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PROCESS DECOUPLING OF PLASMA ENHANCED SYNTHESIS OF CHLORINATED POLYVINYL CHLORIDE (CPVC) PARTICLES IN A CIRCULATING FLUIDIZED BED

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ABSTRACT

Plasma enhanced synthesis of CPVC particles in a gas-solid plasma circulating fluidized bed reactor (PCFBR) is proposed as a novel CPVC synthesizing method. The chlorination process is decoupled into a fast initiation step in a plasma riser and a slow chlorination process in the accompanying bed. The CPVC product has good properties in terms of chlorine content and microstructure.

INTRODUCTION

Chlorinated polyvinyl chloride (CPVC) is produced by chlorination of polyvinyl chloride (PVC) particles. In recent years, CPVC has received much attention as a kind of high-performance thermoplastic which gives better performance in heat stability, mechanical properties and flame retardant ability because of the increase of polarity compared with PVC. Therefore, CPVC can be widely used in hot and cold water pipes, industrial liquid handling and other commercial applications (1).

For the rapid development of the chlor-alkali industry in China, a large amount of excess chlorine has caused a serious problem, i.e., how to balance the noxious chlorine gas or the chlorine ion as in HCl from a sustainability viewpoint. PVC is a major solution to this problem, CPVC provides a further valuable route to immobilize chlorine. By further chlorinating the PVC particles to CPVC, more chlorine gas can be fixed into the solid products. It is known that the chlorine content of PVC is about 56.7 wt%. Most commercial CPVC resins have a chlorine content ranging from 63 wt% to 69 wt%, and even to 74 wt% by special treatments. For example, about 400 kg of chlorine is consumed by chlorinating 1,000 kg of PVC to CPVC with a 69 wt%

chlorine content. Accordingly, the CPVC industry not only consumes the excess chlorine, but also converts PVC into another high-value material.

Among the reported approaches to synthesizing CPVC, the aqueous suspension method is the main production technology at the commercial scale (2-3). However, a gas-solid method is acknowledged as a cleaner process, considering the ease to control and to separate the CPVC products from waste gases, etc. The main challenge of this method is to improve the gas-solid contact efficiency and find an effective initiator. In general the approach is carried out in fluidized beds, utilizing UV light as the initiator. But, the UV light is too easily shielded by PVC particles and the capability of initiation is weakened.

So, finding a more effective and cleaner initiator for the gas-solid chlorination method is of great importance. It is reported that the typical mechanism of PVC chlorination is a series of free radical reactions (4). It was proposed that cold plasma could be an effective initiator instead of UV. Cold plasma can be comprised of many kinds of ions, radicals, UV light, etc. Researchers have shown that cold plasma can be widely applied in the surface treatment of polymer materials (5-6). The mechanism showed that plasma could activate the surface of polymers and reactive gas simultaneously. However, the chlorine absorbed on the surface of a PVC particle must migrate into the core of the particle to chlorinate the bulk of the particle, which is assumed to be a slow diffusion-like process (7). Therefore, the chlorination process can be decoupled into two steps: the first step is the initiation of chlorination by plasma, and the second step is the chlorine diffusion from the surface to the inside of particles in a chlorine atmosphere. In this work, we proposed a novel CPVC synthesizing method in the Plasma Circulating Fluidized Bed Reactor (PCFBR).

EXPERIMENTS

First, a fixed-bed DBD reactor was employed to examine the feasibility of the CPVC synthesizing method. PVC particles were chlorinated with/without plasma at 100 °C. During chlorination, the plasma power source was turned on for 1 minute and then turned off for 10 minutes to simulate the process decoupling method. The power density of the plasma was 8.1 W/cm³ at atmospheric pressure, and the working frequency was 13.8 KHz.

A PCFBR was designed to synthesize CPVC as shown in Figure 1. The riser was assembled by two 0.5 m long straight coaxial quartz tubes with a gap of 4 mm, and the thickness of quartz tubes was ~2 mm. An iron bar was inserted into the inner tube as one electrode while some copper was wound outside the outer tube as the other.

One electrode was connected to the DBD power source (CTP-2000K, Nanjing Suman Electronics Co., Ltd), the other electrode was grounded. The plasma was generated by means of double-dielectric barrier discharge method inside the gap of two tubes. The accompanying bed was made of quartz, the same as the riser. The particle circulation rate was controlled by the flow rate of carrier gas. The chlorine gas had a purity of 99.999%, and the other gases including Ar and N₂ had a purity of 99.9%. The waste gas from the reaction unit was treated by an alkali solution.

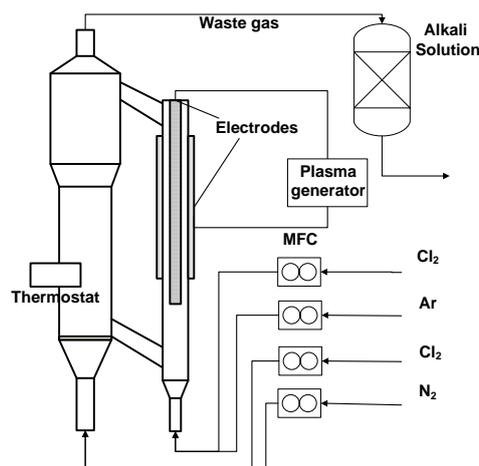


Figure 1 Schematic drawing of the plasma circulating fluidized bed reactor (PCFBR)

Approximately 70 g of PVC particles (SG-5 provided by Xinjiang Tianye Co. Ltd.) with ~150 μm diameter were added to the accompanying bed. The whole apparatus was

purged with N₂ gas in order to exhaust the oxygen in the system and fluidize the particles. The accompanying bed was heated up from room temperature to 70 $^{\circ}\text{C}$, and then the reactant gas, e.g., the mixture of chlorine and N₂, was injected into the accompanying bed from the bottom nozzle. The gas flows were fixed at 1 SLM Cl₂ and 1 SLM N₂. At the same time, a mixture of chlorine and Ar was injected into the riser from the bottom nozzle with two different flow rates of 0.3/2.0 SLM and 0/2.5 SLM. The Cl₂/Ar plasma was generated inside the gap between the two tubes by the DBD method. The power density and frequency were 1.02 W/cm³, 12.7 KHz (Cl₂/Ar=0.3/2.0) and 1.24 W/cm³, 13.6 KHz (Cl₂/Ar=0/2.5, respectively). The particle circulation rate in both situations was ~0.2 g/s. After treating particles at 70 $^{\circ}\text{C}$ for 20 minutes, the temperature was raised to 100 $^{\circ}\text{C}$ for 40 minutes. After that, the particles were chlorinated for different times. At the end of the experiments, the plasma generator, chlorine flow and heating apparatus were turned off but N₂ and Ar were kept flowing for several minutes to purge the remaining chlorine in the apparatus and that absorbed on the particles. Then the particles were exposed in the fume hood for

a day or more so that chlorine gas volatilized thoroughly.

The CPVC products were characterized by several methods. The chlorine content was analyzed by oxygen combustion and electrification method. Each product was characterized for at least 3 times to get an average and the error was found to be less than 0.5%. The distribution of chlorine in CPVC particles was measured by SEM and EDS (JSM-6460LA and EDS were made by the Oxford Instrument Company). The microstructure of CPVC products was characterized by Raman spectrum analysis (RM2000 made in Renishaw, UK.). In the measurements, the laser was Ar-514, with 20X objective lens, 5 μm diameter of facula, 4.7 mw and 30 s scanning time.

RESULTS AND DISCUSSION

Chlorination of PVC particles without a plasma initiator was carried out in the first series of experiments in the fixed bed reactor. The chlorine content of the CPVC particles rose to 69.7 wt% after 12 hours (see Figure 2). It proved that the chlorination process could take place by heating PVC particles at high temperature without any other initiator. However, it is not an effective method due to the low reaction rate. Then an atmospheric pressure DBD plasma was employed as the initiator in the second experimental series. It can be clearly seen that the chlorination process was accelerated significantly by the cold plasma and the chlorine content rose to 67 wt% in only 3 h. Considering that the working time of plasma was only 5 min/h under the intermittent operation, this proved that plasma was an efficient initiator in PVC chlorination.

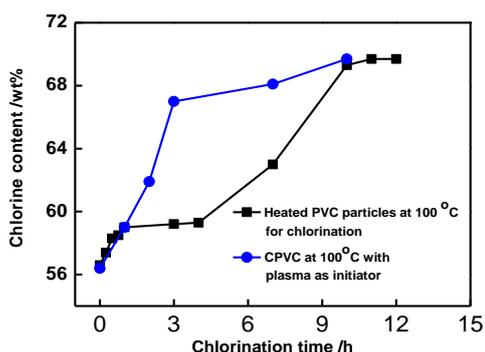


Figure 2 Chlorination curves of PVC particles with/without plasma as the initiator at 100 °C

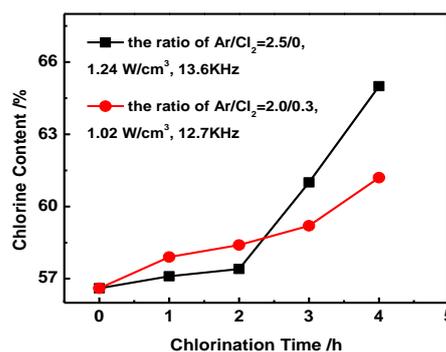


Figure 3 The chlorine content of CPVC by mass as a function of reaction time in PCFBR

The results obtained from fixed-bed DBD reactor proved that the cold plasma was

able to initiate the chlorination effectively. At the same time, the method of process decoupling was feasible and could be operated in a CFB reactor. That was, PVC particles were treated fast in the riser by cold plasma and the chlorination was initiated, then the chlorine slowly diffused into the core of the particles in the accompanying bed with a relatively long residence time. Particles were circulated in the PCFBR several times to be chlorinated sufficiently. The following discussion is based on the experiments in the PCFBR.

The chlorine content of CPVC is shown as a function of reaction time in Figure 3. One series of the results shows the chlorine content increasing up to 65.0% when pure Ar was used as the carrier gas with plasma in the riser. These results revealed that PVC can be chlorinated in the PCFBR. The total residence time of particles in the plasma zone was only about 22.2 s during the 4-hr experiments. In fact, with appropriate optimization of the PCFBR operation, a successful single-run of the chlorination process would be ~1.5 hr, or even much less.

Figure 3 also indicates that under the same power input of plasma, the composition of carrier gas in the riser is very important, because it provides the atmosphere in which plasma is generated, and the reactive species are different in different plasmas. So it is possible to adjust the property of plasma by changing the ratio of Cl_2/Ar . At the same time, the mechanism of chlorination is changed. For example, chlorination can occur in the riser when Cl_2 is introduced, which is different from the case of pure Ar as carrier gas. It was noticed that the chlorine content increases linearly as a function of reaction time in Figure 3 for the case of $\text{Cl}_2/\text{Ar}=2.0/0.3$. This might indicate that when introducing chlorine gas with Ar to generate plasma, not only are the PVC particles activated, but also the surface of the PVC particles is chlorinated rapidly in the plasma zone. However, the chlorine content increased slowly when the chlorination time was lengthened. Another fact is that the discharging of Cl/Ar plasma was weaker than pure Ar plasma so that the initiation effect became weaker. Obviously, work is required for a deep understanding of the complex mechanism and for guiding this optimization of the process design.

CPVC characterization

SEM and EDS can give a semi-quantitative result by comparing two samples under the same conditions. The chlorine content shown in Figure 4 is the mass fraction of chlorine. The total amount of chlorine and carbon elements (hydrogen is not included because EDS cannot discern light elements). So this value is larger than the actual chlorine content of CPVC. Considering that the analysis error of the instrument is less than 5 %, in principle, the results of EDS shown in Figure 4 indicate that the CPVC synthesized in this work has a much higher chlorine content than PVC raw

material. In addition, the scanning area was the interior of the CPVC particles, which proved that chlorination occurred inside the PVC particles, not only on the surface.

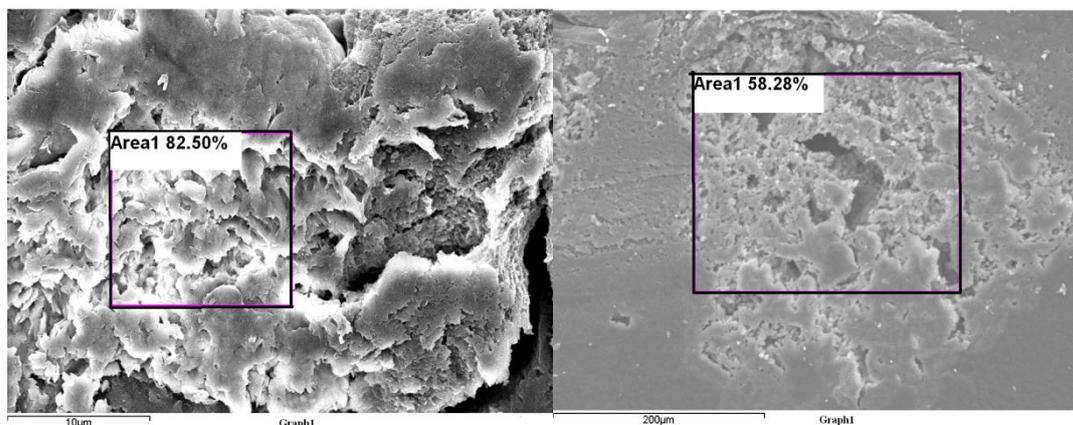


Figure 4 Chlorine distribution in the particle of plasma synthesized CPVC (left), and PVC raw material (right)

The microstructure of CPVC was analyzed by Raman spectral analysis. In Figure 5, five kinds of CPVCs were analyzed, including four samples of CPVC synthesized using PCFBR with Ar plasma as the initiator and one sample of commercial CPVC using the aqueous suspension method. The PVC SG-5 raw material was also analyzed for comparison. In the spectra, the characteristic peak of CPVC is at $300\text{-}500\text{ cm}^{-1}$.

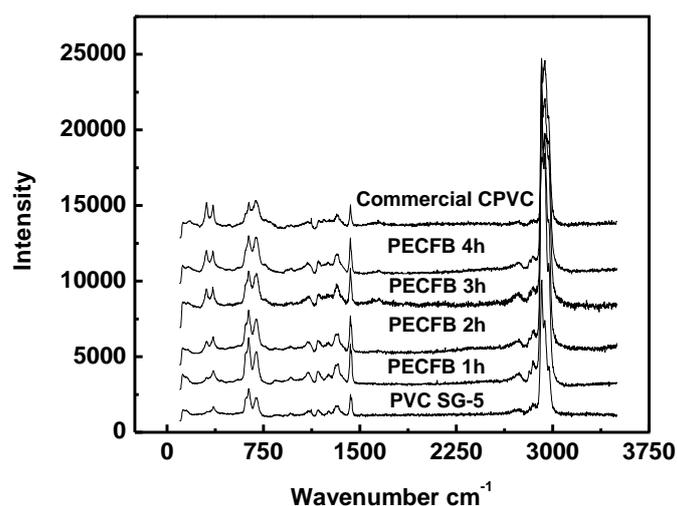


Figure 5 Raman spectra of PVC or CPVCs

In the chlorination process, the increase of the amount of -CCI- can be seen clearly. At the same time, there is essentially no -C=C- group in all of the samples, which has a signal at 1650 cm^{-1} . This proves that almost all the CPVC samples have a fine microstructure. But with it is still evident that there is a very weak -C=C- signal in the spectrum of an every CPVC sample and no signal in the spectrum of PVC, which reveals the influence of Elimination-Addition mechanism. To sum-up, it was shown that chlorination occurred in the bulk of the PVC particles and that the microstructure of plasma synthesized CPVC was comparative to the commercial product by the Raman analysis.

CONCLUSION

In this article, a novel CPVC synthesizing method was proposed that employed plasma as the initiator and which operated in a circulating fluidized bed. The chlorination process consisted of two steps: a fast initiation step and a slow chlorination process. In the chlorination process, the residence time of particles in the plasma zone was only about 22 seconds in the total 4-h reaction time, which indicated that plasma had high initiation efficiency. In the experiments so far, the chlorine content of CPVC product reached 65.0%. Characterizations by SEM and Raman spectrum show that the bulk of the particles were chlorinated. Moreover, the particle product had a uniform chlorine distribution inside the particles and a fine microstructure. The objective of this work was to propose a novel CPVC production method with preliminary demonstration of feasibility. This would also open a specific, potential area for CFB applications. Still, there is lots of work to do in the future, for example, to investigate the operational performances of PCFBR, plasma-related design and optimization, influence of PVC particle properties on the chlorination process, etc.

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