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

TABLE I
Selected Factors and Their Levels

Factors			Levels		
Description	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

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.

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.

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 L_{18} 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
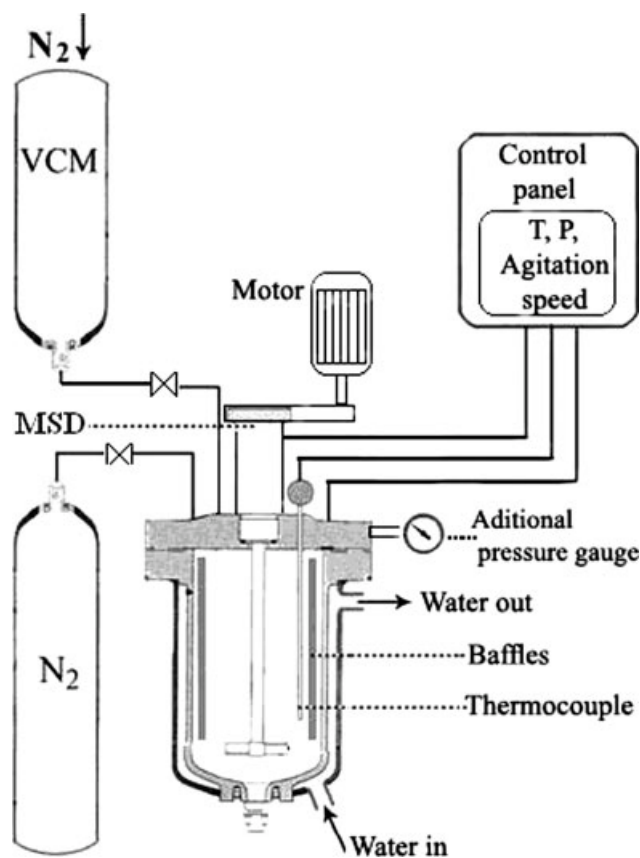
Figure 1 Schematic representation of the experimental set up.

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 μS/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 derive (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×, 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 numbers[23]:

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

Comparing the number of pixels in micrograph width, and the scale given in bottom of micrograph, the ECD is converted to micrometer dimension.
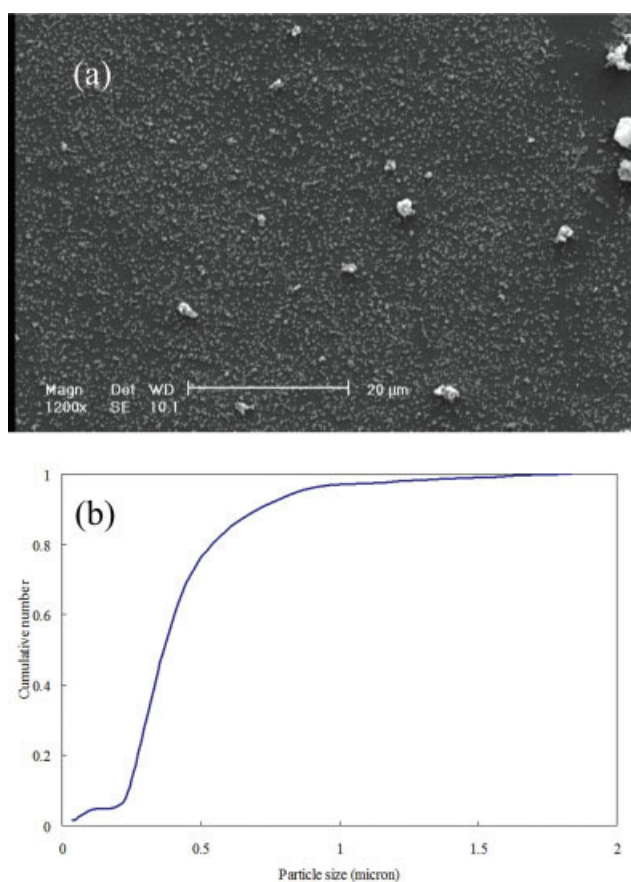
Figure 2 SEM micrograph (a) and corresponding cumulative distribution (b) of emulsion PVC particles (Run no. 7 in Table II). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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:

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

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

where $g(d_i)$ is the number fraction of particles with diameter d_i. One SEM micrograph and its corresponding 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. It is implied from the values in the last column of this table that the emulsifier concentration

TABLE III
Analysis of Variance (ANOVA) for MPS

Factor	DOF	Sums of squares	Variance	F-ratio	Pure sum	Percent
[T]	2	0.001	0.000	0.282	0.000	0.000
[E]	2	0.076	0.038	19.674	0.072	56.75
[I]	2	0.024	0.012	6.393	0.021	16.389
R	2	0.005	0.002	1.535	0.002	1.628
S	2	0.005	0.002	1.52	0.002	1.58
Other/error	7	0.013	0.001			23.653
Total	17	0.128				100.00%

TABLE IV
Analysis of Variance (ANOVA) for PSD

Factor	DOF	Sums of squares	Variance	F-ratio	Pure sum	Percent
[T]	2	0.003	0.001	6.960	0.003	16.585
[E]	2	0.002	0.001	4.116	0.001	8.671
[I]	2	0.000	0.000	0.146	0.000	0.000
R	2	0.005	0.002	9.852	0.004	24.633
S	2	0.006	0.003	11.361	0.005	28.832
Other/error	7	0.001	0.000			21.279
Total	17	0.019				100.00%

has the predominate influence on MPS. On the other hand, according to Table IV, except the initiator concentration, all factors have significant influence on the distribution variance (or PSD). The trends of influence of each factor on the MPS and PSD are discussed in the following.

The other/error term, in the last row of ANOVA tables, contains information about three sources of variability of the results: uncontrollable (noise) factors, factors that are not considered in the experiments, and experimental (random) error.[18,24]

Influence of emulsifier concentration

The emulsifier concentration has been recognized as the key parameter to control the PS in emulsion polymerization of VCM.[2,11,19,25,26] This can be justified as the number of micelles formed and thus the number of particles that are the main sites for polymerization directly depends on the emulsifier type and concentration. The total number of polymer particles per unit weight (kg) of the latex (N_p) can be obtained from following equation.[11] It is observed that the PS (d_i) is inversely proportional to the total number of particles, and hence the control of emulsifier concentration may help to obtain the desired MPS[11,16]:

$$N_p = \frac{\sum n_i}{\rho \frac{\pi}{6} \sum d_i^3 n_i} \qquad (4)$$

where ρ is the density of PVC, and n_i represents the number of particles with size d_i.

Furthermore, emulsifier molecules occupy the particle surface and therefore increase the electrostatic repulsion. A high emulsifier concentration, a greater is the electrostatic repulsion that leads to more colloid stability and so prevents the coagulation of particles due to higher energy barrier.[8,9,27]

The influence of emulsifier concentration on the MPS and distribution variance is shown in Figure 3. As expected, when the concentration of emulsifier is increased from 1 to 4 g/L, the MPS is reduced from 0.34 to 0.2 μm. Notice that the first level of emulsifier concentration is less than the critical micelle concentration (CMC) of SDS, which its average value in the range of temperature in this research is about

3 g/L.[28] Therefore, the particle formation at low level of emulsifier concentration is carried out via the homogeneous nucleation mechanism. The second level of emulsifier concentration however is greater than the CMC, thus heterogeneous nucleation will become predominant and the number of particles will increase relative to the first level of emulsifier concentration. Therefore, according to eq. (4), increasing the number of particles will decrease the MPS in the range of 1–4 g of SDS per liter.

In the third level of emulsifier concentration, a very slightly increase in the MPS can be seen (Fig. 3). It may be attributed to the coagulation phenomena. When the emulsifier concentration increases even more, well above CMC, particles with small size will first produce due to higher number of particles. Very small and large number of particles will increase the probability of collision between the particles. This is because of greater surface to volume ratio of smaller particles. On the other hand, the amount of required emulsifier for stabilization of particles increases with decreasing the particles size. Therefore, the need for emulsifier will be greater than the increased concentration. This leads to a shortage of emulsifier for stability of colloids so that the collision between particles causes the coagulation of particles and increase of the MPS.
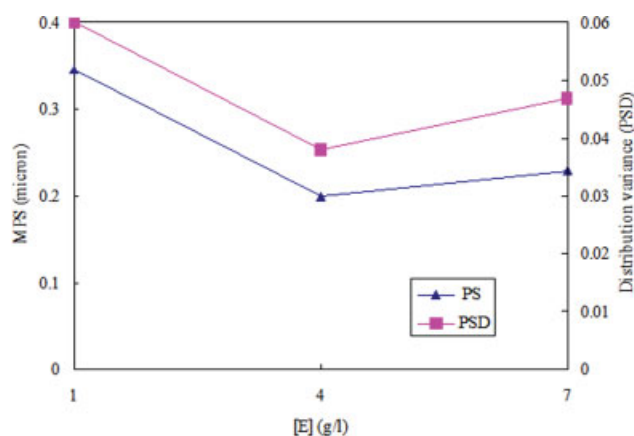

Figure 3 Influence of emulsifier concentration on MPS and PSD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
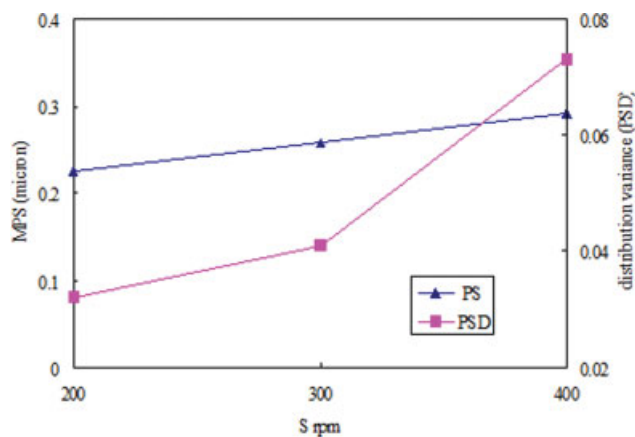
Figure 4 Influence of agitation speed on MPS and PSD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table IV shows that the emulsifier concentration has also significant influence on the PSD. Since the PSD is a consequence of the distribution of times at which different polymer particles are nucleated,[6] any factor affecting the time distribution in the first stage of polymerization, may influence also the PSD. As it is indicated in Figure 3, with increasing the emulsifier concentration from 1 to 4 g/L, two nucleation mechanisms occur simultaneously. This in turn decreases the distribution of nucleation times, and therefore the PSD.

Beside the nucleation, the coagulation phenomena may also affect the PSD. As mentioned above, coagulation of particles may happen in the third level of emulsifier concentration (well above CMC), that leads to a slightly wider PSD (Fig. 3). The influences of emulsifier concentration on the MPS and PSD show similar trends (Fig. 3).

Recently Wutzel and Samhaber, investigated the influence of emulsifier concentration on the PSD in emulsion polymerization of styrene, a monomer with no solubility in water. They suggested that at high surfactant concentrations not all of the surfactant molecules are adsorbed by the generated particles during the initiation phase. The presence of excess micelles after this period leads to formation of new particles throughout the polymerization reaction, and thus results a broadening of the final PSD.[16]

Influence of agitation speed

The trend of influence of agitation speed on MPS and distribution variance (PSD) is shown in Figure 4. Statistical analysis (Tables III and IV) represents that the agitation speed, in the range of variations in this study, has no significant effect on the MPS, as the corresponding F-ratio is less than 4. However, this factor has the most influence on the distribution variance.

Agitation speed can increase the motion of particles and the frequency of collision between polymer particles; therefore coagulation of particles will become more probable. This mechanism is called Shear or orthokinetic coagulation.[9] The coagulation of some particles results in a broader PSD (Fig. 4).

For emulsion polymerization of styrene however, Gu et al.[14] have suggested that the agitation speed has no significance effect on size distribution of particles.

One point in justification of agitation speed influence is that the absolute effect of mixing rate depends strongly on the hydrodynamic aspects of the reactor system. The geometric design of the reactor inside, the shape and position of baffles, type and size of propeller, as well as rheological properties of latex, all affects the mixing phenomena in reaction mixture. Anyway, although the above-mentioned conclusion can not easily be extrapolated to other reactor systems, and some scale-up calculations are necessary to generalize the influences of mixing intensity on the MPS and PSD, however, the responses at different agitation speed levels may be compared in a specified reactor configuration.

Influence of water to monomer weight ratio

The main effect of water to monomer weight ratio on MPS is given in Figure 5. It is implied from the corresponding F-ratio in MPS ANOVA table, that in the range of selected levels of variables, this factor is not an important parameter for controlling the MPS. The factor R however, is in the second rank after agitation speed for affecting distribution variance. It is probably attributed to its influence on homogeneous nucleation, as vinyl chloride is a moderate water soluble monomer. Decreasing the amount of monomer in the system with increasing the R value, will decrease homogeneous nucleation. This in turn will
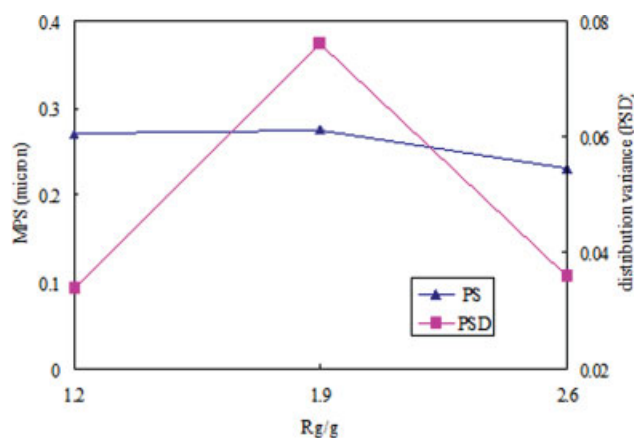

Figure 5 Influence of water to monomer weight ratio on MPS and PSD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cause increasing of nucleation period and affecting the distribution of times at which polymer particles are nucleated. Hence, as R goes up the distribution variance is increased. This behavior can be observed in Figure 5, when R is increased from 1.2 (first level) to 1.9 (second level). Gu et al.[14] on the other hand have obtained that the PSD is independent of R in emulsion polymerization of styrene, probably due to no solubility of monomer they worked.

A different behavior is observed at higher values of R as the distribution variance is narrower relative to that in second level (Fig. 5). As the monomer droplets are stabilized by emulsifier molecules,[15] with decreasing the amount of monomer even more, the number of monomer droplets is also decreased, and therefore a higher amount of free emulsifier will be presented in the system. This in turn leads to a higher number of micelles, and consequently a shorter nucleation period that causes a narrower distribution variance.[5]

Influence of temperature

The temperature does not influence the MPS, in the range of selected levels for this variable (Table III). However, as Table IV indicates, this factor is a significant factor for PSD. Increasing the temperature from 46 to 53°C increases the width of distribution (Fig. 6). This is due to the fact that increasing the temperature will increase the Brownian motion of particles, and thus the probability of coagulation occurrence. This mechanism for aggregation of particles is called Brownian or perikinetic coagulation that widens the distribution variance.[9]

The effect of temperature on distribution variance shows a nonlinear behavior, so that at 60°C the PSD is narrower than 53°C. This can be justified by the influence of temperature on CMC of SDS, as shown in Figure 7.[28] A more required concentration of
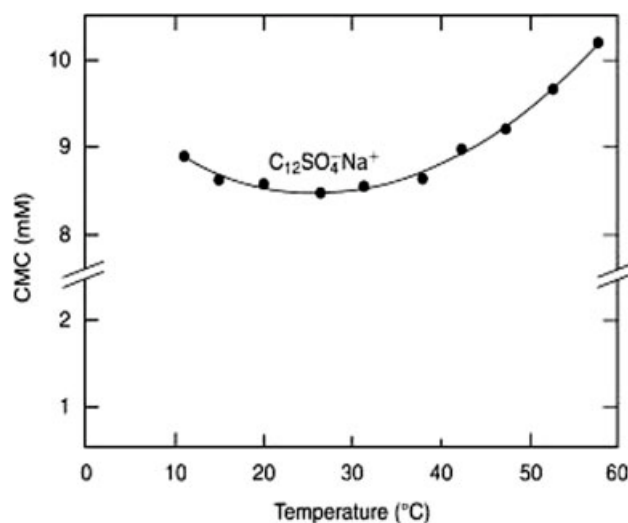
Figure 7 Temperature dependency of the CMC of SDS.[28]

emulsifier to form micelles at higher temperature means a greater amount of free emulsifier up to that temperature. This, in turn, means that there are a lot of emulsifier molecules at higher temperature that could be adsorbed by polymer particles and therefore, an enhanced colloidal stability. More stabilized polymer particles result in less coagulation. Thus, the narrower PSD at 60°C will be expected.

As mentioned above, the temperature has two opposite effects; i.e., the promotion of coagulation due to higher Brownian motion, and the reduction in coagulation due to increasing the CMC. The very low influence of temperature on the MPS may be attributed to balance of these two phenomena.

In emulsion polymerization of styrene, Wutzel and Samhaber have found that as the temperature goes up, the number of particles is also increased and thus the MPS is decreased [see eq. (4)]. This is due to the higher decomposition rate of the thermal initiator in the system, and therefore a higher number of radicals which are available for initiation. Temperature hasn't showed any significance influence on the PSD of polystyrene.[16] The difference in observations is attributed to the fact that the emulsion polymerization of VCM does not obey the classic Smith-Ewart theory, and therefore, the number of polymer particle does not depend on the initiator concentration.[29]

Because of the larger influence of agitation speed relative to temperature, on the MPS and distribution variance, we may conclude that in competition of Brownian and shear mechanisms for coagulation, the latter predominates in emulsion polymerization of VCM.

Influence of initiator concentration

Although in emulsion polymerization of VCM, the number of particles is independent of initiator
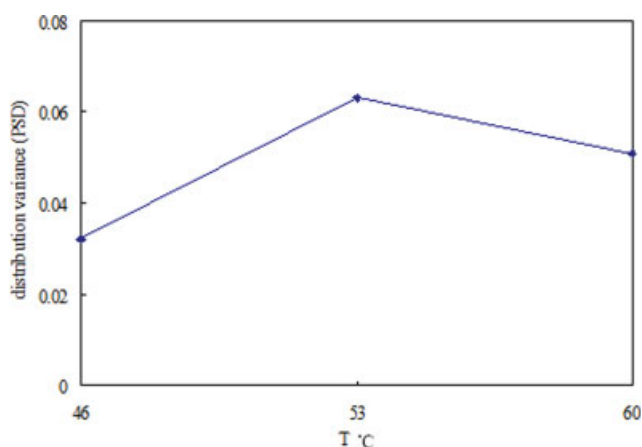

Figure 6 Influence of temperature on PSD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
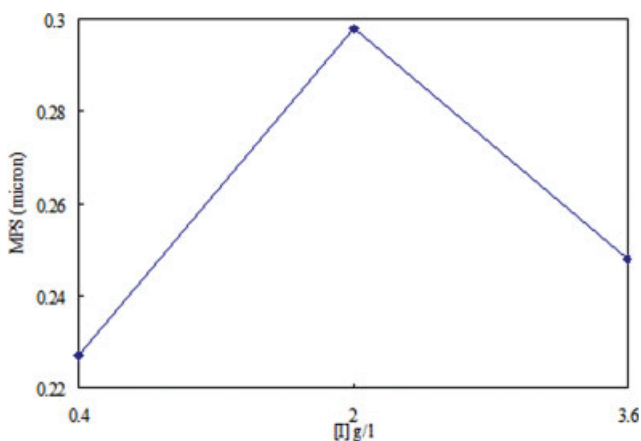
Figure 8 Influence of initiator concentration on MPS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentration,[11,19,26,29] however, as it is observed in Figure 8 and Table III, the initiator concentration affects the MPS. This behavior may be attributed to the role of initiator as a source of electrolyte generation in emulsion system. A high electrolyte concentration results in a lower energy barrier (the sum of the van der Waals attraction and the electrostatic repulsion energies), for approaching particles to coagulate.[9] As the initiator concentration goes from 0.4 g/L to the second level (2 g/L), the electrolyte concentration increases. Thus, the coagulation of
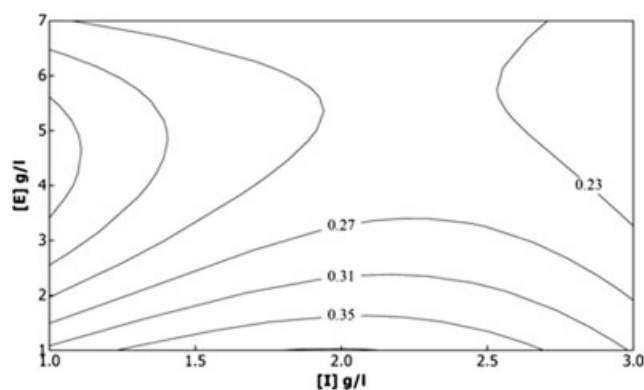

Figure 9 The counter plot for MPS.

particles is enhanced and will increase the MPS (Fig. 8). At the third level of this factor (3.6 g/L), however, the higher concentration of initiator may lead to bi-radical termination reactions and decreases the initiator efficiency,[30] thus the MPS has been decreased.

Counter plot

The counter plot is the locus of the responses with equal values. It is a projection of three dimensional response surface plots on a plane.[24] The contour plot is commonly given as a graph drawn for pairs of most important factors. According to number of
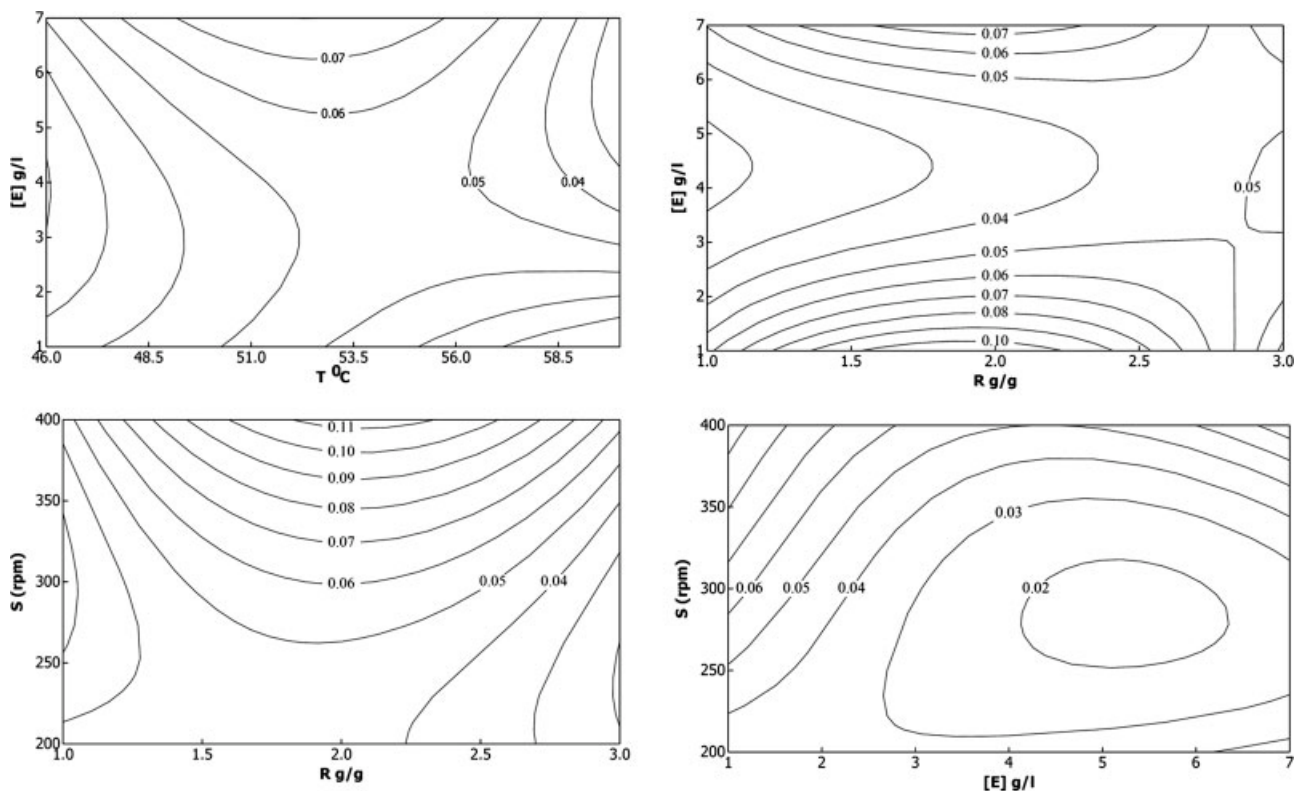

Figure 10 The counter plots for PSD.

TABLE V
Input Values and Conditions for OEC Analysis to Obtain the Optimum MPS and Minimum PSD

	Response	Worst value	Best value	Quality characteristic	Weight factor (%)
1	PS	0.101	0.3	Nominal is better	50
2	PSD	0.116	0.0157	Smaller is better	50

significant factors involved, a counter plots for the MPS and four for distribution variance (PSD) are shown in Figures 9 and 10, respectively. The range of the MPS or distribution variance can be predicted for any given values of parameters.

Optimum condition

The desired values of MPS and width of distribution depend on the application of e-PVC, for which the optimum condition can be determined. Some more experiments are required around the best levels of important factors in a narrower range, while the insignificant factors are kept constant, to find the exact optimum condition for a defined target.

In this article, determination of the relative optimum conditions (the best levels of factors studied in this study) have been illustrated for a typical paste application of e-PVC. Suppose that the target is to get an MPS with a nominal value of 0.3 micron, together with a minimum PSD.[2] Since the optimum conditions for each individual response may differ, an overall evaluation criterion (OEC) is defined according to Taguchi method, to obtain the best conditions at which both responses are close to their optimum values. Thus the problem is to maximize the new transformed response (OEC). For this purpose, the following equation is defined for normalization of responses[18]:

$$OEC_i = \left(1 - \left|\frac{MPS_B - MPS_i}{MPS_B - MPS_W}\right|\right)w_{MPS}$$
$$+ \left(1 - \frac{PSD_i - PSD_B}{PSD_W - PSD_B}\right)w_{PSD} \quad (5)$$

where i, w, and B indices refer to the run number (1–18), the worst, and the best responses, respectively,

TABLE VI
Optimum Conditions for Maximizing the OEC

Factor	Level description	Level	Contribution
T	46°C	1	11.991
[E]	7 g/L	3	0.349
[I]	2 g/L	2	3.465
R	1.2 g/g	1	3.533
S	200 rpm	1	6.536
Total contribution from all factors			25.874
Current grand average of performance			64.986
Expected result at optimum condition			90.860

for MPS and distribution variance. The terms w_{MPS} and w_{PSD} are the weight factors for contributions of MPS and distribution variance to determine the best condition, respectively. The input values for calculation of OEC terms are summarized in Table V. The OEC values at any given condition in Table II are calculated (not shown), and finally this new response is maximized using Qualitek-4 software. The best levels, and the contribution of each factor for improvement of overall performance (OEC) are given in Table VI. As it is observed, although the current grand average of performance according to results in Table II is 64.986 units, setting the factors on optimum conditions increases the OEC by 25.874 units, so that the expected result at optimum condition will be 90.86 units. Hence, a very significant improvement is expected if the optimum condition will be applied.

CONCLUSIONS

The influences of various operating variables on the mean PS and PSD of e-PVC in batch reactor were statistically analyzed using Taguchi experimental design. The main conclusions that are valid in the range of levels considered in this study are as follow:

- The mean PS strongly depends on emulsifier concentration, as this factor influences directly the number of particles in the latex. The initiator concentration is also important factor affecting the MPS. The other operating variables have no significant effects on MPS in the range of levels investigated in this study.
- All factors excluding the initiator concentration have important influences on the width of distribution. Contributions of these factors on distribution of variance are in following sequence, respectively: agitation speed, water to monomer weight ratio, temperature, and emulsifier concentration.
- The effects of important factors on MPS and width of distribution of e-PVC show a nonlinear behavior.
- It is implied from the greater influence of agitation speed relative to temperature on distribution of variance that the shear coagulation predominates the Brownian coagulation, in this system.

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