Aminosilane Grafting of Plasticized Poly(vinyl chloride) I. Extent and Rate of Crosslinking

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ABSTRACT: The grafting of poly(vinyl chloride) (PVC) by reactive aminosilane compounds, which make them moisture-curable, has been investigated. Plasticized poly(vinyl chloride) has been successfully grafted with aminosilane during extrusion. The grafted polymer was crosslinked in the presence of moisture. Although the hydrolysis and condensation of the crosslinking agent is very rapid, the speed of the reaction is controlled by the rather slow diffusion of water in the plasticized PVC. This water diffusion speed follows Fick's Law and is strongly dependent on temperature. To achieve a high crosslinking speed, the extruded PVC has to be placed in warm water or in a steam heated vessel. The effects of catalyst concentration, moisture concentration, and immersion time and temperature on the rate and degree of crosslinking were investigated. Since the formulation used contained a tin stabilizer, the addition of a tin catalyst to the immersion water had little effect. Crosslinking did occur in samples stored at room temperature due to the presence of moisture, but the reaction rate was increased substantially if the sample was immersed in water. Reaction rate was very temperature dependent and followed an Arrhenius relationship. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2111–2119, 1997

Key words: PVC; crosslinking; grafting; aminosilane

INTRODUCTION

Poly(vinyl chloride) (PVC) can be considered as an ideal base for chemical modification due to its chemical structure. Presumably, the chlorine could react as in other chlorine-containing aliphatic compounds, but secondary degradation reactions will occur at the same time. Nevertheless, various functional modification reactions (grafting and crosslinking) have been carried out in solution and in the condensed state.[1–5]

CHEMICAL CROSSLINKING

Modification of PVC by crosslinking has aroused wide interest due to the potential improvements of its thermal properties. Although a number of thermal crosslinking methods for PVC have been presented in the literature[6–13] and in patents,[14,15] the crosslinked products are rarely used commercially. This is most probably due to practical problems during processing (high melt viscosity and/or premature crosslinking) and product quality (thermal stability). Several attempts using different reactive chemicals either in solution, suspension, or in the molten state have been reported. Duchacek and Kuta[13] have crosslinked PVC by tetramethyl–thiuramdisulphide in the presence of zinc oxide. They found the activation energy for the crosslinking reaction to be 106 KJ mol. Mori and coworkers[9–11] have extensively reported the use of dithiol triazines as a crosslinking agent for PVC. Wejchan-Judeck[16] reported the crosslinking of PVC using dithiols, and Gonnu and Michel[17]

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studied the reactivity of alkaline earth salts of dimercaptans as crosslinking agents.

The methods discussed so far have the disadvantage that the crosslinking process is promoted thermally, and it is difficult to separate the grafting from the crosslinking process, even when the reactivity of the polymer towards grafting is greater than the reactivity to crosslinking, as reported by Mori and Nakamura.[10] Due to this, it is likely that crosslinking occurs during the processing step, causing practical problems.

For polyolefins, especially polyethylene, silane crosslinking has been used successfully since the 1970s and is a commercially established process.[18,19] The polyethylene is grafted with unsaturated silanes containing hydrolysable groups, which form crosslinks by hydrolysis and condensation in the presence of water, preferably in the presence of a silanol condensation catalyst. This method has a number of advantages compared to peroxide or radiation crosslinking.[20]

Attempts to crosslink PVC using silane crosslinking agents have also been reported.[21–23] Ryningen et al.[24,25] described a new process to avoid the degradation problems observed by Hearn et al.[26] Kelner and Schatz[27–29] have also successfully crosslinked PVC by grafting mercapto–alkoxysilanes on to the polymer chains without degrading the PVC. They reported that the grafting reaction occurred only in the presence of basic lead salts. In their second article, Kelnar and Schatz[29] studied the crosslinking of PVC using different organosilanes and crosslinking conditions. It was found that the crosslinking rate for samples grafted with mercaptosilanes was higher for samples catalyzed with dibutyltindilaureate, the rate constant for catalyzed and uncatalyzed reactions differing by two orders of magnitude. On the other hand, for PVC grafted with aminosilanes, this difference was only one order.

The present work investigates the kinetics of aminosilane crosslinking of plasticised PVC. In addition, the influence of catalyst concentration, and also moisture concentration, on the rate and degree of crosslinking have been evaluated. Finally, a relationship between the crosslinking and the diffusion process is presented. The grafting and crosslinking reactions are considered in an accompanying article.

EXPERIMENTAL

Materials

Materials used were as follows. Suspension PVC (PVC Corvic S71/102), with a K value of 71, was supplied by ICI Ltd., U.K.; di-2-ethyl hexyl phthalate (DOP) was used as plasticizer; dibutyltinthioglycolate ester (T192), heat stabilizer, and dibutyltin dilaurate (TL) catalyst were supplied by Akros Chemicals. The crosslinking agent was *N*-(2-aminoethyl)-3-aminopropyl-trimethoxy silane, (Z-6020) supplied by Dow Corning, as shown in the following: $NH_2—(CH_2)_2—NH—(CH_2)_3—Si—(OCH_3)_3$.

Preparation

The formulation used contained 100 phr PVC, 50 phr of DOP, 2 phr of T192 heat stabilizer, and 3 phr of aminosilane (in which phr is parts per hundred of resin). The compounds were dry blended in a Henschel intensive mixer. The resin was preheated to 90°C, after which the plasticizer and the other ingredients were added. A total mixing time of 20 minutes was chosen in order to achieve good mixing.

The dry blend was extruded in a 1 in. diameter single screw extruder (Killion 100). The extruder was fitted with a slit die to produce strips of approximately 0.6 mm in thickness.

Crosslinking Process

Crosslinking was carried out by immersing extruded samples in water. The following crosslinking variables were investigated: (1) catalyst concentration (0–5%); (2) immersion time (1–20 h) at an immersion temperature of 80°C and 0–275 h at room temperature; (3) immersion temperatures of 20, 80, 105, and 120°C; (4) moisture content, which was varied by keeping the samples in water, normal air, and in a desiccator.

Analysis and Testing Procedures

Gel content was used to measure the degree of crosslinking. The gel content was determined by Soxhlet extraction for 20 h with tetrahydrofuran. The remaining swollen gel was dried in a vacuum oven at 60°C for at least 20 h, and gel content was expressed as the percentage of the original sample weight, excluding the plasticizer.

Diffusion Experiments

Each of the specimens was immersed in 250 mL of water. All tests were made at four different temperatures, 70, 80, 105, and 120°C (±1°C), with the last two experiments conducted using an autoclave. To monitor weight changes, the sam-

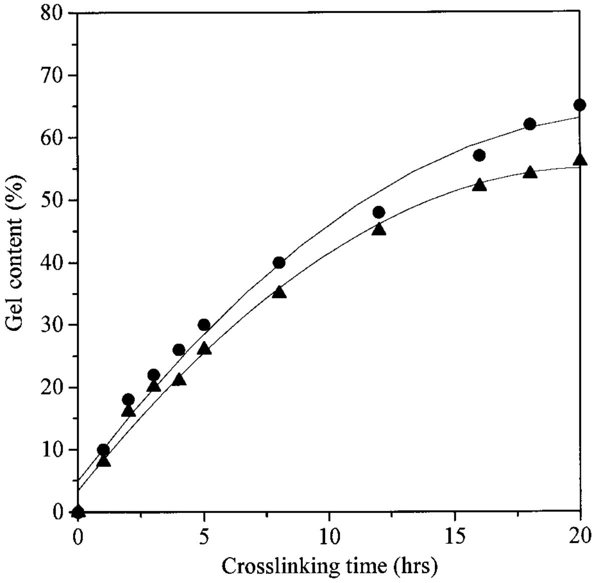

Figure 1 Effect of crosslinking time on gel content for samples crosslinked in (▲) water and in (●) water plus catalyst at 80°C.

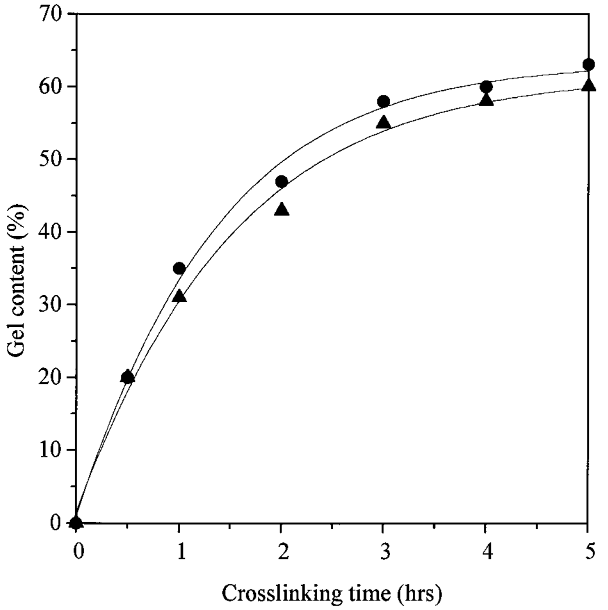

Figure 2 Effect of crosslinking time on gel content for samples crosslinked in steam at 120°C (▲) without catalyst and (●) with 5% catalyst catalyst.

ples were removed from the flask, wiped gently with a tissue, and immediately weighed.

RESULTS AND DISCUSSION

Effect of Catalyst Concentration on Rate and Degree of Crosslinking

To study the effect of the condensation catalyst on crosslinking rate, extruded samples containing 2 phr of aminosilane and 3 phr of tin stabilizer were crosslinked for different periods of time. Figure 1 shows the results of gel content of samples crosslinked at 80°C in water and in water containing catalyst; Figure 2 shows the crosslinking curves for samples crosslinked in steam at 120°C with and without a condensation catalyst.

The method described by Kelnar and Schatz[28] was used to characterize the crosslinking reaction rate. The dependence of the logarithm of relative gel content $\ln\{(G_\infty - G)/(G_\infty - G_0)\}$ on crosslinking time was linear, and the slope is termed the rate constant. Figure 3 presents rate plots for the two samples, and the rate constant values for crosslinking under various conditions are given in Table I. It is interesting to note that the catalyst does not appear to have an important effect on crosslinking rate. The effect of increasing the temperature is more obvious. The rate constant for the crosslinking reaction of samples crosslinked in water and in water plus catalyst at 80°C are about one order of magnitude lower than those obtained when the samples were crosslinked in steam.

Narkis et al.[30] and Kumar Sen et al.[31] in their studies of silane grafted polyethylene pointed out

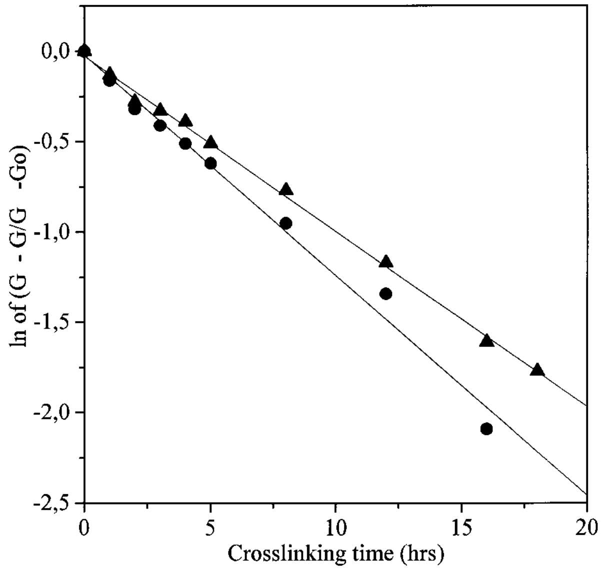

Figure 3 Linear dependence of relative gel content on crosslinking time in (▲) water and in (●) water plus catalyst.

Table I Rate Constants for PVC Crosslinking

	Rate Constant (min^{-1})	
Medium	80°C	120°C
Water	0.0021	0.0100
Water + catalyst	0.0026	0.0120

that the catalyst is vital to shorten the crosslinking time. Narkis et al.,[30] however, mentioned that even in the absence of catalyst, silane-grafted polyethylene will crosslink, though at a much slower rate. On the other hand, Kelnar and Schatz[29] pointed out that the rate constant for PVC grafted with mercaptosilanes was two orders of magnitude lower in presence of catalyst; and for PVC grafted with aminosilanes, it was one order of magnitude lower. They mentioned that the reaction with the aminosilane is more rapid.

The sample used in our study were stabilized with tin stabilizer, which, in effect, is a condensation catalyst. The rate constant for this system at 120°C (0.010 min^{-1}) is similar to that obtained by Kelnar and Schatz[29] (0.0144 min^{-1}) for samples grafted with aminosilane and stabilized with the ester of thioglycolic acid.

Effect of Variation of Moisture Concentration on the Rate and Degree of Crosslinking

To investigate the effect of moisture content on crosslinking rate, extruded samples were placed in three different environments: water, air, and a desiccator at room temperature. Figure 4 shows the crosslinking curves. At room temperature, the crosslinking of the samples in air and in the desiccator occurs very slowly and at an effectively similar rate. A rate constant of 1.84×10^{-6} min^{-1} was found for the samples in air, and a rate constant of 1.79×10^{-6} min^{-1} was found for the samples in the desiccator. These samples reached a gel content of 35% after 275 days. On the other hand, the samples in water were completely crosslinked after 40 days with a maximum gel content of 63%. The rate constant for these samples was 1.14×19^{-4} min^{-1}, which is two orders of magnitude higher.

Surprisingly, the crosslinking process in a dry atmosphere (desiccator at room temperature) is only slightly delayed and not inhibited, although the rate and degree of crosslinking are lower than when the samples were immersed in water. Only a small concentration of water distributed in the grafted PVC is required to produce crosslinking, and it appears that moisture already present in the sample was adequate for this purpose. The samples in the desiccator already contained an equilibrium concentration of moisture, and any diffusion of water either out of the samples, or back into them as existing water reacted with the silane, had little effect. Kelnar and Schatz[29] and Hjertberg and Dahl[34] mentioned that diffusion of water from the external environment has practically no effect on the crosslinking. However, they showed that the rate constant obtained during the crosslinking process at 80°C in water and in air were different (almost one order in magnitude). In our study at room temperature, the crosslinking rate was two orders of magnitude higher for the samples immersed in water, and the degree of crosslinking was also higher. These results suggest that water concentration is an important factor to consider.

Energy of Activation for Crosslinking Reaction

To determine the activation energy (E_a), crosslinking reactions were carried out at different temperatures (20, 80, 105, and 120°C) in water and in water plus 5 phr catalyst. The corresponding gel fraction has been measured against the

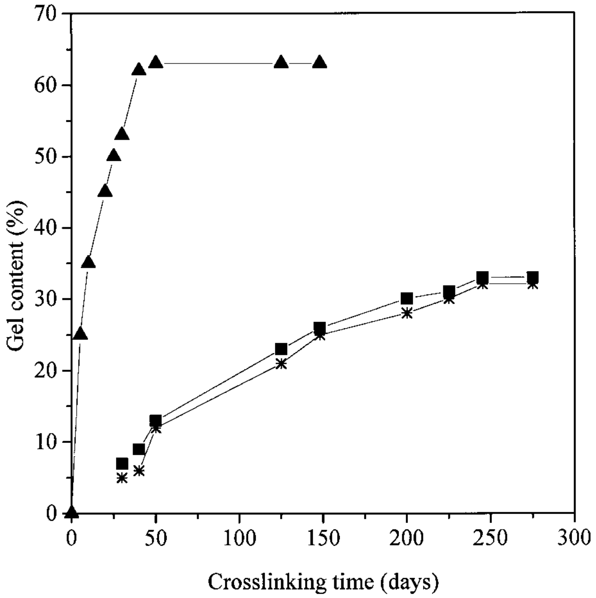

Figure 4 Effect of crosslinking time on gel content for samples placed in three different environments at room temperature: (▲) H_2O, (■) air, and (*) desiccator.

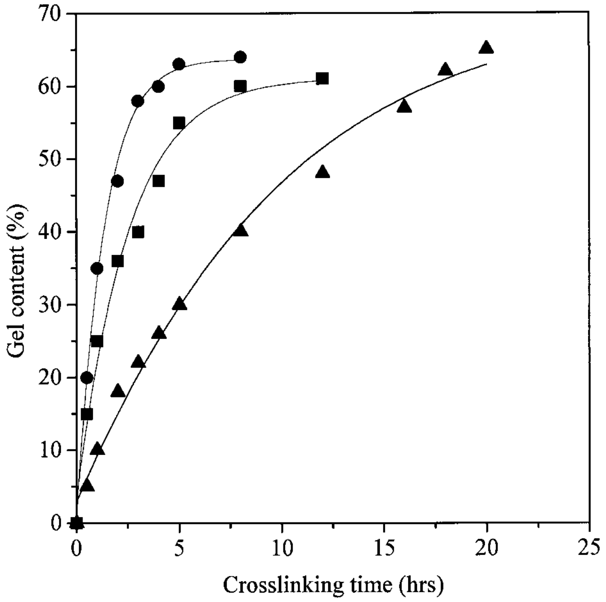

Figure 5 Effect of crosslinking time on gel content for samples crosslinked in water at three different temperatures: (▲) 80, (■) 105, and (●) 120°C.

crosslinking time. Figures 5 and 6 show that the rate and degree of crosslinking increase with temperature. From the rate constants obtained according to the method previously described, Arrhenius plots have been drawn. (Fig. 7). Linear plots are observed in both cases, and the energy of activation (E_a) has been calculated as 10.60 and 10.16 kcal mol for the systems water and water plus catalyst, respectively. The lower the energy of activation, the faster the reaction. However, in this case, the values are approximately equal. Again, the tin stabilizer already in the formulation appears to be acting as a condensation catalyst. Extra catalyst in the water bath does not have a significant effect on the reaction rate.

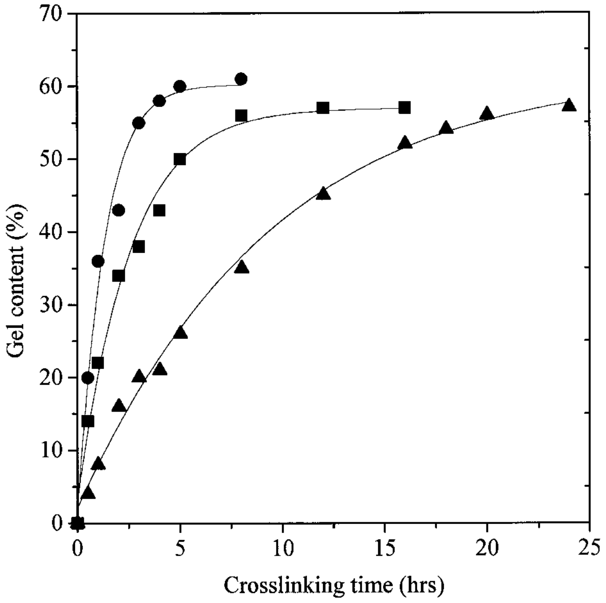

Figure 6 Effect of crosslinking time on gel content for samples crosslinked in water plus catalyst a three different temperatures: (▲) 80, (■) 105, and (●) 120°C.

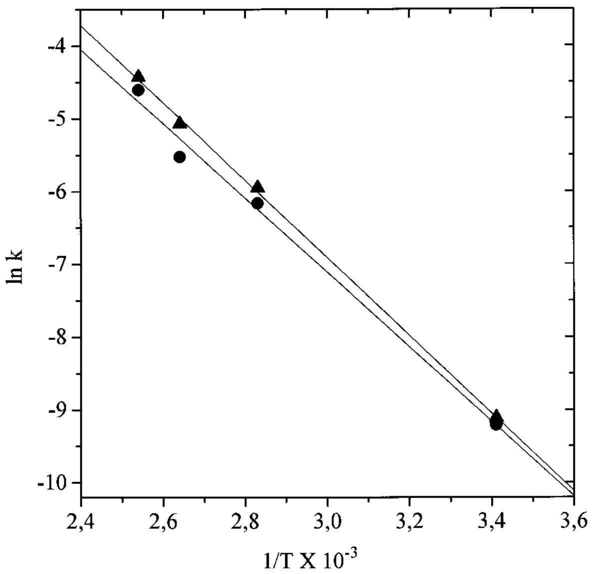

Figure 7 Arrhenius plot for crosslinking in (▲) water and in (●) water plus catalyst.

Diffusion Results

It is necessary to study the water diffusion process in plasticized PVC in order to correlate this with the crosslinking process.

In an attempt to examine the water absorption kinetics, Fickian behavior for a plane sheet was considered as described by the following well-known equation[35]:

$$\frac{q_t}{q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0} \frac{\exp\{-[(2n+1)\pi/l]^2 Dt\}}{(2n+1)^2} \quad (1)$$

Where q_∞ represents the water content at equilibrium, q_t represents the water content at time t, D is the diffusion coefficient, n is an integer, and l is the thickness.

When t is large, D is assumed to be independent of concentration; and eq. (1) may be simplified to give

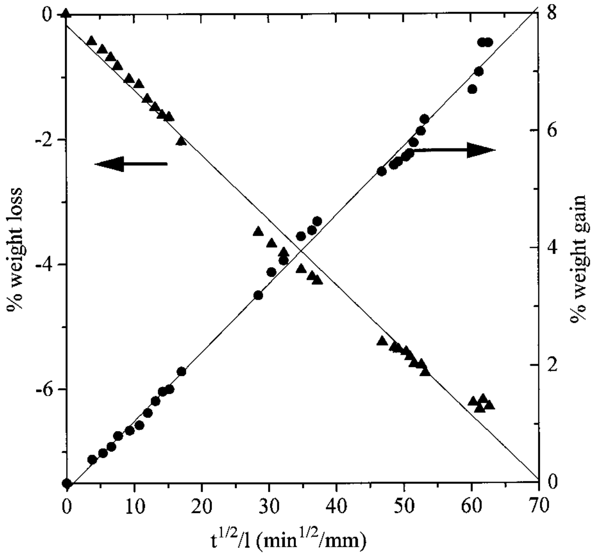

Figure 8 Diffusion plots for the system immersed in (▲) water and (●) water plus catalyst.

$$\frac{q_t}{q_\infty} = 1 - \frac{8}{\pi^2} \exp \frac{\pi^2 Dt}{l^2} \tag{2}$$

By plotting $\ln(1 - qt/q_\infty)$ against t, the diffusion coefficient can be evaluated. The approximation for short times,

$$\frac{q_t}{q_\infty} = \frac{[4]}{[l]} \frac{[Dt]^2}{[\pi]} \tag{3}$$

is also useful. A plot of $qt/q\infty$ against $4(t/\pi l^2)^{1/2}$ is initially linear and has a slope of $D^{1/2}$.

The exact derivation of eq. (3), together with a through discussion on all the assumptions required, has been given elsewhere.[36]

This equation can be rewritten as

$$\% \text{ weight change} = 4\left\{\frac{Dt}{\pi l}\right\}^{1/2} \tag{4}$$

Graphs of % weight change versus $t^{1/2}/l$ will provide the diffusion coefficients.

It has been pointed out[37] for plasticizer migration in PVC that considerable deviation from the linearity was evident when the test was conducted for long times. On the other hand, the results obtained during the initial stages were found to be in accordance with eq. (3).

For this study, it was decided to use eq. (4) because it is intended that the crosslinking reaction takes place in the early stages of the diffusion process.

Figure 8 shows diffusion curves for the system immersed in water and in water plus catalyst. From these figures, it can be seen that the samples immersed in water gained weight; in the investigation of the extract from the samples, a sample of the water was taken, the water was evaporated, and the remaining residue was analyzed using Fourier transform infrared (FTIR) analysis. The FTIR analysis confirmed that the catalyst solution had extracted some plasticizer. The plasticizer content of the immersed samples was evaluated after certain periods of time. The samples immersed in water did not lose plasticizer, but the samples immersed in water and catalyst lost up to 15% in some cases. Clearly, while the plasticizer is insoluble in water alone, the solubility parameter of an aqueous solution of the tin catalyst is such that the plasticizer can dissolve. By calculating the amount of plasticizer that was extracted after a series of times, it was possible to know the water uptake in the system containing the catalyst.

Figures 9 and 10 show the diffusion plots for the two systems at four temperatures. The results presented in Figure 10 are the results after correction for plasticizer loss. In these systems, the temperature has a marked effect on diffusion. As expected, when the temperature increases, the water uptake also increases.

It would be necessary to carry out more experiments in order to obtain quantitative information about the counterdiffusion process observed in the presence of catalyst. However, in spite of this counterdiffusion process, the water and catalyst are well diffused through the plastic and are capable of producing high gel contents.

The above treatment is undoubtedly simplified, ignoring, for instance, boundary layer phenomena; but it may be successfully extended for short-term migration studies.

The calculated diffusion coefficients obtained from the previous graphs are shown in Table II. The correlation factor of the calculation by the method of least squares was at least 0.98 showing a good accord between the experimental values and theory.

The temperature dependence of D is that corresponding to an activation process obeying a relationship similar to the Arrhenius equation, as follows:

$$D = D_o \exp - \left[\frac{E_a}{RT}\right] \tag{5}$$

where D is the diffusion coefficient, D_o is the pre-

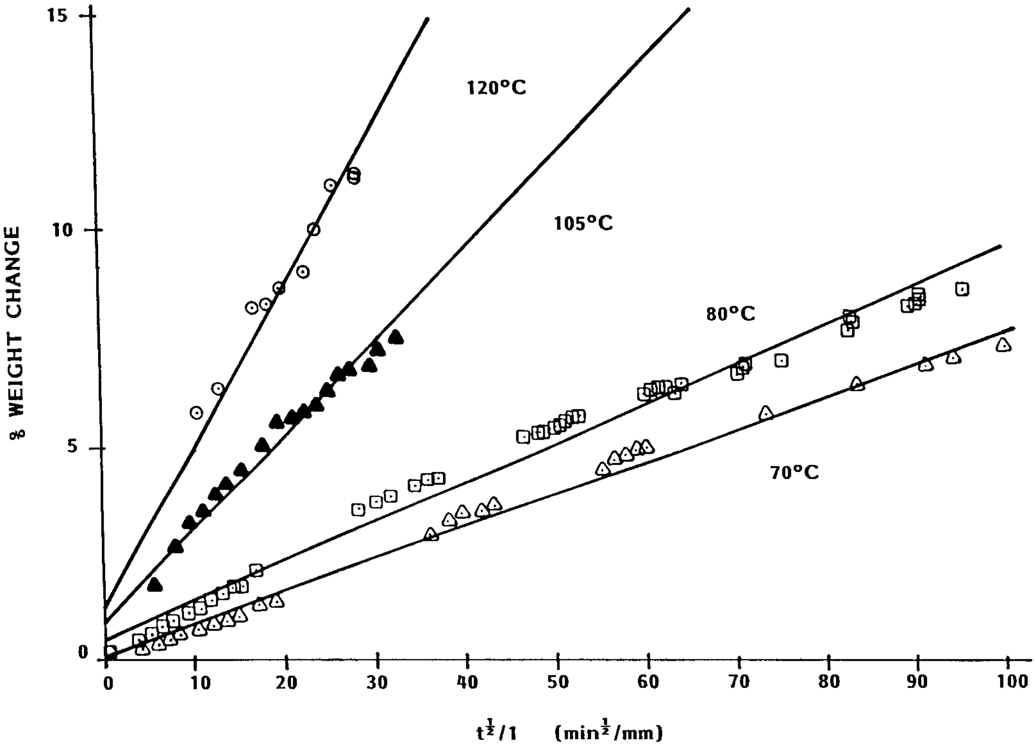

Figure 9 Diffusion experiments in water at (△) 70, (□) 80, (▲) 105, and (○) 120°C.

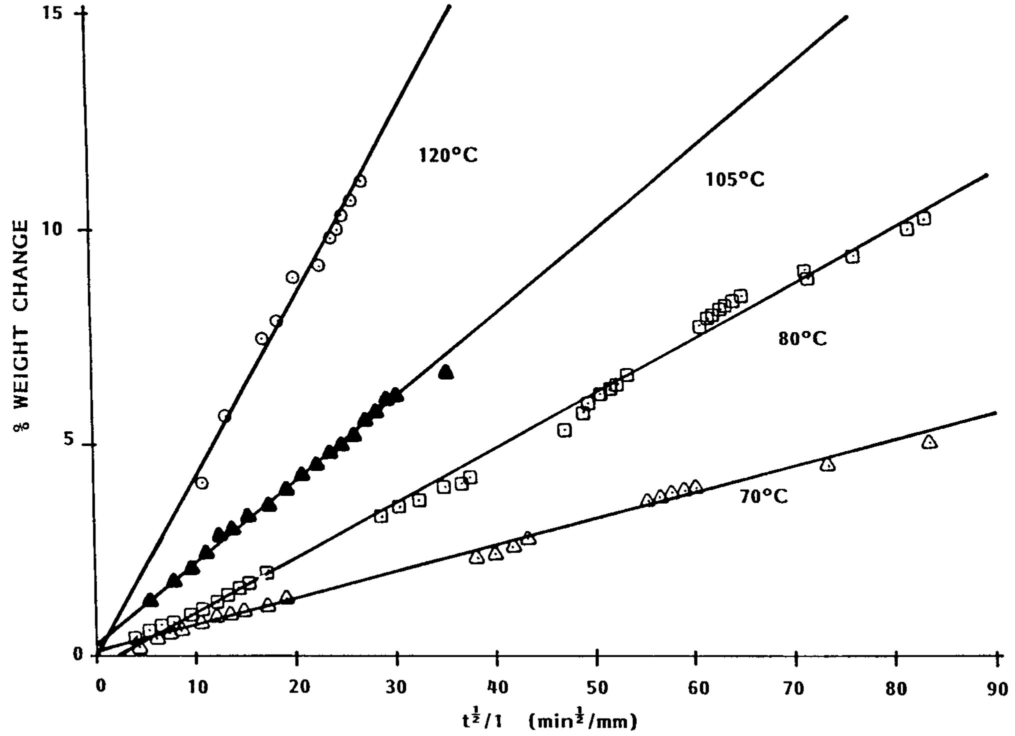

Figure 10 Diffusion experiments in water plus catalyst (△) 70, (□) 80, (▲) 105, and (○) 120°C.

Table II Diffusion Coefficients for Water and Water Plus Catalyst at Four Temperatures

Temperature (°C)	Rate Constant (min^{-1})	
	Water	Water + Catalyst
70	0.622	1.01
80	2.667	1.39
105	6.534	8.0
120	27.24	23.3

exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature in Kelvins.

These results are presented in Figure 11 and 12 and are in good agreement with those obtained for the migration of plasticizers and stabilizers in PVC.[37] The energies of activation (E_a) for the diffusion process have been calculated as 8.46 and 7.72 kcal mol for the system in water and water plus catalyst.

Correlation with the Crosslinking Process

Hochstrasser[38] suggested the following empirical formula to calculate the crosslinking time for polyethylene by using the diffusion coefficient for water, as follows:

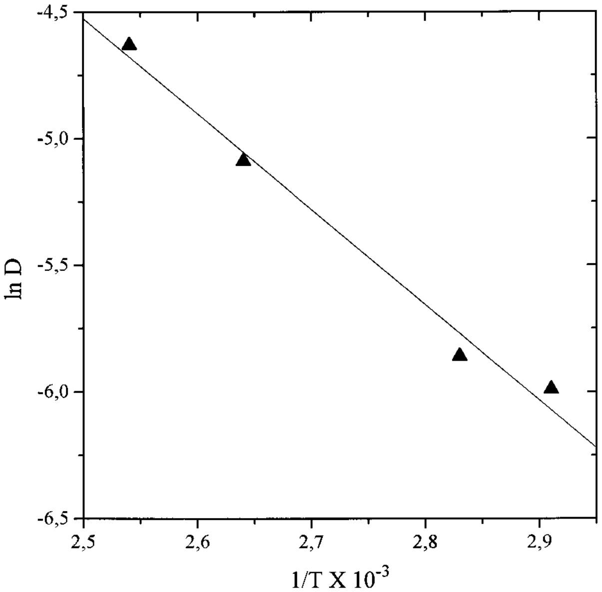

Figure 11 Effect of temperature on diffusion coefficients of samples immersed in water.

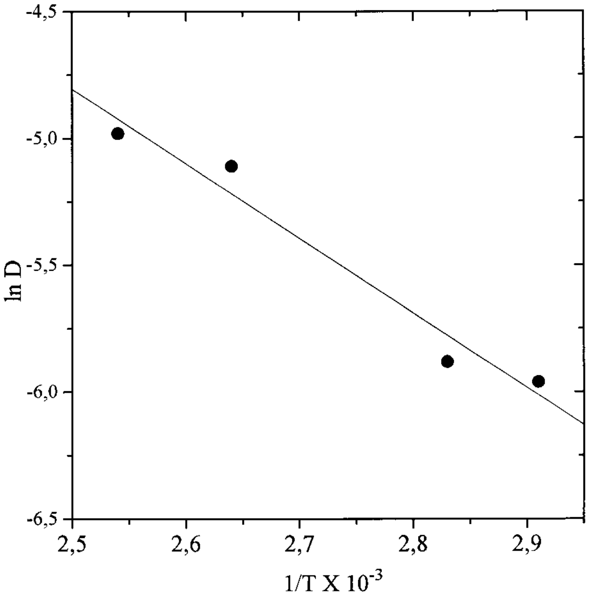

Figure 12 Effect of temperature on diffusion coefficients of samples immersed in water plus catalyst.

$$\text{crosslinking time} = \frac{l^2}{RH \times D} \qquad (6)$$

where l is the thickness; D is the diffusion coefficient; and RH is the relative humidity.

Using a thickness of 0.6 cm (which is the average thickness of the samples used in this study), and a relative humidity of 1, the crosslinking time at different temperatures can be calculated. If these results are compared with the experimental data in Figure 5, it can be seen that the actual times to reach a maximum gel content are very similar. The crosslinking time is dramatically reduced as the temperature is increased, as shown in Table III.

CONCLUSIONS

It is found that the rate constants for the crosslinking of PVC grafted with aminosilane are simi-

Table III Calculated Crosslinking Times at Three Temperatures

Temperature (°C)	Crosslinking Time (h)
80	37
105	15
120	3.6

lar when the samples are immersed either in water or in water containing catalyst. It is therefore suggested that the organotin stabilizer used acts as a silanol condensation catalyst. Neither the degree nor the rate of crosslinking is highly influenced by the external catalyst.

The moisture content has a strong influence on the rate and degree of crosslinking. Samples immersed in water at room temperature were fully crosslinked after 40 days. However, small quantities of water present in the samples are enough to initiate the crosslinking at room temperature, although the crosslinking rate is very slow and very long periods are required for complete reaction.

The water temperature had a significant effect on both the rate and degree of crosslinking. Energies of activation (E_a) for the crosslinking reaction of 10.60 and 10.16 kcal mol have been obtained for the system using water and water plus catalyst, respectively.

The water transfer into PVC was found to obey Fick's Law, and the temperature dependence of the diffusion coefficient could be described by an Arrhenius equation. The activation energy for the diffusion process was 8.46 kcal mol.

Using an empirical equation proposed for diffusion of water in crosslinkable polyethylene,[38] crosslinking times were obtained. These results are in good agreement with actual measurements of gel content. We can conclude in this respect that the diffusion process has a notable influence on the rate and degree of crosslinking for plasticized PVC.

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