# Effects of Silane and the Lowering of pH on the Properties of Phenol–Formaldehyde Resol Resins and Resin Coatings

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**ABSTRACT:** Phenol–formaldehyde resol resins were modified by the addition of silane (3-aminopropyltriethoxysilane) and the lowering of pH (formic acid). The effects of the modifications on the properties of the resins during storage were studied through comparison with the parent resins and by viscosity measurements, NMR spectroscopy, ultraviolet–visible spectroscopy, and differential scanning calorimetry. Resin coatings on paper were prepared to determine the influence of discoloration of the resin solution on the color of the cured resin. A decrease in the pH of the NaOH-catalyzed resin solutions lightened the color of the solutions and corresponding coatings, whereas silane additions made the coatings slightly more yellow. The lowering of pH increased the viscosities and decreased the reactivities of the resin solutions compared with the unmodified reference resins during storage. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1933–1941, 2007

**Key words:** additives; modification; resins

## INTRODUCTION

More intensive study and a better understanding of phenolic resins have led to new methods for exploiting the advantageous properties of cured, highly crosslinked thermoset resins. Resins with good thermal and moisture resistance and mechanical stability have found applications as adhesives, binders, and matrix components in the woodworking, insulation, and foundry industries.[1,2]

Various modifications of phenol–formaldehyde (PF) resins have been made to achieve the properties needed in particular applications. Suitable additives cover a wide range of organic and inorganic compounds, most of them used in proprietary applications. The curing properties of PF resins in wood-based products are improved by the addition of various carbonates, which increase the functionality of the systems and reduce the hot-pressing times.[3–5] Urea is added to reduce the manufacturing costs and to bind the free formaldehyde present in the resol resin solutions.[6,7] Modifications with lignin and starch, in turn, promote the condensation reactions in the resol systems, increase the molar masses of the resins, and replace a portion of the costly phenol component.[6]

Organosilanes are common adhesion promoters and coupling agents in the manufacture of mineral wool mats and foundry sand molds.[1,2] They improve compatibility and adhesion by strengthening interactions or generating bonds between the inorganic components (e.g., glass fibers, sand) and organic resin matrices.[8] The commercial importance of silanes in composite technology is confirmed by the extensive patenting of these systems.[9–12] Silanes, usually alkoxysilanes, can be applied as surface pretreatments to fillers and fibers before their incorporation with resins, or they can be mixed with the resin solution in the manufacturing stage just before use. Silane hydrolyzes in aqueous resin solutions yielding highly reactive silanol groups. The process progresses in self-condensation reactions of the silanols and produces oligomerized silane networks with siloxane bonds. Because the silanol groups are also responsible for the reactions of silanes with the solid substrates, however, the self-condensation reactions must be kept within defined limits. For this, a neutral pH of the solution is effective.[8]

The characteristic red color of NaOH-catalyzed resol resins limits the commercial use of the resins. Moreover, heat curing, moisture, and exposure to light darken the adhesive joints between the veneers of plywood more than the wood itself. Particularly in the furniture industry, red and dark resin joints are considered unattractive and undesirable. Efforts to reduce the discoloration of resol resins include the use of various additives and catalysts and prevention of the oxidation of the resin solutions.[13–19] The lowering of the pH is a well-known approach for the

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production of light colored resol resins,[20] with the assumption that the cause of the discoloration is phenolphthalein-type oxidation products of phenol or phenolic derivatives formed by the radical mechanism.[15] Despite the obvious commercial importance, there are no reports on the color formation of resol resins in the literature.

In this study, we modified three parent PF resol resins, also used as reference resins, by adding aminosilane [3-aminopropyltriethoxysilane (APS)] and lowering the pH (formic acid). The effects of these modifications on the chemical and physical properties of the resin solutions and the color of the cured resins (coatings on paper) were studied during a short storage period. The behavior of the aminosilane in the aqueous resin solutions was clarified, and the effects of the silane additions on the properties of the solutions and the color of the cured coatings were explored. If, as recently indicated, silanes are covalently bonded with cellulose fibers during heat treatment,[21,22] the applications of silane-modified resins could be considerably expanded. The pH adjustments of the resins were of interest to the study of color changes with the aim of reducing discoloration of the solutions and cured resin coatings. Resins were analyzed during storage by viscosity measurements, ^{13}C-NMR, ultraviolet–visible (UV–vis) spectroscopy, and differential scanning calorimetry (DSC). We studied the shelf life of the resin solution by following the change in the viscosity ($\Delta\eta$). The structures of the reference resins and selected modified resins were characterized by ^{13}C-NMR. The transmittance spectra of the liquid resin samples and reflectance spectra of the resin coatings were measured with a UV–vis spectrometer, and the spectra were used in the calculations of CIE [International Commission Illumination (Commission Internationale d'Eclairage)] $L^*$ (lightness coordinate), $a^*$ (red/green coordinate), and $b^*$ (yellow/blue coordinate) color coordinates. The reactivities of the resins were determined by DSC.

## EXPERIMENTAL

### Synthesis and properties of parent resins

The synthesis and characterization of three unmodified PF resol resins, also used as reference resins, were performed by Hexion Specialty Chemicals, Ltd. (Table I, R1–R3, Kitee, Finland). Resins R1 and R2 were considered impregnation or insulation resins, and R3 was considered a matrix resin for abrasive materials. Sodium hydroxide (Finnish Chemicals, Pietarsaari, Finland) was used as a catalyst in the reactions of phenol ($\geq$ 99%, Merck, Hohenbrunn, Germany) and formaldehyde (40 wt % formalin solution, Hexion Specialty Chemicals, Ltd.). We set formaldehyde/phenol (F/P) molar ratios by weighing to 2.25 for resin R1 and 2.60 for resin R2. The pH values (25°C), free formaldehyde contents (wt %; hydroxylamine hydrochloride method), and solids contents (wt %; 3 h/105°C) of the parent resins are shown in Table I. We obtained reference resin R3 from R2 by evaporating water with a rotary evaporator (Heidolph VV 2000, Heidolph, Schwabach, Germany, 4 h at 40°C); thus, R3 contained only traces of free formaldehyde and had a high solids content. Resins were kept frozen until modification or use in the experiments.

Before storage, an excess of urea (pro analysi, Merck, Darmstadt, Germany) relative to the amount of free formaldehyde (wt %) was added to resins R1 and R2 to bind free formaldehyde left in the solutions. Although R3 contained only traces of free formaldehyde, the urea content was adjusted equal to that of resin R2 to facilitate comparison. After the urea modification, the resins, in closed vessels, were shaken 50 times per minute for 60 min in a water bath at 40°C to promote the dissolution of urea.

### Modification of resins

The modifications of resins R1–R3 are presented in Table I. Resin R1 was modified by the addition of APS (technical grade, Degussa-Hüls AG, Düsseldorf,

#### TABLE I
#### Initial Properties and Modifications of Reference Resins R1–R3

| Resin | Code | pH | Free formal (wt %) | Solids content (wt %) | Modifications[a] | |
|-------|------|-----|--------------------|-----------------------|------------------|------|
| | | | | | Preparation | Code |
| Reference resin 1 | R1 | 8.8 | 3.6 | 49.8 | R1 + 1.0 wt % Si | S1 |
| Reference resin 2 | R2 | 9.2 | 3.8 | 52.8 | R2 + pH = 7[b] + SP[c] | P2 |
| | | | | | R2 + pH = 7[b] + SP + 1.0 wt % Si | PS2 |
| Reference resin 3[d] | R3 | 9.1 | —[e] | 79.2 | R3 + pH = 7[b] | P3 |
| | | | | | R3 + pH = 7[b] + 1.0 wt % Si | PS3 |

[a] Urea was added to all modified resins.
[b] The pH was adjusted to 7 with formic acid.
[c] SP = separation of phases.
[d] Obtained from R2 by the evaporation of water.
[e] Traces of free formaldehyde.

Germany) to produce silane resin S1. The silane content of S1 was defined as 1.0 wt % of silicon relative to the solids content of resin R1. Before the silane modification, the urea concentration of S1 was adjusted so that it would be equal to that of R1. After the modification, silane resin S1 was heated in a water bath (40°C) as described for the reference resins.

Reference resins R2 and R3 were used in the pH modifications. We adjusted the pH levels to 7 (pH meter, Consort P901, Consort, Turnhout, Belgium) by dropping and mixing formic acid (pro analysi, Riedel de Haën, Seelze, Germany) into the resins. On modification, the red and transparent R2 solution changed to a light-colored, opaque solution, and two phases formed. The upper, transparent water phase and the lower, opaque resin phase were allowed to separate in a separating funnel at room temperature for 12 h. The upper layer was discarded, and the lower resin layer was weighed and split into two portions to yield resins designated as P2 and PS2. The urea concentrations of P2 and PS2 were calculated according to the amount of free formaldehyde in R2. APS was added to PS2, to achieve a silicon content of 1.0 wt % set in proportion to the weighed mass of the lower phase.

Because of the higher solids content, there was no phase separation during the pH modification of resin R3. The amount of urea in modified resins P3 and PS3 was adjusted to be equivalent to that of reference R3. The silane concentration of PS3 was defined as 1.0 wt % of silicon relative to the solids content of resin R3. The transparency of the pH-adjusted resins returned with the dissolution of urea. The pH-modified resins were shaken and heated in the same way as the reference and silane resins.

Reference and modified resins were stored in nontransparent plastic bottles (250 mL) at room temperature and shaken twice daily for 15 min during storage. Reference resin R1 and silane resin S1 were used to study the short-term effects of silane modification on the properties of resin and resin coatings, whereas the pH-modified solutions and corresponding references were used in the analysis of longer term effects. The number of days of storage is indicated as a number in parenthesis [e.g., R1(7)].

### Preparation of resin coatings

Resin coatings were prepared to study the effects of the modifications and storage of the resin solutions on the color of the corresponding cured resins. We prepared three parallel coating samples at the start and end of the storage period by spreading a resin layer 60 μm thick with a K Hand Coater (R. K. Print Coat Instruments, Ltd., Litlington, United Kingdom) on white paper (Xerox Business, 80 g/m$^2$) taken from the same paper pack and curing the coated papers in a heating chamber at 105°C for 23 h. We labeled the coatings by adding the letter C to the abbreviation of the solution that was used (thus CR1). Days of storage of resin solution are indicated by numbers in parentheses.

### Viscosity measurements

The development of the viscosity of the reference and modified resins during storage was followed by a Brookfield DV-II+ digital viscometer with a small sample adapter and an SCN-31 spindle (Middleboro, MA). The resin samples (10 mL) were poured into the sample adapter and stabilized in a water-circulating jacket (25°C) of the viscometer for about 25 min before the final viscosity measurement. The calibration of the viscometer was performed with viscosity standards of 100, 500, 1000, and 5000 mPa s (Brookfield). The results of the analyses are the average of two parallel determinations.

### $^{13}$C-NMR

The structures of the reference and selected modified resins were characterized with a Bruker AMX-400 NMR spectrometer (Bruker, Karlsruhe, Germany) observing $^{13}$C at 100.623 MHz. Quantitative $^{13}$C-NMR spectra were measured by an inverse gated proton decoupling technique with acquisition parameters of 90°, a pulse of 11.5 μs, a 120.0 s delay time, and 600 scans. Total run time was 20.5 h. We prepared samples in 10-mm NMR tubes (Wilmad, royal imperial grade, Buena, NJ) by dissolving approximately 1 mL of resin in about 3 mL of 99.8% deuterated dimethyl sulfoxide (DMSO-$d_6$; Euriso-top, Gif-Sur-Yvette, France), which was also used as a compound for deuterium lock and as an internal chemical shift standard. The central resonance line of DMSO-$d_6$ ($\delta = 39.5$ ppm) was used for the scaling of the $^{13}$C-NMR spectra. The phenoxy carbon region of 150–158 ppm was assigned the integral value of 1.00, and all other integrated signals or signal groups were related to that value. The $^{13}$C-NMR signals and signal areas of the reference and modified resins were identified with the help of the literature.[23–30]

### UV–vis spectroscopy and color coordinates

Transmission spectra of the liquid resins and reflectance spectra of the nontransparent resin coatings were measured with a PerkinElmer Lambda 900 UV–vis–NIR (ultraviolet-visible-near infrared) spectrometer. The spectra of the liquid resins were determined with 10-mm cuvettes (100-QX Quartz SUPRASIL 300, Hellma, Müllheim, Germany) in a wave-

length area of 380–780 nm at room temperature. An empty cuvette was used as a reference and for the background measurements. The first color determinations of the reference resins were performed immediately after thawing. The reflectance spectra (380–780 nm) of the coatings were measured with the integrating sphere of the UV–vis–NIR spectrometer with white reference disks in the determinations of background spectra. The results of the UV–vis–NIR experiments are given as the average of two parallel analyses.

The color coordinates were defined with Perkin-Elmer Advanced Data Handling software in the wavelength area 380–780 nm. The calculation of the color coordinates was done according to the CIE $L^*a^*b^*$ color space with a 10° observer and D65 standard illuminant. The $L^*$ axis, which is the normal of the plane formed by the $a^*$ and $b^*$ axes, shows the luminosity (lightness) of a color so that 0 refers to ideal black and 100 refers to ideal white. The $a^*$ axis expresses the red green color share of the samples, with positive $a^*$ values indicating redness and negative $a^*$ values indicating greenness. Correspondingly, the $b^*$-axis describes the yellow color shades ($+b^*$) and blue color shades ($-b^*$). The color difference ($\Delta E$) between any two samples in the CIE $L^*a^*b^*$ color space is the distance between the color locations. $\Delta E$ is expressed as $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ are the differences in the coordinates of the resin or coating samples prepared at the start and end of the storage period.

## DSC

The thermal behavior of the resins during the curing was determined with a Mettler Toledo DSC instrument with STARe thermal analysis software (Mettler-Toledo, Columbus, OH). Liquid resin samples (~10 mg) were pipetted into Mettler Toledo high-pressure steel pans and sealed with the gold-plated copper seals. The pans were heated from 25 to 270°C at a heating rate of 10°C/min. The results of the DSC experiments are given as the average of two parallel determinations performed with the same steel pan. The standard deviations for the repeatability and reproducibility of the reaction heat measurements for the liquid resol resins were 5 and 15%, respectively.[31]

## RESULTS AND DISCUSSION

### Effect of the modifications and storage on the resin viscosity

Reference resin R1 (F/P = 2.25) was modified by silane addition (1.0 wt % Si relative to solids content of the resin) to yield silane resin S1 (Table I). Resins P2 and P3 were produced by pH modifications (pH 7) of references R2 and R3 with the same initial F/P molar

**TABLE II**
**Viscosities of Resins Measured 1 or 2 Days After Preparation and Viscosities and Δη's (%) at 8 Days**

| Resin | Viscosity | | | | |
|-------|-----|-------|-----|-------|---------|
|       | Day | mPa s | Day | mPa s | Δη (%) |
| R1  | 1 | 71   |   | —    | —    |
| S1  | 1 | 129  |   | —    | —    |
| R2  | 2 | 63   | 8 | 74   | +17  |
| P2  | 2 | 601  | 8 | 958  | +59  |
| PS2 | 2 | 713  | 8 | 1041 | +46  |
| R3  | 2 | 2442 | 8 | 3093 | +27  |
| P3  | 2 | 3375 | 8 | 5531 | +64  |
| PS3 | 2 | 3921 | 8 | 5663 | +44  |

ratio (2.60) but different solids contents due to the evaporation of water from R3. The addition of APS to P2 and P3 yielded resins PS2 and PS3. The effects of the modifications on the viscosity of resins S1, P2, PS2, P3, and PS3 compared with the reference resins (R1–R3) were followed by measurement of the viscosities of each sample during storage at room temperature (Table II). The viscosity determinations were performed once, after 1 day, for resins R1 and S1, and twice, after 2 and 8 days, for resins R2, R3, P2, PS2, P3, and PS3. The 12-h phase-separation stage was included in the storage time of resins P2 and PS2.

The viscosity of R1 was 71 mPa s at the start of the experiment. The addition of silane affected the viscosity of the resin solution, and the initial viscosity of S1 was about twice that of R1. A probable explanation for the increased viscosity of S1 was the hydrolysis and self-condensation reactions of APS. APS reacts rapidly with water yielding silanol groups, and self-condensations of the silanol groups produce gel-like dimeric and, further, oligomeric silanes through the formation siloxane bridge structures.[32,33] Such structures would have very likely increased the viscosity of the S1 solution.

Reference R2 exhibited the lowest initial viscosity and the smallest percentage increase in viscosity ($\Delta \eta$ = +17%) during storage. The evaporation of water from R2 to yield R3 generated, as expected, high initial and end viscosities. Additionally, the high solids content in R3 probably promoted the reactions between the resin units of the solution and accelerated the development of the viscosity during storage ($\Delta \eta$ = +27%).

The phase separation after the pH adjustments resulted, predictably, in higher initial viscosities in resins P2 (601 mPa s) and PS2 (713 mPa s) than in reference R2 (63 mPa s). The silane in resin PS2 generated an extra increase in viscosity compared with P2, consistent with the effect of silane modification of S1. However, the increase in viscosity during storage was less for P2 ($\Delta \eta$ = +46%) than for PS2 ($\Delta \eta$ = +59%). As was observed in the comparison of pH-modified resin P3 with reference R3, the water solubility of the resins was affected by the pH of the solution so that a decrease in pH reduced the solubil-
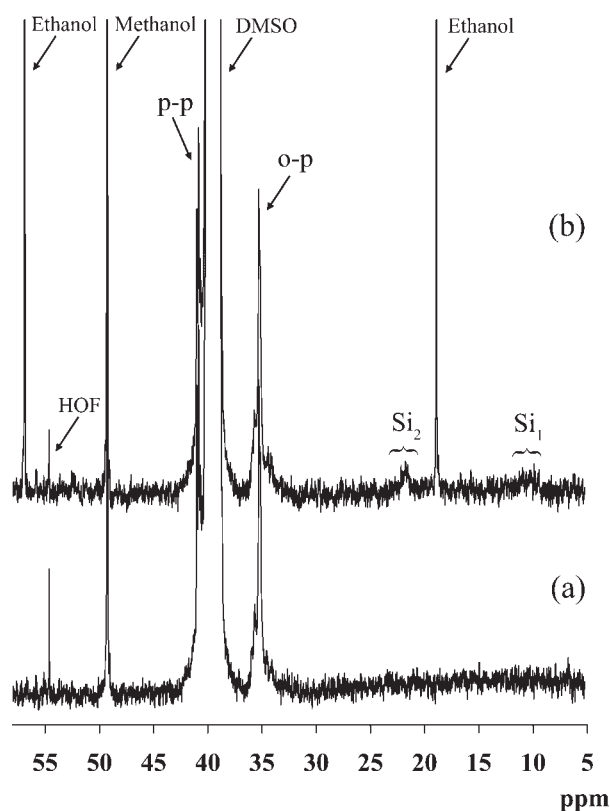
**Figure 1** $^{13}$C-NMR spectra (58–5 ppm) of (a) reference resin R1 (after 10 days) and (b) silane resin S1 (after 11 days) with $^{13}$C resonances of ethanol [O—CH$_2$—CH$_3$ (56.8 ppm) and O—CH$_2$—CH$_3$ (18.9 ppm)], hemiacetal of formalin (HOF), methanol, para–para (p–p) methylene bridges, DMSO (solvent), ortho–para (o–p) methylene bridges, and partially hydrolyzed or oligomerized APS [Si$_1$ (Si—CH$_2$— at 9–12 ppm) and Si$_2$ (Si—CH$_2$—CH$_2$— at 21.0–22.5 ppm)].

ity and increased the viscosity.[34] The effect of silane addition on the initial viscosity and development of viscosity of PS3 compared with P3 was similar to the effect observed for resins PS2 and P2.

**Studies of resin structure by NMR spectroscopy**

The structures of reference resins R1–R3 and modified resins S1, PS2, and PS3 were characterized at the end of the storage period by NMR spectroscopy. The effects of silane and pH modifications on the structures of the resins were of particular interest. The addition of urea complicated the interpretation of the resin spectra due to an overlap of the urea signals next to the phenoxy region ($\sim$158 ppm) and the methylols groups ($\sim$65 ppm). Although the storage periods of the reference and modified resins were not the same, structural differences were clearly evident.

The $^{13}$C-NMR spectrum of silane resin S1 [after 11 days, Fig. 1(b)] differed from that of reference R1 [after 10 days, Fig. 1(a)]. The signals of free ethanol, O—CH$_2$—CH$_3$ (56.8–56.9 ppm) and O—CH$_2$—CH$_3$

(18.9 ppm), appeared in the spectrum of S1 because of hydrolysis of the APS with water and the generation of silanol-containing species through release of ethanol.[33] Also, the $^{13}$C resonances of partially hydrolyzed or oligomerized APS, namely, Si—CH$_2$— at 9–12 ppm and Si—CH$_2$—CH$_2$— at 21.0–22.5 ppm,[33] were observed in the spectrum of S1. However, no signals of Si—CH$_2$—CH$_2$—CH$_2$—NH$_2$ ($\sim$45 ppm) due to hydrolyzed or condensed APS were found. Likewise, the sharp peaks of pure silane close to the shift regions of the partially hydrolyzed or oligomerized silane were not detected in the spectrum, indicating complete hydrolysis of APS. The formation of the silane networks was also observed as increased viscosity of the modified solution (see previous discussion).

The lowering of pH followed by the addition of APS changed the structures of resins PS2 and PS3 compared with references R2 and R3. Ortho–ortho methylene bridges, seldom found in resol resins, were observed in the spectra of PS2 (Fig. 2) and PS3. The formation of these bridges was probably due to the lower pH, which produced structures common for novolac resins condensed under acidic conditions.[2] The addition of silane, which yielded signals of free ethanol and shift areas of hydrolyzed and condensed APS, was also evident in the spectra of PS2 and PS3. In addition, $^{13}$C signals of formic acid resulting from the pH adjustment of the resin solutions were found at 169 ppm.

Neutral pH slows down the self-condensation reactions of silanol groups formed in the hydrolysis
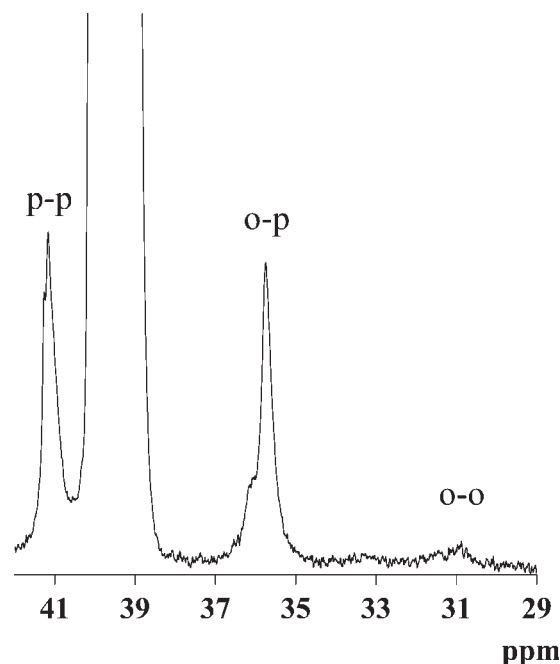


**Figure 2** $^{13}$C resonances of para–para (p–p), ortho–para (o–p), and ortho–ortho (o–o) methylene bridges in the NMR spectrum of PS2.

reactions.[8] However, comparison of the signals and signal areas of silane resin S1 and pH-modified resins PS2 and PS3 revealed no significant differences in the silane-based $^{13}$C resonances of these spectra. Additionally, the $^{13}$C resonance areas of partially hydrolyzed and oligomerized silane were rather broad and overlapped, which complicated the determination of the relative amounts of these structures.

## Effect of modifications and storage on color of liquid resins

The effects of the resin modifications and storage on the color of the aqueous resin solutions were determined by the transmittance method of UV–vis spectroscopy. The $L^*$, $a^*$, and $b^*$ color coordinates (Table III) in the wavelength area of 380–780 nm were calculated according to the CIE $L^*a^*b^*$ color space. Transmittance spectra were not measured for the R1 and S1 solutions due to some opacity in S1.

Color measurements were made on days 0 and 6 for all resins except P2 and PS2. The first measurement of P2 and PS2 was made 1 day later due to the phase separation. At the beginning of storage, references R2 and R3 were yellowish solutions with some green color shades. The color coordinates of R2 and R3 differed at the end of the experiment (after 6 days); both resins darkened, but R2 also turned more reddish. Comparison of the color change values of R2 ($\Delta E = 69.3$) and R3 ($\Delta E = 22.6$) suggested that the evaporation of water after the synthesis was an effective way to slow down the discoloration of resol solutions.

The lowering of pH and subsequent separation of phases yielded very light colored, yellowish liquid resins P2 and PS2, which did not turn red during 6 days. The $L^*$ values of P2 and PS2 were high, over 80, showing the significant effect of pH on the color formation of the resol solutions. In general, the slight decreases in the $L^*$ coordinates and increases in the $a^*$ and $b^*$ coordinates of P2 and PS2 between days 1 and 6 indicated darkening, as in reference R2, but the color changes of P2 ($\Delta E = 10.3$) and PS2 ($\Delta E = 5.6$) were substantially less than with R2 ($\Delta E = 69.3$). Comparison of
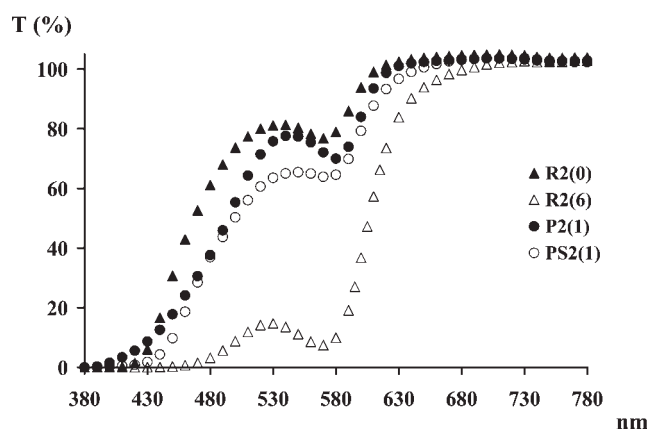


**Figure 3** UV–vis transmittance spectra (T (%), transmittance in percents) of reference resin R2 recorded 0 [R2(0)] and 6 days [R2(6)] after preparation and resins P2 [P2(1)] and PS2 [PS2(1)] recorded 1 day after modification.

the $b^*$ values of solutions P2 and PS2 showed that the addition of silane in PS2 slightly increased the yellow shade, probably due to the pale color of pure APS.

Resins P3 and PS3, which were prepared without phase separation, were not as light in color as P2 and PS2, but the changes over the 6 days were minor ($\Delta E$'s = 2.8 and 4.2 for P3 and PS3, respectively). The silane modification in PS3 increased the lightness [$L^* = 71.8$ (0) and $L^* = 68.5$ (6)] relative to P3 [$L^* = 60.9$ (0) and $L^* = 60.5$ (6)] and, in addition, made the solution more yellow, as was also observed in the comparison of resins P2 and PS2.

Figure 3 presents the UV–vis spectra of resins R2, P2, and PS2. The effect of storage on the color of reference resin R2 was clearly observed in the comparison of the spectra of R2 recorded after 0 days [R2(0)] and 6 days [R2(6)]. The strong absorption of R2(6) in the wavelength area of 430–580 nm, especially at 490–560 nm (bluish green color), increased the perception of the red color in the solutions and gave a high $a^*$ coordinate in the second color analysis. P2 and PS2 were slightly darker than R2 at the first measurement [P2(1) and PS2(1)], but they exhibited considerably less color change ($\Delta E$, Table III) between the first and second measurements, which demonstrated the advantageous effect of pH adjustment and phase separation on the color of the resin solutions.

In this study, the decrease in the transmittance of the unmodified resin solutions during storage was observed particularly at 560–570 nm, and the redness of the solutions was increased. This could have indicated an increase in the amount of phenolphthalein-type chromophores, perhaps formed via oxidation or radical mechanisms. The absorption spectrum of alkaline phenolphthalein solution in the visible region has been observed to show a single absorption maximum at 552.8 nm.[35]

**TABLE III**
**Color Coordinates and $\Delta E$'s for Resin Solutions Measured at 0 or 1 days and Again 6 Days After Resin Preparation**

| Resin | Day | Color coordinate | | | Day | Color coordinate | | | $\Delta E$ |
| | | $L^*$ | $a^*$ | $b^*$ | | $L^*$ | $a^*$ | $b^*$ | |
|---|---|---|---|---|---|---|---|---|---|
| R2 | 0 | 92.0 | −5.9 | 45.8 | 6 | 52.3 | 46.1 | 68.7 | 69.3 |
| P2 | 1 | 91.5 | −5.9 | 50.0 | 6 | 88.5 | −4.5 | 59.8 | 10.3 |
| PS2 | 1 | 85.0 | −1.2 | 62.3 | 6 | 82.0 | 2.6 | 65.1 | 5.6 |
| R3 | 0 | 74.9 | −3.7 | 47.3 | 6 | 59.4 | 6.9 | 59.9 | 22.6 |
| P3 | 0 | 60.9 | 1.5 | 39.6 | 6 | 60.5 | 1.2 | 42.4 | 2.8 |
| PS3 | 0 | 71.8 | 1.6 | 57.3 | 6 | 68.5 | 4.0 | 56.4 | 4.2 |

| Coating | Day | Color coordinate | | | Day | Color coordinate | | | $\Delta E$ |
|---|---|---|---|---|---|---|---|---|---|
| | | $L^*$ | $a^*$ | $b^*$ | | $L^*$ | $a^*$ | $b^*$ | |
| CR1 | 1 | 64.8 | 6.1 | 17.1 | — | — | — | — | — |
| CS1 | 1 | 66.2 | 4.3 | 23.6 | — | — | — | — | — |
| CR2 | 1 | 63.7 | 6.6 | 16.4 | 7 | 63.0 | 6.5 | 17.1 | 1.0 |
| CP2 | 1 | 72.5 | 5.3 | 23.3 | 7 | 77.4 | 2.9 | 18.0 | 7.6 |
| CPS2 | 1 | 74.4 | 2.7 | 26.4 | 7 | 76.7 | 2.1 | 21.2 | 5.7 |
| CR3 | 1 | 59.9 | 8.8 | 13.3 | 7 | 59.0 | 8.6 | 27.3 | 14.0 |
| CP3 | 1 | 66.2 | 7.0 | 16.0 | 7 | 68.8 | 5.3 | 14.5 | 3.4 |
| CPS3 | 1 | 65.2 | 6.6 | 20.7 | 7 | 67.6 | 5.3 | 17.8 | 4.0 |

## Effects of the modification and storage of resin solutions on the color of the resin coatings

Resin coatings were prepared to demonstrate the effects of modifications and storage of the resin solutions on the color of the corresponding cured resins. The color coordinates for the nontransparent coatings were determined from the reflectance spectra of the samples in the wavelength area of 380–780 nm. The first coatings were made 1 day after resin preparation, and second coatings for resins R2, R3, P2, PS2, P3, and PS3 were prepared 7 days after resin preparation. Table IV shows the results of colorimetric analyses of the coatings of the reference (CR1–CR3) and modified resins (CS1, CP2, CPS2, CP3, and CPS3).

The silane modification affected the color formation of coating CS1, slightly increasing the lightness ($L^*$) and yellow ($b^*$) coordinates but decreasing the redness ($a^*$) compared with reference coating CR1.

The darkening of reference solution R2 between days 1 and 7 was reflected only slightly in the $L^*$ coordinates of the corresponding CR2 coatings. In particular, the intense increase in redness of the R2 solution during storage was not seen so strongly in the $a^*$ values of CR2. In addition, $\Delta E$ in the CR2(1) and CR2(7) coatings was only 1.0. The decrease in pH of the resin solution and resultant phase separation was reflected as increased $L^*$ values of coatings CP2 and CPS2 relative to the reference coating CR2. The lightest and least red coatings of the study were CP2 and CPS2 prepared from the pH-modified and phase-separated resins. The addition of silane shifted the color of CPS2 slightly toward yellow (larger $b^*$) compared with CP2. An unexpected trend in the color formation of coatings CP2 and CPS2 was the slightly increased lightness and decreased redness and yellowness of the coatings prepared at 7 days despite the minor darkening of the corresponding resin solutions during storage. The color coordinates of CP2(1) were 72.5 ($L^*$), 5.3 ($a^*$), and 23.3 ($b^*$), whereas those of CP2(7) were 77.4 ($L^*$), 2.9 ($a^*$), and 18.0 ($b^*$).

The CR3 coatings prepared from the R3 solution with high solids content were the darkest reference coatings and also showed the greatest $\Delta E$. The pH modification in solutions P3 and PS3 yielded lighter coatings, CP3 and CPS3, respectively, and minor $\Delta E$'s relative to the two coatings of reference solution R3. The slight lightening of coatings CP3 and CPS3 was contrary to the color formation of the corresponding resin solutions P3 and PS3, respectively, which darkened slightly with storage.

Lowering the pH of a resin solution was an effective method for lightening the color of the cured resin. This was observed in the color comparison of reference coatings CR2 and CR3 with pH-modified coatings CP2, CPS2, CP3, and CPS3. The color analyses of resin coatings CS1, CPS2, and CPS3 prepared from the silane-modified solutions showed the addition of silane to effectively shift the color of the coatings toward yellow (larger $b^*$ values). Such a shift would improve the color compatibility of the cured resin with a variety of substrates. The slightly increased lightness and decreased redness and yellowness of coatings CP2(7), CP2S(7), CP3(7), and CPS3(7) relative to coatings CP2(1), CP2S(1), CP3(1), and CPS3(1), despite darkening of the corresponding resin solutions, was due to further reactions in the resin solutions.

The reflectance spectra of reference coating CR2 and the corresponding modified coatings CP2 and CPS2 are shown in Figure 4. The intense discoloration of reference solution R2 during storage appeared only as a slight darkening in the coatings prepared after 1 [CR2(1)] and 7 [CR2(7)] days of storage. The lightening of pH-modified coatings CP2 and CPS2 was contrary to the color formation of the corresponding solutions P2 and PS2 during storage. The lightening could be seen in a comparison of spectra of CP2(1) with CP2(7) and CPS2(1) with CPS2(7),
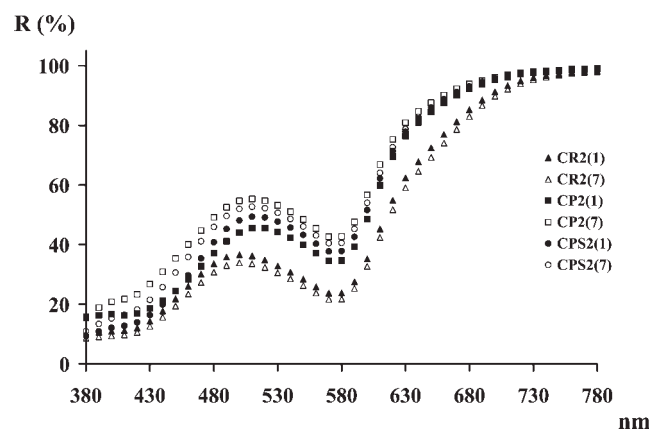


**Figure 4** UV–vis reflectance spectra (R (%), reflectance in percents) of reference coating CR2 and modified coatings CP2 and CPS2 prepared from the corresponding resin solutions 1 and 7 days after resin preparation.

TABLE V
Results of DSC Analysis of the Resin Solutions Carried Out 3, 7, or 15 Days After Resin Preparation

| Resin | Day | $\Delta H$ (J/g) | $T_1$ (°C) | $T_2$ (°C) | Onset (°C) | End (°C) | Day | $\Delta H$ (J/g) | $T_1$ (°C) | $T_2$ (°C) | Onset (°C) | End (°C) |
|-------|-----|------|------|------|------|------|-----|------|------|------|------|------|
| R1 | 3 | −90 | 158 | — | 125 | 200 | — | — | — | — | — | — |
| S1 | 3 | −112 | 155 | — | 121 | 195 | — | — | — | — | — | — |
| R2 | 7 | −165 | 147 | — | 114 | 181 | 15 | −154 | 149 | — | 119 | 189 |
| P2 | 7 | −129 | 160 | — | 118 | 193 | 15 | −124 | 161 | — | 128 | 192 |
| PS2 | 7 | −123 | 160 | — | 129 | 198 | 15 | −137 | 160 | — | 128 | 198 |
| R3 | 7 | −234 | 146 | 190 | 115 | 203 | 15 | −173 | 148 | 189 | 117 | 205 |
| P3 | 7 | −158 | 162 | — | 128 | 211 | 15 | −171 | 160 | — | 126 | 208 |
| PS3 | 7 | −165 | 157 | — | 129 | 200 | 15 | −156 | 158 | — | 128 | 201 |

which were prepared from the corresponding P2 and PS2 resins after 1 and 7 days of resin storage.

## Effect of the modifications and storage on the resin reactivities

DSC analyses provided information about the behavior of the resin systems during the exothermic curing processes. The number of curing signals observed in the DSC curves of resols is a sum of many factors, including the pH of the solution,[7] F/P[24] and NaOH/P[36,37] molar ratios, the amount of free formaldehyde,[38] and the additives[6] present. In this study the shapes of the DSC signals were affected by the urea additions and the pH of the resin solutions.

Two well-separated curing signals appeared in the DSC curves of reference resin R3 [the first curing signal ($T_1$) at 146–148°C and the second curing signal ($T_2$) at 189–190°C; Table V]. $T_1$ reportedly resulted from the formation of methylene bridges in condensation reactions of methylol groups with free phenol and other phenolic components and in reactions of two methylol groups forming dibenzyl ether bridges.[6,24,37] $T_2$ was attributed to the release of formaldehyde in the condensation of a dibenzyl ether bridge to give a diphenyl methylene bridge or to other resin reactions.[24,37] A well-separated $T_2$ is more likely to appear when the alkalinity (pH) of the system is low[24] or when the F/P molar ratio is high (2.15–2.30).[37]

The second curing peak, in the high temperature range (190–200°C), was not observed in the curves of the reference resins R1 and R2 or the silane resin S1; rather, a second exotherm overlapped the first ($T_1$). It was assumed that the source was reactions of urea-based compounds,[6] even though the signal was not present in the thermograms of reference R3 or the pH-modified resins P2, PS2, P3 and PS3, which also had urea added to the solutions. The typical curve shape of resins P2, PS2, P3, and PS3 was one distinct signal without the shoulders of other exotherms.

The effect of urea on the number and shape of the curing peaks was investigated in a DSC run where reference R1 with 3.6 wt % of free formaldehyde was cured without the addition of urea. Two well-separated curing peaks, at about 150 and 214°C, similar to

those of reference R3, appeared. On the grounds of the DSC analyses, it seemed likely that the capture of free formaldehyde by urea played an important role in the curing behavior of the resol resins. Probably the binding of free formaldehyde with urea produced the urea-based curing signals overlapping the first exotherm $T_1$. Reference R3 was an exception among the reference resins because there was little free formaldehyde to be captured by urea and give rise to urea-based curing signals. The production of two distinct signals in the curing of R3 could rather be considered typical for resins with low pH (pH = 9.1) and high F/P molar ratios (F/P = 2.6).[24,37] In a study of the curing of model compounds of methylolphenols with different concentrations of NaOH, Tonge et al.[36] found that the number of curing signals in the DSC curves depended on the NaOH/methylolphenol molar ratio of the system. Thus, only one curing signal was observed when no NaOH catalyst was added. In the case of resins P2, PS2, P3, and PS3, the effect of NaOH in the curing stage was eliminated by the neutralization of the resins, and so, presumably, only one curing signal appeared.

The results of the DSC analyses are presented in Table V. The DSC measurements of R1 and S1 were performed after 3 days of storage. The result of the curing experiment of silane-modified resin S1 indicated complex interactions between the components of the resol solutions, which made interpretation of data difficult. Reference R1 was less reactive than S1, which yielded a lower absolute reaction heat value ($\Delta H$) and a higher curing peak temperature ($T_1$). Also, the onset and end temperatures of the curing of R1 were higher than for the modified resin S1.

The first DSC curves for references R2–R3 and modified resins P2, PS2, P3, and PS3 were recorded after 7 days of storage, and the second curves were recorded 8 days later (i.e., at 15 days). The high reactivity of R3, mainly due to the high solids content, decreased substantially during storage, whereas the reaction heat of R2 stayed at the same level throughout. In the first measurement, the absolute value of the reaction heat of R2 was 69 J/g lower than that of R3, but the difference was only 19 J/g at the end of the period (15 days). This trend was probably

affected by the high viscosity and solids content of R3, which promoted reactions between the resin components and decreased the reactivity of the solution. The temperatures of the curing signals and the onset and end temperatures for R2 and R3 increased between days 7 and 15. The pH modifications clearly reduced the reactivities of resins P2, PS2, P3, and PS3 by decreasing the absolute values of DH and raising the temperatures of the $T_1$'s approximately 10°C above the temperatures of the corresponding reference resins R2 and R3. With the error limits of the DSC analyses taken into account, the reaction heats and $T_1$'s of resins P2, PS2, P3, and PS3 remained nearly constant during storage.

## CONCLUSIONS

Silane and pH modifications effected changes in the physical properties of the resol resins during storage. The addition of silane increased the viscosity of the resin solution due to hydrolysis and the subsequent self-condensation reactions of silane to yield a polymerized product with siloxane bridges. The lowering of the pH increased the viscosity of the resin solutions because of the reduced solubility in water. NMR spectra of the pH-modified resins unexpectedly revealed minor amounts of ortho–ortho methylene bridges. A disadvantage of the lower pH was the reduced reactivity in the curing stage. Light-colored resin solutions and coatings, almost entirely lacking the undesired red component, were obtained by the lowering of the pH, with subsequent separation of phases. The color of the pH-modified solutions remained light during storage. The yellow shades of the coatings were intensified through the addition of silane. Color analyses of the reference and modified resins in the liquid and cured states showed that the discoloration process was complex and that the effects of one particular factor on the color formation of the resins were difficult to determine from the final result. The results of the study nevertheless indicated that resol resins yielding light colored coatings and adhesive joints could be produced by lowering the pH of the resin solution. Moreover, if silane is required to improve the coupling properties of the resols in specific applications, it will not darken the cured resins but rather increase the yellowness, and enhance the color compatibility, for instance, with wood material.

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