

Effect of F/P and OH/P Molar Ratios and Condensation Viscosity on the Structure of Phenol-Formaldehyde Resol Resins for Overlays—A Statistical Study

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ABSTRACT: A two-level full factorial experimental design with three variables, formaldehyde-to-phenol (F/P) molar ratio, hydroxyl-to-phenol (OH/P) molar ratio, and condensation viscosity was implemented to determine the effect of the variables on the structure of phenol-formaldehyde resol resins for paper overlay impregnation. Ten resins were prepared with F/P molar ratios between 1.9 and 2.3, OH/P molar ratios between 0.09 and 0.13, and condensation viscosities between 60 and 180 mPa s. The effect of these three independent variables on the chemical structure was

analyzed by ¹³C-NMR spectroscopy, on the molecular weight distribution by gel permeation chromatography, and on the reactivity by differential scanning calorimetry. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2942–2948, 2004

Key words: resins; ¹³C-NMR; differential scanning calorimetry (DSC); gel permeation chromatography (GPC); experimental design; phenol formaldehyde (PF) resins; paper overlays

INTRODUCTION

Phenol-formaldehyde (PF) resins are polycondensation products of the reaction of phenol with formaldehyde. When alkali catalyst, for example, sodium hydroxide (NaOH), is present, resol resins are produced. Phenolic resol resins are utilized in a variety of applications, such as impregnation and adhesion.^{1,2} The final structure, properties, and performance of the resins produced depend on the condensation parameters. Formaldehyde-to-phenol (F/P) and hydroxyl-to-phenol (OH/P) molar ratios as well as condensation viscosity are the most important parameters in synthesis of the resols. The effect of these parameters on the structure and reactivity of the resins as well as on the reaction mechanisms and kinetics has been researched.^{1–23}

In this study, the effects of F/P molar ratio, OH/P molar ratio, and condensation viscosity on the chemical structures, molecular weights, and reactivity of the phenol-formaldehyde resol resins were studied by ¹³C-NMR spectroscopy,^{1–9,20–44} gel permeation chromatography,^{1–7,10,43–49} and differential scanning calorimetry^{1–4,11,19,20,44–54} utilizing a two-level full factorial experimental design.

EXPERIMENTAL

Experimental design

A two-level full factorial experimental design with three independent variables was generated with one center point, which was repeated. In this design, F/P molar ratio, OH/P molar ratio, and condensation viscosity were defined as independent variables, all receiving two values, a low and a high value. Presenting these three variables in a rectangular coordinate system, a cube-like model is formed, with eight corners, which represent eight of the studied resins (Fig. 1). A center point is added to the design to improve accuracy of the design and this center point is repeated to better estimate the error of the design. The eight corners and one center point (repeated twice) provided a total of 10 resins (Table I). All 10 resins were analyzed with ¹³C-NMR (Bruker AMX-400, Ettlingen, Germany), GPC (Waters, Milford, MA), and DSC (PerkinElmer, Norwalk, CT), and all the results were treated as dependent variables and analyzed with analysis of variance (ANOVA) at the 0.01 significance level. All the analysis results were analyzed by using STATISTICA for Windows software, version 5 (Statsoft, Tulsa, OK).

Resin preparation

Formaldehyde, produced by Dynoresin Oy (Kitee, Finland) from methanol, served as a formalin solution, containing 45% formaldehyde, water, and some meth-

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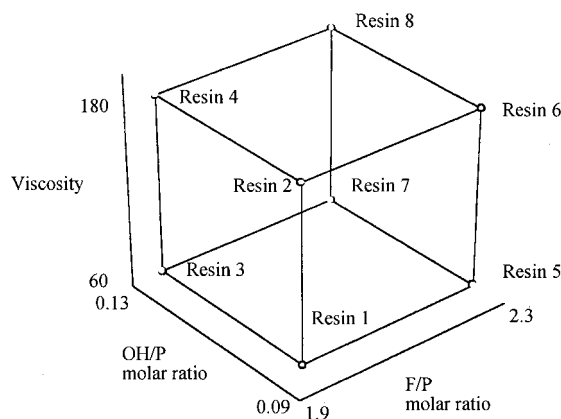


Figure 1 Two-level experimental design of 10 PF resins.

anol. Another starting material, phenol, was purchased from J. T. Baker (Deventer, Holland). All 10 PF resins were produced with NaOH catalyst (produced by Merck, Darmstadt, Germany) and condensed at the 80°C temperature with varying F/P molar ratios, OH/P molar ratios, and condensation viscosities (Table I). The resins were stored frozen at -18°C until analysis.

NMR experiments

Quantitative ^{13}C -NMR spectra of the studied resins were recorded with a Bruker AMX-400 spectrometer at 20°C, observing ^{13}C at 100.623 MHz and using an inverse gated ^1H -decoupling technique. All the spectra of resins were run with a 90° pulse of 11.5 μs , a 120-s pulse delay, 600 scans, and a 20-h acquisition time. Deuterated dimethylsulfoxide (DMSO- d_6 , 99.8% atom %, Riedel-de-Haën, Seelze, Germany) was used as a solvent. The ^{13}C signals of resins were referenced to the central resonance line of DMSO with a δ value of 39.5 ppm.

GPC experiments

The GPC measurements were made with a chromatography system equipped with a Waters 510 pump, a Rheodyne loop injector, and three Styragel columns (1000, 500, and 100 Å, 30 × 0.7 cm) in series. The columns were calibrated with three polystyrene standards ($M_n = 1300, 5460, 30,300$), one dinonylphtalate standard ($M_n = 418$), and one 1-phenylhexane standard ($M_n = 162$). Resin samples were diluted to 20 mg/mL with tetrahydrofuran, which was also used as an eluant at a flow rate of 1.0 mL/min. Separated compounds were detected by means of a Waters 440 UV detector operating at 254 nm. All the resins were measured at room temperature. Retention times and the shapes of the chromatograms were analyzed with Turbochrom navigator 4.1 software (P.E. Division, San

Jose, CA), and molecular weights and polydispersities were calculated with TC*SEC software (P.E. Division).

DSC experiments

DSC measurements were made with a PerkinElmer DSC 7 instrument and 7 Series Unix thermal analysis software (Perkin-Elmer). 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, and the nitrogen gas flow was 20 mL/min.

RESULTS AND DISCUSSION

Studied resins

The independent variables, F/P molar ratio, OH/P molar ratio, and condensation viscosity, were given a high and a low value. By using all possible combinations, eight resin formulations were generated. These eight resins were condensed at the 80°C temperature and represent the corners of the cube (Fig. 1). A center point was added in the design and the resin corresponding to the center point was prepared twice. The center point resins 9 and 10 (Table I) were also condensed at the 80°C temperature.

All 10 resins were analyzed with ^{13}C -NMR for structural information, with GPC for molecular weights and with DSC for resin reactivity. Every analysis result was treated as a dependent result in the statistical study. Direct ^{13}C -NMR integration results for each structural group were defined (Table II), and calculated NMR results (Table III) demonstrated free phenol as a percentage of total phenolic units and *o-p'*/*p-p'* bridges ratios, methylene bridges ratios to methylols, and *o*-methylols ratios to *p*-methylols. The molecular weight average (M_w), the molecular number average (M_n), and polydispersity of the prepared resins are presented (Table IV). The delta H values and

TABLE I
Properties of 10 PF Resins Studied

| PF resin | F/P molar ratio | OH/P molar ratio | Viscosity (mPa s) |
|----------|-----------------|------------------|-------------------|
| 1 | 1.9 | 0.09 | 60 |
| 2 | 1.9 | 0.09 | 180 |
| 3 | 1.9 | 0.13 | 60 |
| 4 | 1.9 | 0.13 | 180 |
| 5 | 2.3 | 0.09 | 60 |
| 6 | 2.3 | 0.09 | 180 |
| 7 | 2.3 | 0.13 | 60 |
| 8 | 2.3 | 0.13 | 180 |
| 9 | 2.1 | 0.11 | 120 |
| 10 | 2.1 | 0.11 | 120 |

TABLE II
NMR Results of the 10 Analyzed PF Resins

| PF resin | Aromatic carbons | | | | Methylol groups | | Methylene bridges | | Formalin hemiacetals | Formalin oxymethylene | Phenolic hemiformals |
|----------|------------------|-------------------|------------------|-------|-----------------|-------------|-------------------|-------------|----------------------|-----------------------|----------------------|
| | Phenoxy | Free <i>ortho</i> | Free <i>para</i> | Other | <i>Ortho</i> | <i>Para</i> | <i>o-p'</i> | <i>p-p'</i> | | | |
| 1 | 1.000 | 0.554 | 0.101 | 4.484 | 1.060 | 0.200 | 0.260 | 0.307 | 0.013 | 0.034 | 0.003 |
| 2 | 1.000 | 0.468 | 0.069 | 4.476 | 1.004 | 0.145 | 0.321 | 0.344 | 0.012 | 0.030 | 0.002 |
| 3 | 1.000 | 0.575 | 0.105 | 4.718 | 1.165 | 0.199 | 0.259 | 0.490 | 0.007 | 0.020 | 0.000 |
| 4 | 1.000 | 0.475 | 0.064 | 4.730 | 1.076 | 0.136 | 0.340 | 0.356 | 0.008 | 0.022 | 0.000 |
| 5 | 1.000 | 0.349 | 0.044 | 4.854 | 1.242 | 0.259 | 0.268 | 0.409 | 0.037 | 0.127 | 0.038 |
| 6 | 1.000 | 0.250 | 0.024 | 5.038 | 1.210 | 0.210 | 0.352 | 0.429 | 0.042 | 0.128 | 0.022 |
| 7 | 1.000 | 0.336 | 0.043 | 4.760 | 1.313 | 0.300 | 0.210 | 0.412 | 0.029 | 0.098 | 0.025 |
| 8 | 1.000 | 0.206 | 0.013 | 4.903 | 1.249 | 0.197 | 0.328 | 0.401 | 0.029 | 0.105 | 0.000 |
| 9 | 1.000 | 0.381 | 0.044 | 4.901 | 1.231 | 0.179 | 0.309 | 0.467 | 0.020 | 0.060 | 0.000 |
| 10 | 1.000 | 0.359 | 0.045 | 4.726 | 1.167 | 0.178 | 0.293 | 0.359 | 0.018 | 0.058 | 0.005 |

The integral values are related to the value of 1.00 of phenoxy carbon.

observed peak temperatures for both exotherm signals are listed as well (Table V).

Statistical analysis results

All dependent variables were analyzed by utilizing ANOVA and the multiple regression model. The ANOVA *F*-test indicates the dependence of the dependent variables with the independent variables, *P* level indicates the statistical significance of the correlation, and *t* values indicate the strength of the correlation between dependent variable and independent variables (Table VI).

The *F*-test results for relations of the amount of *para* methylol phenols with the F/P molar ratio and the condensation viscosity are high, 27.162 and 24.207, respectively, indicating a clear dependence of *para* methylol phenols on the F/P molar ratio and the condensation viscosity. However, for the OH/P molar ratio, the *F*-test result is very low, 0.108. It can also be seen that *P* level values for the relation between the amount of *para* methylol phenols and both F/P molar

ratio and condensation viscosity are under the set *P* level of 0.01, while for the OH/P molar ratio, the *P* value is very high, 0.754 (Table VI). This data indicate that the relations of dependent variable *para* methylol phenols with independent variables F/P molar ratio and condensation viscosity are statistically significant at the 0.01 significance level, while the relation of dependent variable *para* methylol phenols and independent variable OH/P molar ratio is not statistically significant. The same relationship can be seen in Figure 2, where the independent variables are shown in a pareto chart with a significance test (two-tailed *t* test) done with six degrees of freedom.

The effect of independent variables on the resin structure

All 10 resins were impregnation resins with a relatively low OH/P molar ratio and a low condensation viscosity. The resulting ¹³C-NMR spectra all resembled those of low molecular weight resol resins or impregnation resins.³ NMR signals due to different

TABLE III
Calculated NMR Results of 10 PF Resins

| PF resin | Free phenol % ^a | Methylols <i>ortho/para</i> | Methylene bridges <i>o-p/p-p'</i> | Methylene bridges/methylols |
|----------|----------------------------|-----------------------------|-----------------------------------|-----------------------------|
| 1 | 6.09 | 5.30 | 0.85 | 0.45 |
| 2 | 4.59 | 6.92 | 0.93 | 0.58 |
| 3 | 6.29 | 5.85 | 0.53 | 0.55 |
| 4 | 5.23 | 7.91 | 0.96 | 0.57 |
| 5 | 2.58 | 4.80 | 0.66 | 0.45 |
| 6 | 0.98 | 5.76 | 0.82 | 0.55 |
| 7 | 2.65 | 4.38 | 0.51 | 0.39 |
| 8 | 1.26 | 6.34 | 0.82 | 0.50 |
| 9 | 2.65 | 6.88 | 0.66 | 0.55 |
| 10 | 3.02 | 6.56 | 0.82 | 0.48 |

^a Percentage from total phenolic units.

TABLE IV
GPC Results of the 10 Analyzed PF Resins

| PF resin | M_w (g/mol) | M_n (g/mol) | Polydispersity |
|----------|------------------|------------------|----------------|
| 1 | 1027 | 609 | 1.685 |
| 2 | 1494 | 760 | 1.967 |
| 3 | 950 | 610 | 1.557 |
| 4 | 1424 | 820 | 1.736 |
| 5 | 1072 | 746 | 1.436 |
| 6 | 1562 | 979 | 1.595 |
| 7 | 938 | 696 | 1.348 |
| 8 | 1388 | 931 | 1.491 |
| 9 | 1299 | 833 | 1.558 |
| 10 | 1264 | 780 | 1.620 |

structural groups were assigned³ and quantitatively determined (Table II).

Both F/P molar ratio and condensation viscosity had a decreasing effect on the free *ortho* and *para* phenols, causing the amount of free positions to decrease as the condensation viscosity and F/P molar ratio increase (Table VI). OH/P had no statistically significant effect.

F/P molar ratio had an increasing effect on *ortho* and *para* methylol phenols. The higher the F/P molar ratio, the higher was the amount of *ortho* and *para* methylol phenols. The increasing condensation viscosity had a decreasing effect on *para* methylol phenols.

The ratio of *ortho* methylols to *para* methylol groups was calculated and analyzed. Condensation viscosity had an increasing effect indicating that more *ortho* methylol phenols are formed as the reaction proceeds. OH/P molar ratio did not have a statistically significant effect, which is an interesting detail. These results suggest that the amount of catalyst, at these levels, does not have a direct effect to either *ortho* or *para* methylol positions.

Only condensation viscosity had a statistically significant effect on *o-p'* methylene bridges, with the higher the condensation viscosity, the higher the amount of *o-p'* bridges. None of the variables had a significant effect on *p-p'* methylene bridges. This response is mainly caused by the difficulty in the integration of the *p-p'* methylene NMR signal, caused by partial overlap of DMSO solvent signal with the *p-p'* bridge signal.

The ratio of *ortho-para* bridges to *para-para* bridges was also calculated and analyzed. Condensation viscosity had an increasing effect on the ratio of *o-p'* bridges to *p-p'*, indicating that more *ortho-para* bridges are formed as the reaction proceeds. F/P molar ratio and OH/P did not have statistically significant effects. These results suggest that neither molar ratios at these levels had directing effects on the methylene bridge ratio.

The amount of phenolic hemiformal groups were not affected by any of the three independent variables.

At the same time, the F/P molar ratio had an increasing effect on formalin hemiacetal as well as on the formalin oxymethylene. When more formaldehyde is present, more formalin hemiacetals and oxymethylenes are formed. The higher the OH/P molar ratio is, the lower the amount of the hemiacetals.

The effect of all three independent variables was evaluated on free phenol determinations. It was found that F/P molar ratio and condensation viscosity have a decreasing effect on the amount of free phenol, F/P molar ratio having a stronger effect. The higher the amount of formaldehyde or the higher the degree of condensation, the lower the amount of free phenol in the resin. OH/P had no statistically significant effect in the studied resin design range.

From the integrated NMR results, the ratio of methylene bridges to methylol groups was calculated (Table III). In the studied resins, none of the independent variables (F/P and OH/P molar ratio, or condensation viscosity) had a statistically significant effect on this ratio.

The effect of independent variables on the resin molecular weights

The condensation viscosity had an increasing effect on the weight-average molecular weight (M_w), suggesting that M_w is very dependent on the degree of condensation (Table IV). The OH/P molar ratio had a decreasing effect, suggesting that the higher the OH/P molar ratio, the lower the M_w . F/P molar ratio did not have an effect on M_w .

Condensation viscosity had a similar, but not as strong, increasing effect on M_n . The F/P molar ratio had an increasing effect, indicating that the higher the amount of formaldehyde, the higher the M_n . The OH/P molar ratio did not have an effect on M_n . All three independent variables had an effect on polydispersity, M_w/M_n . Both molar ratios had a decreasing effect, while condensation viscosity had an increasing effect.

TABLE V
DSC Results of the 10 Analyzed PF Resins

| PF resin | Curing enthalpy delta H (J/g) | Curing temperatures | |
|----------|----------------------------------|---------------------|------------|
| | | T_1 (°C) | T_2 (°C) |
| 1 | -202.83 | 150.7 | 164.0 |
| 2 | -190.08 | 150.0 | 165.0 |
| 3 | -239.12 | 149.0 | 159.3 |
| 4 | -197.98 | 149.0 | 158.7 |
| 5 | -153.80 | 144.3 | 186.0 |
| 6 | -90.40 | 145.3 | 184.7 |
| 7 | -234.09 | 142.3 | 181.0 |
| 8 | -155.05 | 143.3 | 178.0 |
| 9 | -188.48 | 146.2 | 168.7 |
| 10 | -194.60 | 145.7 | 169.0 |

TABLE VI
F-test Results, P Level Values, and t Values for All Variables of 10 PF resins

| | Aromatic carbons | | Methylol groups | | Methylene bridges | | Formalin hemiacetals | Formalin oxymethylene | Phenolic hemiformals | Free phenol |
|------------------------|-------------------|------------------|-----------------|-------------|-------------------|-------------|----------------------|-----------------------|----------------------|-------------|
| | Free <i>ortho</i> | Free <i>para</i> | <i>Ortho</i> | <i>Para</i> | <i>o-p</i> | <i>p-p'</i> | | | | |
| F-test results | | | | | | | | | | |
| F/P Molar ratio | 199.059 | 83.898 | 71.124 | 27.162 | 0.155 | 0.829 | 163.635 | 260.595 | 10.256 | 116.028 |
| OH/P molar ratio | 0.193 | 0.307 | 11.654 | 0.108 | 1.313 | 1.011 | 16.713 | 11.517 | 2.564 | 0.757 |
| Condensation viscosity | 39.553 | 27.459 | 8.218 | 24.207 | 37.936 | 0.271 | 0.435 | 0.076 | 2.827 | 16.472 |
| P level values | | | | | | | | | | |
| F/P Molar ratio | 0.000 | 0.000 | 0.000 | 0.002 | 0.707 | 0.398 | 0.000 | 0.000 | 0.019 | 0.000 |
| OH/P molar ratio | 0.676 | 0.600 | 0.014 | 0.754 | 0.295 | 0.354 | 0.006 | 0.015 | 0.160 | 0.418 |
| Condensation viscosity | 0.001 | 0.002 | 0.029 | 0.003 | 0.001 | 0.621 | 0.534 | 0.792 | 0.144 | 0.007 |
| t values | | | | | | | | | | |
| F/P Molar ratio | -14.109 | -9.160 | 8.434 | 5.212 | -0.394 | 0.911 | 12.792 | 16.143 | 3.203 | -10.772 |
| OH/P molar ratio | -0.439 | -0.554 | 3.414 | 0.328 | -1.146 | 1.005 | -4.088 | -3.394 | -1.601 | 0.870 |
| Condensation viscosity | -6.289 | -5.240 | -2.867 | -4.920 | 6.159 | -0.520 | 0.659 | 0.275 | -1.681 | -4.059 |

| | Methylene bridges <i>o-p/p-p'</i> | Methylene bridges/methylols | Methylols <i>ortho/para</i> | M_w | M_n | Polydispersity | Curing enthalpy delta H | Curing temperatures | | |
|------------------------|-----------------------------------|-----------------------------|-----------------------------|---------|--------|----------------|-------------------------|---------------------|---------|--|
| | | | | | | | | T_1 | T_2 | |
| F-test results | | | | | | | | | | |
| F/P Molar ratio | 3.207 | 4.563 | 9.798 | 0.386 | 25.116 | 75.208 | 10.947 | 179.481 | 245.075 | |
| OH/P molar ratio | 2.992 | 0.027 | 1.275 | 18.923 | 0.112 | 19.801 | 10.123 | 14.720 | 18.500 | |
| Condensation viscosity | 14.726 | 8.749 | 19.256 | 323.406 | 56.442 | 37.749 | 10.909 | 0.614 | 0.553 | |
| P level values | | | | | | | | | | |
| F/P Molar ratio | 0.124 | 0.077 | 0.020 | 0.557 | 0.002 | 0.000 | 0.016 | 0.000 | 0.000 | |
| OH/P molar ratio | 0.134 | 0.875 | 0.302 | 0.005 | 0.749 | 0.004 | 0.019 | 0.009 | 0.005 | |
| Condensation viscosity | 0.009 | 0.025 | 0.005 | 0.000 | 0.000 | 0.001 | 0.016 | 0.463 | 0.485 | |
| t values | | | | | | | | | | |
| F/P Molar ratio | -1.791 | -2.136 | -3.130 | 0.621 | 5.012 | -8.672 | 3.309 | -13.397 | 15.655 | |
| OH/P molar ratio | -1.730 | -0.164 | 1.129 | -4.350 | -0.335 | -4.450 | -3.182 | -3.837 | -4.301 | |
| Condensation viscosity | 3.837 | 2.958 | 4.388 | 17.983 | 7.513 | 6.144 | 3.303 | 0.783 | -0.744 | |

The effect of independent variables on the resin reactivity

For all 10 resins, DSC curves had two separate signals, which were analyzed for the total curing enthalpy (delta H), and individual curing temperatures (Table V). None of the variables had a statistically significant effect on delta H. The peak value of the first exotherm decreases as F/P or OH/P molar ratio increases. The F/P molar ratio had an increasing effect and the OH/P molar ratio had a decreasing effect on the second exotherm. As the OH/P molar ratio increases, the second exotherm gets closer to the first one. Typically only one wide exotherm is observed for resins with higher alkalinity.²⁰ Condensation viscosity had no statistically significant effect on the two exotherms.

CONCLUSION

The present study proved that experimental design is a very valuable and capable tool for evaluating multiple variables in resin production. All three production variables have a significant effect on both structure and reactivity.

The F/P molar ratio and condensation viscosity were found to have the most frequent effect on structural parameters. Both F/P molar ratio and condensation viscosity had a decreasing effect on free *ortho* and *para* positions. F/P molar ratio showed an increasing effect on both *ortho* and *para* methylol phenols, while condensation viscosity demonstrated a decreasing effect on *para* methylol phenols.

Hemiacetal and oxymethylene groups were dependent on the F/P molar ratio, which had an increasing effect on both groups. Surprisingly *o-p'* bridges were only affected by the condensation viscosity, which had an increasing effect. It was found that the F/P molar ratio and the condensation viscosity showed a decreasing effect on the amount of free phenol, while OH/P demonstrated no statistically significant effect.

The condensation viscosity and the F/P molar ratio were found to have the strongest effect on molecular weight values. The condensation viscosity always had an increasing effect, whereas the OH/P molar ratio had a decreasing effect. The effect of the F/P molar ratio on the molecular weights varied. Both molar ratios had a decreasing effect on polydispersity,

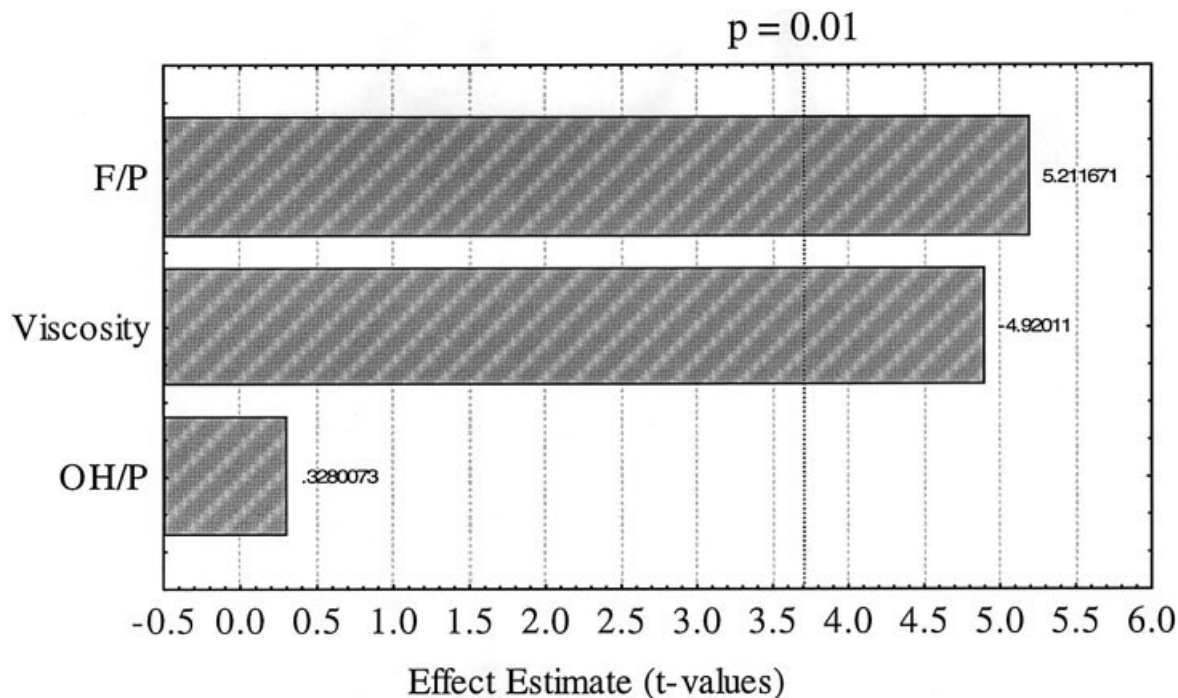


Figure 2 Pareto chart (*t*-values) for the effect of independent variables (F/P, viscosity, OH/P) on the amount of *para* methylol phenol.

M_w/M_n , whereas the condensation viscosity showed an increasing effect.

An increase in the OH/P molar ratio shifts both first and second curing exotherm to the lower value, whereas an increase in the F/P molar ratio shifts the first exotherm to a lower value and a second exotherm to the higher value, separating signals from each other. Condensation viscosity had no effect on the first or second exotherms.

All the studied resins showed two separate exotherms, a result different from the one obtained by Park et al.¹¹ When the studied resins were compared to ones studied by Park et al.,¹¹ three notable differences were observed. In all studied resins, M_w 's are higher than those of Park's resins.¹¹ In addition, the OH/P molar ratios used in this study are considerably lower, resulting in a wider polydispersity in the studied resins. The results could indicate that due to the lower OH/P molar ratio, a wider range of molecules is produced, giving a different kind of thermal behavior. At the same time, as indicated in this study, increasing the OH/P molar ratio brings the second exotherm closer to the first one. Further studies are required to study the phenomenon.

References

- Knop, A.; Scheib, W. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: Berlin, 1979.
- Gardziella, A.; Pilato, L. A.; Knop, A. *Phenolic Resins, Chemistry, Applications, Standardization, Safety and Ecology*, 2nd ed.; Springer-Verlag: Berlin, 2000.
- Holopainen, T.; Alvila, L.; Rainio, J.; Pakkanen, T. T. *J Appl Polym Sci* 1997, 66, 1183.
- King, P. W.; Mitchell, R. H.; Westwood, A. R. *J Appl Polym Sci* 1974, 18, 1117.
- So, S.; Rudin, A. *J Appl Polym Sci* 1990, 41, 205.
- Bouajila, J.; Raffin, G.; Waton, H.; Sanglar, C.; Paise, J. O.; Grenier-Loustalot, M.-F. *Polym & Polym Composites* 2002, 10, 341.
- Kim, M. G.; Nieh, W. L.; Sellers, Jr., T.; Wilson, W. W.; Mays, J. W. *Ind Eng Chem Res* 1992, 31, 973.
- Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P. *Polymer* 1996, 37, 639.
- Lenghaus, K.; Qiao, G. G.; Solomon, D. H. *Polymer* 2001, 42, 3355.
- Haupt, R. A.; Sellers, T., Jr. *Ind Eng Chem Res* 1994, 33, 693.
- Park, B. D.; Kim, Y. S.; So, W. T. *J Appl Polym Sci* 2002, 83, 1415.
- Puglia, D.; Kenny, J. M.; Manfredi, L. B.; Vazquez, A. *Mater Eng* 2001, 12, 55.
- Manfredi, L. B.; Riccardi, C. C.; de la Osa, O.; Vazquez, A. *Polym Int* 2001, 50, 796.
- Manfredi, L. B.; de la Osa, O.; Galego Fernandez, N.; Vazquez, A. *Polymer* 1999, 40, 3867.
- Haupt, R. A.; Sellers, Jr., T. *For Prod J* 1994, 44, 69.
- Kelley, S. S.; Gollob, L.; Wellons, J. D. *Holzforchung* 1986, 40, 303.
- Astarloa Aierbe, G.; Echeverria, J. M.; Martin, M. D.; Etxeberria, A. M.; Mondragon, I. *Polymer* 2000, 41, 6797.
- Pizzi, A.; Stephanou, A. *Holzforchung* 1994, 48, 150.
- Pizzi, A.; Stephanou, A. *Holzforchung* 1994, 48, 35.
- Luuikko, P.; Alvila, L.; Holopainen, T.; Rainio, J.; Pakkanen, T. T. *J Appl Polym Sci* 2001, 82, 258.

21. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1993, 49, 2157.
22. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Leca, J.-P.; Bedel, D. *Polymer* 1994, 35, 3046.
23. Grenier-Loustalot, M.-F.; Larroque, S.; Grande, D.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 1363.
24. Fisher, T. H.; Chao, P.; Upton, C. G.; Day, A. J. *Magn Res Chem* 2002, 40, 747.
25. Fisher, T. H.; Chao, P.; Upton, C. G.; Day, A. J. *Magn Res Chem* 1995, 33, 717.
26. Lenghaus, K.; Qiao, G. G.; Solomon, D. H. *Polymer* 2000, 41, 1973.
27. Luukko, P.; Alvila, L.; Holopainen, T.; Rainio, J.; Pakkanen, T. T. *J Appl Polym Sci* 1998, 69, 1805.
28. Kim, M. G.; Wu, Y.; Amos, L. W. *J Polym Sci, Part A: Polym Chem* 1997, 35, 3275.
29. Kim, M. G.; Amos, L. W. *Ind Eng Chem Res* 1991, 30, 1151.
30. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 955.
31. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 939.
32. Sojka, S. A.; Wolfe, R. A.; Dietz, Jr., E. A.; Dannels, B. F. *Macromolecules* 1979, 12, 767.
33. Panamgama, L. A.; Pizzi, A. *J Appl Polym Sci* 1995, 55, 1007.
34. Maciel, G. E.; Chuang, I.-S.; Gollob, L. *Macromolecules* 1984, 17, 1081.
35. Chuang, I.-S.; Maciel, G. E. *Macromolecules* 1991, 24, 1025.
36. de Breet, A. J. J.; Dankelman, W.; Huysmans, W. G. B.; de Wit, J. *Angew Makromol Chem* 1977, 62, 7.
37. Bryson, R. L.; Hatfield, G. R.; Early, T. A.; Palmer, A. R.; Maciel, G. E. *Macromolecules* 1983, 16, 1669.
38. Werstler, D. D. *Polymer* 1986, 27, 750.
39. So, S.; Rudin, A. *J Polym Sci, Polym Lett Ed* 1985, 23, 403.
40. Fyfe, C. A.; McKinnon, M. S.; Rudin, A.; Tchir, W. J. *Macromolecules* 1983, 16, 1216.
41. Pasch, H.; Goetzky, P.; Gründemann, E. *Acta Polym* 1985, 36, 555.
42. Pasch, H.; Goetzky, P.; Raubach, H. *Acta Polym* 1983, 34, 150.
43. Kim, M. G.; Amos, L. W.; Barnes, E. E. *Ind Eng Chem Res* 1990, 29, 2032.
44. Myers, G. E.; Christiansen, A. W.; Geimer, R. L.; Follensbee, R. A.; Koutsky, J. A. *J Appl Polym Sci* 1991, 43, 237.
45. Rudin, A.; Fyfe, C. A.; Vines, S. M. *J Appl Polym Sci* 1983, 28, 2611.
46. Gobec, G.; Dunky, M.; Zich, T.; Lederer, K. *Angew Makromol Chem* 1997, 251, 171.
47. Schultz, G.; Gnauck, R.; Ziebarth, G. *Plaste Kautschuk* 1982, 29, 398.
48. Wellons, J. D.; Gollob, L. *Wood Sci* 1980, 13, 68.
49. Li, P.; Coleman, D. W.; Spaulding, K. M.; McClennen, W. H.; Stafford, P. R.; Fife, D. J. *J Chromatogr, A* 2001, 914, 147.
50. Chow, S.; Steiner, P. R. *J Appl Polym Sci* 1979, 23, 1973.
51. Pizzi, A.; Mtsweni, B.; Parson, W. *J Appl Polym Sci* 1994, 52, 1847.
52. Christiansen, A. W.; Gollob, L. *J Appl Polym Sci* 1985, 30, 2279.
53. Balcerowiak, W.; Hetper, J.; Kaledkowski, B.; Gryta, M. *Thermochim Acta* 1998, 320, 209.
54. Focke, W. W.; Smit, M. S.; Tolmay, A. T.; van der Walt, L. S.; van Wyk, W. L. *Polym Eng Sci* 1991, 31, 1665.