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The Effects of Initiators Mixture on Suspension Polymerization of Vinyl Chloride and its Comparison with other Productivity-Enhancing Procedures

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Abstract

Molecular and morphological properties of poly(vinyl chloride) grains produced by suspension polymerization of VCM in the presence of a mixture of three kind of initiators (i.e. fast, mild and slow) (named as Cok process) was experimentally investigated in a pilot-scale reactor. The results obtained here were initially compared with a isothermal regular process (named as control process) and then with those obtained already for other productivity-enhancing polymerization techniques (i.e. nonisothermal and fast initiator dosage process). The results showed that, in contrast to nonisothermal and fast initiator dosage process, the addition of initators mixture at the beginning of the reaction has the smallest influence on molecular weight and polydispersity index compared to control process. It is obvioused that Cok-PVC grains have the lowest cold plasticizer absorption and porosity among these mentioned processes. Scanning electron microscopy (SEM) showed that the particles produced by Cok process are more regularly shaped, with a smoother surface compared with the control product. According to the literatures, all three productivity-enhancing techniques lead to an apparent quality enhancement, higher flowability and greater bulk density of final grains. While both processes of continous initiator dosage and nonisothermal polymerization broaden the particle size distribution of final PVC grains, applying initiator mixture produces particles with the same particle size distribution as control process. The SEM images processing showed that Cok process deccelerates the formation of a three-dimensional skeleton of primary particles relative to the control polymerization. In comparison with nonisothermal trajectory and continous fast initiator dosage system, the Cok polymerization process leads to the most delay of motionless conversions and fusion time as well.

Keywords: VCM suspension polymerization, initiator mixtures, molecular characteristics, morphological properties

Introduction

Vinyl choride monomer suspension polymerization is performed in a batch-wise process. As, the productivity of this high demand product is still low, improving the productivity of the batch polymerization process has been always considered as a challenging issue [1–5]. The enhanced productivity in VCM suspension polymerization process can be effectively achieved by reducing the batch time so that predefined specifications of final product do not change remarkably. The polymerization of vinyl chloride monomer (VCM) is conventionally carried out isothermally in commercially producing plants. The cooling system of the reactors must be designed in such a way that it is able to remove the heat developed at the exothermic peak (figure 1). The typical trend of heat removal rate versus raection time in vinyl chloride polymerization indicaes the full capacity of the cooling system remains idle most of the time during the course of the polymerization[2].

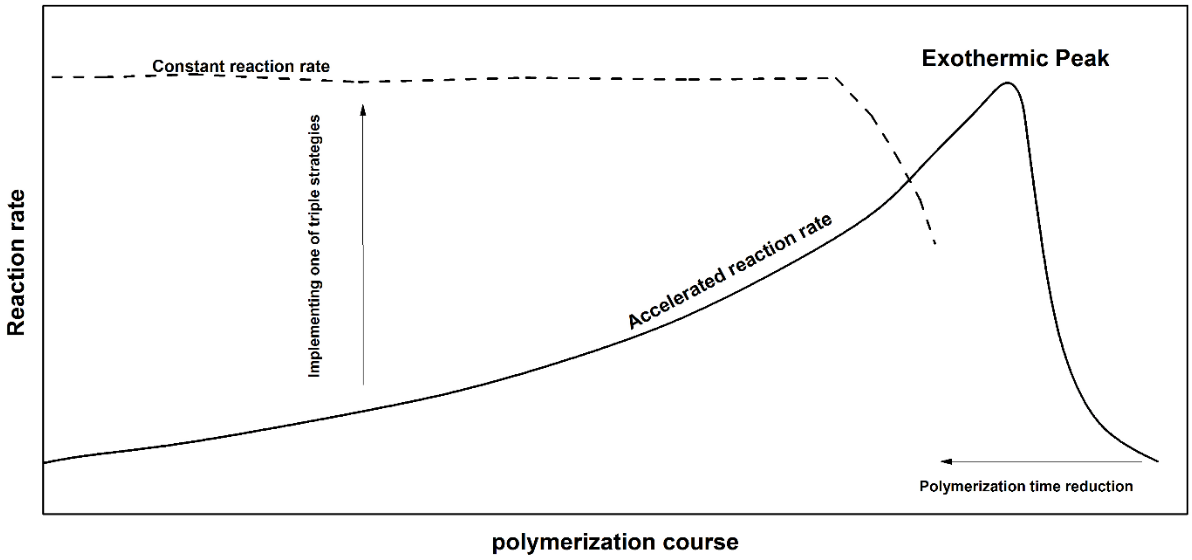


Figure 1. comparison of the variation of reaction rate versus time between a regular and a productivity-enhancing process

As a consequent, the spread of the concentrated heat load at exothermic peak of reaction over the entire course of the polymerization can lead to a constant reaction rate and thus reduced reaction time and hence enhanced productivity. The decomposition rate of the initiator and the polymerization temperature are strategic factors that can be manipulated to control the reaction rate at its maximum constant value. It is found that there are three ways to install the full capacity of the cooling system for achieving an almost constant rate of polymerization; temperature programming, cocktail of initiators and fast initiator dosage system. In all the strategies the polymerization reaction and correpounding heat removal rates are kept constant at a desired value. Feldman et al. [4] suggested a temperature-programmed VCM suspension polymerization with a constant rate to improve productivity. They used a simple model developed by Abdel-Alim et al [6] to develop a temperature trajectory for constant rate polymerization reaction. They used a 0.5-L laboratory scale reactor to carry out nonisothermal VCM polymerization. In their programmed temperature policy, the temperature was decreased from 64 to 40C, followed by a constant temperature at 40 C for a period of time, and then an increase to 68 C. This temperature profile led to a reduction in time of reaction with slightly deteriorated volumetric properties and better thermal stability of the product relative to the PVC obtained isothermally. Longeway and Witenhafer 117] proposed that programmed temperature of a series of the polymerization reactors measuring 40 m3 each (the first at 57 C and the last at 36 C, with an 80% final conversion) could decrease the total reaction time by 28%. Tacidelli et al. [8] proposed a heat kick policy in which the final temperature of the reaction increased to reduce the reaction time. Recently, we have successfuly implemented a variable temperature trajectory during the course of the reaction to improve productivity by reducing the polymerization time for a predefined K value [9-11]. In this procedure , the reaction temperature was raised to higher value than that of corresounding isothermat process at the beginning of polymerization and then decreased gradually over the process time to a lower value than that of isothermal one. Pinto et al [12] applied the technique of adding a mixture of different initiators to reactor at the beginning of the raction and at a isothermal condition. To take advantage of this technique, it is essential to apply an optimal formulation of three types of initiators having low (fast), moderate (mild) and high (slow) half-lives of activation energies for the decomposition. For the first time, Akzo Nobel Company (Netherlands) suggested the process of fast initiator dosage system to enhance the productivity. Recently, Bijanmanesh et al [13], have applied continuous dosage of a fast initiator during polymerization reaction and had success in reduceing time reaction by 40%.

From the kinetic point of view, the course of VCM suspension polymerization consists of three stages; the early stage when only the monomer phase exists, when polymerization proceeds in both polymer and monomer phases and once only the polymer-rich phase is present. The evolution of conversion of vinyl chloride monomer to polymer chains is accompanied with several physical transitions during the polymerization. Polymer phase is changed from the aggregation of the precipitated macro-radicals to nano-domains and then domain and finally to a three-dimensional network of primary particles which are surrounded in a rigid skin. The process variables such as polymerization temperature, the type and concentration of initiator and the method of initiator addition have been found to have a significant influence on the internal structures and molecular characteristics of PVC resin [1, 8–14]. In other word, the final characteristics of final PVC is influenced by the conditions governed by the strategy implemented to enhanced productivity. In the present work, two PVC resin is obtained by two initiator systems; an optimal mixture of fast, mild and slow initiators (named Cok process) and a single initiator (named control process). The morphological and molecular properties of the product are compared to the case in which only one initiator is optimally chosen. Two experiments are performed under equivalent thermal conditions. Further comparisons were conducted between the characteristic of PVC grains produced by three strategies, namely, the continous fast initiator dosage system, the adition of the mixture of initiators at the beginning of the reaction and the temperature trajectory. The way of obtaining the optimal formulation of an initiator mixture to achieve a constant reaction rate and hence a lower reaction time is described in our previous article [14].

EXPERIMENTAL

Materials

Vinyl chloride monomer (VCM) was supplied by Bandar Imam Petrochemical Company, Mahshahr, Iran; hydroxypropyl metylcellulose (Methocel 65SH-50); hydroxylpropylcellulose (KlucleJ) and sorbitan monolaurate (Span 20) as suspending agents were supplied by Shin-Etsu Chemical Co. (Tokyo, Japan), Hercules International, Ltd., and Beckmann Chemikalien KG (Bassum, Germany; Becksurf 7125), respectively. Three initiators, diisobutyryl peroxide (named Fast: E = 109.06 kJ/mol and A = 3.7E+14), Di (3methoxybutyl) peroxydicarbonate (named Mild: E = 143.29 kJ/mol, A = 9.09E+18) and dimyristylperoxydicarbonate (named Slow: E = 124.1, A = 2.82E+15) was supplied by Akzo Nobel Co. (Amersfoort, The Netherlands) and used as initiators. Suspension polymerizations of VCM were carried out under both isothermal and nonisothermal conditions with an identical recipe in a 15-L stainless-steel jacketed reactor with two baffles of circular cross-section and two 8-flat blade turbines. The reactor temperature was controlled manually by the flow of water regulated by a valve on a 12-L circulator. In all these producible experiments, the amount of VCM and water charged were 2,800 and 4,100 g, respectively. For the Cok process an optimal formulation of an initiator mixture (Fast= 3.1×10^{-3}, Mild= 5×10^{-4}, Slow= 1.2×10^{-3} mol) added to the reactor before the VCM charge. The used initiator for the control process was the Mild (6.1×10^{-3}mol) . The reactor was purged with nitrogen before the start of the reaction. The mixture of reaction was heated up to the polymerization temperatures of 52°C for all experiments by flowing hot water in the jacket. The polymerization process was stopped after the pressure in the reactor dropped by 0.5 bars, corresponding approximately to a conversion of 80%. Sampling is carried out by stopping the reaction by immediately quenching the content of the reactor to about 15°C. In all experiments, after venting the unreacted vinyl chloride via a valve on the top of the reactor vessel to the VCM recovery unit, the reactor content's temperature was raised again to 60°C to remove the residual monomer. The final conversion was obtained by weighing the final dried powder. The K value was calculated from the dilute solution viscosity measurements of the PVC samples in cyclohexanone by an Ubbelohde viscometer according to ASTM D 1243-95. Fusion behavior and dynamic thermal stability are demonstrated by a Brabender® Plastograph EC apparatus equipped with an electrically heated mixing head (W 50 EHT mixer) and non-intermeshing rotors having a 50-cm^3 volume capacity.

Characterization of the suspension-poly (vinyl chloride) (s-PVC) Particles.

The mean particle sizes and particle size distributions of the PVC grains were measured with a Malvern Model 2603LC particle size analyzer (Worcestershire, UK). 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 (ASTM D 3367-95). The bulk density 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 skin and inner structure of the grains. The interior of particles was studied via the fracturing of particles. For this purpose, samples frozen in liquid nitrogen were mechanically broken down. Then, the fractured samples were coated with a thin layer of gold with a gold sputter coater (Model SCD005; Bal-Tec, Hannover, Germany) in vacuum, and then micrographs were prepared. The SEM images were analyzed by using image processing software (ImageJ) to measure the sauter mean diameter (D) and coefficient of variation (CV, defined as the ratio of the standard deviation to the mean diameter) of primary particles in different conversions using the Eqs. 1 and 2, respectively [5, 7, 15]. At least 120 primary particles for three different broken particles at each conversion were analyzed to calculate the parameters

$$D_{32} = \frac{\sum_1^n D_i^3}{\sum_1^n D_i^2} \qquad (1)$$

$$CV = \frac{\sqrt{\sum_1^n (D_i - \bar{D})^2}}{\bar{D}} \qquad (2)$$

The flow properties were determined by passing the powder through an aperture according to ISO 6186. The test results are expressed as flow time in seconds. Also, the MW and its distribution were measured by gel permeation chromatography (ALC, Waters) with a Styragel 6e column, a tetrahydrofuran solution of PVC at 408C, and a 1 mL/min flow rate. Specifications are summarized in Table 1.

Table 1. comparison of the specifications of PVC grains produced by four procedures

sample	K-value	Bulk density (g/L)	CPA (g/[100 g of PVC])	Specific surface area (m2/g)	Mean particle (µm)	Flowability (s)	Weight-averaged molecular weight (g/mol)	Polydispersity index
Control sample	71.5	400	36	0.0563	101.1	38.3	213000	2.5
COk-PVC	71.1	410	28	0.0483	103	36.2	211000	2.51
Non-PVC[1]	70.5	4009	54	0.0603	106.6	30.5	224000	2.4
Fast-PVC[2]	70.8	390	56	0.076	113	34.4	218000	2.3

The effect on productivity

As mentioned above, three kinds of initiators with different half –life were used in Cok process. The choice of the optimal formulation of an initiator mixture is made in such a way that the maximum possible reaction rate is obtained over the course of polymerization. For this purpose, the amounts of each initiator in the mixture was first mathematically optimized with details provided in our earlier work[14]. The “Fast” initiator possessing lower half-life, decomposes more quickly than others and initiate the free-radical polymerization with the highest rate, at the very early stages of the reaction. After finishing the “Fast” initiator, the polymerization will proceed at the same rate through the “Mild” initiator. The decomposition of the “Slow” initiator at the end of the reaction compensate for the reduction of the mild initiator concentration, once again resulting in a constant reaction rate . Figure 2 shows the evolution of conversion and reaction rate in time for both Cok and control processes. As it can be seen, in the polymerization of VCM initiated by a mixture of three initiators (Cok), the reaction rate remains almost constant for the entire range of conversion, while the “Control process” results in a sensible acceleration of the reaction and consequently an excessive demand for heat removal when approaching the depletion of the liquid monomer phase.

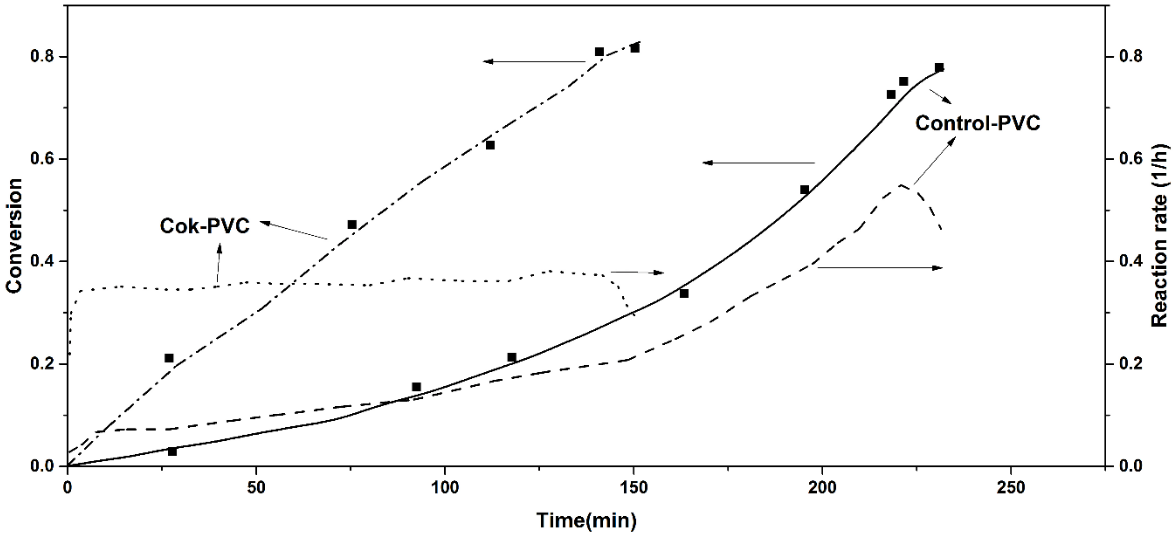


Figure 2. Comparison between polymerization rate and monomer conversion for both Cok and control polymerization process.

The figure also shows that the higher average rate of reaction along the batch time is achievable by using the optimal mixture of initiators, resulting in the reduction up to 36% in total processing time, relative to the control case. It can be calculated that the average reaction rate during the entire course of the polymerization, is 63% of the maximum reaction rate.

Among works performed on the enhanced productivity of PVC through temperature-trajectory [2-8], in earlier work [9-11] we suggested the most reduction in the polymerization time up to 33%. Bijanmanesh et al [13] reported that continuous dosing of a fast initiator during suspension polymerization of vinyl chloride enhanced productivity by 40%. According to the results reported here, it seems that the best approach to reduce the polymerization time of a typical VCM suspension polymerization is continuous dosage of a fast initiator. This is why the K value of PVC resin and molecular weight are only governed by the polymerization temperature and is very slightly affected by the initiation rate. Therefore, the higher average rate of reaction can be possibly achieved by manipulating the initiation rate which was, in turn, influenced by initiator decomposition rate. An appropriate temperature trajectory which can adjust the final MW to the predefined value produces only less than half as much average reaction rate as possible maximum reaction rate (corresponding to maximum cooling capacity of the reactor) [15-17].This is while the averge reaction rate can reach up to 80% as much as possible maximum reaction rate using continous dosage of fast initiator [13]. The Cok process represents the second most significant strategy for enhancing the productivity of VCM suspention polymerization.

The effect on molecular characteristics

Gel permeation chromatography results and the measured K values for products obtained by both Cok and control suspension polymerization processes are summarized in Table 1and figure3. As shown, there is no significant effect on K-value and the MW and its distribution (polydispersity index) as well when an optimal mixture of initiators is used for enhanced productivity.

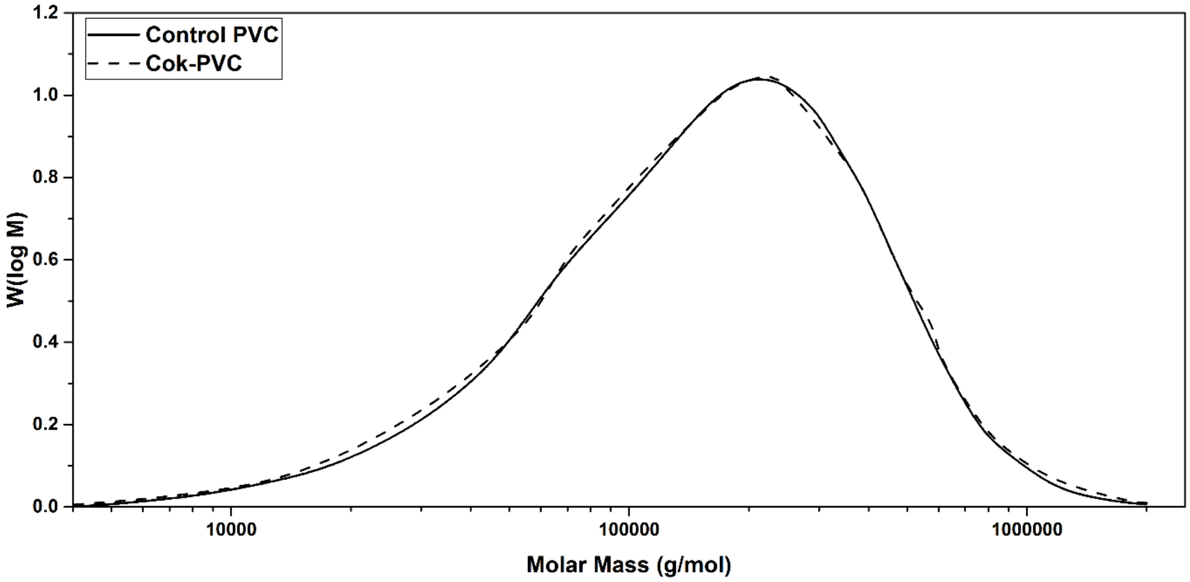


Figure 3. Molecular weight distribution. Effect of using optimal mixture of initiators

In both productivity-enhancing techniques of “Cok” and “continuous dosage of a fast initiator”, enhanced productivity is caused by manipulating only the initiation rate of VCM polymerization. Therefore, both of them follow the same behaviour with regard to molecular weight and subsequent K value when compared to a those of conventional VCM suspension polymerization [18]. On the other hand, temperature variation affects strongly all of the reaction rate constants and termination and transfer reactions as well. The terimination rate coefficient increases more rapidly with temperature than initiation and propagation rates, thereby resulting in the change in the molecular weight and its related properties. Nevertheless, it is proved that if temperature trajectory is optimally chosen for enhanced productivity, it has only slight effect on molecular characteristics such as molecular weights and molecular weight distribution[19].

The effect on grain morphology

Effect on Particle Size and Its Distribution

Particle size distribution of the final PVC grains produced under both Cok and control conditions are shown in figure 4.

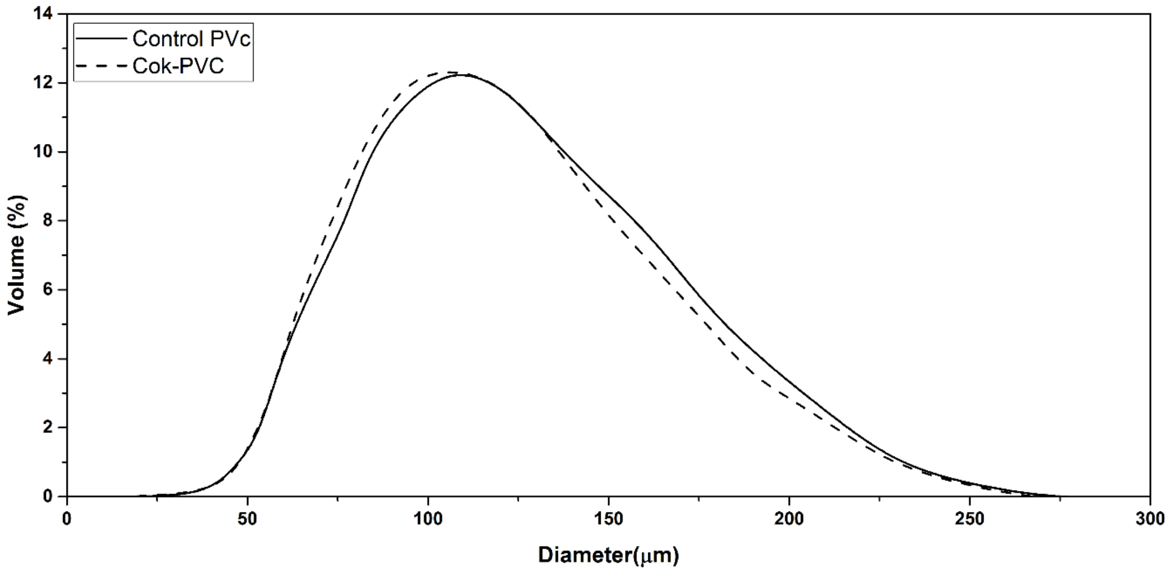


Figure 4. Comparison between particle size distribution of the PVC grains formed by Cok and control conditions

As shown in figure 4 and table 1, no change is observed in the mean particle size and the particle size distribution of the PVC resin using technique of initiators mixture. This is because that the coalescence rate of the particle/droplets depends on the type and concentration of suspending agents used and not on the type and concentration of initiators used [20].

This is while other productivity-enhancing strategies of nonisothermal trajectory and continuous initiator dosage broaden the particle size distribution slightly and enlarge mean particle size compared those of a control VCM suspension polymerization [19-20]. In the continuous fast initiator dosage system, the initiator is likely to produce free radicals in the aqueous phase and consequently the ultrafine particles which is subsequently adhered on the skin of the grains. In this case, both temperature trajectory and Cok process show the same manner as a conventional VCM suspension polymerization.

Effect on Grain Shape

The SEM micrographs taken at similar magnification from final grains were used to examine the appearance quality of the particles produced by control and Cok-PVC conditions. These micrographs are shown in Figure. 5.

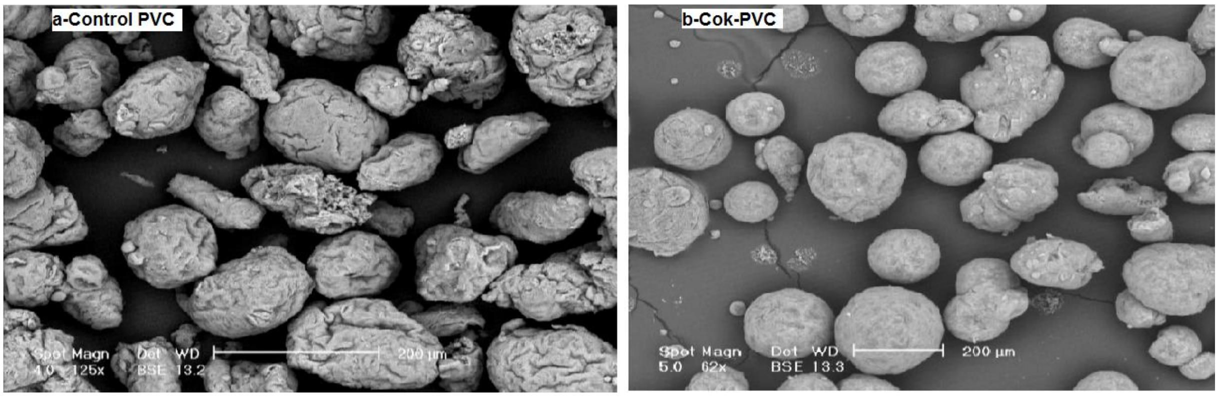


Figure 5. The SEM photographs showing the appearance quality of the particles produced by control (a) and Cok(b) process

By comparing these micrographs, it can be seen that the PVC grains prepared by Cok-PVC conditon are more spherical with smoother surfaces than those produced by control condition. the thick sorrounding skin as well as the uniform and large size of primary particles inside grains forming a kind of strong inner skeleton prevent the droplet from collapsing [9]. The larger primary particles in size and number at the early stage of the reaction, are more likely to collides to the inner surface of the droplets and thus strengthens the skin [10]. This early formed primary particles acts also as a turbulence damper and resists the change of spherical shape of the particles into an irregular shape that can be seen in the cotrol condition.

According to above, it can be expected that the skin porosity of the PVC grains prepared nonisothermal is greater than that in the PVC grains produced by other productivity-enhancing techniques. The results provided by Bijanmanesh et al show that the fast initiator dosage system create the thickest surrounding skin of the final PVC grains. As would be expected in such a system, initiator enters into the monomer phase from aqueous phase, as a consequent the formation of polymer phase starts from the inner surface of the particle and continues to grow inward, toward the center of the droplet. These results suggest that the primary particles has the most compacted form near the particle surface and the amount decreased toward the center of the particle.

Figure 6 shows the SEM images of the surface of the grains prepared under Cok and control conditions. It is evident from the figures that a few ultrafine particles are adsorbed at the skin of the particles in Cok polymerization.

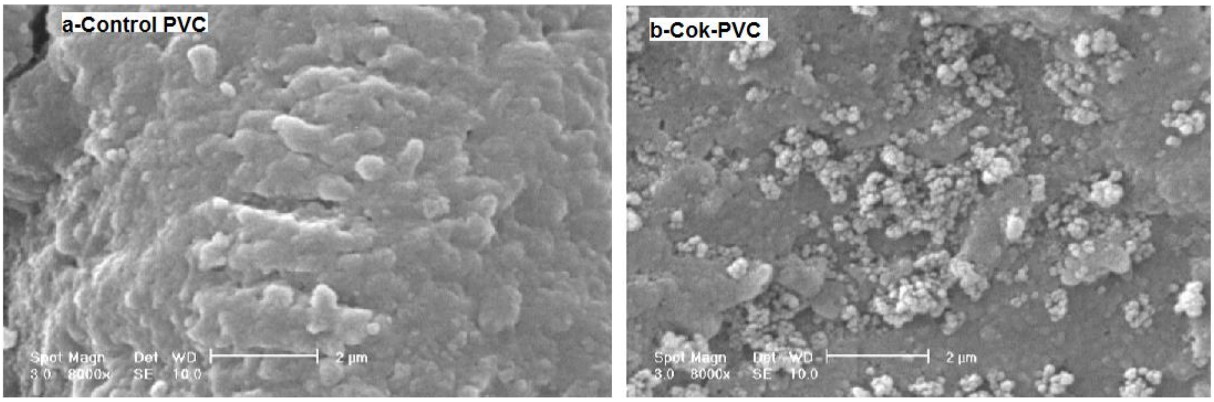


Figure 6. The SEM photographs of the surface of the particles produced by control (a) and Cok(b) process

By using a mixture of different initiators, the chance of polymerization outside the monomer droplets and thus the formation of fine particles increases. The monomer polymerization initiated by the free dispersed initiator in the aqueous phase and the corresponding oligo-radicals precipitate on the surface of the monomer droplets and continue to grow. The results obtained from micrographs of the final PVC grains given in the literature [9-10], indicate that the PVC grains prepared by variable temperatures are more spherical in shape with smoother surfaces than those produced by two other procedures.

Effect on primary particles

Figure 7 shows SEM micrographs of fractured PVC grains prepared by control and Cok experiments, respectively. The final primary particles size in the PVC resins prepared by Cok condition are greater than that in the grains formed under the control condition.

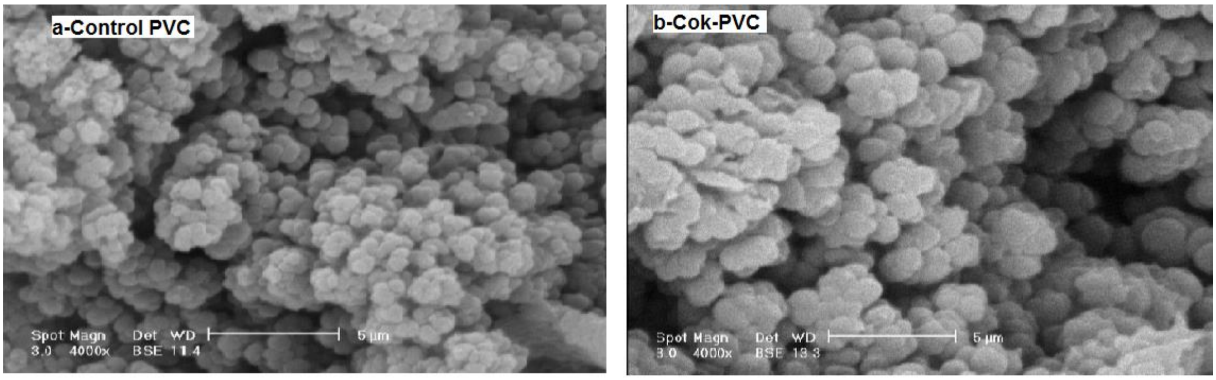


Figure 7. PVC primary particles at final conversion for control (a) and Cok(b) process

In other words, the grains produced in cok condition are composed of considerably larger, more uniform and distinct primary particles compared to the control case. The higher initiation rate at the very early stage of the Cok reaction, the greater the conversion take place throughout the droplet and thus the more the number of the nano-domains are nucleated [19]. When the fast initiator decomposed completely, the number of the primary particle nuclei does not change significantly anymore and newly formed nano-domains coats the existing primary particles causing the primary particles, as will be shown in the next section, grow uniformly.

Among three productivity-enhancing approaches, continuous dosage of fast initiator has the most effect on primary particle structure and morphology. The dosage system of fast initiator changes the mechanism of nucleation and growth in favor of decreasing the primary particle size. The most difference between the Cok and continuous dosage process is the rate and the period of nucleation of a new primary particles. The fast initiator produces a larger number of nucleus per volume, which tends to aggregate and form newly formed primary particles. A similar phenomenon occurs also in the Cok process at the beginning of the reaction, due to presence of fast initiator. After finishing the fast initiator, the nucleation rate and subsequently the number of newly formed nuclei decrease significantly over time. Thereafter, the newly formed nuclei are more likely to be deposited on the surface of the elder primary particles. In continuous dosage system, however, the fast initiator concentration is kept high intentionally, to obtain a constant reaction rate, resulting in a high nucleation rate over all time periods.

While the Cok process causes the more spherical and uniform primary particle shape, almost similar to that seen in control VCM polymerization process, the final primary particles produced by two other techniques of the temperature trajectory and initiator dosage systems decrease in size and are less fused, resulting in an increased porosity of the PVC grains . In other word, the final size of the primary particles formed by the initiator mixtures and the control process is larger than that of PVC grains produced by the other two methods. A temperature or initiator dosage trajectory results in the formation of an early three-dimensional skeleton with finer primary particles and subsequently higher internal porosity.

Motionless conversion

The extent of the fusion of primary particles is influenced by conversion. At a certain conversion, the drop is completely occupied with polymer particles. The polymer particles form a structure solid enough not to distort easily (motionless point) [20]. At this stage, monomer fills the interstitial pores formed between the primary particles. If polymerization continues beyond this conversion, the interstitial pores between the primary particles will be filled with the polymer, and the packed primary particles are thus formed. Also, after critical conversion, in which no monomer exists in interstitial pores formed between the primary particles, the volume fraction of the pores remains constant, and the whole structure only shrinks. The motionless conversion can be estimated by a procedure described in the previous work published [14]. Figure 8 shows CPA measurements versus conversion for resins produced both Cok and control condition. They both follow a similar trend in which CPA increases with conversion, reaching a maximum at motionless conversion, then falling to the final value.

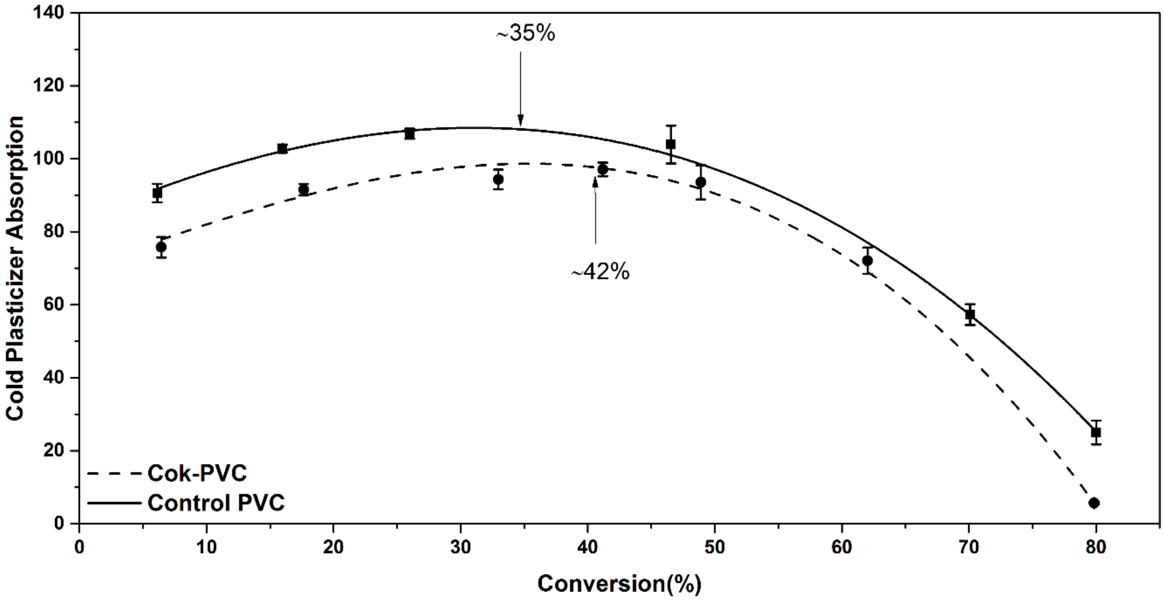


Figure 8. CPA versus conversion for two samples

Since at the beginning of the reaction, the number of primary particles in the Cok-experiment is greater, so more porosity is created, resulting in a greater CPA. With increasing conversion, the total number of individual primary particles remain nearly unchanged, and only their size grows. Under these circumstances, the interstitial pores of the primary particles inside networks are gradually diminished, resulting in decreasing in CPA relative to control case. Decreasing in the interstitial pores leads to a delay in the occurrence of the motionless point, thereby resulting in less filling of the pores at higher conversions. In control conditions, on the other hand, the newly formed particles are rather stable and elder particles can individually grow, and thus both small and large particles coexist inside the droplets. As a consequent, the larger free volumes or cavities (discrete zones) are induced by different sizes of primary particles (see figure7).

The main reason for delayed motionless point in Cok process is that when primary particles radius increases, surface to volume ratio decreases, resulting in decreasing accessibility of the more interior micropores of the primary particles. Although Cok process has a similar behavior in delaying motionless conversion as nonisothermal and fast initiator dosage, the mechanism of this delay is different. The results show that continuous initiator dosage system causes the most delay in the motionless conversion due to the very early aggregation of very fine primary particles, leading to the formation of large amounts of intestinal pores and discrete zones as well [14]. In temperature trajectory, however, a monomer condensation from gas phase into the polymer phase due to the temperature reduction during reaction results in a delay in the occurrence of the motionless point[9].Our results show that both nonisothermal and Cok give approximately the same delay in motionless conversion.

The mean sauter diameter of primary particles (d_{32}) at different conversions was estimated with the image analyzer software. Figure9 exhibits the evolution of the primary particle size with conversion for both control and Cok and conditions.

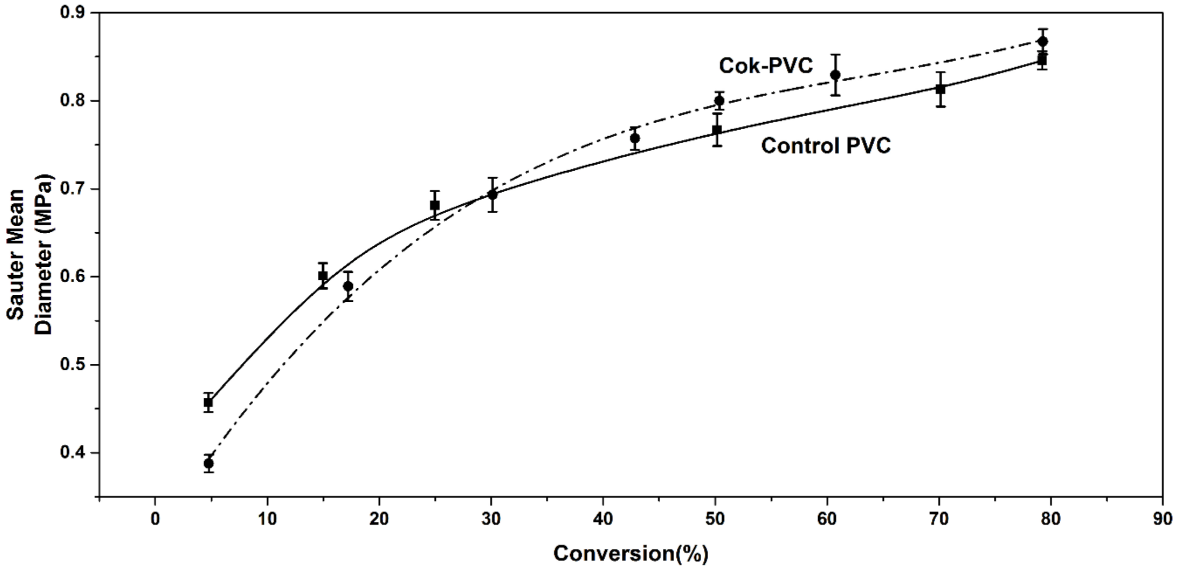


Figure 9.Mean Sauter diameter of primary particles (obtained by image processing) versus conversion.

As can be seen, the sauter mean diameter of primary particles obtained by cok-condition polymerization initially displays a smaller value compared with those formed by normal expriment but gradually increases to a larger final value after a certain conversion. Moreover, both curves experience an increase in the primary particle size with the extent of reaction up to certain conversion, after which d_{32} continue at a much slower rate. This conversion corresponds to the formation of a three-dimensional network of the primary particles occurring at significantly larger conversions for Cok condition. This means that applying the Cok- condition decelerates the primary particles networking. Also, the final size of the primary particles formed by the Cok condition is larger than that of PVC grains produced by control experiment, as was verified from SEM micrographs (see Figure. 7). The evolution of the primary particle size distribution is analyzed through its coefficient of variation (CV) and reported in Figure. 9. The polymerization in Cok- condition results in almost constant CV in the whole conversion range whereas normal polymerization results in increasing CV with conversion. The figure also shows that the primary particles are more narrowly distributed in Cok suspension polymerization of vinyl chloride compared with the normal polymerization. At a higher decomposition rate of initiator in Cok polymerization at the beginning of the reaction, the rate of primary particle nucleation are larger, offering the earlier sites for further growth of primary particles. These sites are homogenously distributed in all over the droplet in such a way they attract easily any newly formed PVC chains. In this situations, newly formed PVC chains precipitate on theses prepared sites homogenously, resulting in the formation of the larger particles with the same size. This causes the primary particles with almost uniform size distribution to be obtained. In control conditions, on the other hand, the composition rate of initiator is lower in the beginning of the reaction, leading the rate of primary particle nucleation not to be enough to form primary sites for further growth. As a consequently, both small, newly formed and large particles coexist inside the droplets, resulting in broadening the primary particles size distribution.

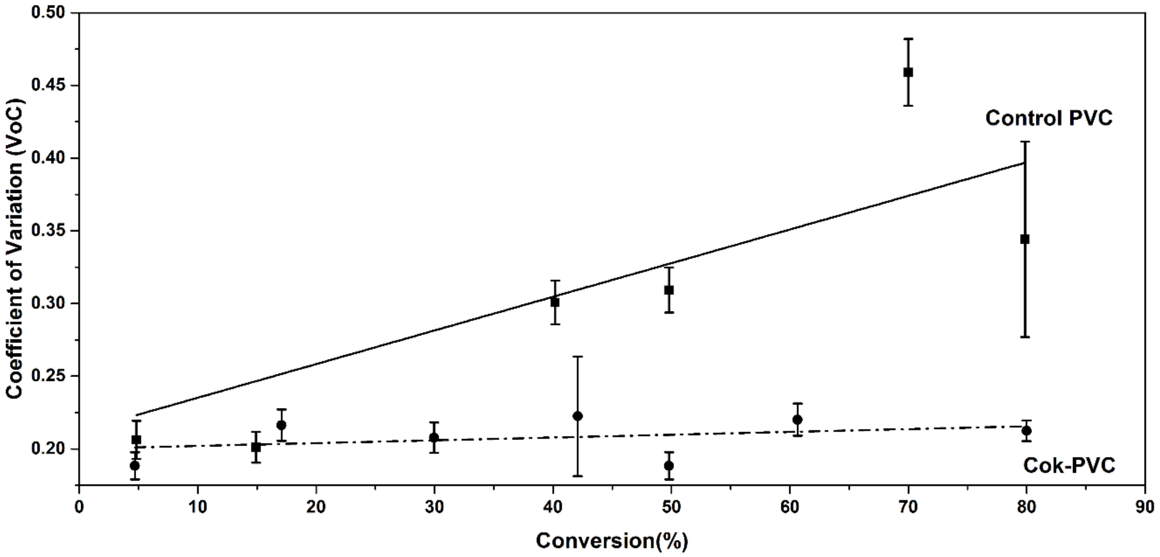


Figure 10. Coefficient of variation of primary particle size distribution versus conversion plotted for control and Cok conditions.

When the primary particle increase in size, they tend to grow individually rather than fuse or interknit. The primary particles grow individually in size to an extent after which tends to fuse or interknit with each other [19]. This three-dimensional network prevents the individual primary particles from continued growth.

Comparison of our results with the data provided by Bijanmanesh et al [13] show that the continues fast initiator dosage system provide the most rapid formation of three-dimensional network of the primary particles and the lowest CoV. The higher the initiation rate, the smaller the primary particle size and the earlier the aggregation take place, thereby resulting in more uniform size distribution of smaller primary particles. Due to their larger size, Cok-PVC primary particles experience the most delayed formation of three dimensional network. It is worthy to note that all three productivity-enhancing procedures have the same trend toward the variation of primary particle size distribution as a function of conversion.

Effect on Porosity

It is found that Cold Plasticized Absorbent decreases with conversion after motionless point. As can be seen, the cold plasticizer adsorption in the grains obtained by cok-condition polymerization displays a smaller value at all conversion compared with those formed in control condition. This can be due to the fact that the larger the diameter of the primary particles , the greater internal cavities are trapped and become inaccessible to the oil penetration.[17]

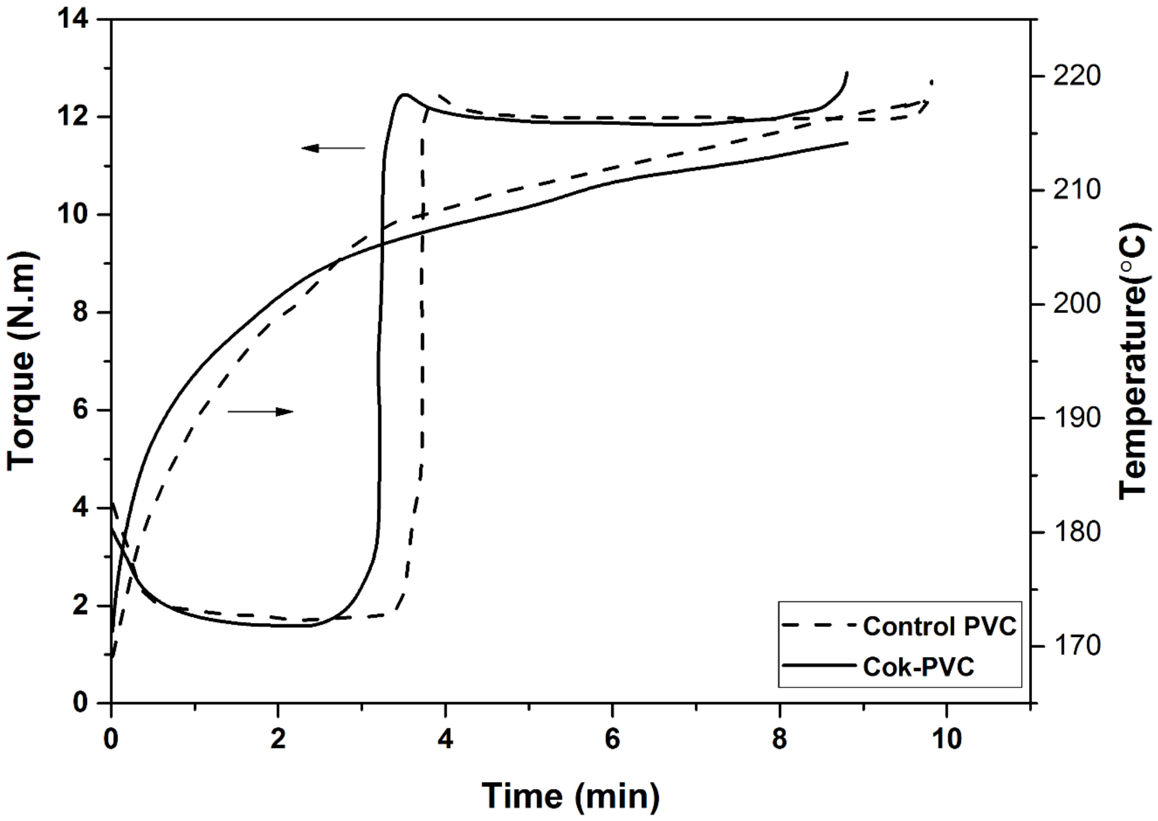
with increasing size, the primary particles become more stabilized and therefore agglomerate slower which form a delayed three dimensional inner skeleton of bigger particles with lower interstitial voids[9-11].

Effect on the Bulk Density

As expected, with a decrease in the porosity of the grains, the bulk density increases [17-18]. Table 1 shows the difference between the bulk densities of the grains obtained by Cok and control conditions. PVC grains prepared with a Cok condition have a lower porosity and thus a greater bulk density . Although final PVC grains prepared by each of the trajectories possess higher porosity, the bulk density of the particles is also comparable to the resin prepared regularly.

The effect on the fusion behaviour

The torque/time curve obtained from the compounds of PVC resins produced Cok and control conditions are shown superimposed in Figure. 3.



As can be seen the both Cok and Control grades of PVC have nearly the same stability time (the time between the maximum torque and the point where the torque value starts to rise again) and so may have the same stability. The fusion torques in both grades of PVC are also equal due to almost the same fusion temperatures. Very important is the fact that the Cok produced PVC also shows a significant effect on the fusion behavior of the PVC compound so that it needs a very longer time to reach the maximum torque in the fusion plot. The Brabender® plastograph data indicated that the final PVC synthesized with the Cok condition showed longer fusion time and probably lower thermal stability. The primary particles of PVC grains produced under Cok conditions are relatively large in size which prevents them fusing rapid; therefore, frictional forces and subsequent viscous shear heating are low, which causes the increase in melt temperature. Thus, the thermal stability is likely to decrease as the fusion temperature increases. One of the interesting results is obtained for PVC synthesized using suspension polymerization at variable polymerization in temperatures or initiator dosage trajectory, in which the Brabender plastograph data indicate a lower fusion time and higher stable time. The number of labile chlorines, internal double bonds, and dehydrochlorination rates in the PVC chains synthesized with these two policies decreases in compared with a regular process. As a result, the thermal stability can be improved if either a variable temperature or continuous initiator dosage is applied.

Conclusions

suspension polymerization of VCM in a pilot-scale reactor was performed by addition of a mixure of three types initiators at the beginning of the reaction (named Cok polymerization), which provides a constant reaction rate over the entire time course of the polymerization. It was observed that the MWD and MW of produced resin remained almost unchanged in a such circumestance. Although the particle size and particle size distribution also remained unchanged, the initiator mixture provided particles with a more regular shape and a smoother surface. The SEM micrographs showed that larger amounts of ultrafine particles attached to the surface of grains produced by Cok condition. Moreover, a Cok condition results in the formation of a late three-dimensional skeleton with bigger primary particles and subsequently lower internal porosity. PVC grains prepared by Cok polymerization entertain higher bulk density compared to the resin prepared by control condition. A comparison of data obtained from the present study with data from previous studies[], it can be concluded that the cocktail initiator mode leads to the grains with the nearest properties to that of a conventional polymerization process of VCM. The greatest productivity, however, can be obtained by initiator dosage system. This is while the purchased cost would spend more in the initiator dosage strategy and in a lower extent, in the temperature programming, because of special equipment needed to satisfy two modes. Therefore it seems to achieve an enhanced productivity accompanied with the equivalent properties of a conventional VCM suspension polymerization, in terms of molecular and morphological characteristics, the best approach is using cocktail initiator system.

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