

A Review on Enhanced Productivity Approaches in VCM Suspension Polymerization



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Abstract

VCM suspension polymerization is performed as the batch-wise process. For this, the productivity of this high demand product is low. As VCM suspension polymerization is an exothermic process, the full capacity of the cooling system remains idle most of the time during the course of the polymerization. There are three strategies for keeping the reaction rate constant during the entire polymerization process. Fast initiator dosage during reaction, cocktail initiator system and the temperature trajectory are the strategies that one can utilize to maintain the polymerization reaction rate at a constant value close to the allowed maximum rate. There are several reports that investigated separately the PVC resin properties obtained by these modes of polymerization. However, no report is published to compare the specifications of each mode together and also the PVC resin properties prepared by these policies. Literature review shows that 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.

Keywords: PVC; Initiator dosage; Temperature trajectory; Cocktail initiator; Suspension polymerization

Introduction

Suspension polymerization is a process used for producing many commercial resins, including poly(vinyl chloride) (PVC). The suspension polymerization process is typically carried out in well-stirred batch reactors [1]. This process uses mechanical agitation in conjunction with suspending agents to disperse the monomer in water as a continuous phase. The initiator dissolves in the monomer droplets and decomposes after adjusting the temperature, resulting in initiating free radical polymerization in the droplets [2]. Typically, the reaction takes place at a constant temperature. The kinetic aspects of the polymerization reaction and generally final properties of produced resin, strongly depend on the temperature in which the polymerization reaction occurs. As the VCM suspension polymerization is carried out in a batchwise reactors, the productivity of the process has been proven to be low. Therefore, 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. The polymerization of vinyl chloride monomer (VCM) is 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 highest reaction rate where exothermic peak occurs. The typical trend of heat removal rate versus reaction time in vinyl chloride polymerization indicates the full capacity of the cooling system remains idle most of the time during the course of the polymerization.

As a consequent, the distribution of heat load at exothermic peak of reaction over the entire course of the polymerization can lead to 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 corresponding heat removal rates are kept constant at a desired value. Feldman et al. [2] and Feldman and Macoveanu [3] suggested a temperature-programmed VCM suspension polymerization with a constant rate to improve productivity. They used a simple model developed by Abdel-Alim and Hamielec [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 40°C, 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 [4] proposed that programmed temperature of a series of the polymerization reactors measuring 40m³ 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. [5] proposed a heat kick policy in which the final temperature of the reaction increased to reduce the reaction time. Recently, we have successfully implemented a variable temperature trajectory during the course of the reaction to improve productivity by reducing the polymerization time for a predefined K value [1]. Pinto et al. [3] applied the technique of adding a mixture of different initiators to reactor at the beginning of the reaction and at an isothermal condition.

Thereafter, we call these strategies the enhanced productivity caused processes (EPCPs). In any event, the operational condition variations which occur in all three strategies may affect negatively or positively the quality of the final PVC product in terms of morphological and molecular characteristics. The aim of the present paper was to assess the influences which each of EPCPs has on the final product compared to conventional PVC regarded as what reported in the literature so far.

Result and Discussion

From the kinetic point of view, the course of VCM suspension polymerization consists of three stages; 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 in which 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 cycle of PVC production from VCM polymerization is affected by the change of operational conditions made by the abovementioned strategies which are implemented to enhanced productivity.

The effect on productivity

Among works performed on the enhanced productivity of PVC through temperature-trajectory [2], Darvish et al. [3] suggested the most reduction of polymerization time (ca. 100min). While the implementation of cocktail initiator policy could decrease the total reaction time by 20%, Bijanmanesh et al. reported that continuous dosing of a fast initiator during suspension polymerization of vinyl chloride enhanced productivity by 40%; the best approach in order to reduce the polymerization time of a typical VCM suspension polymerization.

The effect on molecular characteristics

None of the performed studies considered the change in the K value of the final product of PVC by implementations of EPCPs. As the molecular weight of polymerized PVC is only slightly affected by the initiation rate, the two modes of using a mixture of different initiators and fast initiator continuous dosage have no effect on molecular weight and subsequent K value when compared to those of conventional VCM suspension polymerization.

The utilization of temperature trajectory for enhanced productivity, however, is founded that have slightly influence on molecular characteristics such as molecular weights and molecular weight distribution[2].

The effect on grain morphology

While initiator cocktail shows no significant effect on the mean particle size of the PVC resin, a non-isothermal trajectory and continuous initiator dosage slightly broaden the particle size distribution towards bigger mean particle size compared that of a regular VCM suspension polymerization. It is believed that continuous fast initiator dosage modes cause polymerization initiated in the aqueous phase and ultrafine particles which is subsequently adhered on the skin of the grains. In this case, both temperature trajectory and initiator cocktail modes show the same manner as a conventional approach. By comparing the results obtained from micrographs related to grain shape from different kinds of literature, we can see that the PVC grains prepared by variable temperatures are more spherical with smoother surfaces than those produced by two others. The skin porosity of the PVC grains prepared nonisothermal was greater than that in the PVC grains produced other than. The most effects on primary particle morphology belong to the mode of fast initiator dosage. While initiator cocktail process causes fused primary particles packed together structure, exactly like to regular process, the grains produced in both temperature trajectory and initiator dosage systems are composed of an agglomeration of smaller primary particles promoting the formation of porous PVC grains. In another word, the final size of the primary particles formed by the cocktail initiator and the conventional process is larger than that of PVC grains produced other than, a temperature or initiator dosage trajectory results in the formation of an early three-dimensional skeleton with smaller primary particles and subsequently higher internal porosity. Although PVC grains prepared by either trajectory entertain higher porosity, the particle bulk density is also comparable to the resin prepared regularly.

The effect on thermal stability

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 Brabenderplastograph 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.

Conclusion

By the assessment of the final properties of PVC grains, 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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