

Effect of Alkalinity on the Structure of Phenol–Formaldehyde Resol Resins

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Received 1 June 2000; accepted 29 January 2001

ABSTRACT: Two phenol–formaldehyde resol resin series with different methylation- and condensation-stage alkalinities were studied. The first series was impregnation resins having a methylation alkalinity between 0.5 and 1.5 wt % and a condensation alkalinity of 1.5 wt %. The second series was adhesive resins with a methylation alkalinity between 0.5 and 3.5 wt % and a condensation alkalinity of 6.0 wt %. The chemical structure was analyzed by ¹³C-NMR spectroscopy, and reactivity, by differential scanning calorimetry (DSC). The methylation alkalinity was found to affect the distribution of the structural groups of both phenol–formaldehyde impregnation and adhesive resins, but not to the same extent as did the total condensation alkalinity. Also, the results of the DSC analysis illustrate best the reactivity differences due to the condensation alkalinity. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 258–262, 2001

Key words: phenol–formaldehyde resin; ¹³C-NMR; DSC; alkalinity

INTRODUCTION

Phenolic resol resins are the polycondensation products of the reaction of phenol with formaldehyde in the presence of an alkali catalyst, for example, NaOH. Alkaline phenol–formaldehyde resins are used as industrial impregnation resins and plywood adhesives.^{1,2} The final structure and, further, the properties of the phenolic resins are dependent on the condensation parameters. One of the most important conditions is the alkalinity in the synthesis of resols. The mechanism and kinetics of the alkali-catalyzed reaction of phenol with formaldehyde, the physical properties of resins under alkaline conditions, and the effects of the curing alkalinity on resins have been widely researched.^{1–11} In this study, the effects of

the methylation alkalinity (first-stage alkalinity after an initial addition of a NaOH catalyst) and the condensation alkalinity (second-stage alkalinity after subsequent addition of a NaOH catalyst) on the chemical structures and reactivity in two phenol–formaldehyde resin series were studied by ¹³C-NMR spectroscopy and differential scanning calorimetry (DSC).

EXPERIMENTAL

Resin Preparation

Formaldehyde was produced by Dynoresin Oy from methanol and used as a formalin solution, which contained 45 % formaldehyde, water, and some methanol. Another starting material, phenol, was purchased from J.T. Baker (Deventer, Holland). A series of 10 resins was condensed with a NaOH catalyst (produced by Merck, Darm-

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Journal of Applied Polymer Science, Vol. 82, 258–262 (2001)
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stadt, Germany) in two stages. Four of the resins (numbers 1–4) were impregnation resins having a methylation alkalinity between 0.5 and 1.5 wt % and a condensation alkalinity of 1.5 wt %. Six resins (numbers 5–10) were adhesives with a methylation alkalinity between 0.5 and 3.5 wt % and a condensation alkalinity of 6.0 wt %. The molar ratio of formaldehyde to phenol was 2.2 in all the resins. The condensation temperature of all the studied resins was 80°C, and the viscosity, 350 mPa s. The resins were stored frozen at –18°C until analysis.

NMR Experiments

Quantitative ^{13}C -NMR spectra of the studied resins 1–10 were recorded with a Bruker AMX-400 spectrometer, observing ^{13}C at 100.623 MHz and using an inverse-gated ^1H decoupling technique. All spectra of the resins were run with a 90° pulse of 11.5 μs in the previously optimized¹² NMR conditions of a 10-s pulse delay, 600 scans, and with 20 mM of the relaxation reagent, $\text{Cr}(\text{acac})_3$ (97%, purchased from Aldrich, Milwaukee, WI.) $\text{DMSO-}d_6$, 99 atom % deuterated dimethyl sulfoxide (Riedel-de Haën, Seelze, Germany), was used as a solvent. The ^{13}C signals of the resins were referenced to the central resonance line of DMSO with a δ value of 39.5 ppm.

DSC Experiments

DSC measurements were made using a Perkin–Elmer DSC 7 instrument and a 7 Series Unix thermal analysis software. The apparatus was calibrated with indium and zinc samples. Liquid resin samples of 10 mg were measured in Perkin–Elmer stainless-steel pressure capsules heated from 25 to 250°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of Alkalinity on the Structural Groups of Resins Analyzed by ^{13}C -NMR Spectroscopy

Four of the resins (numbers 1–4, Table I) were impregnation resins having a methylation alkalinity between 0.5 and 1.5 wt % and a condensation alkalinity of 1.5 wt %. Six resins (numbers 5–10, Table I) were adhesives with a methylation alkalinity between 0.5 and 3.5 wt % and a condensation alkalinity of 6.0 wt %. The quantitative determination of structural groups of the studied

Table I NMR Results of the Analyzed Resins

No. Resin	Methylation Alkalinity (wt %)	Condensation Alkalinity (wt %)	Aromatic Carbons			Methylol Groups			Methylene Bridges			Formalin Hemiacetal ^a	Formalin Oxymethylene	Phenolic Hemiformals
			Phenoxy	Free ortho	Free para	Other	ortho	para	o-p'	p-p'	o-p'			
1	0.5	1.5	1.00	0.272	0.025	4.684	1.042	0.168	0.288	0.334	0.622	0.034	0.018	0.103
2	0.8	1.5	1.00	0.261	0.026	4.759	1.036	0.152	0.265	0.348	0.614	0.037	0.018	0.101
3	1.2	1.5	1.00	0.245	0.022	4.687	1.053	0.150	0.275	0.342	0.617	0.034	0.017	0.091
4	1.5	1.5	1.00	0.233	0.020	4.841	1.115	0.150	0.276	0.361	0.638	0.032	0.016	0.083
5	0.5	6.0	1.00	0.158	0.005	5.069	1.262	0.143	0.264	0.372	0.636	0.004	—	0.023
6	0.8	6.0	1.00	0.150	trace	5.055	1.286	0.143	0.283	0.337	0.620	0.004	—	0.011
7	1.5	6.0	1.00	0.143	0.010	5.075	1.287	0.107	0.282	0.366	0.649	0.004	—	0.009
8	2.0	6.0	1.00	0.118	0.009	5.086	1.304	0.113	0.302	0.345	0.647	0.003	—	0.013
9	2.5	6.0	1.00	0.149	0.004	5.062	1.328	0.121	0.311	0.355	0.666	0.004	—	0.022
10	3.5	6.0	1.00	0.100	0.019	5.198	1.342	0.107	0.302	0.348	0.650	0.006	0.003	0.031

Integral values are related to the value of 1.00 of the phenoxy carbon.

^a Average of two hemiacetal carbon signals.

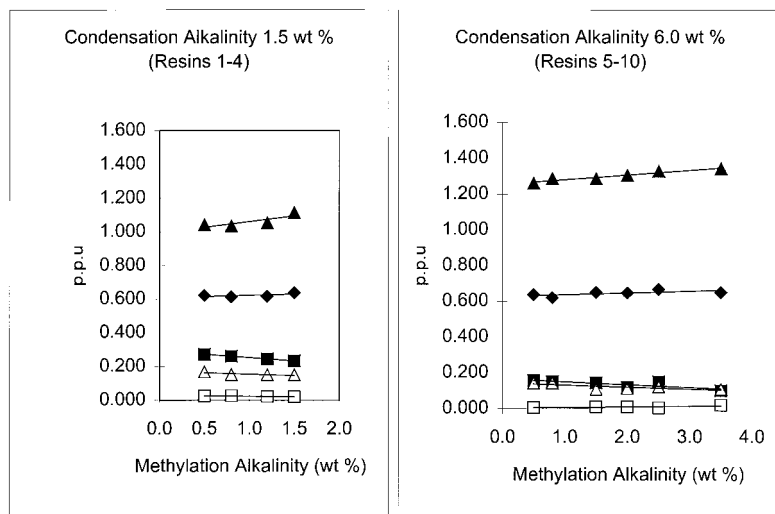


Figure 1 (■) Free *ortho* aromatic groups, (□) free *para* aromatic groups, (▲) *ortho* methylol groups, (△) *para* methylol groups, and (◆) the sum of *p-p'* and *o-p'* methylene bridges of resins 1–4 and of resins 5–10 as a function of methylation alkalinity.

resins (1–10) was done by ^{13}C -NMR spectroscopy, and the structural data are collected in Table I.

The *para* position in phenol is known to show, under alkaline conditions, a slightly higher relative reactivity toward formaldehyde than the *ortho* position.^{1,2} Also, in this study, about 10 times less free *para* than free *ortho* aromatic groups were found to be left, based on the ^{13}C -NMR analysis of the resins. The addition of methylol groups to the *ortho* positions increases the reactivity of the remaining free *ortho* and *para* positions toward further formaldehyde.^{1,2} According to the NMR results in Table I, relatively more *para* than *ortho* methylol groups reacted further to methylene bridges. The most important final reaction in the prepolymer formation under strong alkaline conditions was found to be, indeed, the formation of methylene bridges, while the formation of dihydroxydibenzyl ether is very unlikely under high alkaline conditions.^{1,2,13}

Higher amounts of both free *ortho* and free *para* aromatic groups were present in the impregnation resins (1–4) with a lower condensation stage alkalinity of 1.5 than in the adhesives (5–10) with a higher condensation alkalinity of 6.0 (Fig. 1). This is in accordance with the lower production of methylol groups for the impregnation resins (1–4) than that of the adhesive resins (5–10). However, formalin hemiacetal, oxymethylene, and phenolic hemiformal groups were present in the impregnation resins (1–4), while only trace amounts, if any, of them were found in the adhesives (5–10) (Table I).

Figure 1 illustrates the increasing amounts of *ortho* methylol groups and slightly decreasing amounts of *para* methylol groups as a function of the methylation alkalinity. Figure 1 indicates also that the amount of free *ortho* aromatic groups of all the resins (1–10) decreased as a function of increasing methylation alkalinity, as well as did slightly that of the free *para* aromatic groups of the impregnation resins (1–4). Only traces of free *para* aromatic groups were present in resins of higher condensation alkalinity (5–10). The sum of *ortho-para* and *para-para* bridges had reached the quite stable level and no significant trends as a function of the alkalinity values were found in this study. Phenolic hemiformals of resins 1–4 decreased as expected according to increasing methylation alkalinities much more clearly than did the other formalin-based groups (formalin hemiacetals and oxymethylenes; Fig. 2).

DSC Results

The characteristic temperature range and the heat of reaction of the DSC curves give information on the reactivity. The enthalpy values of the adhesives (5–10) are slightly higher than are those of the impregnation resins (1–4; Table II). The differences in the enthalpy values due to variation in the methylation alkalinity within the two resin series are not as clearly interpreted as they are between these two series, particularly when repeatability of the method is considered to be 5%.¹⁴

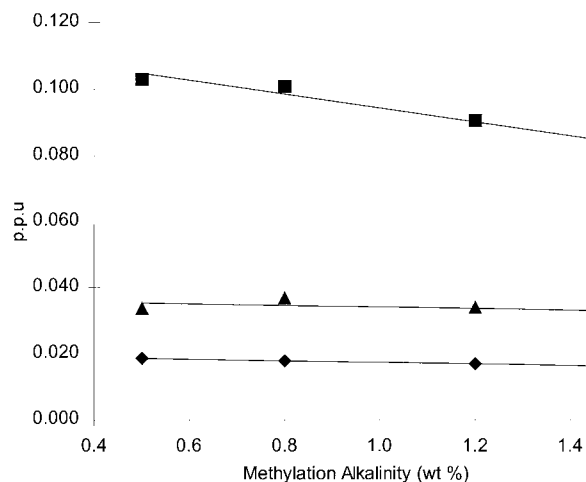


Figure 2 (■) Phenolic hemiformal, (▲) formalin hemiacetal, and (◆) formalin oxymethylene groups of resins 1–4 as a function of methylation alkalinity.

The DSC curves for phenol–formaldehyde resins (1–4) with a low condensation alkalinity of 1.5 wt % contain two well-separated exotherms (Fig. 3). The first signal of the DSC curves having the maximum at the temperature between 146 and 149°C is caused by the condensation of methylol groups with phenolic units to form methylene bridges and by the condensation of two methylol groups to form dibenzyl ether bridges.^{15–18} The second signal of the thermograms (the maximum between 184 and 194°C) of resins 1–4 represents further reactions of the resin—for example, the condensation of the dibenzyl ether bridges to methylene bridges with the elimination of formaldehyde.^{15–18}

In the DSC graphs of the resins (5–10) with a high condensation alkalinity of 6.0 wt %, the

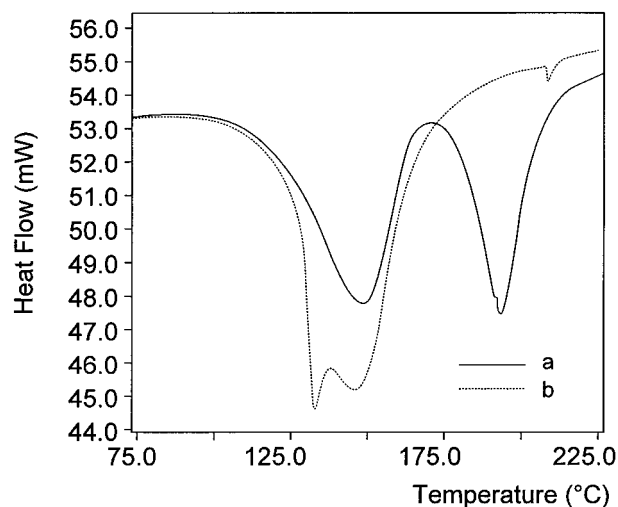


Figure 3 DSC curves of phenol–formaldehyde (a) impregnation resin and (b) adhesive resin.

signal having the peak temperature between 146 and 149°C represents the formation of methylene groups in the condensation of methylol groups with phenolic units (Fig. 3). The formation of dihydroxydibenzyl ether is very unlikely under high alkaline conditions, and the signal due to condensation of ether bridges above 184°C is not found in the DSC thermogram. Instead, a narrow exotherm having the peak temperature between 133 and 136°C overlaps the subsequent signal of the formation of methylene groups. This exotherm is considered to be due to the fast addition reaction of free formaldehyde with free phenol to give methylolphenols, and it is usually overlapped with the signal of methylene group formation.³

Table II DSC Analysis of Resins with Different Alkalinities

No. Resin	Methylation Alkalinity (wt %)	Condensation Alkalinity (wt %)	ΔH (J/g)	T_1 (°C)	T_2 (°C)	$\Delta(T_1 - T_2)$ (°C)
1	0.5	1.5	-162.1	146.9	184.7	37.8
2	0.8	1.5	-170.0	149.5	194.0	44.5
3	1.2	1.5	-169.3	147.4	192.8	45.4
4	1.5	1.5	-161.0	146.6	188.3	41.7
5	0.5	6.0	-201.4	134.7	145.9	11.2
6	0.8	6.0	-183.5	136.5	146.2	9.7
7	1.5	6.0	-172.2	133.7	145.9	12.2
8	2.0	6.0	-182.3	135.4	147.0	11.6
9	2.5	6.0	-173.8	135.6	147.8	12.2
10	3.5	6.0	-180.2	134.8	148.7	13.9

DSC signals at T_1 and T_2 are separate for resins 1–4 and overlapped for resins 5–10.

CONCLUSIONS

This study indicated that alkalinity control is important in resin production. The progress of resin synthesis was found to be dependent mainly on the total condensation alkalinity, but also on the methylation-stage alkalinity. The amount of free *ortho* aromatic groups decreased and also free *para* groups slightly as a function of increasing methylation alkalinity. The highest amount of *ortho* methylol groups were found for the resins with the highest methylation alkalinity. The higher condensation-stage alkalinity favored the production of *ortho* methylol groups, when the proportions of free aromatic groups and formalin-based structures were reduced. The results of the DSC analysis illustrate best the reactivity differences due to the condensation alkalinity.

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