

Silane Cross-linking of PVC. I. Grafting of Mercaptoalkylalkoxysilanes onto PVC: Properties of the Grafted and Cross-linked Product

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SYNOPSIS

The reaction of poly(vinyl chloride) (PVC) with mercaptoalkyltrialkoxysilanes yielded silane-grafted PVC that can be cross-linked by the hydrolytic mechanism. The grafting of the silanes on the plasticized and unplasticized PVC was carried out at 180°C during processing in the presence of basic lead-containing stabilizers. The reaction is favorably affected by the presence of plasticizers and lubricants containing polar, preferably ester, groups. The silane-grafted and cross-linked polymers have satisfactory thermal stability. The results of strength measurements at elevated temperatures after cross-linking by water indicate that the material obtained has greatly improved parameters that are suitable for a number of applications. © 1993 John Wiley & Sons, Inc.

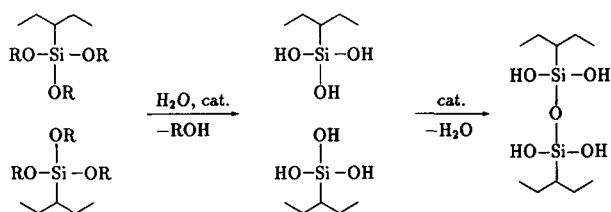
INTRODUCTION

One of the most important ways of improving polymer quality is by cross-linking, which primarily produces better thermal shape stability, improved resistance to solvents, lower permanent deformation, etc.

The cross-linking of poly(vinyl chloride) (PVC) using peroxides or radiation is poorly efficient and the presence of suitable coagents is essential.^{1,2} These cross-linked PVCs have decreased thermal stability and are often discolored. In addition, PVC can be cross-linked using a number of chemical reagents, where the best results were obtained for multifunctional organic mercapto compounds.³⁻⁶ Even in this case, practical applications are prevented especially by processing limitations and also by the decreased thermal stability of the products.

For polyolefins, especially polyethylene (PE), silane cross-linking has been used successfully since the 1970s; this method has a number of advantages compared to peroxide or radiation cross-linking.⁷ Basically, the first step involves the preparation of

the silane (e.g., vinyltrimethoxysilane)-grafted polymer⁸ using peroxides. More recently, the copolymers of ethylene with vinylsilanes have been produced directly.⁹ These polymers are cross-linked after treatment using water or atmospheric humidity in the presence of a suitable catalyst, according to the following reaction scheme:



The first known attempt to silane cross-link PVC is described in a patent awarded to the Dow Corning Co. for the copolymer of vinylsilane with vinyl chloride.¹⁰ A further patent by the same company describes the use of aminosilanes for hydrolytic cross-linking of PVC, where grafting occurred during processing.¹¹ However, in these compounds, the basicity of the amino group leads to elimination of HCl¹²; a decrease in the thermal stability is accompanied by premature cross-linking during the grafting process.¹³ Japanese patents describe the reaction of 3-

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mercaptopropyltrimethoxysilane with halogenated polymers in the presence of various organic amino compounds¹⁴⁻¹⁶ or, e.g., the complex of mercaptosilane with the organic compounds of cadmium.¹⁷

Thus, further additives are necessary for the grafting of mercaptosilanes, which, however, increase the sensitivity of the halogenated polymer to degradation, reflected in the fact that the reactions were carried out at temperatures below 100°C.¹⁴⁻¹⁷

A mixture of PVC with silane-grafted chlorinated PE¹⁸ or ethylene-vinyl acetate copolymer¹⁹ has also been described as cross-linked PVC. A blend of PVC with the copolymer of 3-methacryloyloxypropyltrimethoxysilane with various acrylates has also been patented.²⁰

It is apparent from the work on the cross-linking of PVC with mercapto compounds, especially the derivatives of dimercaptotriazine, that, at processing temperatures in the presence of suitable compounds (MgO, polyols), these compounds can bond onto the PVC chain through nucleophilic substitution of the Cl atom without great participation of competitive elimination of HCl. No detailed study of the thermal stability of these cross-linked PVCs has been published yet.

Consequently, this work was carried out on the grafting of mercaptosilanes to PVC in the presence of suitable thermal stabilizers, where sufficiently high thermal stability of the grafted and cross-linked products was retained.

EXPERIMENTAL

Materials

PVC: Neralit 702 (Chemopetrol, Czechoslovakia)—a suspension PVC ($K = 70$); Slovinyl 702 (CHZWP Nováky, Czechoslovakia)—emulsion paste-forming PVC ($K = 70$); di(2-ethylhexyl)phthalate (DOP, Urxovy závody, Czechoslovakia); Loxiol G 30 (Henkel, FRG)—C₃₂-fatty acid ester; Austrostab MCS 20—tribasic lead sulfate (BWU, Austria); 3-mercaptopropyltrimethoxysilane (MTMS) (Wacker-Chemie, FRG)—bp 212°C; 5-mercaptopentyltriethoxysilane (MTES) (UTZCHT Prague, Czechoslovakia); dibutyltin dilaurate (DBTDL)—Sn content 12.5%.

Composition of PVC mixtures (in parts by weight): Unplasticized PVC: Neralit 702 100 p., thermal stabilizer 6 p., lubricant 1 p., DBTL 0.05 p., silane 1.5–8 p. Plasticized PVC: Neralit 702 100 p., DOP 50 p., thermal stabilizer 5 p., DBTDL 0.05 p., silane 2–8 p. PVC paste: Slovinyl 702 100 p., DOP

70 p., thermal stabilizer 3 p., DBTDL 0.05 p., silane 2–10 p.

Preparation of Silane-grafted PVC

The grafting of silanes on plasticized and unplasticized PVC occurs simultaneously with kneading of the dry mixture in the W50 chamber of a Brabender PlastiCorder at 60 rpm. The material was usually blended for 10 min at 180°C. After removing it from the chamber, the mixture was immediately pressed to form plates with dimensions of 150 × 150 × 1.5 mm at a temperature of 175°C for 3 min, followed by cooling in a cold press at laboratory temperature.

The pastes were prepared in a Collin 111 mixer; the thermal stabilizer was first ground in a mortar with a small amount of plasticizer. The 0.5 mm foil was fused in a Werner Mathis apparatus at a temperature of 180°C for 15 min.

Cross-linking of Silane-grafted PVC

This process was carried out for a period of 6 h, where the samples were suspended in steam at a temperature of 100°C.

Analyses

The degree of grafting of silane on the PVC was evaluated indirectly on the basis of the degree of cross-linking after exposure in water. The gel content was determined after extraction with boiling tetrahydrofuran for 12 h. The gel content values for the plasticized mixtures were not recalculated to PVC. Further, the cross-linking density was determined by swelling the samples in cyclohexane at laboratory temperature for 15 days. Calculations were carried out using the Flory-Rehner equation²¹; the interaction parameter for the PVC-cyclohexane system has a value of 0.249.

Thermal Stability

The time period during which HCl is not lost from the sample at a temperature of 200°C was evaluated.

Strength Tests

The strength at break and the corresponding elongation of the samples were measured on an Instron 1122 instrument. The crosshead speed was 50 mm/min. Measurements were carried out at laboratory

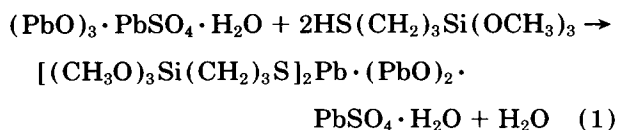
temperature and at 80, 100, 120, and 150°C using a heated chamber in the clamp space.

The change in the properties of the grafted plasticized PVC with the storage time was characterized by the study of the pressure deformation with increasing temperature at time intervals of 4 h and 1, 4, and 21 days after grafting of silane. This method²² is based on the study of the deformation of the material with a thickness of approximately 1 mm by a tip with an area of 1 mm², to which a variable load in the range 4–5 N and frequency of 1 Hz is applied. The sample was heated at a rate of 6°C/min in the range 50–250°C.

RESULTS AND DISCUSSION

The Effect of Thermal Stabilizers on the Grafting of Mercaptosilanes

The grafting of MTMS on plasticized and unplasticized PVC stabilized with basic types of thermal stabilizers was studied. It can be seen from the results in Table I that, under the test conditions, grafting occurred only in the presence of basic lead salts. This is probably a consequence of their ability to form a nucleophilic agent from the MTMS with a poorly reactive thiol group. These stabilizers react with MTMS at laboratory temperature to yield a yellow compound according to eq. (1):

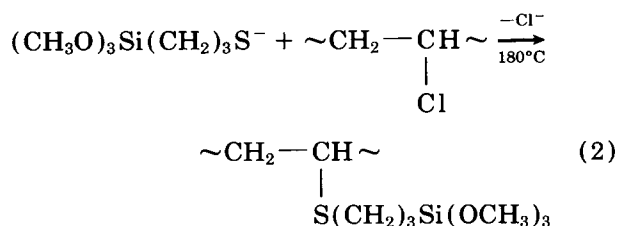


Dissociation of this compound at processing temperatures then leads to the formation of the thiolate

Table I Effect of the Thermal Stabilizer (5 phr) on the Gel Content in PVC Grafted with MTMS (5 phr) for 10 min at 180°C

Type of Stabilizer	Gel Content (%)	
	Plasticized PVC	Unplasticized PVC
Ba/Cd soap	0	0
Ca/Zn soap	0	0
Organotin (IV)	0	0
Tribasic lead sulfate	66	85
Dibasic lead sulfate	60	78
Dibasic lead stearate	61	—

anion, which is capable of substituting a chlorine atom in the PVC chain according to eq. (2):



Plasticized mixtures containing further lead(II) compounds as given in Table II were also yellow in color, but grafting with silane occurred only for PbO. It is further evident from these results that even a combination of basic lead stabilizers or PbO with the other types of stabilizer does not lead to the grafting reaction in the test period (max. 20 min). Grafting practically also did not occur in the mixture without stabilizer, where the mercaptosilane was activated using various organic amino compounds (e.g., tributylamine, hexamethylene diamine, diphenylamine), glycols (polyethylene glycol, diethylene glycol), or metal oxides (MgO, ZnO). These compounds had a positive effect only in presence of basic lead stabilizers.

Because of the relatively short reaction times (10–20 min), it cannot be excluded that these negative results are only a consequence of considerable slowing of the grafting reaction of MTMS on the PVC chain. However, at longer grafting times at the given temperatures, the reaction could be greatly affected by degradation processes, especially for mixtures without thermal stabilizers.

The Effect of the Amount of Mercaptosilane and Tribasic Lead Sulfate

It is apparent from the dependence in Figure 1 that, under the given grafting conditions (10 or 15 min at 180°C) and at a content of 5 phr of tribasic lead sulfate, the maximum gel content is achieved for plasticized and unplasticized mixtures at an MTMS content of about 5 phr. The relatively great increase in the gel content at an amount of silane equal to about 2 phr is connected with attainment of the gel point. The slower dependence obtained for the plasticized PVC obtained by fusion of the paste can apparently be attributed to the considerable dilution of the polymer by the plasticizer.

Under the same conditions, the gel content and thermal stability were studied in dependence on the content of tribasic Pb sulfate at an MTMS content of 5 phr. The curves in Figure 2 are similar in shape

Table II Effect of Further Additives on the Gel Content in Plasticized PVC Grafted with MTMS (5 phr) at 180°C

Compound	Amount (phr)	Stabilizer ^a	Processing Time (min)	Gel Content (%)
PbO	5	—	10	63
Pb stearate	5	—	15	0
Basic Pb acetate	5	—	15	2.5
MgO	5	—	15	0
Diethylene glycol	5	—	15	0
PEG 600	5	—	15	0
PbO	5	Ba/Cd soap	12	0
PbO	5	Ca/Zn soap	12	0
PbO	5	Organotin	12	0
ZnO	5	Ba/Cd soap	12	2
1-Naphthylamine	1	Ba/Cd soap	12	0
1-Naphthylamine	1	Ca/Zn soap	12	2
Tribasic Pb sulfate	5	Ba/Cd soap ^b	10	1

^a 5 phr.^b 3 phr.

to those for increasing contents of MTMS (Fig. 1); however, for the unplasticized mixture, the gel point is shifted to lower amounts of stabilizer compared to the plasticized PVC, apparently connected with the better dispersibility of the solid stabilizer as a consequence of the higher shearing forces in blending of unplasticized PVC.

Sufficient cross-linking was achieved in both mixtures at a stabilizer content of 5–6 phr, i.e., at a weight ratio of silane and stabilizer of about 1 : 1 (molar ratio of about 5 : 1). As mentioned above, silane reacts with the basic Pb stabilizer exotherm-

ically to form a solid yellow compound according to eq. (1). As the mixtures usually contain a fivefold molar concentration of MTMS compared to stabilizer, reaction to a higher degree can be expected (reaction of 2–3 PbO). In addition, the reaction occurs in practice first on the surface of the stabilizer particles during the preparation of the dry mixture and thus the stabilizer cannot react quantitatively. The better distribution of the stabilizer during the blending of the unplasticized PVC and also the fact that the mixture is not diluted by the plasticizer apparently led to the presence of the gel at approx-

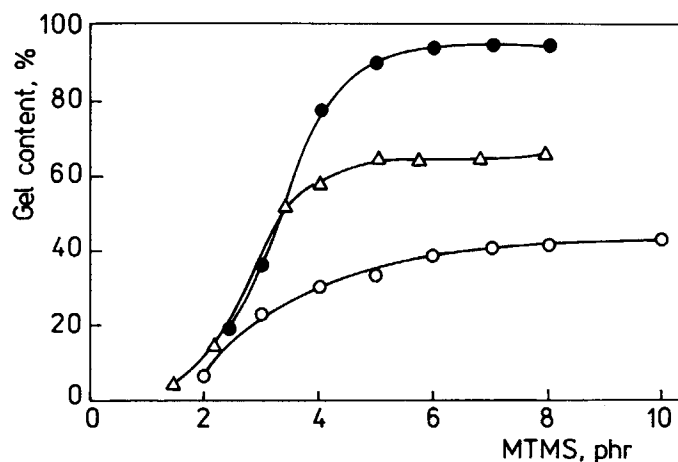


Figure 1 Dependence of the gel content on the amount of MTMS: (Δ) plasticized PVC, processed for 10 min at 180°C; (\bullet) unplasticized PVC, processed for 10 min at 180°C; (\circ) PVC paste, fusion for 15 min at 180°C.

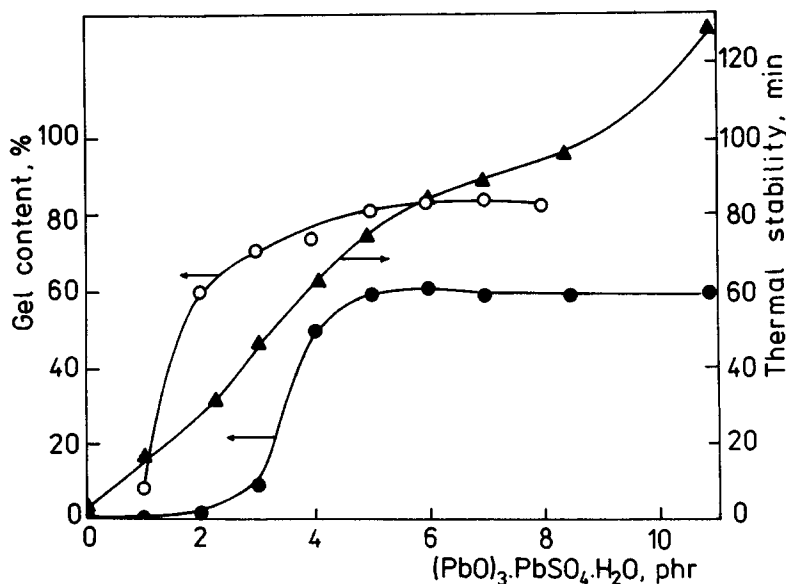


Figure 2 Dependence of the gel content and thermal stability on the content of tribasic lead sulfate: (\blacktriangle , \bullet) plasticized mixture containing 5 phr MTMS; (\circ) unplasticized mixture containing 5 phr MTMS; processed for 10 min at 180°C.

imately one-half of the stabilizer content, i.e., 1 phr (Fig. 2) compared with plasticized PVC.

It is further apparent from Figure 2 that the reaction of the stabilizer [eq. (1)] and the grafting reaction of MTMS on PVC [eq. (2)] practically do not decrease the thermal stability.

The grafting of MTES on PVC was studied under conditions similar to those for MTMS; the results are given in Table III. It is apparent that this silane can also be employed for cross-linking PVC. Its higher molecular weight makes it necessary to employ larger amounts. In addition, it was found that the cross-linking with water is slower than for MTMS.²³

The Effect of the Processing Conditions

It follows from the dependence in Figure 3 that the efficiency of the grafting reaction increases with in-

creasing temperature. However, in practice, it is necessary to also bear in mind processing limitations, especially for plasticized mixtures. In case of unplasticized PVC, the participation of elimination reactions apparently increases at temperatures of about 200°C. This is also reflected in the observed partial cross-linking of these mixtures during grafting of silanes, apparently as a consequence of loss of HCl (Fig. 3).

The increase in the gel content with blending time of the plasticized PVC in the Brabender Plastograf is apparent from Figure 4. The relatively marked dependence on the blending intensity is apparent from the dependence of the gel content on the blender blade rotation rate in Figure 5. In addition to faster heating of the mixture during more intense blending, the improved homogenization, especially of the stabilizer, is important here. A further increase in the degree of cross-linking for the now insoluble polymer with the time of thermal exposure at a temperature of 180°C was studied in swelling tests. The increase in the cross-linking density is given in Table IV.

Table III Cross-linking of PVC with MTES

	Plasticized PVC				Unplasticized PVC
Amount of silane (phr)	3.4	4.3	5.1	6	5
Gel content (%)	34	49.5	59.5	61	53

The Effect of the Plasticizer

It is apparent from the values of the gel content in dependence on the plasticizer employed (Table V) that the grafting reaction occurs best in the presence

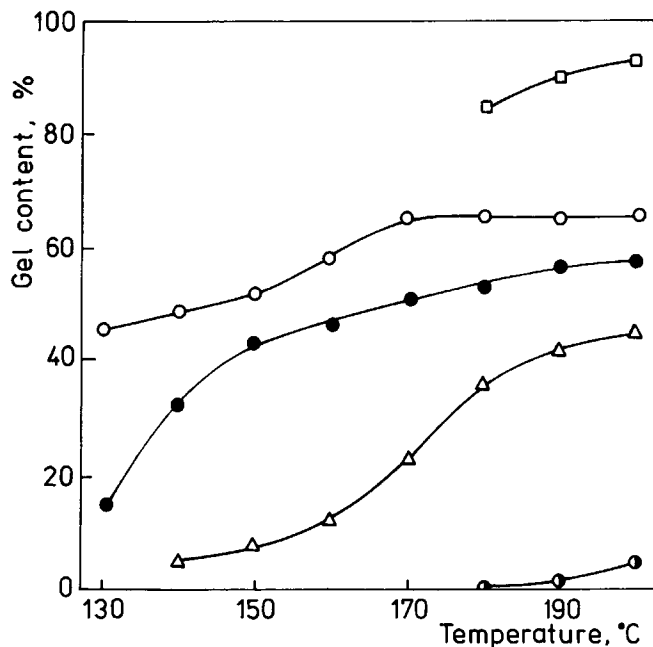


Figure 3 Dependence of the gel content on the processing temperature: plasticized PVC [(●) 3.4 phr MTMS, (○) 5 phr MTMS]; (△) PVC paste (5 phr MTMS); unplasticized PVC (6 phr MTMS) (●) after grafting with silane, (□) after cross-linking by water.

of plasticizers containing ester groups. The favorable effect of these polar groups is best seen for the esters of phthalic acid, where the gel content decreases with increasing shielding by higher alkyls (Table V). This fact is in agreement with data found for the cross-linking of PVC by derivatives of dimercaptotriazines, where the reaction rate increased with increasing plasticizer polarity.²⁴

The thermal stability values given in Table V are approximately 10% lower than those for similar mixtures without grafted silanes and correspond well to the known effect of the type of plasticizer on the thermal stability of PVC: The highest values were obtained for DOP. It is apparent from the dependence of the gel content on the DOP content in the PVC paste (Fig. 6) that dilution with the plasticizer

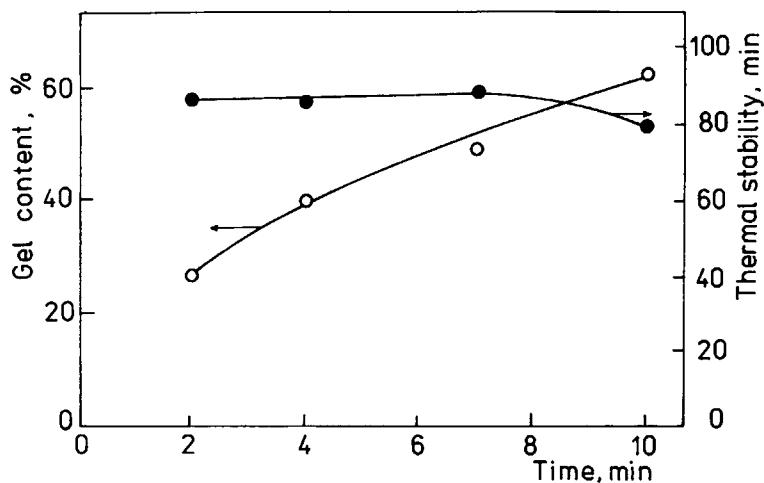


Figure 4 Dependence of the gel content and thermal stability of plasticized PVC on the processing time.

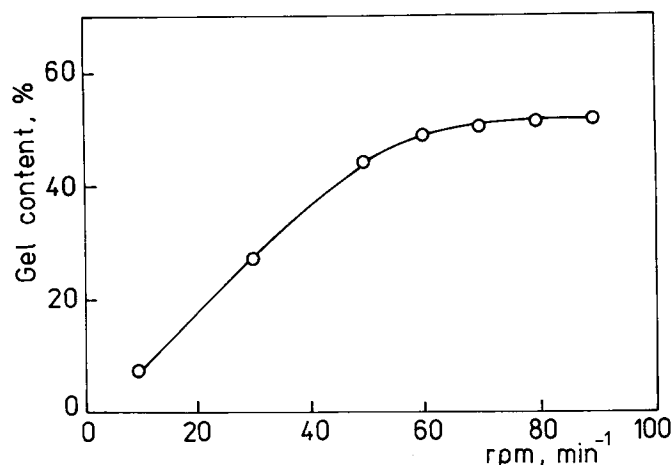


Figure 5 Dependence of the gel content on the velocity of the Brabender Plastograf blades for plasticized PVC (blending time 10 min).

only slightly decreases the efficiency of grafting with MTMS. Thus, highly plasticized systems can be cross-linked.

In the presence of tributyl phosphate (Table V), the gel was found to be present (6%) after the grafting reaction and thus the use of the esters of organic acids seems preferable.

Mechanical Properties of Silane-cross-linked PVC

It can be seen from the dependence of the strength and elongation on the gel content (Fig. 7) for a mixture containing 70 phr plasticizer that the strength increases with increasing cross-linking at both the test temperatures, i.e., 20°C and 120°C.

The dependence of the strength and elongation on the temperature were studied in greater detail on mixtures containing 50 phr plasticizer at three different gel contents (14, 29, and 63%). The decrease in the strength of these samples with increasing temperature is apparent from Figure 8; at 150°C, the strength at a gel content of 63% attained a value of almost 2 MPa. The strength of the uncross-linked samples was practically zero at temperatures greater than 80°C.

The variation of the elongation with the gel content at various temperatures is interesting (Fig. 8). At temperatures of 20 and 80°C, the elongation decreases with increasing cross-linking, similarly as for more plasticized samples from pastes [Fig. 7]; at temperatures above 80°C, the more cross-linked samples have higher elongation and the dependence is similar to that for the strength [Figs. 7 and 8]. This is apparently a result of the fact that, at lower gel contents, the structure of the network is not yet sufficiently homogeneous and the sample is thus destroyed at lower elongation. In general, the dependence of the elongation on the temperature always passes through a maximum, which is shifted to higher temperatures with increasing degree of cross-linking.

Table VI gives the strength and ductility values for unplasticized PVC at temperatures of 20, 120, and 150°C. It is apparent that the dependence is similar to that for the plasticized mixture containing 50 dsp of plasticizer (i.e., a gradual decrease in strength, first an increase in elongation at 120°C, and then a decrease at 150°C). However, the great increase in the elongation at elevated temperatures is quite different; here, similar values to those for plasticized mixtures were obtained (Fig. 8).

Table IV Dependence of the Cross-linking Density in PVC on the Processing Time at 180°C

	Plasticized PVC		Unplasticized PVC	
	7	12	5	10
Processing time (min)	7	12	5	10
Gel content (%)	93.5	94	63	63
Cross-linking density (mol m ⁻³)	57	94.5	12.7	14.6

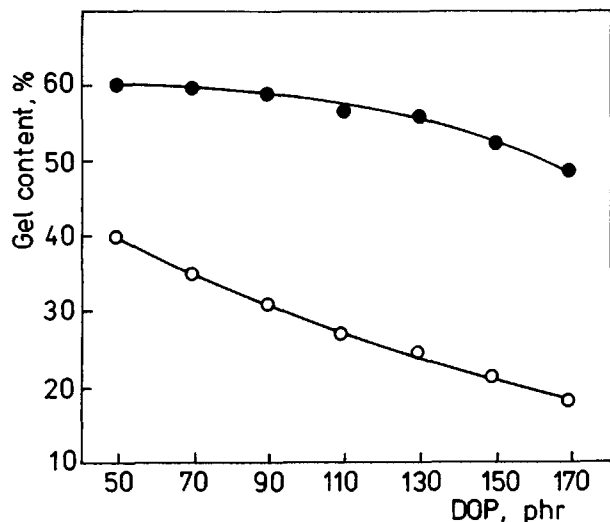


Figure 6 Dependence of the gel content on the content of DOP in PVC paste (5 phr MTMS, fusion for 15 min at 180°C): (○) gel content in the mixture; (●) gel content recalculated to PVC.

The Properties of Silane-grafted PVC

Because of the relatively high content of silane either grafted to the PVC chain or freely distributed in the mixture, it seemed useful to study the change in the properties of cross-linkable PVC with the storage time in the absence of a condensation catalyst, especially taking into consideration the decreased

Table V The Effect of the Type of Plasticizer on the Gel Content and Thermal Stability of Plasticized PVC (5 phr MTMS, Kneaded for 10 min at 180°C)

Plasticizer	Gel Content (%)	Thermal Stability (min)
Diethyl phthalate	69	66
Dibutyl phthalate	60	65
Di(2-ethylhexyl) phthalate	63	78
Diisodecyl phthalate	58	72
Di(tridecyl) phthalate	24	—
Di(2-ethylhexyl) adipate	59	74
Diocetyl sebecate	16	—
Tricresyl phosphate	45	—
Tributyl phosphate	53	—
Epoxidized butyl esters of fatty acids	0	—
Butadiene-fumaric acid copolymer	30	—

processability of the material. It was found that this effect can best be studied using a method in which the variation in the pressure deformation (penetration of a tip loaded by a constant force into the sample) is studied in dependence on the temperature. Figure 9 indicates that this method can also be used to characterize the degree of cross-linking, as es-

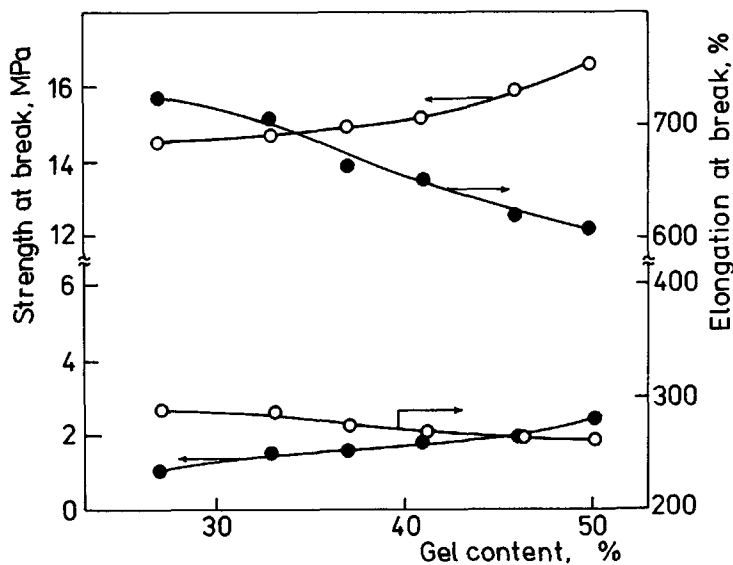


Figure 7 Dependence of the strength and elongation at break on the gel content for plasticized PVC from paste containing 70 phr DOP: (○) 20°C; (●) 120°C.

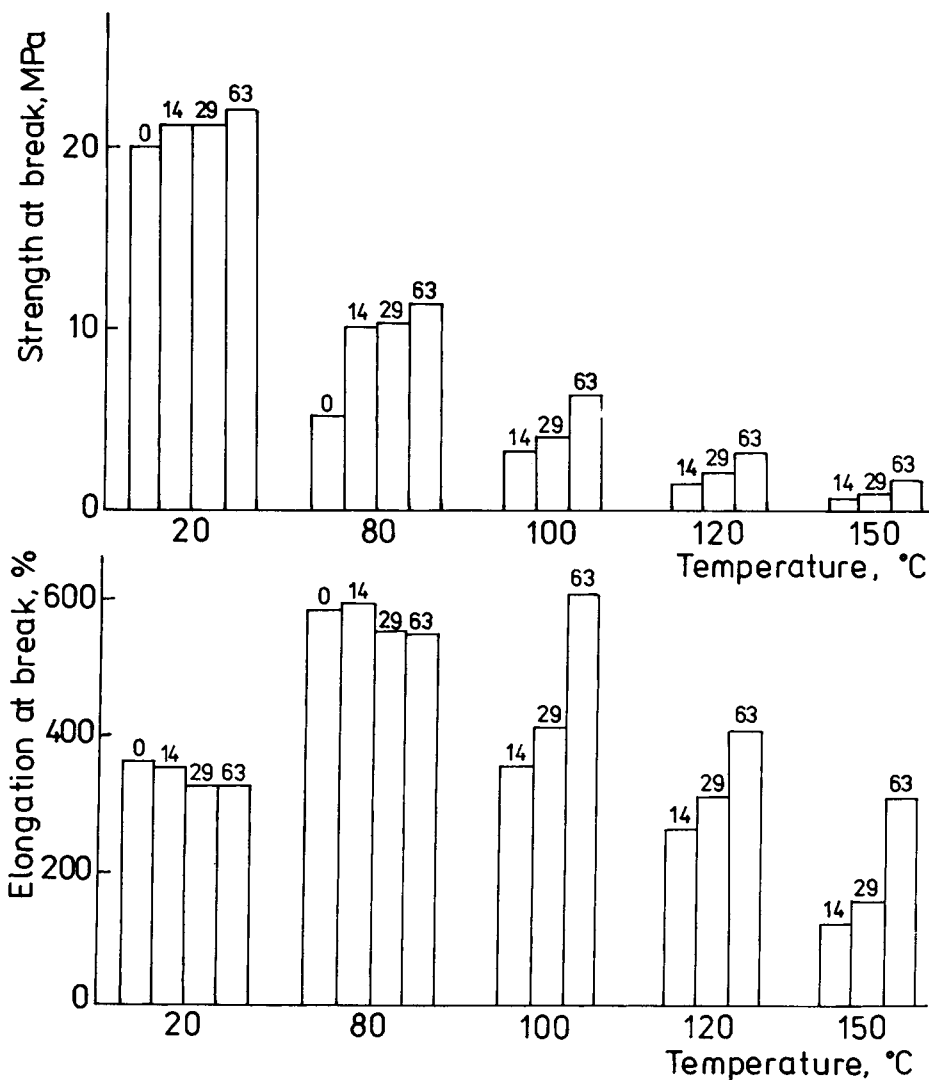


Figure 8 Dependence of the strength and elongation at break of plasticized PVC (50 phr DOP) on the temperature for various degrees of cross-linking (the numbers in the columns are the corresponding gel contents in %).

pecially incomplete deformation at temperatures of about 250°C corresponds well to the determined gel content.

The pressure deformation was studied for a plasticized mixture with grafted MTMS (Fig. 10), MTES (Fig. 11), and also aminosilane¹³ (Fig. 12) (samples without DBCDL). The measurements were carried out immediately after grafting of the silane and then after 1, 4, and 21 days.

It is apparent from the dependencies in Figures 10 and 11 that the deformation at temperatures above 200°C was maximal for mixtures with mercaptosilanes, i.e., the samples did not contain a gel. In addition, these samples were still completely soluble in THF after 12 months; consequently,

branching of the macromolecule (i.e., an increase in the mol. wt.) through condensation reactions with the grafted silane can be practically excluded in the

Table VI Tensile Tests of Unplasticized PVC Cross-linked with MTMS

Temperature (°C)	Strength at Break (MPa)		Elongation at Break (%)	
20	46 ^a	45.5 ^b	23 ^a	25 ^b
120	6.1 ^a	6.3 ^b	290 ^a	370 ^b
150	1.85 ^a	2.7 ^b	200 ^a	215 ^b

^a Gel content 48%.
^b Gel content 85%.

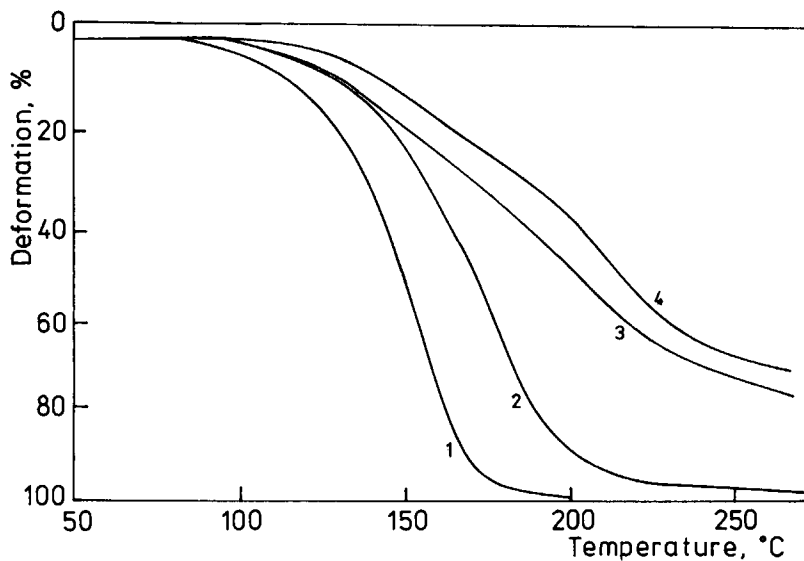


Figure 9 The variation in the pressure deformation with increasing temperature for plasticized PVC with various gel contents: (1) 0%; (2) 12%; (3) 27%; (4) 63%.

test period of 21 days. On the contrary, the incomplete deformation of samples with grafted aminosilane (Fig. 12) is connected with both the determined gel content after grafting and the tendency

of the aminosilanes to undergo further cross-linking even in the absence of a condensation catalyst.

On the other hand, the shift of the beginning of pressure deformation to higher temperatures com-

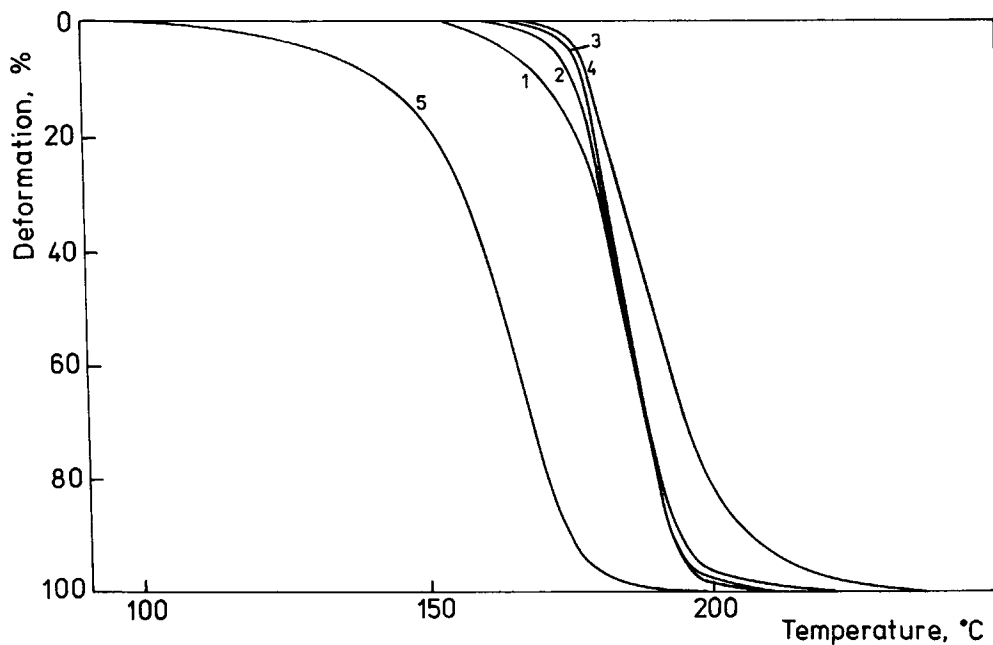


Figure 10 The variation in the pressure deformation with increasing temperature for plasticized PVC with grafted MTMS at various times after grafting: (1) 4 h; (2) 24 h; (3) 4 days; (4) 21 days; (5) ungrafted.

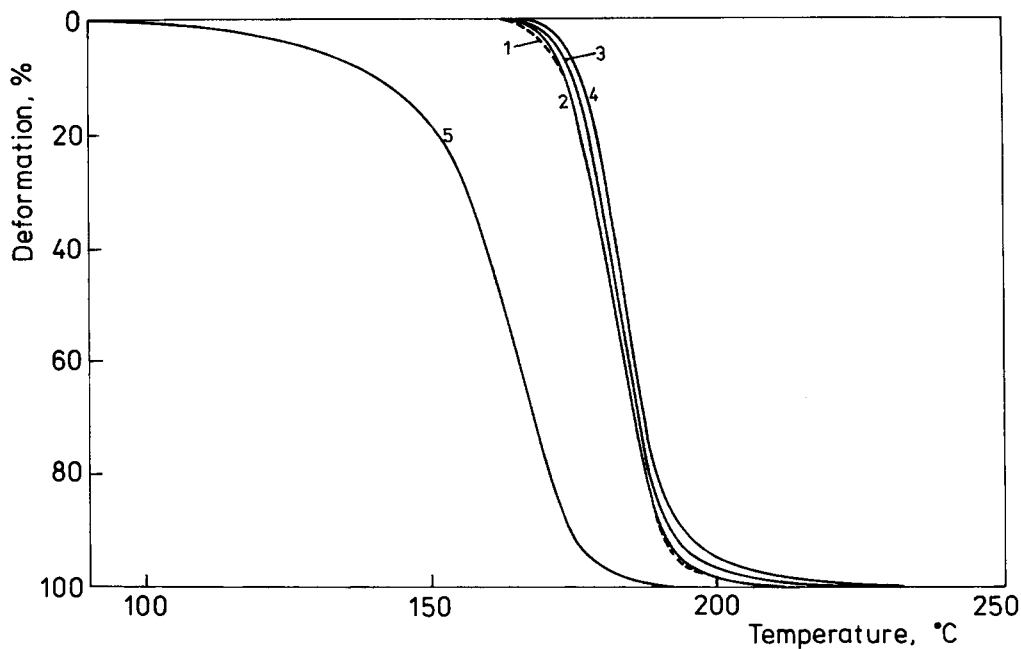


Figure 11 The variation in the pressure deformation with increasing temperature for plasticized PVC with grafted MTES at various times after grafting: (1) 4 h; (2) 24 h; (3) 4 days; (4) 21 days; (5) ungrafted.

pared to samples without silane (Figs. 10-12) and the decrease in the rate of the deformation with increasing temperature in the range approximately 170-220°C with storage time indicates a certain de-

gree of hardening of the mixture in the presence of silanes.

The smallest differences between the shapes of the individual curves at various times were observed

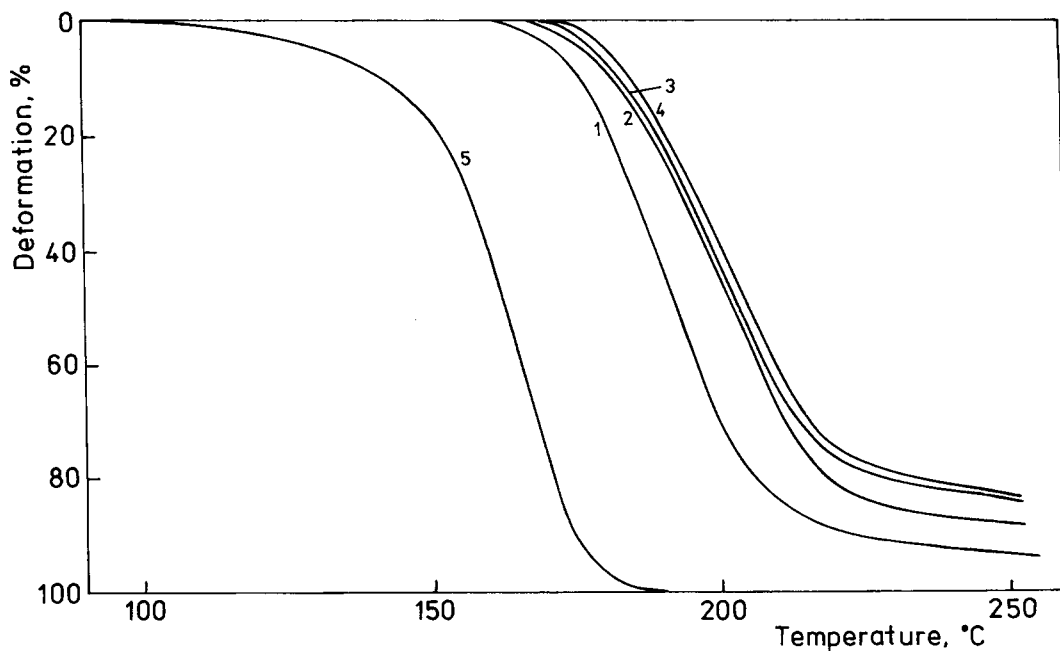


Figure 12 Variation in the pressure deformation with increasing temperature for plasticized PVC with grafted ATES at various times after grafting: (1) 4 h; (2) 24 h; (3) 4 days; (4) 21 days; (5) ungrafted.

for MTES (Fig. 11), corresponding to the observed easy workability even after storage, apparently connected with the known low reactivity of this silane during the cross-linking reaction.²³ The more different shapes of the curves for mixtures with MTMS (Fig. 10) reflect its somewhat greater hardening, especially after 21 days storage. Finally, this effect of hardening is most evident for PVC grafted with 3-aminopropyltriethoxysilane (ATES) (Fig. 12).

CONCLUSIONS

The possibility of grafting MTMS and MTES onto PVC was studied in order to obtain a water-cross-linkable product. It was found that both these silanes can be grafted under suitable conditions on the PVC chain through nucleophilic substitution of the Cl atom. However, the presence of basic lead stabilizers is essential as they form the actual nucleophilic reagent through reaction with silane.

The reaction is favorably affected by the presence of plasticizers and lubricants containing polar, preferably ester, groups. The grafting proceeds sufficiently rapidly at temperatures of about 180°C, so that it can be carried out during the processing of the PVC mixture.

It was found in examination of the effect of further compounds on the grafting of mercaptosilane that other thermal stabilizers minimally decelerate this reaction even at relatively low contents. In contrast, the grafting reaction even occurs in the presence of relatively high plasticizer contents and PVC pastes can be cross-linked. It was found from measurements of the dependence of the pressure deformation on the temperature that the relatively high silane contents in the mixtures (grafted onto PVC or free) lead to a certain "hardening" during storage, which decreases the workability even in the absence of the condensation reaction of the alkoxy group of the silane. This negative effect was less marked for MTES. The measured strength and ductility values at elevated temperatures indicate that the hydrolytic cross-linking of PVC yielded a material with improved parameters and, for plasticized PVC, with almost unchanged thermal stability.

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