

# Thermal and Mechanical Properties of Silane-Crosslinked Poly(Vinylchloride)

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**ABSTRACT:** A comparative study has been made of the crosslinking of plasticized PVC by grafting of  $\gamma$ -aminopropyltriethoxysilane (ASi) and sodium  $\gamma$ -mercaptopropyltrimethoxysilane (NaMSi) during processing. The influence of type of reagent and concentration, and the rheological behavior were investigated to obtain a crosslinked material with improved mechanical properties and good thermal stability. Depending on the reagent concentration, different gel contents, ranging from 0–100%, were obtained with both reagents. For all crosslinked systems the mechanical properties above  $T_g$  were improved. In the case of ASi-crosslinked PVC, the thermal stability deteriorated significantly but, for NaMSi-crosslinked PVC, thermal stability remains close to that of raw PVC, and the separation of the grafting and crosslinking processes is more viable in this case. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 865–872, 1998

**Key words:** crosslinked poly(vinylchloride); organosilanes grafting; gel content; mechanical and thermal properties; reactive processing

## INTRODUCTION

The crosslinking of polyolefins and polyvinylchloride with organosilanes grafted on the polymer<sup>1–3</sup> has lead to improved properties and performance of polymers used in the production of electric cables and wires. Although a multistep process (first the introduction of a reactive group into the polymer chain, and second the crosslinking) has the advantage of easy characterization of the modified polymer leading to defined networks,<sup>4,5</sup> one-step crosslinking processes, which lead directly to a network structure, are feasible processes if the polymer is not too reticulated during processing.

Continuous and discontinuous reactive processing of PVC has been extensively studied in the literature,<sup>6–10</sup> but only a few studies have been published by different authors concerning silane crosslinking of PVC,<sup>11–16</sup> in which aminosilanes are reported to be the most reactive. Other authors claim that aminosilane crosslinked PVC is very unstable, while mercaptosilane crosslinked PVC is more stable, although with a lower reactivity. In previous work in our laboratory<sup>17</sup> we carried out a preliminary study, which, on the one hand, investigated crosslinking reactions of PVC with amino- and mercaptosilanes, and on the other, crosslinking of the azide-modified polymer (PVC-N<sub>3</sub>) with vinyl- and acryloxysilanes, and in which the processing conditions for the reaction were established.

The objective of this article is to compare the thermal and mechanical properties of polyvinylchloride crosslinked with  $\gamma$ -aminopropyltriethoxysilane and  $\gamma$ -mercaptopropyltrimethoxysilane.

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**Table I** Experimental Conditions and Formulations Employed in the Processing of PVC with Organosilanes

Organo Silane	Silane Conc.		DOP (phr)	DBTDL (phr)	Stearic Acid (phr)	Temp (°C)	Processing Time (min)
	phr	Molar % <sup>a</sup>					
NaMSi	0	0	30	3	1	140	20
NaMSi	2	0.57	29.1	3.3	1	140	20
NaMSi	4	1.15	29.6	3.2	1	140	20
NaMSi	6	1.74	30	3.2	1	140	20
NaMSi	8	2.29	30.5	3.2	1	140	20
NaMSi	10	2.87	30.9	3.3	1	140	20
NaMSi	10	2.87	30.9	3.3	1	140	50
NaMSi	10	2.87	30.9	3.3	1	160	30
NaMSi	10	2.87	30.9	3.3	1	160	50
NaMSi	30	8.60	30.2	3.3	1	140	20
NaMSi	45	12.90	30	3.2	1	140	20
ASi	2	0.57	30.8	3.3	1	140	20
ASi	4	1.13	29.4	3.1	1	140	20
ASi	6	1.70	29.7	3.2	1	140	20
ASi	8	2.26	30	3.2	1	140	20
ASi	10	2.83	30	3.2	1	140	20
ASi	30	8.84	30.2	3.3	1	140	20
ASi	45	12.72	29.3	3.2	1	140	20

<sup>a</sup> Expressed with respect to the amount of polymer.

The processing and reaction with both organosilanes are also compared.

## EXPERIMENTAL

### Materials

The polymer is a commercial bulk polymerized PVC with a molecular weight of  $M_n = 32,000$ , determined by osmometry, and tacticity  $i = 19.6$ ,  $h = 49.8$  and  $s = 30.7$  determined by <sup>13</sup>C-NMR spectroscopy.

The sodium salt of  $\gamma$ -mercaptopropyltrimethoxysilane (NaMSi) was synthesized from the corresponding thiol, generously supplied by Quimidroga (Spain), and sodium hydride in heptane. The  $\gamma$ -aminopropyltriethoxysilane (ASi) was also supplied by Quimidroga.

Diethylphthalate (DOP), dibutyltin dilaurate (DBTDL), and stearic acid were used without further purification.

### Processing and Reactions

The reactions of PVC with NaMSi and ASi were carried out in a Haake Rheocord 9000 unit coupled to a Rheomix 600 mixer with two roller ro-

tors. The components—PVC, organosilane, lubricant (stearic acid), plasticizer (DOP), and crosslinking catalyst (DBTDL)—were premixed to obtain an homogeneous mixture. Blank reactions were also carried out for comparison. The materials obtained by reactive processing were pressed in a hot press to obtain thin samples of thickness 0.5–1 mm. To complete the crosslinking process, the systems were immersed in hot water at 80°C for 5 h.

Table I shows the different reaction conditions employed.

### Characterization

#### Silane Incorporation

The silane grafting on PVC was followed by IR spectroscopy using a Nicolet 520 FTIR spectrometer on films of noncrosslinked PVC of between 15–40  $\mu$ m obtained by the evaporation of 20 mg of purified modified PVC dissolved in 0.5 mL THF. For crosslinked polymers, KBr pellets were obtained from extracted networks.

Qualitative information on the incorporation of silane in the polymer chain is obtained from this study, and in some cases semiquantitative information can be deduced.

### Network Dimensions

Circular samples were cut from the pressed polymer sheets. The gel content was determined after Soxhlet extraction first for 24 h in THF, and then in ethyl ether for 12 h. The remaining gel was dried in a vacuum oven at 60°C for 24 h. The amount of THF-insoluble material, i.e., the gel content, is expressed (in %) by the ratio of the weight of the dried gel to the weight of the original sample, excluding the plasticizer.

To determine the molecular weight between crosslinks ( $M_c$ ), extracted samples as described above were swollen in THF at 40°C for 3 days. The number-average molecular weight between crosslinks was determined using the Flory-Rehner equation expressed by

$$M_c = \frac{\rho_2 V_0 V_r^{1/3} (1 - 2/\phi)}{\ln(1 - V_r) + \chi V_r^2 + V_r}$$

$$V_r = \frac{1}{1 + \frac{\rho_2 w_s - w_o}{\rho_1 w_o}}$$

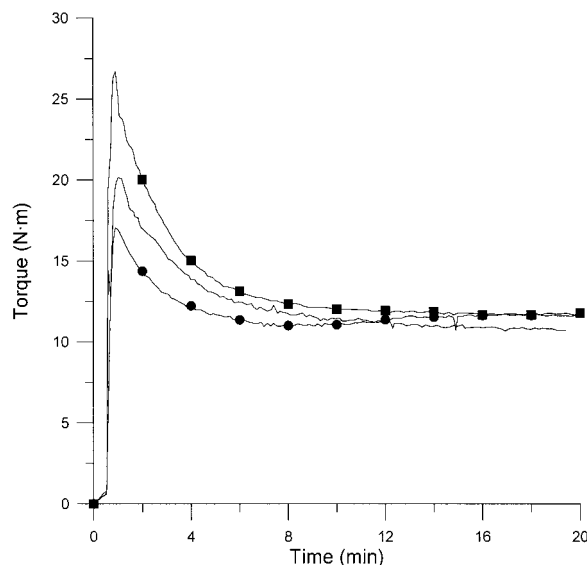
where  $\rho_1$  and  $\rho_2$  are the solvent and polymer densities, respectively,  $V_0$  is the molar volume of solvent,  $\phi$  is the crosslinking functionality, and  $\chi$  is the polymer-solvent interaction parameter.  $V_r$  is the volume fraction of polymer in the swollen network, determined as expressed above. The parameters  $w_o$  and  $w_s$  are the initial and swollen weights of the network, respectively.

### Thermal Properties

The thermogravimetric analysis of the polymers obtained by the reactions with ASi and NaMSi was carried out with a Perkin-Elmer TGA-T7 thermal analyzer. The temperature was varied from 35 to 400°C at a heating rate of 2, 5, 10, and 25°C/min under a N<sub>2</sub> purge. Thermograms were corrected with the aid of standards, using Alumel and Nickel as internal references in each of the experiments.

### Mechanical Properties

The study of the mechanical properties was carried out from the stress-strain curves obtained in an Instron 4031 universal testing machine. Measurements were carried out using a 0.1 KN load cell, with a testing speed of 50 mm/min, at room temperature and at 110°C, employing dumbbell-



**Figure 1** Processing rheograms at 140°C; — PVC, ● PVC + ASi (10 phr), and ■ PVC + NaMSi (10 phr).

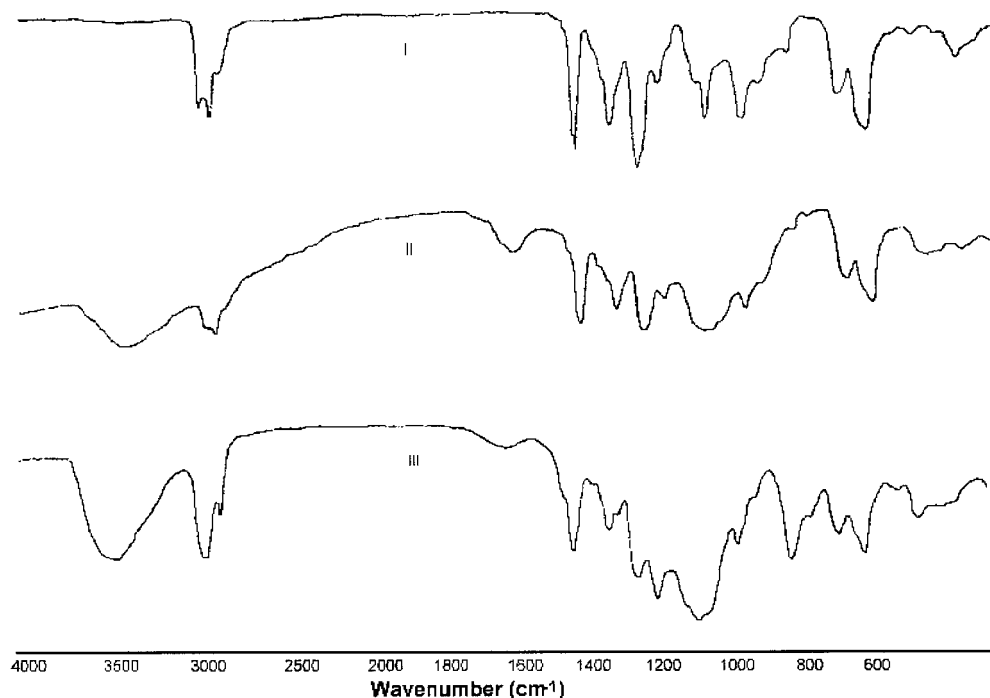
shaped test samples cut from crosslinked polymer sheets.

## RESULTS

### Processing

Figure 1 shows the evolution of torque as a function of time, at 140°C, for the processing of plasticized PVC, plasticized PVC with 10 phr of ASi, and plasticized PVC with 10 phr of NaMSi. From the figure it can be observed that the torque value, that is energetic consumption, is lower for the PVC processed with aminosilane than that processed with mercaptosilane, or even than of plasticized PVC. This is in agreement with the liquid and solid state of both reagents employed. At longer times, in the case of PVC processed with NaMSi, a plateau after the first peak can be seen, while for PVC processed in the presence of ASi an increase in the torque parameter is observed, as a consequence of premature crosslinking of the polymer. This is confirmed later in the study of the gel content of the processed polymers.

Although not shown here, changes in the processing conditions of the PVC-NaMSi system, such as increasing temperature to 160°C and time to 50 min, do not affect the shape of the rheogram, other than the obvious decrease in the value of the torque. In this case, premature crosslinking is prevented and, therefore, the practical applica-



**Figure 2** IR spectrum of different polymers processed for 20 min at 140°C. (I) PVC; (II) PVC + ASi (30 phr) processed for 20 min at 140°C; (III) PVC + NaMSi (30 phr).

tions of this system seem to be more promising when compared with the PVC–ASi system.

### IR Characterization

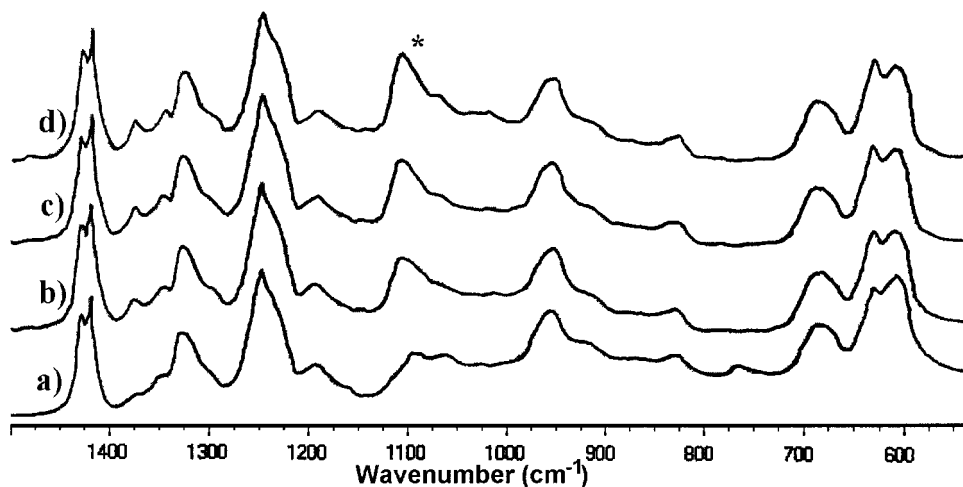
In Figure 2 the IR spectra of PVC, ASi-crosslinked PVC and NaMSi-crosslinked PVC are compared. From this comparison we can conclude that the reactive processing of plasticized PVC with both organosilanes leads to the corresponding modified polymers, clearly shown by the appearance of new bands in the spectra as a consequence of the silane grafting, between 1150–1010  $\text{cm}^{-1}$  [ $\nu(\text{Si}-\text{O})$  and  $\nu(\text{Si}-\text{O}-\text{Si})$ ]. Further, the hydrolysis of the siloxane groups, which takes place prior to the crosslinking reaction, leads to the appearance of the bands at 3600–3200  $\text{cm}^{-1}$  due to the OH groups. It is important to point out that the difference in intensity of the band at 1640  $\text{cm}^{-1}$ , corresponding to the C=C bonds [ $\nu(\text{C}=\text{C})$ ] between both crosslinked polymers, indicates a higher degree of degradation in the case of PVC processed with aminosilane, with respect to the mercaptosilane-crosslinked polymer. This is explained on the basis of the purely nucleophilic character of the  $-\text{S}^{\ominus}$  group, while the  $-\text{NH}_2$  group exhibits a significantly basic character.

In Figure 3 the IR spectra of PVC processed under the same experimental conditions with different amounts of NaMSi are compared. It can be observed that increasing the amount of organosilane during processing results in a higher degree of grafting, because the band at 1116  $\text{cm}^{-1}$  (noted with \* in the figure) increases in intensity; thus, a higher degree of crosslinking is reached, as is found in the study of the network dimensions.

### Network Dimensions

The gel content (gel %) and molecular weight between crosslinks ( $M_c$ ) of ASi–PVC and NaMSi–PVC crosslinked systems were determined from extraction and swelling experiments, as described in the Experimental section. To observe the degree of premature crosslinking during the processing, two different series of samples were studied; those taken directly from the molten polymer, and those after 5 h in hot water at 80°C.

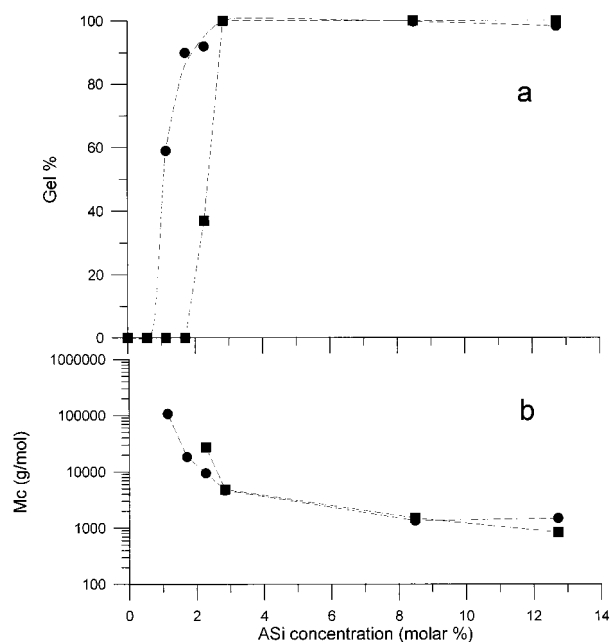
Figures 4 and 5 show the evolution of gel % and  $M_c$  for plasticized PVC processed at 140°C and 40 rpm with different amounts of ASi and NaMSi, respectively. Both systems exhibit similar behavior, with increasing gel content and decreasing of  $M_c$ , as the concentration of organosilane increases, rising to 100% gel content. Furthermore,



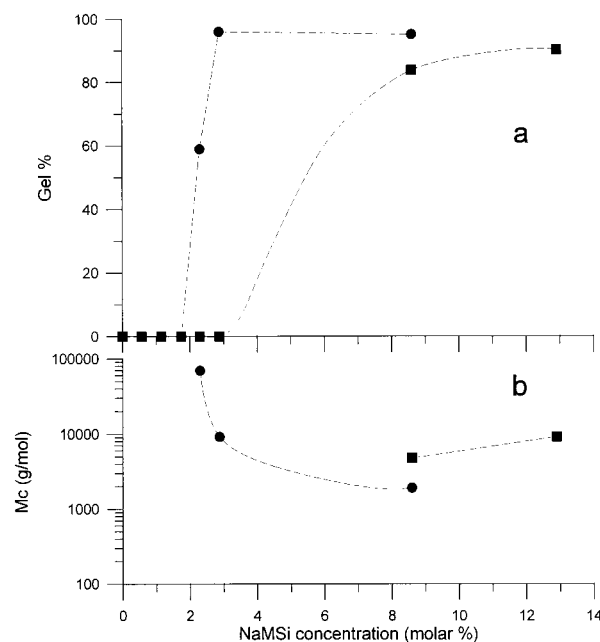
**Figure 3** Evolution of IR spectrum of PVC processed with different amounts of NaMSi for 20 min at 140°C. (a) Raw polymer; (b) 2 phr; (c) 4 phr; and (d) 10 phr.

it is observed that in the case of the ASi-PVC system a lower concentration of organosilane is required to obtain a crosslinked polymer, and differences between treated and untreated samples in hot water are lower in comparison to that of the NaMSi-PVC system. In fact, for NaMSi-PVC,

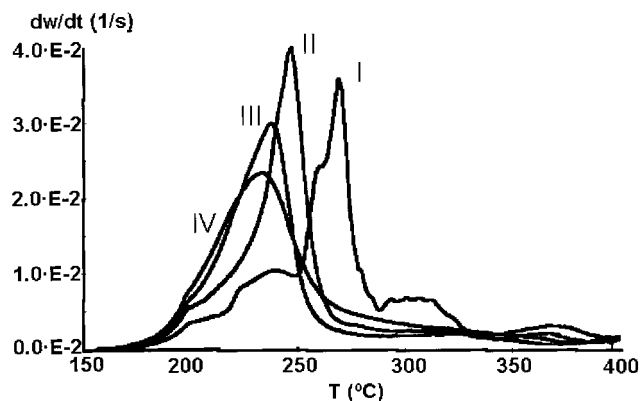
concentrations above 1.7% molar were needed to obtain effective crosslinking, compared with the value of 0.6% molar of ASi-PVC. This can be explained by considering the aggressivity of the  $\text{—NH}_2$  group. This group leads to higher degrees of grafting than NaMSi, although accompanied by



**Figure 4** Influence of the concentration of ASi on the network dimensions of the ASi-crosslinked polymers, obtained during processing at 140°C for 20 min. (a) Gel content; (b) molecular weight between crosslinks. ■ Samples directly after processing; ● Samples after 5 h in hot water at 80°C.



**Figure 5** Influence of the concentration of NaMSi on the network dimensions of the NaMSi-crosslinked polymers, obtained during processing at 140°C for 20 min. (a) Gel content; (b) molecular weight between crosslinks. ■ Samples directly after processing; ● Samples after 5 h in hot water at 80°C.



**Figure 6** Differential thermograms of PVC processed for 20 min at 140°C with different amounts of ASi. (I) Raw polymer; (II) 2 phr; (III) 6 phr; and (IV) 10 phr.

secondary reactions and premature crosslinking during processing, giving rise to a thermal destabilization of the polymer, as is confirmed later in the thermal study.

To explain the premature crosslinking of some of the formulations studied we suggest that, in the absence of thermal stabilizers, the formation of small amounts of HCl by degradation of the polymer (acting as crosslinking reaction catalyst), the presence of water adsorbed in the polymer or the atmospheric humidity, and the high temperature could lead to crosslinking. The extent of this phenomenon should be greater at higher amounts of organosilane or with the employment of substances promoting the polymer degradation, such as aminoorganosilanes.

From these results we can conclude that, using the appropriate experimental conditions in the NaMSi-PVC system, it is more feasible to separate both the organosilane grafting and the crosslinking process.

### Thermal Properties

Figure 6 shows the thermograms obtained for plasticized PVC and plasticized PVC processed at 140°C and 40 rpm with increasing amounts of ASi. The plasticized polymer exhibits thermal behavior different to the amino-grafted PVC. For polyvinylchloride three well-separated steps can be found, corresponding to the loss of DOP, the loss of HCl, and the degradation of the hydrocarbonated chain, respectively. Aminosilane-crosslinked PVCs apparently only exhibit a broad degradation peak. In actuality, this is due to a shift of the second peak (degradation of the polymer) to

lower temperature, thus overlapping with the loss of the plasticizer.

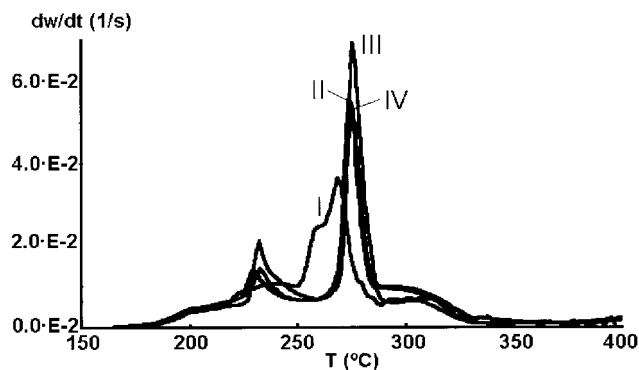
From these results it can be concluded that the reaction of PVC with aminosilane leads to the destabilization of the polymer, and this effect is higher with a higher concentration of aminosilane.

Figure 7 shows the thermograms obtained for plasticized PVC and plasticized PVC crosslinked with NaMSi in the same conditions as above. It can be appreciated here that the behavior of PVCs-mercaptosilane is very similar to that of PVC, all samples presenting the same number of peaks. It is observed that, although the first peak does not shift, narrower peaks are obtained. This case can be interpreted on the basis of greater polymer-plasticizer interaction due to the chemical and physical modification of the polymer chains.

The second peak also exhibits a narrowing as the concentration of mercaptosilane increases and there is a small shift to higher temperature, thus indicating a stabilization of the polymer.

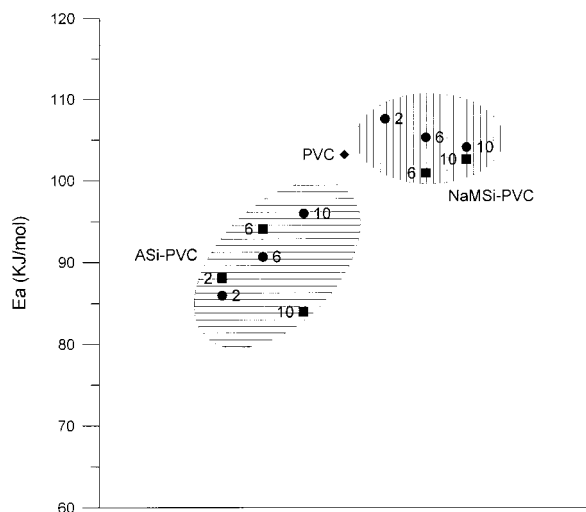
The kinetics of the degradation for both series has been analyzed in terms of activation energy, by applying the Flynn and Wall kinetic model.<sup>18</sup> In the ASi-PVC series the activation energy has been determined for the first peak and for PVC and NaMSi-PVC for the second one, that is, that corresponding to the main degradation of the polymer. To obtain these data, the degradation of the sample was carried out at different heating rates ranging from 2–25°C.

In Figure 8 the values of  $E_a$  obtained are compared. A destabilization for PVC-ASi systems is observed. In the case of the mercaptosilane-crosslinked PVCs, the  $E_a$  values obtained are similar to that of PVC.



**Figure 7** Differential thermograms of PVC processed for 20 min at 140°C with different amounts of NaMSi. (I) Raw polymer; (II) 2 phr; (III) 6 phr; and (IV) 10 phr.





**Figure 8** Activation energies for the degradation of crosslinked polymers obtained by the processing of PVC with different amounts of organosilane 20 min at 140°C. C. ♦ PVC; ● Samples directly after processing; ■ Samples after 5 h in hot water at 80°C. Concentration of organosilane (phr) is noted near dots.

Briefly, thermal destabilization of ASi-PVC crosslinked systems takes place derived from the HCl lost and premature crosslinking during processing. However, the thermal stability of NaMSi-PVC networks is similar to that of PVC.

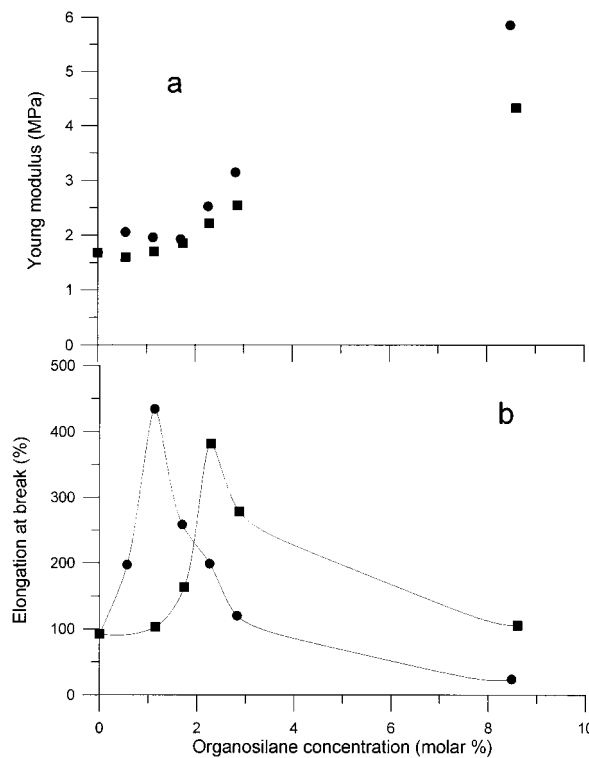
### Mechanical Properties

The mechanical properties of different samples prepared by the reactive processing of plasticized PVC with ASi or NaMSi have been evaluated from the stress-strain curves at 110°C obtained as described in the Experimental section. An experiment at temperatures above the  $T_g$  of the polymer was necessary to confirm the formation of a three-dimensional network, because, as expected, in the test carried out at room temperature differences were not significant.

Figure 9 shows the evolution of Young modulus and elongation at break measured at 110°C for both systems, ASi-PVC and NaMSi-PVC processed at 140°C and 40 rpm, and treated in hot water at 80°C for 5 h. The results obtained indicate similar behavior in both systems: at low concentration of organosilane, the Young modulus values are close to those of PVC; meanwhile, elongation at break is higher as the organosilane concentration increases. There is a limiting concentration above which both systems exhibit a change in the behavior of the measured magni-

tudes, in the sense that the modulus becomes higher and the elongation lower as organosilane concentration increases. This can be explained on the basis of the formation of a very weakly crosslinked network at low concentrations that allows the polymer chains to slip without breaking the sample, leading to longer elongations but no change in the modulus. On the other hand, at high organosilane concentrations, the dense network formed prevents the chains slipping, leading to a decrease in the elongation at break and higher modulus.

Differences observed between both series of crosslinked polymers can be explained by the higher degree of crosslinking reached in the ASi-PVC system at the same concentration to that of the NaMSi-PVC. As has been established previously, the larger reactivity of the amino group with respect to the thiolate leads to a higher degree of grafting; thus, a larger crosslinking density.



**Figure 9** Influence of the concentration of organosilane on the mechanical properties measured at 110°C of polymers obtained by processing 20 min at 140°C. (a) Young modulus; (b) elongation at break. ● ASi-PVC, ■ NaMSi.

## CONCLUSIONS

Different rheological changes are observed for PVC processed with  $\gamma$ -aminopropyltriethoxysilane and the sodium salt of  $\gamma$ -mercaptopropyltrimethoxysilane. For the former, the energy consumption is lower than for the latter, but in the amino system undesirable crosslinking is favored. Both reagents allow the development of high gel contents and crosslinking densities, depending on the organosilane concentration employed. Furthermore, in the polymers processed with mercaptosilane, it is more feasible to separate the grafting and crosslinking reactions.

Thermal stability for the NaMSi-crosslinked PVCs is similar to or higher than that of PVC, while for ASi-crosslinked PVCs it is lower than for the raw polymer. The mechanical properties above  $T_g$  of the crosslinked polymers are improved in both series of crosslinked polymers.

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