

Effect of the Phase Ratio on the Particle Properties of Poly(vinyl chloride) Resins Produced by Suspension Polymerization

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ABSTRACT: The effects of the dispersed phase to continuous phase ratio (weight of VCM (gr)/weight of water (gr) ($\phi = g_{\text{VCM}}/g_{\text{water}}$)) on the particle properties of a poly(vinyl chloride) (PVC) suspension were investigated experimentally. A series of experiments were performed with different ϕ values in a pilot-scale reactor. The cold plasticizer absorption of the resin decreased with ϕ . Scanning electron micrographs showed that by the reduction of ϕ , many of the produced particles had a regular shape,

a smooth surface, and greater porosity. An increase in ϕ caused a wider and multimodal particle size distribution of the produced PVC particles. The mean particle size and bulk density also increased with ϕ , whereas the molecular weight and polydispersity index did not change. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2748–2755, 2008

Key words: particle size distribution; poly(vinyl chloride) (PVC); processing

INTRODUCTION

Suspension polymerization is a commercial process for manufacturing poly(vinyl chloride) (PVC). Approximately 80% of the world's PVC is produced by the suspension polymerization process.¹ Droplets of liquid vinyl chloride are dispersed in water by a combination of vigorous agitation and a suspending agent. Polymerization occurs inside the droplets as a result of an oil-soluble initiator. In suspension polymerization, each droplet behaves as a minibulk reactor. The particle size distribution (PSD), molecular weight (MW), morphology, and porosity of the formed PVC grains are important characteristics of particles of poly(vinyl chloride)s produced by suspension polymerization (S-PVCs) for end-use applications.

The drop size and PSD of dispersed phase droplets are determined as a result of the rates of breakage and coalescence of droplets. Because of the complexity of the process, problems involving mass transfer, chemical reactions, and its dependence on a large number of parameters, many scientists have worked with noncoalescing clean systems without surfactants² and with a low dispersed to continuous phase ratio (ϕ) or with liquid–liquid dispersion systems without polymerization.^{3,4} Several investigators

have worked on the effects of surface-active agent(s) on both liquid–liquid dispersion and suspension polymerization systems and derived a number of models to predict the drop size.^{5–10} Chatzi and Kiparissides¹¹ presented a model for the prediction of the steady-state drop size distribution. Their model was assessed with experimental data obtained with an *n*-butyl chloride/water dispersed system. Also, Maggioris et al.¹² studied the effect of turbulence on the PSD of droplets in a suspension polymerization system experimentally. ϕ in their experiments was 0.75. Zerfa and Brooks³ correlated the vinyl chloride drop size with the parameters affecting dispersion with a low vinyl chloride monomer (VCM)/water ratio (maximum $\phi = 57$ wt %) and obtained a complete relationship for the drop size, volume fraction of VCM, and Weber number. The effect of the agitator speed on the VCM drop size^{3,9} and on the mean particle size of PVC grains^{13,14} was investigated. Increasing the agitator speed was found to reduce the mean particle size.

One of the most important properties of S-PVC powder is its porosity. Studies have shown that higher porosity makes the stripping of unreacted VCM easier and also results in greater plasticizer uptake, which aids processing.¹ Some investigators have changed the types and concentrations of suspending agents to attain higher porosity.¹⁵ Nilsson et al.¹⁵ reported the influence of poly(vinyl alcohol) and hydroxypropyl methylcellulose (HPMC) on resin porosity. Cebollada et al.¹⁶ studied the effects of the HPMC structure and concentration on the porosity of PVC resins experimentally. Bao et al.¹⁷

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TABLE I
Suspension Polymerization Recipe

Ingredient	Ratio
VCM/water (ϕ ; g/g) (3.5 wt % HPMC in water)/ water (g/g)	0.41, 0.58, 0.84, 0.86, 1.1 0.02–0.022
(3.5 wt % HPC in water)/ water (g/g)	0.019–0.02
Span 20/distilled water (g/g)	0.0013–0.0144
MYPC/VCM (g/g)	0.00106

investigated the influence of the degree of hydrolysis of poly(vinyl alcohol) on the porosity and particle morphology of PVC resins. Also, Bao and Brooks¹⁰ investigated the influence of the temperature, conversion, and nonionic surfactant on the mean particle size, porosity, and morphology of PVC powder in a bench-scale reactor. They observed that with the reduction of the polymerization temperature and conversion, the amount of the plasticizer absorption increased.¹⁰ Recently, Bao and Brooks¹⁸ studied the influence of a new heterogeneous polymerization process on particle features in which *n*-butane was the reaction medium. They reported that PVC resins prepared by this polymerization process had a lower number-average particle size and higher porosity. Also, a regular particle shape was observed in the produced PVC particles.

In this article, the effects of the ratio of VCM to water (ϕ) on the particle properties of S-PVC resins in a pilot-scale reactor are presented. Most of the previous investigations were carried out with bench-scale reactors. The maximum ϕ value studied was 57 wt %.³ Some results have been obtained for systems without polymerization reactions.^{3,9,19} In this work, all the conditions were followed according to an industrial recipe in a pilot-scale reactor with ϕ values ranging from 50 to 110 wt %. Materials used in the experiments were provided by Bandar Imam Petrochemical Co. (Mahshahr, Iran).

EXPERIMENTAL

Materials

VCM was supplied by Bandar Imam Petrochemical Co.; hydroxypropyl methylcellulose (HPMC) (Methocel 65SH-50); hydroxypropylcellulose (HPC) (Klucel J), and sorbitan monolaurate (Span 20) as the suspending agents were supplied by Shin-Etsu Chemical Co. (Tokyo, Japan), Hercules International, Ltd., and Beckmann Chemikalien KG (Bassum, Germany; Becksurf 7125), respectively. Dimyristyl peroxydicarbonate (MYPC), used as an initiator, was supplied by Akzo Nobel Co. (Amersfoort, The Netherlands) under the trade name Perkadox 26.

Polymerization procedure

VCM polymerization was carried out in a 15-L stainless steel jacketed reactor with two baffles with a circular cross section and an agitator consisting of two eight-flat-blade turbines.

The following recipe was followed in agreement with the Bandar Imam Petrochemical procedure. Demineralized water, suspending agents, and an initiator were weighed and charged to the reactor (Table I). Then, the reactor was closed and purged with nitrogen, and a weighed amount of VCM (Table I) was charged to the reactor at $17 \pm 2^\circ\text{C}$. The mixture was agitated vigorously for 20–30 min to dissolve the initiator in VCM droplets while cold water was flowing in the jacket of the reactor. After that, the contents of the reactor were heated up to $52 \pm 1^\circ\text{C}$ by hot water flowing in the jacket. The warming took about 25 min. The timing of the polymerization was started when the temperature reached 52°C . The temperature was kept constant during the reaction. Finally, the polymerization was ended when the pressure in the reactor dropped by 0.3 bar. The reactor was quickly cooled with the circulation of cold tap water in the jacket. The unreacted VCM vented, and the produced PVC was discharged. The produced PVC resin was filtered, and the resulting wet cake was dried in a vacuum oven at 50°C for 24 h. The dried PVC was weighed, and the final conversion was calculated by gravimetry.

A series of experiments were performed with different VCM/water ratios (as shown in Table I) to investigate the effect of ϕ on particle properties while the other parameters were kept unchanged. In these experiments, the weight phase ratio of VCM to water was varied while the other operating conditions and the concentrations of other agents were fixed.

Characterization of the S-PVC particles

The mean particle sizes and PSDs of the dried PVC samples were measured with a Malvern model 2603LC particle size analyzer (Worcestershire, UK). The standard deviation (*s*) and particle coefficient of variation (*cov*) were calculated with the following formulas:

$$s = \sqrt{\sum_i w_i (d_i - \bar{d})^2} \quad (1)$$

$$\text{cov} = s/\bar{d} \quad (2)$$

where w_i is the weight fraction of the particle with a mean diameter d_i and \bar{d} is the mean particle size of the whole sample produced in one batch.

The porosity of the samples was characterized by cold plasticizer absorption (CPA) according to the standard test method for the plasticizer sorption of PVC resins under an applied centrifugal force

TABLE II
CPA, BD, and K Values of PVC Resins Prepared with Different ϕ Values

Run	ϕ	CPA (g/100 g of PVC)	BD (g/L)	K value	SD _{CPA} (g/100 g of PVC)	SD _{BD} (g/L)	SD _K value
1	0.41	72.4	323	68	1.49	0.65	1.96
2	0.58	73.7	280	67	3.30	1.9	2.32
3	0.84	36.4	426	69	0.34	0.6	1.07
4	0.86	44.8	384	70	2.20	1.1	0.35
5	1.1	46.1	374	69.5	1.13	1.6	0.78

SD = standard deviation.

(ASTM D 3367-95). The bulk density (BD) was measured by the DIN 53466 standard method.

Scanning electron microscopy (SEM; model XL30, Philips Co., Eindhoven, The Netherlands) was used to study the quality of produced particles as well as the underlayer surface porosity. The internal structure of the particles was studied via the sectioning of particles. For this purpose, the samples were soaked in distilled water overnight and while still wet were quickly frozen by liquid nitrogen and sectioned. Then, the prepared samples embedded in epoxy resin were coated with a thin layer of gold with a gold sputter coater (model SCD005, Bal-Tec, Hannover, Germany) *in vacuo*, and then micrographs were prepared.

The number calculated from the dilute solution viscosity measurements of a polymer, used to denote the degree of polymerization or molecular size, is the K value. This parameter depends on the relative viscosity (η_{rel}):¹

$$\log \eta_{rel} = \left(\frac{75K^2 \times 10^{-6}}{1 + 1.5Kc \times 10^{-3}} + K \times 10^{-3} \right) c \quad (3)$$

where c is the concentration of the dilute solution of PVC (g/dL). η_{rel} was measured with the viscometry method according to the standard test method for the dilute solution viscosity of a PVC resin with cyclohexanone (Merck, Darmstadt, Germany) as a solvent in 30°C in an oil bath (Townson & Mercer Co., Manchester, UK) and with an Ubbelohde viscometer (ASTM D 1243-95). Also, the MWs and polydispersity indices of the samples were measured by gel permeation chromatography (GPC; ALC, Waters) with a Styragel 6e column, a tetrahydrofuran solution of PVC at 40°C, and a 1 mL/min flow rate.

The CPA, BD, and K values of the PVC resins prepared with different ϕ values are shown in Table II. Each sample characterization was performed at least three times, and standard deviations are also included.

RESULTS AND DISCUSSION

Effect of ϕ on the particle size and size distribution

As shown in Figure 1, an increase in ϕ increases the mean particle size of a PVC resin. This could be due

to an increase in the coalescence rate of the droplets. At greater ϕ values, the probability of the collision of droplets and the coalescence rate increase. Thus, the coalescence rate is more significant, and a greater number of particles are produced. Similar observations were made by Zerfa and Brooks³ for stabilized and dispersed droplets of VCM in agitated aqueous solutions of hydrolyzed poly(vinyl acetate) in the absence of polymerization. Zerfa and Brooks carried out their experiments in a bench-scale vessel with ϕ ranging from 0.015 to 0.57 (with a volume fraction between 0.01 and 0.4). They concluded that the size of the droplets increased with ϕ . Our experiments in a pilot-scale reactor expanded the range of the variation of ϕ to 1.1, which was almost twice what was studied by Zerfa and Brooks.

PSD of the produced powder is shown in Figure 2 at different ϕ values, and the particle coefficients of variation of these samples are shown in Figure 1. Increasing ϕ results in an increase in the coefficient of variation. Thus, the dispersity of the particle size increases, and the size distribution becomes wider. Also, Figure 2 shows that with an increase in ϕ , the size distribution changes from a monomodal distribution to a multimodal distribution. Zerfa and Brooks³ obtained similar results for a dispersed VCM system at a low agitator speed. PSD in suspension polymerization is affected by the turbulence intensity. Turbulence intensities in stirred reactors

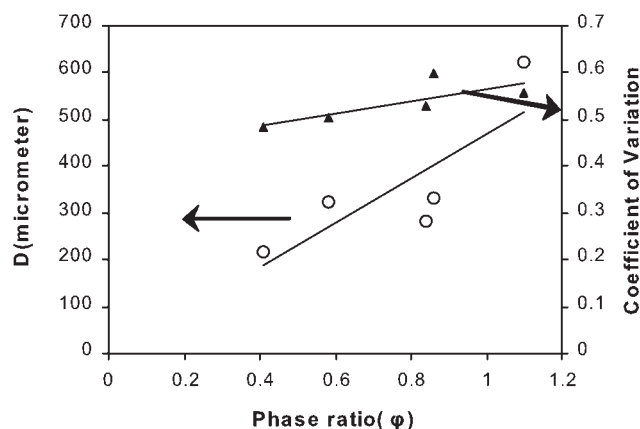


Figure 1 Mean particle size (D) and coefficient of variation for different ϕ 's.

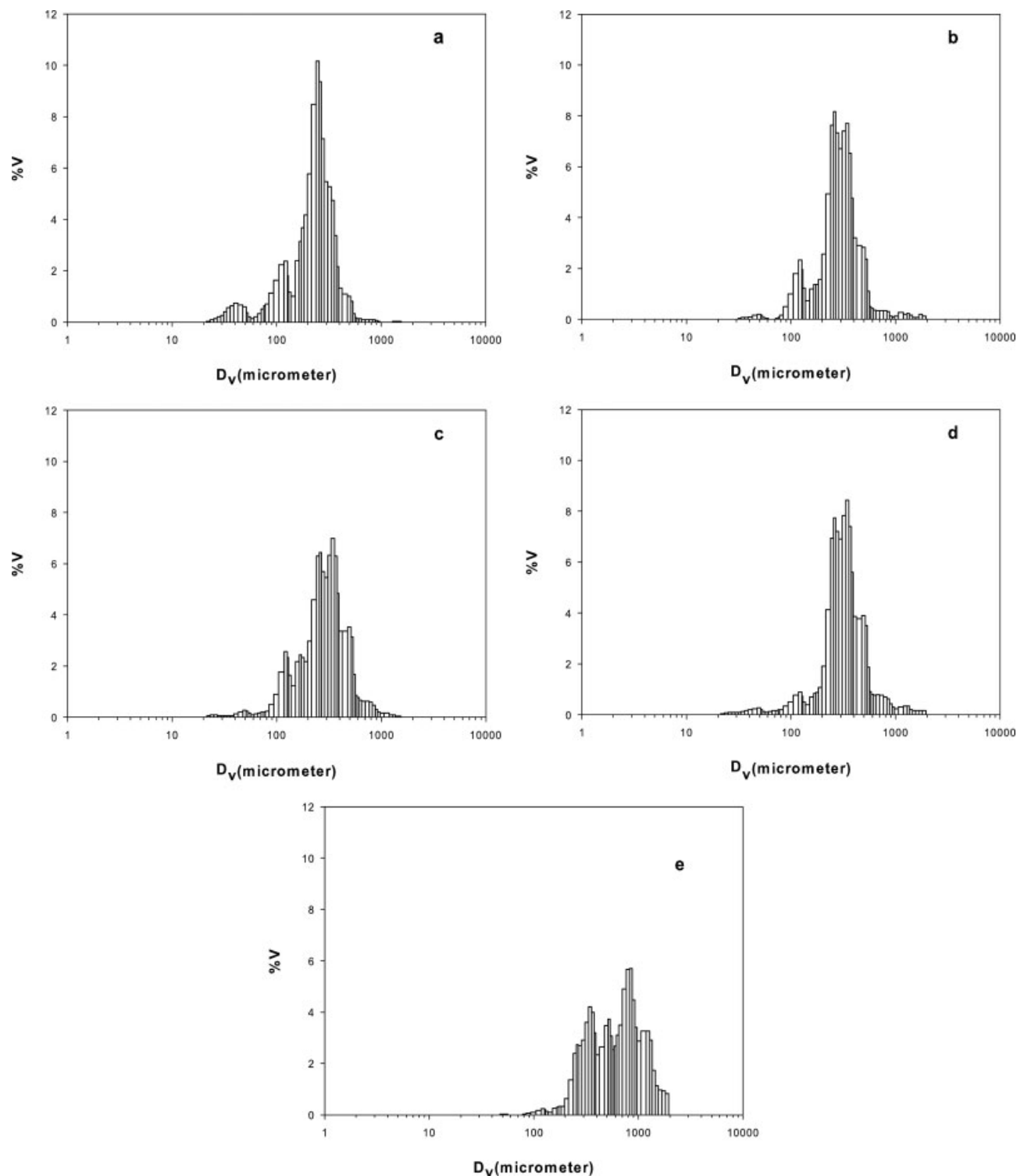


Figure 2 Variation in PSD of PVC at different ϕ 's: (a) 0.41, (b) 0.58, (c) 0.84, (d) 0.86, and (e) 1.1 (D_v = mean particle size; % V = percentage of volume).

vary in different regions of the reactors. It has been stated that the impeller region is dominated by drop breakage and that the circulation region is dominated by drop coalescence.¹¹ Several scientists have indicated that the effects of the turbulence intensity, coalescence, and breakage region on the drop size distribution is

very important.^{4,11,12} ϕ affects the regions of breakage and coalescence similarly to the turbulence intensity but to a lesser extent and, therefore, changes the mean particle size and size distribution.

Turbulence is damped by the dispersed phase. At smaller ϕ values, the damping effect is not

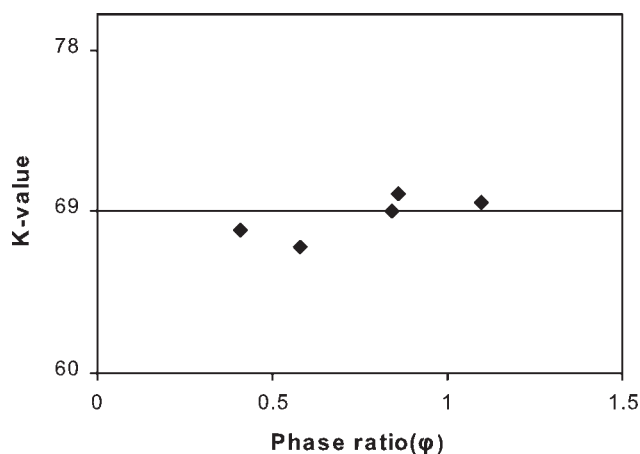


Figure 3 K values of PVCs produced with different ϕ 's.

significant; therefore, perfect mixing exists, and the system is perfectly homogeneous. Homogeneity of the reactor content results in a narrow distribution of particles. With an increase in ϕ , the number of VCM droplets in a unit of volume increases, and the probability of the collision of droplets and the coalescence rate increase, particularly in the early stages of polymerization, during which the viscosity of droplets has not reached an extent at which droplet breakup and coalescence are prevented. Moreover, the effect of turbulence damping by the dispersed phase becomes more significant, and it has been postulated that the coalescence region increases in volume and the degree of inhomogeneity of the vessel content increases. This means that the mean particle size of PVC particles shift to greater values (Fig. 1), and multimodal PSD is also observed (Fig. 2). As shown in Figure 2, with an increase in ϕ , the width of the distribution increases, and the mean particle size of PVC particles shifts to greater values (as shown in Fig. 1). At low ϕ [$\phi = 0.41$; Fig. 2(a)], one sharp peak can be observed at $\sim 250 \mu\text{m}$. In Figure 2(e) ($\phi = 1.1$), big peaks can be distinguished at 300, 500, and 800 μm because of the inhomogeneity of the vessel content. These results were obtained at a constant agitation speed in a VCM suspension polymerization system, whereas Zerfa and Brooks³ made similar observations for nonreacting VCM droplets in a dispersed system in which the agitation speed was variable. They observed that at a high ϕ value ($\phi = g_{\text{VCM}}/g_{\text{water}} = 0.57$) and low agitation speed, the size distribution of the droplets became multimodal.

Effect of ϕ on the K value and MW

Figure 3 shows the measured K values versus ϕ . The K value of each batch was measured four times. As shown in Figure 3, the K value does not change with ϕ . A GPC analysis of the samples gave similar

TABLE III
GPC Analysis of the PVC Samples

Run	ϕ	$M_w \times 10^{-4}$	$M_n \times 10^{-3}$	M_w/M_n
1	0.41	124.8	50.90	2.45
2	0.58	113	47.15	2.4
3	0.84	123.4	52	2.37
4	0.86	112	51	2.20
5	1.1	117	45.5	2.55

M_w = weight-average molecular weight; M_n = number-average molecular weight.

results (Table III). It indicated no appreciable variations in the corresponding MW. The MW of a polymer in a free-radical system is usually affected by the polymerization temperature and particularly by the choice and concentration of the initiator. Thus, in our experiments with a similar temperature and initiator, the K values and MWs were almost constant.

Effect of ϕ on porosity

Figure 4 shows the variation of CPA at different ϕ values. Increasing ϕ decreases CPA. A decrease in ϕ reduces the mean particle size, as shown in Figure 1. When the mean diameter of the particles decreases, the surface area of the PVC grains increases, whereas the length of the pores inside the particles decreases. Therefore, the permeation of DOP in inner pores takes place with less resistance, and this shows an increase in CPA.

A scanning electron microscope was used to examine the quality of the particles produced with different ϕ values. SEM micrographs of the entire section of PVC grains with two different ϕ values are shown in Figure 5. Both micrographs were prepared with a 140 \times magnification. Some pores in the inner structure of the grains were observed, as shown in Figure 5(a,b). The number of pores per

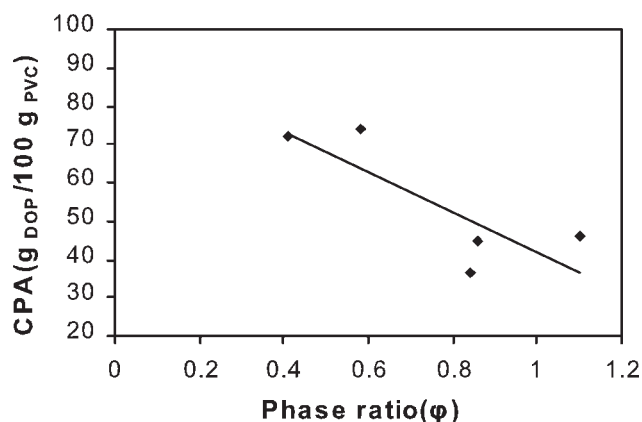


Figure 4 CPA of PVC grains produced with different ϕ 's.

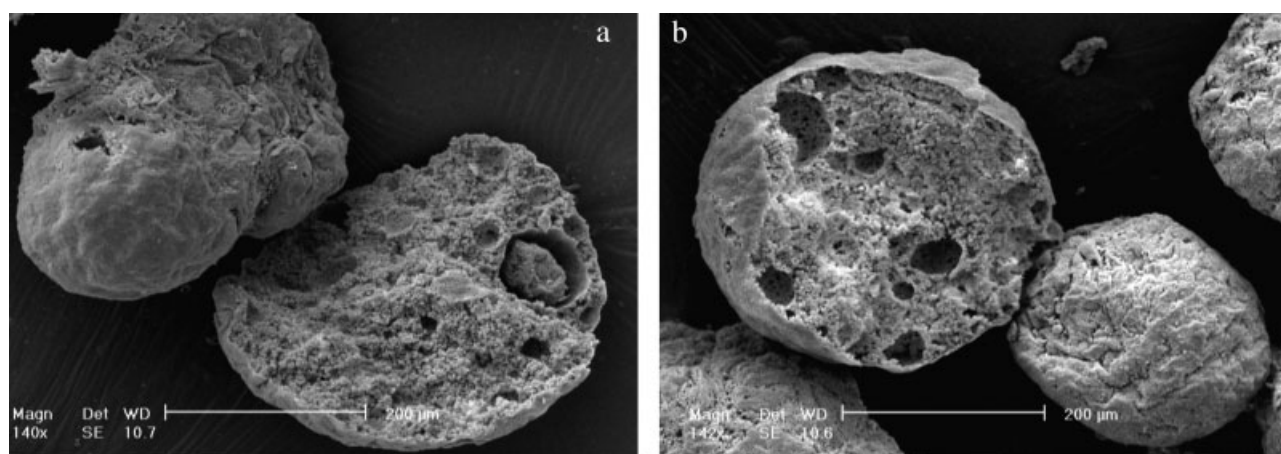


Figure 5 Scanning electron micrographs of the entire section of a PVC grain at $\phi =$ (a) 0.86 and (b) 0.41.

unit of surface area in the PVC grain prepared at a lower ϕ value [Fig. 5(b)] is greater than that in the PVC grain prepared at a higher ϕ value [Fig. 5(a)].

Figure 6 shows SEM micrographs of sectioned PVC grains prepared with two different ϕ values (0.41 and 0.86). The primary particles in the PVC resins prepared with the higher ϕ value [Fig. 6(b)] are greater than the primary particles formed in the grains prepared with the lower ϕ values [Fig. 6(a)]. The grains produced with the higher ϕ value are composed of many fused primary particles packed together, whereas in the PVC grains prepared with the lower ϕ value [Fig. 6(a)], the compositions of the primary particles are separate aggregates, resulting in more free space between the primary particles and greater porosity. It is believed that with ϕ decreasing, the amount of the continuous phase increases, and the applied shear of the agitator is rapidly transferred to the polymerizing VCM droplets because the effect of the turbulence damping by the dispersed phase is small. In the presence of

shear, the primary particles in the droplets will not pack closely together. Shear transferred to droplets causes the primaries to be aggregated to form a continuous open network at low conversions, and the product has a high porosity. Data in this respect are scarce. Only in one special case did Bao and Brooks¹⁸ obtain similar results for two different VCM/*n*-butane ratios in a new polymerization process. They also observed that with a reduction of the VCM/*n*-butane ratio, the porosity of grains became higher.

Particle morphology of the PVC resins

Figure 7 shows SEM micrographs of particles produced with two different ϕ values. Both of these micrographs were taken with the same magnification and scale. By comparing these micrographs, we can see that the PVC grains prepared with the lower ϕ value have a smaller mean particle size than those with the higher ϕ value. These results confirm the

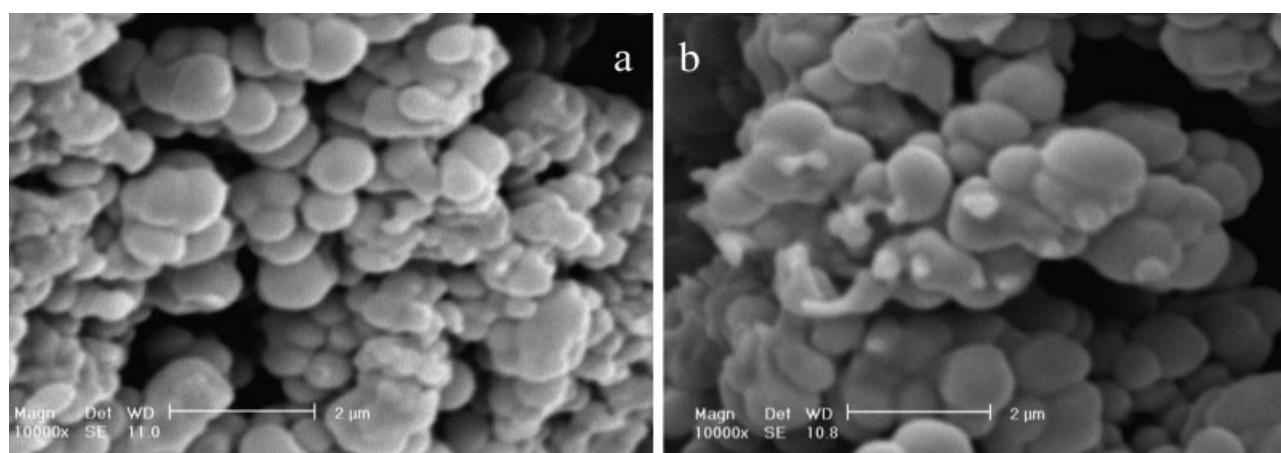


Figure 6 SEM micrographs of the center parts of a PVC grain at $\phi =$ (a) 0.41 and (b) 0.86.

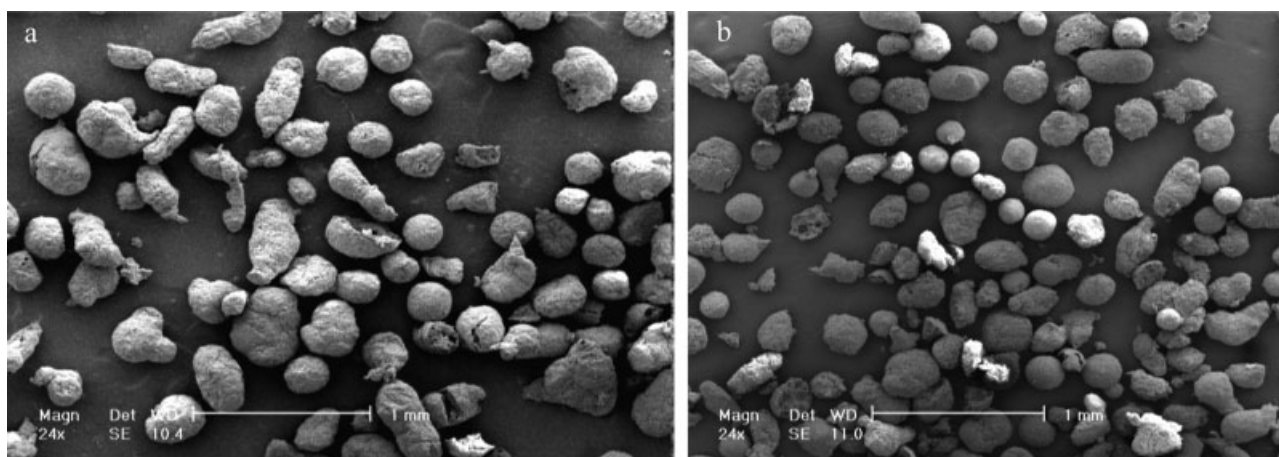


Figure 7 Some particles of PVC grains obtained from two different ϕ 's: (a) 0.86 and (b) 0.41.

results obtained from PSD analysis (Fig. 1). A greater uniformity of particles (a more regular shape and a smoother surface) can be observed with a lower ϕ value, as shown in Figure 8. There are many particles like those shown in Figure 8(a,b) at low and high ϕ values, respectively. It seems that because of the increase in ϕ , the probability of the collision of particles increases spatially in the early stages of polymerization; therefore, a greater number of subgrains are agglomerated, and the grains become rough and irregular in shape.

Effects of ϕ on the BD

The BD of a PVC powder is mainly affected by the external particle morphology and the internal structure of the particles. Regularity in grains leads to an increase in the BD of a PVC powder. Also, with a reduction of the porosity of the grains, the BD increases. Figure 9 shows the variations of the BD of the grains when the ratio of VCM to water changes.

The results indicate the increasing trend of the BD with ϕ . PVC grains prepared with a higher ϕ value have lower porosity (Figs. 4 and 5), whereas the particle shapes become irregular (Fig. 8); these parameters are in conflict with increasing BD. It seems that the influence of the decreasing porosity in increasing BD of PVC grains is more significant than the effect of the regularity of grains. Therefore, the overall observed trend is BD increasing with ϕ .

CONCLUSIONS

PVC powder was prepared with different ϕ ratios (VCM/water) through the suspension polymerization of vinyl chloride in a pilot-scale reactor. A decrease in ϕ was found to lead to a significant decrease in the particle size and narrower PSD. With an increase in ϕ , the PSD changed from monomodal to multimodal as a result of greater nonhomogeneity in the reactor content. Reducing ϕ resulted in a higher porosity and a lower BD. SEM micrographs

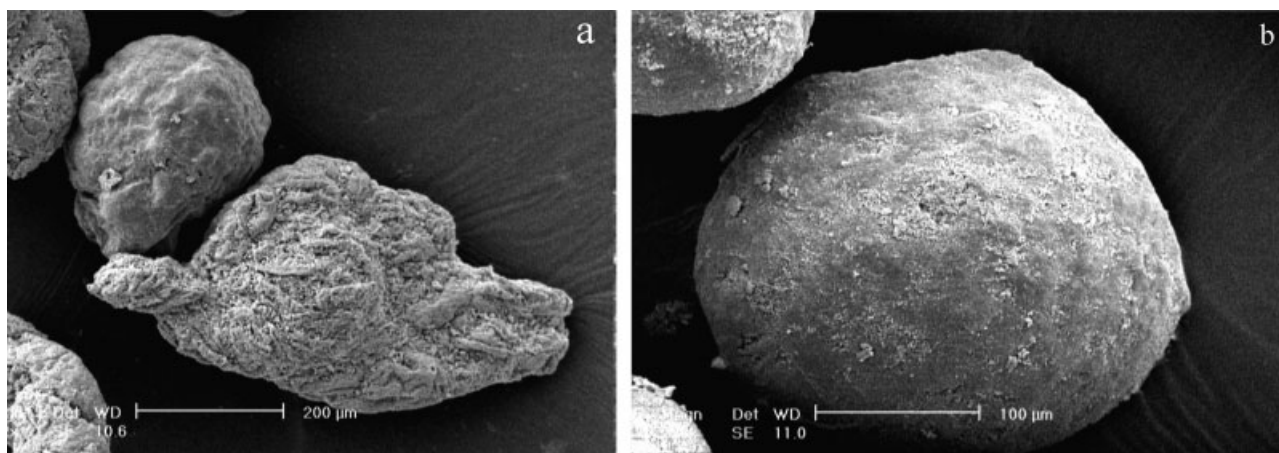


Figure 8 SEM micrographs of PVC grains prepared by two systems with $\phi =$ (a) 0.86 and (b) 0.41.

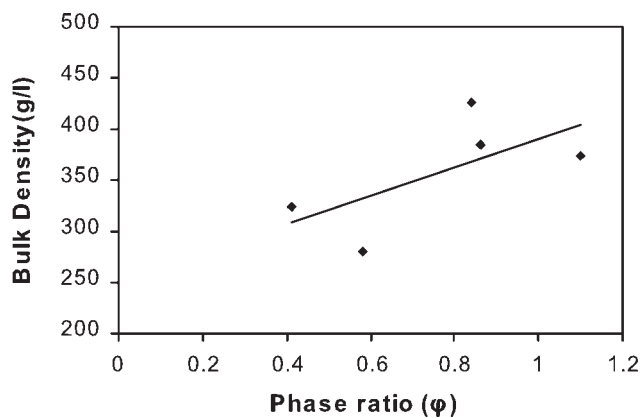


Figure 9 BD of PVC grains produced with different ϕ 's.

showed that the degree of agglomeration of primary particles increased with ϕ and that the particles became irregular in shape with rough surfaces at higher ϕ values. GPC analysis and measurements of the K values of the samples indicated that the MW and polydispersity index of the PVC resin did not change with ϕ .

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