperatures of 75% MFR (resin E) solutions and of wood/MFR blends ($w/w = 80{:}20$) with 25% solvent content and dielectric constants (D) of the solvents

solvent	crosslinking temperature (°C) of 75% MFR solution	crosslinking temperature (°C) of wood/MFR blend	D
without	205	190	–
water	201	163	78.5
methanol	205	178	32.6
ethanol	205	180	24.3
butanol	205	186	17.1

Table 7. Crosslinking temperatures of resin A/wood (NH_3 pre-treated) blends

resin A/wood blend (*w*/*w*) = 80:20	crosslinking temperature (°C)	*pH*
untreated	165	5.1
1 h ammonia treatment	165	5.4
2.5 h ammonia treatment	162	6.1
4 h ammonia treatment	160	6.4
6 h ammonia treatment	158	6.5

Dependence on Ammonia Pre-Treatment of Wood

Applying ammonia pre-treatment on wood, we expected an increase in the crosslinking temperature compared to unmodified wood/resin compounds, because we assumed that ammonia neutralizes the acidic groups of wood. It's known that the carboxyl groups of wood react with ammonia to amides [4], which are less acidic than carboxylic acids (pK_a (CH_3COOH) = 4.75, pK_a (CH_3CONH_2) = 15) [5]. Due to the higher *pH* of ammonia treated wood (Table 7), higher crosslinking temperatures of blends of resin and ammonia treated wood are expected.

Experimental data showed however, that ammonia pre-treatment does not lead to an increase on the crosslinking temperature of wood/MFR compounds. On the contrary, we observed a slight decrease with increasing ammonia treatment time, although the *pH* of the ammonia modified wood increased. Out of this result another effect, which exceeds the neutralization of wood must be relevant. *Weimer et al.* [4] found a degradation of the wood components during the ammonia treatment. These degradation products, containing amide and amine structures may also influence the crosslinking behavior of the wood/MFR blend.

Experimental

The applied resins and their properties are listed in Table 8, typical structures for this resins are shown in Fig. 1. The resins were characterized with ^{13}C NMR, ^{1}H NMR, SEC, DSC/TGA, and FTIR.

Wood (trade name Lignoflok E140) was purchased from J. Rettenmaier & Söhne, Rosenberg, Germany. Lignoflok E140 are spruce particles with particle sizes from 60 to 140 μm, the pH is 5.5 ± 1. The thermal degradation starts at 170°C. For the experiments the material was dried at

Table 8. Resin types

Name	Trade name	Manufacturers	Properties
Resin A	Hilamin PA 43	Dynea Austria GmbH	low molecular weight MFR, M:F = 1:2.5–3, partially methylated
Resin B		Dynea Austria GmbH, experimental product	low molecular weight MFR, M:F = 1:2.5, partially methylated
Resin C		Dynea Austria GmbH, experimental product	low molecular weight UFR, high U:F ratio, highly methylated
Resin D		Agrolinz Melamine International, Austria, experimental product	low molecular weight MFR, M:F = 1:3.5, fully methylated
Resin E		Agrolinz Melamine International, Austria, semi technical product	higher molecular weight MFR, M:F = 1:3.5, fully methylated

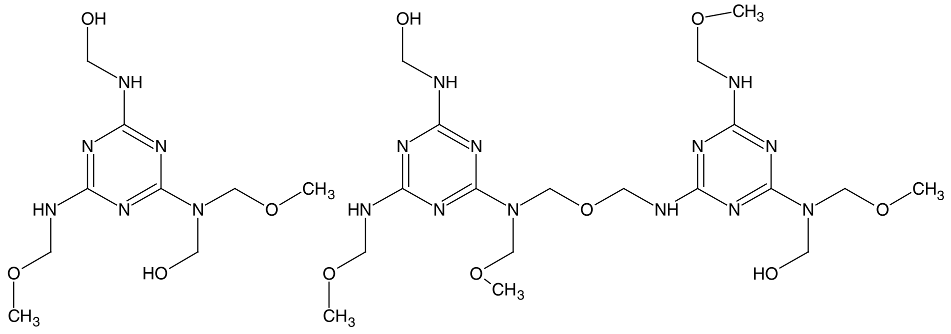

Fig. 1. Typical structures of low molecular weight MFR

103°C for 24 h. Cellulose Type 402–600 was also purchased from J. Rettenmaier & Söhne, Rosenberg, Germany. The particle sizes ranged from 40 to 100 μm. The applied xylan was a gift of Lenzing AG, Austria, lignin was conventional Organosolv Lignin from Aldrich. The ammonia pre-treated wood was a gift of Wood K plus and the Institute for Chemical Technology of Organic Materials, University Linz, Austria.

For the measurement of the crosslinking of resins in the presence of wood and wood components oven-dried wood particles and dried resins (25 mbar, 30°C, 24 h) were intimately mixed to a paste. The ratios (*w*/*w*) resin to wood were chosen 100:0, 95:5, 80:20, 50:50. Immediately after mixing measurements were realized with a DMA (Rheometrix Dynamic Spectrometer Model RDS-II (RSI Orchestrator/Rheometric Scientific) and/or with DSC/TGA (Netzsch STA 449C).

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