Modification of Phenol–Formaldehyde Resol Resins by Lignin, Starch, and Urea

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ABSTRACT: Lignin-based chemicals, starch, and urea were used as modifiers for phenol–formaldehyde resol resins. The effects of the addition stage of the modifiers used in the synthesis of the resins and the type of modification reagent on the structures of the resins and their molar masses and reactivities were investigated. The modifications with corn starch and lignin promoted condensation; this was verified by increased molar masses and high ratios of methylene bridges to the sum of free ortho and para aromatic groups with respect to the corresponding reference resin without a modification reagent. The later the modifier was added to the resin condensation mixture, the more methylene bridges were formed with respect to the amounts of free ortho and para aromatic groups. In addition, when urea or wheat starch was added in the later condensation stage, the final condensation also reached high stages. The modifications with lignosulfonate and starch, as well as the early addition of urea, enhanced p–p' bridge structures. The lowest condensation stage and, therefore, the highest reactivity were found when wheat starch was added with the starting reagents. The curing heat of the wheat-starch-modified resins decreased according to the deferred addition point of starch. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 582–588, 2003

Key words: resins; modification; NMR; gel permeation chromatography (GPC); differential scanning calorimetry (DSC)

INTRODUCTION

Many different studies have been performed to find modifiers, additives, and even economically and environmentally applicable substitutive starting materials for phenol in the manufacturing of phenol–formaldehyde (PF) resins. These materials contain lignin from kraft lignin[1–9] (degraded and chemically modified lignin from sulfate pulping), black liquor[10–14] (a lignin-rich byproduct from the pulp industry), lignosulfonate[1,2,15–17] (lignin recovered as lignosulfonates from sulfite pulping), or organosolved lignin[18–21] (pulping liquor prepared from wood materials, an aqueous polar organic solvent, and an acid catalyst). Also, studies have been made with urea in cocondensed resins with phenol and formaldehyde.[22,23]

Lignin is a highly crosslinked, three-dimensional aromatic polymer with phenylpropane units linked together by carbon–carbon or ether bonds and with phenolic and alcoholic hydroxyl groups similar to those of PF resins. In the chemical pulping process, lignin is dissolved as soluble fragments in pulping liquor after the bonds between phenylpropane units break.[3] In the pulp industry, lignin is a waste product and is usually used as a fuel in pulp mills; this has made it an attractive raw material for adhesives. In the base-catalyzed process, formaldehyde reacts mainly with the free ortho position of phenolic units of lignin and very rarely with the side chain of lignin.[4,5,24] A PF resin can also copolymerize with lignin in the reaction of methylol groups of a resin with free ortho carbons of phenolic units in lignin fragments.[3] However, lignin is often modified (e.g., premethylolated) for better reactivity in resin formation and a phenol replacement level of over 20%.[25a–c] However, under acidic conditions, lignin can be first condensed with phenol before being treated with formaldehyde for resin production.[10,11]

The salts of lignosulfonates are formed in the sulfite pulping process during the reaction of ammonium, sodium, calcium, or magnesium sulfites or bisulfites with wood at low pHs and at elevated temperatures. Lignosulfonates contain compounds of increasing molecular size and increasing monomeric units.[25a] Kraft lignin is known to be more reactive than lignosulfonate in the resin formation reaction with formaldehyde, and for increased reactivity, lignosulfonate-containing sulfite liquor has been treated with mineral acids and oxidizing reagents.[15] Also, the PF precursor with a low formaldehyde/phenol molar ratio is known to react with lignin, especially with lignosulfonate, into the phenol–formaldehyde;–lignin precursor and further with formaldehyde into the final phenol–formaldehyde;–lignin–formaldehyde resol.[16]

Starch, a natural polysaccharide, has been added to phenolic resins during manufacturing for dry-out re-

TABLE I
Modification and ¹³C-NMR Results of the Resins

Resin	Modification reagent			Condensation viscosity (mPas)	Methylene bridges/ free ortho and free para aromatic carbons	Methylene bridges/ methylols	Methylene bridges o–p'/p–p'
	Reagent	Addition stage	wt %				
1	Reference resin without a modification reagent			174	2.50	0.68	1.37
2	Lignosulfonate	With starting reagents	4.9	490	3.05	0.88	0.62
3	Lignin-bearing lye	With starting reagents	9.4	290	3.53	0.64	1.70
4	Corn starch	With starting reagents	3.6	243	3.97	0.78	0.95
5	Corn starch	After condensation of 45 min	3.6	225	4.74	0.95	0.96
6	Corn starch	At the end of the resin condensation	3.6	230	5.05	0.95	0.74
7	Wheat starch	With starting reagents	3.4	820[a]	0.87	NC	0.92
8	Wheat starch	After condensation of 45 min	3.4	1060[a]	1.84	NC	0.96
9	Wheat starch	At the end of the resin condensation	3.4	244[b]	3.63	NC	0.87
10	Urea	With starting reagents	4.9	266	1.96	NC	0.81
11	Urea	After condensation of 45 min	4.9	245	2.66	NC	0.93
12	Urea	At the end of the resin condensation	4.9	158	3.11	NC	1.68

NC = not calculated; methylol signals also include uric methylols.
[a] Viscosity before extra urea addition.
[b] Viscosity after extra urea addition.

sistance and improved prepress tack.[22] Also, starch has been examined as an extender in the kraft lignin–formaldehyde resin.[26] Starch was dehydrated in an acid-catalyzed reaction into 5-hydroxymethylfurfural (HMF) in the presence of phenol and formaldehyde, and phenolic resins with incorporated HMF structures were formed.[27]

Trace amounts (usually up to 2 wt % of total solids) of urea have been added to phenolic adhesive resins to catch free formaldehyde. Urea in higher amounts (>4 wt % of total solids) is used in PF adhesives as a phenol replacement reagent to cut manufacturing costs and to increase the reactivity of the resin.[22] Co-polymerized resins between phenol resins and urea resins are used in many industrial applications. For the necessary desirable properties to be obtained, specific reaction parameters should be chosen that favor a copolymerization reaction instead of separate ho-mopolymerization. The reaction rate between methyl-olphenols and urea is strongly related to the pH of the reaction media, and a weak acidic environment favors the methylolphenol reaction with urea.[28] Phenol–u-rea–formaldehyde (PUF) resins were condensed un-der acidic conditions in the reaction of urea and poly-methylolphenols or in the reaction of phenol with a urea–formaldehyde resin.[23]

In this study, the PF resin was modified with ligno-sulfonate, lignin-bearing lye, wheat starch, corn starch, or urea. The effects of the addition stage in the synthesis and the type of modification reagent on the structures of the resin and their molar masses and reactivities were investigated.

EXPERIMENTAL

Resin synthesis

In this study, 12 resol resins were condensed in a 6-dm³ glass reactor equipped with a stirrer, a con-denser, and external cooling and internal heating units. One of the resins (**1**, Table I) was a reference without a modification reagent. In the other resins (**2–12**, Table I), different modifiers were used with phenol (purchased from J.T. Baker, Deventer, Hol-land).

The reference resin was prepared by a simple pro-cedure. Phenol, formaldehyde (produced from meth-anol; Dynoresin Oy, Bakelite Oy, Finland), and NaOH (used as a catalyst; Merck, Darmstadt, Germany) were mixed, and the temperature was raised to the conden-sation temperature (88°C). Condensation continued for 3 h until the viscosity reached 174 mPa s. Then, the resin was cooled to room temperature (25°C), and the alkalinity was adjusted to 7.0–7.1 wt %. The total experiment time (including the rise in temperature, condensation, and cooling) was 3.5 h.

Modified resins **2–12** (Table I) were synthesized ac-cording to the preparation method of the reference resin with a constant 3-h condensation time. The amounts of the modification reagents were 3.4–9.4 wt % of the amounts of the liquid resins. Sodium ligno-sulfonate (solid; Ligno Tech Finland OY, Tampere, Finland) and lignin-bearing lye (liquid; UPM-Kymmene, Pietarsaari, Finland) were added with starting materials at the beginning of the condensation reaction. Wheat starch (Roquette, Lestrem, France) as

a suspension in water, solid corn starch (Cerestar Scandinavia A/S, Holte, Denmark), and solid urea (technical-grade; Kemira Chemicals B.V., Rozenburg, The Netherlands) were added at three different stages so that the effects of various addition points could be studied. The points were at the beginning (with phenol, formaldehyde, and NaOH), in the middle of the condensation (45 min after the beginning), and at the end of the condensation reaction.

The condensation viscosities of modified resins **2–6** and **10–12** were 158–490 mPa s, depending on the modification reagent and the addition stage. Wheat starch swelled and increased the condensation viscosities of resins **7–9** even over 1000 mPa s. Therefore, extra urea (3 wt % of the amounts of the liquid resins) was added to the wheat-starch-modified resins at the end of the condensation reaction, just before the alkalinity adjustment, to control the viscosity at the end stage. A viscosity of 244 mPa s was obtained for resin **9** because of concurrent urea addition with wheat starch.

Also, the alkalinities of cooled modified resins **2–12** were adjusted to 7.0–7.1 wt %. The formaldehyde/ phenol molar ratios of both the reference resins and the modified resins were 2.0. After the synthesis, the resins were kept frozen at $-18°C$ until the analytical measurements.

^{13}C-NMR spectroscopy

The resins were characterized by quantitative ^{13}C-NMR spectroscopy with a Bruker AMX-400 spectrometer (Bruker, Ettlingen, Germany) with ^{13}C at 100.623 MHz and with the inverse-gated ^{1}H decoupling method. The measurements were made at room temperature with 600 scans, a delay time of 120 s, a 20-h acquisition time, and a 90° pulse of 11.5 μs.

Deuterated dimethyl sulfoxide (DMSO-d_6; 99.8 atom %; Riedel-de Haën, Seelze, Germany) was used as a solvent. The central resonance signal of DMSO-d_6 with a δ value of 39.5 ppm was used as an internal standard.

Gel permeation chromatography (GPC)

The GPC system (Waters, Milford, MA) included a Waters 510 pump, a Rheodyne loop injector, and a Waters 440 UV detector operating at 254 nm or a refractive-index detector. Styragels with pore sizes of 1000, 500, and 100 Å were used as column packing materials. The calibration of the columns was performed with three polystyrene standards (molecular weight = 30,300, 5460, or 1300). In addition, dinonylphthalate (molecular weight = 418) and 1-phenylhexane (molecular weight = 162) standards were used. The resins were dissolved in filtered tetrahydrofuran (THF; 20 mg/mL), which was also used as an

eluent. The sample size was 250 μL, and the eluent rate was 1.0 mL/min. The measurements were made at a room temperature.

The retention times and the shape of the chromatograms were determined with Turbochrom Navigator 4.1 software (P. E. Nelson Division, San Jose, CA), and TC*SEC software by P.E. Nelson was used to calculate the number-average molecular weights (M_n's) and weight-average molecular weights (M_w's), as well as the polydispersity.

Differential scanning calorimetry (DSC)

The DSC analysis was made with a PerkinElmer DSC 7 instrument (Perkin Elmer, Norwalk, CT) and 7 series Unix thermal analysis software (Perkin Elmer). The equipment was calibrated with indium and zinc samples. A resin sample of 10 mg was sealed in air in PerkinElmer stainless steel pressure capsules. Samples were heated from 25 to 250°C at a rate of 10°C/min, and the nitrogen gas flow was 20 mL/min.

RESULTS AND DISCUSSION

Effect of modification on the structures of the resins according to ^{13}C-NMR spectroscopy

The studied resins had high alkalinity, and the signals of phenolic carbons shifted downfield (150–165 ppm) with respect to lower alkalinity resins (150–157.5 ppm).[29] In this phenolic ^{13}C range, the broad signals of high molar mass compounds and the carbonyl signals of urea compounds [—NC(O)N—] in the middle of the phenolic range (158–163 ppm[23,30,31]) of resins **7–12** (Table I) produced poor signal dispersion. Therefore, the integration of the carbons of phenolic origin was not reliable enough to use in a comparison with other resin carbons.

The methylol groups at 60.5–64.5 ppm were assigned together because of the indistinguishable ortho and para methylol signals. Also, ^{13}C signals of uric methylols [—C(O)NHCH$_2$OH] formed from the added urea (in resins **7–12**) appeared in the same spectral region (62.2–66.8 ppm)[30,31] as the methylol groups of phenolic resins. Moreover, the chemical shifts of both free ortho and free para aromatic groups were integrated together with enough accuracy in the range of 115–118 ppm. Free formaldehyde was not present in any form (hemiacetals, hemiformals, or oxymethylenes) in the spectra of the modified resins.

The effects of modification on the structures of the resins could be evaluated by a presentation of the ratio of methylene bridges to the sum of free ortho and para aromatic groups, the ratio of methylene bridges to methylols (condensation stage), and the ratio of ortho–para methylene bridges (ca. 35 ppm) to para–para methylene bridges (ca. 41 ppm; Table I). Although the

TABLE II
DSC and GPC Results of the Modified Resins

Resin	Modification reagent	GPC results			DSC results			
		M_n (g/mol)	M_w (g/mol)	M_w/M_n	ΔH (J/g)	T_1 (°C)	T_2 (°C)	T_3 (°C)
1	Reference resin without a modification reagent	1030	3150	3.1	−122.5	157.2		
2	Lignosulfonate[a]	ND	ND	ND	−129.4	151.6		
3	Lignin-bearing lye[a]	1190	3600	3.0	−106.6	151.9		
4	Corn starch[a]	1180	4070	3.4	−106.8	156.6		
5	Corn starch[b]	1090	4050	3.7	−105.5	156.8		
6	Corn starch[c]	1160	3760	3.2	−111.2	153.3		
7	Wheat starch[a]	ND	ND	ND	−184.7	152.0	176.1	
8	Wheat starch[b]	ND	ND	ND	−140.3	147.6	172.8	
9	Wheat starch[c]	ND	ND	ND	−127.7	149.0	172.8	
10	Urea[a]	1000	3050	3.0	−130.0	132.1	145.2	172.6
11	Urea[b]	1050	3910	3.7	−135.6	133.0	147.5	172.3
12	Urea[c]	1150	4010	3.5	−118.8	138.1	150.6	169.1

ΔH = curing enthalpy (J/g); T_1, T_2, T_3 = temperature of first, second, and third DSC exotherm, respectively; ND = molecular weights were not determined (incomplete solubility of resins in THF).
[a] With starting reagents.
[b] After condensation of 45 min.
[c] At the end of the resin condensation.

^{13}C-NMR technique is a powerful tool for analyzing resin structures, the molar concentration of lignin or starch was not high enough to reveal whether or not these reagents were contributing to the resin structure. For urea-modified resins 10–12, the carbonyl signals [–NC(O)N–] of the prepolymers formed from urea and formaldehyde could be assigned, but the cocondensation of urea, phenol, and formaldehyde to PUF resins would not even be expected under alkaline conditions.[23]

The later the modification reagent was added to the resin condensation mixture, the more methylene bridges were formed with respect to the amounts of free ortho and free para aromatic groups. The highest ratios of methylene bridges to these free aromatic groups was reached by modifications with lignin-based reagents (resins 2 and 3) and corn starch (resins 4–6) or in the late-stage addition of wheat starch (resin 9) or urea (resins 11 and 12). When resins 3–6, 11, and 12 were analyzed, the GPC results also indicated high condensation stages.

When added with starting reagents (resin 10), urea reacted with formaldehyde into urea methylols. This formaldehyde bonding naturally decreased methylolation occurring mainly at the beginning of resin synthesis; therefore, during further condensation, the amount of methylene bridges remained low, this being indicated as a low ratio of methylene bridges to free ortho and free para aromatic carbons. For resin 11, the methylolation stage was already high after 45 min of condensation when urea was added, and the final value of the ratio of methylene bridges to free ortho and free para aromatic carbons was higher (2.66) than

that of resin 10 (1.96). When added at the end of the condensation of resin 12, urea acted as a catcher of residual free formaldehyde without affecting methylolation anymore and further methylene bridge formation.

In resins 1–6, more methylol groups were quantified than methylene bridges. The highest ratios of methylene bridges to methylols were obtained with cornstarch modification. The lignin-bearing lye-modified resin 3 had more o–p′ methylene bridges and methylol groups than the lignosulfonate-modified resin 2. In a base-catalyzed process, formaldehyde is known to react mainly to the free ortho position of phenolic units of lignin forming methylol substituents, which are further condensed into methylene bridges.[4,5,24,25d] Also, in this study, the modification of a resin with lignin (resin 3) promoted the highest o–p′/p–p′ ratio. Generally, the quantitative determination showed that modifications with starch (resins 4–9) or the addition of urea during active resin synthesis (resins 10 and 11) favored p–p′ bridge structures.

Molar mass distributions of the modified resins

PF adhesive resins are used in plywood gluing. Therefore, the molar mass distribution of the prepolymer is very important. If the prepolymer molecules in the hot pressing procedure are too small, they penetrate too deeply into the porous structure of wood and, therefore, give a poor adhesion effect. If the prepolymer molecules are too large, they do not penetrate into the wood enough, and this causes the same weak bonding effect.
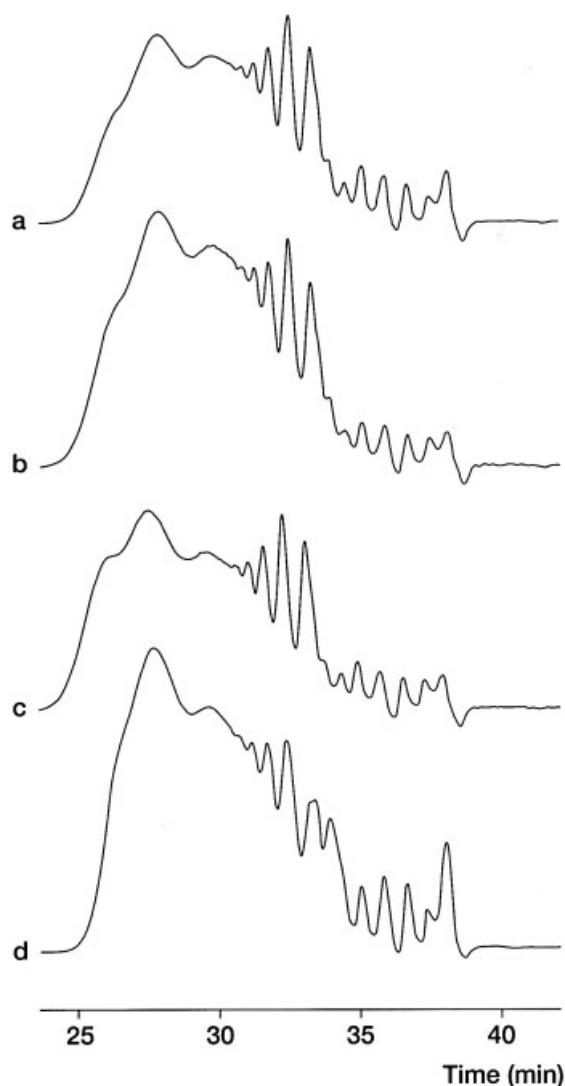
Figure 1 GPC curves of the resins: (a) the reference resin (**1**), (b) the lignin-bearing lye-modified resin (**3**), (c) the corn-starch-modified resin (**4**), and (d) the urea-modified resin (**10**). The modification reagents were added with starting reagents.

The results collected from the GPC measurements are presented in Table II. The GPC curve of the lignin-bearing lye-modified resin **3** was slightly different from that of reference resin **1** (Fig. 1). The proportion of large molecules was higher. Both the M_n and M_w values of **3** were slightly higher than those of **1**, but the polydispersity values of **1** and **3** were almost identical.

Modifications with corn starch seemed to increase the M_w value of resins **4** (Fig. 1), **5**, and **6** compared with that of the reference resin. The M_n and polydispersity values were slightly higher than those of the reference resin. The resins with the highest molar mass values arose when corn starch was added at the beginning of the condensation reaction.

The M_w values of the urea-modified resins **10** (Fig. 1), **11**, and **12** increased when urea addition was

moved toward the end of the condensation reaction. The M_n values were very similar to those of the reference resin, and the M_w values were clearly higher for the resins in which urea was added in the middle or at the end of the condensation reaction.

Curing and reactivity of the modified resins

DSC measurements give valuable information concerning the curing and reactivity of resins. Barry and coworkers[2,6] investigated, using DSC, the effect of the lignin content on the curing properties of PF resins. The cure exotherm of lignin–phenol–formaldehyde resins decreases as the lignin content increases, but to a lesser extent for methylolated lignins than for non-methylolated lignins. This is considered to be an indication that methylolation increases the reactivity of lignins. Also, the peak temperature decreases with an increasing lignin content.[2] Similarly, Ysbrandy et al.[32] found that the replacement of phenol with lignin shifts the cure exotherm toward lower temperatures and decreases the heat of a curing reaction.

In this study (Table II), both lignin-derived resins, the lignosulfonate-modified resin **2** and the lignin-bearing lye-modified resin **3**, showed a DSC exotherm with one broad signal at the peak temperature of 152°C, and the reference resin **1** showed a peak temperature of 157°C. The curing reaction seemed to be more exothermic for the lignosulfonate-modified resin than that for the reference or the lignin-bearing lye resin. The peak temperatures of the signals of both modified resins were lower than that of the reference resin. A single exotherm of the curing of the PF reference resin can be attributed to the formation of methylene bridges.[29,33,34] Also, the DSC signals of lignin-modified resols appearing in the same temperature region as that of the reference resin represent the chain-building and methylene bridge-forming condensation reactions.

The corn-starch-modified phenol resins **4–6** showed DSC curves with one exotherm as resin **1** without a modification reagent. The heat generated during the curing of the corn-starch-modified resins was lower than the curing heat of the unmodified resin because of a higher condensation degree. The peak temperatures were at the same level as those of the reference resin.

The wheat-starch-modified resins **7–9** showed two exotherms in their DSC curves (Fig. 2). The first signal at 147–152°C represents phenolic curing.[29,33,34] Extra urea was added to **7–9** at the end of the condensation reaction to capture the residual free formaldehyde and to control the viscosity. The second exotherm at 172–176°C can be associated just with urea-derived compounds. When wheat starch was added at the beginning of the reaction, the total curing heat and the curing heats of both individual exotherms were high-

est. This was due to the low condensation stage verified by the low ratio of methylene bridges to free aromatic carbons. When added at the same time to the final reaction solution, wheat starch and urea competed in binding free formalin, and the heat of the second curing was lower. No correlation between the addition stage of wheat starch and the peak temperatures was found.

The urea-modified resins **10–12** produced three DSC signals (Fig. 3). The first exotherm at 132–138°C represents the fast addition reaction of free formaldehyde with free phenol, which gives methylolphenols.[35] The second signal with the peak temperature between 145 and 151°C is considered to be due to the formation of methylene bridges.[29,33,34] The third signal at about 170°C can again be considered the exotherm associated with urea-containing compounds. The later urea was added to the reaction solution, the higher the curing heat was of the third exotherm around 170°C and the lower the peak temperature was in this third signal. However, no correlation between the total enthalpy and the urea addition stage could be found.

CONCLUSIONS

In comparison with the unmodified PF reference resin, most exothermic curing reactions were found with the
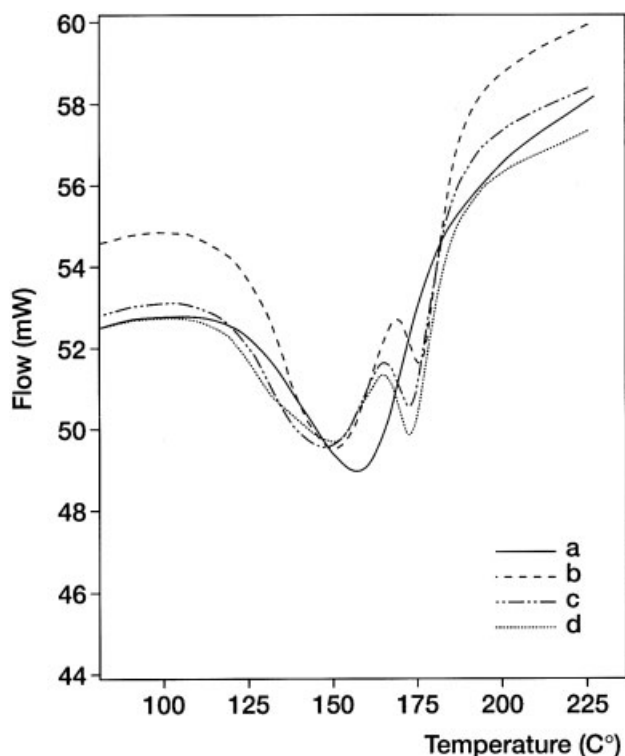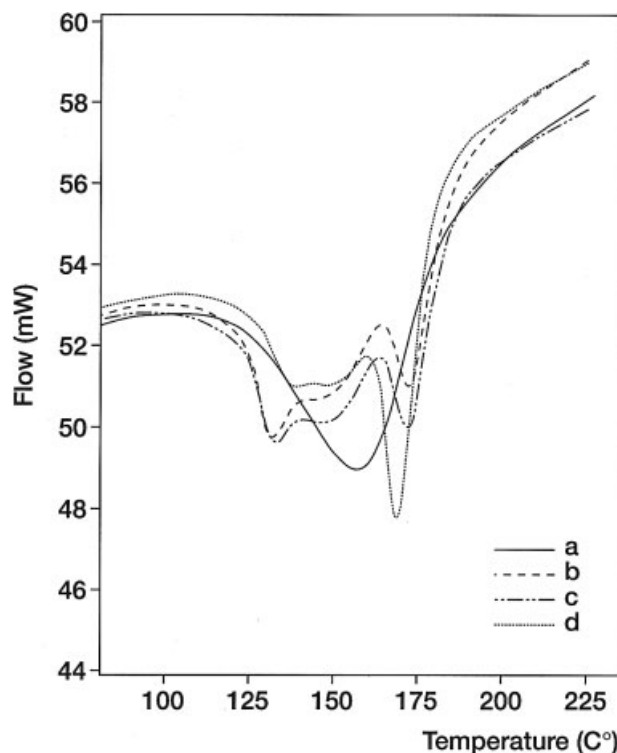

Figure 3 DSC curves of (a) the reference resin (**1**) and (b–d) the resins modified with urea [(b) added with starting reagents (**10**), (c) after 45 min of condensation (**11**), and (d) at the end of the resin condensation (**12**)].

wheat-starch-modified resins. Almost as high and even slightly higher exotherms were reached with the lignosulfonate-modified or urea-modified resins than with the reference. Modifications with corn starch, a lignin reagent, or urea were proven to increase M_w values with respect to the values of the reference resol.

The addition stage of the studied modifiers had a significant effect on the resin reactivity only for the wheat-starch-modified resins. The curing heat decreased when the addition point of wheat starch was deferred. The M_w values of the urea-modified resins increased when the modification reagent was added at the end of the condensation. The later the modifier was added to the resin condensation mixture, the more methylene bridges were formed. Especially high ratios of methylene bridges to free ortho and para aromatic groups were reached during modification with lignin-based reagents or corn starch or in the late-stage addition of wheat starch or urea. Except for the ortho-directing lignin-bearing lye, the modification of the reference resol typically enhanced $p–p'$ bridge structures.

Figure 2 DSC curves of (a) the reference resin (**1**) and (b–d) the resins modified with wheat starch [(b) added with starting reagents (resin **7**), (c) after 45 min of condensation (resin **8**), and (d) at the end of the resin condensation (resin **9**)].

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