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# Random-design for the Technology of Emulsion Polymerization with High Solid Content and the Statistical Analysis of the Resultant Data

Chen Yang Zhao*, Shao Ying Li, Ying Gao, and Jin Song Ma

College of Materials Science and Engineering, Hebei University of Science Technology, Hebei, Shijiazhuang-050054, P.R.China

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## ABSTRACT

A novel randomly-arranged experimental design method (random-design) was employed to optimize the technology of emulsion polymerization with high solid content. In the case of the emulsion copolymerization of styrene, butyl acrylate (BA), and acrylic acid, six principal factors were chosen for random-design process. Then, regression analysis was used for the random-design experimental results by a known statistical analysis system (SAS). In turn, the optimal regression equations were established between the principal factors and the emulsion properties. It is shown that the particle size and size distribution are greatly affected by the following factors: the square values of the solid and emulsifier contents and the interactions between the initiator concentration and functional monomer concentration, BA concentration and reaction temperature, emulsifier content and reaction temperature, solid content and reaction temperature, and BA and functional monomers.

**Key Words:**

emulsion polymerization;
high solid content;
random-design method;
statistical analysis system;
interaction.

(*) To whom correspondence to be addressed:
E-mail: zhaojsh2005@163.com

## INTRODUCTION

The aqueous polymer latex synthesized by emulsion polymerization has been widely used in many fields due to its particular properties such as non-flammability, non-toxicity, odorless, and inexpensive. Nevertheless, the use of water also brings the disadvantages such as slow drying rate, high energy requirement in the drying process of coatings, storage, and transport. To enhance the solid content of the emulsion polymerization is a way to solve the above problems [1-3]. The viscosity of the reaction system, however, is sharply increased with increase in solid content, which in turn leads to the failure of emulsion stabilization. Until now, substantial research has been carried out on the

technology of emulsion polymerization with high solid content [4-6]. Emulsions with high solid content up to 70% and low viscosity have been studied at the same time [7,8].

It is recognized that the emulsion polymerization system is fairly complicated by the reaction factors which commonly interact and eventually affect the emulsion properties [9,10]. Thus, it is of great importance to understand the interactions among various reaction factors, and consequently to work out a desirable technology for emulsion polymerization with high solid content.

Experimental design plays a very important role in chemistry research, which still to a great extent within science it is a discipline based on experiments. An experiment with good design not only efficiently provides useful information, but also makes it convenient to achieve optimal experimental conditions. Up till today, there have been three major experimental design methods, including factorial design such as fractional factorial design and orthogonal design (OD) [11], optimal regression design, and uniform design (UD) [12-13]. OD Method has been a popular experimental design since 1950s which is widely used in various industrial or commercial fields. Optimal regression design method was originally introduced by Kiefer based on a pre-specified regression model. Later, Fang et al. proposed a uniform design concept based on quasi-Monte Carlo method or number-theoretic method which allows experimental points to be scattered uniformly over the domain. All the above experimental design methods share the same characteristic that when the practical factor-level combination fills the given matrix, it may change the uniformity of the original matrix. More recently, Zhang proposed a novel random-arranged experimental design method which intrinsically originated from orthogonal design method and was on the basis of uniform distribution experiments [14]. This method can directly give random experimental plans from the factor-level combinations by the computer in accordance with the three principles of experimental design. Subsequently, some of desirable plans were selected as the eventual experimental designs, according to five optimality criteria. The unique advantage of random design is that it is not restricted by the number of experimental factors and given values and it can directly fill the practical values in the matrix.

In this paper, we employed the random-design method for the study of emulsion polymerization with high solid content. Subsequently regression analysis was made for the random-designed experimental results by a known statistical analysis system (SAS) [15-17]. The method used in experimental design and analysis of high solid content emulsion is a new attempt. The interactions among influential factors were investigated and the regression models between the influential factors and the emulsion properties were settled to achieve a quantitative prediction of emulsion properties which is the main innovation of the article.

## EXPERIMENTAL

### Materials

Styrene (St) and butyl acrylate were purchased from Beijing Oriental Chemical Co., Acrylic acid (analytical grade) was obtained from Tianjing Institute of Chemical Reagent. AES was acquired from Beijing Hongkai Yongsheng Refinery Chemical Engineering Ltd. Co. OP-10 was bought from Guangzhou Huicai Coating Chemicals Ltd. Co. Ammonium persulphate (analytical grade) was purchased from Bejing Second Chemical Reagent Company. Sodium hydrogen carbonate (analytical grade) was obtained from Tianjing First Chemical Reagent Factory. *tert*-Butyl hydroperoxide (chemical grade) was obtained from Center Factory of Shanghai Chemical Reagent Exchange Station. Sodium formaldehyde sulphoxylate dehydrate (chemical grade) was purchased from Beijing Xudong Chemical Factory.

### Emulsion Preparation and Characterization

The monomers, emulsifier, cushioning reagent and deionized water were added into a 500 mL three-necked flask. Then the mixture was stirred at room temperature for 2 h to form pre-emulsion. One third of the above pre-emulsion was added into a 500 mL four-necked flask equipped with a mixer, thermometer and reflux condenser. After purging with nitrogen for 20 min, the reactor was subjected to a water bath with 55±1°C. When the required temperature was attained, the initiator was added dropwise. After polymerization, the remaining pre-emulsion was slowly added dropwise for some time. The polymerization continued for certain time and then it was stopped by cooling.

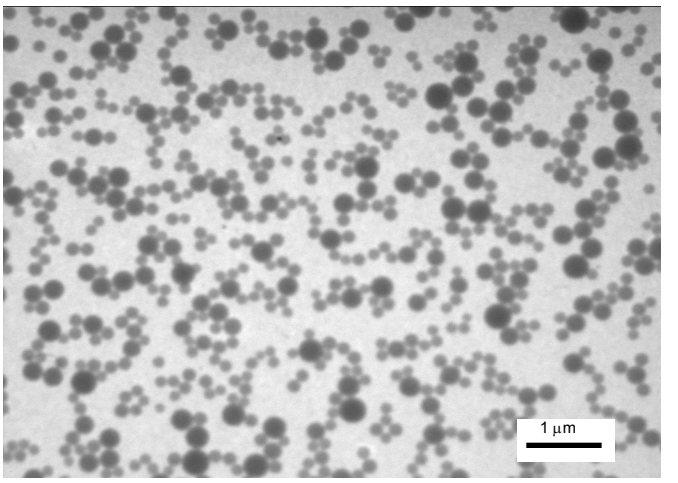
Diluted latexes were dropped onto a copper net with

a supporting membrane, TEM (Hitachi H-800, Japan) and SEM (S-250 SEM, Cambridge, England) techniques were employed to view the morphology of the latexes. The TEM micrographs were also used to measure the average particles size and for measuring their distribution an image analyzer (Kontron IBAS, Germany) was used. More than 5000 particles were covered in computation.

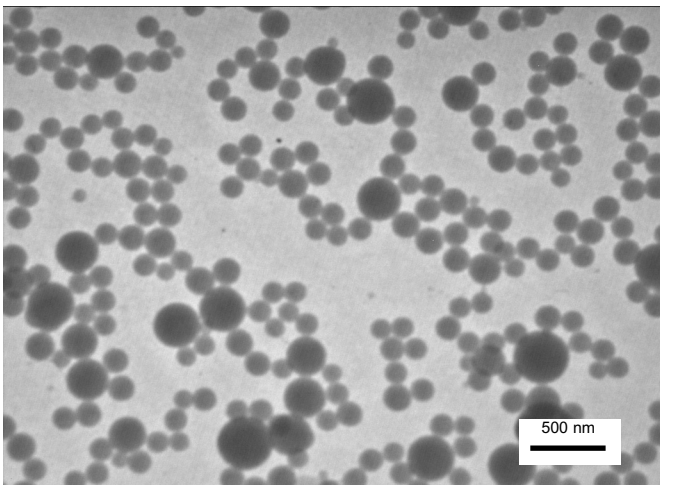
## RESULTS AND DISCUSSION

### Morphology of the Emulsion Particle with High Solid Content

Usually high solid content emulsion polymerization exhibits poor stability due to the higher viscosity that leads to failure of the whole reaction. In order to resolve this problem, larger particle diameter and expanded range of the particle size were chosen. Accordingly, particles were able to distribute extensively. Based on this modification, St/BA/AA copolymerized emulsion was prepared by means of pre-emulsification semi-continuous polymerization. The pre-emulsion semi- continuous polymerization makes sure that all the distributions of monomers are in the micelles of the emulsion and therefore a stable reaction to be achieved. Performance was characterized by TEM technique (Figures 1a and 1b). It can be seen in these figures that the particles have regular spherical shape and are bigger than those particles being formed in a normal process. This indicates that when the higher solid content is applied, the emulsion particle size also grows larger. The average diameter obtained is about several hundred nanometers. Meanwhile, the diameter of emulsion particle is randomly distributed. Smaller particles have greater chance to penetrate into the space between the larger particles, and in this way, the density is increased utmost.




(a)




(b)

**Figure 1.** TEM images of high solid content latex: (a) magnification ×1000 and (b) magnification × 2000.

### Random-design for the Experimental Plan

We carried out the random-design study in the case of the emulsion copolymerization of styrene (St), butyl acrylate (BA) and acrylic acid (AA). On the basis of some preliminary experiments, we have chosen six principal factors for random-design process, i.e., emulsion

**Table 1.** Selected experimental factors and the given values.

| Factors | Symbols | Given values |
|---|---|---|
| Emulsion solid content (wt%) | $a_1$ | 55.0 58.0 60.0 62.0 65.0 |
| Amount of monomer BA (wt%) | $a_2$ | 25.0 28.0 30.0 |
| Concentration of emulsifier (wt%) | $a_3$ | 2.0 2.5 3.0 |
| Concentration of initiator (wt%) | $a_4$ | 0.2 0.3 0.4 0.5 |
| Temperature of polymerization (°C) | $a_5$ | 50.0 54.0 58.0 62.0 65.0 |
| Concentration of functional monomer (wt%) | $a_6$ | 1.0 1.5 2.0 2.5 |

**Table 2.** Five optimality indices in experiment design matrix.

| Cn | De | Sd | Ao | Do |
|---|---|---|---|---|
| 2.71886 | 0.8337 | 187.6 | 1.1180 | 0.94780 |

solid content ($a_1$), concentration of monomer BA ($a_2$), concentration of emulsifier ($a_3$), concentration of initiator ($a_4$), temperature of polymerization ($a_5$) and concentration of functional monomer ($a_6$). Table 1 shows the experimental factors and the given values.

By using the random-design program on the computer, some design matrixes were randomly given from the above factor-levels. Then we tested the optimality and uniformity of the designs to find out a good plan in terms of five criteria including condition number squared (Cn), discrepancy (De), the maximum symmetric difference (Sd), A-optimality (Ao), and D-optimality (Do), as shown in Table 2.

The approach of Cn to 1.0 would indicate a better orthogonalization of the design matrix and normally an acceptable value could be less than 10.0, while a high value of Sd and low values of De, Ao, and Do would mean better optimality. On the basis of these criteria, the design gave 12 experimental plans and subsequently we conducted all these random-designed experiments. These results were presented in Table 3.

**Statistical Analysis of the Resultant Data**

Using statistical analysis system (SAS) software we conducted a regression analysis of the results of the experiments arranged by the random-design method. Besides the independent variables of $a_1 - a_6$ shown in Table 2, we have also reproduced 21 dummy variables in the regression model of SA, in view of the interaction effects among the reaction factors. These newly built variables are: $a_7 = a_1 \times a_1$; $a_8 = a_2 \times a_2$; $a_9 = a_3 \times a_3$; $a_{10} = a_4 \times a_4$; $a_{11} = a_5 \times a_5$; $a_{12} = a_6 \times a_6$; $a_{13} = a_1 \times a_2$; $a_{14} = a_1 \times a_3$; $a_{15} = a_1 \times a_4$; $a_{16} = a_1 \times a_5$; $a_{17} = a_1 \times a_6$; $a_{18} = a_2 \times a_3$; $a_{19} = a_2 \times a_4$; $a_{20} = a_2 \times a_5$; $a_{21} = a_2 \times a_6$; $a_{22} = a_3 \times a_4$; $a_{23} = a_3 \times a_5$; $a_{24} = a_3 \times a_6$; $a_{25} = a_4 \times a_5$; $a_{26} = a_4 \times a_6$; $a_{27} = a_5 \times a_6$, representing the interaction effects among the corresponding variables, respectively.

**Regression Analysis of Particle Size by SAS Software**

It is recognized that the linearity constant $R^2$ increases with the number of variables, and meanwhile the equation shows good stability. Many regression equations have been obtained by SAS software. However, in accordance with the principles of regression analysis as well as the knowledge of emulsion polymerization, we eventually selected $a_7$, $a_9$, $a_{20}$, and $a_{26}$ as the variables of optimum regression equation ($D_n$) of average particle size. The corresponding linearity constant $R^2$ was 0.83 and the range of condition number was 1.09-16.89 which indicated that the linearity and stability of the regression equation was fairly good. From the data in

**Table 3.** Design matrix obtained by adopting the random-design method and the corresponding experimental results.

| No. | $a_1$ (wt%) | $a_2$ (wt%) | $a_3$ (wt%) | $a_4$ (wt%) | $a_5$ (°C) | $a_6$ (wt%) | $D_n$ (nm) | U |
|---|---|---|---|---|---|---|---|---|
| 1 | 60.0 | 25.0 | 2.0 | 0.3 | 62.0 | 1.0 | 256 | 1.56 |
| 2 | 58.0 | 28.0 | 3.0 | 0.2 | 62.0 | 1.5 | 190 | 1.31 |
| 3 | 60.0 | 28.0 | 2.0 | 0.5 | 62.0 | 2.0 | 290 | 1.54 |
| 4 | 65.0 | 25.0 | 2.5 | 0.3 | 58.0 | 2.5 | 306 | 1.43 |
| 5 | 62.0 | 30.0 | 3.0 | 0.5 | 58.0 | 2.5 | 328 | 1.25 |
| 6 | 55.0 | 28.0 | 2.5 | 0.4 | 54.0 | 2.0 | 184 | 1.09 |
| 7 | 58.0 | 28.0 | 2.5 | 0.2 | 50.0 | 1.5 | 152 | 1.28 |
| 8 | 65.0 | 30.0 | 2.5 | 0.4 | 54.0 | 1.0 | 297 | 1.46 |
| 9 | 58.0 | 28.0 | 2.5 | 0.5 | 54.0 | 1.5 | 214 | 1.12 |
| 10 | 62.0 | 28.0 | 3.0 | 0.4 | 65.0 | 1.5 | 223 | 1.06 |
| 11 | 60.0 | 30.0 | 2.0 | 0.3 | 65.0 | 2.5 | 279 | 1.69 |
| 12 | 62.0 | 25.0 | 2.5 | 0.3 | 58.0 | 2.0 | 201 | 1.32 |

$D_n$: the number average size of latex (nm); U: coefficiency of dispersion.

**Table 4.** Four groups of optimum combinations constructing $D_n$ linear model prediction.

| $a_1$ (wt%) | $a_2$ (wt%) | $a_3$ (wt%) | $a_4$ (wt%) | $a_5$ (°C) | $a_6$ (wt%) | $D_n$ (nm) |
|---|---|---|---|---|---|---|
| 65.0 | 30.0 | 2.0 | 0.5 | 65.0 | 2.5 | 397 |
| 65.0 | 27.0 | 2.0 | 0.5 | 65.0 | 2.5 | 380 |
| 64.0 | 28.0 | 2.0 | 0.5 | 65.0 | 2.5 | 375 |
| 65.0 | 28.0 | 2.5 | 0.5 | 65.0 | 2.5 | 370 |

Table 4 we reached the regression equation of particle size as follows:

$$D_n = -278.7966 + 0.1042\ a_7 - 8.0510\ a_9 + 0.0848\ a_{20} + 83.8146\ a_{26} \quad (1)$$

since the dummy variables were $a_7 = a_1 \times a_1$, $a_9 = a_3 \times a_3$, $a_{20} = a_2 \times a_5$, and $a_{26} = a_4 \times a_6$, then eqn (1) could be converted into:

$$D_n = -278.7966 + 0.1042\ a_1 \times a_1 - 8.0510\ a_3 \times a_3 + 0.0848\ a_2 \times a_5 + 83.8146\ a_4 \times a_6 \quad (2)$$

by making linear replacement of the equation parameters, we obtained a standardized form of the regression equation as follows:

$$D_n = 0.65989\ a_1 \times a_1 - 0.26285\ a_3 \times a_3 + 0.25688\ a_2 \times a_5 + 0.43899\ a_4 \times a_6 \quad (3)$$

from the above standardized regression equation, it is possible to find out how the selected variables affect the dependent variables as well as their direction. Thus some significant conclusions can be obtained as follows.

1. The contribution of influential factors to average particle size follows this sequence: solid content of emulsion squared, the interaction between the concentrations of initiator and functional monomer, amount of emulsifier squared and the interaction between the amount of BA monomer and reaction temperature.
2. The solid content of emulsion affects the average particle size in a positive way. The higher the solid content, the larger the latex particles would reach.
3. Positive interactions also exist between the concentrations of initiator and functional monomer. The higher the initiator concentration, the more notable would be the contribution of functional monomer to the average particle size.
4. The amount of emulsifier has negative effect on particle size, which means that the average particle size would become small with increase in emulsifier concentration.
5. Positive interactions exist between the amount of BA monomer and reaction temperature, indicating that when the amount of BA monomer is high the reaction temperature has greater influence on the average particle size.

From numerous optimum combinations for particle sizes predicted according to this equation we have selected four combinations as presented in Table 4.

**Regression Analysis of Particle Size Distribution by SAS Software**

Similarly, we also obtained many regression equations by SAS software with regard to the particle size distri-

**Table 5.** Comparison between experimental data and model predictions*.

| $a_1$ (wt%) | $a_2$ (wt%) | $a_3$ (wt%) | $a_4$ (wt%) | $a_5$ (°C) | $a_6$ (wt%) | d (nm) | u | $D_n$ (nm) | U | $\delta_1$ | $\delta_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 65.0 | 28.0 | 2.0 | 0.5 | 55.0 | 1.0 | 301 | 1.48 | 324 | 1.39 | -7.1 | +9 |
| 65.0 | 30.0 | 2.5 | 0.3 | 58.0 | 1.0 | 284 | 1.45 | 315 | 1.56 | -9.8 | -7 |
| 64.0 | 29.0 | 2.5 | 0.4 | 65.0 | 1.5 | 308 | 0.231 | 285 | 0.209 | +7.5 | +9.5 |

(*) d and u are the predicted values obtained by equations (3) and (6), $D_n$ and U are the experimental values; $\delta_1$ and $\delta_2$ are the errors of the predicted values from models $D_n$ and U, respectively. The calculation is as follows: $\delta_1 = (d - D_n)/D_n$; $\delta_2 = (u-U)/U$

**Table 6.** Four groups of optimum combinations constructing U linear model prediction.

| $a_1$ (wt%) | $a_2$ (wt%) | $a_3$ (wt%) | $a_4$ (wt%) | $a_5$ (°C) | $a_6$ (wt%) | U |
|---|---|---|---|---|---|---|
| 65.0 | 30.0 | 2.0 | 0.2 | 65.0 | 2.5 | 1.9 |
| 65.0 | 30.0 | 2.0 | 0.2 | 65.0 | 1.5 | 1.8 |
| 64.0 | 25.0 | 2.0 | 0.2 | 65.0 | 2.0 | 1.8 |
| 65.0 | 29.0 | 2.0 | 0.2 | 65.0 | 1.5 | 1.8 |

bution. We have selected $a_4$, $a_{16}$, $a_{21}$ and $a_{23}$ as the variables in optimum equation of particle size distribution. The $R^2$ of the equation is 0.82, and the range of condition number is 1.21-18.13. The linearity and stability of the equation is good. From the data in Table 5 we have obtained the regression equation of particle size distribution as follows:

$$U = 0.92753 - 0.54542\ a_4 + 0.00042\ a_{16} + 0.00160\ a_{21} - 0.00646\ a_{23} \quad (4)$$

since $a_{16}=a_1\times a_5$, $a_{21}=a_2\times a_6$, and $a_{23}=a_3\times a_5$, eqn (4) can be converted into:

$$U = 0.92753 - 0.54542\ a_4 + 0.00042\ a_1\times a_5 + 0.00160\ a_2\times a_6 - 0.00646\ a_3\times a_5 \quad (5)$$

eqn (6) is the standardized form of the regression equation:

$$U = -0.29699\ a_4 + 0.74706\ a_1\times a_5 + 0.12740\ a_2\times a_6 - 0.80815\ a_3\times a_5 \quad (6)$$

From the regression equation, we reach the following conclusions:

1. The contribution of the influential factors to particle size distribution follows the sequence: the interaction between emulsifier and reaction temperature, the interaction between solid content and reaction temperature, and the interaction between BA and functional monomers.
2. The emulsifier and reaction temperature affect the particle size distribution in a negative way. The higher the emulsifier content, the less likely the reaction temperature affected the particle size distribution.
3. The solid content and reaction temperature affect the particle size distribution in a positive way. The higher the solid content, the greater the reaction temperature affected the particle size distribution.
4. The amount of initiator affected the particle size distribution in a negative way. The higher the amount of initiator, the narrower the particle size distribution would be.
5. The concentrations of BA and functional monomers affected the particle size distribution in a positive way. At higher BA monomer concentration, the concentration of functional monomer affected the particle size distribution more.

From numerous optimum combinations for particle size distributions predicted according to this equation, we have selected four combinations as presented in Table 6.

**Reliability Test of the Regression Equation**

SAS has also made a diagnosis of the established regression equation and has worked out the optimized values from the model. In order to test the reliability of this model, we carried out two other experiments. These experimental results in combination with the predicted results are shown in Table 5.

From the data in Table 5, we can find that there exist some errors between the predicted values from models $D_n$ and U and the experimental values. This may result from the fluctuation of the technological process in emulsion preparation and the measurement error. However, the error is not higher than ±10% indicating that these models can be reasonably used to describe the actual cases.

## CONCLUSION

In view of the complexity of the reaction factors in emulsion polymerization and the results obtained we can conclued as follows:

- By selecting six principal factors to conduct the ran-

dom-design process, the optimum experimental conditions for emulsion polymerization with high solid content were achieved.

- Using SAS software, the experimental results were analyzed. The major influential factors to average particle size are solid content of emulsion squared, the interaction between the concentrations of initiator and functional monomer, amount of emulsifier squared, and the interaction between the amount of BA monomer and reaction temperature.
- The major influential factors on particle size distribution were found to be the interaction between emulsifier and reaction temperature, the interaction between solid content and reaction temperature, and the interaction between BA and functional monomers.

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