

Batch Emulsion Polymerization of Vinyl Chloride: Application of Experimental Design to Investigate the Effects of Operating Variables on Particle Size and Particle Size Distribution

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ABSTRACT: In this article, the influences of operating variables on the particle size (PS) and particle size distribution (PSD) of emulsion poly(vinyl chloride) in batch reactor were investigated using Taguchi experimental design approach. The variables were temperature (T), water to monomer weight ratio (R), concentrations of initiator ([I]) and emulsifier ([E]), and agitation speed (S). Scanning electron microscope was used together with image analysis software to determine the PS and PSD. Statistical analysis of results revealed that the PS of emulsion poly(vinyl chloride) strongly depends on emulsifier and initiator concentrations, respectively, whereas the other factors have no significant

effects in the range of levels investigated in this study. Except initiator concentration, all factors have important influence on the PSD (significance sequence: $S > R > T > [E]$). It is implied from the greater influence of agitation speed relative to temperature on PSD that the shear coagulation predominates the Brownian coagulation in this system. The relative optimum condition for a typical paste application was also determined using overall evaluation criteria. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 338–347, 2009

Key words: emulsion polymerization; particle size distribution; poly(vinyl chloride); electron microscopy

INTRODUCTION

The particle size (PS) and particle size distribution (PSD) in emulsion polymerization of vinyl chloride are two important characteristics influencing the processability of the latex, and the final quality of product.¹ One of the most conventional forms of emulsion poly(vinyl chloride) (e-PVC) applications is plastisol (a stable dispersion of e-PVC particles in plasticizer).² The application properties of plastisol such as rheology and film formation are strongly dependent on the PS and PSD. Small particles in plastisol result in high viscosity media, whereas in paste applications (like in manufacturing of artificial leather), the presence of large particles is essential to prepare low viscosity plastisol, and a wide PSD is desirable.² In processing of e-PVC, when the plastisol is heated up to 180–200°C, it undergoes two processes, known as gelation and fusion. It is dem-

onstrated that the gelation rate increases with decreasing the PS due to more interactions between particles and plasticizer.³ Furthermore, the proper shape and size distribution affect the fusion phenomenon which is of importance in efficient performance of the processing machines.⁴

During the emulsion polymerization, PS and PSD are governed by interplay of three major phenomena, called nucleation, growth, and aggregation of the polymer particles. Although the nucleation period is quite short, the generation of particle nuclei during the early stage of the polymerization plays a crucial role in determining the mean particle size (MPS) and PSD of final latex.⁵ The PSD is believed to be a consequence of the distribution of times at which different polymer particles are nucleated.⁶ As vinyl chloride monomer (VCM) is slightly soluble in water, the particle nucleation occurs through both homogeneous and heterogeneous mechanisms. Entering the radicals into the micelles, and then reaction with diffused monomer, lead to heterogeneous or micellar nucleation. On the other hand, the reaction of dissolved monomers in water with the radicals, forms polymer particles that grow until they reach a critical size and then precipitate (homogeneous nucleation).⁷ The particles formed by these two mechanisms don't differ essentially and are

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TABLE I
Selected Factors and Their Levels

Description	Factors		Levels		
	Unit	Symbol	1	2	3
Temperature	°C	T	46	53	60
Emulsifier conc.	g/L	[E]	1	4	7
Initiator conc.	g/L	[I]	0.4	2	3.6
W/M ratio	g/g	R	1.2	1.9	2.6
Agitation speed	rpm	S	200	300	400

known as primary particles. These primary particles then may simply grow by conversion of monomer to polymer within these particles, or undergo aggregation. The aggregation of particles decreases the number of particles and thus affects both MPS and PSD.⁸

The formation of aggregates in the latex is caused by a loss of colloidal stability of the particles. Destabilization may be accelerated by reducing the electrostatic repulsion between the particles and also by increasing the average kinetic energy of the particles. The former can be affected by physicochemical parameters like initiator and emulsifier concentrations. But, the kinetic energy of particles is influenced by process variables; say agitation speed and temperature.^{9,10}

The process and reaction variables may affect the nucleation, growth, and aggregation mechanisms, and thus the PS properties.^{4,11-16} In spite of various articles published on this field, no report is available suggesting application of experimental design for quantified and comparative analysis of operating variables effects on the MPS and PSD, especially for emulsion polymerization of VCM.

In this study, the influences of temperature (T), emulsifier and initiator concentrations ([E] and [I]), water to monomer weight ratio (R) and agitation speed (S), on MPS and PSD of e-PVC in batch reactor have been statistically investigated using Taguchi experimental design approach. Scanning electron microscopy (SEM) with an image analyzing software has been utilized for PS and PSD determination.

EXPERIMENTAL

Experimental design

The conventional approach in process evaluation involves changing one parameter at a time. This approach requires numerous experimental runs to fully explore the entire parameter space. In this respect the experimental design approach including Taguchi method can reduce the number of experiments while retaining data collection quality.

The first important step in design of experiment is the proper selection of factors and their levels. In this study, five operating factors (temperature, emulsifier and initiator concentrations, water to monomer weight ratio, and agitation speed) were considered in three levels (Table I). The factors and their levels have been chosen according to a literature review on previous publications on the emulsion polymerization of vinyl chloride. For design of experiments with five factors and three levels for each factor, a standard L₁₈ orthogonal array was employed (Table II). Each row of the matrix represents one run at specified condition. To avoid the systematic bias, the

TABLE II
Taguchi Experimental Design Based on Coded Levels, and the Statistical Parameters Obtained from Image Analysis of SEM Micrographs

Run no.	Factors and their levels					Measured parameters			
	T	[E]	[I]	R	S	d _{min} (μm)	d _{max} (μm)	MPS (μm)	PSD (variance)
1	1	1	1	1	1	0.0740	2.3730	0.2890	0.0220
2	1	2	2	2	2	0.0740	0.9490	0.2250	0.0226
3	1	3	3	3	3	0.0409	2.0300	0.2160	0.0422
4	2	1	1	2	2	0.0409	1.4560	0.3590	0.0984
5	2	2	2	3	3	0.0740	2.5140	0.2690	0.0854
6	2	3	3	1	1	0.0409	3.2250	0.2100	0.0487
7	3	1	2	1	3	0.0372	1.8900	0.4780	0.0744
8	3	2	3	2	1	0.0409	2.2460	0.2030	0.0470
9	3	3	1	3	2	0.0409	0.9250	0.1422	0.0197
10	1	1	3	3	2	0.0409	1.7400	0.3318	0.0314
11	1	2	1	1	3	0.0573	0.7630	0.1683	0.0157
12	1	3	2	2	1	0.0371	1.9930	0.2410	0.0395
13	2	1	2	3	1	0.0573	1.8420	0.3150	0.0233
14	2	2	3	1	2	0.0746	2.9550	0.2280	0.0207
15	2	3	1	2	3	0.0746	4.8580	0.3100	0.1110
16	3	1	3	2	3	0.0573	5.2200	0.2890	0.1160
17	3	2	1	3	1	0.0409	1.1230	0.1010	0.0190
18	3	3	2	1	2	0.0543	1.5950	0.2690	0.0326

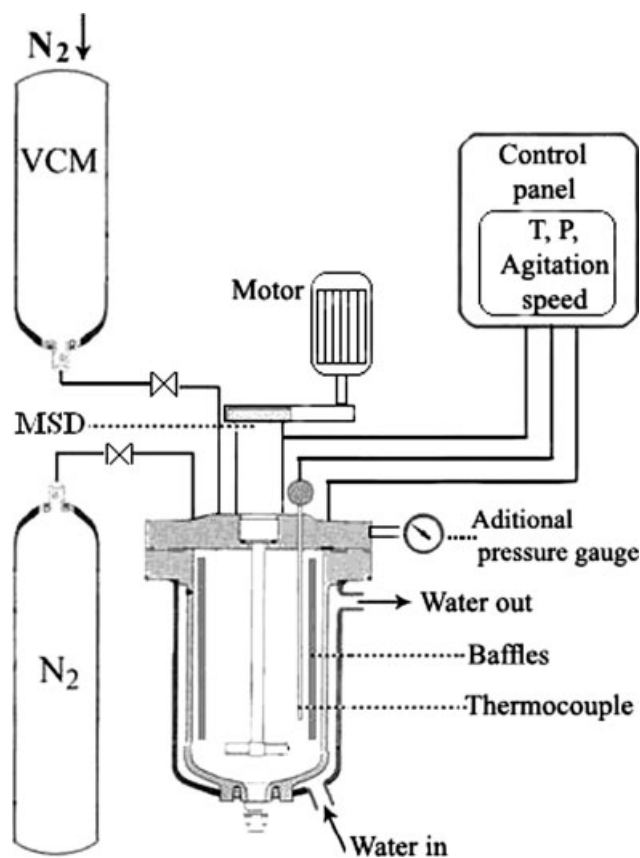


Figure 1 Schematic representation of the experimental set up.

sequence in which these runs were carried out was randomized.^{17,18}

Materials

VCM was kindly supplied by Bandar Imam Petrochemical Company (Iran). A gas chromatography analysis showed a purity of 99.994% for this monomer. Merck grades of potassium persulfate, sodium dodecyl sulfate (SDS) and sodium bicarbonate (all with purity over 99.99%), were used as initiator, surfactant and pH regulator, respectively. Deionized water (with conductivity below 0.9 $\mu\text{S}/\text{cm}$ at 25°C) was used throughout the work.

Emulsion polymerization

A 6-L jacketed stainless steel reactor was used for batch emulsion polymerization of VCM. The reacting mixture was stirred by a turbine type impeller, which was connected to a magnetic seal drive (MSD) to prevent gas leakage. The reactor wall was equipped with two rectangular baffles. The emulsion temperature was measured by a thermocouple placed inside the reactor, and was controlled by a circulating water system. A schematic of experimental set up is shown in the Figure 1.

For polymerization, the reactor was first charged with water. The system was then warmed up (to about 40°C) and purged by nitrogen while stirring, to eliminate the dissolved oxygen. The emulsifier was used in compressed form to control the foaming in the reactor before charging the VCM.¹⁹ The initiator (in powder form) and pH regulator (0.1 N) were also added. The reactor was then heated to reaction temperature, and the desired amount of VCM was charged by nitrogen pressure. This time was considered as the start of reaction. The reaction was followed for 3 h and at the end of reaction hydroquinone was added to the reaction mixture to terminate the polymerization.¹⁴

Characterization method

Among various methods including dynamic light scattering, sieving, sedimentation, centrifugation, coulter counter, and electron microscopy; SEM plus image analyzer software have been proved to be a reliable method for determination of MPS and PSD.^{3,4,20–22} The most advantages of this method, is its sensitivity to PSs as small as 0.1 μm , and also its capability to give additional information on morphology.

In this study, the MPS and PSD of the final latex was measured using SEM and image analysis software. The latex sample was first diluted with bidistilled water, to eliminate the emulsifier. The solution was then put in ultrasonic bath to disperse the particles, and finally one drop was placed on a slide, and dried.²¹ This method was applied identically to all 18 samples to keep a similar condition for sample characterization and analysis.

For viewing in SEM (Phillips XL30), a 50 nm gold film was sputtered on the surface with a Sputter Coater (BAL-TEC. SCD 005) to make it conductive and to prevent charging in the electron beam.²¹ Mahmud et al.⁴ have suggested that for statistical validation of the results, the number of PVC particles in the SEM micrograph should be more than 430. We chose a 1000 times dilution and magnification of 1200 \times , to satisfy these criteria.

The average PS in each micrograph was determined by means of Sigma Scanpro5[®] software (version 5.0), in which the surface area of each particle was measured by filling the surface with pixels. The number of pixels (NP) is then equaled to the surface area of a circle, so that the equivalent circular diameter (ECD) is obtained in dimension of pixel numbers²³:

$$\text{ECD} = \left(\frac{4(\text{NP})}{\pi} \right)^{1/2} \quad (1)$$

Comparing the number of pixels in micrograph width, and the scale given in bottom of micrograph, the ECD is converted to micrometer dimension.

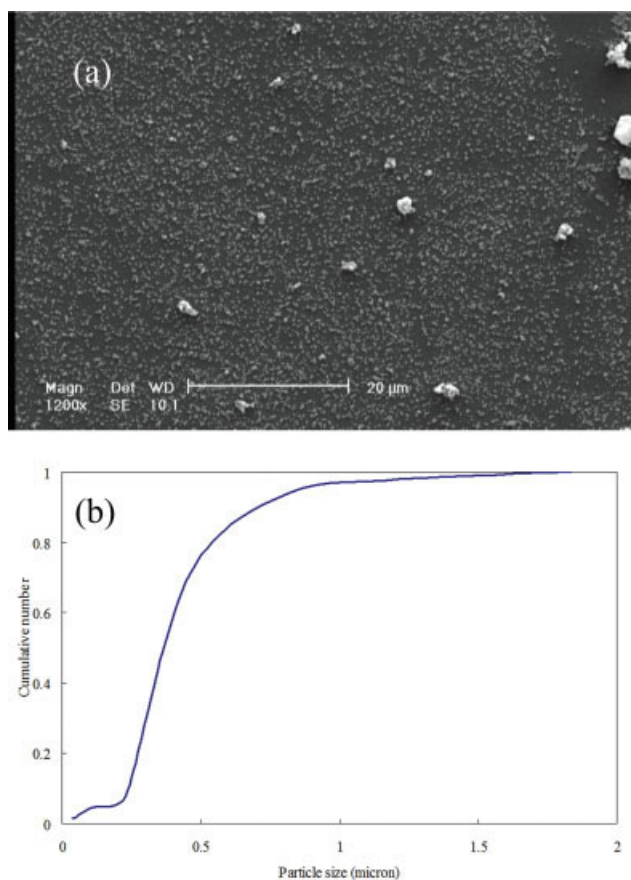


Figure 2 SEM micrograph (a) and corresponding cumulative distribution (b) of emulsion PVC particles (Run no. 7 in Table II). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The output of image analysis software could be readily converted into the cumulative PSDs. The number-average PS (MPS) and the distribution variance, σ^2 as a quantified criterion for broadness of PSD, can be calculated from following equations:

$$\text{MPS} = \sum g(d_i)d_i \quad (2)$$

$$\sigma^2 = \sum (d_i - \text{MPS})^2 g(d_i) \quad (3)$$

where $g(d_i)$ is the number fraction of particles with diameter d_i . One SEM micrograph and its corre-

sponding cumulative distribution curve obtained for one of the samples are illustrated in Figure 2. The calculated parameters including maximum and minimum diameter (d_{\max} and d_{\min}), MPS, and distribution variance (or PSD), obtained from SEM analysis of any sample, are summarized in Table II.

RESULTS AND DISCUSSIONS

Analysis of variance

The analysis of variance (ANOVA) is a powerful technique in Taguchi method that explores the percent contribution of factors affecting the response. This statistical table also screens the significant factors from those with less significance. The strategy of ANOVA is to extract from the results how much variations each factor causes relative to the total variation observed in the result.^{18,24} The statistical analysis of the results was carried out using Qualitek-4 (Nutek) and Minitab (Minitab) software.

Tables III and IV shows the ANOVA statistical terms for MPS and PSD, respectively. There are many statistical terms in ANOVA table, among them few are more meaningful. The F-ratio is a criterion for distinguishing the important factors from those with less significance. A low value of F-ratio for a factor means that the variation of response with respect to changes of this factor is equal to or smaller than the variations due to errors. If the F-ratio of a control factor is greater than about 4 (confidence level of 95%), then the factor has a significant influence on the response. It should be emphasized that the interpretation of ANOVA table is valid just in the range of levels considered for any factors. If the F-ratio for a factor is less than 4, it does not mean that the factor has no effect on the response absolutely, but just in the range of selected levels, the variation on response due to changes in factor levels has been insignificant comparing with errors. That's why the selection of levels is vital in design of experiment.^{18,24}

Table III indicates that just the emulsifier and initiator concentrations are of importance for affecting the MPS.

References

1. Fortuny, M.; Graillat, Ch.; McKenna, T. F. *Ind Eng Chem Res* 2004, 43, 7210.
2. Saeki, Y.; Emura, T. *Prog Polym Sci* 2001, 27, 2055.
3. Garcia, J. C.; Marcilla, A. *Polymer* 1997, 39, 431.
4. Mahmud, F.; Atiquallah, M.; Jarrah, N.; Hussain, I. *Eur Polym J* 1992, 28, 1039.
5. Chern, C. S. *Prog Polym Sci* 2006, 31, 443.
6. Odian, G. *Principles of Polymerization*; 4th ed.; Wiley: New Jersey, 2004; Chapter 1.
7. Ugelstad, J.; Hansen, F. K. *Rubber Chem Technol* 1976, 49, 536.
8. Fitch, R. M.; Watson, R. C. *J Colloid Interface Sci* 1978, 68, 14.
9. Kemmere, M. F. *Batch Emulsion Polymerization: A Chemical Engineering Approach*. Ph.D. Thesis. Eindhoven: Technische Universiteit Eindhoven, 1999.
10. Melis, S.; Kemmere, M.; Meuldijk, J.; Storti, G.; Morbidelli, M. *Chem Eng Sci* 2000, 55, 3101.
11. Boieshan, V. *Acta Polym* 1990, 41, 298.
12. Boieshan, V. *Acta Polym* 1990, 41, 303.
13. Arshady, R. *Colloid Polym Sci* 1992, 270, 717.
14. Gu, S.; Mogi, T.; Konno, M. *J Colloid Interface Sci* 1998, 207, 113.
15. Capek, I.; Lin, Sh. Y.; Hsu, T. J.; Chern, Ch. Sh. *J Polym Sci Part A: Polym Chem* 2000, 38, 1477.
16. Wutzel, H.; Samhaber, M. W. *Monatsh Chem* 2007, 138, 357.
17. Park, S. H. *Robust Design and Analysis for Quality Engineering*; Chapman and Hall: London, 1996.
18. Roy, K. R. *Design of Experiments Using Taguchi Approach: 16 Steps to Product and Process Improvement*; Wiley: New York, 2001.
19. Ugelstad, J.; Mork, P. C.; Dahl, P.; Ranges, P. J. *J Polym Sci Part C* 1969, 27, 49.
20. Ito, F.; Ma, G.; Nagai, M.; Omi, Sh. *Colloids Surf A* 2002, 201, 131.
21. Alvarez, A. E.; Ressoa, J. A.; Aparacio, L. V.; Samoria, C.; Valles, E. M.; Brandolin, A. *Lat Am Appl Res* 2001, 31, 317.
22. Garcia, J. C.; Marcilla, A. *Polymer* 1997, 39, 3507.
23. Davidson, J. A.; Etter, A. A.; Thomas, M.; Butler, R. S. *Part Part Syst Char* 1992, 9, 94.
24. Montgomery, D. C. *Design and Analysis of Experiments*, 4th ed.; Wiley: New York, 1997.
25. Peggion, E.; Testa, F.; Talamini, G. *Die Makromol Chem* 1964, 71, 173.
26. Friis, N.; Hamielec, A. E. *J Appl Polym Sci* 1975, 19, 97.
27. Chern, C. S.; Hsu, H.; Lin, F. Y. *J Appl Polym Sci* 1996, 60, 1301.
28. Tadros, F. Th. *Applied Surfactants Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2005.
29. Gao, J.; Penlidis, A. *Prog Polym Sci* 2001, 27, 403.
30. Pourmehr, M.; Shahbazian, A.; Navarchian, A. H.; Hajian, M.; Iranian Chemical Engineering Congress (ICHEC); Kish island, Iran, 2008.