Studies in the Process Optimization and Characterization of Low Formaldehyde Emission Urea-Formaldehyde Resin by Response Surface Methodology

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ABSTRACT: Stringent control of formaldehyde emission standards the world over has intensified research and development effort to explore several paths for reducing formaldehyde release. A new generation of low odour resins is currently being developed and some resin manufacturers are now programming formaldehyde and urea additions at two or more stages in the overall reaction. This article reports on the studies conducted on a four-stage condensation process consisting of the first stage involving a high acid environment followed by an alkaline condensation, a condensation under a pH 6, and finally neutralization to pH 7. A programmed variation consisting of changing ''the number of additions'' and ''the duration between additions'' of urea to formaldehyde was considered as an effective method to control the molecular weight, molecular weight distribution, and the oligomeric structures. Response surface methodology was employed to optimize the above conditions to produce particle boards with minimum formaldehyde emission and maximum internal bond strength. The studies showed that sequential addition of urea [''the duration between additions'' and the ''number of additions''] improved the internal bond strength and reduced formaldehyde emission of the particleboards. Detailed resin characterization in terms of the number and weight average molecular weights, molecular weight distribution, polydispersity, percentages of reactive moieties, and interlinking units present in the oligomer could be stipulated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2709–2719, 2007

Key words: UF resin; low formaldehyde emission; optimization; response surface methodology; polydispersity; methylene groups; methylene ether groups; hydroxymethyl groups

INTRODUCTION

UF resins are traditionally produced by reacting urea and formalin in three stages, first in the mild alkaline medium, followed by condensation in the acid medium, and finally neutralized. Additional urea is then added after neutralization to control both the formaldehyde emission (in the case of low formaldehyde emission resins) as well as to extend the storage life of the resin.

Deviation from this method has been covered by patents by Williams[1,2] describing the process of producing low emission UF resins by a new four stage procedure consisting of (1) carrying out the condensation of urea and formaldehyde under a very high acid environment and large excess of formaldehyde; (2) continuing the reaction in the alkaline medium after additional urea is added to effect a predetermined molar ratio U/F; (3) carrying out the reaction under a low pH of about 5 to allow further condensation until desired viscosity is reached; (4) neutralizing the product and addition of a final amount of urea to obtain a desired low HCHO to urea ratio. The reduced formaldehyde emission from this resin system has been attributed to the predominance of methylene linkages in the cured resin. The present investigation was taken up to study in detail the effect of sequential and incremental addition (number of additions and the duration between the additions) of the urea to the reaction mixture in the second stage of the reaction to exercise control over the final working properties such as the internal bond strength and emission of HCHO through a precise control of functional groups and interlinking units of the oligomers, their molecular weight, molecular weight distribution, and polydispersity. Levenspiel[3] refers to this type of influence of sequential addition of reactants on the product distribution in terms of what he calls the influence of ''contacting pattern'' of the reactants to control complex reactions. According to Levenspiel,[3] the use of proper ''contacting pattern'' is a critical factor in obtaining favorable distribution of products of complex reactions. This concept is particularly important for a step wise polymerization reaction such as between urea and formaldehyde. The mode of sequential addition, as will be discussed in this article, has been found to control not only the nature of reactive functional groups (methylol groups) and the nature of the interlinking units present in the oligomers but also the molecular weight and the molecular weight distribution

in such a manner as to influence the ultimate performance characteristics of the resin. Two important earlier works that are the fore-runners of the present investigation require to be cited in this connection: (1) Pizzi et al.,[4–7] who reported that the increase of the number of additions of urea during the preparation of the resin increases the bond strength; (2) Kim,[8] who reported on the migration of hydroxymethyl groups to the second urea component leading to the reaction of migrating methylol groups with the free amide groups that are added in the final stage in the alkaline medium. It has to be mentioned that the initial condensation of urea and formaldehyde under a high acid environment has been reported to effect direct condensation of the reactants leading to oligomers, thus by-passing the monomeric methylol ureas, and to produce products with predominantly methylene groups in the polymer chain (an innocuous group for formaldehyde emission) rather than methylene ether bridges, which are known to be responsible for the emission of formaldehyde.[4] These chain-extended oligomers, the product of the first stage of condensation between urea and formaldehyde, undergoes cleavage under the alkaline conditions of the second stage, whereby the hydroxymethyl groups present in the oligomers are jettisoned and allowed to migrate to the molecules of added urea or another oligomer of different chain lengths. The manipulation of the second stage of the process in this manner is akin to the ''equilibration process'' carried out in the case of silicone chemistry wherein there is a rupture and recombination of the polysiloxane chains in the reaction medium to produce products of desired molecular weight distribution. The objective of the present study was (1) to determine the effect of ''number of additions'' and ''duration between the additions'' on the molecular weight, molecular weight distribution, polydispersity, internal bond strength, and formaldehyde emission of the UF resin; (2) to optimize the process conditions to maximize the internal bond strength and minimize the formaldehyde emission; and (3) to specify exactly what should be molecular weight, molecular weight distribution, and polydispersity of the UF resin corresponding to the established optimum conditions. For the purpose of accomplishing the above objectives, response surface methodology (RSM)[9] was employed.

MATERIALS AND METHODS

Materials

Urea used for preparation of urea formaldehyde resins in this study was supplied as free sample by Borden Chemical, Malaysia. Fifty percent formaldehyde that was used to prepare the urea formaldehyde resins was kindly supplied as free samples by Borden Chemical, Malaysia. Ammonium chloride was supplied by R and

M Chemical, United Kingdom. Dimethyl sulfoxide (DMSO) was used as a solvent for urea formaldehyde resins as well as the mobile phase in the HPSEC analysis. Deuterated DMSO was used for the NMR analysis. Both the grades were obtained from Fluka Chemical, Switzerland. Lithium chloride was supplied by Fluka Chemical, Switzerland. Ammonium acetate used in this study was supplied by Fisher Chemicals, United Kingdom. Acetylacetone was used to prepare the Nash reagent (acetylacetone method) for formaldehyde emission test using photometric method. The chemical was supplied by Fluka Chemical, Switzerland. Ammonium sulfate was supplied by Ajac Chemicals, Australia. Aluminum sulfate used as one of the curing agents was supplied by R and M Chemical, UK.

Methodology

Response surface methodology

Response surface methodology (RSM)[9] is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize the response.

The two independent variables were identified for the purpose of RSM in the preparation of low formaldehyde emission urea formaldehyde. They are:

1. Number of addition of urea.
2. Duration between the addition.

Central composite rotatable design, one of the accepted designs for response surface methodology, was adopted for the experimental runs.

Since nonlinear trend in the functional relationships between the process variables and the response were considered likely, an efficient class of experimental design known as central composite design (CCD) of second order was used to generate the experimental treatment combinations.[6] The basic CCD for k variables consists of a 2^k factorial design with each factor at 2 levels (-1, $+1$) augmented by $2k$ axial points and a number of replications at the central points. Thus the two factors would take in the CCD the following values expressed as coded variables:

Lowest value	$-\alpha$
Low value	-1
Central value	0
High value	$+1$
Highest value	$+\alpha$

The value of ''α'' is given by $(n_f)^{1/4}$ where n_f is the number of experiments in the factorial portion of the design (i.e., 2^k). In the present case, the value of ''α'' is 1.414.

TABLE I
CCD Matrix in Real Levels for the Preparation of Urea Formaldehyde Resins

Standard	Run	Type	Factor A: Number of additions	Factor B: Duration between additions (min)
1	10	Factorial	2	10
2	3	Factorial	4	10
3	1	Factorial	2	20
4	13	Factorial	4	20
5	5	Axial	1	15
6	6	Axial	5	15
7	4	Axial	3	7.93
8	8	Axial	3	22.07
9	12	Center	3	15
10	7	Center	3	15
11	9	Center	3	15
12	2	Center	3	15
13	11	Center	3	15

The analysis of the data generated by the designed experiments leads to the establishment of functional relationship between the responses and process variables. The validity of the above mathematical function is established by the analysis of variance (ANOVA) by the ''Design Expert Software.'' The software executes three dimensional plots as well the perturbation plots of the mathematical functions. In the ''perturbation plots,'' the responses are plotted by changing only one factor over its range, while holding all the other factors constant. The terms used in connection with the RSM are defined as follows.

Definition of terms

R-*squared values.* They are the multiple correlation coefficients, a number between −1 and 1 that indicated the degree of relationship of the response variable to the combined linear predictor variables.
p-*Values.* Probability values relating to the risk of falsely rejecting the null hypothesis.
Lack of fit. Variation between model prediction and the experimental points are compared with pure error to test the lack of fit. In the statistical output lack of fir should be insignificant. A small F-value and a high P value are good in this test.
Perturbation plots. The Perturbation plots show the effect of changing one factor, while holding the rest constant. This plot is useful when trying to decide which factor has the most complex behavior (most curved or steepest change rate).

By default, DESIGN-EXPERT sets the reference point at the midpoint (coded 0) of all the factors. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor. If there are more than two factors, as in the present

case, the perturbation plot can be used to find those influential factors that most affect the response.

Thus the response surface plots and the perturbation plots can be used to give the scientific interpretations of the phenomena involved in the process under study as well as to determine the optimum conditions to give maximum degree of substitution.

The design matrix in coded values employed for the RSM is shown in Table I.

The relationship between the coded and real variables is shown in Table II. The analysis of results was carried out by standard methods of Montgomery and Myers,[10] using the Design Expert Version 5 software. Wherever necessary, transformations were carried out.

Preparation of low formaldehyde emission type UF resin

These resins were synthesized from commercial urea and 50% formalin as described below.

Hundred and twenty grams of 50% formaldehyde solution was charged into a reaction flask. Its pH was adjusted to pH 1.0 using 50% sulfuric acid at 40°C. The required amount of urea was added in 15 equal increments over a duration of 15 min at 40°C to finally reach a F/U molar ratio of 3.25 : 1. The reaction is exothermic. The temperature was controlled at 50°C. After the required amount of urea was added to produce an initial F/U ratio of 3.25, the reaction mixture was held at the final temperature for about 10 min. The pH of the resulting solution was then adjusted to 7.5 using 50% sodium hydroxide solution. Then, the urea was added sequentially to the above reaction mixture varying (1) the number of additions and (2) duration between the additions in accordance with the central composite rotatable design. The experimental design adopted is shown in the Table I. A final molar ratio of F/U (=1.5) was maintained in all experiments. pH of the mixtures was adjusted to pH 7.5 after each addition of urea. When the F/U ratio of 1.5 was reached, the reaction mixture was brought to gentle reflux for 15 min. The pH was then adjusted to 6.0 with 30% formic acid. Then reflux was continued until a Gardner viscosity of $J+$ was reached. The pH

TABLE II
The Coded and Real Values of the Central Composite Design for the Preparation of Urea Formaldehyde

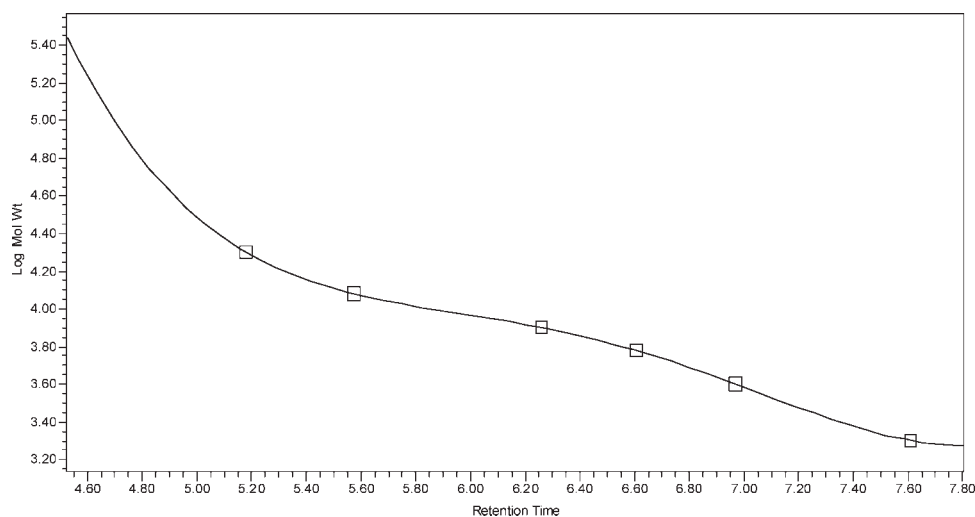| Number of additions (A)	Duration between the additions (B) (min)	Factors Coded and real levels	
1	7.93	−α	−1.41
2	10	−1	−1.00
3	15	0	0.00
4	20	1	1.00
5	22.07	α	1.41

Figure 1 Calibration plot of PEG standards from Fluka Chemical.

was then adjusted to 7.5 with NaOH and cooled immediately to room temperature. Then, the final required amount of urea was added to achieve a final F/U molar ratio of 1.1 with stirring until all the urea added was dissolved. The pH was again adjusted to 7.5. The resins so produced were used (1) to make particleboards for formaldehyde emission and internal bonding testing (2) HPSEC and NMR analysis.

Physicochemical methods for characterization of the urea formaldehyde resins: Size exclusion chromatography

Preparation of UF samples for size exclusion chromatography. Samples of the UF resin (0.5 g solid basis) prepared made from Runs 1–13 (Table I) was dissolved in 3 mL of dimethylsulfoxide containing 2% of lithium chloride at room temperature. All the UF-DMSO solutions were filtered through a 0.45 μm Whatman glass syringe filter to remove any extraneous particles prior to SEC measurements. DMSO-LiCl

mobile phase was filtered using Whatman universal membrane filter and Millipore vacuum filter to remove any impurities and then sonicated for 15 min using Cole-Parmer soniccator bath to remove any gases and air bubbles.

Determination of molecular weight distribution. The molecular weight measurements for the UF-DMSO solutions were carried out by a Waters Alliance HPLC System equipped with a Waters 2410 Differential RI Detector. A PL-Gel 10 μm 500 Å column supplied by Polymer Laboratories was used. DMSO containing 2% of LiCl was used as the mobile phase[11,12] with the sensitivity of the detector set to a suitable value (×16), 100 μL of sample solution was injected onto the column via the sample loop. The SEC column was thermostated at 80°C using an external column heater and the flow rate of the mobile phase was adjusted to 1 mL/min.

A calibration plot (Fig. 1) was obtained using polyethylene glycol supplied by Fluka Chemical as standard.

TABLE III
Experimental Data on the Responses

| Std | Run | A | B | Response | | | | | |
				a	b	c	d	e	f
1	10	2	10	−107.539	2311	5391	2.33	0.40	2.4694
2	3	4	10	−70.820	3470	6497	1.87	0.73	1.8241
3	1	2	20	−146.586	3656	7412	2.03	0.62	1.6451
4	13	4	20	−164.347	3624	7140	1.97	0.25	2.0074
5	5	1	15	−111.193	2605	6157	2.36	0.29	2.5296
6	6	5	15	−104.914	3632	7607	2.09	0.88	2.2670
7	4	3	7.93	−111.926	2475	9341	2.36	0.19	2.6326
8	8	3	22.07	−102.918	3393	5980	1.76	0.77	1.8139
9	12	3	15	−114.759	3983	8634	2.17	0.69	2.6610
10	7	3	15	−110.532	4156	9215	2.25	0.73	2.5206
11	9	3	15	−80.840	4068	8896	2.17	0.63	1.6819
12	2	3	15	−124.688	4106	9156	2.17	0.56	2.2500
13	11	3	15	−136.692	3965	9268	2.22	0.51	2.0219
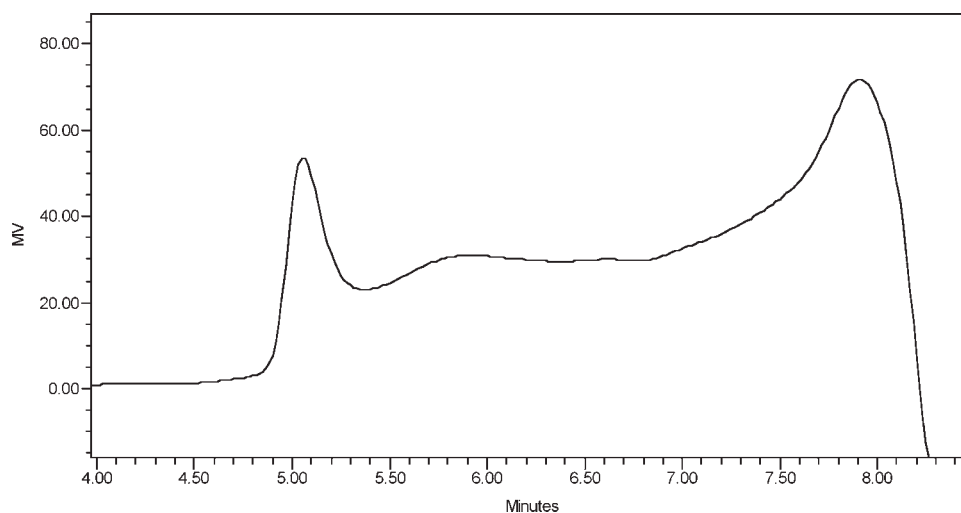
Figure 2 SEC plot of a typical UF resin (Run 13).

Preparation of laboratory particleboards and the determination of mechanical properties and formaldehyde emission

Preparation of laboratory particleboards. Resin samples from Runs 1–13 and a commercial UF resin sample were used to bond the particleboards. Dried rubber wood particles were obtained from Mieco Chipboard in Negeri Sembilan, Malaysia from which single layer particleboards of density 700 kg/m^3 were made. UF resin was sprayed on the particles. The resin content in the particleboards was maintained at 10%, based on the oven-dry weight of the particles. Two percent of the ammonium chloride was added to the resin as a catalyst, based on the solid content of resin, and mixed well before spraying. The resinated particles were formed into a mat of dimensions 200 mm × 200 mm. The mat was prepressed and further hot-pressed at 160°C for 3 min to produce a board of density 700 kg/m^3 with the dimensions of 200 mm × 200 mm × 10 mm. Boards were trimmed and conditioned to a constant mass in an atmosphere of (20 ± 2)°C and a relative humidity of (65 ± 5)% [or (45 ± 5)% relative humidity in the case of formaldehyde test] and then cut into test pieces for the determination of formaldehyde emission (WKI method) and internal bonding test.
Determination of internal bond strength. Internal bond strength was determined by employing BS 5669 : 1989.
Determination of formaldehyde emission. The WKI Method/Flask Method[13] was used to determine the formaldehyde emission values for all the experiments. The Desiccator Method (JANS 16:1998) and the Perforator Method (BS 5669:1989) were employed for the purpose of comparison. These comparisons were made with respect to the particleboard samples made from the UF resin prepared under the optimum conditions established by the response surface method.

RESULTS AND DISCUSSION

The results of the RSM experiments are tabulated in Table III. The results are discussed as follows.

Effect of ''number of additions'' and ''duration between additions'' on polydispersity

The molecular weight and molecular weight distribution of urea formaldehyde resin are the most important characteristics of the resin, which influence several of its properties, e.g., viscosity and flow behavior, wetting behavior of wood surface, adhesion potential, and penetration into the wood surface. Higher the molar mass, the lower the water dilutability of the resin, lesser the quantity of resin that can remain soluble in water. This results in difficulty to handle during particleboard making. UF resin consisting predominantly of lower molecular weight species leads to excessive penetration of the resin into the wood surface, causing starvation of adhesive on the surface of wood particles[14] despite its ability for better wetting. UF resins consisting mostly of polymer molecules of higher molecular weight will in contrast cause insufficient wetting of the substrate surface as described by Dunky.[15] Higher molecular weight species are however very important for the cohesive strength of the resin. As the molecular weight is increased, the cohesive strength rises, caused by a greater density of molecular entanglements.[16] It is therefore obvious that an efficient bonding of the particles can be achieved by the coexistence of both high and low molecular weight species at an optimum level so that the low molecular weight species can enhance the wetting (thereby promoting adhesion), while the high molecular weight species contribute to the cohesive strength.

The molecular weight and the molecular weight distribution of the samples were determined, as discussed under ''Determination of Molecular Weight
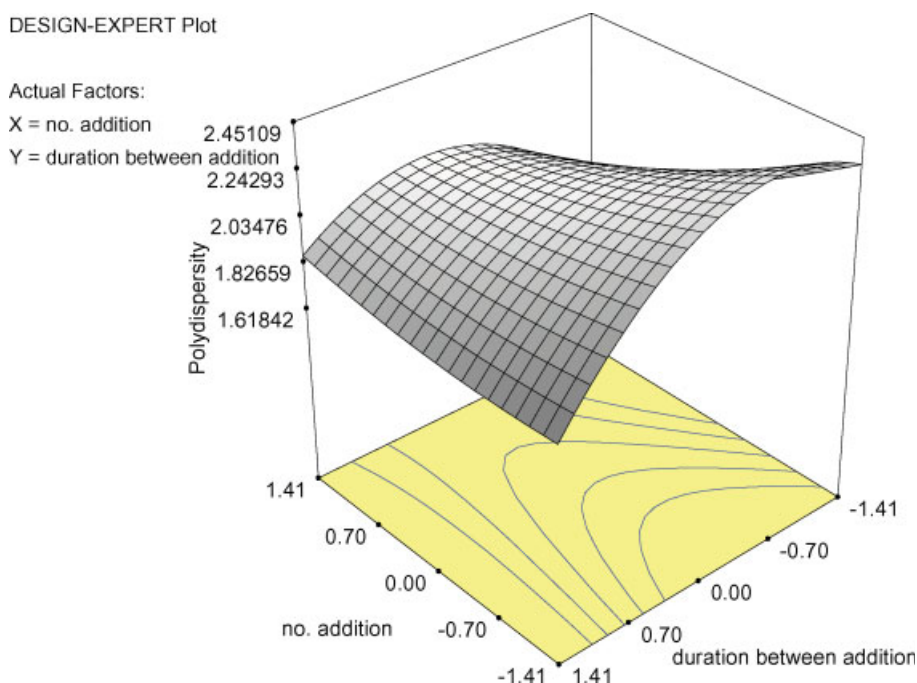
Figure 3 3D response surface plot of polydispersity as a function of number of additions and duration between additions in UF resins preparation in coded value. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Distribution'' in ''Physicochemical Methods for Characterization of the Urea Formaldehyde Resins'' section. The calibration curve showing the relationship between the retention time and the molecular weight for the PEG standard column is shown in Figure 1.

A typical SEC plot for the resin of Run 13 is given in Figure 2. It may be observed that UF resin contains molecules of different molar masses ranging from monomeric species to oligomers of different molecular masses and that the column has a good resolution to effectively separate the species for a quantitative determination of the molecular weights. It can also be seen from the Figure 2 that UF resin prepared by the acid cooking protocol consists predominantly two major category of species one with high molecular weight and the other with relatively very low molecular weight. This is an ideal situation wherein the high molecular weight polymer can impart high value of internal bond strength, while the low molecular weight species can promote good surface wetting and can thus be favorable for good adhesion.

Experimental data of polydispersity of UF resins are given in Table III. The data given in Table III were analyzed by Design-Expert Version 5 Software. A quadratic model (R-squared $= 0.98$; model $P = 0.0001$ and lack of fit $P = 0.44$) was found to fit the experimental data adequately. Besides the above statistical parameters, the adequacy of the quadratic model was further established by normal probability plots. The distribution of points close to a straight line (not shown) establishes the validity of the re-

sponse function for the data points. The quadratic model is depicted as 3D response surface in Figure 3.

The perturbation plots in Figure 4 show that there is an initial increase of polydispersity of UF resin followed by subsequent decrease when the ''duration between the additions'' increases from 7.93 to 22 min. On the other hand, the polydispersity decreases with the increasing ''number of additions.''
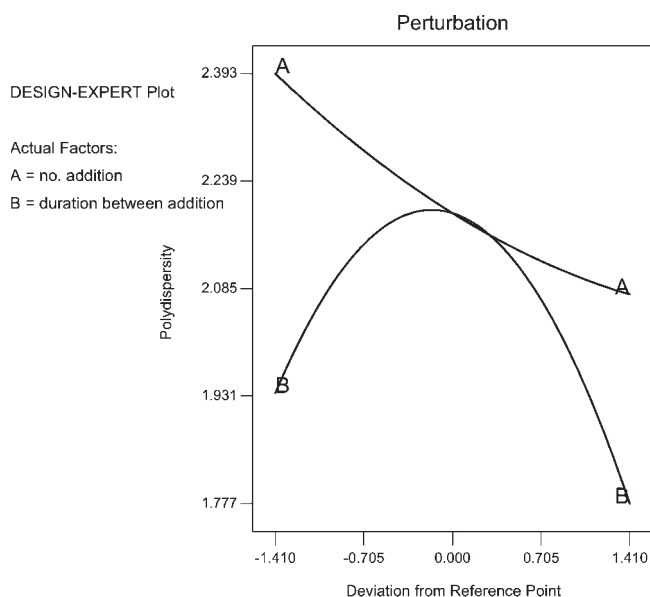

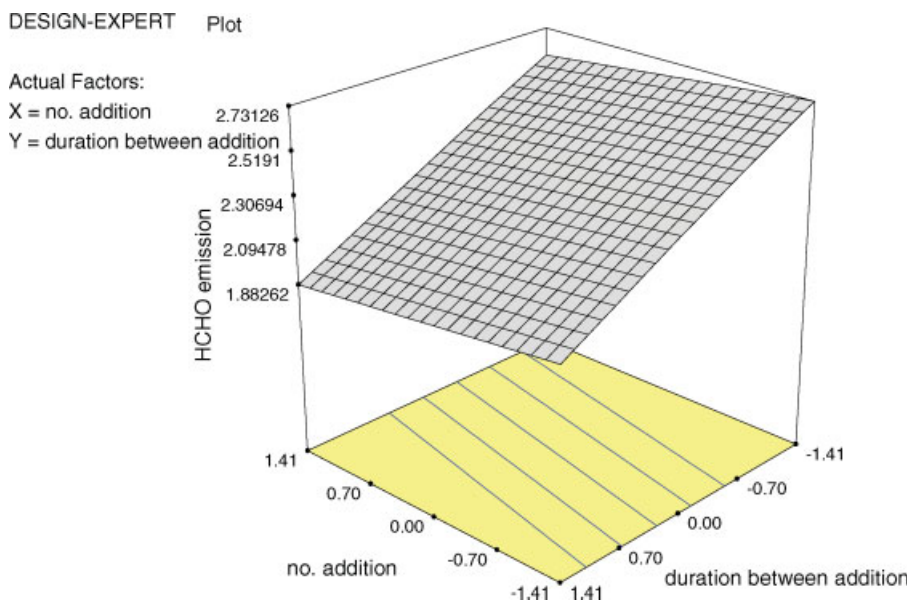**Figure 4** Polydispersity as a response of two factors UF resins preparation in perturbation plot.

Figure 5 3D response surface plot of formaldehyde emission as a function of number of additions and duration between additions in UF resins preparation in coded value. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Before trying to explain these findings, it is necessary to point out the implications of the variation of the "number of additions" and "the duration between the additions." For the same molar ratio between the formaldehyde and urea, as has been maintained in the present study, the total quantity of urea added to formalin is the same in all cases. However, when the "number of additions" is large, the quantity of urea added in each installment is small and *vice versa*. Similarly as the "duration between the additions" is more, more time is allowed between successive additions for the reaction to take place.

At the low levels of "number of additions" (i.e., as the number of additions of urea is small), the quantity of urea added to the reaction mixture for each installment (in Stage 2) is relatively large. It is likely that significant quantity of urea remained unreacted and as such carried forward to the next stage (Stage 3) of the reaction under reduced pH. The reaction product at the end of Stage 2 will thus consist predominantly of urea, some monomeric methylol ureas, and oligomers derived from Stage 1. In the Stage 3, the unreacted urea can undergo condensation reaction either with formaldehyde or with monomeric methylol ureas. The product of reaction after the Stage 3 will be (a) Oligomers, of relatively very low molecular weight, newly formed in Stage 3, (b) oligomers carried forward from Stage 1 whose molecular weight can be relatively higher. This system will be more heterogeneous with respect to molecular weight. Thus the polydispersity is high. But as the "number of additions" increases, the quantity of urea added in each installment is small. Urea can participate in methylolation reaction to a

greater extent to produce monomeric methylol ureas. Sufficient time is also available for favorable migration of hydroxyl methyl groups from oligomeric species (produced during the Stage 1 under strong acid environment) to unreacted urea. The ultimate result under these conditions is that the product is less heterogeneous. Therefore as the "number of additions" increases the polydispersity comes down.
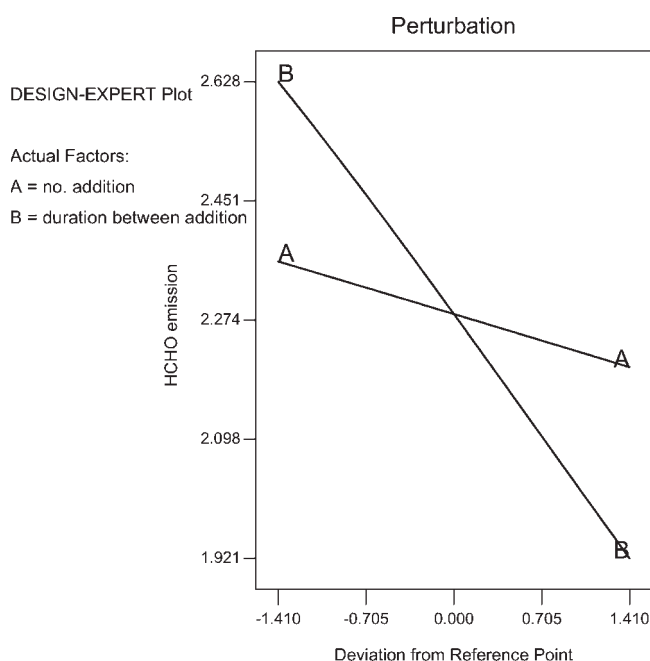

Figure 6 Formaldehyde emission as a response of two factors UF resins preparation in perturbation plot.
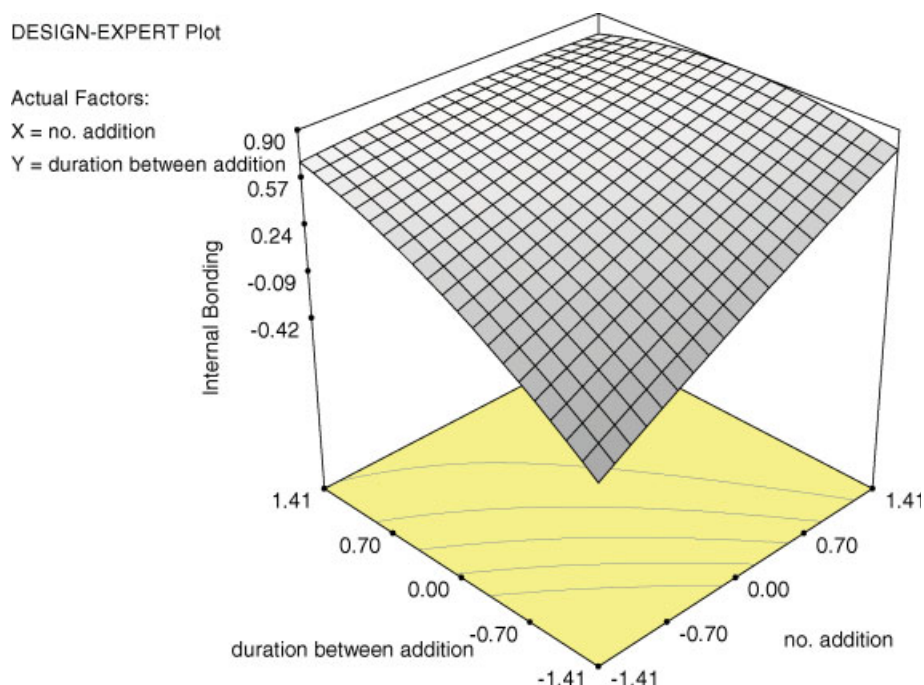
Figure 7 3D response surface plot of internal bonding as a function of number of additions and duration between additions in UF resins preparation in coded value. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Thus an equilibrium phenomenon similar to what is encountered in the silicone chemistry occurs. Accordingly, the sequential addition of urea and carrying out the reaction in the alkaline medium (Stage 2) followed by the reaction under the acidic conditions as adopted in the present study can be considered as an integrated equilibrium process where the polymer chain branches (methylol groups) are cleaved and transferred to added urea or other oligomers in a manner similar to the "equilibration process" known in the silicone chemistry.[17] Thus the technique of sequential addition of urea can be used as a means of preparing urea formaldehyde resins of a desired and unique molecular weight distribution for use in particleboards making.

Effect of "number of additions" and "duration between additions" on formaldehyde emission

Experimental data collected on formaldehyde emission from the particleboard made from urea formaldehyde resins are tabulated in Table III. It was analyzed by Design Expert 5.5 software and a linear model with appropriate transformation (Logit) [R-squared = 0.72; model $P = 0.02$ and a lack of fit $P = 0.78$] was found to fit adequately with the experimental data. The adequacy of the linear model is established by normal probability plot.

The effects of "number of additions" and "duration between of additions" on the formaldehyde emission are shown as 3D curve in Figure 5. Perturbation plot

in Figure 6 indicates that the formaldehyde emission levels decrease with the increasing of "number of additions" as well as the "duration between the additions." Furthermore, the duration between the additions was found to bring greater effect toward the formaldehyde emission, since the slope of line BB is steeper compared to AA. All these observations are again due to degree of conversion of urea on the one
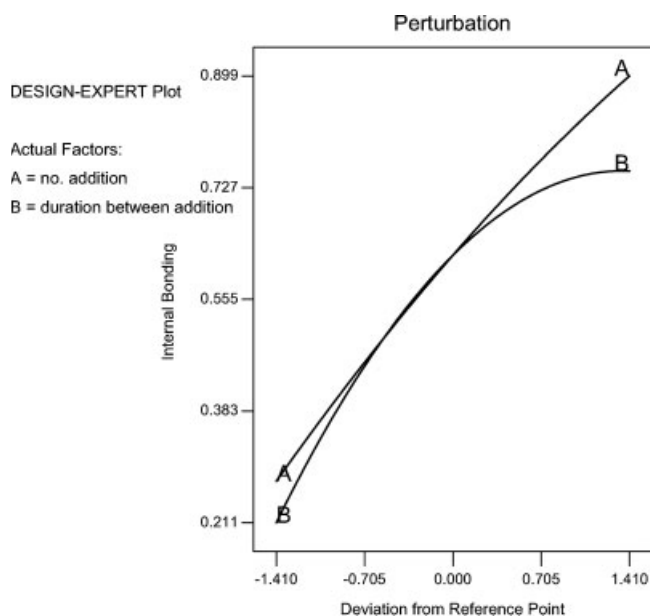

Figure 8 Internal bond strength as a response of two factors UF resins preparation in perturbation plot.

TABLE IV
Criteria for the Preparation for the
Environmental-Friendly UF Resins

Name	Goal
Number of addition	2.00–4.00
Duration between the additions (min)	10.00–20.00
ΔH (J/g)	−154.347 to −70.82
Weight average molecule, M_w (g/mol)	2475–9341
Number average molecule, M_n (g/mol)	2311–4156
Polydispersity	1.75–2.36
Internal bonding (N/mm^2)	Maximum
Formaldehyde emission (mg/100 g of boards)	Minimum

hand and the migration of the hydroxymethyl groups on the other, as discussed earlier. This is a phenomenon conducive to produce ideal oligomeric species favorable to the reduction of formaldehyde emission.

Lowest level of formaldehyde emission can be achieved at the point A when both number of additions and duration between the additions assume highest values within the range of studies as can be seen in Figure 5.

Effect of ''number of additions'' and ''duration between additions'' on internal bond strength of particleboards

Experimental data collected on internal bonding of particleboards made from the urea formaldehyde resins are given in Table III. The results when analyzed by Design Expert 5.5 software and a quadratic model (R-squared = 0.92; model $P = 0.01$ and lack of fit $P = 0.65$) was found to fit adequately with the experimental data. The adequacy of the quadratic model was further established by normal probability plot. The distribution of points close to a straight line establishes the validity of the response function chosen.

The effect of ''number of additions'' and ''duration between the additions'' on the internal bond strength of the particleboards made is shown in Figures 7 and 8. It can be observed that the increase in internal bond strength is associated with the increase in the ''number of additions'' as well as ''duration between

the additions.'' These results are suggestive of the possibility that the molecular weight distribution resulting from sequential addition procedure adopted in this work is favorable for a high internal bond strength. These results also agree with the observation by Pizzi,[4] who reported that the increase of the number of additions of urea during the preparation of the resin increases the bond strength. It is quite evident that the preparation of low-formaldehyde UF resins is based on existence of optimum proportions of oligomeric species of different molecular weights. The optimum amount of methylolated species on the polymer is necessary to maintain a high crosslink density and cohesion, and hence strength of the board.

The internal bond strength of the particleboard depends both on the strength of adhesion between the resin matrix and the particles, as well as on the cohesive strength within the resin matrix. This in turn depends on the molecular weight distribution in the resin. An efficient resin system should contain both low molecular weight as well as higher molecular weight oligomers. Low molecular weight species are efficient in wetting the wood particles and enhance adhesion, while the high molecular weight species contribute to the cohesive strength in the matrix phase. An efficient resin system is therefore one which ensures a compromise between the high molecular weight and low molecular weight species with a well defined polydispersity. The molecular weight distribution studies have shown how the polydispersity is influenced by the two factors ''number of additions'' and the ''duration between the additions.''

The RSM has been effective in uniquely defining the optimum molecular weight distribution, which would maximize the internal bond strength and minimize the formaldehyde emission.

Optimization

Optimization was an important aspect in the present work, which involved searching for a combination of factor levels that simultaneously satisfied the requirements placed on each of the several responses. Establishment of the appropriate mathematical model for each factor was the prerequisite for optimization. In the various subsections of the ''Results and Discussion''

TABLE V
Suitable Combination Resulting from the Numerical Optimization for the Preparation
of Environmental-Friendly UF Resins

Solutions	Number of additions	Duration between the additions (min)	ΔH	M_w	M_n	Polydispersity	Internal bonding	Formaldehyde emission	Desirability
1	2	16	−154.34	7696	3718	2.02	0.82	2.0568	0.808
2	2	16	−154.34	7731	3731	2.03	0.82	2.0584	0.806
3	1	16	−154.34	8275	3943.00	2.03	0.79	2.0914	0.765

TABLE VI
Comparison among Predicted Responses and Actual Experiments

Condition and Responses	Number of additions	Duration between the additions (min)	ΔH	M_w	M_n	Polydispersity	Internal bonding	Formaldehyde emission	Desirability
Solution 1	2	15.82	−154.34	7696	3717.92	2.02	0.82	2.0568	0.808
Sample	2	15.82	−152.22	7899	3882.65	2.05	0.79	2.0269	–

section above, various models have been experimentally determined and their validities have already been established. Now the final problem was

1. to determine the optimum levels of "number of additions" and the "duration between the additions," which maximized the internal bond strength of the particleboards and minimized the formaldehyde emission.
2. to determine the characteristic properties (namely the molecular weight).
3. to determine the molecular weight distribution and polydispersity.

Both the problems described above were solved by an elegant optimization method described by Myers and Montgomery[10] intended for application to practical situations involving multiple responses (as in the present work). In such systems where it is not possible to maximize or minimize all the responses simultaneously, some sort of compromise or "trade off" of some properties would become necessary. This method was based on an interesting procedure developed by Derringer and Suich[18]. The concept of "desirability function" has been introduced, which enables investigators to apply their own priorities and desires into the optimization procedure. This optimization method when applied creatively to the present system enabled us not only to establish optimum conditions for the process of making the UF resin but also to specify a complete characterization of the resin at the molecular level.

The above optimization was carried out numerically by employing the Design Expert Software. The desired goal for each parameter and response is first chosen. The allowable goals are (i) to maximize the response, (ii) to minimize the response, (iii) to target a specific level of parameter or response, and (iv) to keep the parameter or response within a specific range. Table IV stipulates the intended goal. The computer generates three solutions corresponding to the maximum internal bond strength and minimum formaldehyde emission as given in the Table V. This table also contains the important characteristics $\overline{M}_w$, $\overline{M}_n$, polydispersity) of the UF resin, which produces these optimum performance.

The optimum values corresponding to Solution 1 are adopted for the preparation of the UF resin. The properties of the UF resin so produced are given in Table VI. The predicted and the actually determined values are very close.

CONCLUSIONS

The effect of the sequential addition ("number of additions " and "duration between additions") of the urea to 50% formalin was studied for the preparation of the UF resins. On the basis of these studies, the process was optimized. Response surface methodology was employed for the studies. The responses were number and weight average molecular weights, polydispersity, internal bond strength, formaldehyde emission, percentages of reactive moieties, and inter-unit linkages of the oligomers. Size exclusion chromatography was used for the molecular weight distribution. Mathematical relationships between the process variables and the responses have been established. The results showed that the sequential addition ("number of additions" and "duration between the additions") of urea played a significant role in reducing the formaldehyde emission and increasing the internal bond strength. Further the variables have a strong effect on the molecular weight distribution, formaldehyde emission as well on the internal bond strength of the particleboards made by using the resin as adhesive. Optimum conditions of the preparation of the UF resin has been proposed by the aid of Design Expert software.

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