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A study on the effects of reaction conditions on the characteristics of resol resins for foams by statistical analysis

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Abstract−A two-level full factorial experimental design with three variables, formaldehyde-to-phenol (F/P) molar ratios, hydroxy-to-phenol (OH/P) wt%, and reaction temperature was implemented to determine the effect of the variables on the properties of phenol-formaldehyde (PF) resol resins for insulation foam. Ten resins were prepared with F/P molar ratios between 1.5 and 2.5, OH/P wt% between 0.5 and 1.5 and reaction temperature between 80 and 90 °C. The effect of three independent variables on the resin properties was analyzed by using three-way ANOVA of SPSS. All three production variables had a significant effect on resin properties. The F/P molar ratio and OH/P wt% were found to have the most frequent effect on resin properties. F/P molar ratio and OH/P wt% had an increasing effect, while reaction temperature showed a decreasing effect on free formaldehyde. The present study confirms that experimental design is a very valuable and capable tool for evaluating multiple variables in resin production.

Key words: Resol Resin, Experimental Design, Statistical Analysis, ANOVA, Condensation Reaction

INTRODUCTION

Phenol-formaldehyde (PF) resins were synthesized by the addition and condensation reaction of phenol with formaldehyde. When alkali catalyst, for example, barium hydroxide ($Ba(OH)_2$), was present, resol resins were produced [Gardziella et al., 2000]. Phenolic resol resins are utilized in a variety of applications, such as aeronautical, building, impregnation, adhesion and frame retardants [Knop and Pilato, 1985; Gardziella et al., 2000]. The synthesis of resol is a two step process. The first step, addition reaction, leads to five monocyclic compounds polyfunctionalized by hydroxymethyl groups. In the second step, condensation reaction, low molecular PF resol resins are formed by removing condensed water. It is known that at the initial stage of the condensation the methyrol substituted phenols (primary reaction products) could react with formaldehyde to form hemiformal compounds.

The final structure of resins produced depends on the reaction conditions. Formaldehyde to phenol (F/P) and hydroxyl to phenol (OH/P) wt% as well as reaction temperature were the most important parameters in the synthesis of resol. The influence of catalyst type on reaction mechanism and kinetics was studied by Grenier-Loustalot et al. [1996]. They also studied the reactivity of initial monomer towards formaldehyde [1996] and the effect of F/P ratios [1996]. The authors concluded that the rate at which phenol disappeared from the reaction mixture was dependent on not only the metal valence in the hydroxide catalyst but also the size of hydrated metal cation. Mondragon et al. studied kinetics of resol formation catalysed by sodium hydroxide and triethyamine [1998], catalysed by barium hydroxide [1998], and catalysed by zinc acetate [1999]. Synthesis of resol resins in the presence of trialkyamines [Hepter et al., 1999] and tetraalkylammonium hydroxide [Hepter and Kaledkowski, 2000] was investigated. The authors ascertained that resols obtained by trialkylamines, as compared to conventional resins, offered different properties which sometimes were advantageous from the viewpoint of the applicability of resin.

As shown above, every parameter for resol synthesis had been studied thoroughly by many research groups using all kind of techniques. In a previous paper, the evolution of products formed from the addition of formaldehyde onto phenol and later condensation reaction had been analyzed. Molecular species of resol had been determined by GC after trimethylsilylation of samples. The effect of initial F/P and OH/P wt%, and reaction temperature on the chemical structure (mono-, di- and tri-substitution of methyrol group, methylene bridge, phenolic hemiformals, etc.) was studied by utilizing a two-level full factorial experimental design [Nam et al., 2006].

In this study, the effect of initial F/P and OH/P wt%, and reaction temperature on the free phenol and formaldehyde, molecular weights, and viscosity of prepolymer were studied by GC, GPC, and viscometer utilizing a two-level full factorial experimental design.

EXPERIMENTAL

1. Experimental Design

A two level full factorial experimental design with three independent variables was generated with one center point, which was repeated [Holopainen et al., 2004]. In this design, F/P molar ratio, OH/P wt%, and reaction temperature were defined as independent variables, all receiving two values, a high and a low value. Presenting these three variables in a rectangular coordinate system, a cube-like model was formed, with eight corners, which represent eight of the studied resins (Fig. 1). One center point (repeated twice) was added to improve accuracy of the design, and this center point was repeated to better estimate the error of the design. The eight corners and center point provided a total 10 resins as shown in Table 1. All 10 resins were analyzed with GC, GPC, and viscometer, and every

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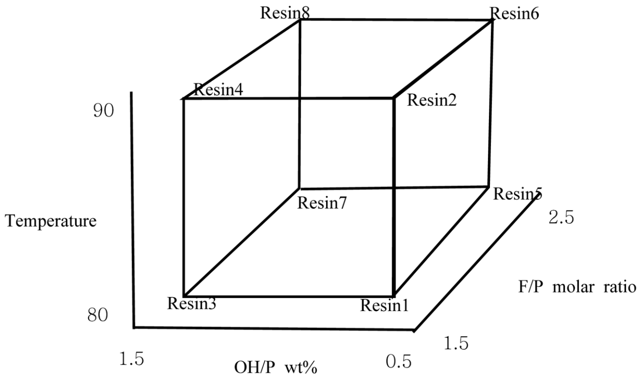

Fig. 1. Two-level experimental design of 10 PF resins.

Table 1. Properties of 10 PF resins studied

PF Resin	F/P molar ratio	OH/P wt%	Temperature (°C)
1	1.5	0.5	80
2	1.5	0.5	90
3	1.5	1.5	80
4	1.5	1.5	90
5	2.5	0.5	80
6	2.5	0.5	90
7	2.5	1.5	80
8	2.5	1.5	90
9	2.0	1.0	85
10	2.0	1.0	85

analysis result was treated as a dependent variable and analyzed with analysis of variance at the 0.05 significance level. All the analysis results were analyzed by using three-way ANOVA of SPSS.

2. Synthesis of Resols

Phenol (>98%), $Ba(OH)_2$ (>97%), and formaldehyde (37% aqueous solution) were commercial products used without further purification. All 10 PF resins were produced with two-step process using $Ba(OH)_2$ as catalyst. The first step, addition reaction, proceeded for 300 min with varying F/P molar ratio, OH/P wt%, and reaction temperature as shown in Table 1.

Phenol was melted at 40 °C for 30 minutes and weighed formaldehyde was added slowly. The mixture was heated to 10 °C lower than reaction temperature. Measured amount of catalyst was added into the reactor at that time and the reactor was purged with N_2 gas. Zero time was defined as time taken for the mixture to reach the reaction temperature. After 5 hours, reaction mixtures were moved into a vacuum oven, and condensation reaction proceeded at 120 °C. A vacuum pump was connected to the vacuum oven to remove water vapor formed during condensation reaction. Products were sampled every 30 minutes until resins were cured. All samples were stored frozen at −18 °C until analysis.

3. GC Analysis

Molecular species in resol were analyzed by GC (Hewlett Packard Co., 6890 A) equipped with a flame ionisation detector after trimethylsilylation of sample with N,O-bis(trimethylsilyl)-trifluoracetamide in pyridine [Prokai, 1985]. Free formaldehyde and free phenol were analyzed without trimethylsilylation of samples. Samples were prepared by dissolving with tetrahydrofuran and filtered by PTFE filter. A glass column (3 m×2 mm I. D.) packed with 3% OV-1 on 100-120 mesh Chromosorb W HP was applied. Injection port and detector temperature were maintained at 280 °C, and the oven was programmed from 120 to 300 °C at 8 °C/min.

4. GPC Measurement

The GPC measurements were made with GPC (Younglin, Acme GPC system) and three Styragel columns (HR1, HR2, and HR5E, 7.8×300 mm) in series. The columns were calibrated with ten polystyrene standards. Resin samples were diluted to 10 mg/mL with THF, which was also used as an eluent at a flow rate of 1.0 mL/min. Separated compounds were detected by refractive index detector (RI 750F). All the resins were measured at 50 °C.

5. Viscometer Measurement

An A&D SV-10 viscometer was applied to determine the viscosity of resins. A tuning-fork vibration method was used to determine the viscosity of samples. Viscosity from 0.3 to 10,000 mPa·s could be measured at room temperature. The amount of sample required was 35-45 mL.

RESULTS AND DISCUSSION

1. Studied Resins

All 10 resins were analyzed with GC for free phenol and formaldehyde and with GPC for molecular weights after 300 min of addition reaction. The results are shown in Table 2. Every analysis result was treated as a dependent result in the statistical study.

All 10 resins were further condensed at 120 °C and under pressure removing water vapor. Resin viscosities were measured at every 30 min and the results are presented in Table 3. Condensation time of 120 min was chosen to study the effect of three independent variables on the resin property based on Table 3. Table 4 demonstrates free phenol and free formaldehyde as a weight % of full mixture, molecular weight average (Mw), molecular number average (Mn), and poly dispersity of the prepared resins.

2. Statistical Analysis Results

All dependent variables were analyzed by utilizing ANOVA and the multiple regression model of SPSS for Windows software, version 12.0. The ANOVA F-test indicates the dependence of dependent variables with the independent variables. P level indicates the

Table 2. Characteristics of 10 PF resins after 300 min of addition reaction

PF resins	Free phenol wt%*	Free formaldehyde wt%*	Mw
1	18.65	12.44	191
2	16.59	12.27	473
3	10.62	13.41	611
4	9.19	11.41	2389
5	16.05	17.72	545
6	16.10	12.72	533
7	8.31	15.96	641
8	8.32	15.50	750
9	10.96	14.21	705
10	11.09	14.31	685

*indicates wt% of full mixture

Table 3. Variation of viscosities during condensation reaction

PF resin / Time (min)	1	2	3	4	5	6	7	8	9	10
30				1380[a]						
60				4140						
90			119	H[b]						
120	36	416	1970		20	21	46	88	110	114
150	38	6080	H		87	41	305	1510	H	H
180	188	H		797	210	H	H			
210	F[c]			3130	383					
240					4200	531				
270					F	H				

[a]The unit of viscosity is mPa·s
[b]H indicates hardened resin
[c]F indicates viscosity exceeding 13,000 mPa·s

Table 4. Characteristics of 10 PF resins after 120min of condensation reaction

PF resin	Free phenol wt%	Free formaldehyde wt%	Mw	Mn	Poly dispersity	Viscosity (mPa·s)
1	20.80	7.97	617	574	1.08	36
2	24.65	5.78	640	583	1.10	416
3	11.07	11.78	1226	828	1.48	1970
4	-	-	-	-	-	F
5	18.53	10.51	565	538	1.05	20
6	22.11	12.02	565	536	1.05	21
7	7.69	10.97	763	679	1.12	46
8	10.10	10.25	865	723	1.20	88
9	11.41	10.41	930	686	1.35	110
10	11.50	10.47	934	676	1.38	114

Table 5. Results of statistical analysis for free phenol and free formaldehyde

	Addition reaction		Condensation reaction	
	Free phenol	Free formaldehyde	Free phenol	Free formaldehyde
F test results				
F/P molar ratio	581.55	3825.42	3825.42	1648.85
OH/P wt%	14170.15	31.92	32785.13	189.27
Temperature	174.03	1455.42	2880.11	170.57
P level values				
F/P molar ratio	.026	.010	.014	.016
OH/P wt%	.005	.112	.004	.046
Temperature	.048	.017	.012	.049
t-value results				
F/P molar ratio	−.192	.748	−.292	.564
OH/P wt%	−.946	.068	−.911	.462
Temperature	−.105	−.461	.306	−.218

statistical significance of correlation, and t-values indicate the strength of the correlation between dependent and independent variables. The range of t-value from 0.7 to 1.0 means highest positive correlation, from 0.3 to 0.7 means medium positive correlation, from 0.1 to 0.3 means little positive correlation, from −0.1 to 0.1 means no correlation. The minus sign means negative effect.

Results of statistical analysis for free phenol and free formaldehyde in addition reaction and in condensation reaction are shown in Table 5. The effects of F/P molar ratio, OH/P wt% and addition reaction temperature on the molecular weight, on the poly dispersity, and on the viscosity of resin were analyzed by statistical study in Table 6.

3. The Effect of Independent Variables on Free Phenol and Free Formaldehyde

Table 6. Results of statistical analysis for viscosity and molecular weight of resins

	Viscosity	Mn	Mw	Poly dispersity
F-test results				
F/P molar ratio	150414.7	1273.11	8836.00	802.77
OH/P wt%	112672.1	7267.56	28224.00	1521.00
Reaction temperature	4958.50	75.11	434.02	1521.00
P level values				
F/P molar ratio	0.0002	0.018	0.007	0.022
OH/P wt%	0.0002	0.007	0.007	0.022
Reaction temperature	0.0009	0.073	0.031	0.095
t-value results				
F/P molar ratio	−0.545	−0.216	−0.314	−0.364
OH/P wt%	0.409	0.897	0.766	0.594
Reaction temperature	−0.262	−0.182	−0.190	−0.145

The F-test results for the relations of the free phenol in addition reaction with amount of catalyst (OH/P wt%) were very high, indicating a clear dependence of free phenol on OH/P wt% (Table 5). However, for the F/P molar ratio and reaction temperature, the F-test was not high, 581.55 and 174.03, respectively. It could also be seen that P level values for the relation between the free phenol and OH/P wt% were under the set P level of 0.05. P level values for the relation between the free phenol and both F/P molar ratio and reaction temperature were under the set P level of 0.05 also. This data indicated that the relation of dependent variable free phenol with three independent variables was statistically significant at the 0.05 significance level.

The t-value results showed the negative effect of three independent variables on free phenol, which meant that the higher the values of three independent variables, the lower the free phenol. However, the effect of each independent variable on free phenol was different in strength. The OH/P wt% showed highest negative correlation, while the F/P molar ratio showed little negative correlation and the reaction temperature showed no correlation. So, the higher the OH/P wt%, the lower was the amount of free phenol. The catalyst amount kinetically and mechanistically affected the prepolymer formation. The higher the OH/P wt% the higher reactant consumption rate and product formation rates. These results followed the trends similar to the values obtained by Grenier- Loustalot et al. [1996] and Aierbe et al. [2000a].

It could be seen that the relations of free formaldehyde with both F/P molar ratio and reaction temperature were statistically significant at the 0.05 significance level, while the OH/P wt% was not statistically significant. F/P molar ratio had a very strong increasing effect on free formaldehyde. The lower the F/P molar ratio, the lower was the free formaldehyde content. The influence of the initial F/P molar ratio on the formation of a resol resin was investigated by Aierbe et al. [2000b]. They found that free formaldehyde concentrations increased with the initial amount of formaldehyde used.

The reaction temperature had a medium negative effect on free formaldehyde, causing the amount of free formaldehyde to decrease as the reaction temperature increased. On increasing the reaction temperature, reactant consumption rates and first formed addition products increased, condensation times decreased as well [Aierbe et al., 2002]. Residual phenol and formaldehyde concentrations and the amount of free unreacted ortho and para positions decreased with temperature.

After 300 min of addition reaction, the molecular species of 10 PF resins would be different in composition. Sixteen molecular species in resol were identified by GC. They were categorized as substituted monomers (mono-, di-, and tri-substituted), condensed dimers, and phenolic hemiformals [Nam et al., 2006]. The difference in composition of molecular species of 10 PF resin would cause different resin properties, even if the condensation reaction proceeded under the same conditions. The effect of three independent variables on the free phenol during condensation reaction was similar to that of addition reaction. The effect of three independent variables on free phenol was statistically significant. F/P molar ratio had a little negative correlation and OH/P wt% had a very strong negative correlation, same as addition reaction. Only the effect of reaction temperature on free phenol changed from 'no correlation' to 'little positive correlation'.

All of the three independent variables showed statistically significant effects on the amount of free formaldehyde. F/P molar ratio and OH/P wt% had an increasing effect, while reaction temperature showed a decreasing effect on free formaldehyde. In consequence, the higher the catalyst content, the lower the F/P molar ratio, and a higher reaction temperature would be recommended to reduce the amount of free phenol and free formaldehyde in resol resins.

4. The Effect of Independent Variables on the Resin Molecular Weights and Viscosity

As published in the literature [Aierbe et al., 2000b], phenolic *ortho* and *para* unreacted sites decreased with F/P molar ratios as a consequence of the higher possibility of hydroxymethyl addition to occur and favored conditions of these groups to condense giving rise to methylene and ether bonds. Formation of phenolic rings connecting bonds depended on the initial F/P ratio. Dibenzyl ether bonds and methylene bonds formed on the prepolymer increased with F/P. In this study, however, the F/P molar ratio and addition reaction temperature had a decreasing effect on weight-average molecular weight (Mw), indicating that the higher the F/P molar ratio and increasing the addition reaction temperature, the lower the Mw.

OH/P wt% had a strong increasing effect, suggesting that the higher the catalyst content, the higher the Mw. The effect of increasing the amount of catalyst reported in the literature [Grenier-Loustalot, 1996; Aierbe et al., 1998] by using NMR and HPLC, basically affected the activation and rate of polymerization reaction, thus reaching higher polymerization degrees on the prepolymer formation.

The OH/P wt% had a strong increasing effect also on Mn. F/P molar ratio had a little decreasing effect, suggesting that the higher the F/P molar ratio, Mn decreased slightly. Addition reaction temperature did not have an effect on Mn. Similar to Mn, addition reaction temperature did not have an effect on poly dispersity. The effects of F/P molar ratio and OH/P wt% on poly dispersity were same as those of Mw.

The OH/P wt% had a strong increasing effect on Mn and Mw, and had a strong decreasing effect on free phenol. When the molecular weight needed to be controlled, especially for insulating resol foam which required Mw less than 1000, care had to be taken for the level of OH/P wt%.

All three independent variables had an effect on viscosity. Both F/P molar ratio and addition reaction temperature had a decreasing effect, while OH/P wt% had an increasing effect. As shown in Table 6, effects of three independent variables on viscosity were same as those on Mw.

5. Reaction Conditions for Preparing Insulation Resol Foams

To prepare insulating resol foam, both molecular weight and viscosity of resol resin should be controlled. Molecular weight less than 1,000 and viscosity less than 6,500 cP were necessary conditions for foaming of resol resin. Another important factor to be met for insulation foam production was the lowering of free formaldehyde content in the resol prepolymer. As discussed, the higher the catalyst content, the lower the F/P molar ratio, and higher the addition reaction temperature would be helpful to reduce the amount of free phenol and free formaldehyde in resol resins. The above conditions, except addition reaction temperature, caused increasing of both viscosity and molecular weight of resol resin. So, to prepare resol prepolymer for insulation foam, proper control of condensation time would be essential.

To confirm the statistical analysis results, new reaction conditions were determined. F/P molar ratio decreased from 2.0 to 1.2, OH/P wt% increased from 1.0 to 1.5, and reaction temperature increased from 85 °C to 90 °C, respectively. After 300 min of addition reaction and followed by condensation reaction for 20 min, free formaldehyde wt% of resol prepolymer dropped from 10.44% (center point) to 2.38% (modified condition). This result showed the validity and usefulness of statistical analysis.

CONCLUSIONS

The present study showed that experimental design is a very valuable and capable tool for evaluating multiple variables in resin production. All three production variables had a significant effect on resin properties. The F/P molar ratio and OH/P wt% were found to have the most frequent effect on resin properties. F/P molar ratio and OH/P wt% had an increasing effect, while reaction temperature showed a decreasing effect on free formaldehyde. So, the higher the catalyst content, the lower the F/P molar ratio, and a higher reaction temperature would be recommended to reduce the amount of free phenol and free formaldehyde in resol resins. According to the statistical analysis, F/P molar ratio decreased from 2.0 to 1.2, OH/P wt% increased from 1.0 to 1.5, and reaction temperature increased from 85 °C to 90 °C, respectively. After 300 min of addition reaction and followed by condensation reaction for 20 min, free formaldehyde wt% of resol prepolymer dropped from 10.44% (center point) to 2.38% (modified condition).

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