

Preparation of Chlorosulfonated Polyethylene by the Gas-Solid Method

RUOFEI ZHAO, SHUJUN CHENG, YAN SHUN, YONGJUN HUANG

Research Institute of Material Science and Engineering, East China University of Science and Technology, Shanghai, People's Republic of China

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ABSTRACT: Chlorosulfonated polyethylene (CSM) has been prepared by the gas-solid method in a tank reactor using chlorinated polyethylene (CPE) and a gaseous mixture of chlorine and dioxide sulfur. Sulfur content of CSM determined by element analysis is used as a reference for the quantitative determination of the degree of chlorosulfonation. The effects of reaction temperature, effective gaseous mixture concentration, particle size of CPE, and the ratio of chlorine to dioxide sulfur on chlorosulfonation are investigated. The results indicate that with the increment of reaction temperature within the range of from 30 to 50°C, the rate of chlorosulfonation during the later reaction period (15–25 min) is markedly increased and the prepared CSM has higher sulfur content. It was also found that the rate of chlorosulfonation increases with the effective gaseous mixture concentration, and that the ratio of chlorine to dioxide sulfur is preferably 1 : 1. It was proven that HCl, by-product of the chlorosulfonation, can accelerate the rate of chlorosulfonation when the volume concentration of HCl is lower than 40%, and that the presence of oxide results in higher sulfur content of the resultant CSM. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3582–3588, 2001

Key words: chlorosulfonated polyethylene; chlorinated polyethylene; chlorosulfonation; gas-solid method

INTRODUCTION

CSM is a widely used special synthesized rubber, which is, in general, manufactured commercially by the solution method. The gas-solid method is a novel way to prepare CSM. Compared to the conventional solution procedure it is inexpensive, and no environment pollution as no solvent is used. There are many patents available on preparation of CSM by the gas-solid method using polyethylene (PE) and a gaseous mixture of chlorine and sulfur dioxide.^{1–4}

Chlorosulfonation of PE by the gas-solid method is not a problem-free procedure. The crys-

tallinity of the starting material PE is so high that chlorosulfonation cannot be carried out successfully unless the reaction temperature reaches the melting point of PE. This chlorosulfonation temperature will lead to agglomeration of PE particles, which may prevent the progress of reaction. Noeske et al. disclosed a process for chlorosulfonation of PE in a fluidized bed within a temperature range of 40 to 80°C.¹ However, the chlorosulfonated materials prepared in accordance with the procedure are generally not amorphous materials due to sufficient residual crystallinity. Another method developed by Blanchard et al. consisted of reacting amorphous CPE with a gaseous mixture of chlorine and sulfur dioxide in a fluidized bed.⁵ The crystallinity of amorphous CPE is less than 15 wt %, and chlorination does

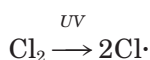
Correspondence to: R. Zhao.

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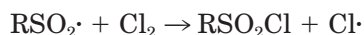
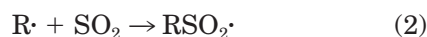
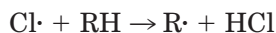
not occur in chlorosulfonation, so the reaction can be carried out at lower temperature than using PE. The reaction was carried out at a temperature range of 25 to 100°C, for a period of 2 h or less. This process is more attractive than using PE as the starting material, but the reaction has not been comprehensively studied. The chemical equation of the chlorosulfonation of CPE is shown as eq. (1). Additionally, the chlorosulfonation of CPE takes place via a free radical chain mechanism as shown in the sequence of eq. (2).



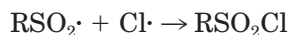
Initiation



Propagation



Termination



It has been proven that in amorphous CPE with relatively random chlorine distribution, a fraction of the chlorinated units CHCl can crystallize with the CH₂ units, forming a certain degree of cocrystallinity where the CHCl groups are treated as defects.⁶⁻⁸ Due to such defects the cocrystalline has lower melting point than perfect crystalline of CH₂ segments. If and to what extent the cocrystalline affects the chlorosulfonation will be taken into account in this article. When the chlorosulfonation was carried out in a fluidized bed, either using PE or CPE as the starting material, because the reaction gaseous mixture was not circulated in the bed, the reaction gaseous mixture contain no HCl. The effect of HCl, by-product of the chlorosulfonation, on this reaction was always neglected. Moreover, the chlorosulfonation takes place via a free radical mechanism. Oxygen is an effective inhibitor for reactive free radical. So the presence of oxygen will affect the reaction. In the present work, CSM was prepared using CPE by

the gas-solid method in a tank reactor. The effects of reaction temperature, concentration of reaction gaseous mixture, the ratio of chlorine to sulfur dioxide, concentration of HCl, and concentration of oxygen on chlorosulfonation were comprehensively investigated.

EXPERIMENTAL

Materials

Chlorinated polyethylene (CPE) was supplied by Wei Fang YaXing Chemical Company (CPE135A), which is synthesized in suspension from high-density polyethylene with weight-average molecular weight of approximate 220,000. Chlorine content determined by element analysis is 35.4 wt %. The particle size of CPE is in the range of 50 to 315 μm.

Chlorosulfonation Procedures

Chlorosulfonation was carried out by the gas-solid method in a three-neck reaction flask (Pyrex) using CPE and a gaseous mixture of chlorine, sulfur dioxide, and nitrogen, initiated by ultraviolet light. The ultraviolet source is a high-pressure mercury lamp (500 W) with a wave length suitable for producing chlorine free radicals manufactured by the ShangHai YaMing Bulb Company. In the reaction, chlorine absorbs the impinging light, producing chlorine radicals Cl· thereby initiating the chlorosulfonation as shown in the sequence of eq. (2).

In a typical reaction the reaction conditions and the reaction procedure are described as follows. The ratio of the three gases was Cl₂ : SO₂ : N₂ = 1 : 1 : 1.6, so the concentration of the effective reaction gaseous mixture of chlorine and sulfur dioxide was 56 vol %. The millitre equivalent of chlorine to 1 g CPE was 40 mL at 30°C. Twenty grams of CPE were placed in the reactor, then the reaction system was pumped vacuum. Cl₂, SO₂, and N₂ preheated to reaction temperature were simultaneously fed into the reaction system. The reactor was placed in a constant-temperature water bath. The reaction was carried out under ultraviolet radiation. The solid CPE particles were stirred with a magnetic stirrer and well dispersed on the bottom of the reactor. The pressure of the reaction system kept equal to atmospheric pressure, while decreasing in the reaction process due to the consuming of chlorine and sulfur dioxide.

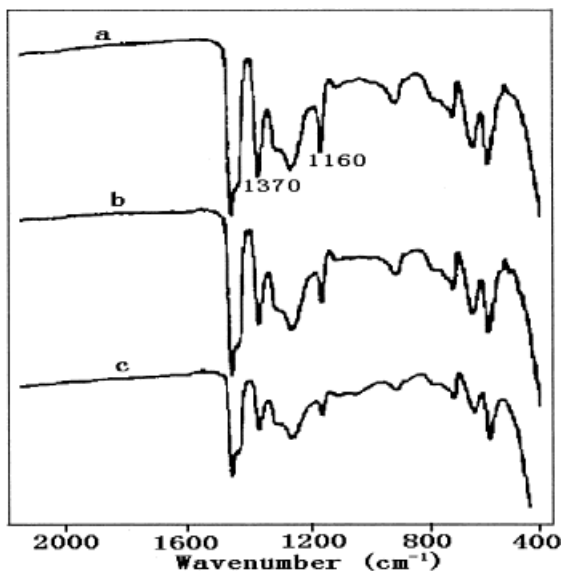


Figure 1 IR spectra of CSM of various sulfur contents. Sulfur content: (a) 0.94 wt %; (b) 0.51%; (c) 0.26%.

After a desired period, the UV light was discontinued. The chlorosulfonation was stopped by blowing a stream of dry nitrogen through the reaction system. The residual gaseous mixture blown off by nitrogen was absorbed by 15 wt % $\text{Na}_2\text{S}_2\text{O}_3$ solution and 10 wt % NaOH solution.

Characterization

Infrared (IR) spectra were recorded on a Nicolet Magna-IR550 spectrophotometer. Chlorine content of CPE and Sulfur content of CSM were determined by element analysis using a Dionex-2010I Ion Chromatograph. The melting curve was obtained by a Universal V2.3C TA instrument with $10^\circ\text{C}/\text{min}$ heating rate in nitrogen.

RESULTS AND DISCUSSION

Fourier Transform (FTIR) Spectra

Three CSM samples differing in sulfur content were prepared using CPE135A and the gaseous mixture of chlorine and sulfur dioxide through different reaction time in a tank reactor. IR spectra of three CSM samples cast from toluene solutions are shown in Figure 1. The spectrum of CSM shows two absorption bands at 1160 and 1370 cm^{-1} , which are characteristic peaks of $-\text{SO}_2\text{Cl}$ present in CSM. It is apparent from Figure 1 that with the increasing of sulfur content of CSM the

two characteristic peaks intensity increases. In our studies sulfur content is used as a reference for the quantitative determination of $-\text{SO}_2\text{Cl}$.

Effect of Reaction Temperature

Figure 2 shows the effect of reaction temperature on chlorosulfonation. From the results we can see that a time period of 5 min is sufficient to attain the desired sulfur content, and that at each temperature sulfur content exhibits a sharp increase followed by a gradual leveling off beginning at 5 min. When the reaction time is short (less than 5 min), a slight increase of the rate of chlorosulfonation with increasing temperature is seen. However, during the later stage (15–40 min) the effect of temperature is enhanced, resulting in a significant increase of sulfur content at 40 or 50°C comparing to a plateau region at 30°C . To avoid undesirable agglomeration of polymer particles, the temperature employed in the chlorosulfonation is preferred lower than 60°C . Chlorosulfonation of particles of CPE with chlorine and sulfur dioxide is a gas-solid phase reaction, including gas diffusion and inherent reaction. When reaction temperature is raised, both the rates of gas diffusion and inherent reaction speed are increased so that the rate of chlorosulfonation is increased. In addition, the morphology of CPE also plays an important role in affecting chlorosulfonation. The melting behavior of CPE135A characterized by DSC is shown in Figure 3. The DSC run performed on CPE135A does not evidence any residual crystalline melting transition, whereas it shows two endothermic peaks at 30 and 58°C , and the enthalpy values are 5.5 and 3.4 J/g, respectively.

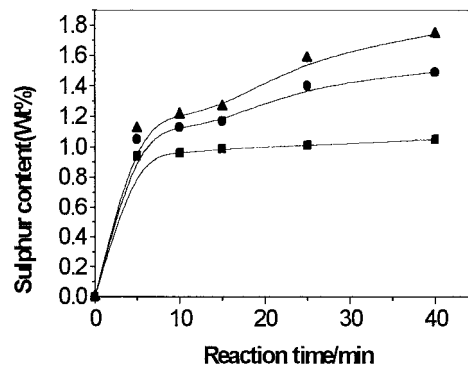


Figure 2 Effect of reaction temperature on chlorosulfonation. Reaction gaseous mixture concentration: 56 vol %. Reaction temperature (■) 30°C ; (●) 40°C ; (▲) 50°C .

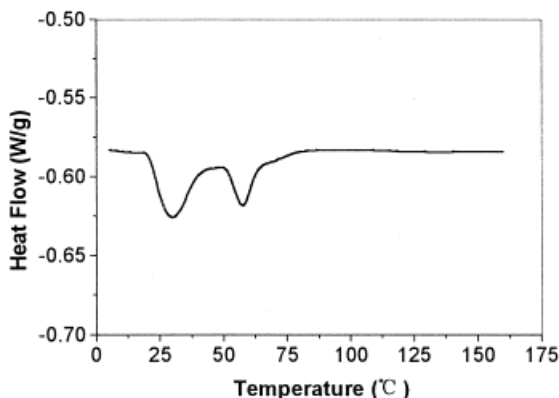


Figure 3 DSC thermogram of CPE135A.

The same phenomenon was observed with solution chlorinated polyethylene containing 32% chlorine by B.H. Chang. Evidence that part of $-\text{CHCl}-$ groups in CPE can cocrystallize with the $-\text{CH}_2-$ groups has been reported in various literature.⁶⁻⁸ Two endotherms observed in the DSC thermogram result from an orthorhombic-to-hexagonal phase transition of the cocrystalline at the lower temperature and the melting point of the hexagonal form at the higher temperature.⁸ The cocrystalline is inaccessible during the course of chlorosulfonation at 30°C. However, it may become accessible during the later stage of the reaction at 40 and 50°C due to part or total of the cocrystalline melting, which is responsible for the abnormal increase of the reaction rate during the later stage of the reaction.

Effect of Particle Size

The size of solid particles may affect the rate of the gas-solid reaction with respect to the interdiffusion of the gaseous reactant in the solid particles. The starting material CPE consists of a wide-size distribution of solid particles. To study the effect of particle size on chlorosulfonation, four size distributions of particles were obtained by screening. Figure 4 shows the significant effect of particle size on chlorosulfonation. It is apparent that with the decreasing of the particle size the rate of chlorosulfonation increases, and that when the particle size as small as 104–147 μm the effect is no longer significant.

This result indicates that the interdiffusion of gaseous reactant in the particles plays an important role in determining the rate of chlorosulfonation. With the decreasing of the particle size the specific surface area increases, which results in a

larger reaction area of chlorosulfonation. At the same time the diffusion resistance decreases, as the distance from the particle surface to the core is shorter. So the reaction rate is increased. Because the particle of CPE is porous, the interdiffusion is relatively easy. When the particle size is so small, the step of the interdiffusion of gaseous reactant is too quick to affect the rate of chlorosulfonation.

Effects of the Concentration of Effective Reaction Gaseous Mixture and the Ratio of Chlorine to Sulfur Dioxide

There are four gases in the reaction system including chlorine and sulfur dioxide as effective reaction gases, nitrogen as inert gas, and small amount of HCl produced in chlorosulfonation. The ratio of chlorine to sulfur dioxide was fixed at 1 : 1, the concentration of effective reaction was changed. The effect of the concentration of effective gaseous mixture of chlorine and sulfur dioxide on chlorosulfonation is shown in Figure 5, from which we can see that with the concentration increases the rate of chlorosulfonation increases significantly, and that the resultant CSM has higher sulfur content. When the total concentration of chlorine and sulfur dioxide is higher than 60 vol %, the effect is no longer noticeable.

The effect of the ratio of chlorine to sulfur dioxide on chlorosulfonation is shown in Table I. The data presented in Table I clearly shows that the most rapid rate of chlorosulfonation was obtained at the ratio of 1 : 1, and that with the increasing of the difference in concentration of

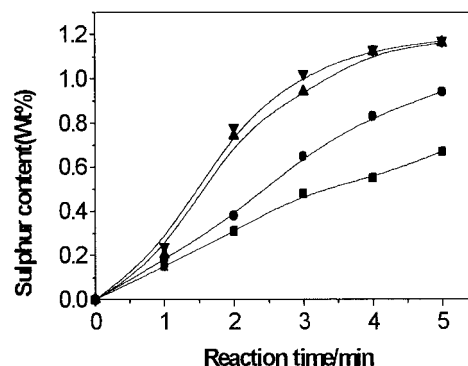


Figure 4 Effect of diameter of CPE particles on chlorosulfonation. Reaction temperature: 30°C; effective reaction gas concentration: 56 vol %; diameter of CPE particle: (■) 417–833 μm ; (●) 147–417 μm ; (▲) 104–147 μm ; (▼) 50–104 μm .

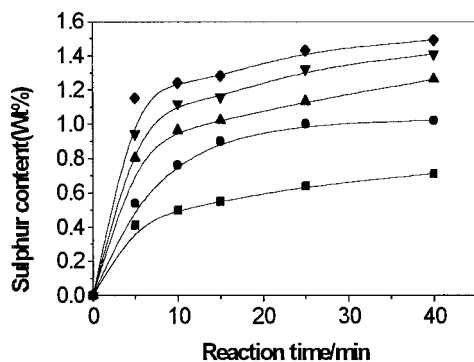


Figure 5 Effect of effective reaction gas concentration of effective on chlorosulfonation. Reaction temperature: 30°C; effective reaction gas concentration: (■) 28 vol %; (●) 40%; (▲) 50%; (▼) 60%.

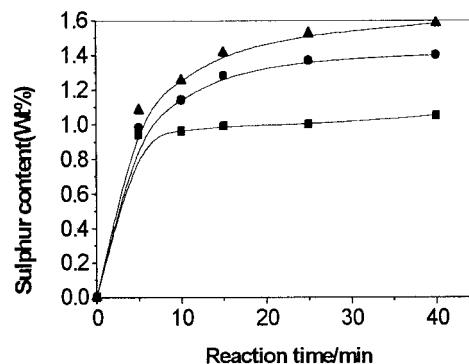


Figure 6 Effect of concentration of HCl on chlorosulfonation. Reaction temperature: 30°C; effective reaction gas concentration: 56 vol %; concentration of HCl: (■) no HCl was fed in; (●) 15 vol %; (▲) 20%.

chlorine and sulfur dioxide, the rate is decreased. Similar results were reported by Robert et al.⁵

Effect of HCl

HCl is produced in the process of chlorosulfonation, and the concentration of HCl was increased progressively in the course of the reaction. Dry HCl was fed into the reaction system to study the effect of HCl on the chlorosulfonation. This effect is plotted in Figures 6 and 7. Figure 6 shows the marked effect that HCl has upon chlorosulfonation and the final product. Contrary to what might otherwise be expected, with the concentration of HCl increases the reaction rate is increased and the final product has higher sulfur content. It is shown in Figure 7 that with the increasing of HCl concentration, when it is lower than 20% the enhancing effect on chlorosulfonation is increased; however, when it exceeds 20% the effect is decreased. When the concentration of

HCl is higher than 40%, HCl has a negative effect on chlorosulfonation, resulting in lower sulfur content of the final product.

Dehydrochlorination of CPE under the conditions such as heating and radiation by ultraviolet is well known. In the literature a free radical mechanism has been suggested for the dehydrochlorination of CPE.^{9,10} It was also reported that HCl can accelerate the rate of dehydrochlorination via free radical mechanism.¹¹ The free radical mechanism dehydrochlorination takes place in the chlorosulfonation system under ultraviolet as shown in the sequence of eq. (3).

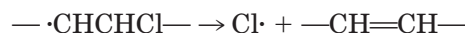
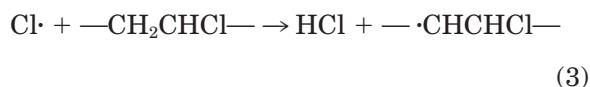
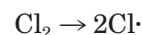


Table I Effect of Ratio of Chlorine to Dioxide Sulfur on Chlorosulfonation

Reaction Time (min)	Sulfur Content				
	5	10	15	25	40
Cl ₂ : SO ₂					
3 : 1	0.72	0.75	0.80	1.09	1.16
2 : 1	0.73	0.95	1.00	1.22	1.60
1 : 1	1.21	1.29	1.34	1.35	1.59
1 : 2	0.68	0.85	1.06	1.19	1.47
1 : 3	0.66	0.94	0.98	1.01	1.25

Reaction temperature: 30°C.
Effective reaction gas concentration: 100%.

To explain the positive effect of HCl on chlorosulfonation, it is considered that the increasing of HCl concentration promotes the dehydrochlorination via the free radical mechanism, thus increasing the concentration of the free radical $\text{—}\cdot\text{CHCHCl—}$ as the reactive point of chlorosulfonation. On the other side, as the chlorosulfonation is the gas-solid phase reaction, gases diffusion including the process of HCl produced inside the particles of CPE diffusion towards the outside affects the reaction rate. When the concentration of HCl increases, the rate of the diffusion of the produced HCl decreases, which reduces the reaction rate.

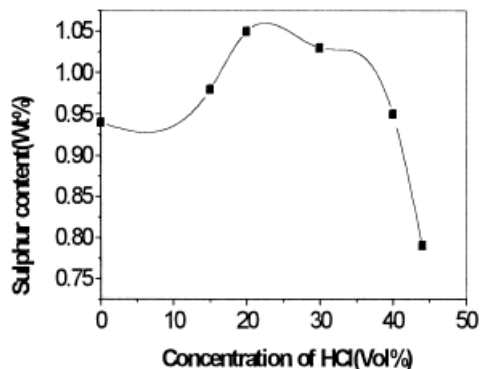


Figure 7 Effect of concentration of HCl on sulfur content of CSM. Reaction temperature: 30°C; effective reaction gas concentration: 56 vol %; reaction time: 5 min.

Both the two sides together affect the reaction, leading to the results shown in Figures 4 and 5. When the concentration of HCl < 40%, the positive effect dominates. The negative effect surpasses the positive effect as HCl concentration > 40%. At the level of 20%, the rate of chlorosulfonation reaches the maximum.

Effect of Oxygen

Oxygen is an effective inhibitor for reactive free radical. The chlorosulfonation proceeds via the free radical mechanism, so the presence of oxygen affects the reaction. It was claimed that the concentration of oxygen should be controlled at the level of lower than 100 ppm.⁵ The concentration of oxygen in the reaction system in our study was controlled at lower than 300 ppm by vacuum pumping. To investigate the effect of oxygen on

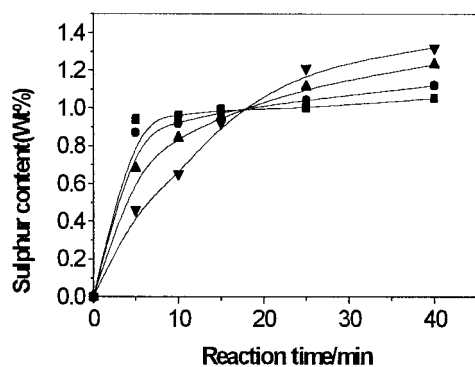


Figure 8 Effect of oxide concentration on chlorosulfonation. Reaction temperature: 30°C; effective reaction gas concentration: 56 vol %; concentration of oxygen: (\blacksquare) < 300 ppm; (\bullet) 0.2 vol %; (\blacktriangle) 0.5%; (\blacktriangledown) 1.0%.

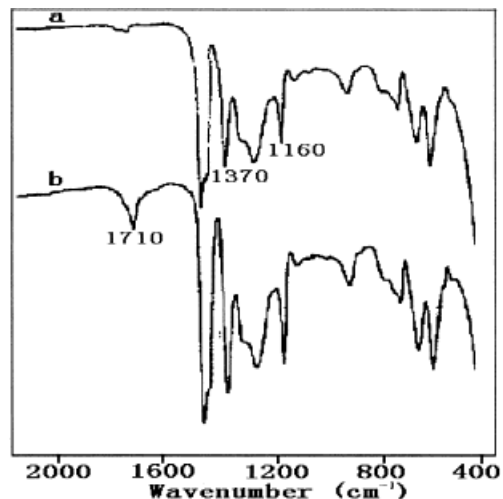


Figure 9 IR spectra of CSM synthesized in the presence of oxide with different concentrations. Reaction temperature: 30°C; effective reaction gas concentration: 56 vol %; reaction time: 40 min. Concentration of oxide: (a) < 300 ppm; (b) 1.0%; sulfur content: (a) 1.05 wt %; (b) 1.32%.

chlorosulfonation, oxygen was fed into the reaction system. The result is shown in Figure 8. It is seen that with increasing the oxygen concentration, initially the reaction rate shows slight decreases, but after 20 min the reaction rate is increased significantly and results in higher sulfur content of the final product. This result indicates that oxygen has no dramatic effect on the chlorosulfonation.

Infrared spectra of two CSM products prepared at different level of oxygen concentration through a reaction time of 40 min are shown in Figure 9. The most obvious difference between the two samples is the appearance of the carbonyl groups at 1710 cm^{-1} of Sample b prepared at 1 vol % level of oxygen. Figure 7 also shows that the intensities of the absorption peaks at 1160 and 1370 cm^{-1} of Sample b are stronger than Sample a, in accord with the sulfur content determination.

With respect to the effect of oxygen on the chlorosulfonation of CPE, a tentative explanation was presented. It is well known that oxygen is an effective inhibitor for reactive free radicals.¹² The chlorosulfonation takes place via a free radical mechanism, as shown in eq. (2). During the chlorosulfonation process, oxygen can react with chain radicals of CPE producing peroxy radicals, as shown in eq. (4).



The peroxy radical $\text{ROO}\cdot$ is too inactive to propagate the chlorosulfonation. At the same time, the concentration of the reactive chain radical $\text{R}\cdot$ is decreased. As a result, the reaction rate of the chlorosulfonation during the earlier stage decreases to some extent with increasing oxygen concentration.

With the progress of chlorosulfonation, the concentration of oxygen decreases. The oxidation of CPE results in the formation of carbonyl groups along the CPE chain, evidenced by the IR spectra (Fig. 9). It was suggested that the higher reaction rate during the later stage of the chlorosulfonation probably is associated with the formation of carbonyl groups in the CPE. The chlorine distribution in the CPE exploited in this work is not virtually homogenous, evidenced by the NMR analysis in the previous work.¹³ A fraction of segments with fewer chlorine atoms arrange in an intimate way. In consideration of the steric hindrance effect of the bulky groups $\text{CH}-\text{Cl}$, these segments are prone to chlorosulfonation. However, the gas permeability of the phase composed of these segments is poor. The formation of carbonyl groups can effectively expand the distance among these segments, thus enhancing the gas permeability of the solid particles and thereby promoting the chlorosulfonation during later reaction stage. For the same reason the formation of carbonyl groups makes more segments accessible to chlorosulfonation, which is attributable to the higher sulfur content of the final product.

CONCLUSION

Chlorosulfonated polyethylene was prepared by gas-solid method in a tank reactor. Under the conditions (a) the millilitre equivalent of chlorine to 1 g CPE of 40 mL, (b) the ratio of chlorine to sulfur dioxide of 1 : 1, (c) the concentration of the gaseous mixture of chlorine and sulfur dioxide of 56 vol % CSM with desired sulfur content was obtained in a reaction time of 5 min at 30°C. The reaction was no longer extended at this temperature when time was long up to 40 min. However,

sulfur content was significantly increased during the later stage of the reaction at 40 or 50°C due to the melting of the cocrystalline of CPE. Smaller particle size of CPE is favorable to the chlorosulfonation. The preferable particle size is about 100 μm . With increasing concentration of the reaction gaseous mixture the rate of chlorosulfonation increases. When the ratio of chlorine to sulfur dioxide is 1 : 1, the reaction rate is the highest. HCl with the concentration lower than 40% can accelerate the reaction because the presence of HCl is beneficial to increase the concentration of the free radical chain of CPE. The chlorosulfonation is insensitive to oxygen. When the concentration of oxygen is lower than 300 ppm, the reaction is not affected. With increasing oxygen concentration the initial reaction rate is decreased slightly, however, the reaction rate during the later stage is markedly increased, and the resultant polymer has higher sulfur content.

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