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Experimental Study and Modeling of UV-Enhanced PVC Chlorination to CPVC Using a Gas–Solid Process

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Experiments were carried out in a vibrated fluidized bed to investigate the dynamic process of UV-enhanced synthesis of chlorinated polyvinyl chloride (PVC) using a gas–solid method, where a UV-Vis online analysis system was used to record the kinetics of chlorination. Meanwhile, a comprehensive mathematical model incorporating the distributed activation energy model was established to describe the hindrance effect of Cl atoms already inserted on the PVC polymer chain on the later insertion during the chlorination process. Each of the hypotheses in the model was validated by the well-designed experiments, and the model predictions matched well with the experimental data under various operating conditions. Sensitivity analyses of three primary operating parameters, that is, temperature, chlorine concentration, and UV intensity, were made for better understanding of the mechanism of PVC chlorination. It is anticipated that the modeling methodology in this work would be also suitable for similar gas–solid reaction systems. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2235–2243, 2014

Keywords: polymer processing, multiscale modeling, chlorinated polyvinyl chloride, gas–solid method, UV radiation

Introduction

Further chlorination of polyvinyl chloride (PVC) to produce chlorinated polyvinyl chloride (CPVC) is a process with great value in three ways. First, CPVC is a high-value product with superior physical and chemical properties. For example, CPVC can withstand corrosive solutions at temperatures higher than PVC, allowing commercial application of CPVC for broader markets like hot water delivery, fire sprinkler systems and so forth. Second, further chlorination of PVC means more consumption of chlorine. Because the chlorine is the excessive, toxic product in the chlor-alkali industry, the production of CPVC can help to alleviate this problem to a certain degree by immobilizing the chlorine into the solid-state resins. Third, with increased heavy chlorine atoms in the resins, the mass fraction of carbon in the CPVC product decreases markedly, making CPVC a typical low-carbon product.

The synthesis of CPVC has been commercialized since 1950s, mainly adopting the aqueous suspension method.[1] However, the batch-operation process of the aqueous method is inevitably accompanied by the discharge of a large amount of waste water (e.g., about 20 ton discharged water per ton CPVC), which causes serious concern to the environment.[2] On the contrary, the gas–solid method is a much cleaner process with nearly no waste disposal, where dry gases atmosphere during the chlorination allows for the easy handling of solid particles and effluent gases (i.e., HCl/Cl_2). To promote the chlorination performance, UV radiation is often facilitated for process intensification.

It is acknowledged that the chlorination of PVC is a free radical chain reaction. Unfortunately, there is no accurate and reliable conclusion on the mechanism of chlorination reaction so far. Some researches focusing on the investigation of the actual chlorination route have been performed.[3–7] By proper simplification, the chlorination is considered to be a radical substitution reaction, where chlorine radicals preferentially substitute the hydrogen atoms that are connected to the methylene carbon.[8] The reaction route is assumed as follows.

First, chlorine is decomposed into chlorine radicals under UV radiation

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \tag{1}$$

Then, the chlorine radicals attack and substitute the hydrogen atoms on the methylene

$$Cl\cdot + -(CH_2-CHCl)- \rightarrow -(CH\cdot-CHCl)- + HCl \tag{2}$$

$$-(CH\cdot-CHCl)- + Cl_2 \rightarrow -(CHCl-CHCl)- + Cl\cdot \tag{3}$$

Finally, chorine radicals collide to each other and the reaction terminate

$$2Cl\cdot \rightarrow Cl_2 \tag{4}$$

Based on the above chlorination route, the kinetic expression of the reaction can be accordingly deduced, and this will be clarified in detail in the following section.

Apart from the complex chlorination reaction mechanism, the simultaneous transport phenomenon in the process of CPVC synthesis using a gas–solid method is sophisticated. When it comes to process modeling, it can be categorized as

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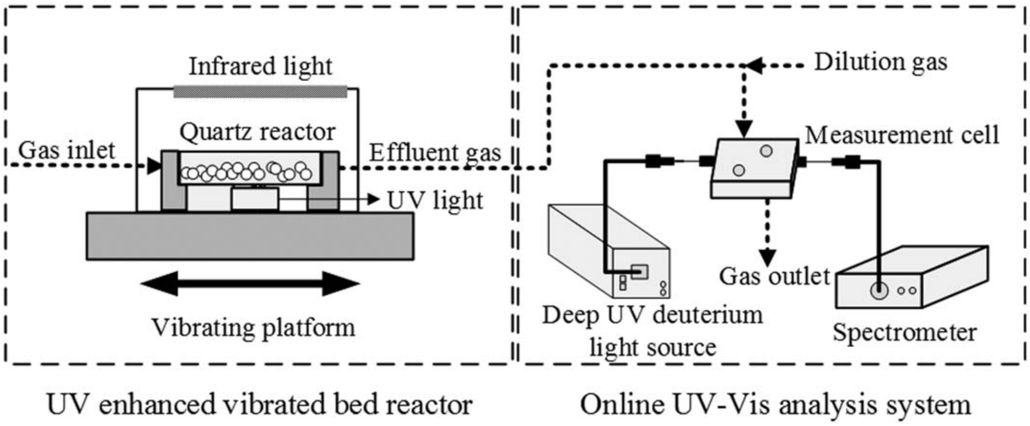

Figure 1. Schematic diagram of the experimental setup.

noncatalytic gas–solid reaction. Ramachandran and Doraiswamy[9] and Wen[10] made thorough overviews on the noncatalytic gas–solid models applied in different systems considering the different structural features of the solid as well as the contact mode between the gas and the solid. Nevertheless, no reliable model has been reported suitable for the gas–solid synthesis of CPVC specifically. Barrière et al.[8] theoretically calculated the chlorination process and analyzed different circumstances of reaction-limited regime and diffusion-limited regime. Wachi et al.[11] studied the conversion distribution in the gas–solid synthesis of CPVC with a simplified model, but the model is unsubstantial with little experimental validation and the calculation is also simplistic.

The aim of this study is to build a comprehensive model to predict the chlorination process of PVC using the gas–solid method. The model is to be validated by experiments under various conditions. Besides, the critical factors affecting the chlorination process will be discussed experimentally and expressed explicitly in the model.

Experimental

Experimental setup

The experimental setup consists of two parts: the reaction system and the measurement system, as shown in Figure 1. The chlorination of PVC takes place in a cylindrical quartz reactor with thickness of 6 mm and diameter of 50 mm. Chlorine gas and argon gas are supplied by cylinders with 99.999% and 99.9% purity, respectively, to flow into the reactor and interact with the PVC grains. A vibration platform is used during the experiments to enhance the contact efficiency between the PVC grains and the chlorine gas in the reactor. Frequency of the vibration platform is 0–5 Hz and its amplitude is fixed at 20 mm horizontally. A UV lamp (4 W, Philips Company) is placed right beneath the reactor. Besides, an infrared lamp (800 W, Philips Company), as the heating source, is fixed at the top of the vibration box. Temperature is recorded from thermocouple adhered to the upper surface of the reactor. Temperature programming is applied to control the temperature accurately during the experiments by adjusting the heating power of the infrared lamp. The concentration of chlorine gas is controlled by tuning the flow rates of chlorine and the dilute gas (Ar), respectively. The online UV-Vis spectral analysis system allows for the dynamic recording of the chlorine concentration in the effluent gas continuously. The specification of the apparatus and the measurement principle have been given in detail in one of our previous articles.[12]

PVC grains are provided by Qilu Petrochemical Corporation in China. The mean diameter is 150–250 μm and the pore diameter is 300–1000 nm measured by sieving method and mercury intrusion porosimetry, respectively.

UV enhanced chlorination of PVC

Before starting each experiment, the inert gas (Ar) is introduced and flows through the entire gas circuit to remove other gases to protect the PVC grains. The amount of the PVC sample placed in the reactor is about 4 g. Then, the reacting gas (Cl_2) and the dilute gas (Ar) are turned on and tuned to a certain ratio to flow through the reactor and contact with PVC grains. After the online UV-Vis spectral analysis system is all set, the infrared lamp is turned on to heat up the whole reaction system gradually, which is controlled by temperature programming. Once the temperature reaches the set value, UV lamp is turned on and the chlorination is initiated immediately. The chlorination rate can be deduced from the recorded data of the chlorine concentration in the effluent gas using the UV-Vis analysis system.

Dissolution of chlorine gas in PVC grains

The unique properties of PVC as a polymer make it soluble for chlorine gas.[13] To investigate the dissolution mechanism and acquire the basic dissolution parameters, experiments were carried out using the above experimental setup.

After setting about 4 g of PVC samples in the reactor, the weight of the reactor is measured and recorded. Similar to the chlorination experiments, the reactor is fixed on the vibration platform. After the temperature is stable, the chlorine gas, along with the dilution gas (Ar), is introduced into the reactor and interact with the PVC polymer. About 10 min later (the time needed for the solubility equilibrium explored by the experiments), the reactor is taken out and the weight is measured again. Subtracting the initial weight, the mass of chlorine dissolved in the PVC polymer is obtained as well as the basic laws between the chlorine concentration in polymer phase and the gas phase.

Mathematical model

As mentioned earlier, the chlorination of PVC using the gas–solid method involves simultaneous mass transfer and chemical reaction. Obviously, the mass transfer between the gas and the solid is greatly affected by the structure of the PVC grains, so it is necessary to take a deep look at the PVC structure before the model development. At a macrolevel, PVC is porous grains with diameter of 50–250 μm and porosity of around 60%, and the pore diameter ranges from 300 to 1000 nm. At a microlevel, many microparticles with diameter of 2–10 μm, namely the secondary particles, exist inside each macro PVC grain. The secondary particles are arranged randomly with pores separating apart.[14] When the chlorine gas contacts PVC grains with such multiscale structure, it would first diffuse through the voids and then come into contact and interact with the solid secondary particles. The effect of the intragrain gaseous diffusion through the pore was estimated by Wachi et al. and they concluded that it could be neglected compared to the gaseous diffusion through the continuous secondary particles.[11] This is similar to the particle-grain model proposed by Szekely and Evans.[15–18] Further, with neither external mass-transfer limitation nor internal diffusion effect ideally, the chlorination process is essentially focused on the interaction between the chlorine gas and the PVC secondary particles. This is the first assumption made for developing our mathematical model.

PVC is a polymer with free volume existing between the polymer chains, which makes PVC grains exhibit unique properties distinct from common solids, like being soluble and permeable for chlorine gas.[19–21] Hence, when the chlorine gas contacts the PVC secondary particles, it would dissolve in the polymer surface and diffuse into the bulk polymer phase gradually with simultaneous chlorination reaction taking place under proper conditions. To model the complex process, it is necessary to characterize the dissolution and the diffusion mathematically. Based on the work conducted in the literature, we naturally assume that the dissolution of chlorine gas in PVC polymer obeys the Henry's Law, that is, the concentration of chlorine dissolved in PVC polymer is proportional to the concentration of chlorine in the bulk gas phase at dissolution equilibrium. This is the second assumption for the mathematical model.

The third hypothesis is the spherical assumption of the secondary particle and neglecting the change of particle size during the chlorination process at the same time. As the model is focused on one single secondary PVC particle, we also assume that all secondary particles inside the PVC free grain are uniform and the physiochemical change of the secondary particles is corresponding to the change of micro PVC grain which could be directly obtained by experiments.

To summarize, the model assumptions are listed as follows:

1. There is no external or internal mass-transfer limitation in the gas–solid chlorination process;
2. The dissolution of chlorine gas in the PVC polymer accords with the Henry's Law;
3. The diameter of PVC/CPVC secondary particle is considered to maintain constant.

As discussed above, these hypotheses were first made by theoretical analysis or adopting suggestions from former researchers. To assure the reliability of the model, these assumptions will be tested experimentally and the results will be discussed in the subsequent section.

Based on the above assumptions, the model can be described mathematically. The core equation is the mass balance expression of the chlorine gas in a PVC secondary particle, which is given as

$$\frac{\partial C_B}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C_B}{\partial r}\right)-S \tag{5}$$

where C_B is the chlorine concentration in PVC polymer phase, t is time, r is the radial position along the spherical secondary particle, D is the diffusion coefficient of chlorine in PVC polymer that changes with temperature, and S represents the source term for the kinetics of the chlorination reaction.

The reaction rate expression is determined by the reaction mechanism clarified previously. Applying the pseudo-steady-state hypothesis to the reactive radicals $\mathrm{Cl}\cdot$ and $-(\mathrm{CH}\cdot-\mathrm{CHCl})-$, it follows from Eqs. 1–4 that

$$2k_1[\mathrm{Cl}_2]=2k_4[\mathrm{Cl}\cdot]^2 \tag{6}$$

and

$$\frac{d[\mathrm{Cl}_2]}{dt}=\frac{d[\mathrm{MH}]}{dt}=k_2[\mathrm{MH}][\mathrm{Cl}\cdot]=k_2[\mathrm{MH}]\sqrt{\frac{k_1}{k_4}}[\mathrm{Cl}_2] \tag{7}$$

where k_1, k_2, k_4 is the reaction rate constant in the radical reactions (1), (2), (4), respectively, and $[\mathrm{Cl}_2]$ (mol/m^3)and [MH] (mol/g) is the local concentration of chlorine and the unchlorinated PVC repeat unit, respectively.

Defining a new parameter k as

$$k=k_2\sqrt{\frac{k_1}{k_4}} \tag{8}$$

the reaction rate is then expressed as

$$S=k[\mathrm{MH}][\mathrm{Cl}_2]^{0.5} \tag{9}$$

The reaction rate constant k follows the form of Arrhenius equation, which is presented as follows

$$k=A\exp\left(-\frac{E}{RT}\right) \tag{10}$$

where A is the pre-exponential factor, and E is the activation energy for the chlorination reaction. Normally, A and E remain constant in a regular reaction. However, in the chlorination reaction, the substitution of the relatively big Cl atoms for H atoms may cause steric and other chemical effect, increasing the difficulty for subsequent chlorine atoms introduced onto the polymer chain as a whole.[22] In other words, the chlorination reaction would get harder and harder, which can be represented by the increase of activation energy during the reaction. Thus, the distributed activation energy model (DAEM) is incorporated.[23–26] The existence of the hindrance effect has been further supported by pyrolysis chromatography result of CPVC product with graded chlorine contents both from our experiments and from literature, which is presented in Appendix A.[27,28]

Before the chlorination reaction takes place, a rather long time is needed for heating the experimental system to the required temperature, during which the chlorine gas and the PVC grain keep in contact. Since it only takes about 10 min for the dissolution of chlorine gas in PVC polymer to reach equilibrium, it is safe to conclude that the dissolution equilibrium has achieved before the reaction starts. Thus, the initial condition is expressed as

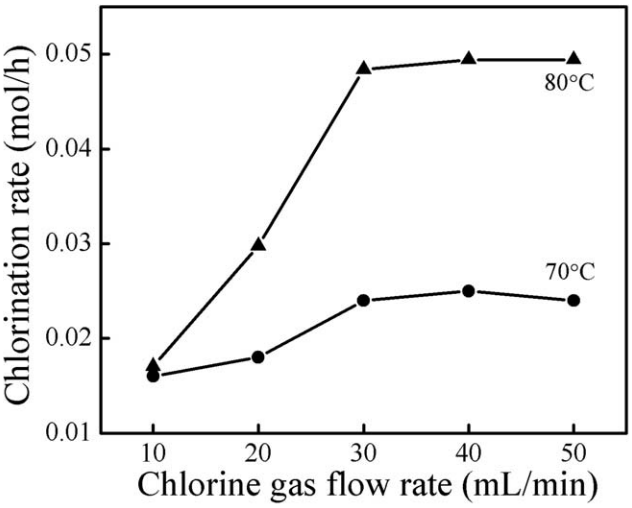

Figure 2. Effect of flow rate of the chlorine gas on chlorination rate.

$$t=0, C_B=Hy \tag{11}$$

where H is the Henry coefficient, which could be obtained by experiments and will be provided later, and y is the concentration of chlorine gas in the bulk gas phase.

The boundary conditions are given by

$$t>0, \begin{cases} r=0, \dfrac{\partial C_B}{\partial r}=0 \\ r=R, C_B=Hy \end{cases} \tag{12}$$

Here, it should be pointed out that such boundary condition is imposed based on the third assumption stated above that the radius change of the secondary PVC particle is neglected. When there is remarkable volume expansion of solid, radius change should be incorporated in the model, and in that case model equations in a dimensionless form is preferential.

Combining Eqs. 5, 9, 11, and 12, chlorine concentration in PVC polymer C_B at any position and any time can be theoretically calculated. The finite volume method was adopted to discrete the equations.[29]

To compare the calculated results with the experimental results effectively, the chlorine content, that is, the mass fraction of chlorine in the whole PVC/CPVC sample, has been chosen to be the target indicator, whose change with time represents the dynamic chlorination process. The chlorine content in the model is calculated as

$$\text{Cl wt}\,\%=\frac{w_{\text{MCl}}\cdot 97}{w_{\text{MH}}\cdot 62.5+w_{\text{MCl}}\cdot 97}\cdot 100\% \tag{13}$$

where w_{MCl} and w_{MH} is the mass fraction of reacted and unreacted chlorinated PVC repeat unit, namely $-(\text{CHCl}-\text{CHCl})-$ and $-(\text{CH}_2-\text{CHCl})-$, respectively.

Results and Discussion

Validation of model hypotheses

It is well acknowledged that the existence of external and internal diffusion can be investigated by the influences of gas velocity and particle size on the reaction rate, respectively.[30] If the reaction rate is not affected by these two factors, it can be concluded that there is neither external nor internal mass-transfer limitation. Experiments were conducted to explore these effects, and the results are presented in Figures 2 and 3.

As shown in Figure 2, the chlorinated rate grows with increasing the flow rate of chlorine gas at the beginning. But noticeably, when the flow rate is higher than 30 mL/min, the chlorination rate becomes independent of the gas velocity. In other words, by increasing the gas velocity, the external mass transfer limitation can be eliminated. As a high gas velocity is usually adopted in most of our experiments as well as industrial operations, it is reasonable to consider that no external diffusion affects the chlorination process.

Figure 3 indicates that under experimental conditions with no external mass-transfer limitation (80°C and 40 mL/min of chlorine gas), changing PVC grain size causes no noticeable differences on the chlorination process. Hence, it can be concluded that there is no external and internal diffusion during the process as long as the gas velocity is high enough. Thus, the assumption of the direct interaction of chlorine gas with the secondary particles is verified.

Although it is difficult to observe the structural change of PVC secondary particles directly, the mass and the density changes can be obtained by weighing and density meter measurement, which allow for the acquisition of the volumetric and the diameter changes further on. The detailed calculations are presented in Appendix B.

Figure 4 shows the changes of true density and calculated density (assuming there is no volumetric change) with the chlorine contents of CPVC product and Figure 5 gives the calculated results of volumetric change and diameter change. It can be seen that expansion of the PVC/CPVC sample does exist during the chlorination process. But as to the diameter change, the expansion ratio is only 5% at most when the chlorine content reaches as high as 69%. When it comes to secondary particle, the diameter change would be even less. Such minor change is considered to have little effect on the chlorination process.

The third hypothesis is about the Henry's Law. To study the relationship of the chlorine concentration in the bulk gas phase and the PVC polymer phase under dissolution equilibrium, experiments were carried out and the results are presented in Figure 6.

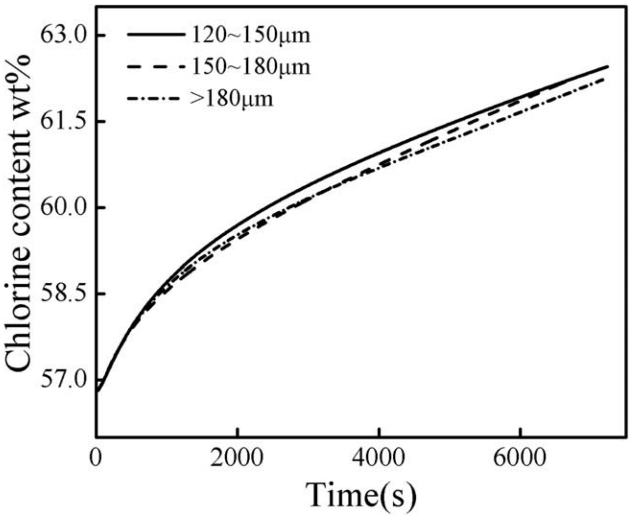

Figure 3. Effect of PVC grain size on the chlorination process at 80°C and 40 mL/min of chlorine gas.

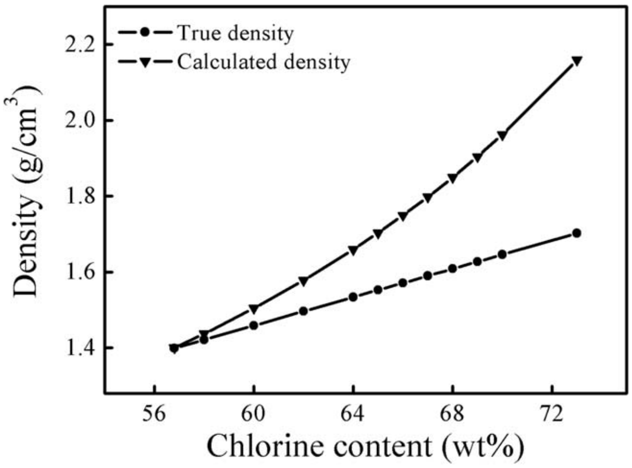

Figure 4. True density and calculated density of CPVC products with various chlorine contents.

Figure 6 exhibits linear relationship of the chlorine concentration in the two phases, which confirms the Henry's Law assumption firmly. Furthermore, the Henry coefficients at different temperatures can be obtained from the slopes of the fitting lines in Figure 6. As it is solely dependent on temperature, the Henry coefficient can be expressed as a function of temperature by proper regression. Regression of ln H as function of $1/T$ leads to a linear coefficient of 0.99, as shown in Figure 7. Thus, H can be expressed in the form of a prefactor multiplied by an exponential factor, the parameters of which are the slope and intercept of the linear fitting line

$$H = 0.0466\exp\left(\frac{15,072}{RT}\right) \tag{14}$$

So far, the three hypotheses made for building the model have been confirmed by experiments, respectively, making the model substantial with firm supports from experiments.

Model validation

Six parameters in the model are to be determined, namely five kinetic parameters A, E_0, δ, x_a, x_b (parameters in the DAEM), and one structural parameter R (the equivalent diameter of PVC secondary particle). The physical property parameter D (the diffusion coefficient of chlorine in PVC polymer) can be obtained from reference[11]

$$D = 9.19\times10^{-7}\exp\left(\frac{-49,100}{RT}\right) \tag{15}$$

Both the changes of H and D due to the chlorination reaction are neglected. The rest of the above parameters were obtained by least-squares fit of one set of experimental data, and the results are shown in Table 1. With determined parameters, the chlorination processes under other operating conditions can be calculated.

Based on our previous study, temperature is considered to be a key factor as it affects the chlorination process both on chemical reaction and physical properties of PVC/CPVC. In the model, the influence of temperature is presented in the expressions of reaction rate constant, Henry coefficient as well as the diffusion coefficient.

Figure 8 shows the calculated results at different temperatures in the form of chlorine content vs. time, along with corresponding experimental results. It can be seen that the

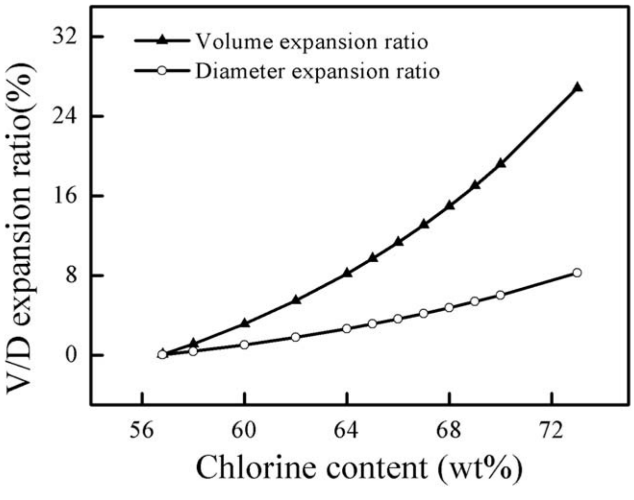

Figure 5. The volume expansion and diameter expansion of CPVC products with various chlorine contents.

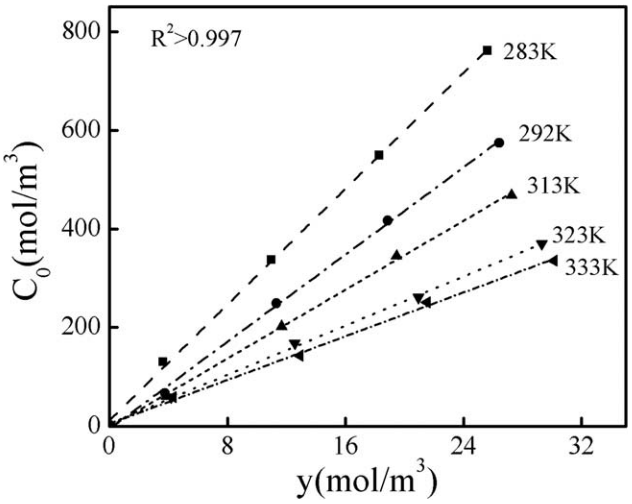

Figure 6. Chlorine concentrations in two phases and linear fits under dissolution equilibrium at different temperatures.

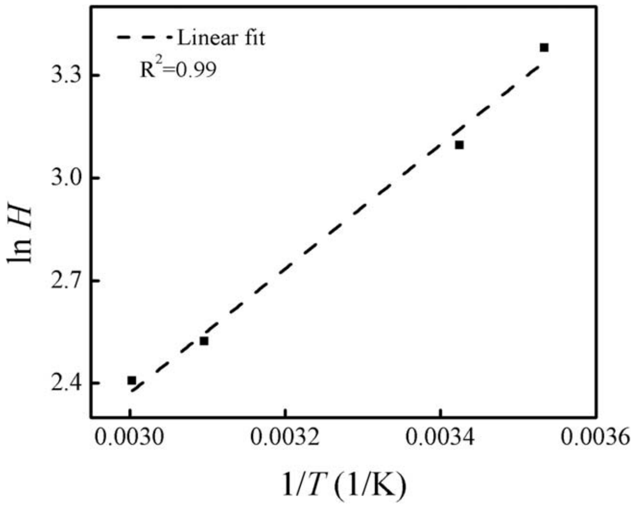

Figure 7. Regression of ln *H* with 1/*T*.

Table 1. Values of Model Parameters

Parameters	A (g/s·(mol·m^3)$^{1/2}$)	E_0 (J/mol)	δ (J/mol)	x_a	x_b	R (m)
Values	14018	62727	1937.7	−16.28	727.32	3.44×10^{-6}

model predictions match well with the experimental data throughout the entire chlorination process. The results also display the great dependence of chlorination process on temperature, which is accordant with the previous theoretical analysis.

The experimental and predicted results under different chlorine concentration conditions are shown in Figure 9. Again, good agreement is obtained between the model predictions and the experiments. From these results, one can see that the influence of the concentration of chlorine gas on the chlorine process is not as significant as that of temperature, despite the fact that the chlorine is one of the reactants. It is suspected that when the chlorine contents fall into this range, the chlorination process is limited by other factors rather than the chlorine gas. Considering the fact that the PVC solid is always abundant, it is likely to be the diffusion of chlorine in the polymer that limits the whole chlorination process.

To illustrate the necessity of incorporating the DAEM to represent the hindrance effect, a comparison between the model calculation considering the hindrance effect and the one without was made, which is shown in Figure 10. Obviously, deviation is inevitable in the model without considering the hindrance effect, that is, the calculated chlorine contents are lower than the experimental results at the beginning part, whereas higher at the ending part. The model considering the hindrance effect, however, shows good agreement with the experimental results all along the whole process. Thus, it is a significant improvement thanks to the introduction of the DAEM.

The chlorination experiments discussed earlier were conducted under UV radiation with the same UV intensity so that the model has not taken this factor into account yet. As a matter of fact, UV intensity could have great effect on the chlorination process by affecting the generation of chlorine radicals.[31]

By controlling the UV intensity that the reactor received quantitatively, chlorination experiments can be conducted with different UV intensities affiliated. Here, the UV intensity, I (J/mol), is defined as the UV energy received by per mole of chlorine gas that flows through the reactor.

From the mechanism point of view, UV radiation initiates the chlorination of PVC by decomposing chlorine gas into radicals, as expressed in Eq. 1, and UV energy intensity could affect the quantum yield for chlorine dissociation. Based on the pseudo-steady-state approximation on the chlorine atom concentration, the overall rate should be proportional to square-root of light intensity.[32] A linear correlation between the experimental data of chlorination rate and square-root of light intensity was made, as shown in Figure 11. It can be seen that a general linear relationship does exist between these two parameters. Similar result was reported by Decker et al.,[33] in which they also proved the chlorination rate is proportional to $I^{0.5}$. Therefore, we may express the effect of UV intensity in the chlorination rate expression with $I^{0.5}$ as a factor. Because the chlorination could also take place without any UV radiation, the relation is expressed as

$$S = S_0 + 0.0089 \times I^{0.5} \tag{16}$$

where S_0 is the chlorination rate under the same condition only without UV radiation.

Using the above correlation, chlorination process under different UV energy intensities could be calculated. Figure 12 shows the comparison of the calculated results with the experimental data. It can be seen that they are reasonably matched, proving that such correlation of $I^{0.5}$ and chlorination rate could basically reflect the effect of the UV intensity.

As stated earlier, temperature, chlorine concentration, and the UV intensity are three major operating factors to affect the chlorination of PVC using gas–solid method intensified

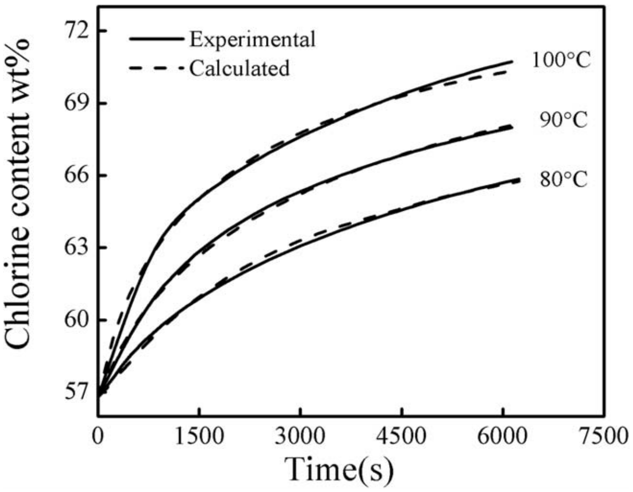

Figure 8. Comparison of experimental results with model predictions at different temperatures (50% and 45 mL/min of chlorine gas).

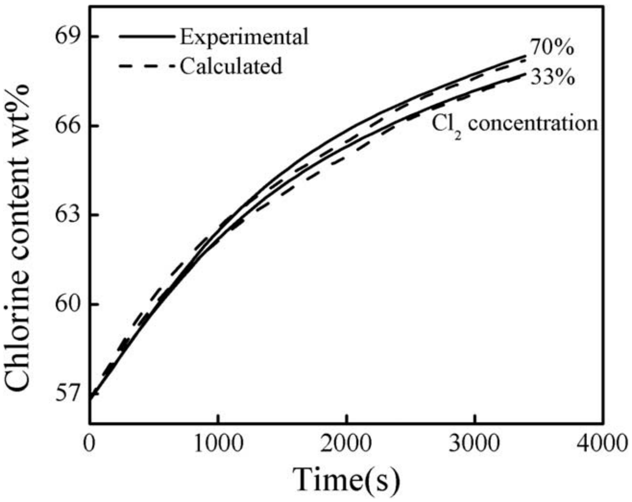

Figure 9. Comparison of experimental results with calculated results at different chlorine concentrations in the gas phase (100°C and 45 mL/min of chlorine gas).

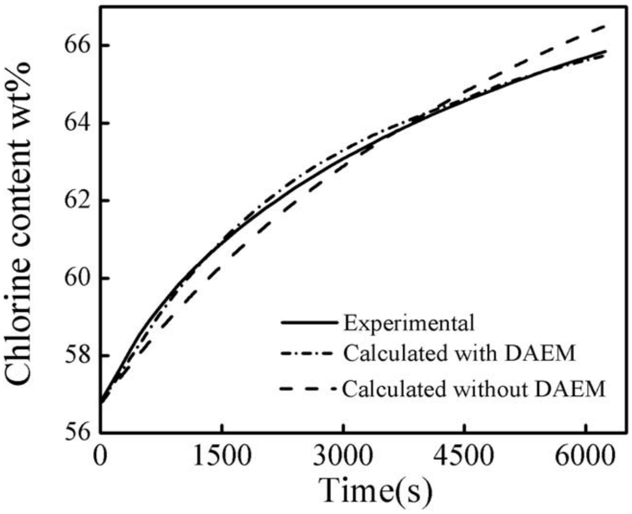

Figure 10. Comparison of the model predictions with or without incorporating DAEM (80°C and 50% of chlorine gas).

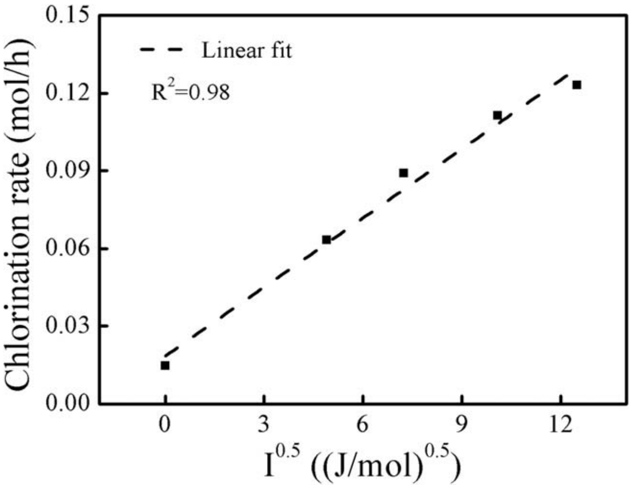

Figure 11. The effect of UV energy intensity on the chlorination rate.

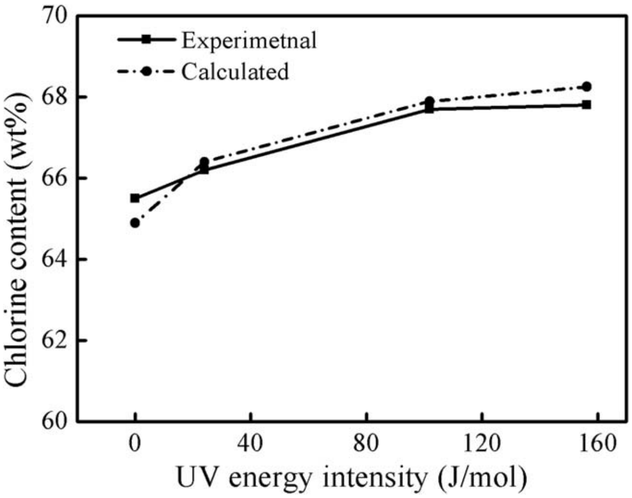

Figure 12. Comparison of experimental data with calculated results at different UV energy intensities.

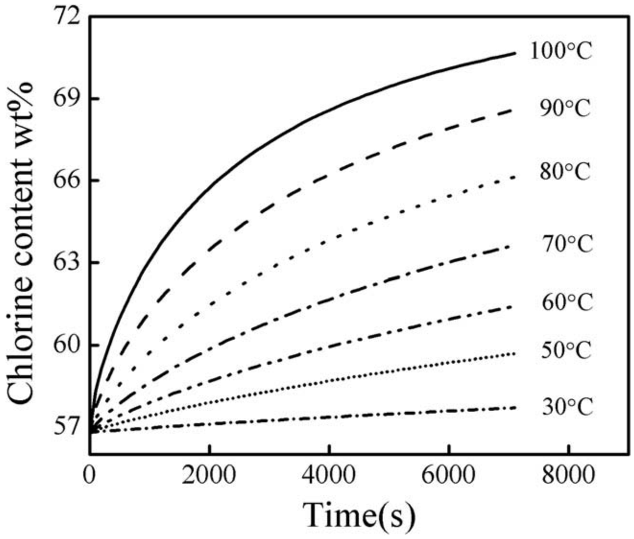

Figure 13. Calculated chlorination results at different temperatures (50% of chlorine gas).

by UV radiation. The effects of these important factors are reflected in the model directly or indirectly. As it is time-consuming and not practical to investigate chlorination process under all conditions experimentally, predictions based on the validated model become a more convenient way. Therefore, sensitivity analyses of these operating parameters were conducted, as shown in Figures 13–15.

Figure 13 illustrates that the chlorination process is highly dependent on temperature. Generally, the chlorination experiments and industrial operation are conducted between 70–100°C, where small difference of temperature can cause distinct chlorination results. Thus, the temperature should be accurately controlled in industrial operation. Conversely, it is also concluded that we could improve the chlorination efficiency by raising the temperature properly. The sensitivity analyses of chlorine concentration and the UV intensity are displayed in Figures 14 and 15. Both factors affect the chlorination process sensitively at relative small values. But

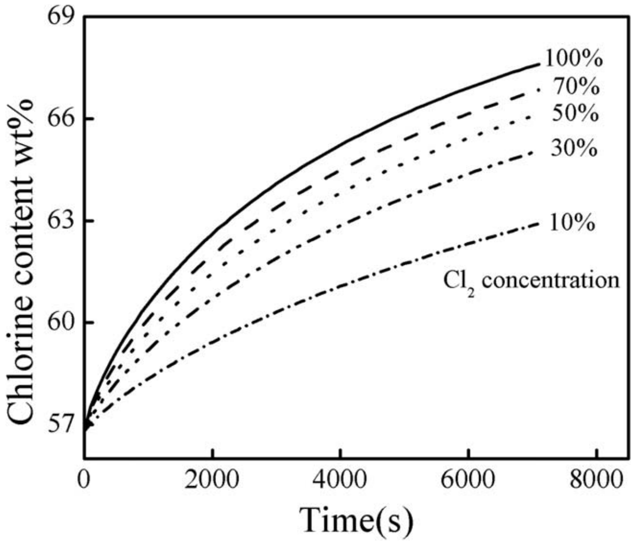

Figure 14. Model predictions at different chlorine concentrations (80°C and 156.3 J/mol of UV radiation).

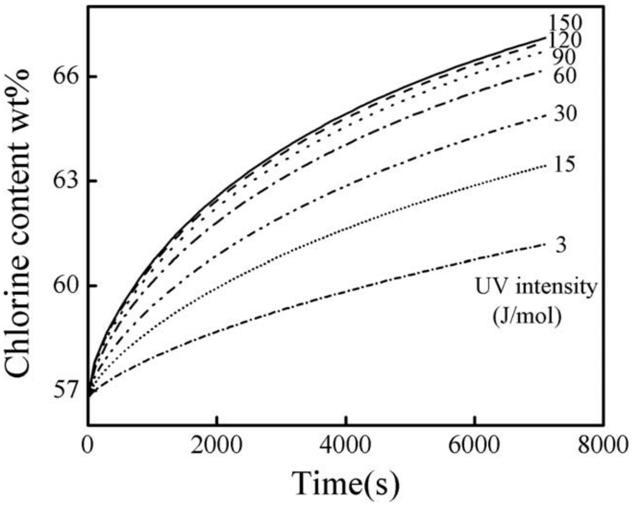

Figure 15. Model predictions under different UV intensities (80°C and 50% of chlorine concentration).

with the increase of the parameter values, the intensification effects are less evident anymore. Such results are useful when determining if it is reasonable to promote the chlorination process through adjusting these parameters.

Conclusions

In this article, we thoroughly investigated the characteristics of the gas–solid PVC chlorination intensified by UV radiation experimentally and theoretically. Based on several hypotheses that were verified by experiments, a comprehensive mathematical model was developed to describe the whole chlorination process. Innovatively, the DAEM was incorporated in the model to describe the hindrance effect of Cl atoms already inserted on the PVC polymer chain on later insertion, which resulted in good agreement of model predictions with the experimental data under various operating conditions. In addition, sensitivity analyses of three primary operating parameters, that is, temperature, chlorine concentration, and UV intensity, were conducted. The results show that temperature is the most sensitive factor in the PVC chlorination process in a wide range, and that the effects of chlorine concentration and UV intensity are only significant when they are relatively small.

Conversely, it should be admitted that the current model is applicable for lab-scale gas–solid PVC chlorination process only as the assumptions are validated by lab experiments. For a larger scale process, new factors brought by scaling up, such as external mass transfer resulted from lower gas–solid contacting efficiency, uneven distributions of reactant concentration and the temperature, need to be taken into consideration. By incorporating these factors with the current model, a more comprehensive model to describe the whole reactor performance can be built, which should be capable of simulating the chlorination process in a practical reactor, thus providing straightforward guidance to industrial operation.

Acknowledgment

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Notation

A = pre-exponential factor, g/s·(mol·m^3)$^{1/2}$
C_B = chlorine concentration in PVC, mol/m^3
D = diffusion coefficient of chlorine in PVC, m^2/s
E = activation energy, J/mol
E_0 = activation energy at one point, J/mol
H = Henry coefficient
I = UV intensity, J/mol
k = chlorination reaction constant, g/s·(mol·m^3)$^{1/2}$
k_1 = the first elementary chlorination reaction constant, 1/s
k_2 = the second elementary chlorination reaction constant, g/(s·mol)
k_4 = the fourth elementary chlorination reaction constant, 1/s·(mol·m^3)$^{1/2}$
R = radius of the PVC secondary particle, m
r = radius of PVC/CPVC secondary particle, m
S = chlorination reaction rate, mol/m^3·s
S_0 = chlorination reaction rate without UV radiation, mol/m^3·s
T = temperature, K
t = time, s
w = chlorine content
w_{MH} = mass fraction of MH in PVC/CPVC
w_{MCl} = mass fraction of MCl in PVC/CPVC
x_a = lower limit of activation energy deviation ratio
x_b = higher limit of activation energy deviation ratio
y = chlorine concentration in gas phase, mol/m^3

Greek letters

δ = activation energy deviation constant, J/mol

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Appendix A

PVC and CPVC can be decomposed into benzene and its chlorine-substituted isomers as well as hydrogen chloride in a pyrolyzer under proper condition. Experiments were conducted at the temperature of 460°C. Hydrogen chloride evolved during the thermal decomposition of the polymers was eliminated by precut column containing NaOH, and only the aromatic compounds such as benzene and its chlorine-substituted isomers were separated to record pyrograms.

To investigate the chlorine distribution on the CPVC polymer chain at different stages during the chlorination process, CPVC products with graded chlorine contents were chosen to be decomposed. The representative results of pyrolysis products are displayed in Figure A1. It can be seen that there is at most one Cl atom added on every three —CH_2—CHCl— units for quite a long stage until chlorine content reaches 62%. Similarly, no more than two Cl atoms are added on six carbons of CPVC chain when the chlorine content is below 67%. Such distribution pattern shows that Cl atoms tend to substitute H’s bonded to the carbons that are far away from the carbons with Cl atoms added, which is believed to be caused by the hindrance effect of the newly inserted Cl atoms.

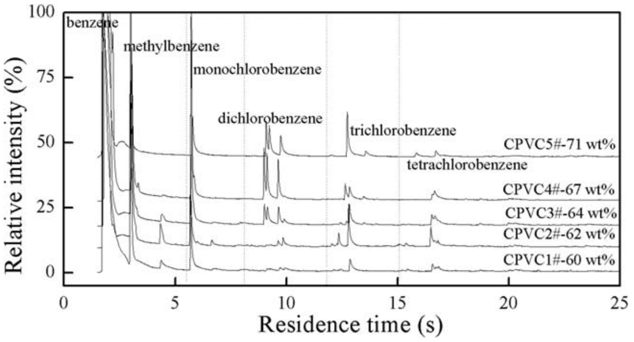

Figure A1. Distribution of pyrolysis products of CPVC with graded chlorine contents.

Appendix B

The density of CPVC ρ_2 is defined as

$$\rho_2=\frac{\rho_1 V_0+\Delta m}{V_2} \tag{B1}$$

where ρ_1 is the density of PVC sample (1.44 g/cm^3 in our experiments), V_0 is the initial volume of PVC, $\Delta m$is mass increase of the sample after being chlorinated, which is presented as

$$\Delta m=\frac{\rho_1 V_0(w-0.568)}{1-w} \tag{B2}$$

where w represents the chlorine content of the CPVC products. Assuming that there is no volumetric change during the chlorination process, that is, the volume of the CPVC product remains V, then the calculated CPVC density can be acquired

$$\rho_2{}'=\frac{\rho_1 V_0+\Delta m}{V_0} \tag{B3}$$

Incorporating with Eq. B2, we can get

$$\rho_2{}'=\frac{0.432\rho_1}{1-w} \tag{B4}$$

Combing Eqs. B1, B3, and B4, the volumetric change can be obtained

$$\frac{V_2}{V_0}=\frac{0.432\rho_1}{\rho_2(1-w)} \tag{B5}$$

The diameter change is then given as

$$\frac{d_2}{d_0}=\left(\frac{V_2}{V_0}\right)^{1/3} \tag{B6}$$

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