Chemical Reactions in Crosslinking of Copolymers of Ethylene and Vinyltrimethoxy Silane

T. HJERTBERG,[*,1] **M. PALMLÖF,**[1] **and B.-Å. SULTAN**[2]

[1]Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden, and
[2]Neste Polyeten AB, S-444 86 Stenungsund, Sweden

SYNOPSIS

The crosslinking reactions of a new type of polyethylene, an ethylene vinyltrimethoxy silane (EVS) copolymer, when reacted with water has been studied. Samples of EVS were treated in water at 90°C. The kinetics of the crosslinking was followed by measuring the gel content and by determination of the content of different structures ($-Si-OCH_3$, $-Si-OH$, and $-Si-O-Si-$) using FT-IR. The observations show that a maximum gel content of 70–75% is obtained after 25 h treatment in water at 90°C. On the other hand, the absorption index for the crosslinks, $-Si-O-Si-$, continues to increase until about 100 h, i.e., more crosslinks seem to be formed without a simultaneous increase in gel content. Mechanical measurements showed decreased elongation at break even after very long treatments. Thermo-oxidative degradation is, however, also responsible for the change in mechanical properties. For properly stabilized samples, the decrease in elongation leveled off after about 100 h of treatment. This indicates that the crosslinks formed after 25 h mainly should be within the already existing gel. The observed synergistic effect of crosslinking and thermo-oxidative degradation emphasizes the importance of a proper stabilizing system.

INTRODUCTION

In many applications there is a need to improve the properties of polyethylene, in particular with respect to heat deformation resistance; but chemical resistance, stress cracking, shrinkage, etc. may be important as well. Crosslinking is then an obvious alternative, and it is used today on a large commercial scale. The most common technique is radical crosslinking[1,2] initiated by peroxides or by irradiation. Both these crosslinking techniques suffer, however, from high investment costs. In the case of radiation initiation crosslinking efficiency decreases with thickness, and thick sections are impossible to crosslink sufficiently. In the case of peroxide crosslinking production, speed is limited by the cure rate and the demands for a certain residence time in the heating zone. The extrusion rate is in itself also limited by the necessity to use a rather low melt temperature.

After the introduction of the Sioplas[3,4] and Monosil[5] techniques in the seventies, silane crosslinking of polyethylene has been an expanding field. In both these processes vinyl silane is grafted to the polymer chains after initiation by a small amount of added peroxide. The crosslinking is then performed by a water treatment after the addition of a catalyst in the final extrusion step. In commercial processes typical conditions to obtain crosslinking may be treatment at 80–90°C at 100% RH or in water. The use of free radicals for the grafting reaction leads to side reactions, in particular molecular enlargement, in the same way as observed in connection with compounding and processing prior to peroxide crosslinking. These reactions negatively influence the surface finish, limit the choice of antioxidants, and lead to increased consumption of antioxidants. Decomposition products from the peroxide may also give a bad smell to the finished product.

Recently, ethylene copolymers containing trimethoxysilane groups in the main chain have been introduced.[6] In this way a crosslinkable polymer can be produced already in the polymerization process

without the need of any special additives. Compared to the grafted compounds, the storage stability and the distribution of silane groups is markedly improved in these copolymers.[7]

In this study we present results from an investigation on the crosslinking reactions of an ethylene vinyl trimethoxysilane (EVS) copolymer, i.e., the silane groups were introduced already during polymerization. The mechanism leading to coupling between the methoxy silane groups are per se well known and involves the following reactions[8]:

$$H_3CO-\underset{\underset{(I)}{OCH_3}}{\overset{\overset{}{\mid}}{\underset{\mid}{Si}}}-OCH_3 + 3H_2O \rightarrow HO-\underset{\underset{(II)}{OH}}{\overset{}{\underset{\mid}{Si}}}-OH + 3CH_3OH \quad (1)$$

$$2HO-\underset{\underset{OH}{\mid}}{\overset{\mid}{Si}}-OH \rightarrow \underset{(III)}{\overset{HO-Si-OH}{\underset{HO-Si-OH}{\overset{\mid}{\underset{\mid}{O}}}}} + H_2O \quad (2)$$
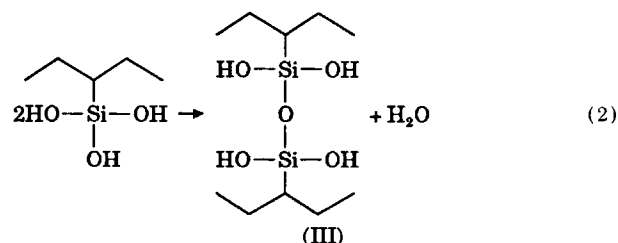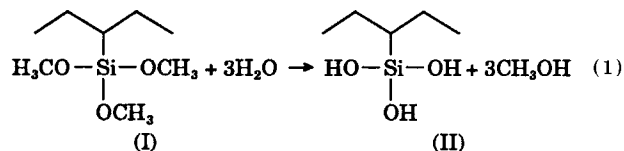
In earlier investigations on silane crosslinking of polyethylene, the graft type material has been studied. The crosslinking has mostly been followed by measuring the changes in mechanical properties and gel content, see, e.g., Ref. 3. In a recent paper, results from an investigation on crosslinking of EVS based on measurements with dynamic mechanical spectroscopy and IR was, however, presented.[9] Using FT-IR we have instead in detail followed the changes in the concentrations of species I–III as a result of treatment in water at 90°C. We have also compared the changes in crosslinking density, i.e., structure III, with the changes in mechanical behavior.

EXPERIMENTAL

Materials

The polymer used in this investigation was an EVS copolymer generously supplied by Neste Polyeten AB, Sweden. The structure of this polymer is schematically

$$EVS: \quad \sim CH_2CH_2\sim \underset{\underset{Si(OCH_3)_3}{\mid}}{CH_2}-CH\sim$$
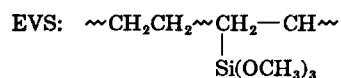
and some general data are given in Table I. For comparison, a conventional LDPE sample was included in some experiments as well.

To increase the crosslinking rate of the EVS copolymer a catalyst, dibutyl–tin–dilaurate (DBTL), was used. Preliminary results indicate that the catalyst decreases the activation energy of the hydrolysis reaction, i.e., structure **I** → **II**. It may also be active in the condensation reaction. It has been reported,[10,11] however, that both steps are catalyzed by Brønstedt acids. No other additives were used in the major part of the experiments. To investigate the influence of thermo-oxidation during crosslinking on the mechanical properties, one series with stabilized EVS was performed as well. The stabilizer consisted of phenolic antioxidants, 0.2% by weight.

Sample Preparation

For the main series, where no stabilizer was used, the catalyst was introduced via a master batch based on conventional LDPE. The catalyst master batch was homogenously mixed with the EVS copolymer to give a catalyst concentration of 0.05% by weight using a laboratory extruder (Axon BX 15) at 160°C. The extrudate was immediately pressed to 0.2 mm films at 150°C and 3.9 MPa for 1 s. The films were then treated in water at 90°C up to 243 h.

In the case of the stabilized material, a commercial master batch (News 1392, Neste Polyeten AB) containing stabilizer as well as catalyst was used instead. The master batch was mixed with EVS in a 19 mm/20 D Brabender extruder. The material was then pressed to 1.3-mm-thick plates at 150°C for 5 min with 25 N/cm² followed by 5 min with 385 N/cm², and finally cooled at 15°C/min. Tensile test specimens were cut from the plates and treated in water at 90°C up to 243 h. To avoid excessive crosslinking before analysis, all samples containing catalysts were stored at −30°C.

Analysis

Transmission spectra were obtained with a Perkin-Elmer 1750 spectrometer. Absorption index for peaks representative for structures **I–III** and oxidation products were calculated using the overtone of CH_2 bending at 2020 cm⁻¹ as internal standard. The gel content was determined with decaline extraction.[12] After milling and sieving (particles larger than 100 mesh), the sample was put into a metal net cushion that was kept in boiling decaline for 7 h. The solvent was replaced after 6 h. After drying the extracted amount was determined gravimetrically. Mechanical properties, elongation at break and ultimate strength, were measured with a JJ Instruments T 30 K tensile test machine at 5 mm/min.

Table I General Data for the Investigated Materials

Sample	Content of Silane (wt %)	T_m[a] (°C)	Degree of Cryst.[a]	Density (kg/m^3)	$M_n \times 10^{-3}$ [b]	$M_w \times 10^{-3}$ [b]
EVS	1.6	108	39	923	18	211
LDPE	—	114	35	923	20	176

[a] DSC.
[b] GPC.

For the nonstabilized material tensile test specimens were stamped from the treated films.

RESULTS AND DISCUSSION

As mentioned in the Introduction incorporation of vinyl silane during polymerization has several advantages compared to the grafting techniques. This is nicely demonstrated by comparing the molecular weight of the EVS copolymer used in this investigation before and after compounding with catalyst master batch, i.e., a process that in a way could be compared with the grafting step in the Sioplas technique. As seen by the values from a GPC analysis given in Table II, hardly any changes could be observed for the EVS copolymer. Even with an on-line LALLS detector, which has a high sensitivity for high molecular weight species, only minor changes could be observed. This behavior is in marked contrast to that observed for grafted materials. Presence of a peroxide normally leads to molecular enlarging reactions and thus an increased amount of high molecular weight material. Use of a LALLS detector has also indicated that a small amount of extremely high molecular weight material, i.e., "microgel," usually is formed.[7] This explains why problems such as bad surface finish might occur for grafted materials.

The strict separation between incorporation of silane and subsequent crosslinking in the case of EVS copolymers is, of course, advantageous in a study concerning the crosslinking mechanism of these materials. To further facilitate a direct FT-IR analysis, we choose to work with 0.2-mm film samples that did not contain any stabilizers. In Figure 1 the gel content developed after treatment in water at 90°C is given as function of time. The rate of gel formation is high during the first hours. Thereafter, the rate decreases and the maximum content of gel, 70–75%, is reached after about 25 h. This is the same level obtained in industrial practice, e.g., when producing cable insulation, with the same material. It should be mentioned that without any catalyst no gel at all is formed as a result of treating this material in water at 90°C for 20 h.

It is important to notice that crosslinking takes place below the melting temperature (peak value 108°C). At 90°C the degree of crystallinity is still about 11% compared to 39% at room temperature. This means that the mobility should be restricted, which could be one explanation for the incomplete crosslinking. This is supported by preliminary measurements that show that the level of gel content after prolonged treatment decreases with decreased reaction temperature, i.e., with increased degree of crystallinity. Another explanation might be the relatively low content of silane groups, about 2 per M_n molecule. The possibility to find molecules without silane groups would thus be rather high. A GPC analysis of the extract obtained from a material with 70% gel showed that the molecular weight of the noncrosslinked material is low; M_n = 1.000 and M_w = 30.000. Assuming a uniform distribution of the silane comonomer before reaction, the M_n molecule in the extract should contain 0.07 silane groups, i.e.,

Table II Molecular Weight of Virgin EVS and after Extrusion with Catalyst

| Sample	$M_n \times 10^{-3}$ [a]	$M_w \times 10^{-3}$ [a]	M_w-LALLS $\times 10^{-3}$ [b]
Virgin EVS	18	211	211
Film after extrusion	14	214	263

[a] GPC.
[b] Low-angle laser light scattering coupled on-line to GPC.
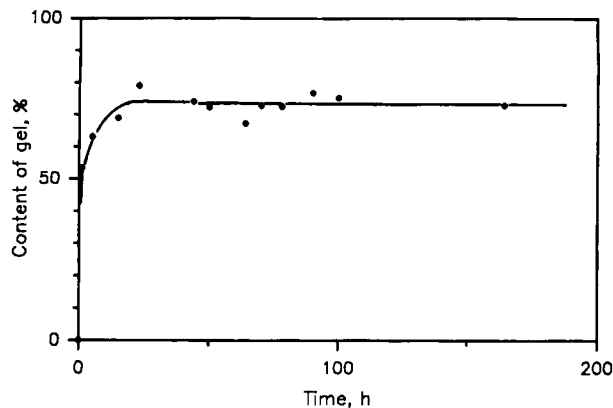
Figure 1   Gel content in EVS as a function of time of treatment in water at 90°C.

one silane group per 14 molecules. An FT-IR analysis of the extract showed furthermore that the content of silane is much lower (ca. 28%) in the extract compared to the average level, probably due to automatic fractionation associated with the crosslinking. An obvious conclusion is that it would be very difficult to reach 100% gel even without any restrictions in mobility.

Figure 2 shows IR spectra of EVS before and after crosslinking as well as a difference spectrum em-
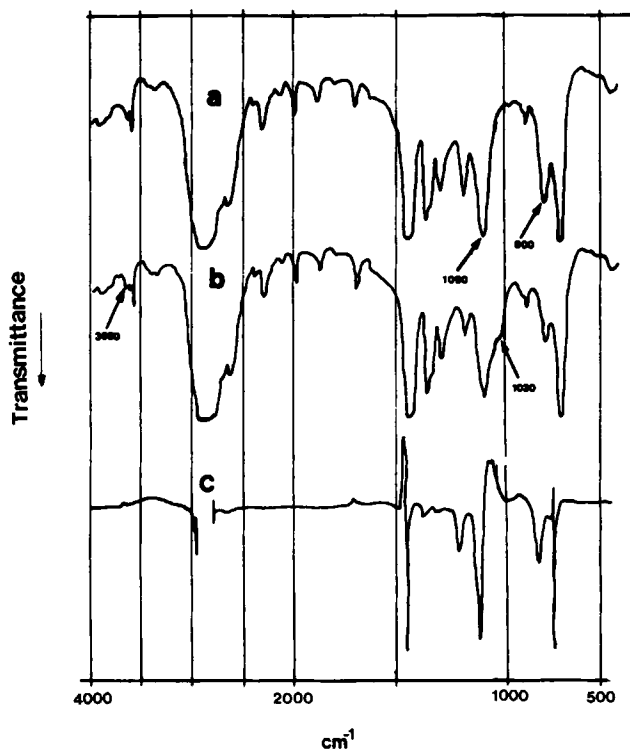

Figure 2   FT-IR spectra of EVS: (a) original sample, (b) sample (0.2 mm film) treated in water at 90°C for 64 h, (c) difference spectrum (b-a).

Table III   Absorption Frequencies Used to Follow the Crosslinking Reactions and Oxidation

Structure	Wave Number (cm^{-1})	Ref.
—Si—OCH$_3$	800 (1090)	13, 14
—Si—OH		
free	3691	14
hydrogen bonded	3549 (3431)	15
—Si—O—Si—	1030	13, 14
C=O; abs. max. in		
oxidized PE	1720	16

phasizing spectral changes. To follow the crosslinking reactions, i.e., changes in the content of structures **I–III**, and the oxidation, the absorption frequencies given in Table III were used. For Si—OCH$_3$ the evaluation is straightforward, but for the two others the situation is more complex. The hydroxyl group of silanols show several bands; free silanols at 3691 and hydrogen bonded at 3549 (and 3431) cm^{-1}. The absorption band of Si—O—Si appears as a shoulder on the larger band due to the Si—O bond in Si—OCH$_3$. In this case one might suspect that the larger peak of SiOCH$_3$ at 1090 cm^{-1} could influence the absorption value of the SiOSi shoulder. Therefore a careful examination of a difference spectrum between a extensively crosslinked sample (X) and an original noncrosslinked one (Y) was made. In the difference spectrum one can easily see the decrease in absorption of the SiOCH$_3$ peak and the increase of the SiOSi absorption. A variation of the factor as given by the equation "Difference = X − aY" represents changes in absorption intensity of sample Y. Such synthetic variations make it possible to see eventual interactions between the two absorption bands. In this case, however, it was not possible to observe any interactions at all, i.e., the intensity of the larger peak did not influence the absorption value of the SiOSi peak.

The disappearance of methoxy is shown in Figure 3. At first the reaction rate is very rapid. It then gradually slows down and becomes constant after about 50 h. Reaction (1) should be of first order with respect to both methoxy groups and water. Considering the permeability coefficient of water in LDPE[17] and the thickness of 0.2 mm, it can be calculated that water should be present in large excess, i.e., the reaction should be a pseudo-first-order reaction. The conversion curve seems to follow such a behavior up to about 10 h. Thereafter, the reaction rate does not decrease toward zero, but instead a
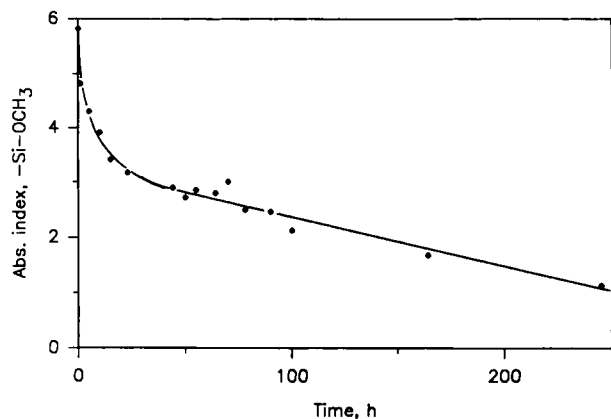
Figure 3 Absorption index for the $-Si-OCH_3$ band at 800 cm^{-1} in EVS treated in water at 90°C.

constant value is obtained. One possible explanation could be that the availability of water is varying depending on the crystalline surroundings. The local permeability coefficient, e.g., within the sperulites, could be much lower than the overall permeability coefficient, resulting in a diffusion-controlled reaction.

The initial rapid decrease in the number of methoxy groups indicates that it should be possible to observe a corresponding increase in the content of Si—OH groups. This is indeed observed for the first 15 h (see Fig. 4). Thereafter, the content of free silanols becomes constant, i.e., silanol groups are consumed at the same rate as they are formed. The high value obtained after 10 h, $A_{3690} = 0.59$, looks somewhat doubtful, but it should be remembered that the rapid initial hydrolysis of the methoxy group slows down markedly between 10 and 20 h. In combination with increased probability of condensation
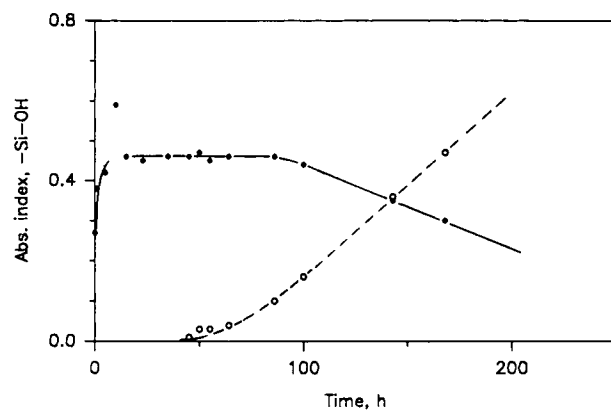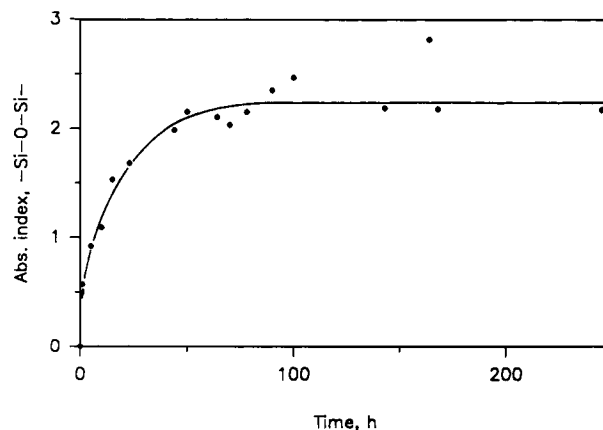
between the silanol groups, a peak value in the content of silanols groups might be plausible.

Consistently, a strong increase in the absorption index of Si—O—Si can be observed (see Fig. 5). The initial high rate of formation of crosslinks is also what could be expected with reference to the fast initial formation of gel. Gradually the formation rate of crosslinks slows down, and after about 100 h no further increase in the content of crosslinks can be observed. As hydrolysis of methoxy groups still occurs (Fig. 3), the number of silanol groups should increase again. On the contrary, the content of free silanol starts to decrease after 100 h (Fig. 4). However, hydrogen-bonded silanol groups begin to appear after about 50 h, and their rate of formation becomes constant after 100 h, i.e., when no silanols are consumed by condensation. An exact quantitative evaluation of the total content of silanols is impossible without knowledge of the extinction coefficients, but a simple addition of the two absorption indices, e.g., $\Sigma A_{Si\text{-}OH} = 0.77$ at 168 h, indicates that the content increases as expected. It can thus be assumed that the remaining silanol groups are isolated and nonmobile. A low mobility is per se what could be expected from the crosslinking process itself, but it should also be remembered that these reactions take place at a temperature where the material still is 11% crystalline.

A comparison between Figures 1 and 5 shows that the formation of Si—O—Si linkages, i.e., crosslinking points, continues a long time after maximum content of gel was obtained. This is illustrated in Figure 6. Possible explanations are shown schematically in the reactions that follow; molecules already part of the network form even more crosslinks, Eq. (3), formation of cyclic siloxanes, Eq. (4), and
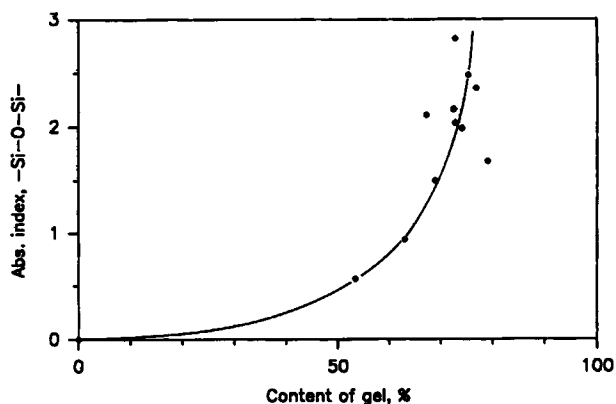

Figure 4 Absorption index for the $-Si-OH$ bands in EVS treated in water at 90°C: ●, ——, free silanol at 3690 cm^{-1}; O, - - - -, hydrogen bonded silanol at 3550 cm^{-1}.

Figure 5 Absorption index for the $-Si-O-Si-$ band at 1030 cm^{-1} in EVS treated in water at 90°C.

reactions between molecules with only one silane group each, Eq. (5):

$$(3)$$

$$(4)$$

$$(5)$$
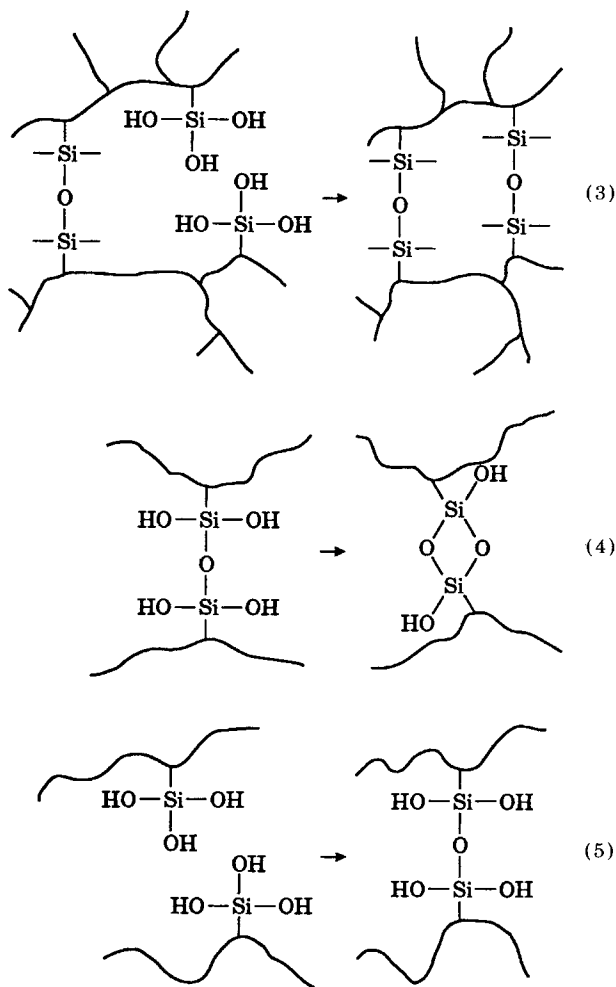
Formation of cyclic siloxanes is, however, less likely as it involves a four-membered ring. This structure has a considerable ring strain and should

Figure 6   Relation between the absorption index for the —Si—O—Si— band at 1030 cm^{-1} and the content of gel.

Table IV   Relative Elongation at Break and Ultimate Strength for Unstabilized EVS[a] Treated in Water at 90°C

| Time of Treatment (h)	Relative Elongation at Break[b] (%)	Ultimate Strength (N)
0	100	32
1	98	42
5	84	
15	74	
23	67	38
44	53	
50	49	34
64	39	
70	36	29
78	32	
90	27	
100	24	27
164	11	17
245	6	18

[a] Film samples.
[b] Normalized to the value of the original sample.

therefore be thermodynamically unstable. To further increase the understanding of the mechanism, elongation at break and ultimate strength were measured. The results obtained with the unstabilized 0.2-mm film samples are presented in Table IV. The elongation at break drops drastically after long water treatment; only 7% retention is observed after 240 h. The results thus indicate an increased crosslinking density within the gel, i.e., according to Eq. (3). Strange enough, the value of elongation at break continues to decrease even after 100 h, i.e., after that point where formation of Si—O—Si ceased. Unexpectedly, ultimate strength decreases as well. It must be noticed, however, that these samples became oxidized during water treatment. After about 50 h a marked increase in the content of carbonyl was observed (see Fig. 7). Considering the temperature (90°C), this indicate that chain scission processes are active.[18] This should, of course, contribute to the impaired elongation properties and decreased ultimate strength.

To eliminate the effect of thermo-oxidative degradation, a new series with the same material but containing 0.2% stabilizer was performed. As the mechanical properties were the most important, we choose to work with small-sized tensile test bars with a thickness of 1.3 mm. In spite of the longer diffusion path FT-IR measurements showed that formation of Si—O—Si linkages had a similar rate as that observed with the 0.2-mm films. This supports that
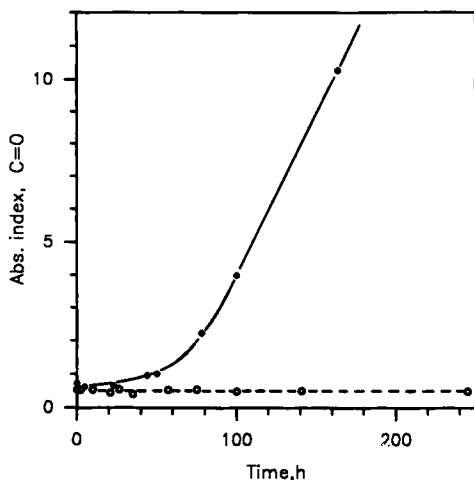
Figure 7 Absorption index for the band of the main oxidation product at 1720 cm^{-1} in EVS treated in water at 90°C: ●, ——, unstabilized EVS; ○, – – –, stabilized EVS.

the reaction rate is not controlled by macroscopic diffusion of water. As expected, the presence of stabilizers prevented thermo-oxidation (see Fig. 7).

The results of the measurements of mechanical properties of the stabilized and crosslinked samples are given in Table V. In contrast to the behavior of the previous series, in which no stabilizer was used, the ultimate strength is not affected by the water treatment. The elongation at break decreases initially as a natural consequence of the crosslinking process, but a constant level around 40% of the original one is reached after about 100 h. The deterioration of the elongation properties at long time

treatments observed for the nonstabilized material can thus conclusively be associated with oxidation processes. The relative values of elongation at break are compared in Figure 8, in which results obtained with a nonstabilized ordinary LDPE are given as well. The LDPE sample gave somewhat scattered data for short times (not shown), but for longer treatments a more stable trend could be observed. Embrittlement of the LDPE sample starts after about 50 h at which point formation of C=O can be observed as well, i.e., similar to what was observed for nonstabilized EVS. An induction period of 50 h at 90°C in water might seem somewhat short. A comparison with another investigation,[19] including ageing of LDPE films in air at 105°C, indicates however that 50 h is quite normal considering the difference in temperature. Diffusion of oxygen through water is thus not a limiting factor. Embrittlement of EVS is, of course, at short times, i.e., up to about 50 h, completely dominated by the crosslinking reactions. Without stabilizer further heat treatment leads to oxidation processes and accompanying deterioration of the mechanical properties. The cooperative effect between crosslinking and thermo-oxidation on elongation properties emphasizes the importance of using a proper stabilizing system for the crosslinkable systems, in particular as they often are intended for applications involving higher temperatures than normal.

A comparison between Figures 5 and 8 indicates that formation of crosslinks, Si—O—Si, and elongation at break behave in a similar way. After an initial rapid change, the rates slow down for both,

Table V Relative Elongation at Break and Ultimate Strength for Stabilized EVS[a] Treated in Water at 90°C

Time of Treatment (h)	Relative Elongation at Break[b] (%)	Ultimate Strength (N)
0	100	80
2.5	100	82
10	67	76
21	45	62
35	48	77
57	64	97
75	45	90
100	32	72
141	41	77
243	44	85

[a] Test bars.
[b] Normalized to the value of the original sample.
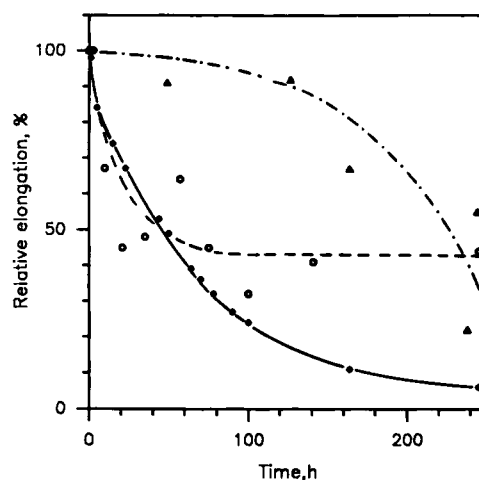
Figure 8 Changes in the relative elongation at break for samples treated in water at 90°C: ●, ——, unstabilized EVS; ○, – – –, stabilized EVS; △, – · – · –, unstabilized LDPE.

Table VI   Elongation at Break for Test Bars of EVS Treated in Water at 90°C for 25 and 96 h

Sample	Elongation at Break (mm)	
	24 h	96 h
1	114	107.5
2	122.5	110
3	123	113
4	125.5	107
5	133	109
6	135.5	101
7	138.5	98
8	141	122
9	150	105
10	153	106.5
Average	134	108
Stand. dev	12	6

and constant levels are reached after about 100 h. This is consistent with the increased amount of Si—O—Si linkages although the gel content does not increase after 25 h. Reactions (4) and (5) should not influence the mechanical properties. Instead the continuing decrease in elongation at break can be explained by increased crosslinking density within the already existing gel, i.e., reaction (3). Admittedly, the elongation data between 25 and 100 h are somewhat scattered. In order to really prove the changes in mechanical properties occurring between 25 and 100 h, a repeated test was performed with two series, each with ten tensile test specimens and treated at 90°C for 24 and 96 h, respectively. As seen by the values in Table VI, a small but significant decrease in elongation at break was indeed observed.

In conclusion this investigation presents the major features of the crosslinking reactions of the new ethylene vinyl silane (EVS) copolymer. FT-IR has been used to study changes in the amount of different chemical structures involved. The maximum gel content, 70–75%, is reached within 25 h only using 90°C and water, although the formation of crosslinks continues until about 100 h. Mechanical measurements have indicated that more crosslinks are formed within already existing gel in the period 25–

100 h, thus explaining the decreased values of elongation at break. Thermo-oxidative processes contribute to this behavior, which emphasizes the importance of a proper stabilizing system for the crosslinkable polymer.

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