Epoxylsilane Crosslinking of Rigid Poly(vinyl chloride)

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ABSTRACT: Crosslinking is an effective way to improve the qualities of poly(vinyl chloride). A crosslinking system consisting of R-glycidoxypropyltrimethoxysilane (KH560) has been first used to introduce crosslinking into rigid poly(vinyl chloride). Different thermal stabilizers (organotin, Ca/Zn stearate, and Ba/Zn stearate) as well as sodium bisulfite additive were tried to promote the grafting of epoxyl group and enhance the degree of crosslinking. FTIR spectra showed that grafting and crosslinking of KH560 with poly(vinyl chloride) could take place, and a gel content of 40% could be obtained when more than 10 phr epoxylsilanes were used in the condition of 2 : 1 (parts by weight) ratio of $BaSt_2/ZnSt_2$ and 1 : 1M ratio of $NaHSO_3/$KH560, while the premature crosslinking was avoided. Thermal properties had been studied. The results showed that the Vicat softening temperature of crosslinked PVC could be improved about $10°C$ when 5 phr epoxylsilane was added, and thermal degradation could be delayed with increase in gel content. Therefore, epoxylsilane-crosslinked PVC will have the potential for extensive applications. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3610–3616, 2007

Key words: crosslinked poly(vinyl chloride); gel content; epoxylsilane; thermal properties

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastics because of its valuable properties, such as low cost, high processability with additives, excellent chemical and fire resistance, etc. However, one of the main drawbacks to use is its low thermal stability and limited range of temperature, where it retains its quality. Crosslinking is an effective way to improve its quality.[1] Usually, crosslinking structure is obtained through exposing the PVC-containing crosslinking agents to a high-energy radiation source.[2,3] Nevertheless, this method is only suitable for thin-layer samples, since for thick-layer products, the surface region will decompose before significant crosslinking occurs in the interior. Peroxides have also been adopted to crosslink PVC in the presence of unsaturated monomers,[4–6] but thermal stability still needs to be improved since bad degradation of PVC occurs during the process of crosslinking.

Recently, the crosslinking of PVC by organofunctional silanes through reactive processing has aroused a great deal of interest, which involves two steps: the organofunctional silanes are initially grafted onto PVC chain by means of reactive extrusion, and then crosslinking structures consisting of Si—O—Si bridges are formed through combination of two or more pendant silane groups when immersing PVC in hot water. Till now, several types of silanes have been utilized to crosslink PVC.[7,8] Thereinto, aminosilane-crosslinked PVC has been extensively studied in the literatures,[9–16] but the aminosilane is prone to producing premature crosslinking and reduces thermal dimensional stability (Vicat softening temperature of crosslinked PVC is lower than raw). Kelner and Schatz[10,17] have crosslinked PVC successfully by grafting mercaptosilane without degrading PVC, but the grafting reaction takes place only in the presence of basic lead stabilizers or lead oxide. Moreover, it is less reactive than the aminosilane, and grafting reaction does not occur so readily. Because of this, Beltran, Hidalgo and coworkers[11,12] synthesized the sodium salt of mercaptosilane, an extremely effective crosslinking agent, from the corresponding thiol by reaction with sodium hydride in heptane. Nevertheless, lead stabilizers and sodium hydride are noxious. So, up to now, both aminosilane and mercaptosilane have not been commercially exploited to crosslink PVC.

It is well known that epoxy compounds are typical nonmetallic stabilizers for PVC, since epoxy group can be grafted onto PVC by creating ether-linkages with polymer backbone[18,19] to prevent the formation of longer polyene chain; moreover, it can also act as a good acceptor for the liberated hydrogen chloride.[19–21] R-glycidoxypropyltrimethoxysilane (KH560), one of the epoxy compounds, is not only expected as an effective stabilizer for PVC, but also a possible crosslinking agent through hydrolysis and condensation of the siloxane groups. So, in this article, KH560 was first used to modify PVC to obtain high-quality crosslinked

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materials. The aim of the present work is to study the feasibility of KH560 crosslinking of rigid PVC in the presence of suitable thermal stabilizers and additives, and investigate the influence of crosslinking on thermal properties.

EXPERIMENTAL

Materials

The PVC resin (WS-1000S) was purchased from Shanghai Chlor-Alkali Company (Shanghai, China). The processing aid acrylic ester (ACR-201) was supplied by Rohm and Hass. Wax Hoechst PE 190 and stearic acid (HSt) as lubricants were from Hoescht (Germany). The dibutyltin dilaurate (DBTDL) catalyst and sodium bisulfite (NaHSO$_3$) additive were from Shanghai Reagent Chemicals (Shanghai, China). The main stabilizers including calcium stearate (CaSt$_2$), barium stearate (BaSt$_2$), zinc stearate (ZnSt$_2$), and organotin were all of industrial grade. The crosslinking agent KH560 was from Nanjing Crompton Shuguang Organosilicon Specialties Co. (Nanjing, China), which is shown in the following:
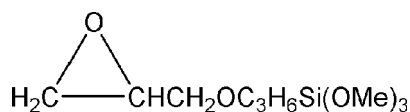
Preparation

The formulation used contained of 100 phr PVC, 3 phr thermal stabilizer, 4 phr ACR-201, 1 phr HSt, 0.4 phr wax Hoechst PE 190, 0.05 phr DBTDL, 0, 3, 5, 10, and 15 phr silane (in which phr is parts per hundred of resin).

Preblending was conducted by placing all the powder components in a laboratory scale Fielder mixer at 2000 rpm. Thermal stabilizer and silane were added when the temperature of the mixture reached 80°C. While the temperature of 120°C was reached, the mixture was dumped to a cooled chamber. Then the mixture was roll-milled at 160°C for 4 min. Irregular sheets obtained by milling were compressed into a 2-mm-thick plate at 180°C using 0.63 a semiautomatic molding press machine. Crosslinking was carried out by immersing compressed samples in water at 90°C for 3 h.

Characterization of the degree of crosslinking

The gel content was determined by Soxhlet extraction for 32 h in tetrahydrofuran (THF). The final residue was dried in a vacuum oven at 60°C for 24 h. The gel content, the percentage of THF-insoluble material, is expressed by the ratio of dried residue weight to original sample weight.

Infrared spectroscopy

The infrared spectra were obtained using a Nicolet 510M FTIR spectrometer in the wave number ranging from 500 to 4000 cm^{-1}. Samples were prepared by compression of the milled samples for 5 min using a pressure of 20 tons to produce sufficiently thin films (50-μm thick), and then thin films were immersed in water at 90°C for 3 h.

Thermogravimetric analysis

Measurements were made in a Setaram TGA Q500 V6.4 Build 193 thermobalance, with a nitrogen flow of 60 mL/min and a heating rate of 10°C/min from 40°C to 550°C. Both weight versus temperature and the derivative of weight versus temperature were recorded; any degradation process is reflected as a weight loss step in the first type of representation, while the same process may appear as a peak in the calculated weight loss derivative plot.

Heat resistance

Vicat softening temperature (VST) of prepared specimens (4-mm-thick) was determined using a heat distortion and Vicat softening point tester (XWB-300F, Hebei Chengde Testing Machine Co., Chengde, China) under a load of 10 ± 0.2 N at a heating rate of 50°C/h.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instrument model 2910 DSC module, at a heating rate of 10°C/min from 30°C to 150°C in nitrogen.

RESULTS AND DISCUSSION

The effect of thermal stabilizers on the grafting of epoxylsilane

Ideally, epoxy groups on the alkoxysilane will form a transition state with labile sites on the PVC chain to produce grafting. Subsequently, the methoxy groups will be hydrolyzed, and condensation reactions will take place to produce crosslinking as shown in Figure 1. During the processing of crosslinking, thermal stabilizers play an important role in stabilizing PVC and synergistic grafting of crosslinking agent. Therefore, it is necessary to choose high effective stabilizers. In our experiments, the grafting of KH560 on rigid PVC stabilized with three different thermal stabilizers, including Ca/Zn stearate, Ba/Zn stearate, and organotin, was studied. It can be seen from Table I that under the test conditions crosslinking of PVC can occur when Ca/Zn or
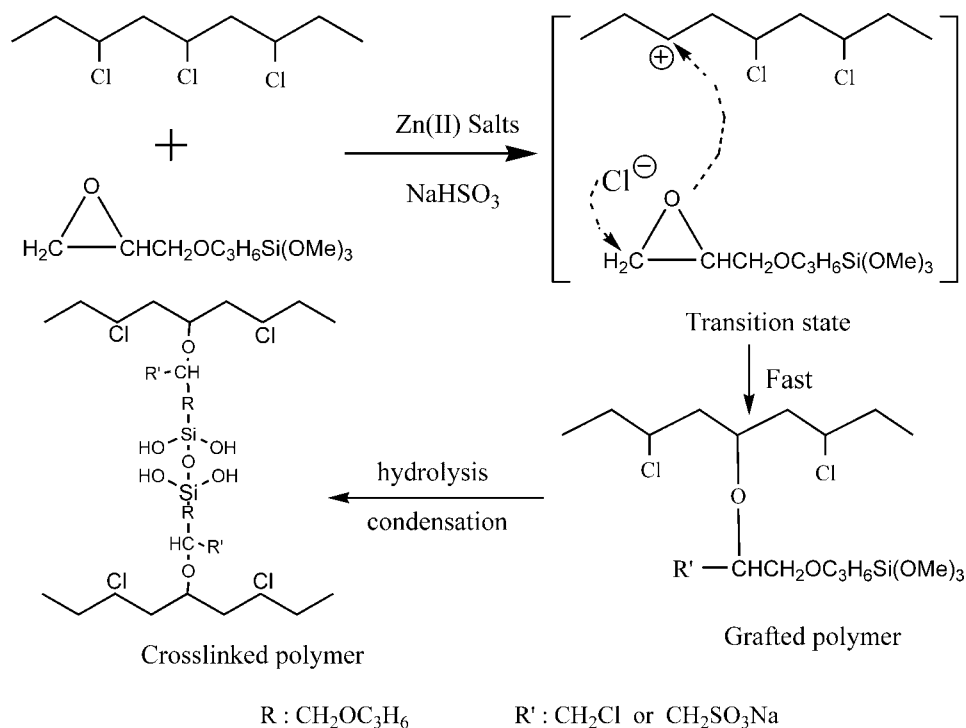
Figure 1 Mechanism of silane-grafting and water-crosslinking process.

Ba/Zn stearate are used, and premature crosslinking can be almost avoided. In addition, the gel content of samples with Ba/Zn stearate is higher than with Ca/Zn stearate. This is due to the formation of a Ca/Zn stearate complex when the two soaps are melted together in the processing conditions,[22] which is easy to substitute allylic chlorides.[23] So epoxy groups of KH560 can form a transition state only with a few tertiary chloride sites in the presence of Ca/Zn stearate complex. However, because Ba/Zn stearate cannot quickly form complex during processing, a transition state of epoxy groups of KH560 with most labile chlorine sites on PVC chain (e.g., allylic and tertiary chlorine sites) predominates over substitution of Ba/Zn stearate stabilizer. Consequently, grafting efficiency is increased and it gives a higher gel content after crosslinking.

Interestingly, the use of organotin stabilizer almost results in a gel content of zero before and after crosslinking process in hot water. This may relate to the strong substitution reactivity of organotin with labile chlorine, correspondingly, few labile chlorine sites on PVC chain are left for the grafting of epoxy groups.[1]

Therefore, Ba/Zn stearate stabilizer was adopted preferentially in our experiment, and how the ratios of Ba/Zn stearate influence the grafting of epoxylsilane will be further discussed in the next section.

## The effect of BaSt$_2$/ZnSt$_2$ ratios (parts by weight) on the grafting of epoxylsilane

To study the effect of BaSt$_2$/ZnSt$_2$ ratios, formulations with different stearate ratios (parts by weight) were prepared as Table II. It is found that the gel content of samples is maximal when a 2 : 1 ratio of BaSt$_2$/ZnSt$_2$ is employed, which indicates that this

TABLE I
Effect of the Thermal Stabilizer (3 phr) on the Gel Content, Before and After Crosslinking in PVC Grafted with 10 phr KH560

Type of stabilizer	Gel content (%)	
	Before	After
CaSt$_2$/ZnSt$_2$ = 2 : 1 (w)	2	15
BaSt$_2$/ZnSt$_2$ = 2 : 1 (w)	5	26
Organotin	0	0

TABLE II
Effect of the BaSt$_2$/ZnSt$_2$ Ratios (Parts by Weight) on the Gel Content, Before and After Crosslinking in PVC Grafted with 10 phr KH560

Stabilizer ratios	Gel content (%)	
	Before	After
BaSt$_2$/ZnSt$_2$ soap		
4 : 1	4	17
2 : 1	5	26
1 : 2	3	20
1 : 4	2	8
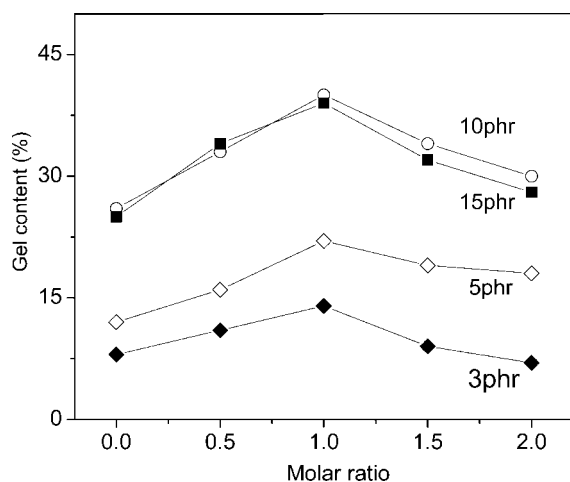
Figure 2 Effect of NaHSO$_3$/KH560M ratio and KH560 concentration on gel content.

ratio not only improves the thermal stability of PVC compound, but also promotes the grafting reaction for KH560. Especially, when BaSt$_2$/ZnSt$_2$ ratio reaches 1 : 4, a lower gel content will be obtained, which may result from the ''zinc burning'' occuring during processing and leading to grafting difficulty as the ZnSt$_2$ concentration increases.

The effect of NaHSO$_3$/KH560 molar ratio and KH560 amount on gel content

Silane is grafted on PVC chain through a process of nucleophilic substitution reaction; therefore, the nucleophilicity of silane will affect its grafting ability. The strong electronegativity of sulfur and nitrogen makes aminosilane and mercaptosilane grafted on PVC easily.[16,17] In terms of epoxy compounds, including epoxylsilane, their grafting was conducted through the formation of a transition state with the labile sites on PVC due to the weak nucleophilicity of epoxy groups.[20] So, the enhancement of epoxylsilane electronegativity will facilitate its grafting. Sodium bisulfite, a kind of weak acid strong alkali salt, can improve the electronegativity of oxygen on epoxy groups through the combination of sodium bisulfite with epoxy groups (Fig. 1). Figure 2 shows the variation of gel content with the molar ratio of NaHSO$_3$/KH560 and silane concentration. It can be seen that the gel content reaches maximum at 1 : 1M ratio for all the samples containing different silane concentration. This may be explained by accelerating the forming of transition states when sodium bisulfite is added during processing. The optimum matching is obtained when a 1 : 1M ratio of NaHSO$_3$/KH560 was employed. It is further apparent from Figure 2 that the gel content increases with increase in epoxylsilane concentration till 10 phr epox-

ylsilane; however, there is no obvious increase in gel content when epoxylsilane is more than 10 phr.

### The effect of crosslinking time on the degree of crosslinking

The crosslinking of KH560-grafted PVC is conducted in water, especially hot water. Generally, the hydrolysis and condensation of the crosslinking agent is very rapid, and so the diffusion of water in the sample will be a key factor to control the degree of crosslinking.[14] Figure 3 shows the evolution of the gel content with time, measured after immersion in hot water. It is observed that the gel content increases rapidly up to 37% within the first 2 h; however, an additional 1 h only yields a further 3% gel content. After 3 h, the samples were completely crosslinked with a maximum gel content of 40%. We know that the deeper the paths along diffusion direction, the lower the diffusion rate is, because of the rise of resistance to water diffusion. So, a duration of 3 h will be chosen as the optimum crosslinking time for all samples.

FTIR spectroscopy analysis

Figure 4 illustrates the comparison of the FTIR spectra of crosslinked samples with different silane concentrations. It can be concluded that the reactive processing of rigid PVC with KH560 leads to the corresponding crosslinked structure, which is clearly shown by the appearance of multiple bands between 1150 and 1170 cm^{-1} as a consequence of the formation of ether linkage (CH—O—CH).[24] This suggests that epoxy groups on KH560 have substituted allylic chlorines on PVC chain to produce grafting. A band at 1145 cm^{-1} [ν(CH$_2$—O—CH$_2$)] is associated with
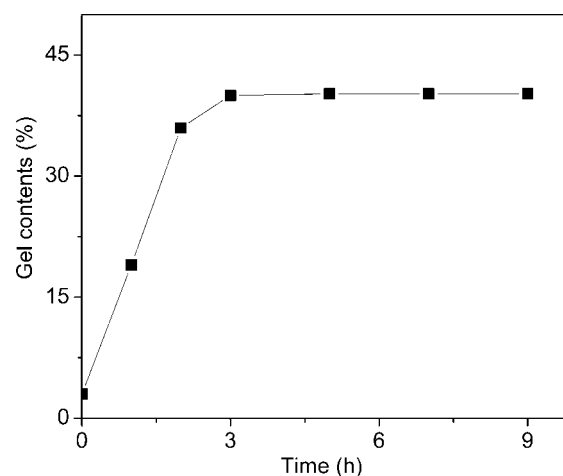
Figure 3 Effect of crosslinking time on gel content for samples crosslinked with 10 phr KH560 in water at 90°C.
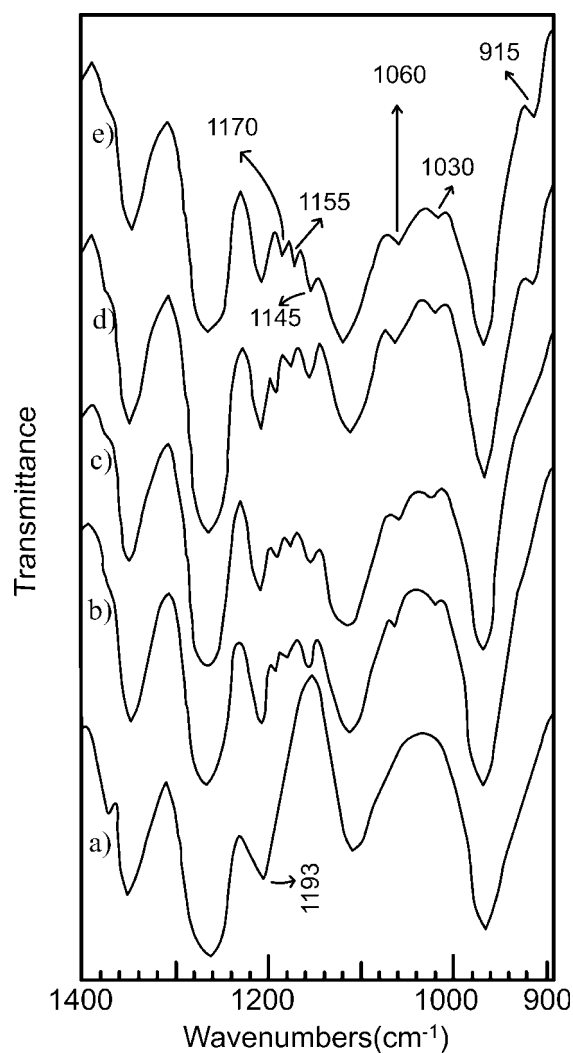
Figure 4 Infrared spectrum of crosslinked samples with various silane concentrations. (a) 0 phr; (b) 3 phr; (c) 5 phr; (d) 10 phr; (e) 15 phr.
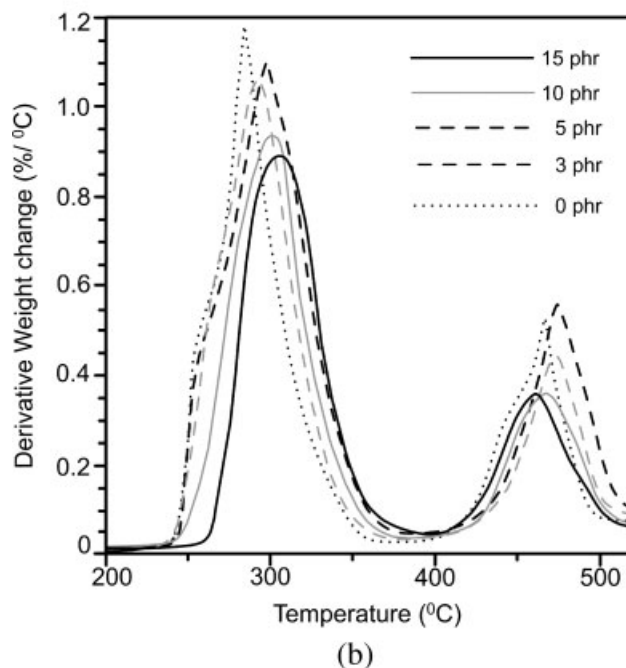
temperature for crosslinked samples with different concentrations of crosslinking agent at a heating rate of 10°C/min. Two successive weight losses can be seen. The first step (observed as a peak in the weight loss derivative trace) at around 290°C is associated with the dehydrochlorination of PVC, while the
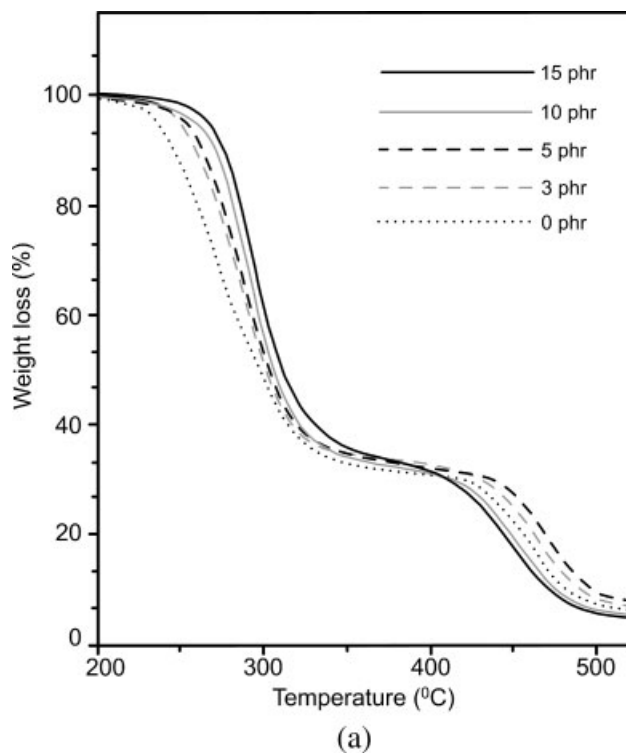
the ether linkage stretching of KH560. Although the tertiary chlorines on PVC chain are also substituted to form ether linkage (C—O—CH), this characteristic absorption may be overlapped by the band of the PVC compound at 1193 cm^{-1}. In addition, the hydrolysis and condensation of the siloxane groups in hot water leads to the appearance of two small shoulders in the region between 1020 and 1070 cm^{-1}, because of the Si—O—Si structure.[25]

Both samples (d) and (e) in Figure 4 have a small band at 915 cm^{-1},[24] corresponding with the band of epoxy group on KH560, and this indicates that excessive KH560 exists in these samples.

Thermogravimetric analysis

Figure 5 shows the weight loss curve and the corresponding derivative ($-dw/dt$) curve versus the

Figure 5 (a) Weight loss and (b) derivative weight change for crosslinked samples with different silane concentrations.

second one (over 460°C) is attributed to the thermal degradation of the remaining polymer. The rigid PVC compounds without crosslinking agent (0 phr) shows a narrow peak in the derivative plot, which corresponds to an early hydrogen chloride loss that takes place at a relatively high rate. In comparison with PVC compounds without crosslinking agent, the samples with different concentrations of cross-linking agent have higher maximum-rate tempera-ture (T_{max}, where the rate of dehydrochlorination reaches maximum) and beginning temperature of the decomposition. This is due to the formation of a three-dimensional —Si—O—Si— type network; moreover, this effect is more remarkable when increasing the amount of the crosslinking agent. Additionally, a wider peak, observed in samples with 10 or 15 phr of crosslinking agent from Figure 5, indicates that excessive epoxy groups on KH560 delay the release of HCl from PVC, and subse-quently, lower the rate of dehydrochlorination.

The second step shows some differences. T_{max} of the second peak rises with the increasing amount of crosslinking agent between 0 and 5 phr; however, T_{max} decreases as 10 and 15 phr crosslinking agent is added. These results probably relate to the special structures of the remains affected by the excessive KH560, but the detail reason will be studied later.

Above all, at the beginning of the reaction, the effect of the grafting of epoxylsilane on lower hehy-drochlorination predominates over thermal stabil-izers when the amount of epoxylsilane is small. However at the end of the reaction, if there is exces-sive silane in the system (such as when more than 10 phr epoxylsilanes were used), it can also act as a good acceptor for the liberated hydrogen chloride.

VST and T_g of the samples

The relationships between the crosslinking agent content and the values of VST and T_g of the samples
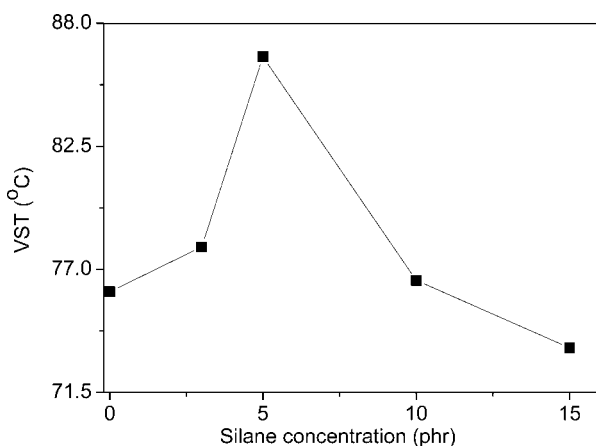

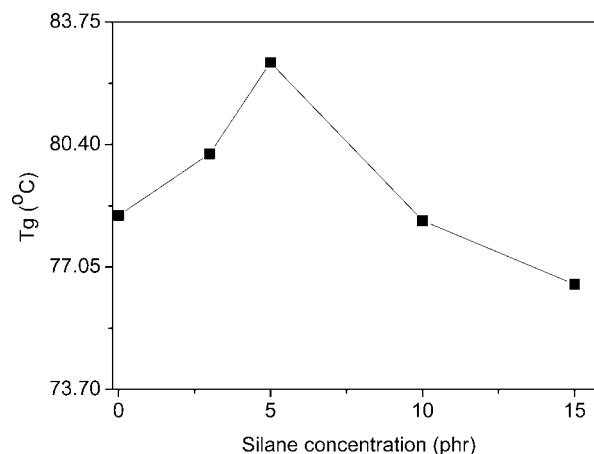**Figure 6** Effect of KH560 concentration on VST.

Figure 7 Effect of KH560 concentration on T_g.

are illustrated in Figures 6 and 7, respectively. As shown in Figure 6, VST of the crosslinked sample increases and reaches its peak when 5 phr of cross-linking agent is added, then decreases with further increasing in the crosslinking agent amount. Appa-rently, the maximum VST is 10.5°C higher than the rigid PVC compound without the addition of a crosslinking agent. The same tendency is also found in Figure 7. The glass transition temperature (T_g) of crosslinked PVC is improved roughly to 4.26°C when adding 5 phr epoxylsilane, compared with rigid PVC without crosslinking.

Both VST and T_g reflect the ability of the chain seg-ments to move. Generally, the more difficult the movement of the chain segments, the higher the VST and T_g are. So, crosslinking can improve VST and T_g of polymer, as has been verified when less than 5 phr crosslinking agent was added. However, the degree of crosslinking does not increase linearly with the amount of epoxylsilanes added. That is to say, when more than 10 phr epoxylsilanes were used, only part of them participated in the grafting, excessive epoxyl-silanes were dispersed in the system to work as plas-ticizer, consequently, the VST and T_g drop down.

CONCLUSIONS

Epoxylsilane KH560 was first used to graft and crosslink rigid PVC in this article. Results showed that with the synergy of metal soaps, especially Ba/Zn stearate, KH560 could be grafted on PVC chain. Then crosslinking would take place through hydro-lysis and condensation reactions. Additionally, the enhancement of electronegativity by combination of sodium bisulfite with epoxy groups would facilitate the grafting of epoxylsilane. As a result, a gel con-tent of 40% had been obtained when more than 10 phr epoxylsilanes were used in the condition of 2 : 1

(parts by weight) ratio of BaSt$_2$/ZnSt$_2$ and 1 : 1M ratio of NaHSO$_3$/KH560. Moreover, thermal dimensional stability and glass transition temperature were improved, and thermal degradation was delayed by the formation of crosslinking.

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