

Application of Taguchi Method to Investigate the Effects of Process Factors on the Performance of Batch Emulsion Polymerization of Vinyl Chloride

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ABSTRACT: In this article, the influences of five operating variables on the molecular weight (or K -value), polydispersity index (PDI), as well as polymerization yield of emulsion poly (vinyl chloride) in batch reactor were investigated simultaneously 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). Statistical analysis of results revealed the significance order of factors affecting the product qualities and quantity. It was found that the reaction temperature is the principal operating factor to control the molecular weight, and this is attrib-

uted to promotion of chain transfer reactions to monomer in this system. The effect of this factor on PDI is also comprehensively discussed. The significance sequences of important factors on yield are: $S > [E] > r$. The polymerization yield increases with S and $[E]$ but decreases as r is increased. The relative optimum condition for a typical paste application was also determined using overall evaluation criteria. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2739–2746, 2009

Key words: emulsion polymerization; poly (vinyl chloride); K -value; polydispersity index; reaction yield

INTRODUCTION

Poly (vinyl chloride) (PVC) is the second widely used commercial thermoplastic, after low-density polyethylene.¹ It can be produced by three different processes: suspension (85%), emulsion (13%), and bulk polymerization (2%).² For many applications, such as artificial leather, emulsion technique is preferred for polymerization of vinyl chloride monomer (VCM).^{3,4}

The mechanism of emulsion polymerization of VCM shows some deviations from conventional Smith-Ewart approach. This is mainly due to the moderate solubility of monomer in water that results in both micellar and homogeneous nucleation.^{5–8} Whenever basic polymer particles are formed, the mass of monomer in liquid phase decreases with time but a thermodynamic equilibrium is established again between monomer concentrations in vapor and liquid phases. As long as monomer exists as separate phase in aqueous media, it will exert its

own vapor pressure so that the total pressure in the reactor will be constant during isothermal polymerization. At a critical degree of conversion (when about 70–80% of total monomer is consumed), the monomer droplets as a separate phase are disappeared, and hereafter the pressure in the reactor begins to drop.^{9,10}

The most important product properties in VCM emulsion polymerization process are mean particle size (MPS), particle size distribution (PSD), K -value, polydispersity index (PDI), and the reaction yield.¹¹ The first two characteristics (MPS and PSD) influence the processability of the latex, such as rheology and film formation.¹² K -value is a measure of molecular weight that strongly affects the melting flow and final mechanical properties of polymer. Also, the MWD which is represented by PDI, has dramatic effects on the processability, miscibility, strength, and modulus of plastics.^{13–15} Finally, the reaction yield that represents the extent of reaction, is important from economic point of view.¹⁶ The recipe and process conditions strongly determine the quality of the latex product. Thus, a well knowledge of the effects of process variables on product qualities is essential to attain desirable properties.

Many authors had already investigated the above mentioned product qualities of VCM emulsion polymerization, using the conventional experimental methods.^{17–22} In these articles, the effect of each

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TABLE I
Selected Factors and Their Levels

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

process parameter has been individually studied on one or a couple of product properties, whereas the other factors were held constant. Alvarez et al. for example have examined the effects of some reaction parameters on conversion and MWD, using a one-at-a-time approach.¹⁷ Despite various studies on the emulsion polymerization of VCM in batch reactor, there is no report available suggesting application of experimental design for statistical analysis of operating variables effects on the performance of this system as a whole.

Using Taguchi experimental design approach, the effects of process variables on MPS and PSD of emulsion PVC have been studied recently by Pourmehr and Navarchian.²³ In the current study, this approach is employed to investigate statistically the influences of temperature, water to monomer weight ratio, agitation speed, and emulsifier and initiator concentrations on *K*-value and PDI of final product, as well as polymerization yield in batch emulsion polymerization of vinyl chloride. The relative optimum condition to obtain the best overall evaluation criteria (OEC) is then determined.

EXPERIMENTAL

Experimental design

The conventional one-at-a-time approach to evaluate the influences of process parameters on product quality or quantity requires numerous experimental runs (particularly when a lot of variables are to be investigated at different levels) to fully explore the entire parameter space. In this respect, the Taguchi experimental design method can reduce the number of experiments while retaining data collection quality. The quantified and comparative analysis of the factor effects is the second advantage of this approach.²⁴

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 as well as industrial recipes for emulsion polymerization of vinyl chloride.^{5,7,9,10,16–23}

For Taguchi-design of experiments with five factors and three levels for each factor, a standard L₁₈ orthogonal array²⁴ was employed (Table II). Each row of the matrix represents one run at specified condition. To avoid the systematic bias, the sequence in which these runs were carried out was randomized.^{24,25} The statistical analysis of the results was carried out using Qualitek-4 (Nutek) software.

Materials

VCM was kindly supplied by Bandar Imam Petrochemical Company (Iran). A gas chromatography (GC) analysis showed a purity of 99.994% for this monomer. Merck grades of potassium persulfate (KPS), 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. Cyclohexanone (Merck grade) was utilized as solvent for *K*-value measurements.

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 details for reactor configurations and polymerization method are given

TABLE II
Taguchi Orthogonal Array for Designed Experiments Based on Coded Levels

Run no.	Operating variables				
	<i>T</i>	[<i>E</i>]	[<i>I</i>]	<i>r</i>	<i>S</i>
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	2	1	1	2	2
5	2	2	2	3	3
6	2	3	3	1	1
7	3	1	2	1	3
8	3	2	3	2	1
9	3	3	1	3	2
10	1	1	3	3	2
11	1	2	1	1	3
12	1	3	2	2	1
13	2	1	2	3	1
14	2	2	3	1	2
15	2	3	1	2	3
16	3	1	3	2	3
17	3	2	1	3	1
18	3	3	2	1	2

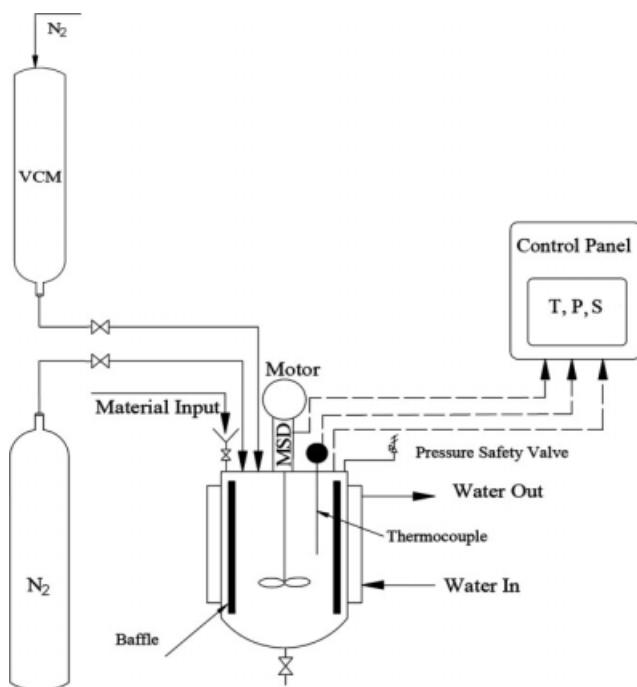


Figure 1 Schematic representation of experimental set up.

elsewhere.^{23,26} A schematic of experimental set up is shown in the Figure 1.

Characterizations

Viscosity measurement

K -values were determined according to ISO 1628 with cyclohexanone as solvent at a concentration of 5 g/l.^{13,14} Relative viscosity (η_{rel}) was determined by an Ubbelohde viscometer ($k = 0.01$, Schott, Germany, Code: 525-10). K -values were implicitly calculated by Fikentscher equation:¹³

$$\log_{10} \eta_{rel} = [75K^2 \times 10^{-6} / (1 + 1.5KC \times 10^{-3}) + K \times 10^{-3}]C \quad (1)$$

in which, K is the K -value and C represents the solution concentration (5 g/l).

The intrinsic viscosities ($[\eta]$) of samples were also determined at 25°C in cyclohexanone by measuring the relative viscosity of five samples with concentrations ranging from 0.1 to 0.5 g/dl.

Molecular weight measurements

The number- and weight-average molecular weights, as well as PDI were determined using gel permeation chromatography (GPC) instrument (Agilent 1100, Japan). A set of PL®-gel columns (500 Å, 10³ Å, and 10⁴ Å), coupled with refractive index detector was used. The polymer samples were diluted in

tetrahydrofuran (THF) with concentration of 1 g/l and were analyzed at 30°C. The injection volume was 20 µl and the flow rate was 1 ml/min. GPC calibration was performed with polystyrene standard samples with molecular weights ranging from 650 to 189,300 g/mol.

Yield determination

In this study, the reaction yield was measured as one of the responses. Samples were taken at the end of reaction, weighed, and dried for 24 hr in vacuum oven at 45°C. The dried product was washed with distilled water to remove the emulsifier and dried again. Finally, it was weighed to determine the yield. The following equation [eq. (2)] was used to calculate the reaction yield (g PVC/l H₂O).^{16,19,21}

$$\text{Yield} = \frac{m_d}{(m_w - m_d)/1000} \quad (2)$$

where m_d and m_w are the grams of final dried as well as initial wet samples, respectively, and 1000 is the density of water (g/l).

RESULTS AND DISCUSSIONS

Eighteen experiments were carried out according to Table II. The results of all measurements are summarized in Table III.

In Taguchi method, the results are statistically analyzed using analysis of variance (ANOVA) to determine the partial contribution of each operating

TABLE III
The Measured Responses for Each Run

Run no.	Measured parameters					
	Yield (g PVC/l H ₂ O)	$[\eta]$ (g/dl)	K -value	M_n	M_w	PDI
1	145.9	1.1213	76.84	97,709	149,670	1.53
2	424.8	1.1109	75.232	90,972	141,410	1.55
3	348.1	1.0936	72.582	87,501	144,790	1.65
4	281.4	0.9005	67.775	78,496	128,920	1.64
5	369.9	0.8795	66.400	65,457	124,665	1.90
6	353.3	0.7484	63.873	59,686	107,450	1.80
7	488.4	0.7109	56.675	43,866	108,080	2.46
8	362.2	0.5484	56.105	32,181	94,948	2.95
9	362.0	0.8030	64.734	60,553	109,060	1.80
10	241.0	1.1176	75.557	94,380	143,130	1.52
11	482.2	1.4190	77.242	103,160	141,240	1.37
12	315.6	1.3282	77.203	101,010	146,170	1.45
13	245.9	0.8856	66.632	66,718	126,200	1.89
14	464.4	0.8976	67.758	69,470	128,720	1.85
15	497.5	0.8564	65.931	63,732	125,960	1.98
16	349.3	0.7208	59.284	45,189	111,930	2.48
17	317.9	0.7372	61.710	59,350	112,550	1.90
18	622.1	0.7267	59.716	48,547	102,750	2.12

TABLE IV
Analysis of Variance (ANOVA) for *K*-value

Factor	Degree of freedom	Sums of squares	Variance	<i>F</i> -ratio	Pure sum	Percent
<i>T</i>	2	782.228	391.114	94.926	773.987	89.986
[<i>E</i>]	2	0.248	0.124	0.03	0	0
[<i>I</i>]	2	31.221	15.61	3.788	22.981	2.671
<i>r</i>	2	3.752	1.876	0.455	0	0
<i>S</i>	2	13.821	6.91	1.677	5.581	0.648
Other/error	7	28.84	4.12	–	–	6.695
Total	17	860.114	–	–	–	100.00%

factor on the response. The strategy of ANOVA calculation is to statistically analyze the variation that each factor cause relative to the total variation observed in the results.^{24,27} This statistical table also screens the significant factors from those with less significance. 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. If the *F*-ratio of a control factor is almost equal to or greater than 4 (confidence level of 95%), then the factor has an important influence on the response.²⁴ It should be emphasized that the interpretation of ANOVA table is valid just in the range of levels considered for any factor. 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.^{24,27}

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

The main effects of factors are determined using average values of response at each level.

Effects of process parameters on *K*-value

Table IV shows the analysis of variance for *K*-value. As it is observed the predominant factor for controlling the *K*-value is the reaction temperature. The initiator concentration may also slightly affect the *K*-value but its contribution percent is very lower than that of temperature. It is implied from data in ANOVA table that the other parameters have no significant influence on *K*-value. These statistical results are similar to that obtained by other authors.^{10,13,15,17,19,20}

Figure 2 indicates that the *K*-value and molecular weight decrease with temperature. It is well known that in conventional free radical mechanism, as tem-

perature increases, the rate of initiator decomposition is also increased, and therefore polymer chains with lower molecular weights will be produced due to faster termination of macroradicals. In VCM polymerization, however, the reduction of molecular weight at higher temperature, can not merely attributed to this reason, because of minor effect of initiator concentration on molecular weight or *K*-value (Table IV). VCM is a non-conjugated weak electron-withdrawing vinyl monomer. Although this monomer has low reactivity, but the propagating radical of VCM is highly reactive and tends to induce chain transfer reactions to all components in the polymerization system particularly monomers.^{1,10,15,19,28} It is noteworthy that the molecular weight of PVC obtained in emulsion polymerization is approximately similar to that obtained in bulk or suspension polymerization, indicating that chain transfer to monomer (C_M) is the predominant factor to determine the molecular weight regardless of polymerization method (or reaction ingredient).¹⁵ The relation between C_M and reaction temperature can be expressed by the following equation¹⁵:

$$C_M = 125 \exp(-7300/RT) \quad (3)$$

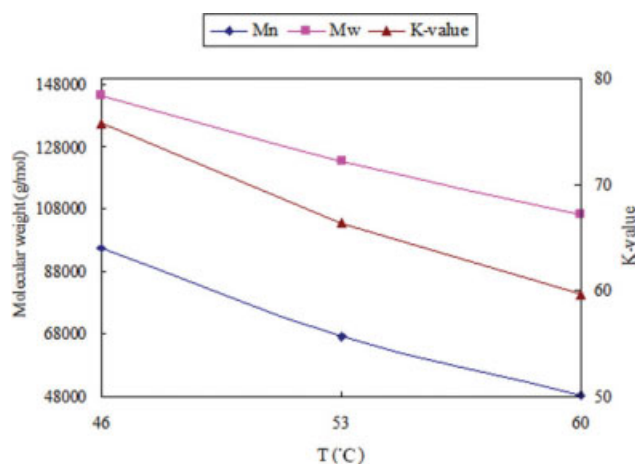


Figure 2 Influence of temperature on *K*-value, M_n , & M_w . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Analysis of Variance (ANOVA) for PDI

Factor	Degree of freedom	Sums of squares	Variance	F-ratio	Pure sum	Percent
[T]	2	1.806	0.903	21.388	1.721	60.625
[E]	2	0.057	0.028	0.682	0	0
[I]	2	0.345	0.172	4.09	0.26	9.189
<i>r</i>	2	0.166	0.083	1.973	0.082	2.893
<i>S</i>	2	0.168	0.084	1.995	0.084	2.96
Other/error	7	0.295	0.42	–	–	24.332
Total	17	2.84	–	–	–	100.00%

where R is the universal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T is temperature (K).

Thus in the case of VCM polymerization, the reduction of K -value with increasing temperature can be justified mainly by promotion of chain transfer reactions to monomers, and the reaction temperature is the principal operating factor to control the molecular weight.

Determination of Mark-Houwink- Sakurada constants (k, α)

In order to find the constants (k and α) of the well-known Mark–Houwink–Sakurada (MHS) equation for emulsion PVC in this study, we plotted the logarithm of $[\eta]$ versus the logarithm of corresponding molecular weights obtained from GPC data for each sample. The resulted equations with reasonable correlation factors for both M_n and M_w are as follow:

$$[\eta] = 3.0543 \times 10^{-4} M_n^{0.7184} \quad (4)$$

$$[\eta] = 3.481 \times 10^{-9} M_w^{1.6516} \quad (5)$$

Effect of process parameters on PDI

The ANOVA data on PDI is shown in Table V. The results show that in the range of levels studied in

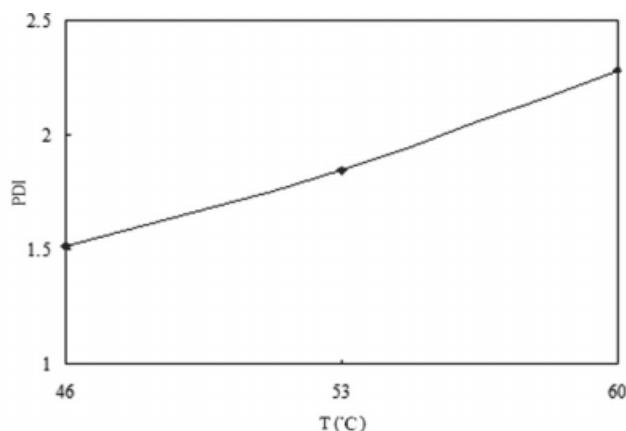


Figure 3 Influence of reaction temperature on PDI.

this article, the only factors affecting PDI are temperature and initiator concentration. Here again, the effect of reaction temperature is more dominant for controlling the PDI. Figure 3 shows that increasing the temperature will cause greater PDI. The higher temperature leads to higher initiator decomposition. Thus as temperature goes up or the initiator concentration is increased more radical will present in system. The radicals produce active centers with different chain lengths that results in a greater PDI as shown in Figure 4.^{17,19}

The influence of temperature on PDI can also be justified by Schultz-Flory distribution hypothesis.⁸ The theoretical PDI in free radical polymerization with disproportionation and combination mechanisms of termination can be expressed by eq. (6):

$$\text{PDI} = \begin{cases} 1 + p, & \text{Disproportionation} \\ \frac{2 + p}{2}, & \text{Combination} \end{cases} \quad (6)$$

where p is conversion of monomers during the reaction. The actual mechanism of termination can be presented as a weight function of contribution of these two termination modes. As the disproportionation mechanism of termination is promoted at higher temperatures,⁸ for any particular conversion a wider MWD is expected as temperature is increased. Furthermore, VCM is more soluble in water at higher temperatures;¹⁷ that slightly leads to a greater

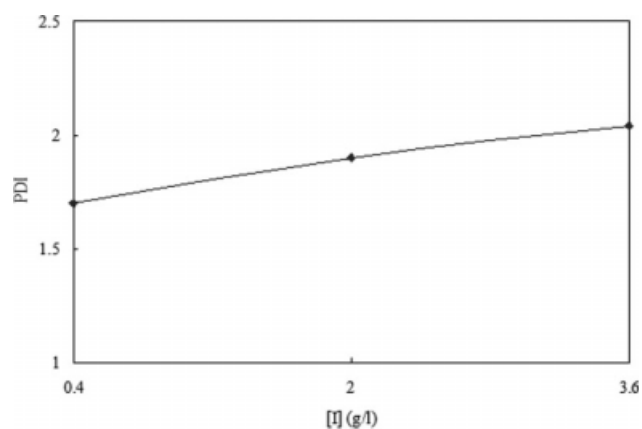


Figure 4 Influence of initiator concentration on PDI.

TABLE VI
Analysis of Variance (ANOVA) for Yield

Factor	Degree of freedom	Sums of squares	Variance	F-ratio	Pure sum	Percent
<i>T</i>	2	24721.772	12360.886	3.914	1840.303	8.544
[<i>E</i>]	2	56208.199	28104.199	8.900	49892.731	23.16
[<i>I</i>]	2	14812.100	7404.050	2.345	31272.171	3.944
<i>r</i>	2	37557.639	18793.819	5.951	53673.455	14.516
<i>S</i>	2	59988.923	29994.461	9.498	53666.754	24.915
Other/error	7	22104.139	3157.734	–	–	24.921
Total	17	215422.775	–	–	–	100.00%

conversion. Therefore, according to Schultz-Flory distribution functions, with increasing the conversion, a greater PDI is observed.

Finally, it is well known that chain transfer reaction to polymer (C_p) results in branching in free radical polymerization. At higher temperatures C_p is enhanced, and the branching in turn leads to more polydispersity and so a broader MWD.⁸

Effects of process parameters on yield

According to ANOVA table for the yield (Table VI), the most important factors which may affect the polymerization yield, are agitation speed, emulsifier concentration and water to monomer weight ratio, respectively. The significance of temperature is in borderline (F -ratio = 3.914), and the initiator concentration is insignificant. Recall that these results are obtained where the factors and their variations are selected based on conventional recipes and therefore the importance sequence may vary if different factors and range of levels were considered.

The last column in ANOVA table contains the contribution percent of each factor affecting the response. About 63% of the effect contributions belong to agitation speed, emulsifier concentration, and water to monomer weight ratio. The ways that these factors affect the reaction yield, are given as follow.

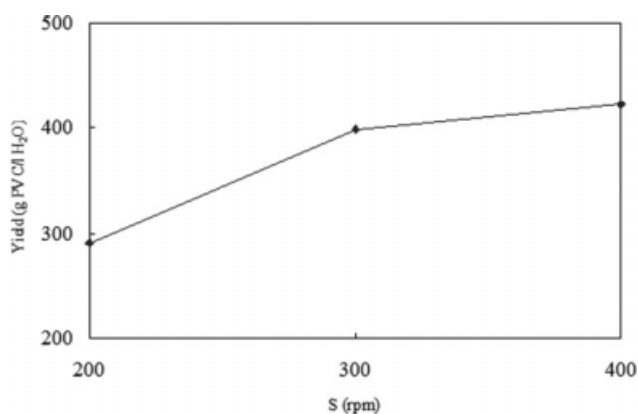


Figure 5 Influence of agitation speed on yield.

Influence of agitation speed

The influence of mixing intensity on the emulsion polymerization yield has been rarely investigated. Figure 5 shows the increasing of the polymerization yield with agitation speed. As the heterogeneous nucleation is the major mechanism in emulsion polymerization of VCM, a higher mixing rate results in a higher yields, because the monomer transfer from droplets to micelles will be enhanced. The results show that this influence is more significant when mixing rates vary from low level to mid level.

As it was discussed also in our previous article,²³ 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 yield, however, the responses at different agitation speed levels may be compared comparatively in a specified reactor configuration.

Influence of emulsifier

As indicated in Figure 6, when the concentration of emulsifier is increased, the yield increases too. This effect is very pronounced when surfactant concentration is varied from 1 g/l to 4 g/l. This is probably due to formation of more micelles as the main sites of polymerization. However, when emulsifier

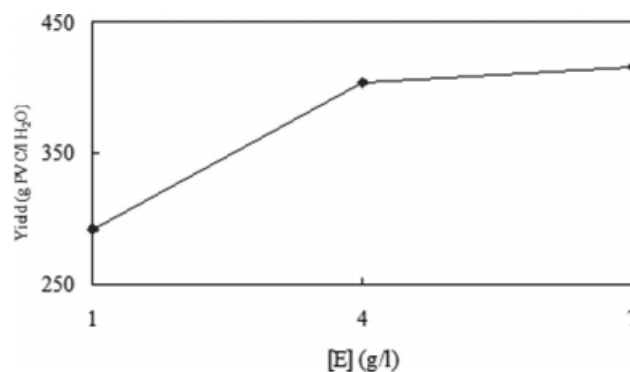


Figure 6 Influence of emulsifier concentration on yield.

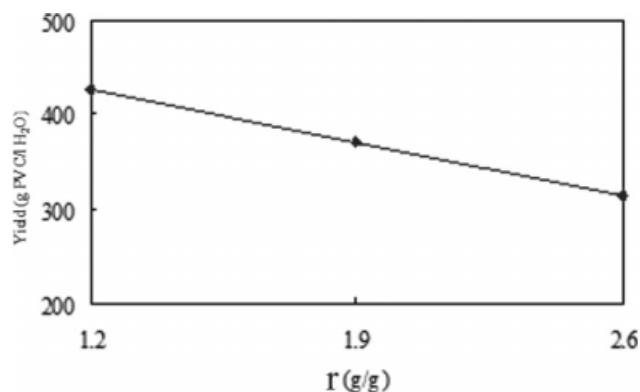


Figure 7 Influence of water/monomer weight ratio (r -value) on yield.

concentration exceeds the critical micelle concentration (CMC) (about 3 g/l)²⁹ the excess amount of emulsifier have very little influence on the yield.

Alvarez et al. examined SDS concentration between 1.0 and 6.1 g/l, in emulsion polymerization of VCM in batch reactor. They also found that increasing emulsifier concentration from 1 to 3 g/l, increase the polymerization rate. Nevertheless, a further increase from 3 to 6 g/l, results in no significant differences between conversion curves.¹⁷ This may be attributed to relative amount of micelles and initiator radicals in polymerization mixture. The initial polymerization rate depends directly on the number of micelles available as polymerization sites. It is well known that this quantity is related to the type and concentration of emulsifier, which in turn, determines the CMC and the amount of emulsifier available to form micelles.^{7,17,18,21,30,31} However, when the emulsifier concentration is much higher than CMC, a lot of micelles will be formed for which there are insufficient amount of radicals for initiation.¹⁷

Influence of water/monomer weight ratio (r -value)

The polymerization yield is decreased linearly with increasing r -value between 1.2 and 2.6, as expected (Fig. 7). Notice that a low r -value corresponds to a higher concentration of monomer. Boieshan has also found that the reaction rate depends almost linearly with r , in the range of 1.13–2.50, and for conversions up to 40%. At higher conversions, however, he observed an auto-accelerated effect, for r values less than 2.25.¹⁸

Optimum condition

The desired values of yield, K -value and PDI depend on the application of emulsion 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, whereas the

TABLE VII
Input Values and Conditions for OEC Analysis to Obtain the Optimum K -value, Minimum PDI, and Maximum Yield

Response	Worst value	Best value	Quality characteristic	Weight factor (%)
1 K-value	56	72	Nominal is better	50
2 PDI	3	1	Smaller is better	25
3 Yield	100	650	Bigger is better	25

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 emulsion PVC. Suppose that the target is to get the reaction yield as high as possible, a K -value equal to 72, and the smallest PDI (narrowest MWD). 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 all 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

$$\text{OEC}_i = \left(1 - \frac{|K_B - K_i|}{|K_B - K_W|}\right) \omega_K + \left(\frac{\text{yield}_i - \text{yield}_W}{\text{yield}_B - \text{yield}_W}\right) \omega_{\text{yield}} + \left(1 - \frac{\text{PDI}_i - \text{PDI}_B}{\text{PDI}_W - \text{PDI}_B}\right) \omega_{\text{PDI}} \quad (7)$$

where i , W , and B indices refer to the run number (1-18), the worst, and the best responses, respectively, each for K -value, yield, and PDI. The terms ω_K , ω_{yield} , and ω_{PDI} are the corresponding weight factors for contributions of these responses to determine the best condition. A set of typical values are used for these factors here, but generally they are selected based on relative importance of product quality or quantities. The input values for calculation of OEC terms are summarized in Table VII. The OEC values at any given condition in Table II are

TABLE VIII
Optimum Conditions for Maximizing the OEC

Factor	Level description	Level	Contribution
T	46 °C	1	13.365
$[E]$	7 g/l	3	5.072
$[I]$	0.4 g/l	1	3.993
R	2.6 g/g	3	4.290
S	300 rpm	2	7.420
Total contribution from all factors			34.140
Current grand average of performance			53.717
Expected result at optimum condition			87.857

calculated using eq. (7), as in the following is illustrated for first run:

$$\text{OEC}_1 = \left(1 - \left| \frac{72 - 76.84}{72 - 56} \right| \right) \times 50 + \left(\frac{145.9 - 100}{650 - 100} \right) \times 25 + \left(1 - \frac{1.53 - 1}{3 - 1} \right) \times 25 = 55.33$$

The new response, OEC, is finally maximized using Qualitek-4 software. The best levels, as well as the contribution of each factor for improvement of OEC are given in Table VIII. As it is observed, a set of $T_1S_2E_3I_1r_3$ is the predicted optimum conditions (with the order of importance) in which the indices show the best level. Although the current grand average of performance according to results in Table VIII is 53.717 units, setting the factors on optimum conditions increases the OEC by 34.140 units, so that the expected result at optimum condition will be 87.857 units. Hence, a very significant improvement on overall performance of system is expected if the optimum condition will be applied.

CONCLUSIONS

For batch emulsion polymerization of vinyl chloride, the influences of five operating variables (temperature, water to monomer weight ratio, concentrations of initiator and emulsifier, and agitation speed) on the K -value, PDI and yield, were statistically analyzed using Taguchi experimental design. The main conclusions are as follow:

- Because of dominant effect of chain transfer to monomer in VCM polymerization, the reaction temperature is the key parameter for controlling the molecular weight. Increasing the temperature will decrease the molecular weight and therefore the K -value.
- Increasing the temperature and initiator concentration will increase the PDI. Temperature is the dominant factor that broadens the MWD through four different ways: more active centers, promotion of disproportionation termination, more VCM solubility in water, and branching of growing chains.
- Agitation speed, emulsifier concentration, and water to monomer weight ratio, has the most effect on the polymerization yield. Polymerization yield will increase with increasing the agitation speed and emulsifier concentration, but decrease with water to monomer weight ratio.

After CMC, the emulsifier concentration has a smaller influence on yield.

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