

The Preparation and Analysis of Chlorinated Ethylene Vinyl Acetate Copolymer as Coating Film in Gas-Solid Phase

Zhao Jing, Lijuan Liu, Shukai Zhang, Jiruo Zhao, Ying Feng

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology, Qingdao, People's Republic of China

Correspondence to: J. Zhao (E-mail: jiruo.zhao@qust.edu.cn)

ABSTRACT: In this article, the feasibility of preparing chlorinated ethylene vinyl acetate copolymer (CEVA) in gas–solid phase is investigated. Furthermore, the structure of the chlorination product and its performance as a coating material are also analyzed. Both the molecular structure and crystallinity of the product are well studied with various characterization methods, including $^1\text{H-NMR}$, Fourier transform infrared, gel permeation chromatography, differential scanning calorimeter, and so forth. The results show that the chlorination of EVA in gas–solid phase is feasible and the chlorine content of CEVA can be made over 60%. It is also found that when the chlorine content is low, chlorination can easily occur in ethylene section but rarely happens in vinyl acetate section. Nevertheless, when the chlorine content of CEVA rises over 35%, $-\text{CH}$ in the vinyl acetate section is also found chlorinated. The removal of hydrogen chloride is induced during chlorination, producing double bonds in the main chain. Besides, the trace of $-\text{CCl}_2$ structure can also be found in the chain of CEVA. After chlorination, the crystallization will change and is negatively correlated with chlorine content. As the film forming material for coating, CEVA has its best performance with 50% chlorine content. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41093.

KEYWORDS: addition polymerization; applications; coatings

Received 27 February 2014; accepted 1 June 2014

DOI: 10.1002/app.41093

INTRODUCTION

In recent years, rapidly development of ethylene vinyl acetate copolymer (EVA) has been made because of its excellent properties and wide applications.^{1–5} EVA has different application depending on the vinyl acetate (VA) content. The VA content of commonly used EVA resin is from 5 to 40 %. As a kind of modified EVA with extended applicable area, chlorinated EVA (CEVA) was first studied in the 1980s and has been well investigated. The chlorine atoms are introduced into ethylene-VA molecules to improve liquidity and solubility in organic solvents, as well as the flame resistance.

There are three methods of preparing CEVA based on free radical polymerization: solution method, water phase suspension method, and solid phase method. The solution method is the first proposed method among the three, but is abandoned now for environment and health reasons. The water phase suspension method is the most widely used currently. However, the water phase suspension method⁶ has high requirements for equipment and the final product needs drying process. Although the continuous big wave drying method⁷ has been proposed to improve the traditional vacuum drying and therefore greatly reduce the

pollution to the environment, it is difficult to avoid the corrosion of the equipment by hydrogen chloride (HCl). In this article, we propose to prepare CEVA via gas–solid phase method, of which the advantage is that not only the pollution of organic solvents but also the corrosion of HCl can be avoided. This is because that the whole reaction goes dryly under normal pressure so that the HCl gas produced can be easily exhausted from the system and then absorbed by water within the tank made from polyvinyl chloride. In recent years, the research of CEVA mainly focus on the lower chlorine content CEVA (the content 12–40%, wt %) used for ink, rubber, and so forth.^{8,9} Meanwhile the study of high chlorine content (more than 48%) CEVA has been rarely seen in the literature.

The main goal of this article is to explore the feasibility, reaction mechanisms and process of preparing CEVA via gas–solid phase method. Particularly, the molecular structure of the product generated by the different stages throughout the process is studied in detail. As EVA molecule is composed of two kinds of sections of ethylene and VA, both the reaction process and product structure are more complicated than that of polythene and polypropylene chlorination. Therefore, the study of the reaction process and product structure is not only important

for EVA chlorination but also meaningful in a more general sense as fundamental work of preparing chlorinated polymers via gas–solid phase method. The increasing of chlorine content changes the location where the replace of hydrogen by chlorine occurs in the molecular chain, which leads to more complicated structure. Some research suggests that chlorination reaction occurs more easily in the acetate section of molecular chain of EVA. However, the process of chlorination occurring in vinyl acetate section still remains unclear. In this article, we especially carry out detailed discussion on this issue, and analyze the chlorination results in different locations in vinyl acetate section. Finally, the performance of CEVA as film forming material for coating is also investigated. In summary, the main contributions of this paper are as following:

1. The feasibility of preparing CEVA of different chlorine content by gas–solid phase method is demonstrated, especially that of chlorine content over 60%;
2. The structure of CEVA of different chlorine content prepared by gas–solid method is studied and analyzed in depth;
3. The application property of CEVA is also discussed according to preparation process as well as the analysis above.

EXPERIMENTAL

Material

EVA, with vinyl acetate content of 28%, particle size is 80 mesh and melt flow index of 150 g/min, was purchased from Jiangyin Lixiang, China. Chlorine gas (Cl_2) was purchased from Hai Jing Chemical Factory, Qing Dao, China. Xylene of analytical reagent grade was purchased from Tianjin BASF chemical trading. SiO_2 was purchased from Qingdao Dongyue Rhodia Chemical, China.

Preparation of CEVA

A round-bottom three-necked flask equipped with a vane stirrer, thermometer, and gas delivery tube was used as the reaction equipment.¹⁰ EVA powder (50 g) and 5 g SiO_2 was mixed in reaction flask for 30 min to ensure the blend uniform. The system was deaerated by chlorine gas (Cl_2) for 10 min at room temperature. The reaction temperature should be controlled below 50°C before the chlorine content go above 10%. In the next phase, as the released reaction heat accumulated, the temperature would rise rapidly, and should be controlled below 80°C before chlorine content reached 35%. Then, raise the temperature to 135°C gradually along with the chlorine content increasing to 45%. Finally, the temperature was maintained at around 135°C until the desired chlorine contents were attained. Hydrogen chloride (HCl) released from the reaction system was absorbed by a triangle flask with 200 mL water. An absorption bottle filled with water is connected to the outlet for exhaust gas and put on a balance. Thus, the amount of HCl can be measured by the weight increment of the bottle. To see more details of measuring method, please kindly refer to Ref. 10. As the desired chlorine content was reached, the chlorine gas was shut off to terminate reaction. The system was then cooled down to below 70°C, and chlorine gas in the reactor was pumped out by vacuum and then air was injected into the reactor. The vacuum and air influx operations were performed

alternately several times to ensure the residual chlorine cleaned out completely. The chlorine content of CEVA polymer can be calculated using the following equation:

$$\text{Cl}\%(\text{Wt}) = \frac{\Delta W + \frac{\Delta W}{34.5}}{W + \Delta W} \times 100\% \quad (1)$$

Where W represents the initial weight of EVA and ΔW represents increased weight of the reaction system.

Characterization

CEVA was purified by precipitation. The CEVA (1 g) was dissolved in xylene (60 mL) and subsequently precipitated in methanol (120 mL). The precipitate was filtered and dried in an oven at 50°C for 2 h. The process was repeated three times and the final product was dried in a vacuum oven at 60°C to constant weight.

Fourier Transform Infrared. The CEVA sample was molded into tablets with KBr powder. Fourier transform infrared (FTIR) spectra of samples were recorded with a FTS-135 IR spectrophotometer (Bio-Rad) in the wavenumber range 400–4000 cm^{-1} to characterize the molecular structure of samples.

$^1\text{H-NMR}$. The $^1\text{H-NMR}$ spectra were recorded using a Varian Unity-500 spectrometer in CDCl_3 , operating at 500 MHz. The contents of different structure units on the molecular chain of CEVA can be calculated using the following formula:

$$X_i = \frac{\frac{W_i}{M_i}}{\sum_{i=1}^n \frac{W_i}{M_i}} \quad (2)$$

Where X_i represents the contents of particular structure units in the molecular chain, W_i represents the integral area of the certain structure, M_i represents the number of hydrogen atoms in the particular structure, and n represents the number of all structure in macromolecule chain.

Gel Permeation Chromatography. The M_n and M_w of CEVA were measured using a WATERS 410 gel permeation chromatography (GPC). The column was calibrated by commercially available narrow distributed polystyrene. THF was used as the mobile phase and the flow rate was 1.00 mL/min.

Differential Scanning Calorimetry. The melting enthalpy of the CEVA was determined using a differential scanning calorimeter (DSC; TA Q100). The analysis was carried out at a constant heating rate of 10°C/min and also at a same cooling rate in the temperature range of –40 to 150°C under a nitrogen atmosphere. The crystallinity of CEVA is calculated using the following formula:

$$\text{crystallinity} = \frac{\Delta H^{*f}}{\Delta H^0f} \times 100\% \quad (3)$$

$\Delta H^0f = 228$ J/g is the melting heat of EVA (28% VA content) with 100% crystallinity, ΔH^{*f} is the melting heat of CEVA.

Property Test of Coating Film

We prepared a CEVA solution in which CEVA was dissolved in xylene to have the concentration of 20% (wt %). The base material is tin plate, of which surface was burnished by abrasive paper.

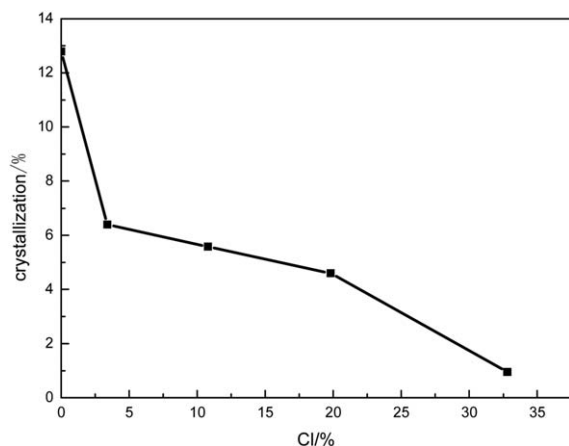


Figure 1. The relationship of chlorine content and crystallinity.

The methods of property test are shown as below:

Viscosity is measured following the standard GB 1723–1993. More specifically, the time of 100 mL solution flowing out from Tu-4 cup viscometer at 25°C is used to quantify the viscosity.

Adhesion is measured by scratch test following the standard GB1720-89. The length of scratch is 75 ± 5 mm. Mark 1,2,3,4,5,6,7 successively from edge of scratch. And check each part film. The area marked 1 were damaged is less than 30% the adhesion is 1level.

Impact strength is measured following the standard GB/T1732-93. The tested film sample is first immobilized horizontally at the bottom of the tester. Then, a falling hemispherical impact body is released to hit the sample, and the damaged condition of the film and base material is recorded. Tests are performed in order of increasing height and the lowest height making the film damaged indicates the impact strength. Measurements are repeated for three times.

Glossiness is measured following the standard GB/T 9754-2007. Gloss meter is used for measurement with correction ahead of the test.

Pencil hardness test is performed following the standard GB6739-86. Using the pencil with already-known hardness, the hardness of the sample is identified by the highest hardness that does not damage the sample.

RESULT AND DISCUSSION

The Chlorine Content and Crystallinity

There is crystallized part in molecular chain of EVA because of ethylene section. Crystallization has a great influence on the performance of the product. During the preparation of CEVA, the polar chlorine atom replaces a hydrogen atom, which destroys the regularity of the molecular chain and made the crystallization broken. The crystallinity is different as the chlorine content is different. The analysis of crystallization is conducted with DSC. The relationship between chlorine content and crystallinity is shown in Figure 1.

From Figure 1, we know that the crystallinity of CEVA decreased as the chlorine content increased. The change was

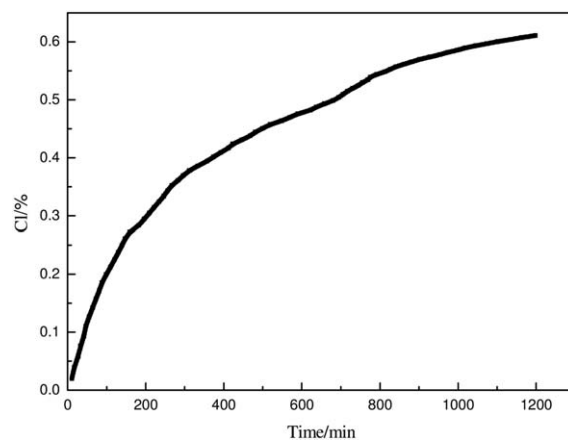


Figure 2. The relationship of The chlorine content of CEVA and time.

most obvious when chlorine content was less than 5%. It shows that the chlorination at the initial stage is more likely to affect crystallization of polymer.

The Feasibility of the Chlorination of EVA in Gas-Solid Phase

The chlorine content of CEVA raised over time as shown in Figure 2. From Figure 2, it can be seen that the chlorine content of CEVA raised gradually in the process and this shows that the chlorination of EVA in gas-solid phase is feasible. The chlorine content of CEVA can be made over 60%. To detect the —C—Cl bonds in the molecular chain, we study the CEVA by FTIR and $^1\text{H-NMR}$. From the FTIR and $^1\text{H-NMR}$ spectrum of CEVA, it can be found that there is chloride substituent in CEVA chain which will be demonstrated in details in the following structure characterization.

The Structure of CEVA

FTIR. Figure 3 shows the FTIR spectra of EVA and CEVA (Cl% is 50%). From the Figure 3, it can be seen that there are characteristic absorption peaks of —C—Cl stretching in the molecular chain. This observation suggests that EVA has been chlorinated successfully, but the location in the molecular chain where chlorination occurs still needs further study. We can take the

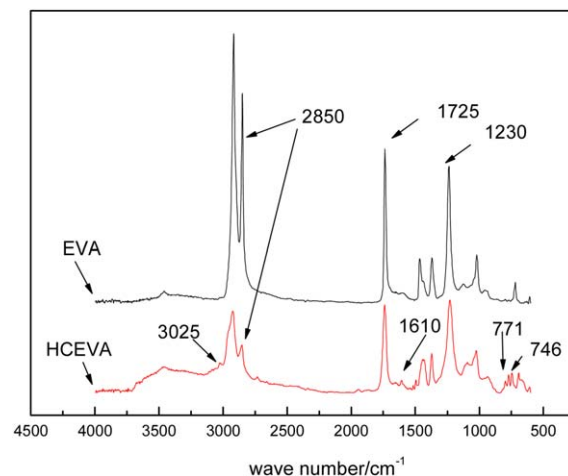


Figure 3. FTIR spectrum of EVA and CEVA (Cl% = 50%, wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Molecular Weight of EVA and CEVA

	EVA	CEVA
Mn	2.2×10^4	3.1×10^4
Mw	1.18×10^5	1.05×10^5
Mw/Mn	5.301	3.381

absorption peak (1723 cm^{-1}) of —C=O for reference because it was not changed during the chlorination reaction. In this way, it can be seen obviously from Figure 3 that the intensity of $\text{—CH}_2\text{—}$ peak at 2850 cm^{-1} of CEVA is weaker than that of EVA. We know the hydrogen atoms in $\text{—CH}_2\text{—}$ of the molecular chain are replaced by chlorine atoms, which represents that the chlorination is easier to react at $\text{—CH}_2\text{—}$ of the molecular chain. We also find that there are double bonds formed during the chlorination reaction. If the oxidative degradation occurred in the EVA molecular, —C=CH_2 would have been produced. There is no peak at 3080 cm^{-1} corresponding to —C=CH_2 in the Figure 3, so the double bonds of the molecular chain were produced by removal of HCl from the chain of CEVA. In summary, FTIR analysis demonstrates that the chlorination of EVA in gas–solid phase is feasible, and the double bonds are produced by the removal of HCl occurring in chlorination.

GPC. From the above analysis, we know that the chlorination reaction is accompanied by removal of HCl, which will produce double bonds in polymer chain. The double bonds in the main chain are easy to induce oxidative degradation and crosslinking reaction, which would affect the molecular weight and change the distribution of CEVA. Figure 4 and Table I show the molecular weight and distribution of EVA and CEVA (Cl% = 50%, wt %) by GPC spectra.

In contrast to EVA, the peak of CEVA shifts to left in Figure 4, indicating that the proportion of the high molecular weight segment becomes higher compared with that of EVA. From Table I, we know that for CEVA Mn is higher, Mw is lower, and distribution is narrower in comparison to that of EVA. These data

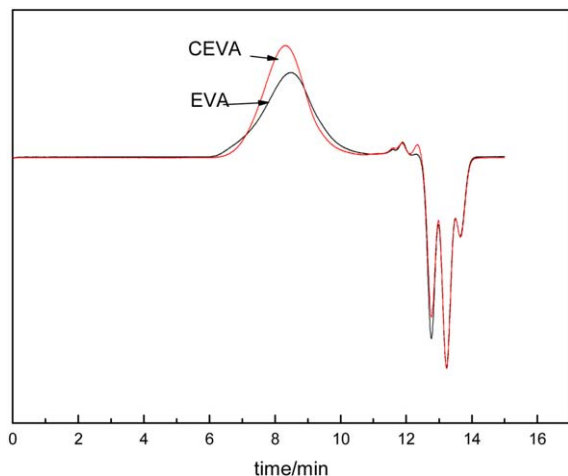


Figure 4. GPC spectrum of EVA and CEVA (Cl% = 50%, wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

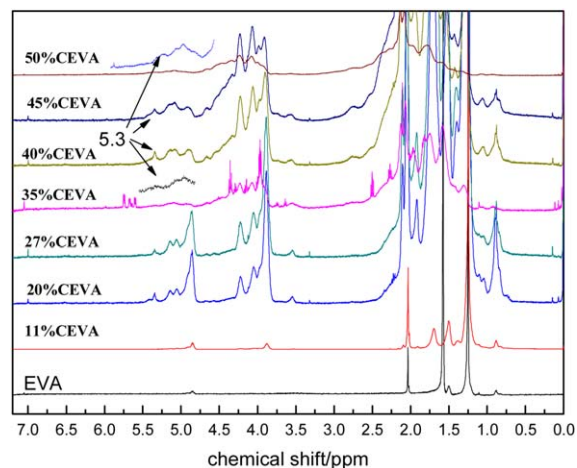


Figure 5. $^1\text{H-NMR}$ spectrum of different chlorine contents of CEVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

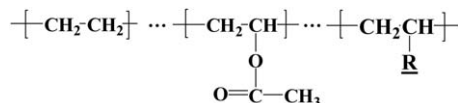
indicate that the double bonds on molecule chains formed by chlorination have no effect on molecular weight, that is, there is no oxidative degradation reaction in the molecular chain during the chlorination. Also, the narrower molecular weight distribution suggests there is no crosslinking reaction during the chlorination. The chlorination reaction first occurs in the low molecular weight section in the ethylene vinyl acetate of EVA, which narrows the molecular weight distribution.

According to the analysis above, it can be concluded that the double bonds in the molecular chain are produced by removal of HCl rather than the oxidative degradation reaction of the polymer containing double bond, and the removal of HCl did not cause crosslinking between molecular chains.

An Investigation of Factors Affecting Structure of CEVA

Effects of Chlorine Content on CEVA Structure. The number of double bonds in the polymer chain which greatly affects the molecular chain structure is related to the chlorine content of CEVA. It is a good method to study the structure of polymers by $^1\text{H-NMR}$. Figure 5 shows $^1\text{H-NMR}$ spectra of CEVA with different chlorine content. And the chemical shifts of various chemical groups are given in Table II.

In Figure 5, $^1\text{H-NMR}$ spectra of the samples with different chlorine content ranging from 11 to 50% are displayed respectively. The structure of EVA is as:



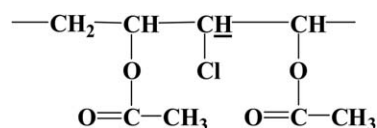
where R is the alkane introduced during the copolymerization process of ethylene and vinyl acetate. The intensity of chemical shift of CEVA at 1.25 ppm , which is assigned to $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$, decreased gradually with increasing of chlorine content compared to that of EVA. The new chemical shifts at 3.5 and 3.6 ppm are assigned to $\text{—CH}_2\text{Cl—}$ and the one at 3.9 ppm is assigned to —CHCl— . So, we infer that the chlorination reaction mainly occurred at $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$ in ethylene section.

Table II. The Chemical Shift Waves of Various Chemical Groups of EVA

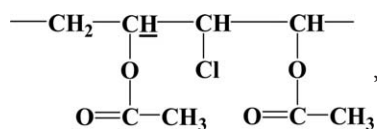
Chemical shift wave (ppm)	Chemical groups of EVA
0.88	$\left[\text{CH}_2\text{CH} \right]_{\text{R}}$
1.25	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$
1.5	$-\text{CH}_2-\text{CH}-$ O O=C-CH ₃
2.0	$-\text{COOCH}_3$
4.8	$-\text{CH}_2-\text{CH}-$ O O=C-CH ₃

We know that there is chlorination in the ethylene section now, but it needs further research about chlorination in vinyl acetate section. We measure the area rate of $-\text{CH}$ chemical shift to $-\text{CH}_3$ chemical shift in the vinyl acetate section to evaluate the chlorination result in vinyl acetate section. The area rate of CH/CH_3 of some samples in low chlorine content which is lower than 27% is shown in Table III.

According to the structure of EVA molecular chain, we know the theoretical rate of CH/CH_3 in vinyl acetate section is 1 : 3.00. As shown in Table IV, the actual rate of CH to CH_3 measured by $^1\text{H-NMR}$ in vinyl acetate section is 1 : 2.94, which fits the theory very well. Moreover, the rates of samples with chlorine content of 11, 20, and 27%, respectively, are almost the same. This suggests that hardly any CH or CH_3 is chlorinated in vinyl acetate section when the chlorine content of CEVA is low, for example, lower than 27%. At the same time, the chlorination of $-\text{CH}_2-$ in the vinyl acetate section is observed. There are chemical shifts appearing at 4.05–4.22 ppm, which are assigned to the structure



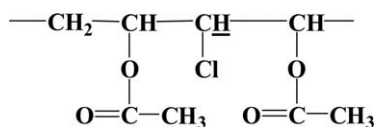
In addition, in the spectrum of 11, 20, 27% CEVA the new chemical shift at 5.0–5.1 ppm are assigned to



which makes the chemical shift of CH conjoint to CH_2 in vinyl acetate section move to lower fields from 4.8 ppm. So we know there is chlorination only at CH_2 in vinyl acetate section with the chlorine content lower than 27%.

To get more details about chlorination in EVA molecular chain, we further investigate on the samples with higher chlorine

content of 35, 40, and 45%. It has been already shown that there is chlorination at CH_2 in both ethylene and vinyl acetate sections with lower chlorine content. Then it is natural to ask how about the chlorination in higher chlorine content. Observing the chemical shift of CEVA with the chlorine content of 35, 40, and 45%, respectively, it can be seen that along with the rising of the chlorine content, the peak shifts from 4.0–4.2 ppm to 4.0–4.5 ppm with the increasing intensity and broadened width. It suggests that chlorination occurs more frequently at



making the chemical shift move from 4.05–4.22 ppm to the lower field 4.0–4.5 ppm. Similarly, the change can be also observed from the peak at 2.3–2.5 ppm assigned to $-\text{CH}_2\text{CHClCH}_2\text{CH}_2-$. Those results prove that there is more chlorination at CH_2 both in ethylene and vinyl acetate section with higher chlorine content than that with lower chlorine content.

To validate whether there is chlorination in the CH and CH_3 in the vinyl acetate section with higher chlorine content, we measure the area rate of CH to CH_3 again. The area rates of CH to CH_3 of 35, 40, and 45% CEVA are shown in Table III. The rates are lower than the ideal date (1 : 3). This result confirms that there is chlorination at CH in vinyl acetate section. But, how the chlorination of CH is affected by different chlorine content in vinyl acetate section is still a question as the data of CEVA with different chlorine content are very close. We also investigate the chlorination at CH_3 in the vinyl acetate section in high chlorine content. In other words, only a small amount of CH is chlorinated as the chlorine content rises.

In addition, there is new shift nearby 5.3 ppm in above CEVA, which can be attributed to the double bonds. This observation denies the occurrence of oxidative degradation, which agrees with the analysis in 3.2.2. Therefore, the appearance of double bonds should be attributed to the removal of hydrogen chloride. Once there are double bonds in the molecular chain, it is possible to produce allyl chlorine substituents, which has higher reactivity. Thereby, conjugated double bonds would be produced due to zipper effect. There is also new chemical shift at

Table III. The Area Rate of CH/CH_3 in Different Chlorine Content

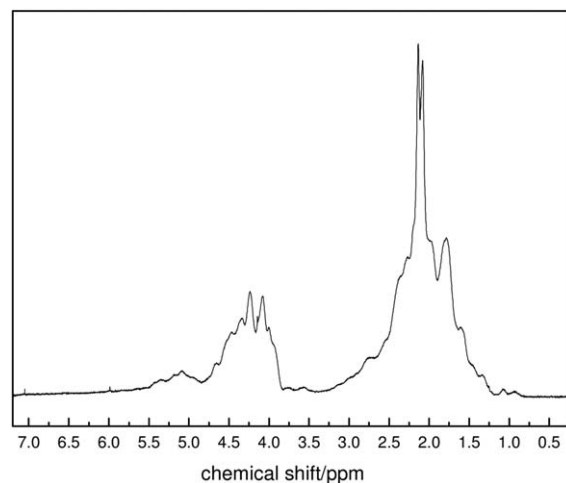
Sample (wt %)	Area rate of CH/CH_3
EVA	1 : 2.94
CEVA 11%	1 : 2.95
CEVA20%	1 : 2.99
CEVA 27%	1 : 3.00
CEVA 35%	1 : 3.56
CEVA40%	1 : 3.51
CEVA45%	1 : 3.48
50% CEVA	1 : 3.38

Table IV. The Chemical Shift of Various Chemical Groups in 50% CEVA

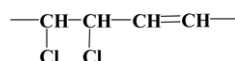
Chemical group	Chemical shift (ppm)	Relative content (%)
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	0.937-1.332	0.41834
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCl}-$	1.4-1.6	2.008032
$-\text{CH}_2\text{CH}_2\text{CHCl}-$	1.61-2.0	19.17252
$-\text{COOCH}_3$	2.03	5.279451
$-\text{CHClCH}_2\text{CHCl}-$	2.1-2.8	23.24716
$-\text{CH}_2\text{CH}_2\text{CCl}_2-$	2.8-3.4	2.388722
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	3.56	0.673527
$-\text{CH}_2\text{CHClCH}_2\text{Cl}$	3.77	0.870147
$-\text{CH}_2\text{CHClCH}_2\text{Cl}$	3.93	5.530455
$-\text{CH}_2\text{CH}(\text{O}=\text{C}-\text{CH}_3)\text{CH}(\text{Cl})-$	3.99-4.65	30.11212
$-\text{CH}(\text{O}=\text{C}-\text{CH}_3)\text{CH}(\text{Cl})-$	4.8-5.1	5.739625
$-\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-$	5.35	3.405288
$-\text{CCl}_2\text{CHCl}_2-$	5.99	1.154618

5.99 ppm, which indicates the structure $-\text{CCl}_2\text{CHCl}_2-$ meaning that a few $-\text{CCl}_2\text{CHCl}_2-$ structures will be formed when the chlorine content is high enough.

To make sure the chlorination at CH_3 in vinyl acetate section, we conduct further research about 50% CEVA in Figure 6. The area rate of CH to CH_3 in vinyl acetate section is 1 : 3.38 for 50% CEVA. Compared to CEVA with lower chlorine content (Table III), it is found that the area rate of CH/ CH_3 with 50% CEVA is greater than that of lower chlorine content CEVA. This result suggests that there is chlorination at CH_3 in vinyl acetate section with 50% CEVA. Besides, the chemical shifts of various chemical groups with 50% CEVA are given in Table IV. In contrast to 45% CEVA, the chemical shift at 5.6–5.8 ppm disappears. It means that conjugated double bonds are destroyed.

**Figure 6.** $^1\text{H-NMR}$ spectrum of 50% CEVA.

The reason is that the chlorine substituent groups become closer in molecular chain with the increasing chlorine content, so the chance of producing the structure



greatly increases and the removal of allyl chlorine and adjacent hydrogen become much rarer, and both contribute to the disappearance of conjugated double bonds.

Chlorination Reaction Temperature and Molecular Structure. Chlorination reaction temperature has a great influence on the structure of the product. The samples are prepared in two stages, the low temperature stage (below melting point) and the high temperature stage (above melting point). The time of low temperature stage, or equivalently the chlorine content achieved after the first stage, affects the structure significantly. The evenness of chlorine substituent group distribution on molecular chain depends on the chlorine content achieved after the low

Table V. Different Chlorine Content Distribution 50% CEVA Structural Sequence and Relative Content

Chemical group	Chemical shift (ppm)	Chlorine content in the first temperature stage (%)			
		29.8%	23.7%	18.6%	12.6%
$-\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-$	5.35	2.87	2.90	2.91	3.41
$-\text{CCl}_2\text{CHCl}_2-$	5.99	1.56	0.78	0.66	0.51
$-\text{CHCl}_2$	2.8-3.4	3.94	2.81	2.67	2.54

Table VI. The Property of CEVA with Different Chlorine Content

Chlorine content (%)	40.9	44.7	51.4	55.3	61.6
Viscosity (s)	40-42	38-39	37-39	36-37	36-37
Hardness (H)	B	B	B	B	B
Adhesion level	3	3	1	1	3
The impact strength (kg cm)	50	50	50	45	30
Glos (60°)%	91	86	80	76	69

Table VII. Various Properties of 50%wt CEVA Coating Film

Chlorine content in the first temperature stage	29.8%	23.7%	18.6%	12.6%
Viscosity (s)	35–37	36–38	37–38	38–40
Hardness (H)	B	B	H	H
The impact strength (kg cm)	50	50	50	50
Adhesion level	1	1	1	1
Gloss (60°)%	55	73	77	87

temperature stage. A series of 50% CEVA are prepared via the process in which they are reacted to different chlorine content in low temperature stage and the chemical shifts and relative content of all groups are shown in Table V. The chlorine content in first temperature stage is 29.8, 23.7, 18.6, and 12.6%, respectively.

From Table V, it is found that the content of the double bonds in 50% CEVA increases with the decreased chlorine content achieved in low temperature stage. The double bonds are sensitive to the temperature. When the reaction takes a long period in the high temperature stage, it is easier to produce double bond. It is also worth noting that reaction temperature has an influence on the content of structure $-\text{CHCl}_2$. The content of structure $-\text{CHCl}_2$ decreases as the final chlorine content in low temperature stage decreases. When the reaction temperature is above the melting point of EVA, the crystallization of EVA is damaged, leaving more sites to take part in reaction and therefore inhibiting the forming of $-\text{CCl}_2$ structure.

Table V shows that reaction temperature has an influence on the double bonds and partial chlorine structure of the molecular chain. And the evenness of chlorine substituent group distribution on molecular chain is that chlorine content is 12.6% in low temperature stage. When the chlorine content attained in the low temperature stage is 12.6%, the distribution of chlorine substituent group is relatively even.

The Properties of Coating

CEVA is very good film material for coating and it has many advantages, such as storage stability, light color retention, flexibility, and so forth. The polar groups in CEVA can improve the adhesion of the coating with metal, pigment dispersion and compatibility with other resin. The properties of CEVA prepared by gas-solid phase as film forming material are shown in Table VI.

The viscosity of CEVA drops slightly with the increasing chlorine content of CEVA, but the change is not obvious when the chlorine content varies from 40.9 to 61.6%. While the impact strength decreases due to the increasing of molecular chain polarity in high chlorine content and gloss decreases with the increasing of chlorine content. Generally speaking, 51.4% CEVA has the best property.

Reflecting the influence of molecular structure on the coating property, the results of test on the property of the samples are shown in Table VII.

Comparing the property of coating film with different chlorine content in low temperature stage, the hardness, and glossiness

of coating films increases with the reaction time in high temperature period prolonged. Comparing the properties of CEVA with different chlorine contents, it can be seen that both the hardness and glossiness are improved with the increasing time of high temperature reaction. More significant improvement to the glossiness can be achieved by means of *in situ* grafted chlorinated modification, which is beyond the scope of this article.

CONCLUSIONS

1. The chlorination of EVA in gas-solid phase is feasible and the chlorine content of CEVA can be made over 60%.
2. Chlorine is easy to react in ethylene section when the chlorine content of CEVA is relative low; Nevertheless, when the chlorine content of CEVA is over 35%, there would be chlorination in $-\text{CH}$ of the vinyl acetate section; when the chlorine content of CEVA is over 50%, there would be a tiny amount of chlorination of $-\text{CH}_3$ in the vinyl acetate section. The double bonds produced during chlorination are found when the chlorine content is higher than 35%, but when the chlorine content rises about 50%, the double bonds disappear.
3. When the reaction takes a long period in the high temperature stage it is easier to produce double bonds. The content of structure $-\text{CCl}_2$ drops with the decreased chlorine content in low temperature stage.
4. The greater the chlorine content is, the lower the crystallinity of CEVA is; the chlorination reaction at the initial stage is more likely to affect crystallization of polymer.
5. CEVA (51.4%) has the best property for coating.

ACKNOWLEDGMENTS

The project was supported by National Natural Science Foundation of China (51173090)

REFERENCES

1. Peeterbroeck, S.; Laoutid, F.; Swoboda, B.; Lopez-Cuesta, J.-M.; Moreau, N.; Nagy, J. B.; Alexandre, M.; Dubois, P. *Macromol. Rapid Commun.* **2007**, *28*, 260.
2. Peeterbroeck, S.; Laoutid, F.; Taulemesse, J. M.; Monteverde, F.; Lopez-Cuesta, J.-M.; Nagy, J. B.; Alexandre, M. and Dubois. *Adv. Funct. Mater.* **2007**, *17*, 2787.
3. Peeterbroeck, S.; Alexandre, M.; Nagy, J. B.; Moreau, N.; DestrE, A.; Monteverde, F. *Compos. Sci. Technol.* **2004**, *64*, 2317.

4. Zanetti, M.; Camino, G.; Thomann, R.; Mühlhaupt, R. *Polymer* **2001**, *42*, 4501.
5. Morlat-Therias, S.; Fanton, E.; Gardette, J.-L.; Peeterbroeck, S.; Alexandre, M.; Dubois, P. *Polym. Degrad. Stab.* **2007**, *92*, 1873.
6. Wang, L. Water phase suspension method for industrial production of chlorinated ethylene/vinyl acetate copolymer; China Patent, CN01121782.0. February 5, **2003**.
7. Chen, R. Continuous big wave drying methods to produce chlorinated EVA; China Patent, CN201210217011.6, October 3, **2012**.
8. Tsebrenko, I. A.; Pakhareno, V. A. *Fiber Chem.* **1999**, *1*, 23.
9. Pretsch, E.; Bühlmann, P.; Affolter, C. Structure Determination of Organic Compounds Tables of Spectral Data, 3rd ed.; Springer-Verlag publishers: Heidelberg, **2000**, p 11.
10. Wang, Y.; Liu, L.; Jing, Z.; et al. *RSC Adv.* **2014**, *4*, 1249.