

Silane Cross-linking of PVC. II. Influence of Silane Type and Conditions on Cross-linking by Water*

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SYNOPSIS

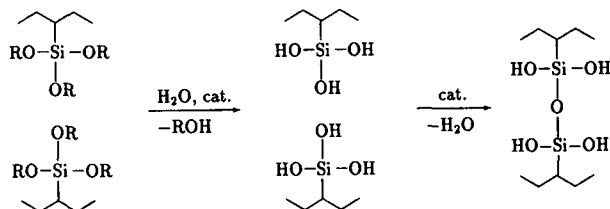
The cross-linking of plasticized and unplasticized poly(vinyl chloride) (PVC) grafted with amino- and mercaptoalkyltrialkoxysilanes has been studied in water and in air at 20–140°C. In both media, the cross-linking occurs faster for plasticized PVC grafted with aminosilanes; however, at temperatures above 100°C, the effect of degradation cross-linking is apparent. For mercaptosilanes, a marked dependence of the cross-linking rate on the silane structure was found; plasticized PVC with grafted 3-mercaptopropyltrimethoxysilane was cross-linked in water at 100°C after 6 h, whereas this process took 12 h for 5-mercaptopentyltriethoxysilane. Practically no cross-linking occurred in unplasticized PVC below T_g , whereas the rate at 100°C was comparable with that for plasticized PVC. The cross-linking rate is affected by the chain mobility, water content, and diffusion of water into the material; a very slight dependence on the thickness of the material was found for plasticized PVC. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

One of the more important ways of improving polymer quality is through cross-linking, leading to an improvement in the thermal dimensional stability and in the resistance to solvents, permanent deformation, stress cracking, etc. In addition to the usual cross-linking through radiation or chemical reagents, the utilization of cross-linking by organofunctional silanes² increased after the introduction of the systems of Sioplas³ and Monosil.⁴

This process is based on the preparation of a silane-grafted polymer using either peroxides and vinyl alkoxy silanes or, more recently, direct preparation of the copolymer of ethylene with, e.g., vinyltrimethoxysilane.^{5,6} After processing, this silane-grafted polymer is cross-linked through the action of water,

which hydrolyzes the alkoxy groups with subsequent condensation to yield siloxane bonds:



To attain a sufficiently fast cross-linking rate, a catalyst is essential, usually dibutyltin dilaurate (DBTDL),³ which decreases the activation energy for the hydrolysis and also catalyzes the condensation. It is stated that both stages are catalyzed by Brönsted acids.^{7,8}

Narkis et al.⁹ carried out a detailed study of the cross-linking of silane-grafted polyethylene (PE); a time period for cross-linking of approximately 10 h was found for exposure to water at a temperature of 80°C, which is two orders of magnitude less than at 23°C. Small differences were found in the cross-

* See Ref. 1.

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linking rate at both temperatures for exposure to water and to humid air.

A detailed study of the cross-linking of ethylene-vinyltrimethoxysilane copolymers was carried out¹⁰; the maximum gel content was achieved in water at 90°C after 20 h of exposure. However, further siloxane bonds continued to be formed up to 100 h of exposure. In the absence of a catalyst, no gel was found under these conditions even after 20 h of exposure; for the unstabilized polymer, the thermooxidation reactions were found to have a negative effect on the mechanical properties of the cross-linked product. Siloxane bonds were formed at comparable rates in cross-linking of samples with a thickness of 0.2 and 1.3 mm, i.e., the rate of the reaction is apparently not controlled by macroscopic diffusion of water.

The cross-linking of these copolymers at processing temperatures was also studied^{6,11} and a marked effect of the thermooxidation reactions on the cross-linking was found. Cross-linking through interaction of the oxidized sites (hydroperoxides) with silane is sufficiently fast even in the absence of DBTDL.

Silane-grafted cross-linked poly(vinyl chloride) (PVC) has recently been successfully prepared^{1,12} through the reaction of PVC with alkoxysilanes containing a mercapto group (e.g., 3-mercaptopropyltrimethoxysilane, MTMS) in the presence of lead-containing stabilizers and suitable plasticizers or lubricants. Silane-grafted PVC can also be prepared through reaction with aminosilanes^{13,14} (e.g., 3-aminopropyltriethoxysilane) and the reaction even occurs at lower temperatures ($\sim 160^\circ\text{C}$) and other thermal stabilizers can be used, but the thermal stability is greatly decreased.

This work describes simultaneous evaluation of the effect of the cross-linking conditions (medium, temperature) and type of silane on the cross-linking reaction. Silane-grafted cross-linkable PVC with various T_g values, permeability for water vapor, and equilibrium water contents were compared.

EXPERIMENTAL

Materials

In addition to the raw materials described in Part I, Ref. 1, the following chemicals were employed: organotin stabilizer (Mark 954, Argus Chemicals), 3-aminopropyltriethoxysilane (ATES) (Union Carbide, USA), bp 217°C, and 3-(2-ami-

noethylamino)propyltrimethoxysilane (ATMS) (Union Carbide, USA) bp 285°C. The PVC mixtures used are identical to those in Part I, Ref. 1.

Preparation of Silane-grafted PVC

In contrast to the conditions in Part I, Ref. 1, only a temperature of 160°C was employed for grafting of the aminosilanes to the PVC.

Cross-linking of Silane-grafted PVC

A study was made of the cross-linking on exposure of the samples in steam at 100°C and in water at temperatures of 80, 50, 30, and 20°C.

Tests of cross-linking by hot air were carried out in a circulating oven at 80 and 100°C. The dependence of the cross-linking rate on the air temperature was tested by exposure for 24 h at temperatures of 50–140°C in steps of 10°C. The average relative humidity of the air was approximately 60% at 20°C. In addition, samples wrapped in aluminum foil were exposed to measure the effect of diffusion of water vapor from the surrounding environment.

The effect on the thickness of the sample on the cross-linking was tested for exposure of samples of plasticized PVC with a thickness of 10 mm at a temperature of 100°C in steam. The gel content in the ca. 1 mm-thick surface layer, in the layer between 2 and 3 mm, and in the center layer between 4.5 and 5.5 mm from the surface was tested for exposure times of 30, 120, 240, 360, and 420 min.

Characterization of the Degree of Cross-linking

The gel content, i.e., the content of insoluble material, was determined after extraction for 12 h in boiling tetrahydrofuran. The gel values found for plasticized PVC were not recalculated to PVC. The cross-linking time was found from the time dependence of the gel content as the time after which the gel content no longer increased.

It was found useful to characterize the rate of the cross-linking reaction using the slope of the straight line in dependence on the logarithm of relative gel content $\ln[(G_\infty - G)/(G_\infty - G_0)]$ (G_∞ = maximum gel content, G_0 = initial gel content) on the cross-linking time. These dependencies were always linear. Because of the similarity with a course of first-order reaction, the parameter (slope) evaluated was termed the "rate constant," K .

RESULTS AND DISCUSSION

The Effect of the Condensation Catalyst on the Cross-linking Rate

A study was made of the rate of cross-linking of plasticized PVC in the absence of a catalyst and the results were compared with cross-linking of the same samples containing 0.05 phr DBTDL. The rate constant values for the cross-linking under various conditions are given in Table I.

It is apparent that the rate constants for the cross-linking reaction in the absence of DBTDL in mixtures with grafted mercaptosilane for exposure to steam at 100°C and to the air at 80°C are about two orders of magnitude lower than those in the presence of the catalyst. No gel was found in samples exposed to the air at laboratory temperature even after 15 months, indicating that this silane-grafted PVC has a long shelf life.

The rate constant for PVC with grafted aminosilane decreased by only about one order of magnitude in the absence of DBTDL. These aminosilanes apparently are capable of accelerating the cross-linking reaction; a number of organic amino compounds have, in fact, been listed as condensation catalysts.¹⁵

Organotin stabilizers have been found to act as quite efficient cross-linking catalysts; a rate constant value of 0.0144 min⁻¹ was found for plasticized PVC with grafted ATES, stabilized with the esters of thioglycolic acid (Mark 954), even in the absence of DBTDL.

The Effect of the Type of Silane on the Cross-linking in Water

Figures 1–3 depict the cross-linking of PVC grafted with various silanes in steam at 100°C; the time required for cross-linking and rate constants are given in Table II.

The difference in the cross-linking rate of mixtures with grafted MTMS compared with 5-mercaptopropyltriethoxysilane (MTES) is particularly interesting. This value is much greater than those for vinylsilanes with methoxy and ethoxy groups used for cross-linking PE. Here, the length of the alkyl chain also seems to have an important influence.

In addition, it was found that the cross-linking of rigid PVC is slower than that for similar mixtures containing a plasticizer. This difference was greatest for MTES, where the cross-linking is twice as fast for plasticized mixtures (Fig. 2).

Compared to the hydrolytic cross-linking of PE, the cross-linking of plasticized PVC grafted with aminosilane and MTMS is faster, while that for un-plasticized mixtures is similar. However, the cross-linking is slower even for plasticized PVC when MTES is employed.

Dependence of the Cross-linking Rate on the Water Temperature

It follows from the dependence in Figure 4 that exposure to water at a temperature of greater than 50°C is necessary to achieve at cross-linking time of the order of hours for plasticized PVC with grafted MTMS. A similar dependence was also found for plasticized mixtures containing aminosilanes. The marked shift to higher temperatures for plasticized PVC with MTES (Fig. 4) corresponds to the lower reactivity of this silane, described in the previous section.

Rather different results were obtained for un-plasticized PVC with grafted MTMS and MTES. No cross-linking occurred at temperatures below T_g , i.e., below about 80°C, even on prolonged exposure in water (e.g., 100 h at 60°C). This fact is also apparent from the rate constant values in Table III, where the constant values for the corresponding de-

Table I Rate of the Catalyzed and Uncatalyzed Cross-linking of Plasticized Silane-grafted PVC

Temperature (°C)	Medium	Silane	Rate Constant (min ⁻¹)	
			0.05 phr DBTDL	No Catalyst
20	Air	MTMS	3.4×10^{-6}	0
80	Air	MTMS	0.0015	7×10^{-5}
100	Steam	MTMS	0.0146	0.0005
100	Steam	ATES	0.022	0.002
100	Steam	ATMS	0.025	0.0026

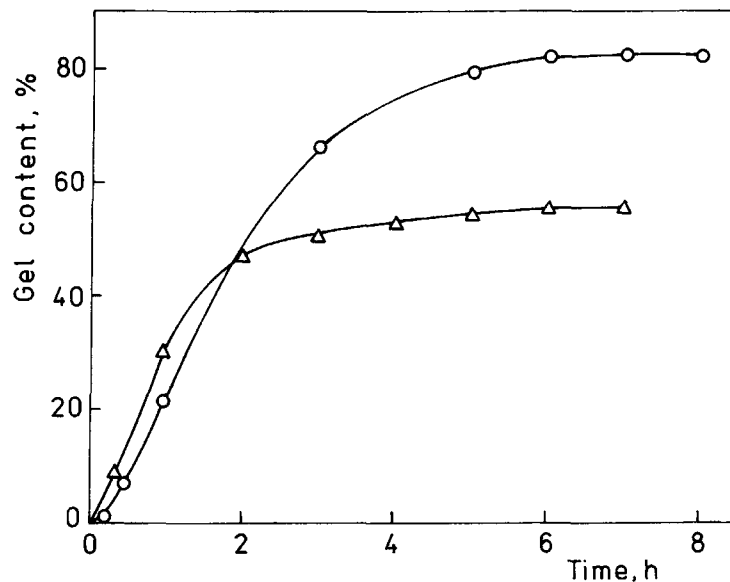


Figure 1 Cross-linking of PVC with grafted MTMS in steam at 100°C: (Δ) plasticized PVC; (○) unplasticized PVC.

pendence of the plasticized mixture with MTMS from Figure 4 are also given.

Cross-linking by Atmospheric Humidity

It is apparent from the curve for the cross-linking of the sample in the air-oven in Figure 5 that plasticized PVC is cross-linked in 10 h at a temperature

of 100°C with a rate constant of 0.0046 min^{-1} . The air had a relative humidity of about 60% at 20°C.

At a temperature of 80°C, plasticized mixtures with MTMS were cross-linked within 30 h, while those with ATEs were cross-linked within 20 h of exposure; in the former case, a rate constant of 0.0015 min^{-1} was found, whereas that for the latter case was 0.0038 min^{-1} . It is apparent from compar-

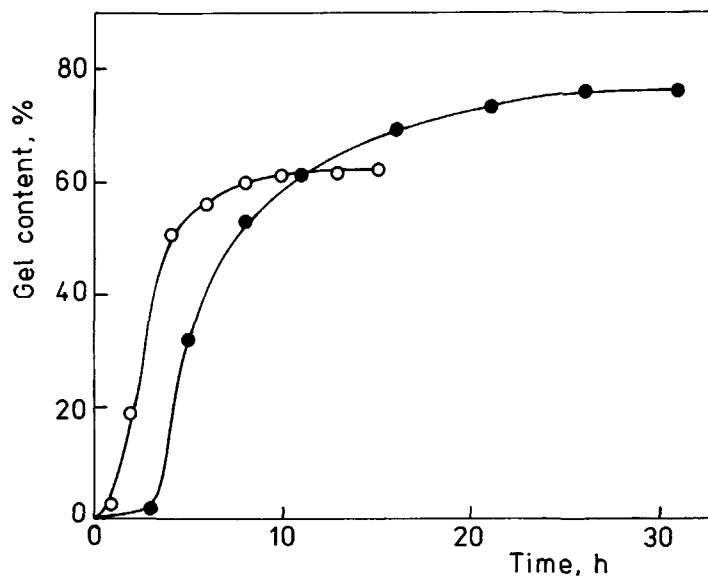


Figure 2 Cross-linking of PVC with grafted MTES in steam at 100°C: (○) plasticized PVC; (●) unplasticized PVC.

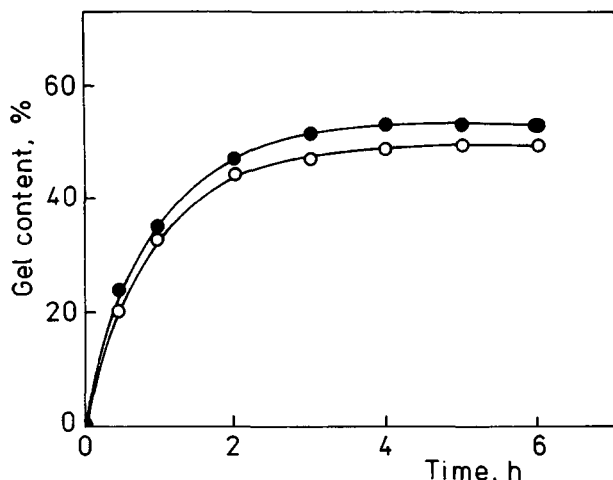


Figure 3 Cross-linking of plasticized PVC with grafted aminosilanes in steam at 100°C: (○) ATES; (●) ATMS.

ison with cross-linking in water at the same temperature (Table III) that the rate constant for MTMS decreased by almost one order of magnitude.

Unplasticized PVC was completely cross-linked at 80°C after approximately 30 days of exposure, in sharp contrast to the value for cross-linking in water (Fig. 4) and the k value was only $4.8 \times 10^{-5} \text{ min}^{-1}$. These values are almost the same as for the cross-linking of silane-grafted PE under similar conditions.⁹

A possible explanation for the much slower cross-linking of rigid PVC could be the lower diffusion of water from the air compared with the plasticized system. To evaluate the effect of this diffusion, identical exposure was carried out in an oven at 80°C for plasticized and unplasticized samples wrapped in aluminum foil. It follows from the results given in Table IV that diffusion of water from the external

Table II Rate of Cross-linking of Silane-grafted PVC and the Time Required for Cross-linking in Steam at 100°C

Silane	Rate Constant (min^{-1})		Time Required for Cross-Linking (h)	
	Plasti-cized	Unplasti-cized	Plasti-cized	Unplasti-cized
MTMS	0.0146	0.0125	6	7
MTES	0.0075	0.0036	12	26
ATES	0.0220	—	5	—
ATMS	0.0250	—	4.5	—

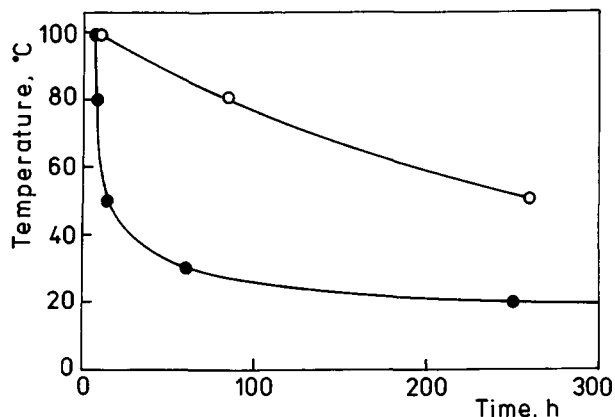


Figure 4 Dependence of the time required for cross-linking on the water temperature for plasticized PVC with grafted (●) MTMS and (○) MTES.

environment has practically no effect on the cross-linking. The cross-linking reaction apparently occurs through the water contained in the reaction mixture.

Consequently, the possibility of increasing the water content in mixtures through short-term exposure (1 h) to steam at 100°C prior to cross-linking in the air at 80°C was tested. It is apparent from the results in Table V that, for plasticized PVC, the cross-linking was only shifted by the initial gel content formed during the exposure to the steam. For unplasticized PVC, the rate constants slightly increased with the "steaming" time, indicating that this increase in the water content increases the reaction rate under these conditions. In addition, the steaming eliminated the relatively long induction period (at least 24 h).

These data thus confirm that the much lower rate of the cross-linking reaction of unplasticized PVC

Table III Rate of Cross-linking of PVC with Grafted MTMS in Dependence on the Temperature of Water

Temperature (°C)	Rate Constant (min^{-1})	
	Plasticized PVC	Unplasticized PVC
100	0.01460	0.0125
80	0.00810	0.0031
50	0.00460	—
30	0.00117	—
20	0.00012	—

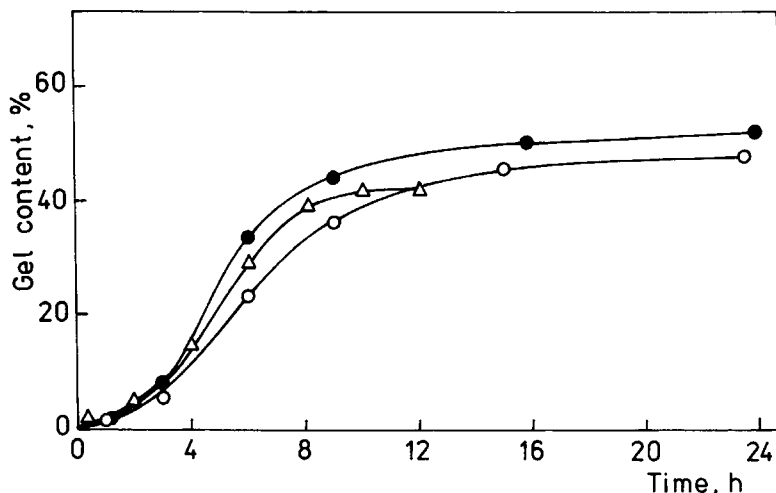


Figure 5 The cross-linking of plasticized PVC in the air at temperatures of 80 and 100°C: (○) ATES at 80°C; (●) MTMS at 80°C; (△) MTMS at 100°C.

above T_g is primarily a result of its lower water content (as a consequence of the low permeability for water vapor) and the rate of the cross-linking is more diffusion-controlled compared to the plasticized mixture.

Dependence of the Cross-linking Rate on the Air Temperature

The gel content was measured after 24 h exposure in an oven at various temperatures. It follows from the dependence in Figure 6 that the cross-linking of plasticized PVC with grafted ATES is fastest, with a maximum gel content at a temperature of 80°C. A further increase in the gel content above 130°C reflects only the consequences of degradation cross-linking, corresponding to the relatively low thermal stability of aminosilane (or other amino compound)-grafted PVC. It is apparent from the similar

Table IV Cross-linking of Silane-grafted PVC at 80°C

Silane	PVC	Exposure Time (h)	Gel Content (%)	
			In the Air	Air Excluded
MTMS	Plasticized	24	55	55.0
ATES	Plasticized	24	52	51.5
MTMS	Unplasticized	24	1	1.0
MTMS	Unplasticized	112	35	34.0

dependence for the plasticized PVC with grafted mercaptosilane (MTMS) that, under the experimental conditions, additional degradation cross-linking does not occur, as the maximum attainable gel content is 63%.

The cross-linking of rigid PVC in the test interval is similar to that for exposure in water (Table III); it occurs at temperatures above 80°C only (Fig. 6).

Cross-linking during exposure to the air at 20°C occurs only very slowly (Fig. 7). A rate constant value of $3.7 \times 10^{-6} \text{ min}^{-1}$ was found for a plasticized PVC with grafted ATES; this parameter for a mixture with MTMS could be found only for the initial interval of about 200 days ($3.4 \times 10^{-6} \text{ min}^{-1}$). Further, the reaction becomes much slower as the cross-linking increases (Fig. 7). (The maximum gel content in the mixture was 63%.) No gel was found in unplasticized PVC under these conditions, in agreement with the values found for cross-linking in water (Table III).

The temperature dependence for cross-linking in the air is greater than that in water. For plasticized mixtures, the rate constant value increased on an increase in the water temperatures from 20 to 80°C by about two orders of magnitude (Table III), while the value in the air increased by approximately three orders (Table I).

The Effect of the Sample Thickness on the Cross-linking

It is apparent from the cross-linking of the individual layers of plasticized PVC grafted with MTMS in

Table V Cross-linking of Silane-grafted PVC in Steam at 100°C and Then in the Air at 80°C

Plasticized MTMS- and ATES-Grafted PVC						
Steaming Time (h)	Gel Content (%)					
	After Steaming		After 24 h at 80°C		After 48 h at 80°C	
	MTMS	ATES	MTMS	ATES	MTMS	ATES
0.0	0	1	50	52 ^a	63 ^a	52 ^a
0.5	42	36	57	52 ^a	63 ^a	52 ^a
2.0	53	48	63 ^a	52 ^a	—	—

Unplasticized MTMS-Grafted PVC							
Steaming Time (h)	Gel Content (%)						Rate Constant (min ⁻¹)
	Reaction Time (h) at 80°C						
	0	1	4	8	11	16	
0	0	1	35	42.5	49	56	4.8×10^{-5}
1	18	33	53	57.5	67	70	5×10^{-5}
3	55	62	68.5	71.3	77	82	5.7×10^{-5}

^a Maximum values.

Figure 8 that the cross-linking of the central layers initially occurs only through water contained in the material; the reaction is comparable with that of a

similar mixture in the air at a temperature of 100°C (Fig. 5), where diffusion of water from the external environment was also not a factor. The subsequent

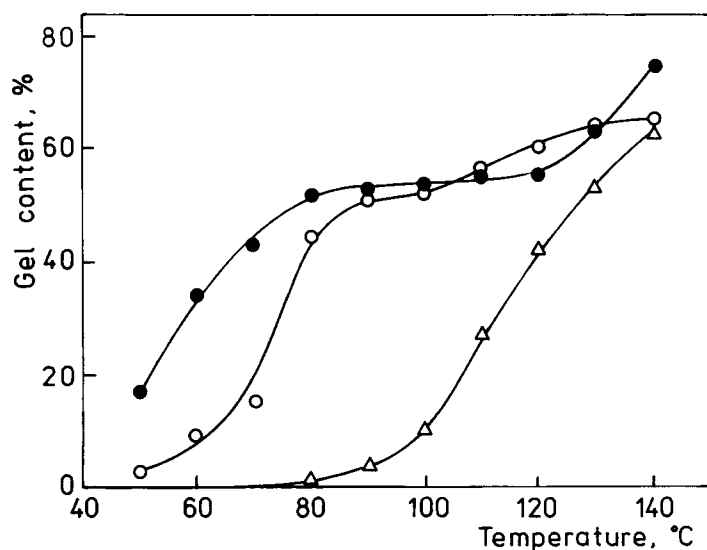


Figure 6 Dependence of the gel content after 24 h exposure in air on the temperature: (O) plasticized PVC with grafted MTMS; (●) plasticized PVC with grafted ATES; (Δ) unplasticized PVC with grafted MTMS.

cross-linking of the central layer reflects the relatively fast diffusion of water into the bulk of the plasticized PVC. Because of these two factors, the cross-linking of plasticized PVC is practically independent of the sample thickness and even a sample with a thickness of 10 mm is cross-linked after 7 h exposure in steam.

CONCLUSIONS

Cross-linking by water occurs fastest for plasticized PVC with grafted aminosilanes and the reaction of MTMS is comparable with that for PE. A surprisingly low cross-linking rate was found for mixtures with grafted MTES (apparently as a result of the length of the alkyl chain). The cross-linking of unplasticized PVC with grafted MTMS above 80°C is only slightly slower; however, below this temperature, practically no cross-linking occurs, indicating a critical dependence on the chain mobility. For plasticized PVC, the cross-linking occurs sufficiently fast through simple exposure to the air at elevated temperatures, where practically only the water contained in the mixture is utilized and diffusion from the external environment is not a factor. These facts also confirmed the determined low dependence of the cross-linking on the sample thickness.

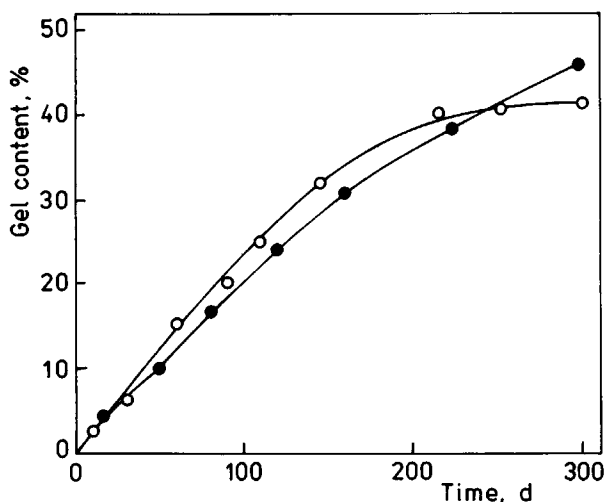


Figure 7 Cross-linking in the air at 20°C for plasticized PVC with grafted 3-mercaptopropyl trimethoxysilane (○) and 3-aminopropyl trimethoxysilane (●).

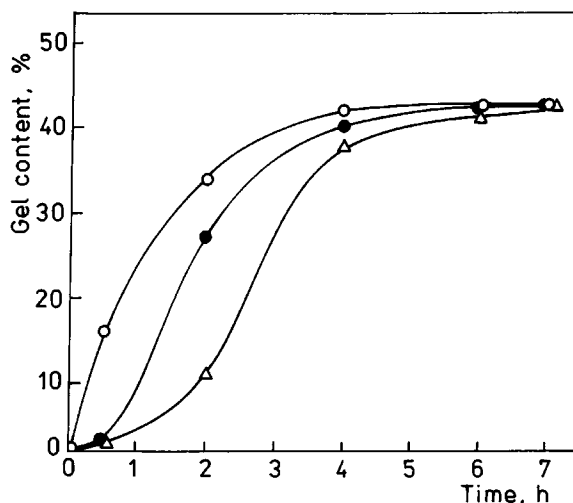


Figure 8 Cross-linking of the layers of a 10-mm sample of plasticized PVC with grafted MTMS in steam at 100°C: ○, 0-1-mm layer (surface); ●, 2-3-mm layer; △, 4.5-5.5-mm layer (center).

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