Investigation of the Effect of Delayed Reflux on PVC Grain Properties Produced by Suspension Polymerization

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ABSTRACT: The effects of the condenser operation on properties of polyvinyl chloride (PVC) particles produced by suspension polymerization process were investigated in a pilot scale reactor. It was observed that delaying reflux operation increased the cold plasticizer absorption of the final resin. Both bulk density and K-value of the PVC powder decreased by increasing time delay in the reflux operation. It was also found that commencement of refluxing before 20% conversion resulted in bimodal particle size distribution (PSD), while monomodal PSD was obtained for longer delays in refluxing. SEM micrographs showed that surface of produced particles were rough and smooth when reflux started before and after 20% conversion, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2506–2514, 2010

Key words: polymerization; suspension; morphology; reflux; polyvinyl chloride; particle size

INTRODUCTION

The great number of applications of polyvinyl chloride (PVC) is largely due to its particle morphological characteristics together with its low price. Particle morphology is an important factor influencing the removal of unreacted vinyl chloride monomer (VCM), plasticizer uptake, processability and bulk density (BD) of the powder, which are important for downstream processing. In general, the morphology of suspension polymerization (S-PVC) particles is determined by the size distribution, shape, and the average porosity of the grains.

About 80% of the global PVC production is by suspension polymerization process.[1] In suspension polymerization process, VCM is dispersed as droplets into the continuous aqueous phase containing suspending agents by vigorous agitation. Each dispersed droplet acts as a minibulk polymerization reactor. The polymerization reaction is strongly exothermic (1540 kJ/kg). Batch reactors which are used to carry out the polymerization reaction at constant temperature are equipped with a cooling jacket for removal of the reaction heat. Large scale reactors are also equipped with overhead condensers to remove part of the reaction heat through the evaporation and subsequent condensation of the monomer. The operation of the reflux condenser affects the particle morphological properties of the final PVC grains.

Particle formation can be described considering the fact that PVC is not soluble in its own monomer. PVC molecular chains start to precipitate from monomer phase inside droplets at very low conversions ($X < 0.1\%$). By increasing the conversion, formation of primary particle nuclei takes place. Because of limited stability, primary particle nuclei rapidly undergo coagulation leading to the formation of primary particles ($X < 1\%$).[2–4] Primary particles grow by coagulation to form a continuous "cloud" inside the dispersed droplets ($\sim 4.5\%$ conversion[4]). Continuous three-dimensional primary particle network within the droplets has formed at critical conversion ($X_C = 15$–20%).[5] Primary particles grow further and fuse until the limiting conversion in which monomer rich phase disappears is reached (X_f). Although the effects of polymerization temperature, quality of agitation, type, and concentration of the suspending agents on properties of the final PVC particles have been studied,[3,6–16] very few reports are available in the literature addressing the effect of the reflux condenser operation on the final product properties.

Koyanagi et al.[17] used a 1-m³ polymerization reactor equipped with a multitubular condenser and showed that the commencement of refluxing before 5% conversion resulted in coarser final product. Kobayashi et al.[18] reported that monomer refluxing increased porosity and decreased BD of the final product. Cheng and Langsam[19] investigated the interaction between some process variables such as: rate of heat removal by the condenser, the reflux start time and suspending agent concentration on

porosity, bulk density, and particle size distribution (PSD) of the produced S-PVC powder in a 14-L reactor equipped with internal cooling coil in the vapor phase. It was observed that the fraction of coarse particles increased with the earlier start of refluxing, while particle coarsening effect became negligible when the refluxing introduced after 30% conversion. It was also reported that the BD of final PVC product was not affected by monomer refluxing while increased with concentration of suspending agents. Zerfa and Brooks[20] investigated the influence of the condenser operation on the S-PVC particle properties in a 1-L vessel experimentally. They observed bimodal PSD for the final PVC particles produced in the presence of refluxing. Porosity of PVC particles was found to increase by time delay in refluxing. Visentini[21] claimed that time delay in refluxing decreased porosity of the final product in contrary to what was previously reported.[20]

Reports on the effects of the time delay in refluxing on the properties of the final product of vinyl chloride suspension polymerization are scarce. Previous investigations so far have been limited to small phase ratios in bench-scale reactors[20] or have reported interaction effects of different process parameters on particle morphology[19] or have not reported complete particle properties.[17,18,21]

In this work, the effects of the time delay in refluxing on the particle properties of S-PVC produced in a pilot scale reactor (15 L) are presented. All the conditions have been followed according to the recipe being used at BIPC (Bandar Imam Petrochemical Company, Iran) with dispersed phase to continuous phase weight ratio (VCM/water) of 0.6. Experiments also covered a wide range of time delays in refluxing with a constant reflux rate.

EXPERIMENTAL PROCEDURE

Materials

VCM was supplied by BIPC (Bandar Imam Petrochemical Company, Iran), Hydroxypropyl methylcellulose (Methocel 65SH-50), Hydroxylpropylcellulose (Klucle J), sorbitan monolaurate (span 20) as the suspending agents were supplied by Shin-Etsu Chemical, Japan, Hercules International, Wilmington, Delaware, USA and Beckmann Chemikalien KG (Becksurf 7125), Germany, respectively. Dimyristyl peroxydicarbonate (MYPC) was supplied by Akzo Nobel under the trade name Perkadox 26 as initiator.

Polymerization procedure

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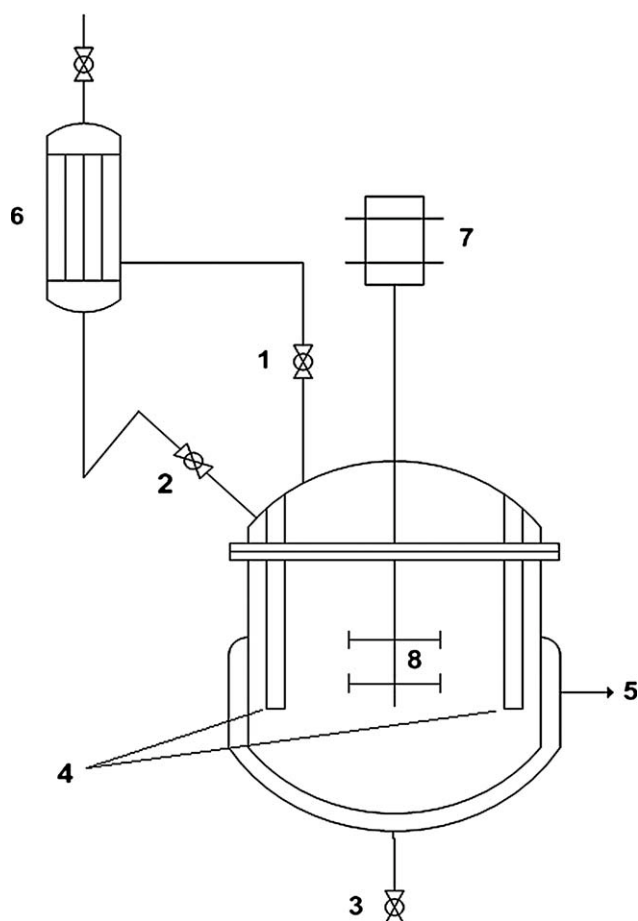

Figure 1 Schematic diagram of polymerization reactor: (1) VCM to condenser valve, (2) condensate output valve, (3) discharging valve, (4) baffles, (5) jacket, (6) condenser, (7) motor, and (8) stirrer.

tor was equipped with a vertical shell & tube heat exchanger as reflux condenser with 0.29 m² surface area. Condenser was isolated (Fig. 1). The flow rate of the cold water was regulated by a valve on the shell-side and VCM condensed on the tube side of the condenser. Reflux rate was calculated from energy balance on the isolated condenser [eq. (1)].

$$\dot{m}_{VCM}\lambda = \dot{m}_{water}C_p\Delta T \qquad (1)$$

where $\dot{m}_{VCM}$ is the flow rate of condensed VCM, λ is the latent heat of vaporization of VCM at reaction temperature (52°C). The latent heat of vaporization of VCM at reaction temperature was calculated making use of Watson equation[22] to be 292.59 kJ/kg. $\dot{m}_{water}$, C_p and ΔT are the mass flow rate of cold water on the shell-side of the condenser, the heat capacity of water, and the temperature difference between the inlet and outlet water on the shell-side, respectively. By regulating the cold water flow rate to the condenser, the reflux rate was controlled at 178 ± 5 mL min^{-1} in all runs. Materials were

TABLE I
Suspension Polymerization Recipe

Ingredient	Ratio
VCM/water (Phase ratio, φ) (g/g)	0.6
(3.5%wt%HPMCin water)/ Water (g/g)	0.015
(3.5%wt%HPCin water)/ Water (g/g)	0.0143
Span20/distilled water (g/g)	0.00073
MYPC/VCM (g/g)	0.00106

All acronyms are defined under Materials section.

charged to the reactor; according to Table I. Contents of the reactor were heated up to a reaction temperature of 52 + 1°C by flowing hot water in the jacket. The instance when the temperature of the reactor contents reached 52°C was defined as the reaction start time. The hot and cold water flow to jacket and condenser were regulated separately to achieve both constant reaction temperature and reflux rate. After 4 h from the start time of the reaction, the reactor was cooled down to about 20°C, and the excess vinyl chloride was slowly vented through the extractor via a venting valve on top of the condenser. The reactor contents were heated up to 60°C to remove the residual VCM afterwards. The produced PVC particles were filtered and the resulting wet cake was dried in a vacuum oven at 40°C for 24 h. The dried PVC was weighed. The weight of the final dried powder divided by the weight of the monomer initially charged to the reactor gives the final conversion.

Characterization of the S-PVC particles

The mean particle size (D_v) and PSD of the dried PVC samples were measured with Malvern particle size analyzer, model 2603LC (Worcestershire, UK), which works based on the principle of laser ensemble light scattering. The dried powder was placed into a feed tray, and distributed into a dispersing air jet. A monochromatic beam of light from a low power (2 mW) Helium–Neon laser (633 nM wavelength) with 9-mm beam expansion was shed on the jet of the air containing particles. The receiver was Fourier Transform Lens Mount Range Lenses 63, 100, and 300 mm focal lengths that covers 0.5–1880 microns size range. The light scattering was monitored by detector electronics. Built in software converted the measurements to PSD.

The porosity was characterized by cold plasticizer absorption (CPA) according to standard test method for plasticizer sorption of poly(vinyl chloride) resins under applied centrifugal force (ASTM D3367-95). The BD was measured according to standard method DIN 53466.

Scanning Electron Microscopy (SEM; Philips, model XL30, The Netherlands) was used to study the quality and shape of the produced particles. Dried powder was soaked in distilled water overnight and while still wet were quickly frozen by making use of liquid nitrogen. Some samples were sectioned for imaging. Samples embedded in epoxy resin were gold-coated in vacuum by using gold sputter coater. The images of the prepared samples were taken at 6 kV and with secondary detector with different magnifications.

The number calculated from the dilute solution viscosity measurements of the PVC, used to denote the degree of polymerization or molecular size, is the K-value. This parameter depends on the relative viscosity (η_{rel}), [eq. (2)]:

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

where c, K, and η_{rel} are the concentration of the dilute solution of PVC (g/dL), K-value and relative viscosity, respectively. 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, Manchester, UK) and with an Ubbelohde viscometer (ASTM D 1243-95).

RESULTS AND DISCUSSION

To study the effect of the start time of refluxing on the particle properties, a series of experiments was performed with constant reflux rate and different time delays in refluxing. It is well known that at 70–75% conversion (X_f) the monomer rich phase disappears in the droplets[6,23] therefore, experiments were performed with a final conversion of less than X_f, about 60%, to make sure that monomer rich phase existed to provide refluxing.

The effect of the time delay in refluxing on the PSD

Figure 2 shows the variation of PSD with different time delays in refluxing. Bimodal PSD are observed for the time delays less than 120 min in refluxing [Fig. 2(a–d)], while monomodal distributions are obtained for longer time delays [Fig. 2(e–g)]. According to the available rate data for the current recipe (provided by BIPC), conversion reaches 15 and 20% after 120 and 180 min, respectively.

Table II shows the Sauter mean diameter related to the left peak of PSD diagrams [Fig. 2(a–d,h)]. It can be seen that the Sauter mean diameter of the left peak for the final PVC particles produced in the presence of refluxing is greater than those of
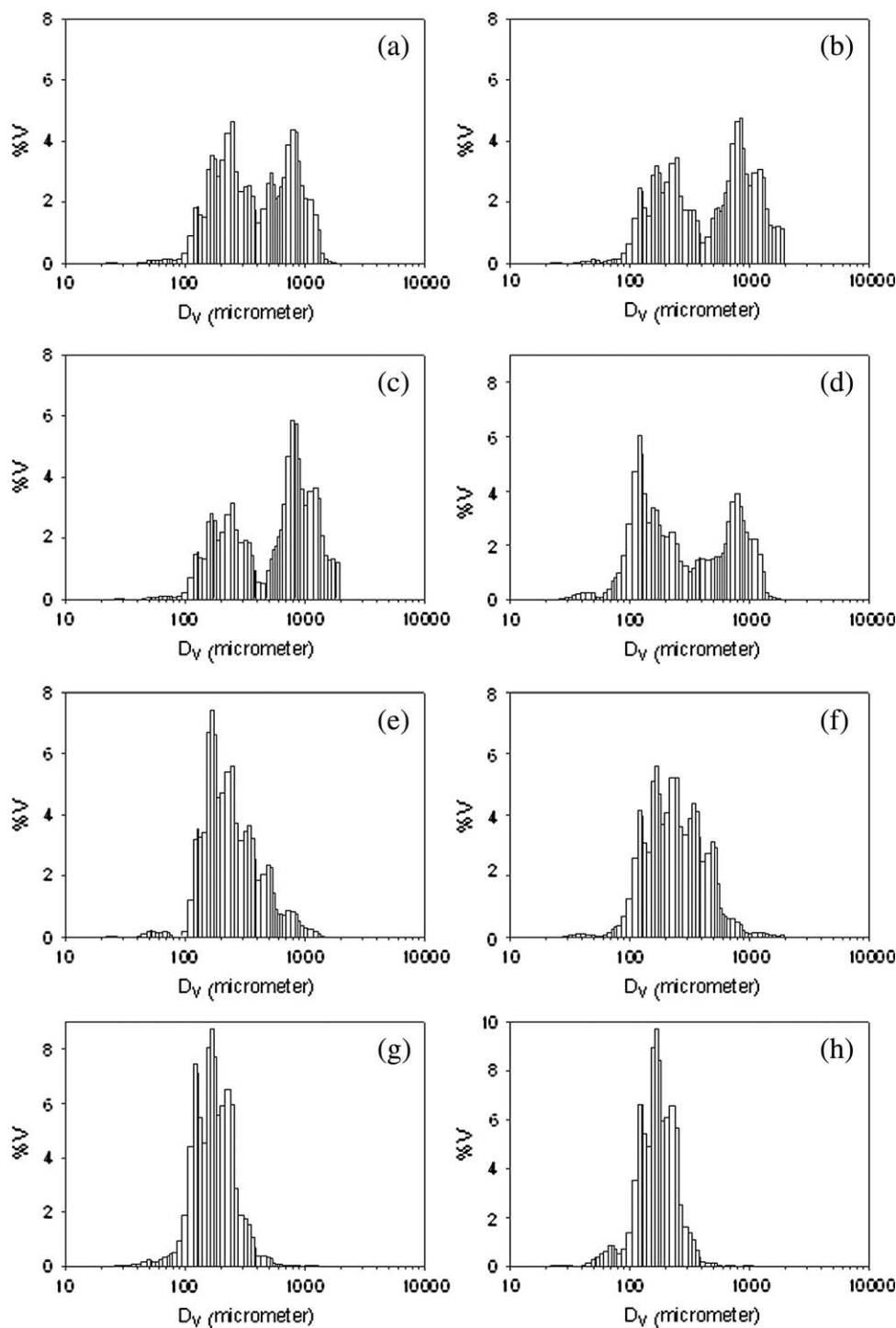
Figure 2 PSD of PVC powder produced by reflux start time at (a) $t = 0$ min, (b) $t = 15$ min, (c) $t = 30$ min, (d) $t = 60$ min, (e) $t = 120$ min, (f) $t = 150$ min, (g) $t = 220$ min, and (h) no reflux condition.

particles produced in the absence of refluxing. Zerfa and Brooks[20] reported that the peak on the left-hand side of the PSD diagram represented the particles produced by the "old" (not returning from the condenser) VCM droplets. Our findings do not follow the mechanism proposed by Zerfa and Brooks,[20] which may be due to the different phase ratio used in this work. They performed their experiments with

a phase ratio of 0.1, while the phase ratio in this work was 0.6 (based on the industrial recipe).

The following mechanism is proposed to illustrate the fate of the returning monomer droplets from the condenser.

Some of the droplets returning from the condenser ("new" droplets) develop their polymerized internal structure without blending with other droplets

Reflux start time (min)	Sauter mean diameter on left peak in PSD (μm)
0	184.7
15	191.0
30	182.9
60	126.1
No reflux	120.2

acquiring initiator by diffusion via continuous phase. The rest of the droplets returning from the condenser coalesce with old droplets forming bigger droplets in which polymerization reaction proceeds. Figure 3 shows the schematic diagram of the fate of the returning monomer droplets from the condenser based on the proposed mechanism.

When the reflux starts at the early stages of polymerization ($X < X_C$) the old droplets had yet "sticky" state[24] and coalesce with the "new" droplets returning from the condenser, forming bigger droplets. Polymerization proceeds in these bigger droplets producing final particles represented by the right peak in the diagrams shown in Fig. 2(a–d). As the phase ratio used in this work is far greater than previous investigation,[20] coalescence of the old and
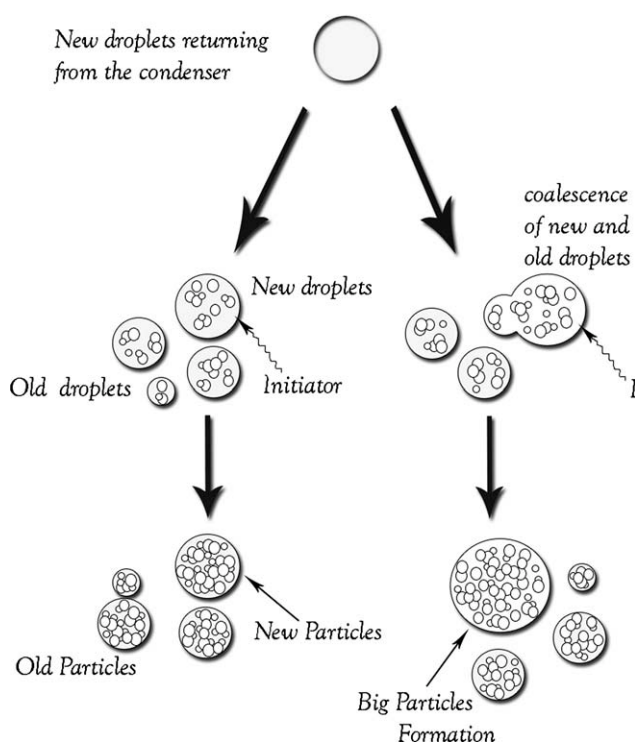
new droplets is more pronounced. Therefore, many bigger droplets are formed ending in bigger particles represented by distinct peak at greater sizes. Polymerization in new and old droplets without coalescence also proceeds resulting in final particles represented with the left peak in PSD.

When commencement of refluxing is delayed to greater conversions ($X > X_C$), however the monomodal PSD is obtained. After critical conversion (X_C), primary particles are formed as a continuous three-dimensional network in the droplets. At this stage, the droplets are much less sticky and are not susceptible to coalescence with returning droplets from the condenser. Therefore, the right route in Figure 3 which produces large particles is blocked and the right peak in the PSD diagram disappears.

The Sauter mean diameter of the particles produced by the time delays in refluxing equal or greater than 120 min are presented in Table III. It is clearly seen that the time delay in refluxing results in particles with greater Sauter mean diameter compared with the case of no refluxing. Existence of the old nonsticky droplets and addition of the "new" bigger droplets returning from the condenser produce a monomodal PSD with a greater particle Sauter mean diameter compared with the case of no refluxing.

Effect on porosity and bulk density of PVC

As shown in Figure 4, when the reflux was delayed to later stages of the polymerization, the porosity of the final PVC particles increased, showing a maximum at time delay of about 150 min. Critical conversion in which continuous three-dimensional primary particle network within the droplets formed was between 15 and 20% conversion.[2,5,6,25] As mentioned earlier, conversion reaches 15 and 20% after 120 and 180 min from the start of the reaction, respectively.

Monomer refluxing is in fact another way of increasing the agitation that is felt inside the forming grains.[21] According to previous studies in the presence of shear, the porosity of PVC grains increased.[6,26] By reflux operation and transfer of monomer from droplets to the vapor phase, primary

Figure 3 Schematic diagram of the fate of the returning monomer droplets from condenser (proposed mechanism).

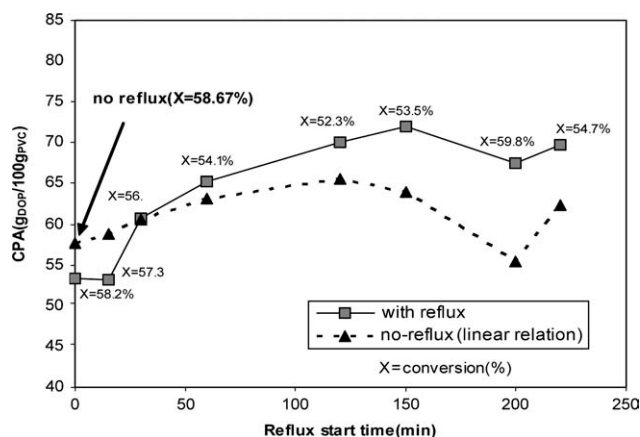| Reflux start time (min)	Sauter mean diameter (μm)
120	175.8
150	186.2
220	140.3
No reflux	120.2

Figure 4 CPA of PVC grains produced with different reflux start times (■) and calculated for no reflux with linear relationship (▲).

particles undergo shear being prevented to pack closely together. Therefore, it is expected that the use of condenser increases the porosity of the particles. Kobayashi et al.[18] also reported increased CPA by refluxing.

It has been tried to control the final monomer conversions at about $X = 60\%$ in the experiments. The calculated conversions for different runs are shown in Figure 4 (by symbol (■)). Regarding the effect of start time of the reflux on CPA, allowance must be made for the extent of the monomer conversion because porosity decreases with conversion during the course of the polymerization reaction. Bao & Brooks[14] carried out experiments in a 1-L vessel in the absence of refluxing and using poly(vinyl alcohol) as suspending agent. They found a linear decrease of CPA of the polymer with increase in conversion with a slope of -1. Cebollada et al.[3] used a 30-L polymerization reactor and a cellulosic suspending agent for producing PVC. It can be shown from their experimental data that particle porosity of the powder decreased linearly by increasing conversion with a slope of -1.4 in the range of 50–70% conversion. A linear relationship between CPA and conversion was adopted in this work. The slope of the linear relationship was taken from Ref. 3 due to the similar suspending agents used in both works. Intercept was determined such that the CPA and conversion measured for no-reflux case were met (CPA $= 57.01g_{DOP}/100g_{PVC}$, conversion $= 58.67\%$). The linear relationship is given by eq. (3):

$$CPA = -1.4X + 139.15 \qquad (3)$$

CPA was calculated from eq. (3) and plotted in Figure 4 (by symbol (▲)). The difference between the two plots solely shows the effect of refluxing on CPA.

When reflux operation was delayed to 150 min from the start of the polymerization ($\approx X_C$), the PVC particles have already formed and kept their structure even after losing some of their VCM by evaporation during the reflux operation. As can be seen from Figure 4, PVC particles produced by 150 min delay in refluxing showed maximum CPA. Similar results have been reported at a smaller phase ratio.[20] However, Visentini[21] found that lower porosity was obtained by time delay in refluxing. Experimental details were not reported by Visentini to compare the polymerization conditions and explain the contrary.

If refluxing is delayed after 150 min from the start of the reaction, porosity will decrease gradually. This could be due to the decreasing effect of conversion on CPA.[3,14] According to the proposed mechanism for particle formation,[2,6] at low conversions primary particles exist in separate or lightly agglomerated form, and porous structures occupy a large fraction of the droplets. At higher conversions the primary particles grow and fuse substantially. Both processes result in a continuous decrease in the final particle porosity. Monomer inside the pores of the formed particles (for $X > X_C$) undergo polymerization and decrease porosity of the particles. Refluxing takes out monomer from pores and decelerates porosity decrease.

Figure 5 shows the BD of PVC particles produced with different time delays in refluxing. As it is seen, BD shows an opposite trend compared with the porosity. That means, by increasing time delay in reflux operation BD decreases and then rises gradually.

Scanning electron microscope was also used to examine the quality of produced particles with different time delays in refluxing. Figure 6 shows SEM micrographs of the entire section of a typical PVC grain prepared with two different time delays in refluxing. It can be seen that pore diameters
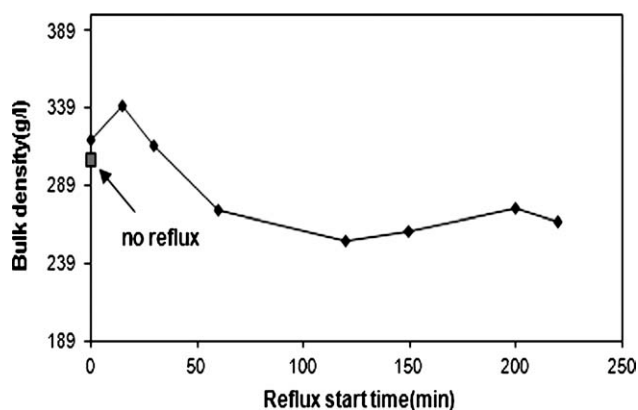

Figure 5 BD of PVC grains produced with different time delays in refluxing.
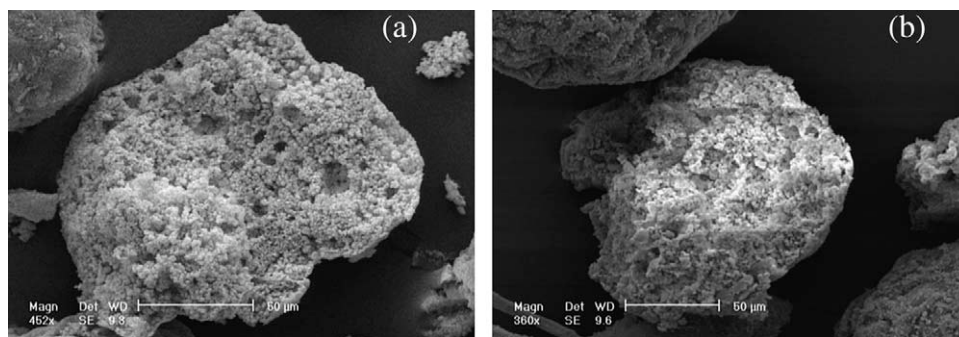
Figure 6 SEM micrographs of the entire section of a PVC grains at different time delays in refluxing: (a) $t = 200$ min and (b) $t = 30$ min.

appeared on the PVC grains prepared with longer time delay in refluxing [Fig. 6(a)] are greater than the pores appeared on the PVC particles prepared at shorter time delay in refluxing [Fig. 6(b)]. When the refluxing begins before critical conversion (X_C) in which particle skeleton becomes rigid, the droplets-particles shrink by evaporation of VCM, and thus, the pores inside the final particles become smaller [Fig. 6(b)]. When the reflux begins after X_C the 3D primary particles network has already formed. Evaporation pulls out monomer from the pores and water substitutes monomer therefore, greater pores will be seen in the final particles [Fig. 6(a)].

To examine the composition of the primary particle structures under different time delays in refluxing, SEM micrographs of cross section of PVC grains are shown in Figure 7. The Primary particles prepared by commencement of refluxing before X_C [Fig. 7(b)] are lightly aggregated with small pores and separated, whereas in the particles prepared by commencement of refluxing after X_C [Fig. 7(a)], the primary particles are fused showing greater diameter pores.

Effect on external morphology

Figure 8 shows SEM micrographs of typical particles produced with two different reflux start times and also without reflux as reference. It can be seen that the PVC grains produced without reflux [Fig. 8(e, f)] have generally spherical shape and smooth surface, while the PVC grains produced with reflux [Fig. 8(a,c)] have rough surfaces due to drop shrinkage caused by evaporation of VCM from the polymerizing droplets. It is also seen that a large fraction (36% by counting method) of the particles produced by a 30-min delay in refluxing are irregular in shape owing to coalescence of "new" and "old" droplets, while this fraction (27%) is less for 200-min delay in refluxing. This is due to the much less coalescence of new and old droplets after critical conversion, which is reached somewhere between 120 and 180 min from the start of the reaction in the experiments.

Effect on K-value

Figure 9 shows changes in K-value of produced S-PVC under condenser operation with different time delays in reflux. It can be seen that condenser operation generally decreases K-value. K-value slightly decreases with time delay in reflux, as well.

Several investigators have shown that molecular weight of the final PVC product slightly decreases with increasing initiator concentration.[25,27,28] Molecular weight significantly depends on polymerization
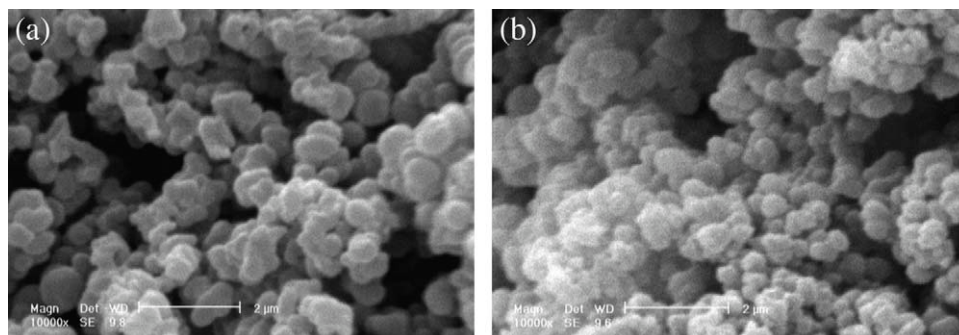

Figure 7 Fractured PVC particle detailing internal structure at different time delay in refluxing: (a) $t = 200$ min and (b) $t = 30$ min.
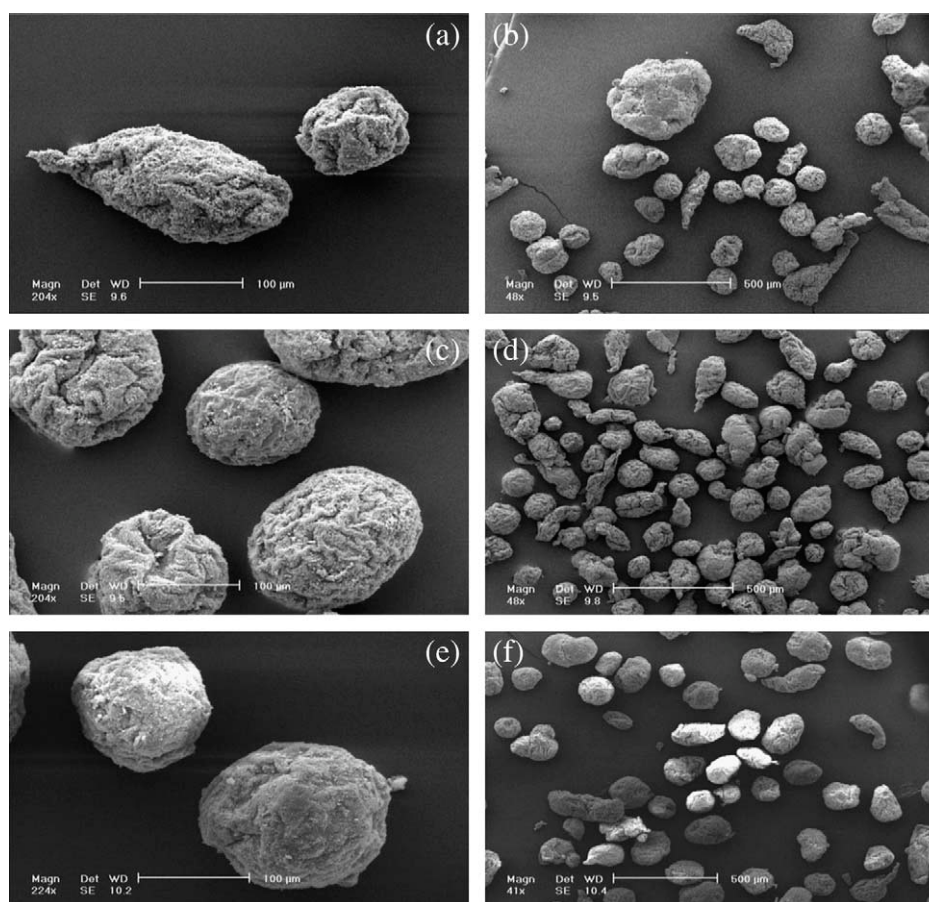
Figure 8 SEM micrographs of PVC grains at different delays in refluxing: (a,b) $t = 30$ min, (c,d) $t = 200$ min, and (e,f) no reflux condition.

temperature and dominance of chain transfer to monomer reactions. Xie et al.[25] indicated that chain transfer to monomer reaction rate constant to propagation rate constant ratio (C_M) for conversions less than X_f was constant, but C_M in polymer rich phase was greater than that in the monomer rich phase. Some monomer evaporates from the droplets during reflux operation causing initiator concentration to increase inside the droplets. This results in molecular weight decrease. When reflux begins at later stages of polymerization, the ratio of polymer rich phase to monomer rich phase in the droplets increases sharply. Since chain transfer to monomer is more pronounced in higher molecular weigh polymer rich phase and the contribution of the higher molecular weight polymer rich phase in producing the final product increases by delaying the reflux, more profound decrease in K-value is seen by increasing the time delay in refluxing.

CONCLUSIONS

This work investigated influences of time delay in refluxing on final PVC particle properties. The main conclusions are:

- Commencement of monomer refluxing before critical conversion ($X_C \sim 15$–20%), results in bimodal PSD while refluxing after X_C, results in monomodal PSD.
- A new mechanism was proposed to describe the features of the PSD of the final PVC particles produced in large phase ratios.
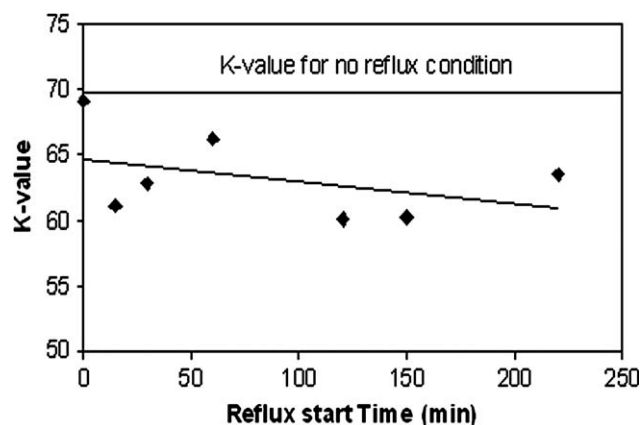

Figure 9 K-value of PVC reins produced by different time delays in refluxing at 52°C.

- Reflux operation generally causes porosity increase. If refluxing begins around X_C, porosity shows a maximum.
- SEM micrographs show that when reflux is started at early stages of polymerization (conversion less than X_C), PVC particles acquire irregular shape and rough surface, whereas refluxing after X_C produces smoother particles.
- Condenser operation in general and time delay in particular decreases K-value.

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