CHAPTER 5

DESIGNED EXPERIMENTS

5.1 Factor Selection

As NaOH is used to make melamine-formaldehyde resins reach pH 8.8 to 9.0, the factors involving the change in volume of NaOH at the reactor are F/M ratio, pH of melamine crystal, pH of formalin, and pH of water.

5.1.1 F/M ratio

As mentioned before in Chapter 3, F/M ratio is molar ratio of formalin to melamine crystal. Now the company employs F/M ratio of 2.0 in its process because this formula gives the company less material cost , in comparison with less F/M ratio such as 1.6 and 1.8. The F/M ratio of 1.6 and 1.8 are the most popular this industry as the European regulations for melamineware for food require no more than F/M ratio of 2.0. Also F/M ratio affects the curing time by the company's experience.

5.1.2 pH of melamine crystal

The pH of melamine crystal in the industry can broadly be divided into pH 8.0-8.7and pH 8.7-9.5. Melamine crystal pH 8.0-8.7 usually uses more volume of NaOH than its pH 8.7-9.5 to reach pH 8.8-9.0 of melamine-formaldehyde resin in each batch. Moreover, price by weight of melamine crystal is more expensive than that of formalin.

5.1.3 pH of formalin

In general, the pH of formalin of manufacturers is in the range of 4.0 to 5.0. However, the company uses the narrow range of formalin pH 4.5 to 4.8 .

5.1.4 pH of water

The pH 7.3-7.9 of water for using in the company's reactor is processed by a carbon tank and a resin tank. This two tanks are used together to produce softener water, which has suitable conditions for reaction in the reactor.

In addition, F/M ratio, melamine crystal pH, and formalin pH are independent each other, because F/M ratio represents proportion of formalin and melamine crystal by weight or volume, that is popular in the industry. Therefore, there will be only three types of product ratio as 1.6 or 1.8 or 2.0. Finally, we will define F/M ratio as another independent factor in this research.

Moreover, other factors at the reactor are temperature and stirring speed, which are fixed as a constant value of the company. Thus, the two factors will not be studied in this reseach.

5.2 Experiments and Statistical Tools

In this study, the four designed experiments consist of the factor screening experiments, the preliminary experiment, the experiment of finding suitable conditions, and the confirmation experiment. The statistical tools for these experiments are as follows.

5.2.1 Factor Screening Experiments

In the factor screening experiment, the 2^k factorial design for the four factors (k=4), each at two levels that are minimum and maximum level is employed to determine which factors affect the curing time or to screen some factors that do not affect the curing time out.

5.2.2 Preliminary Experiment

The method of 2^k factorial design for the two factors (k=2), each at two levels, is used to ensure the effects of F/M ratio and melamine crystal pH selected at random from the two tolerances, before an experiment for finding suitable conditions will be performed, so this experiment is called the preliminary experiment.

5.2.3 Experiment for Finding Suitable Conditions

In this experiment, the two-factor factorial design for 2 levels of melamine crystal pH and 3 levels of F/M ratio with the fixed effects model is employed to find suitable conditions in each level of the two factors.

5.2.4 Confirmation Experiment

The method of hypotheses testing is used to test the differences between two means and variances of the curing time in the laboratory and the process. Since the previous experiments are performed using the laboratory equipment, the curing time means and variance in each condition resulting from the laboratory equipment should be compared with those of the process.

Thus, the difference between the two curing time means and variances resulting from the laboratory and the process is tested using t-test and F-ratio test, respectively.

5.3 Equipment and Measuring Equipment for Experiments

5.3.1 Equipment for Experiment

The equipment used for the experiments comprises a laboratory reactor, a laboratory kneader, a drier in the process, and pot mills in the laboratory. The equipment can be used to produce small quantity of melamine compound that has the same characteristics as it produced by the process.

5.3.1.1 Laboratory Reactor

A laboratory reactor is used to produce melamine-formaldehyde resins of 1.6 kilograms a batch by heating and stirring melamine crystal, formalin, and water together. In Figure 5.1, elements of the laboratory reactor consist of

1. A heater can keep a heat level at 90 degrees of celsius.
2. A pot contains water, which transfers $90^{\circ}C$ heat to the mixture of raw materials in a reactor glass.

3. A reactor glass contains the mixture of melamine crystal, formalin, and water.
4. A thermometer.
5. A stirring system mainly comprises a stirring shaft and a motor.

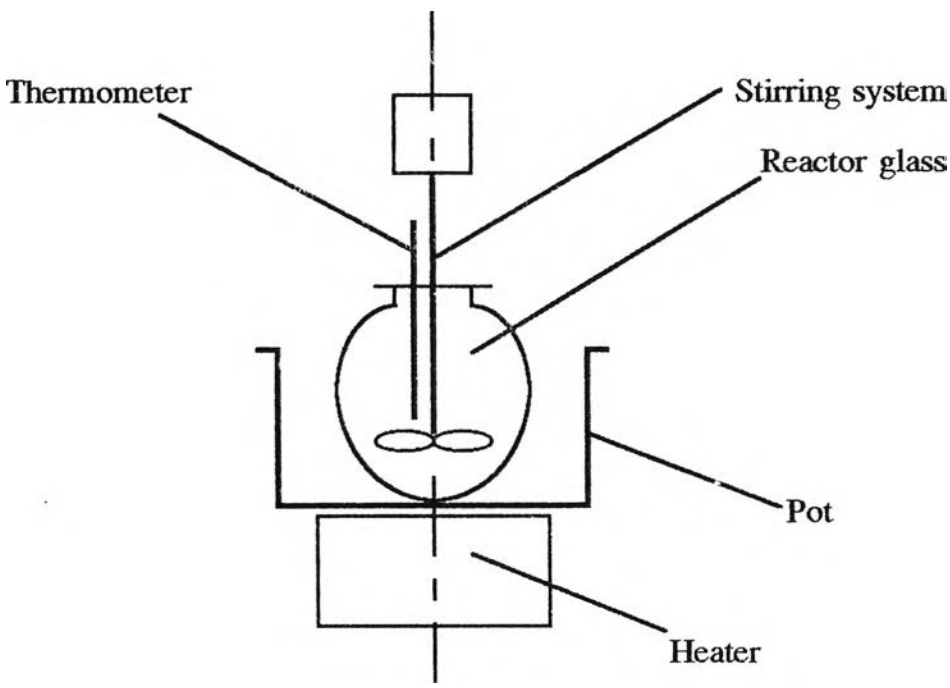

Figure 5.1 : The Laboratory Reactor

5.3.1.2 Laboratory Kneader

Pulp is broken, and then mixed with melamine-formaldehyde resin by this kneader comprising two solid blades and a kneader body as shown in Figure 5.2.

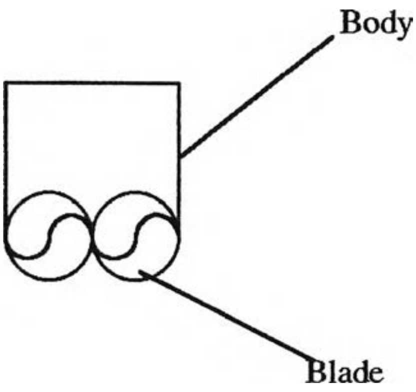

Figure 5.2 : The Laboratory Kneader

As the result of doing this experiment, wet popcorn about 1.8 kilograms a batch is produced.

5.3.1.3 Drier

A drier of the process is employed to dry wet popcorn by steam heating about 80-90°C. After finishing tis process, wet popcorn becomes dried popcorn.

5.3.1.4 Pot Mill

Pot mills of laboratory perform the same function as both turbo mills and ball mills of the process. Dried popcorn is ground by a pot mill, becoming nutural compound. The natural compound is milled again and is mixed with other additives by this pot mill, resulting in melamine compound.

The three parts of a pot mill consist of balls, a pot, and a rotating system as shown in Figure 5.3.

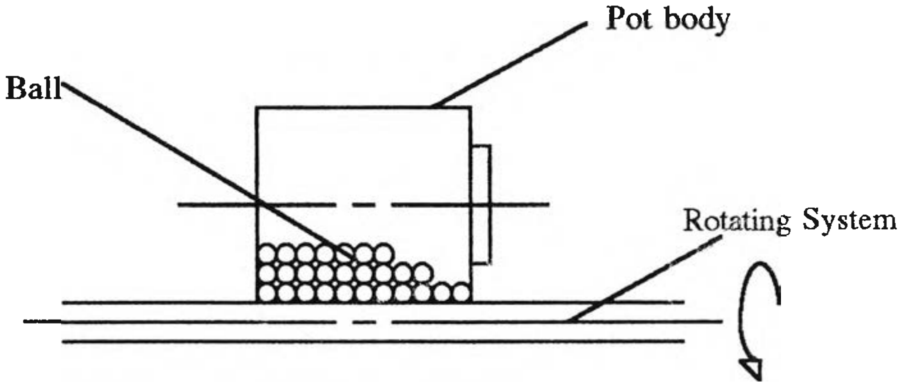

Figure 5.3 : The Pot mill

5.3.2 Measuring Equipment

The measuring equipment for the designed experiments comprises the pH meter that has accuracy of two-digit decimal for measuring pH of substances and the Rheometer for measuring the curing time of melamine compound.

5.4 Procedure for Experiments

The procedure for the four designed experiments are the following steps.

<u>At Laboratory Reactor</u>

1. Using pH meter for measuring pH of melamine crystal, formalin, and water used in each experiment.
2. Loading water, formalin, and melamine crystal into a reactor glass depending on the following formulas.

- F/M ratio of 1.6 uses 637 grams melamine crystal, 546 milliliters formalin, and 356 millimeters water for a batch of reactor.
- F/M ratio of 1.8 uses 616 grams melamine crystal, 596 milliliters formalin, and 324 millimeters water for a batch of reactor.
- F/M ratio of 2.0 uses 600 grams melamine crystal, 643 milliliters formalin, and 295 millimeters water for a batch of reactor.

3. The mixture in the reactor glass is heated and stirred at $90^{\circ}C$ and 200 rounds per minute.
4. After starting step 3. 10 minutes, checking pH of mixture. If the pH of mixture is less than 6.8, NaOH will be added to the mixture until pH 6.8.
5. After step 4. about an hour, breaking reaction and adjusting pH of the mixture, melamine-formaldehyde resin, by adding NaOH to the resin until its pH is 8.8-9.0.
6. Cooling the resin down till $45^{\circ}C$.

At Laboratory Kneader

7. Loading the resin of 1500 grams into the kneader.
8. Feeding pulp 300 grams to the kneader.
9. Adding 4.5 milliliters curing agent type 1 to the the mixture, after finishing step 8 about 30 minutes.
10. Adding 0.5 milliliters NaOH to make the wet popcorn reach pH 8.8-9.0.

At Drier

11. Bringing the wet popcorn to the drier in the process to be dried.

At Pot Mill

12. Loading the dried popcorn into a pot mill, and then it will be ground about 8 hours.
13. Adding 0.63 grams curing agent type 2 and 2.00 grams lubricant to natural compound in that pot mill.
14. Milling the mixture in the pot mill about 3 hours results in melamine compound.

At Rheometer

15. Measuring the curing time of the melamine compound.

5.5 Data Analysis

The data collected from the the four experiments is analyzed by the statistical tools as follows.

5.5.1 Factor Screening Experiments

The analysis of variance (ANOVA) can be employed to draw conclusions about the effect of the four factors, by comparison F_o with F_{α, v_1, v_2}, and α =0.05.

If F_o is more than F_{α, v_1, v_2}, the factor significantly affects the curing time.

If F_o is less than F_{α, v_1, v_2}, the effect of factor is not significant.

5.5.2 Preliminary Experiment

The ANOVA is used to analyse the main effect of factors and the interaction effect as follows.

The average effect of factor A, which is F/M ratio, factor B, which is melamine crystal pH, and interaction are :

$$A = \frac{1}{2n}[a + ab - b - (1)]$$

$$B = \frac{1}{2n}[b + ab - a - (1)]$$

$$AB = \frac{1}{2n}[ab + (1) - a - b]$$

where n replicates, a represents the treatment combination of A at the high level and B at the low level, b represents A at the low level and B at the high level, and ab represents both factors at the high level, and (1) is used to denote both factors at the low level.

And sum of squares are computed as follows.

$$SS_A = \frac{1}{4n}[a + ab - b - (1)]^2$$

$$SS_B = \frac{1}{4n}[b + ab - a - (1)]^2$$

$$SS_{AB} = \frac{1}{4n}[ab + (1) - a - b]^2$$

$$SS_T = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{n} y_{ijk}^2 - \frac{y_{...}^2}{4n}$$

$$SS_E = SS_T - SS_A - SS_B - SS_{AB}$$

The Analysis of Variance is summarized in Table 5.1.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_o
A treatments	SS_A	1	$MS_A = \frac{SS_A}{1}$	$F_o = \frac{MS_A}{MS_E}$
B treatments	SS_B	1	$MS_B = \frac{SS_B}{1}$	$F_o = \frac{MS_B}{MS_E}$
Interaction	SS_{AB}	1	$MS_{AB} = \frac{SS_{AB}}{1}$	$F_o = \frac{MS_{AB}}{MS_E}$
Error	SS_E	4(n-1)	$MS_E = \frac{SS_E}{4(n-1)}$	
Total	SS_T	4n-1		

Table 5.1 : The Analysis of Variance Table for Preliminary Experiment

If F_o of A treatments is more than $F_{0.05,\ 1,\ 4(n-1)}$, we conclude that factor A significantly affects the curing time. In the same way, if F_o of B treatments is more than $F_{0.05,\ 1,\ 4(n-1)}$, we conclude that factor B significantly affects the curing time. And if F_o of interaction is more than $F_{0.05,\ 1,\ 4(n-1)}$, we conclude that there is an interaction effect between the two factors on the curing time.

And the model adequacy of the experiment is checked by a normal probability plot and plots of residuals versus F/M ratio, melamine crystal pH, and fitted values. If the plot resembles a straight line in the normal probability plot and the largest standardized residual is not more than 3 or 4, and quite the same variance in the plots of residuals versus F/M ratio, melamine crystal pH, and fitted values. We can conclude that the model is adequate for the analysis of variance.

5.5.3 Experiment for Finding Suitable Conditions

The analysis of variance, which is employed for this experiment, is summarized in Table 5.2 . And the sums of squares in the table are computed as follows.

$$SS_T = \sum_{i=1}^{3}\sum_{j=1}^{2}\sum_{k=1}^{8} y_{ijk}^2 - \frac{y_{...}^2}{48} ,$$

$$y_{...} = \sum_{i=1}^{3}\sum_{j=1}^{2}\sum_{k=1}^{8} y_{ijk}$$

$$SS_A = \frac{1}{16}\sum_{i=1}^{3} y_{i..}^2 - \frac{y_{...}^2}{48}$$

$$SS_B = \frac{1}{24}\sum_{j=1}^{2} y_{.j.}^2 - \frac{y_{...}^2}{48}$$

$$SS_{AB} = \frac{1}{8}\sum_{i=1}^{3}\sum_{j=1}^{2} y_{ij.}^2 - \frac{y_{...}^2}{48} - SS_A - SS_B$$

$$SS_E = SS_T - SS_A - SS_B - SS_{AB}$$

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_o
F/M ratio	SS_A	2	$MS_A = \frac{SS_A}{2}$	$F_o = \frac{MS_A}{MS_E}$
Melamine Crystal pH	SS_B	1	$MS_B = \frac{SS_B}{1}$	$F_o = \frac{MS_B}{MS_E}$
Interaction	SS_{AB}	2	$MS_{AB} = \frac{SS_{AB}}{2}$	$F_o = \frac{MS_{AB}}{MS_E}$
Error	SS_E	42	$MS_E = \frac{SS_E}{42}$	
Total	SS_T	47		

Table 5.2 : The Analysis of Variance Table for the Experiment for Finding Suitable Conditions

If F_o of F/M ratio is more than $F_{0.05,\ 2,\ 42}$, we conclude that F/M ratio significantly affects the curing time. In the same way, if F_o of melamine crystal pH is more than $F_{0.05,\ 1,\ 42}$, we conclude that melamine crystal pH significantly affects the curing time. And if F_o of interaction is more than $F_{0.05,\ 2,\ 42}$, we conclude that there is an interaction effect between the two factors on the curing time.

And the model adequacy of the experiment is checked by a normal probability plot and plots of residuals versus F/M ratio, melamine crystal pH, and fitted values. If the plot resembles a straight line in the normal probability plot and the largest standardized residual is not more than 3 or 4, and quite the same variance in the plots of residuals versus F/M ratio, melamine crystal pH, and fitted values. We can conclude that the model is adequate for the analysis of variance.

Moreover, Duncan's multiple range test is employed to compare difference between the individual means of either factor at a particular level.

If the difference between two means resulting from two treatments is more than $R_p = r_\alpha(p,f)S_{\bar{y}_{ij.}}$, there is significant difference between the pair of means.
If the difference between two means resulting from two treatments is less than $R_p = r_\alpha(p,f)S_{\bar{y}_{ij.}}$, there is no significant difference between the pair of means.

5.5.4 Confirmation Experiment

The hypotheses testing is done for the following hypotheses.

$$H_0 : \sigma_1^2 = \sigma_2^2$$
$$H_1 : \sigma_1^2 \neq \sigma_2^2$$

where, σ_1^2 represents the variance of the curing time in the laboratory.

σ_2^2 represents the variance of the curing time in the process.

The two hypotheses are tested by computing $F = \dfrac{\sigma_1^2}{\sigma_2^2}$.

If F is between $F_{1-\frac{\alpha}{2}, n_1-1, n_2-1}$ and $F_{\frac{\alpha}{2}, n_1-1, n_2-1}$, we can not reject H_0 and conclude that the two variances are not different.

And the two hypotheses about two means of the curing time in the laboratory and the process are also tested :

$$H_0 : \mu_1 = \mu_2$$
$$H_1 : \mu_1 \neq \mu_2$$

where, μ_1 represents the mean of the curing time in the laboratory.

μ_2 represents the mean of the curing time in the process.

by $$T = \frac{\bar{x}_1 - \bar{x}_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

and $$S_p = \sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}}$$

If T is between $t_{-\frac{\alpha}{2}, n_1+n_2-2}$ and $t_{\frac{\alpha}{2}, n_1+n_2-2}$, we can not reject H_0 and conclude that there is no difference between the two means.