

Continuous dosing of fast initiator during vinyl chloride suspension polymerization: Polymerization rate and PVC properties

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ABSTRACT: Continuous dosing of a fast initiator during the suspension polymerization of vinyl chloride has been carried out in a pilot-scale reactor. The kinetics course of this polymerization and the particle features of the resulting grains were discussed and compared to the conventional polymerization with the same conversion and maximum reaction rate. It was found for the system used that a suitable dosage trajectory allows the reaction rate to remain constant during polymerization. This decreases the polymerization time up to 53% compared with the conventional suspension polymerization, while the molecular weight distribution and molecular weight of the final grains remained almost unchanged. SEM micrographs revealed that PVC grains prepared using this polymerization process had irregularly shaped, uneven particle surfaces and larger particle sizes. The grains also featured high porosity with loosely aggregated smaller primary particles that led to low levels of residual unreacted monomer. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 44079.

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INTRODUCTION

Poly(vinyl chloride) (PVC) is produced by the polymerization of vinyl chloride monomer (VCM) using emulsion, suspension, and bulk polymerization techniques. Almost 80% of total PVC is produced by the suspension process. Despite the high level of demands for this commodity polymer, the industrial suspension polymerization process is still conducted in batch-wise reactors.^{1,2} In conventional suspension polymerization of VCM, the monomer is dispersed into the continuous aqueous phase as separate droplets using a combination of stirring and the use of suspending agents. The oil-soluble initiator is initially added to the monomer droplets. The polymerization occurs in the monomer droplets by means of thermal decomposition of the initiator molecules that formed polymer chains via a free-radical polymerization mechanism.^{3,4}

In seeking to achieve higher productivity in this process, there are two policies that can be implemented: increasing reactor capacity and reducing the batch time process. However, given that VCM polymerization reaction is highly exothermic, heat transfer as a principal limiting will be more pronounced when larger-capacity reactors are used. In such circumstances, more efficient equipment is required for heat removal. On the other hand, reducing the batch time strategy is sometimes possible, but only when there is a change of process conditions without any technological modifications. In order to reduce the

polymerization time of suspension-PVC (S-PVC), the reaction rate is maintained at an almost constant permission value.^{2,5} In this regard, several methods are proposed; Feldman *et al.*⁶ and Darvishi *et al.*^{7,8} applied temperature programming in such a manner that the reaction rate remained constant during the process. The properties of the PVC product such as molecular weights, microstructure, and morphological characteristics, on the other hand, are affected by variations in the temperature.^{8,9}

However, the performance of such temperature programming, which is exerted by manipulation of water flow in jacket, may be inefficient in the case of large-scale industrial reactors. Pinto and Giudici² used a mathematical model proposed by Xie *et al.*¹⁰ and found that the polymerization rate can be kept constant through the use of an optimized mixture of initiators being added to the reactor at the beginning of the reaction. They determined that polymerization time is reduced by 30% when only a single initiator is used. No details were reported on resin morphological and molecular characteristics in this work. Akzo Nobel^{11–14} reported another technique for decreasing the polymerization time of S-PVC. This involved the use of continuous dosages of a fast initiator during the reaction. In this method, by dosing of a fast initiator, it was possible to obtain a polymerization reaction rate for which the heat of polymerization remained virtually constant at the maximum cooling capacity of the reactor over time. The reaction rate was

controlled by varying the amount of initiator during the course of polymerization. However, there was no a complete report available regarding the quality of PVC product. Mrázek *et al.*¹⁵ applied a solid initiator dosage strategy during the S-PVC polymerization using a special developed apparatus. The reactor productivity was almost unchanged in such system due to the initiator half-life. An overview of previous reports on this issue indicates that many important aspects, including molecular and morphological characteristics, have not yet been well studied.

In general, in the suspension polymerization of vinyl chloride, the morphological properties of the PVC grains are governed by polymerization conditions¹⁶ such as the initiator addition method,^{17–19} polymerization temperature,^{20,21} quality of agitation,^{22–24} type and concentration of the suspending agents,^{25–27} the polymerization VCM/water ratio,²⁸ monomer reflux conditions,^{29,30} and the conversion.^{17,21,26} The molecular weight (MW) and molecular weight distribution (MWD) of PVC resin are only governed by the polymerization temperature as a result of the great importance of chain transfer to monomer.^{31–33}

There are extraordinary advantages to be obtained by using continuous dosages of a fast initiator for the reduction of batch time polymerization and the consequent enhancement of productivity of S-PVC. However, there are no reported studies regarding the characterization of PVC resins produced by choosing an initiator continuous dosage strategy. It is, therefore, necessary to understand the influence of dosing of a fast initiator on the final PVC resin properties.

In this work, we present two VCM polymerization processes with identical maximum reaction rates: polymerization using an optimum initiator continuous dosage trajectory and the conventional suspension polymerization. They are then compared in terms of the reaction kinetic and molecular and morphological properties of PVC products. The method of manipulating an initiator continuous dosage trajectory in order to achieve a pre-defined conversion and maximum reaction rate with a lower reaction time has been described as an optimum initiator continuous dosage trajectory in our previous study, involving mathematical modeling and optimization algorithm and verifying by using several experiments.³⁴

EXPERIMENTAL

Materials

The apparatus used in this work for suspension polymerization experiments included a 48 L stainless steel-jacketed reaction vessel equipped with four tubular baffles and an agitator consisting of six flat-blade turbines. The temperature of the mixture in the reactor was kept constant during polymerization at the desired value by means of flowing cold water in the jacket. The temperature of the reaction mixture, jacket input/output and reactor pressure were recorded by the data logger at intervals of 3 s. A specially designed 250 mL sampler device was constructed on the reactor for the purpose of extracting samples during the process. A schematic diagram of polymerization reactor is shown in Figure 1.

The materials used are listed in Table I. Diisobutyl peroxide as a fast initiator was synthesized according to US 70,053,161(2006),

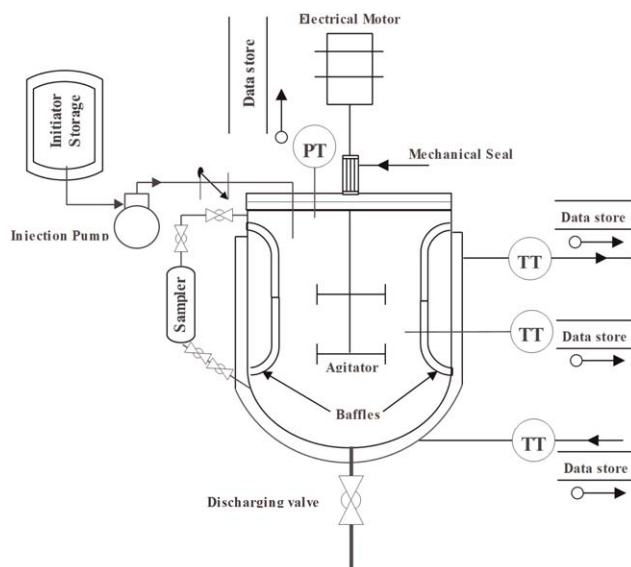


Figure 1. Schematic diagram of S-PVC polymerization reactor.

using potassium hydroxide (KOH), hydrogen peroxide (H_2O_2), isobutyl chloride (*i*-BuCl), and *n*-hexane. This initiator was obtained with a purity of 29.7 wt % in *n*-hexane and its active oxygen was 2.73%. The physical and chemical properties of the obtained diisobutyl peroxide was equivalent to Trigonox 187-C30 produced by the Akzo Nobel company.

Polymerization Procedure

Suspension polymerizations of VCM were carried out under two procedures for initiator addition: a conventional process used in commercial producing plants, wherein a mild initiator (Perkadox 26) is entirely charged at once at the beginning of the polymerization process and, a second process in which a fast initiator (diisobutyl peroxide) is dosed into the reactor during the course of the polymerization reaction. In conventional experiments (Exp. a), the reactor was initially fed demineralized water (DI) and other additives according to Table II. After sealing the reactor, it was purged with nitrogen and vacuumed to remove the air. The given amount of VCM was then charged in the stirred reactor with an agitation rate of 152 rpm. The reactor contents were heated to the desired temperature (52°C) in order to start the polymerization. The temperature of the reaction was maintained until a dramatic decrease in the reaction rate of the polymerization occurred (after critical conversion). The reaction mixture was then heated to 62°C in order to achieve a final conversion and remove unreacted VCM. Sampling was carried out during the course of polymerization through the use of a sampler device. Finally, the reactor was rapidly cooled to 30°C , followed by the condensation of the remaining VCM in the storage vessel. The final PVC grains were obtained after filtering and drying in a vacuum oven set at 55°C .

In the second series of experiments (Exp. b), the diisobutyl peroxide was used as a very fast initiator that was continuously dosed into the reactor during polymerization process. The polymerization process method was the same as described above. The only difference between these two methods of the

Table I. Material Used in the Suspension Polymerization of Vinyl Chloride

Name	Role	Trade name	Manufacturer
Vinyl chloride (VC)	Monomer		Arvand Petrochemical Co., Iran
Hydroxypropyl methylcellulose (HPMC)	Primary suspending agent	Methocel 65SH-50	Shin-Etsu Chemical Co., Tokyo, Japan
Hydroxypropyl cellulose (HPC)	Primary suspending agent	Klucel J	Hercules International, Ltd., Huntington, WV
Sorbitan monolaurate	Secondary suspending agent	Span 20	Beckmann Chemikalien KG (Becksurf 7125), Bassum, Germany
Dimyristyl peroxydicarbonate (MYPC)	Initiator	Perkadox 26	Akzo Nobel Co. (Amersfoort, The Netherlands)
Diisobutyl peroxide	Initiator		Petrochemical Research & Technology Co.

polymerization process was the addition procedure of initiator in the form of continuous dosages at the beginning of the reaction polymerization, which was stopped at the point of critical conversion (X_f).

It should be noted that each series of experiments was performed at least three times so as to ensure the repeatability of the polymerization processes.

Characterization of S-PVC Grains

The final conversion was calculated by gravimetry method for dried PVC. The conversion during process was obtained by using two methods: weighing the extracted samples and the energy balance around the isolated reactor. The conversion versus time relationship was obtained by weighing each sample, according to²⁶:

$$X = \frac{m_p(1+f_r)}{m_t f_r} \quad (1)$$

where X denotes conversion, m_p is the mass of dried polymer in the sample, m_t is the total mass of the sample, f_r is the VCM/water mass ratio initially present in the reactor. Another method for measuring the conversion is energy balanced around the isolated reactor according to³⁵:

$$V_{\text{mix}} \rho_{\text{mix}} C_{p_{\text{mix}}} \frac{dT}{dt} = -\Delta H_r M_0 \frac{dX}{dt} - U_t(T - T_j) \quad (2)$$

where V_{mix} , ρ_{mix} , and $C_{p_{\text{mix}}}$ are the volume, density, and specific heat of the reactor mixture in the reactor, ΔH_r is the enthalpy of the reaction, T and T_j are the temperatures of the reaction mixture and jacket flow. U_t is the overall heat transfer coefficient of the mixture in the reactor to cool water in the jacket that was obtained experimentally. The porosity of the grains were characterized by mercury porosimetry (Porosimeter Pascal 440 Thermo Finnigan, Italy) from 0.1 to 350 MPa and cold plasticizer absorption (CPA) according to the standard test method for plasticizer sorption of poly(vinyl chloride) powder under an applied centrifugal force (ASTM D3367-95). The bulk density (BD) was measured based on the DIN 53466 standard method. The mean particle size, particle size distribution (PSD), and specific surface area of the final grains of PVC samples were determined by a particle size analyzer, model Master size 2000, Malvern, Version 5.20, U.K. The Surface mean diameter is also known as the Sauter mean diameter (SMD), and was calculated by³⁶:

$$\text{SMD} = D_{32} = \frac{\sum D_i^3}{\sum D_i^2} \quad (3)$$

where, D is the particle diameter.

Table II. Suspension Polymerization Recipe

Ingredient	Units	Value	
		Exp. a	Exp. b
VCM/water	(g/g)	0.66	0.66
(3.5 wt % HPMC in water)/water	(g/g)	0.0132	0.0132
(3.5 wt % HPC in water)/(3.5 wt % HPMC in water)	(g/g)	0.96	0.96
Span 20/(3.5 wt % HPMC in water)	(g/g)	0.068	0.068
Perkadox 26/VCM	(g/g)	0.00117	—
Diisobutyl peroxide/VCM	(g/g)	—	0.00098
Temperature	(°C)	52	52
Agitator speed	(rpm)	152	152

Span is a measure of the width of the distribution, and is defined as:

$$\text{Span} = \frac{D_{90} - D_{10}}{D_{50}} \quad (4)$$

where, D_{90} , D_{50} , and D_{10} are diameters where 90%, 50%, and 10% of the population lies below these values, respectively.

Scanning electron microscopy (SEM; Philips Company, model XL30) was used to visualize the internal and external structure of PVC grains. The SEM images were analyzed by using image processing software (Image J) to measure the Sauter mean diameter (D_{32}) and the coefficient of variation (CV) of the primary particles in different conversions (at least 100 primary particles for three different broken PVC grains at each conversion were used).^{26,28,37} The coefficient of variation is defined as the ratio of the standard deviation to the mean diameter according to:

$$\text{CV} = \frac{\text{STDEV}}{\bar{d}} = \frac{\sqrt{\frac{\sum_{i=1}^n (d_i - \bar{d})^2}{n-1}}}{\bar{d}} \quad (5)$$

where, n is the number of particles with diameter, d_i , and \bar{d} is the average diameter.

The K value as a molecular characteristic was calculated from dilute-solution viscosity measurements of PVC samples via a viscometer (LAUDA, Proline, pv15) according to (ISO D3105-1994). The molecular weight distribution (MWD) indices of the samples were measured by gel permeation chromatography (GPC Agilent 1100) with PLgel, 10 μm , 300 \times 7.5 mm columns, a tetrahydrofuran (THF) solution of PVC at 30 $^{\circ}\text{C}$, and a 1 mL/min flow rate. The flow properties of PVC samples were determined by passing the 150 \pm 1 g PVC powder through a standard funnel (10 \pm 0.05 mm in diameter) according to ISO 6168. The test results are expressed as flow time in seconds. The unreacted residual monomer in PVC grains was determined using gas chromatographic analysis by means of a Varian 3900 GC coupled to headspace sampler HS 40.

RESULTS AND DISCUSSION

This work aims to investigate the effect of continuous dosages of a fast initiator on PVC resin quality which is used to enhance productivity. For this purpose, the properties of PVC grains produced by continuous dosages of a fast initiator (Exp. b) were compared to those of the PVC grains produced by the conventional polymerization process in which a mild initiator is totally added to the reactor at the beginning of the process (Exp. a). According to our previous work,³⁴ dosages of the initiator (diisobutryl peroxide) are initially kept constant about 0.36 g min⁻¹ for 20 min, and were then decreased to 0.0686 g min⁻¹ from 21 to 56 min, and were once again decreased to 0.04 g min⁻¹ within a 60 min time period. Initiator dosages were stopped at critical conversion (at which the monomer phase was exhausted as a separate phase and the reaction rate was sharply decreased). Figure 2 shows the initiator continuous dosage trajectory of the fast initiator in Exp. b. The implementation of such an optimal initiator continuous dosage strategy causes the reaction rate over the course of the polymerization

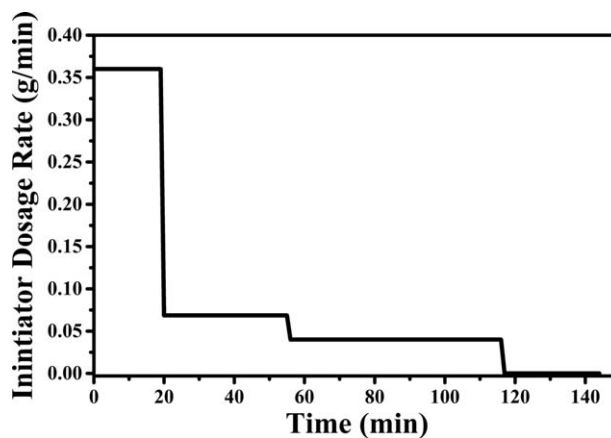


Figure 2. Initiator continuous dosage trajectory of Diisobutryl peroxide in Exp. b.

to be kept constant, based on the maximum rate in the conventional case (Exp. a).

The results of productivity (polymerization time, final conversion) and molecular characteristics, including morphological properties such as CPA, BD, and other properties of PVC grains such as flowability of grains, residual VCM, SMD, span, and specific surface area for two series of experiments are shown in Table III. Standard deviations (STDEV) for final sample characterization and experiment based on at least three times repeated are included.

The Effect on the Kinetics of Polymerization

The evolution of conversion and reaction rate for conventional (Exp. a) and initiator continuous dosage (Exp. b) processes which are calculated based on the energy balance around the reactor [eq. (2)] are illustrated in Figures 3 and 4, respectively. In addition, conversions obtained by the gravimetric procedure [eq. (1)] are superimposed on the Figures 3. It can be clearly seen that the polymerization time and reaction rate of the VCM suspension polymerization have been significantly affected by continuous dosages of the fast initiator. Applying a fast initiator continuous dosage strategy causes the polymerization reaction rate to be kept constant at the maximum permissible value during most of the reaction time. This leads to a 53% reduction in polymerization time compared with a conventional polymerization conducted on the same conversion level.

The difference between the reaction rates of the two processes is more pronounced at the beginning of the process. The fast initiator (diisobutryl peroxide) has a shorter half-life, and this enables control of free radical production and the tuning of the reaction rate at the start of polymerization. A high dose of the initiator is required to achieve the maximum reaction rate at the beginning of the reaction. Then the initiator dosage rate is decreased by approaching to diffusion-controlled reactions and the auto acceleration stage so that the reaction proceeds at the same rate.

Another point to be noted is that the initiator dosing during the early stages of polymerization needs to pass through the continuous aqueous phase and cross the VCM droplets/water

Table III. Characteristics of the Final PVC Grains for the Conventional (Exp. a) and the Initiator Continuous Dosage (Exp. b) Polymerizations

Parameter	Unit	Exp. a	STDEV	Exp. b	STDEV
Initiator type		MYPC	—	Diisobutryl peroxide	—
Initiator dosage		Non-continuous	—	Continuous	—
Initiator amount	(g)	14.3	—	12	—
Polymerization time	(min)	315	3.8	145	4.4
Conversion	(%)	83	1.7	84	1.6
Weight-averaged molecular weight	(g/mol)	198,000	2900	189,000	3100
Number-averaged molecular weight	(g/mol)	83,000	1400	78,000	1300
K value		70.4	0.50	69.8	0.45
CPA	(g Dop/100 g PVC)	30	1.8	40	1.6
BD	(g/L)	495	3.3	480	3.7
Flow ability	(s/150 g)	22	0.5	30	0.82
Residual VCM	(ppm)	4.4	0.065	0.18	0.045
SMD	(μm)	128	3.5	148	4.1
Span		1.15	0.032	1.228	0.036
Specific surface area	(m^2/g)	0.047	0.0012	0.039	0.0015

interface in order to diffuse into monomer phase. After skinning the monomer droplets, some initiator decompose at that point on the surface of the particles and some of them penetrate into the surface of the particles. The later can increase the partition coefficient in the polymer to the monomer phase than is the case for the conventional process, and the most of the initiator remains in the polymer phase due to the affinity of peroxy initiators to PVC chains.¹⁵ Therefore, the diffusion-controlled reaction is more pronounced and these results in an increase in the reaction rate.

On the other side, initiator molecules which are decomposed on the interface of the polymerizing VCM droplets, consume the monomer dissolved in aqueous phase. Therefore monomer mass transfer happens during the vapor phase or droplet to the interface for monomer supplying. In these conditions, the pressure of the reactor gradually starts to fall at low conversion.

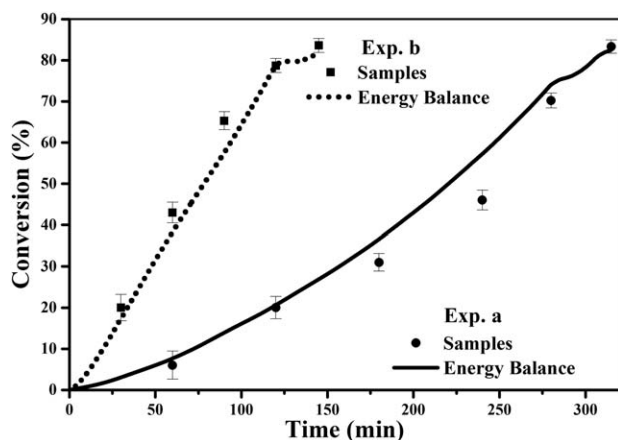
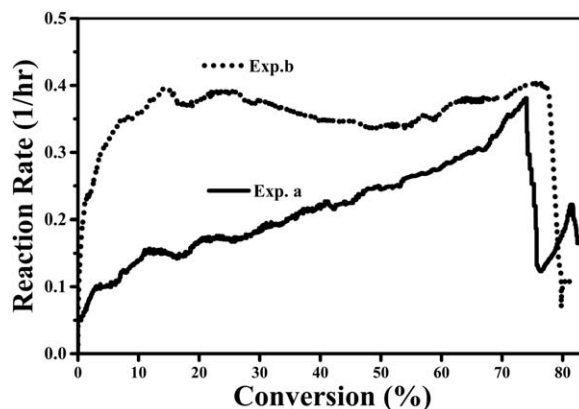
**Figure 3.** Conversion during processes for Exp. a and Exp. b.

Figure 5 shows the reactor pressure versus conversion for both processes.

Note that in the conventional polymerization, the pressure drop begins when the reaction volume shrinks because of the conversion of monomer to polymer and increment of the volume of vapor phase (about 55% to critical conversion). During in this stage of dropping pressure, the reaction rate reaches the maximum. Increasing of the conversion in the reactor leads to the pressure dropping dramatically due to both the volume increase during the vapor phase and the monomer transfer from the vapor phase to the polymer phase (beyond critical conversion). During this stage, the reaction rate decreases immediately due to the consumption of liquid monomer phase.^{38–41} The critical conversion (X_f), is specified at this stage of pressure drop. At this point of conversion, the reactor pressure and the reaction rate decrease dramatically.^{10,38,39,42} In conventional polymerization (Exp. a), critical conversion can be determined based on the drop in reactor pressure. But in the case of polymerization

**Figure 4.** Reaction rate versus conversion for Exp. a and Exp. b.

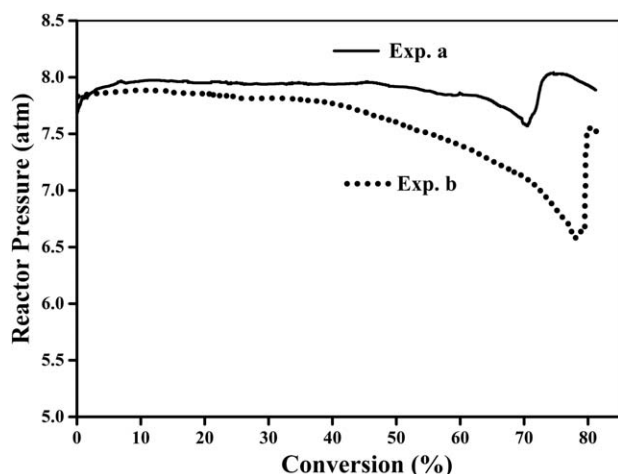


Figure 5. Reactor pressure versus conversion for Exp. a and Exp. b.

with initiator continuous dosage (Exp. b), the reactor pressure starts at a low conversion due to initiator dosages. Critical conversion was determined according to sharp decreases in the reaction rate (Figure 4) and reactor pressure (Figure 5).

Figure 5 shows that, in the initiator continuous dosage system, the drop in pressure starts at about 40% conversion where the surrounded skin is sufficiently rigid.^{43,44} After the critical conversion for both processes, the temperature of the mixture in the reactor was raised to increase the reaction rate and remove VCM unreacted.

Therefore, in the polymerization process with initiator continuous dosage, there are three main zones which are reaction sites, i.e. monomer, polymer and the interface. The occurrence of reactions at the interface causes an increase in critical conversion (X_c) due to consumption of the monomer which exists in the aqueous and vapor phases. This result is evident in the conversion values obtained by both gravimetry and energy balance (Figure 3). These measurements show that critical conversion for the conventional and initiator continuous dosage processes occurred in the ranges of 70 to 73% and 76 to 79% respectively.

The Effect on MW and MWD

Figure 6 shows the evolution of K value with conversion for both processes. Because the decomposition rate of the fast initiator is rapid, the initial concentration of free radicals and macro radicals during the process with continuous dosages is higher than in the case of conventional process. Thus, the chances of chain termination reactions increases, and thereby results in the reduction of the kinetic chain length and molecular weight. This phenomenon is more pronounced at the beginning of the polymerization process due to a higher initiator concentration and a homogenous reaction. The difference between the K values of two processes gradually decreases with conversion due to decrease in the level of initiator dose and increasing diffusion controlled reaction as well.

The average molecular weight of PVC increases slightly with conversion that occurs before critical conversion, and then decreases gradually with conversion due to an increase in transfer reactions as a result of a decrease in monomer

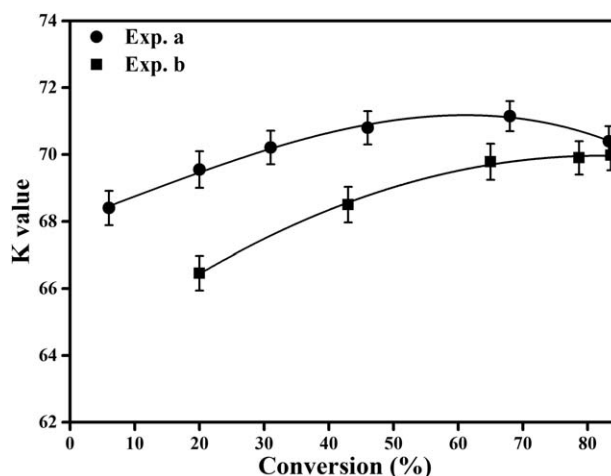


Figure 6. K value versus conversion for grains for the conventional (Exp. a) and the initiator continuous dosage (Exp. b) polymerizations.

concentrations.^{45,46} According to Figure 6, in the case of conventional polymerization, the molecular weight of PVC increases during polymerization up to a critical monomer conversion of beyond 70%, due to the increasing contribution of polymerization during the polymer-rich phase. Beyond this conversion, a distinct decrease in molecular weight is observed as a result of the increasingly diffusion-controlled propagation rate and the increasing importance of chain transfer to monomer. Under initiator continuous dosage conditions, however, the occurrence of critical conversion is delayed compared with conventional polymerization. After X_c , the shorter half-life of the fast initiator results in the initiator concentration being very low. Therefore, a continuous increase in K value was observed during the polymerization to reach the final monomer conversion. This balances the low fractions of chains formed early in the process, thereby resulting in similar final molecular weights and molecular weight distributions for the chains formed under the conventional process. These results are consistent with

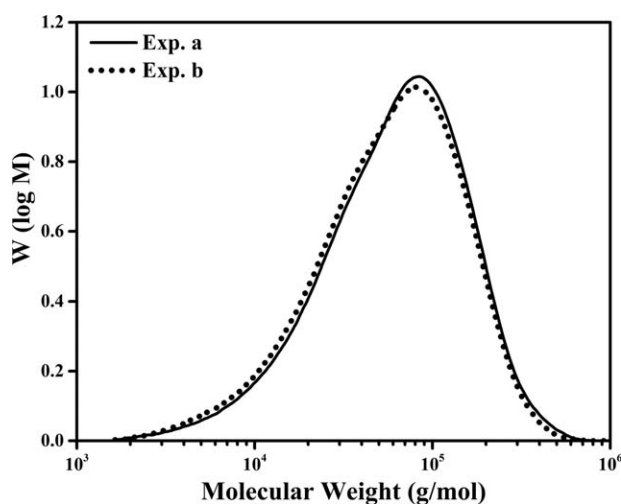


Figure 7. Average molecular weight distribution for grains for the conventional (Exp. a) and the initiator continuous dosage (Exp. b) polymerizations.

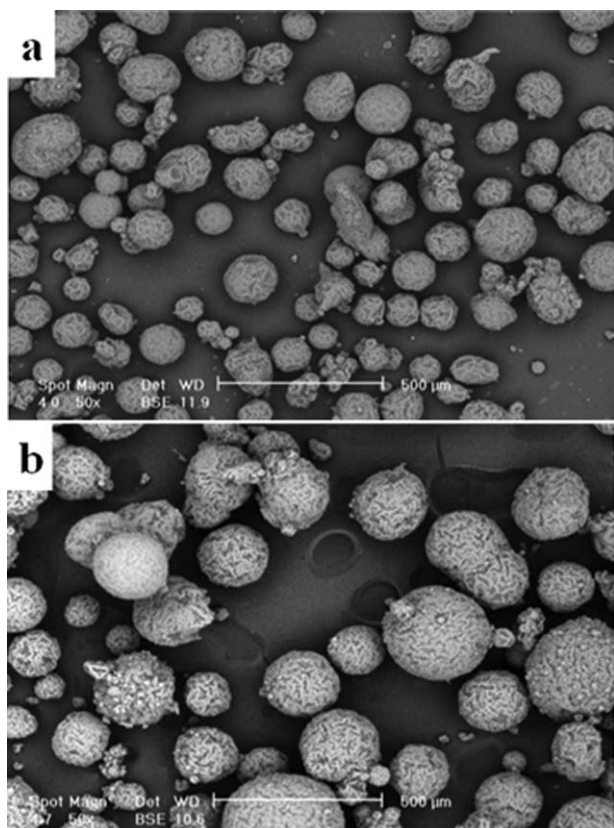


Figure 8. SEM micrographs of PVC grains produced by the conventional process (a) and the initiator continuous dosage process (b).

research to the effect that the molecular weight of PVC is slightly affected by initiator concentration and is significantly affected by polymerization temperature.^{31,32,45,47} Figure 7 compares the average molecular weight distributions of the final PVC produced by two processes. It is evident that the molecular weight distribution of PVC resins obtained from two the processes remained almost unchanged.

The Effect on PSD and External Morphology of Grains

The exteriors of PVC grains prepared by the two different processes were studied by analyzing SEM images and appeared in Figure 8. It was observed that the larger PVC grains with rough surfaces produced by the initiator continuous dosage procedure have different appearance qualities than PVC grains produced by the conventional process.

The slight degree of solubility of VCM in water means that some latex-like particles might form on the surfaces of these polymerizing monomer droplets, i.e., on the water/polymer interface. The poor solvent characteristics of water to solve PVC causes an earlier precipitation of the polymer chains on the surfaces of the monomer droplets, and also produces very short oligoradicals. At low conversion in which the grain crust contains a sufficient amount of pores these oligoradicals enable to migrate into the polymer-rich phase and continue growing. The pores of the polymer-rich phase gradually hills and these short chains encounter increasingly more difficulties for joining to the polymerization medium in the interior of the particles, and therefore remain on the interface while starting to form some latex-like particles.^{37,48,49} This phenomenon is more pronounced under initiator continuous dosage systems, due to the greater

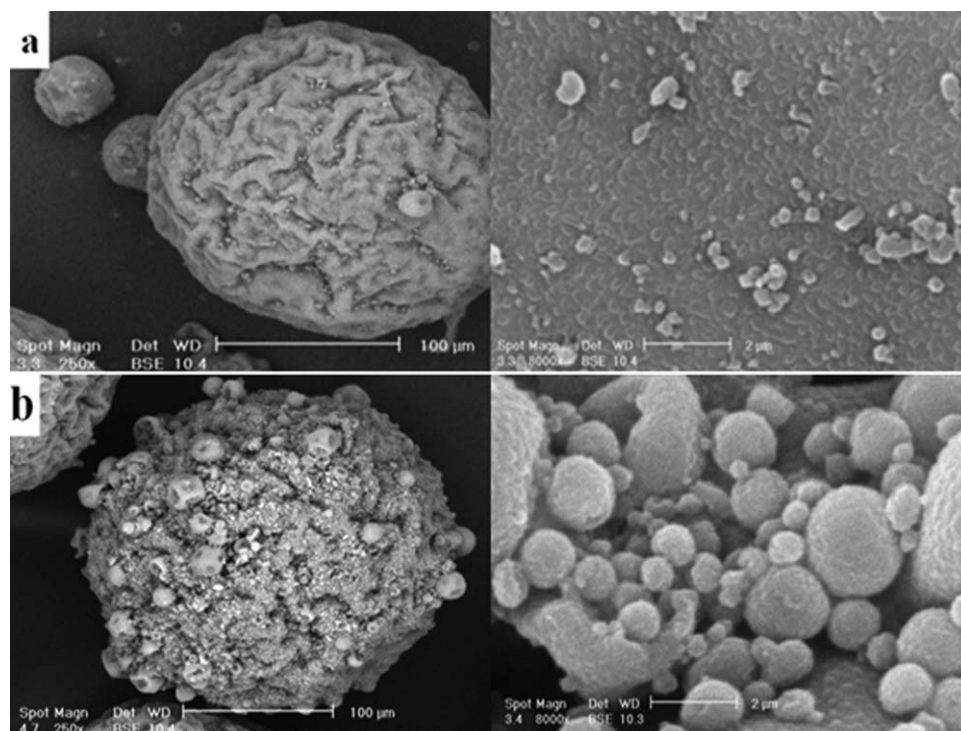


Figure 9. SEM micrographs of PVC grains surface produced by the conventional process (a) and the initiator continuous dosage process (b).

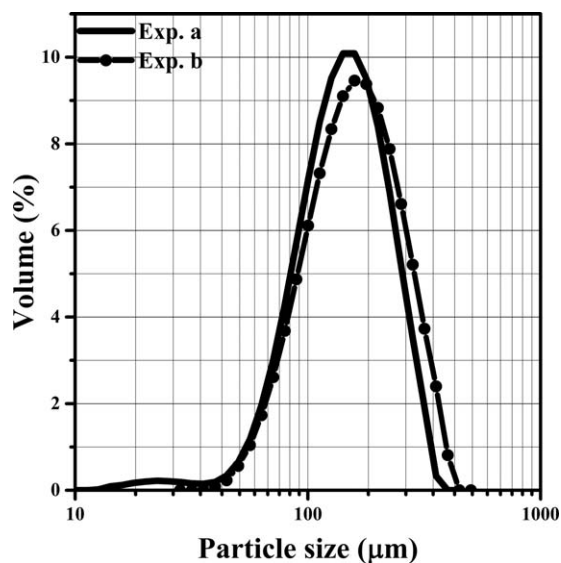


Figure 10. Particles size distribution of PVC grains prepared by the conventional process (Exp. a) and the initiator continuous dosage process (Exp. b).

availability of initiator on the interface at the moment. This causes a large number of newly-formed particles (big blisters) on the grains surface. This in turn produces large particles with rough surfaces due to the presence of newly-adhered particles. The micrographs of the surface of PVC grains prepared by the two processes at higher magnifications appear in Figure 9. The big blisters are obvious in Figure 9(b). In contrast, in conventional polymerization, in which initiator is insufficient during the aqueous phases, the latex-like particles formed are quite small. Some of these latex-like particles adhere to the grains surface while others remain in the system as discrete particles [Figure 9(a)].

Particle size distributions of PVC grains prepared by the conventional process (Exp. a) and the initiator continuous dosage process (Exp. b) appear in Figure 10. The particle size distribution of the PVC grains prepared by Exp. b is slightly broader than that in Exp. a (as characterized by span values given in Table III).

The particle size distribution of PVC grains vary in accordance with the three stages of the polymerization process: an initial low-viscosity stage (drop breakage), the sticky stage (drop/particle coalescence), and the final stage (particle stability).^{4,50,51} In conventional PVC polymerization, prior to monomer conversion, the 35 to 40% drop/particle coalescence rate is significantly reduced and the particle size distribution is established up to this conversion.^{4,26,52} In the case of polymerization involving initiator continuous dosage, particles size distribution is influenced by initiator dosing. Therefore, the particle size produced by Exp. b is larger, and particle size distribution is broader, due to adhered newly formed particles on the surface during the process. The PVC grains prepared by this experiment have a higher Sauter mean diameter (SMD) and a lower surface area for particles as a consequence (see Table III).

The long tail of the distribution curve of particles prepared by Exp. a, on the other hand, arises with the inclusion of latex-like particles formed during the aqueous phase. In contrast, in polymerization with initiator continuous dosage these ultrafine particles can grow during the process due to the presence of sufficient initiator during the aqueous phase. These ultrafine particles reduce the SMD of particles and increase the surface area of PVC grains consequently.

The Effect on Internal Morphology

Figure 11 shows SEM micrographs of cross section of the fractured grains obtained during Exp. a, and Exp. b. in various conversions. The extent of the fusion of primary particles is influenced by conversion.^{17,43,53} The figure reflects what appears to be a more noticeable change in the nature of internal structure for the grains produced by the conventional condition (Exp. a) as opposed to another condition (Exp. b) when conversion increases.

Increasing the concentration of free radicals increases nucleation, and thus the number of initial primary particles increases, which results in PVC grains with more porous internal structures.⁵⁴

Using dosages of the fast initiator during polymerization increases the concentration of free radicals (particularly at the beginning of the polymerization) and the number of the primary particles, which produces PVC grains with large numbers of pores. In addition, during the polymerization with initiator continuous dosage, the coalescence rate of primary particles reduced owing to the earlier establishment of the primary particles due to the high conversion rate. Figure 11 shows that in the conventional process (Exp. a) the number of primary particles was reduced with conversion, and the size of the primary particles increased, but the number and the size of primary particles in Exp. b was slightly changed.

Another point is that using initiator continuous dosage, and the consequent polymerization on the surface of the grains, caused the pores of skins to close more rapidly. Therefore initiator cannot easily diffuse into the droplets, and polymerization reaction rate relatively reduces inside the droplets. Therefore, the number and size of interior pores are slightly changed when conversion increases. In contrast, in grains produced by the conventional polymerization (Exp. a), interparticle volumes are regularly filled with polymer when conversion increases.

The sizes of the final primary particles in the PVC grains prepared conventionally [Figure 12(a)] are bigger than those in the grains formed by the initiator continuous dosage system [Figure 12(b)]. In other words, the grains produced in Exp. a are composed of fused primary particles packed together. This result in lower porosity compared with PVC grains produced by Exp. b with many smaller loose primary particles. This promotes the formation of porous PVC grains, and has been observed in that case of the initiator continuous dosage.

An evolution of the Sauter mean diameter of primary particles with conversions was obtained for both conditions with the image analyzer software. Figure 13 shows these trends. Both curves clearly exhibit a trend of increasing primary particle size

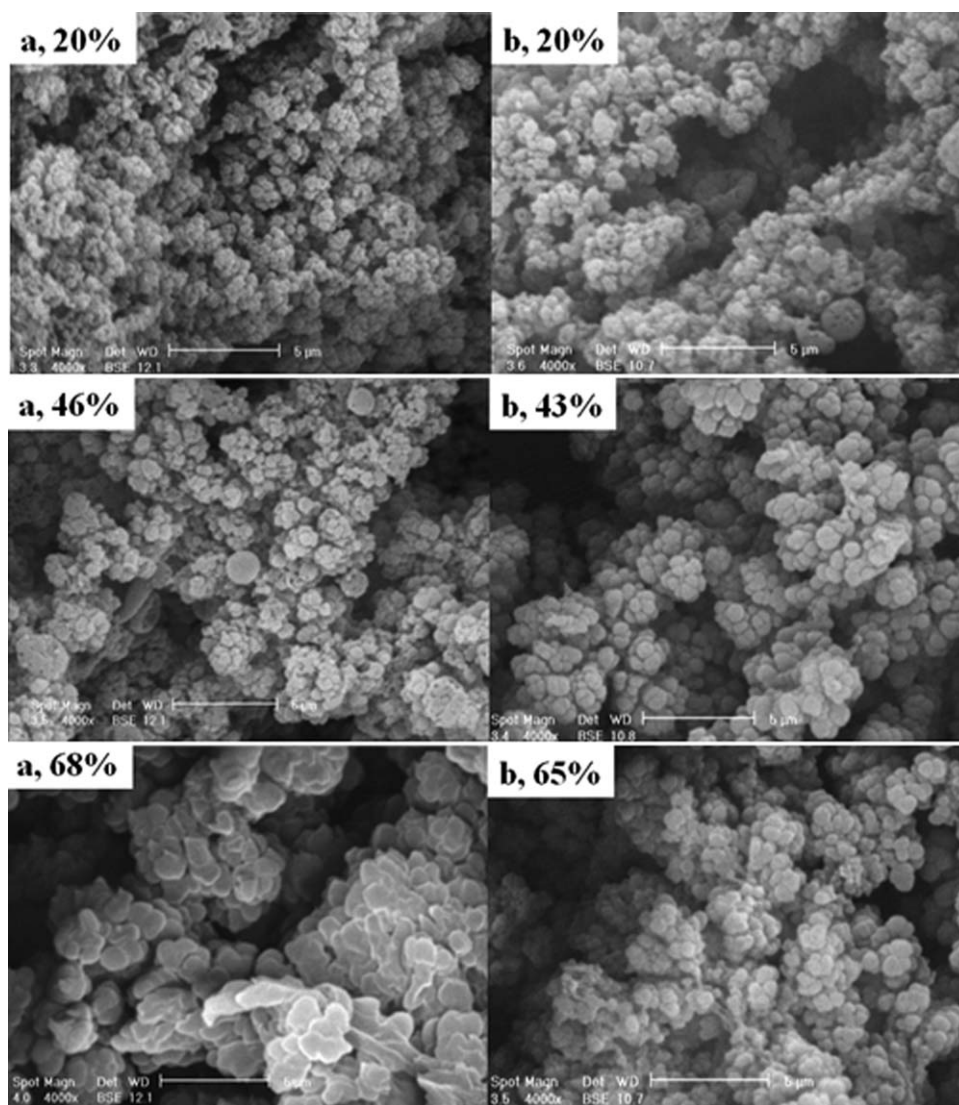


Figure 11. SEM micrograph of interior of PVC grains at different conversion for the conventional process (a) and the initiator continuous dosage process (b).

with conversion. The stability of the primary particles occurs at a significantly smaller extent for Exp. b. This means that using an initiator continuous dosage system accelerates the formation and establishes of three-dimensional (3D) networks between the primary particles inside the polymerizing monomer droplets.

The final sizes of the primary particles formed by the conventional condition (Exp. a) are larger than in the case of PVC grains produced through initiator continuous dosage, as was verified by SEM micrographs (see Figure 12). The variation of the primary particle size distribution with conversion was investigated by its coefficient of variation (CV) and is reported in Figure 14. Coefficient of variation of primary particle size is almost constant in the whole conversion range, for the initiator continuous dosage system. In the conventional polymerization process, this value increases with conversion. This means that the primary particles produced by initiator continuous dosage system is more narrowly distributed compared with conventional polymerization. In a polymerization process with initiator continuous dosage, the high rate of primary particle nucleation

led to the earlier formation of 3D network and stability of primary particles. Therefore, every primary particle reaches a limiting size and tends to fuse rapidly with an elder network of primary particles.³ This 3D network reduces initiator diffusion into the particles and prevents the individual primary particles from continued growth. In conventional polymerization, the rate of nucleation is lower and primary particles have sufficient time to grow individually. Thus, both small and large particles can exist inside the grains.

Figure 15 shows cold plasticizer adsorption (CPA) for PVC samples obtained by the conventional and the initiator continuous dosage processes. The CPA as estimation of internal porosity of the PVC grains decreases with increasing monomer conversion, as the free volume between primary particles is filling up by further polymerization.^{17,26,43} The cold plasticizer adsorption for the grains obtained during polymerization by the initiator continuous dosage initially displays a lower amount compared with those formed by conventional process, but gradually increases to a larger final amount after a certain conversion. At

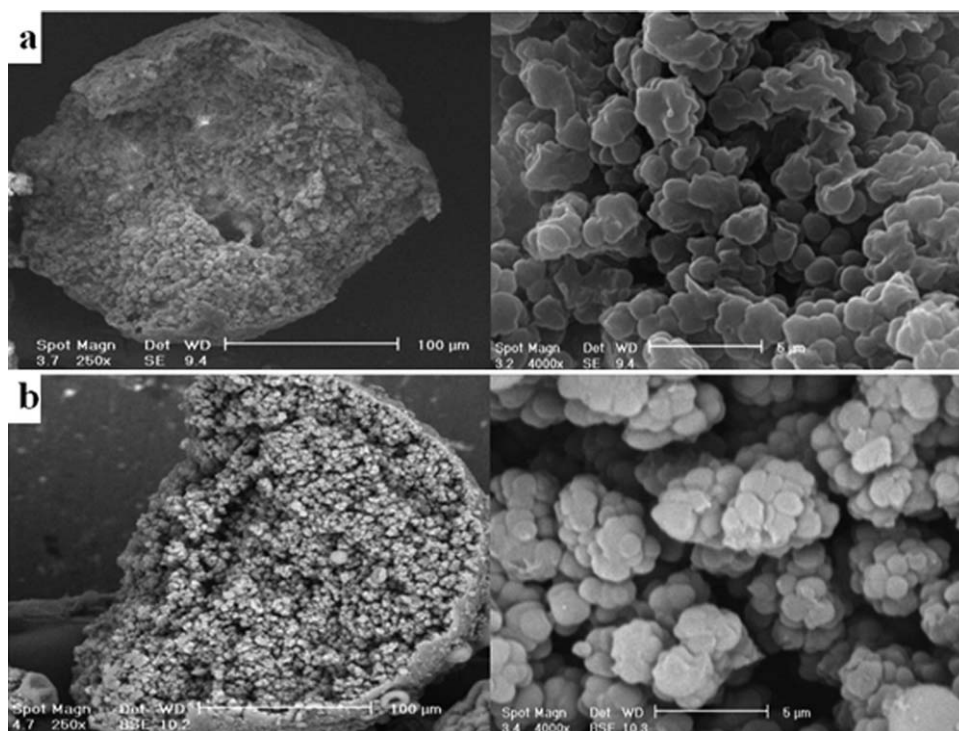


Figure 12. SEM micrograph of interior of final PVC for the conventional process (a) and the initiator continuous dosage process (b).

low conversion, it is postulated that in the grains formed in the continuous dosages system, the formation of numerous primary particles caused to earlier aggregation, and decreases intra-particle volume and thus CPA. Using a fast initiator increases the nucleation rate of primary particles. This in turn increases the chance of particle encounters. For this reason, primary particles will aggregate earlier, forming a kind of inner skeleton which prevents the droplets from shrinking too much during polymerization and increasing monomer conversion, finally resulting in more porous particles.

A second reason for the higher porosity of the final grains obtained by the initiator continuous dosage process is the

presence of a tougher skin due to interface polymerization. The skin lowers the availability of initiator to the internal monomer phase. For this reason, some monomer remains unreacted in some of the micro-pores in the grains, once again results in a higher porosity in the PVC grains.

The quantitative results obtained from mercury porosimetry analysis corroborated the high porosity of PVC grains that are produced by initiator continuous dosage polymerization (see Table IV). The total cumulative pore volume of grains was obtained by the volume of mercury that permeates into the pores of the sample at maximum applied pressure. The total surface area of the pores is the surface area of the pore walls at

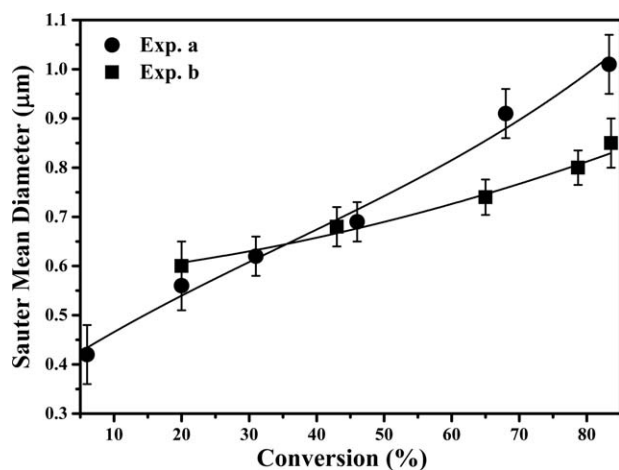


Figure 13. Sauter mean diameter of primary particles (obtained by image processing) versus conversion for the conventional process (Exp. a) and the initiator continuous dosage process (Exp. b).

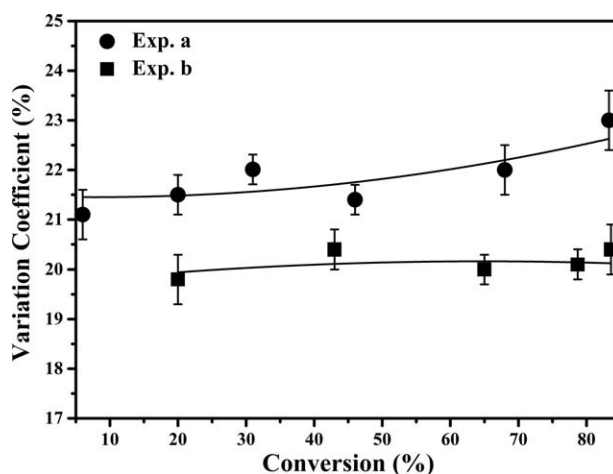


Figure 14. Coefficient of variation of the primary particle size distribution versus conversion for Exp. a and Exp. b.

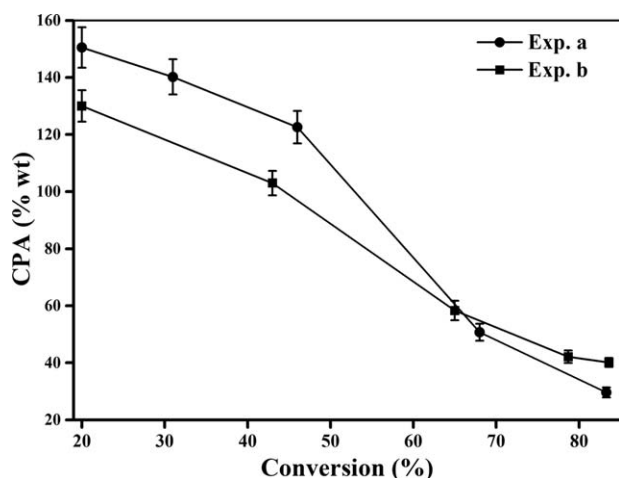


Figure 15. CPA versus conversion for the conventional process (Exp. a) and the initiator continuous dosage process (Exp. b).

this pressure. The porosity of the sample gives the percent portion of these pores in the sample volume.⁵⁵ Table IV shows that the PVC grains obtained by the initiator continuous dosage have high total pore volumes, surface areas and porosity. Figure 16 shows the volume of mercury pores penetrating into the PVC grains against the applied pressure. The required pressure to get intrusion mercury into the pores is inversely depended on size of the pores. In polymerization by initiator continuous dosage, the grains crust is thicker which resists to mercury diffusion at low pressure. The lack of mercury penetration into PVC grains causes a decrease in the median pore diameter of grains.

The Effect on Residual Monomer and Initiator

The porosity of PVC grains is important for ease of the removal of residual unreacted VCM at the end of the polymerization process.^{56,57} In an industrial context, VCM polymerizations are not allowed to proceed to 100% conversion, and some unreacted VCM which is swollen in polymer phase remained in final PVC grains. The amount of residual VCM in PVC grains has a great effect on product quality due to the toxicity of VCM. It is necessary to remove the unreacted monomer in order to ensure a PVC product of consistent quality. The residual unreacted VCM can be stripped efficiently from the PVC grains with high porosity at lower temperatures, thus avoiding problems of thermal degradation of the PVC at higher temperatures.⁵⁸

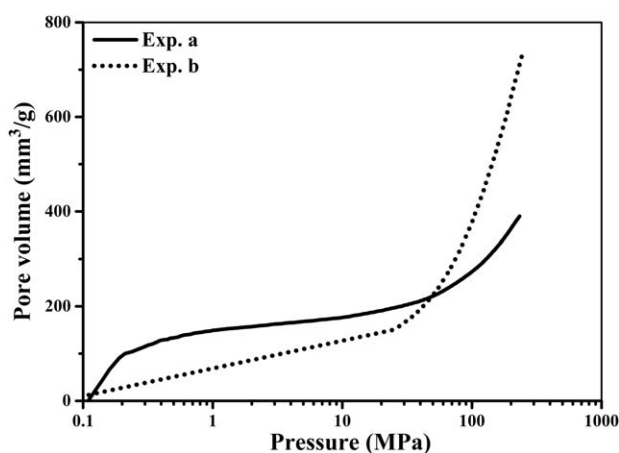


Figure 16. Pore volume–pressure curve of PVC grains prepared by the conventional process (Exp. a) and the initiator continuous dosage process (Exp. b).

The grains produced by initiator continuous dosage polymerization process have smaller primary size that causes swollen monomer content become lesser. Also, these grains have numerous pathways through which the monomer must diffuse into the exterior of the grain. Hence, its removal is facilitated, and the residual unreacted monomer decreases dramatically (see Table III). The fast initiator has a shorter half-life, and it was found that the final grains produced by initiator continuous dosage have a smaller residual mole of initiator than those produced conventionally.^{11–14}

The Effect on Bulk Density and Flowability of PVC Grains

Table III shows the difference between the bulk densities of the PVC grains obtained by the conventional polymerization and the initiator continuous dosage process. The bulk density of grains is a function of morphological characteristics such as polymer particle size (increasing particle size grains, increase bulk density), shape (grains with regular shape and smooth surface have higher bulk density than grains with irregular shape and rough and coarse surface), and the porosity of the particles (grain porosity is inversely proportional to the grain bulk density).^{31,59} PVC grains prepared by the initiator continuous dosage condition have higher particle sizes, but their higher porosity and coarse surface lower the grains' bulk density. The flowability of PVC grains is determined by the velocity of a given amount of dry grains through a standard funnel (ISO 6168). Table III shows that the PVC grains obtained by the initiator continuous dosage

Table IV. Mercury Porosimetry Analysis of PVC Grains Prepared by the Conventional Process (Exp. a) and the Initiator Continuous Dosage Process (Exp. b)

Experiment	Cumulative volume (mm ³ /g)	Total surface area (m ² /g)	Median pore diameter (nm)	Total porosity (%)
Exp. a	390	66	847	35.3
STDEV	22.6	6.5	27.3	1.62
Exp. b	740	204	633	50.9
STDEV	47.5	16.2	44.2	3.12

process have poor flow properties compared with that is the case for PVC obtained by the conventional condition. The flow properties of PVC grains is a complex function of morphological properties such as grain shapes, grain surfaces, particle size distributions, and degrees of porosity.^{59,60} The shapes, degrees of internal friction, the roughness of the particle surfaces and the size distributions of grains obtained by initiator continuous dosage system can all contribute to this observation.

CONCLUSIONS

Continuous dosing of a fast initiator during suspension polymerization of VCM in a pilot-scale reactor was performed by applying an initiator continuous dosage trajectory which provides a maximum reaction rate and conversion identical with a predefined regular condition. It was found that this strategy decrease the total polymerization time up to 53% in comparison with the conventional case, while the molecular weight distribution and molecular weight of final grains remained almost unchanged. The morphology of PVC grains is quite different from grains prepared by the conventional polymerization process. The resulting PVC grains showed irregularly shaped and uneven particle surfaces with obvious more ultrafine particles attached to the surface of grains, wider particle size distributions, and larger grains compared with those obtained by the conventional polymerization. SEM micrographs from fractured grains showed that using an initiator continuous dosage system results in the formation of early 3D networks with the agglomeration of many smaller primary particles which subsequently have higher internal porosity. The CPA and mercury porosimetry analysis confirms the high porosity of the grains produced by initiator continuous dosage system. The PVC grains prepared by the initiator continuous dosage process entertain lower bulk density, residual unreacted monomer and initiator, and higher flow properties compared to PVC produced by the conventional polymerization.

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