

Crosslinking of Plasticized Poly(vinyl chloride) by Substitution and Free Radical Reaction

M. HIDALGO, L. GONZÁLEZ, and C. MIJANGOS*

CSIC, Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva 3, 28006 Madrid, Spain

SYNOPSIS

Two new methods to obtain crosslinking plasticized poly(vinyl chloride) (PVC) are shown. One is by the substitution reaction of PVC with the sodium salt of γ -mercaptopropyl trimetoxysilane and the other is by the free-radical reaction of azide-modified PVC with γ -acryloxypropyltrimetoxysilane and vinyltri(2-metoxietoxy)silane. The content of gel and the number average molecular weight between crosslinking (M_c) were determined by Soxhlet extraction and by using the Flory–Rehner equation. The reactions of PVC with the above organosilanes under normal processing conditions of the polymer lead to high gel contents and, therefore, low M_c . The ultimate tensile strength and elongation at break at 110°C of these polymers are greatly enhanced over those of the uncrosslinked polymer. The results are improved compared to those taken from literature for similar systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most versatile materials in the modern world, although it has some limitations, such as its moderate upper-service temperature limit. This may generally be improved by introducing a three-dimensional structure into the linear polymer, using crosslinking agents. The production of crosslinking polymers by reactive processing with organofunctional silanes has aroused great deal of interest due to the improvement of mechanical properties at high temperatures. In the case of polyolefins this is usually done with vinyl or acryloxysilane in the presence of peroxide initiators,¹ and in the case of PVC by substitution reaction with mercaptopropylsilane, aminopropylsilane, and other silane derivatives.^{2–5} A number of crosslinking methods for PVC have been known to exist for some time^{6–12}; nevertheless, with few exceptions,^{6,8} the crosslinking products are rarely useful on a practical or commercial level.

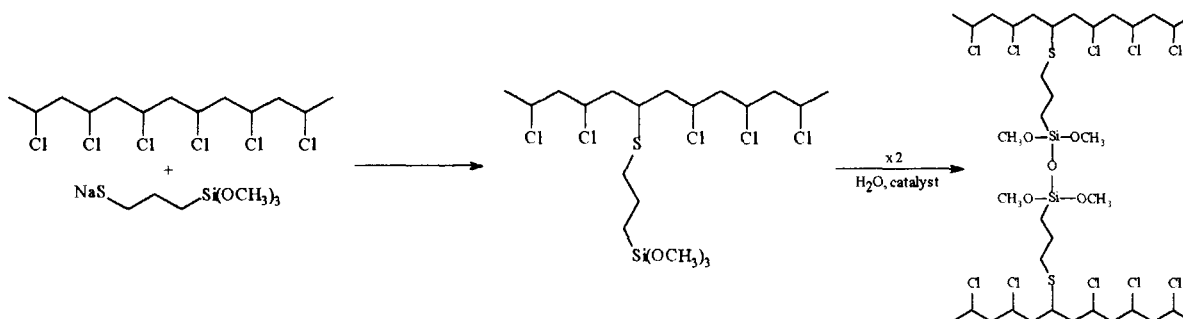
To our knowledge, vinylsilanes have never been grafted successfully onto PVC, since free-radical-

initiated reactions are poorly efficient for this polymer and involve many unfavorable side reactions. On the contrary, as has been reported,^{3,4} aminosilane is a very effective crosslinking agent for PVC, leading to a high gel content and improved tensile strength. However, the thermal stability of the crosslinked polymer is inferior to that of the original. Mercaptopropylsilane is also an efficient crosslinking agent for PVC⁵ although it requires the presence of an activating agent, such as the basic lead salt, to form the nucleophilic agent. Moreover, thiol-substituted PVC presents enhanced thermal stability, as has already been reported.¹³

To overcome these problems, we propose two new methods for crosslinking PVC under normal processing conditions. One method involves crosslinking PVC by a controlled substitution reaction with the sodium salt of mercaptopropylsilane, and the other by a free-radical reaction of the azide-modified polymer with vinyl and acryloxysilane. The latter reaction implies the previous grafting onto the PVC chain of a chemical group, i.e., an azide group, able to deliver free radicals by heating.

These proposed methods are based on recently reported results^{14–21} which show, first, that during continuous or discontinuous processing of PVC, thiolate-derivate reagents, such as sodium benzene-

* To whom correspondence should be addressed.



Scheme 1

thiolate, sodium isoocetyl thiosalicilate, sodium isoocetylthioglicolate, etc.,¹⁴⁻¹⁸ can be incorporated into the polymer chain by a substitution mechanism. And second, that azide-modified PVC is known to give ulterior reactions, as has been extensively reported by Okawara and Ochiai,¹⁹ and can thermally decompose generating free radicals. Consequently, it makes the introduction of vinyl monomers in the PVC chain possible.^{20,21}

In this work the reactions of PVC with sodium mercaptosilane and azide-modified PVC with vinyl- and acryloxysilanes are studied, with the aim of obtaining quantitative and fundamental information for the development of practical applications of crosslinked materials.

EXPERIMENTAL

Materials

The initial polymer was a bulk-polymerized PVC kindly supplied by Elf Atochem (Burgos, Spain) with a molecular weight, determined by osmometric measurements, of $M_n = 32,000$; and tacticity $i = 19.6$, $h = 49.8$, and $s = 30.7$, determined by ¹³C-NMR spectroscopy.

The azide-modified PVC (N_3 -PVC) was obtained by the reaction of PVC with sodium azide in DMF at 25°C. The azide content of the polymer, expressed in mol %, was determined by infrared (IR) spectroscopy by measuring the band at 2100 cm^{-1} corresponding to the azide group with the help of a calibration curve, as detailed by Martínez and colleagues.^{20,21}

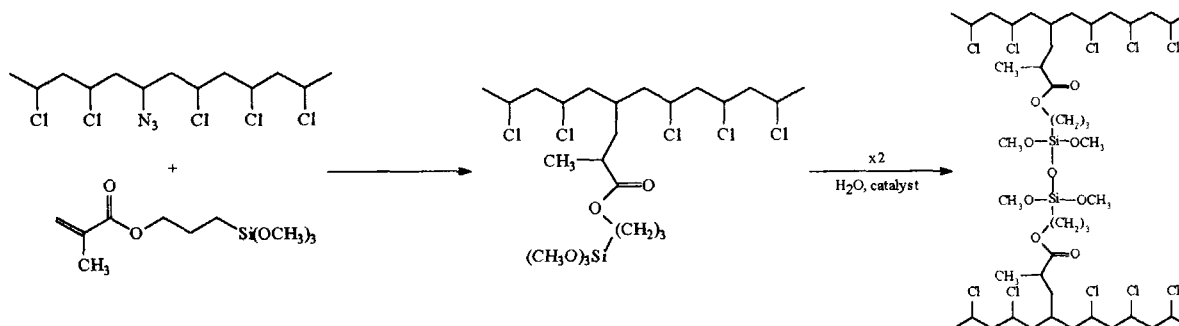
The sodium salt of γ -mercaptopropyltrimethoxysilane (NaMSi) was synthesized from the corresponding thiol, kindly supplied by Quimidroga (Barcelona, Spain), and sodium hydride in heptane.

The aminopropyltriethoxysilane (ASi), the γ -acryloxypropyltrimethoxysilane (AcSi) and vinyltri(2-methoxyethoxy)silane (VSi) also kindly supplied by Quimidroga, were used without further purification.

Tetrahydrofuran (THF) was distilled in the presence of lithium aluminium hydride. Dioctyl phthalate (DOP) and dibutyltindilaureate (DBTD) were used without further purification.

Crosslinking Reactions

Reactions of PVC with NaMSi were carried out in a Brabender Plasticorder at 140°C and 40 rpm. For each reaction the components were premixed to obtain the initial reactive mixture: PVC, NaMSi, plas-



Scheme 2

Table I Conditions and Experimental Results of N₃-PVC Crosslinking in the Melt at 120°C and 30 min

Reagent	Amount (molar %)	Equipment	Directly from Melt			After 5 H in H ₂ O at 80°C		
			Gel (%)	M_c	ν_e	Gel (%)	M_c	ν_e
Control	—	Brabender plasticorder ^b	0	—	—	0	—	—
Acryloxysilane ^a	10	Brabender plasticorder ^b	0	—	—	0	—	—
Acryloxysilane	10	Two-roll mixer	79	1800	5.50×10^{-4}	98	400	2.50×10^{-3}
Vinylsilane ^a	10	Brabender plasticorder ^b	0	—	—	0	—	—
Vinylsilane	10	Two-roll mixer	95	?	?	99	?	?

^a Reaction with PVC in presence of Trigonox-C as radical initiator.

^b 40 rpm.

ticizer (DOP), and crosslinking catalyst (DBTD). The same kinds of reactions were also carried out in a two-roll mixer.

For comparison, reactions of PVC with ASi were also carried out.

Reactions of N₃-PVC with VSi and AcSi were undertaken in a laboratory-designed Brabender prototype, under the same conditions as above. Blank reactions of PVC with VSi and AcSi in the presence of free-radical initiator were also carried out, for comparison.

To complete the crosslinking process, the systems were immersed in hot water at 80°C for 5 h.

Analysis and Measurements

The gel content was determined by Soxhlet extraction for 24 h in THF. The remaining swollen gel was dried in a vacuum oven at 60°C for 24 h. The percentage of THF-insoluble material, the gel con-

tent is expressed by the ratio of the weight of the dried gel to the weight of the original sample, plasticizer excluded.

To determine 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

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

$$V_r = \frac{1}{1 + \frac{\rho}{\rho_{\text{THF}}} \frac{\omega_s - \omega_0}{\omega_0}}$$

where ρ is the polymer density, V_0 is the molar volume of solvent, V_p is the ratio of the deswollen network weight (ω_d) to the initial network weight (ω_0),

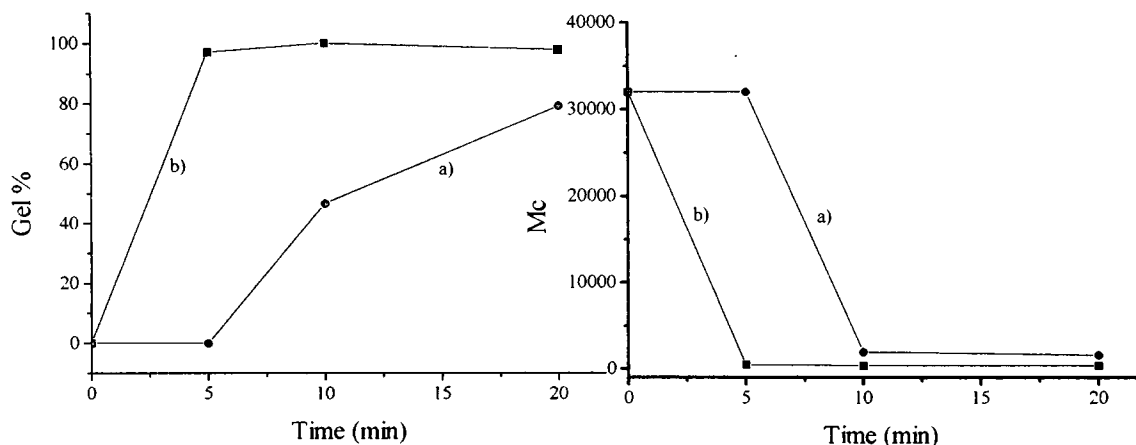


Figure 1 Plot of gel content and M_c vs. time for crosslinked PVC with acryloxy silane: (a) directly from the melt; (b) after immersion in water.

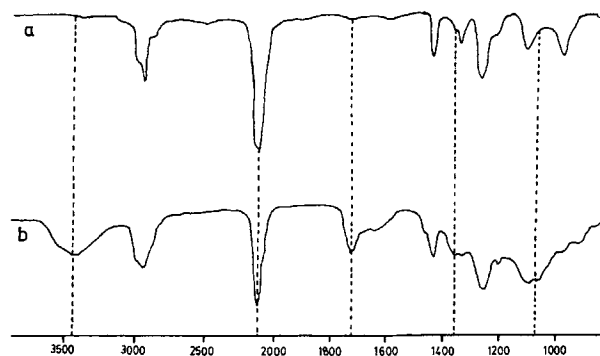


Figure 2 IR spectrum of (a) original N_3 -PVC and (b) crosslinked N_3 -PVC with acryloxysilane after 5 min of reaction.

χ is the polymer-solvent interaction parameter, V_r is the volume fraction of PVC in the swollen network, and ω_s is the swollen network weight.

The ultimate tensile strength (UTS) and elongation at break were measured on an Instron Model 4031 universal testing machine. Measurements were carried out on load of 1 KNw at room temperature, and at 110°C using a heated chamber.

RESULTS AND DISCUSSION

The aim of this work is to develop new crosslinking processes to be used under industrial conditions for plasticized PVC, and to compare these processes with other methods described in the literature. One of the new methods used is controlled substitution reaction of PVC with crosslinking agents, and the parallel or posterior crosslinking reactions, as shown in Scheme 1. The advantage of the direct substitution of PVC with sodium mercaptosilane, easily synthesized apart, is beyond doubt, since no other reaction agents are required which would contaminate the material. Also, in the melt reactions of this polymer, the reactivity of the sodium salt of mercapto derivatives is much higher than that of the acid form.

The other method is by free-radical reaction of a vinyl crosslinking agent with a lightly azide-modified PVC able to generate free radicals by heating, as shown in Scheme 2. It is well known that the free-radical grafting of vinyl monomers on PVC with external free-radical initiators is not a successful reaction even under severe conditions. Nevertheless, as has been extensively reported,¹⁹⁻²¹ PVC can easily be functionalized with the N_3 group by the reaction of PVC with sodium azide. This grafted azide group is very reactive and susceptible to posterior reac-

tions, as has been studied in detail by Okawara and Ochiai,¹⁹ and Gonzalez and colleagues,²² and is able to decompose thermally, thus generating free radicals which act as initiators.²⁰ By this method, styrene monomers have been grafted onto PVC.²¹ Therefore one might presume that the vinylsilanes, either AcSi or VSi, could be grafted onto the azide-modified PVC.

PVC Crosslinking by Free Radical Reaction

The reaction conditions for N_3 -PVC with different amounts of acryloxy- and vinylsilane units, temperatures, and times, are reported in Table I, together with gel content, M_c , and ν_e . The results are compared with those of unmodified PVC. From these results it follows that the N_3 -PVC system, contrary to what one might expect, cannot be crosslinked in the absence of monomers, and that the free-radical reaction of PVC with vinyl and acryloxysilane in the presence of free radicals is not possible either. These findings confirm that the generation of free radicals in the PVC chain by this method is unsuccessful. Further, it can be observed that vinyl- and acryloxysilane can be grafted onto N_3 -PVC, thus leading to the crosslinking of the polymer. Vinylsilane is a more effective crosslinking agent than acryloxysilane.

Figure 1 shows the evolution of the gel content with time, measured directly from the melt and after immersion in water. It is observed that crosslinking is completed in about 5 min of reaction, even before immersion in water. Until this time it is possible to separate crosslinking from grafting, thus allowing characterization studies as shown in Figure 2. This figure gives the IR spectrum of original N_3 -PVC and

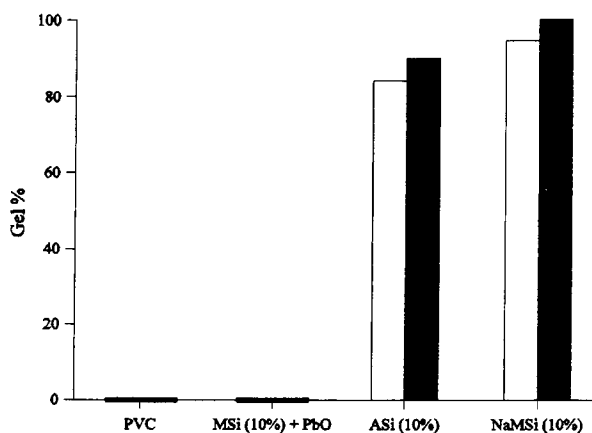


Figure 3 Dependence of gel content on the nature and amount of organosilane. White columns: directly from the melt; black columns: after 5 h in H_2O at 80°C.

that of the purified sample after 5 min of reaction. The appearance of new bands at 3400, 1710, and 1090 cm^{-1} corresponding to the silane can be clearly correlated with the decrease in band intensity at 2110 cm^{-1} corresponding to the N_3 group. The M_c values of these samples are also plotted in Figure 1. These results are in agreement with the spectroscopic data, and indicate a high number of crosslinking points. Although not the objective of this preliminary work, it is possible to optimize the results by adjusting the amount of N_3 , time, and amount of vinylsilane.

Crosslinking by Substitution Reaction

The reaction conditions of PVC with sodium mercaptosilane, aminosilane, and mercaptosilane plus activating agent are given in Table II. This table also shows the gel content, molecular weight between crosslinking, and network density for each set of conditions. These results are illustrated in Figure 3, where the dependence of gel content on the nature and amount of organosilane is plotted. It can be seen that with these experimental conditions, crosslinking of PVC with mercaptosilane plus activating agent as employed by Kelnar and Schatz⁵ is not effective. The difference is that here the experimental reaction conditions are weaker. On the contrary, if we compare these results with those of the sodium mercaptosilane, the latter are very much enhanced. This is not surprising because, according to our experience with chemical reactions of PVC in solution with mercapto derivatives, they have poor grafting efficiency when compared to the sodium salt of mercapto derivatives, the differences being larger in the melt state. Moreover, PbO can be a contaminant agent in the resulting material. From Figure 3 it can be concluded that the reaction of PVC with aminosilane also gives high gel content. Nevertheless,

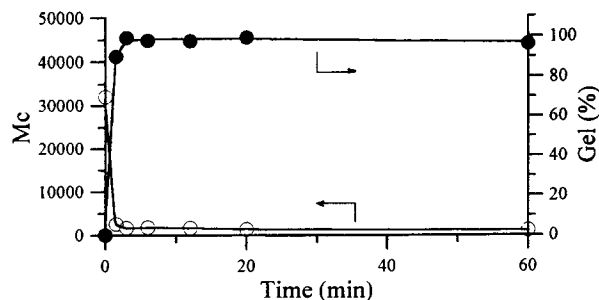


Figure 4 Dependence of M_c and gel content on time for crosslinked PVC with 6% mol of sodium mercaptosilane at 160°C.

aminosilane is too aggressive and reduces the thermal stability of PVC, giving an orange coloration.

Figure 4 shows the dependence of gel content and M_c with time for the reaction of PVC with 6% molar sodium mercaptosilane with DBTD as the crosslinking catalyst at 160°C. The gel content increases sharply at the beginning of the reaction, indicating the effectiveness of this metallic thiolate as a crosslinking agent for PVC.

Finally, we can say that sodium mercaptosilane is not only the most effective crosslinking agent for PVC as far as gel content and properties (as discussed later) are concerned, but it is also the most stable system thermally. This is derived from the fact that thiolates give no side reactions because they are not basic reactants, and the final materials are consequently colorless.

Properties of Silane-crosslinking PVC

The principal reason for crosslinking plasticized PVC is to increase its mechanical properties, especially at higher temperatures ($>T_g$). In Figures 5 and 6 the UTS and elongation at break are compared for various organosilanes at room temperature and

Table II Conditions and Experimental Results for PVC Crosslinking at 140°C and 30 min

Reagent	Amount (molar %)	Equipment	Directly from Melt			After 5 H in H_2O at 80°C		
			Gel (%)	M_c	ν_e	Gel (%)	M_c	ν_e
Aminosilane	3	Two-roll mixer	32	25000	3.90×10^{-5}	43	35800	2.80×10^{-5}
Aminosilane	10	Two-roll mixer	84	8000	1.25×10^{-4}	90	6700	1.50×10^{-4}
Mercaptosilane + PbO	10	Two-roll mixer	0	—	—	0	—	—
Sodium mercaptosilane	3	Brabender plasticorder ^a	0	—	—	20	28000	3.60×10^{-5}
Sodium mercaptosilane	6	Brabender plasticorder ^a	52	5000	2.00×10^{-4}	73	5100	2.00×10^{-4}
Sodium mercaptosilane	10	Two-roll mixer	94	3200	3.10×10^{-4}	100	2900	3.40×10^{-4}

^a 40 rpm.

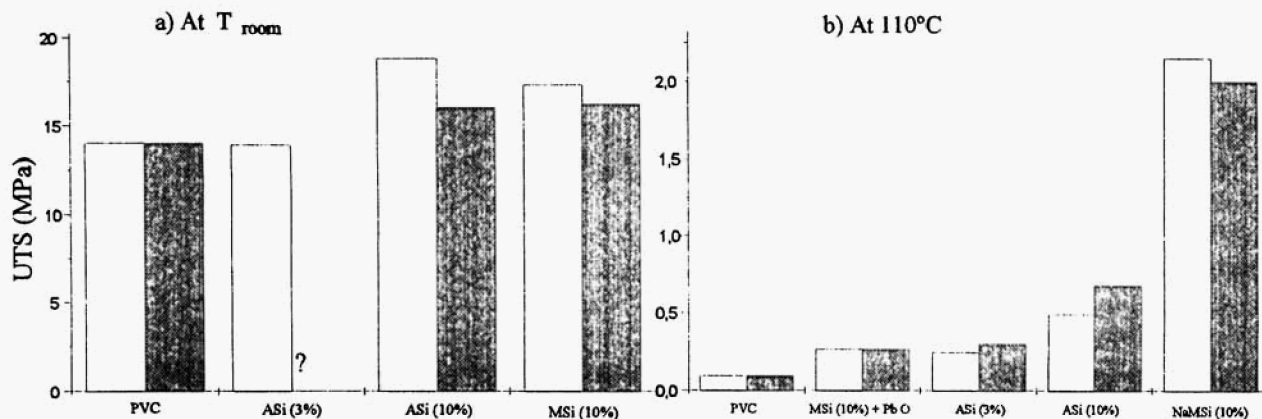


Figure 5 Dependence of the UTS on the nature and amount of organosilane: (a) at room temperature; (b) at 110°C. White columns: directly from the melt; black columns: after 5 h in H₂O at 80°C.

at 110°C. As expected, no appreciable differences were observed for the room-temperature UTS values between the crosslinked and uncrosslinked polymers. This is in agreement with the results of previous studies.²⁻⁵

The beneficial effects of crosslinking for reduction of flow are appreciated at 110°C, since for the same reaction conditions and the same molar amount of organosilane, the UTS values of the sodium mercapto system are very much improved over those for aminosilane and mercaptosilane with PbO. It is worth mentioning that although the crosslinking systems of Dahl and coworkers² seem to give good material properties, we cannot compare our results to theirs because they do not specify either the nature of organosilane employed or the process followed.

From this study we believe that the process of crosslinking PVC using sodium mercaptosilane has potential applications in the cable industry.

CONCLUSIONS

Obtaining crosslinked plasticized PVC using sodium mercaptosilane by a substitution mechanism under conditions similar to those encountered in an industrial environment is a feasible process. The free-radical reaction of vinylsilane and acryloxysilane on azide-modified PVC also leads to a crosslinked polymer. These crosslinked PVCs' gel contents, UTS, and elongation at break at 110°C are very much higher than for uncrosslinked PVCs, and

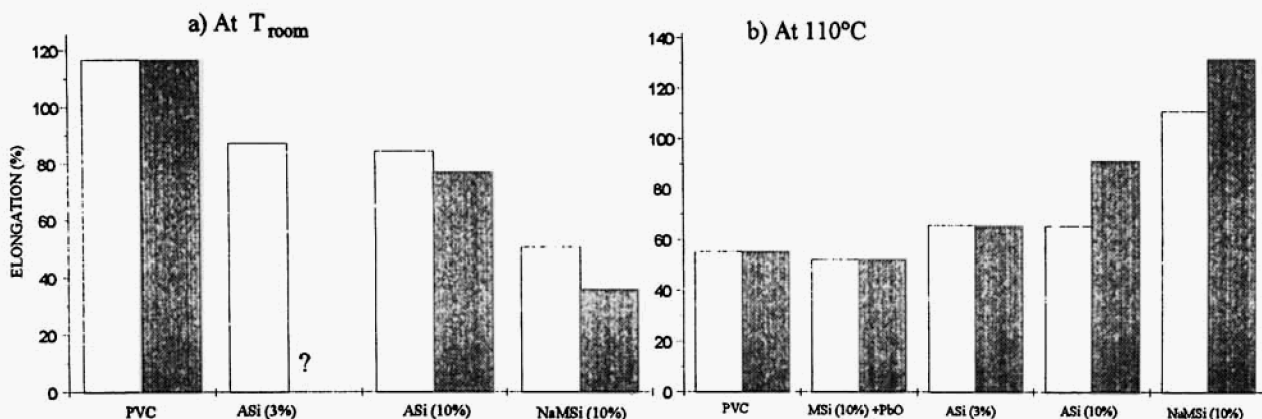


Figure 6 Dependence of the elongation at break on the nature and amount of organosilane: (a) at room temperature; (b) at 110°C. White columns: directly from the melt; black columns: after 5 h in H₂O at 80°C.

higher than values reported in the literature for similar systems.

We are grateful to the Comisión Interministerial de Ciencia y Tecnología (CICYT), No. MAT 95-0013E and 96-0615, for financial support.

REFERENCES

1. A. K. Sen, B. Muherjee, A. S. Bhahacharyya, P. P. De, and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **44**, 1153 (1992).
2. R. Dahl, A. Rynningen, M. Lundquist, and M. Rogested, *PVC93. The Future. Technical, Commercial, Environmental Strategy for Survival*, Brighton, U.K., 1993.
3. O. Rodríguez-Fernández, Ph.D. Thesis, Loughborough University of Technology, England, 1994.
4. M. S. Hears, J. D. Baird, L. P. Nethsinghe, and M. Gilbert, *Polym. Commun.*, **31**, 194 (1990).
5. I. Kelnar and M. Schatz, *J. Appl. Polym. Sci.*, **48**, 657 (1993).
6. T. N. Bowmer and W. I. Vroom, *J. Appl. Polym. Sci.*, **28**, 3527 (1983).
7. K. Mori and Y. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1981 (1978).
8. J. Oravec, Y. Oishi, H. Hirahara, and K. Mori, *Polym. Int.*, **32**, 303 (1993).
9. M. Behal and V. Duchacek, *J. Appl. Polym. Sci.*, **37**, 429 (1989).
10. M. Gonnu and A. Michel, *Makromol. Chem. Macromol. Symp.*, **25**, 219 (1989).
11. T. Hjertberg, R. Dahl, and E. Sörvik, *J. Appl. Polym. Sci.*, **37**, 1239 (1989).
12. H. Reinecke and C. Mijangos, *Makromol. Chem. Rapid Commun.*, **17**, 15 (1996).
13. W. H. Starnes, Jr., I. M. Plitz, D. C. Hische, D. J. Freed, F. C. Schilling, and M. L. Schilling, *Macromolecules*, **11**(2), 373 (1978).
14. C. Mijangos, A. Michel, G. Martínez, and J. Millán, *Eur. Polym. J.*, **20**, 1 (1984).
15. C. Mijangos, G. Martínez, and A. Michel, *Eur. Polym. J.*, **22**(5), 1417 (1986).
16. C. Mijangos, J. M. Gómez-Elvira, G. Martínez, and J. Millán, *J. Appl. Polym. Sci.*, **38**, 1685 (1989).
17. C. Mijangos, P. Cassagnau, and A. Michel, *J. Appl. Polym. Sci.*, **44**, 2091 (1992).
18. M. Hidalgo, D. López, and C. Mijangos, *J. Vinyl. Tech.*, **16**(3), 162 (1994).
19. M. Okawara and Y. Ochiai, *Modification of Polymers*, ACS, Washington, DC, 1980, Chap. 4, p. 121.
20. G. Martínez, M. Gómez-Daza, C. Mijangos, and J. Millán, *Rev. Plást. Mod.*, **398**, 213 (1989).
21. M. Gómez-Daza, G. Martínez, C. Mijangos, and J. Millán, XXII Reunion Bienal de la Real Sociedad de Química, Murcia (España), Sept. 1988.
22. L. Gonzalez, A. Rodriguez, and J. L. De Benito, *Rubb. Chem. Tech.*, **65**, 869 (1992).

Received March 21, 1995

Accepted January 14, 1996