

Crosslinking Reactions of Ethylene Vinyl Silane Copolymers at Processing Temperatures

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SYNOPSIS

The crosslinking reactions of ethylene vinyltrimethoxy silane (EVS) copolymers at processing temperatures have been studied. Samples were heated in inert atmosphere with or without water at 130–350°C. The crosslinking reactions were followed by determination of the gel content and by analyzing the structural changes using FT-IR. As expected, no gel could be observed in pure EVS after treatment in nitrogen, whereas 30% was obtained if the nitrogen was presaturated with water. Addition of a catalyst, dibutyltindilaurate, increased the reaction rate considerably and a final gel content of 70–75% was obtained above 300°C. In contrast, neither water nor catalyst was needed for the formation of gel in a terpolymer of EVS containing butylacrylate as well. During heat treatment the acrylate units formed carboxylic acid, and blends of EVS and an ethylene acrylic acid (EAA) copolymer were therefore used as a model to study the reactions in detail. Despite absence of water these blends started to form gel at low temperatures, 150–200°C. This could mainly be related to internal production of water due to reaction between carboxylic groups leading to anhydride. Both cyclic and noncyclic anhydrides were detected by FT-IR analysis. A larger amount of EAA in the EVS–EAA blend increased the rate of gel formation and decreased the onset temperature, but no corresponding change in the formation of noncyclic anhydride was observed. Another kind of crosslink, formed by reaction between carboxylic acid and silanol groups, can possibly be one explanation to this behavior.

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.

After the introduction of the Sioplas^{3,4} and Monosil⁵ techniques in the seventies, silane crosslinking of polyethylene has been an expanding field. In both processes vinyl silane is grafted to the polymer chains after initiation with 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. Recently, ethylene copolymers containing trimethoxy silane groups attached to the main chain have been introduced.⁶ In this way a crosslinkable polymer can be produced without the need of any special additives. For the copolymers as well as the grafted materials, the typical conditions to obtain the subsequent crosslinking in commercial production may be treatment at 80–90°C at 100% RH or in water.

In a previous paper⁷ we have presented results from an investigation on the crosslinking reactions of an ethylene vinyltrimethoxy silane (EVS) copolymer, i.e., the silane groups were introduced already during polymerization. The results showed that the maximum content of gel, 70–75%, will be reached after 25 h if 0.2-mm-thick films are treated in water at 90°C. On the other hand, IR measure-

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ments showed that the number of crosslink elements, Si—O—Si, continues to increase until about 100 h, i.e., more crosslinks can be formed without a simultaneous increase in the gel content. Measurements of mechanical properties indicated that the formation of crosslinks after 25 h occurred within the already existing gel.

In this study we present results from our continued investigation on the chemical reactions taking place in ethylene vinyl silane copolymers. The crosslinking experiments have been performed at temperatures above that used in commercial processes (90°C), and the results are thus more relevant to the processing conditions. Recently, a paper addressing similar questions was published.⁸ It is, of course, important that no reactions leading to crosslinking, or even molecular enlargement, take place within the processing equipment. In the case of the EVS copolymer this is possible to control, but for a copolymer containing butyl acrylate as well (EVSBA) premature crosslinking occurs much more readily.⁹ To examine the influence of external parameters, the effect of water, temperature, and catalyst, on the crosslinking behavior of EVS have been investigated. The major part is, however, concerned about the crosslinking and related reactions of EVSBA when heated in a dry nitrogen atmosphere. It turns out that despite the absence of an external water supply a substantial amount of gel is formed in this material at temperatures above 250°C. In order to elucidate the reaction pattern for EVSBA, blends of EVS and ethylene acrylic acid (EAA) copolymers have been studied as well.

EXPERIMENTAL

Materials

The copolymers containing silane were kindly supplied by Neste Polyeten AB, Sweden, while com-

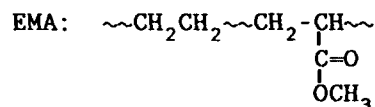
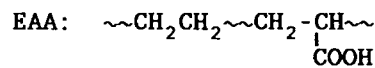
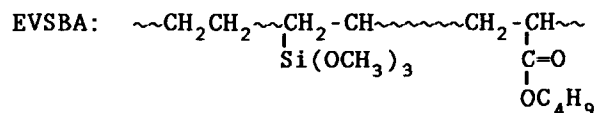
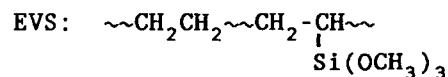


Figure 1 Schematic structures of polymers used in this investigation.

mercially available samples of an EAA and an ethylene methyl acrylate (EMA) copolymer were used. Some data of the polymers used are presented in Table I, and their structures are schematically shown in Figure 1. Different mixtures based on these raw materials (see Table II) were studied as well, which explains the use of two different EVS qualities. EVS-I is the same sample as was used in the previous investigation, while EVS-II was introduced in this work as its MI value was closer to that of the EAA sample, which facilitated a homogenous mixing. In most cases no additives, except a crosslinking catalyst (dibutyl tin dilaurate, DBTL) in some experiments, were used.

Sample Preparation

The different materials were compounded in a laboratory extruder (Axon BX 15) at either 150 or 170°C. The holdup time was short enough for crosslinking reactions not to occur to any noticeable extent. The extrudate was immediately pressed to ca 0.2 mm films at 150°C and 3.9 MPa for 1 s. The films were then treated in an oven, designed to allow

Table I Data on Investigated Materials

Material	MI ₂ (g/10 min)	Density (kg/m ³)	Content of Comonomer ^a (wt %)			
			Silane	BA	AA	MA
EVS-I	0.7	923	1.6	—	—	—
EVS-II	4.5	923	1.6	—	—	—
EVSBA	4.0	928	2.3	20.0	—	—
EAA	10	940	—	—	9.0	—
EMA	2	—	—	—	—	9.0

^a BA, butyl acrylate; AA, acrylic acid; MA, methyl acrylate.

Table II Blended Materials and Their Heat Treatments^a

Materials	Proportion	Extrusion Temp. (°C)	Heat Treatment, (°C)
EVS-II : EAA	95 : 5	150	130, 180, 200, 220, 240, 260, 300, 320
EVS-II : EAA	50 : 50	150	160, 180, 200, 220, 250, 300, 350
EVS-II : EMA	50 : 50	160	250, 350

^a Heat treatment of 0.2-mm films in nitrogen for 10 min.

good control of atmosphere and temperature as well as to give a rapid heating of the sample,¹⁰ for 10 min as shown in Table II. In order to keep the water content as low as possible, the films were kept in a desiccator for at least 10 h before the heat treatment in the oven. To avoid unwanted crosslinking while waiting for analysis or further treatment all samples were kept in a freezer at -30°C .

Analyses

Transmission spectra were obtained with a Perkin-Elmer 1710 FT-IR spectrometer. Absorption indexes were calculated using the overtone of CH_2 bending at 2020 cm^{-1} as internal standard. The content of gel was determined with a decalin extraction method.¹¹ After milling and sieving, the sample (particles larger than 100 mesh) 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. The molecular weight distribution of the soluble part of EVS-I was analyzed by size exclusion chromatography (SEC). Trichlorobenzene at 135°C was used as solvent, and after the dissolution procedure (4 h at 135°C) the solution was filtered through a $0.4\text{-}\mu\text{m}$ pore size filter. The SEC instrument was equipped with on-line low-angle laser light scattering (LALLS) and viscosity detectors. The experimental details of the SEC analysis have been described earlier.^{12,13}

RESULTS AND DISCUSSION

First, the results of treating EVS-I at elevated temperatures will be discussed. The gel content obtained after 10 min treatment is shown in Figure 2. In pure nitrogen hardly no gel at all was formed, which, of course, is what could be expected as water is the actual crosslinking agent. In this respect the behavior of EVS is very similar to that of ordinary LDPE when heated in an inert atmosphere up to 290°C for

10 min.¹² In fact, a reference sample of LDPE showed the same behavior, i.e., measured gel contents of ca. 3–6% independent of temperature. It should be pointed out, however, that the extraction technique used is less well suited for a definite differentiation at these low levels. In their work, Bullen et al.⁸ used a dynamic mechanical spectrometer to continuously follow the changes in storage modulus during heat treatment of EVS above 140°C . This technique is very sensitive toward molecular enlargement before major crosslinking occurs. Without catalyst and using dry nitrogen as atmosphere, the storage modulus was constant for at least 60 min at 200°C , indicating that no molecular enlargement occurred under these conditions.

When the same material is heated in nitrogen saturated with water, on the other hand, formation of gel can be observed (dashed line in Fig. 2). The amount of gel increases with temperature and at

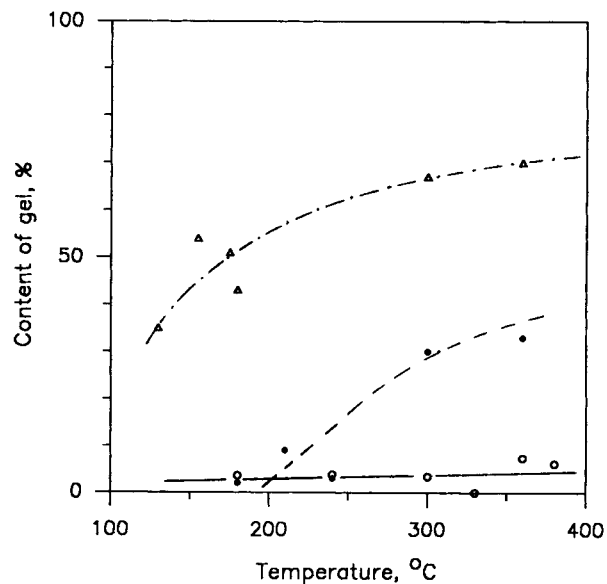


Figure 2 Gel content of EVS-I after heat treatment for 10 min under different conditions: O, — nitrogen; ●, - - - -, nitrogen presaturated with water; Δ, - · - · - · -, nitrogen presaturated with water, catalyst added.

360°C a gel content of 33% was obtained. Still higher temperatures should most likely lead to higher contents of gel until thermal chain scission processes dominate. The third curve in Figure 2 represents the behavior of EVS-I containing catalyst (DBTL) and heated in nitrogen saturated with water. In this case a very rapid formation of gel is observed. Most striking is the considerably lower onset temperature. The maximum content of gel for this material, ca. 75%, is reached at a temperature between 200 and 250°C. It should be emphasized, however, that the conditions used are much more favorable than those in commercial processes. As a comparison it can be mentioned that 75% gel is obtained after 20 h in water at 90°C.⁷

The overall reaction was also followed qualitatively by SEC analysis of the soluble part. Figure 3 shows the M_w values obtained by the on-line LALLS detector. As expected, the molecular weight increases rapidly even at very low levels of gel. This emphasizes the necessity to avoid crosslinking reactions during processing in order to maintain proper processing properties. At somewhat higher contents of gel the M_w value drops drastically. This is expected as larger molecules should be more easily attached to the gel compared to smaller ones. This is demonstrated even more clearly by the recordings from the LALLS detector (see Fig. 4). All high molecular weight material has disappeared from the soluble part after heating at temperatures above 180°C.

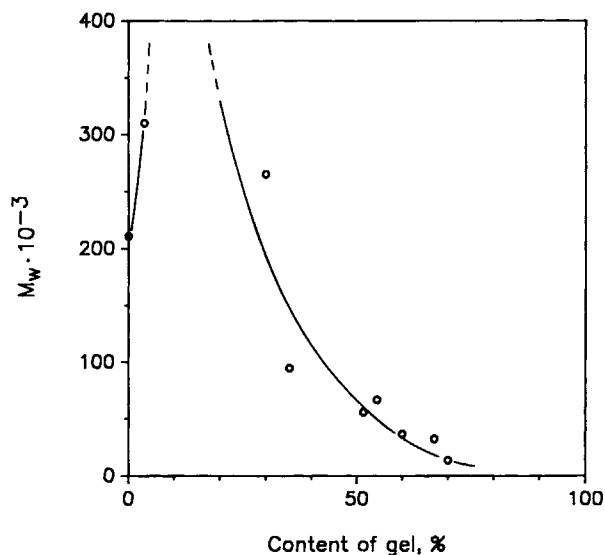


Figure 3 M_w values of EVS-I determined by LALLS, coupled on-line to SEC, as a function of the content of gel.

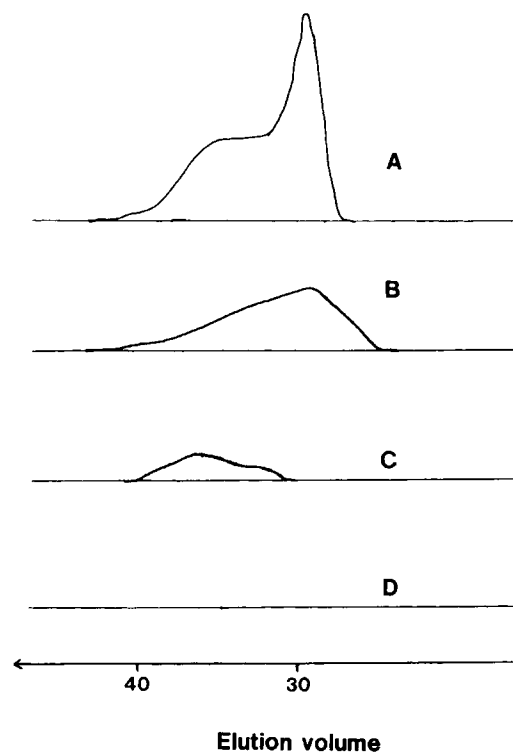


Figure 4 Recordings from the LALLS detector for EVS-I after different heat treatments: (A) 180°C in N_2 saturated with water, 0% gel; (B) 135°C in N_2 saturated with water, catalyst added, 35% gel; (C) 180°C otherwise as for (B) 43% gel; (D) > 180°, otherwise as for (B) > 43% gel.

In conclusion, the results obtained with EVS-I show that an external supply of water as well as heat and catalyst are important factors for the development of gel in this material. It is also possible to control these factors to an extent that formation of gel can be avoided during processing. This is, however, much more difficult in the case of the terpolymer EVSBA, which, besides the trimethoxy silane side groups, contains another functional group, butyl ester. In Figure 5 the content of gel is plotted against the heating temperature for treatments of EVSBA in dry nitrogen and without added catalyst. Up to 240°C only minor amounts of gel was formed, but at about 250°C the rate of crosslinking starts to increase markedly. At the highest temperature investigated, 360°C, as much as 70% was formed. This is quite surprising as there is no water present during the heat treatment. It can instead be assumed that water must be supplied from an internal source.

One possible explanation could, of course, be the relatively high content of water in EVSBA after drying compared to EVS (see Table III). The reason for this difference can be explained by the lower

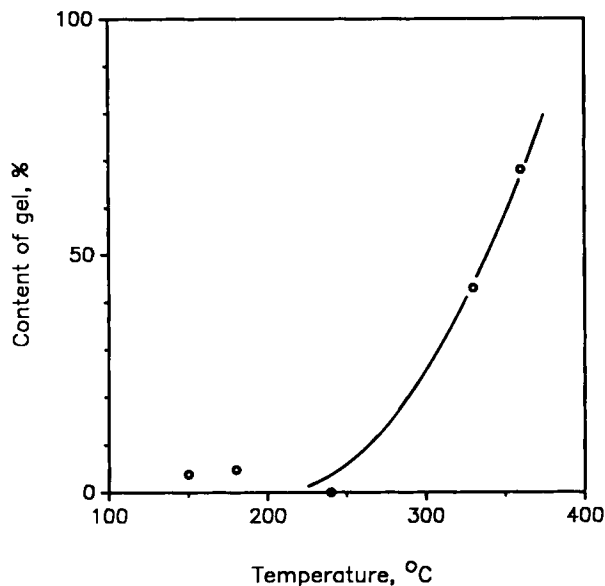


Figure 5 Gel content of EVSBA treated in dry nitrogen for 10 min at different temperatures.

crystallinity of EVSBA and the hydrophilic nature of the ester group. Calculations show, however, that the included amount of water is not sufficient to account for the observed gel content; the content of water should have been 3 to 4 times higher to match the obtained results. Another explanation may be the formation of water through chemical reactions within the polymer. It has been shown¹⁴ that butyl ester groups in ethylene butyl acrylate (EBA) copolymers are degraded, at least at 280°C, under formation of butene and carboxylic acid groups along the chain. The carboxylic acid groups may react with each other and thus form anhydride under simultaneous formation of water.

The same reactions are likely to occur with the butyl ester groups in a EVSBA copolymer as well. In this case the formation of water within the polymer should initiate the crosslinking reactions. To evaluate this possibility mixtures of EVS and EAA were prepared. In EAA, i.e., an ethylene acrylic acid

Table III Moisture Content^a of Silane Copolymers after Drying in Desiccator for More than 10 h

Sample	Content of Water (ppm)
EVS-I	135
EVSBA	342

^a Determined by Karl Fisher titration.

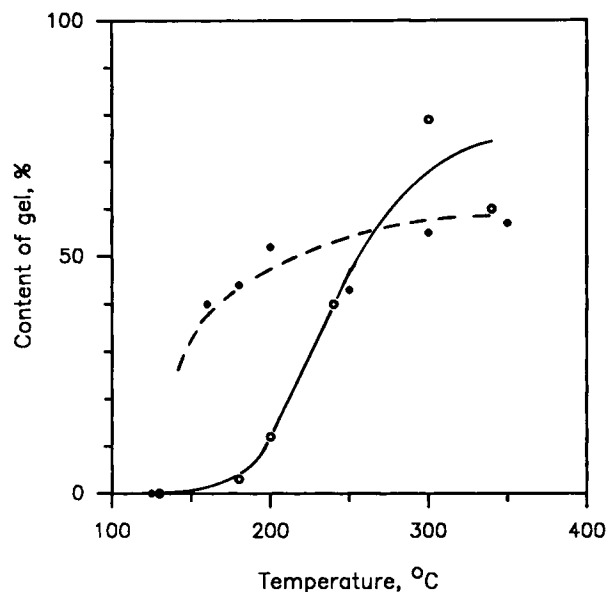


Figure 6 Gel content of blends of EVS-II and EAA treated in dry nitrogen for 10 min at different temperatures: ○, —, 5 wt % EAA; ●, - - - - , 50 wt % EAA.

copolymer, carboxylic acid groups are present already from the very beginning along the polymer chains. EAA can thus be regarded as EBA with completely degraded butyl ester groups. In Figure 6 the solid line shows the gel content of EVS-II containing 5% by weight EAA after heating for 10 min as a function of temperature. It is important to note that the formation of gel starts at a considerably lower temperature than in the case of EVSBA, ca. 200 compared to 240°C. At high temperatures the maximum content of gel is obtained.

Figure 7 shows the spectral region for C=O stretching vibrations of FT-IR spectra of the EVS-EAA mixture before and after heat treatment for 10 min at 300°C in dry nitrogen (for band assignments see Table IV). Before heating, the C=O stretching band of EAA (curve A) is dominated by the absorption at 1705 cm⁻¹ representing dimers of carboxylic acid groups. The small shoulder at 1740 cm⁻¹ shows, however, that there is a certain amount of free acid. After heating the band at 1705 cm⁻¹ is considerably reduced in favor of other frequencies. The most obvious is the absorption at 1810 cm⁻¹, which is typical for anhydrides. Saturated noncyclic anhydrides, which could be formed by intermolecular reactions or an intramolecular reaction between two well-separated acrylic acid units, have another band around 1750 cm⁻¹. Although not seen as a separate band, but only as a broadening of the main band in Figure 7, a band at 1745 cm⁻¹ (see spectra below) can be assigned to noncyclic anhydrides. If, on the

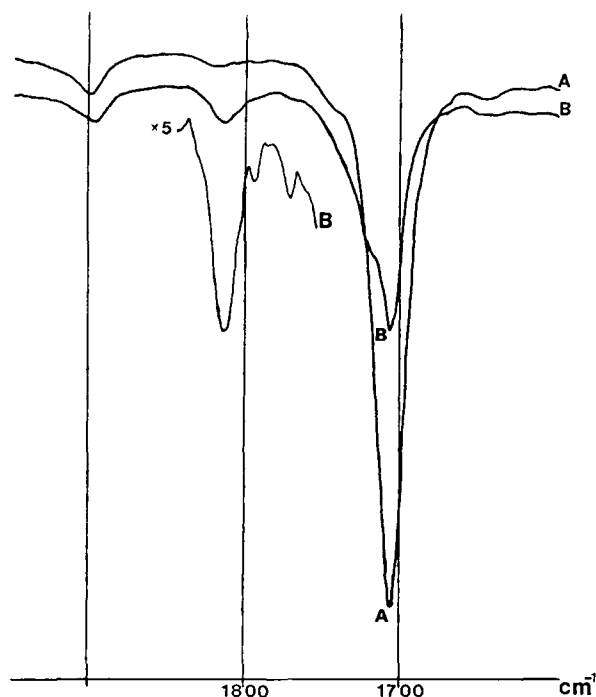


Figure 7 FT-IR transmittance spectra showing the carbonyl stretching region for a blend of 5 wt % EAA in EVS: (A), original sample; (B) after heat treatment at 300°C for 10 min.

other hand, an intramolecular reaction between two acrylic acid units that are adjacent or separated by one or two ethylene units should occur, a cyclic anhydride having C=O stretching bands at higher frequencies would be formed. The small band at 1765 cm^{-1} indicates that this might occur.

The liberation of water within the polymer melt is, of course, favorable with respect to gel formation.

Table IV Absorption Frequencies for Some Important Structures

Structure	Wave Number (cm^{-1})	Ref.
	1705	15
—C—OH	1740	15
Cyclic anhydride	1810, 1765, 900	16
Noncyclic anhydride	1810, 1745, 1025	16
—Si—OCH ₃	1090, 800	17, 18
—Si—O—Si—	1030	17, 18
—Si—O—CO—	1720	18

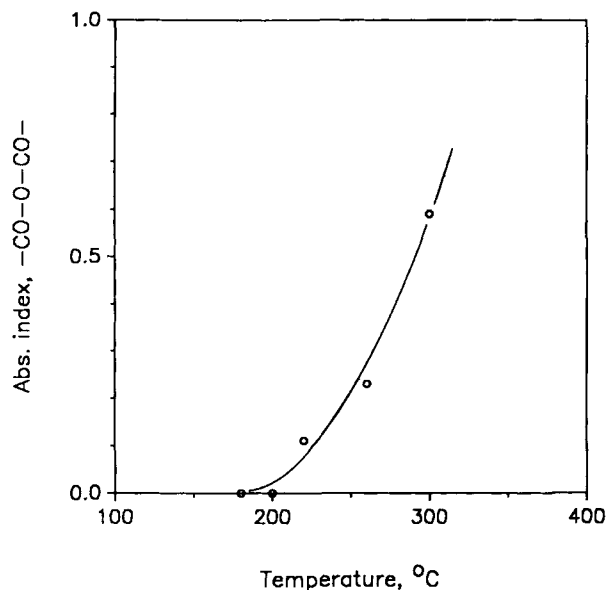
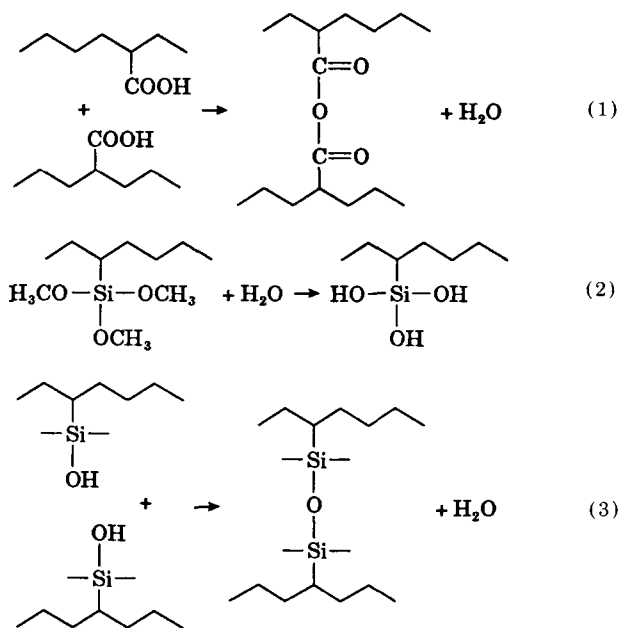


Figure 8 Absorption index for the anhydride band at 1810 cm^{-1} in blends of EVS-II and EAA (95 : 5) treated for 10 min in dry nitrogen.

This is confirmed by the absorption index for the band at 1810 cm^{-1} (Fig. 8), which shows that anhydride formation very much parallels that of the gel, c.f., Figure 6. If the results on the model system EVS-EAA then is transferred to EVSBA, the faster crosslinking of the latter compared to EVS thus seems to be related to degradation of the butyl ester groups to carboxylic acid and their subsequent combination to anhydride. This was further tested using a mixture of EVS-I and an ethylene methyl acrylate (EMA) copolymer. Analysis of the mixture EVS-EMA (95 : 5) after treatment at 350°C in dry nitrogen did not give any evidence of formation of either gel or anhydride. This is consistent with the observation that the degradation of poly(methyl acrylate) starts at a higher temperature compared to poly(butylacrylate). Furthermore, the degradation pattern of poly(methylacrylate) is quite different, which, e.g., has the consequence that no carboxylic acid groups on the polymer chains are formed.¹⁹⁻²¹

These experiments show that the carboxylic acid groups should be responsible for the formation of gel in the EVS-EAA system, and, most likely, in the EVSBA terpolymer as well. In the latter case the butyl ester groups must first be thermally degraded to carboxylic acid. Reaction between carboxylic acids in the polymer leads to formation of anhydride and is accompanied with internal production of water [Eq. (1)]. The —Si—OCH₃ groups can then be hydrolyzed [Eq. (2)] and crosslinked [Eq. (3)]:

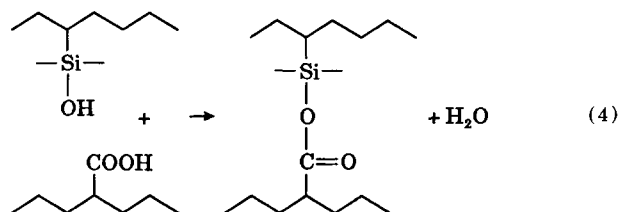


In low molecular weight material the hydrolysis, Eq. (2), is easily accomplished without any catalyst present. In fact, methoxy silane compounds are very sensitive to humidity and must be stored carefully in order to avoid condensation.²² In a polymeric material, however, a catalyst is needed if the crosslinking rate should be high enough from a commercial aspect. This is clearly demonstrated by the results in Figure 2.

If carboxylic acid groups are present, their concentration should reasonably have an influence on the reaction kinetics and possibly affect the temperature at which gelation starts. In another series of experiments with EVS-EAA mixtures the content of EAA was increased from 5 to 50% by weight. As can be seen in Figure 6, this leads to an increased rate of crosslinking. Most notably is the considerable drop for the onset of gelation. Even after heat treatment at 160°C as much as 40% gel was found, whereas no gel at all was formed during the extrusion at 150°C. It can therefore be assumed that the critical temperature is somewhere in the range of 150–160°C.

One explanation to the increased crosslinking rate might, of course, be the expected larger amount of water formed due to anhydride formation, Eq. (1). Second, the carboxylic acid group being a Brønsted acid might have a catalytic effect.²³ It is, however, important to note that the maximum content of gel obtained at 350°C is 57%. This is more than could be expected if the mixture is assumed to contain 50% of a component with maximum gel content of 75% (EVS) and 50% of another without any pos-

sibility to form gel (EAA). A third explanation could, therefore, be the existence of other kinds of crosslinks besides $-\text{Si}-\text{O}-\text{Si}-$. An obvious alternative is crosslinking of EAA due to the formation of anhydride, Eq. (1). Another possibility is reaction between silane methoxy and carboxylic acid groups, Eq. (4):



The FT-IR spectra of samples treated at 160–300°C (Fig. 9) contain several bands of interest concerning the discussed reactions. For the lower temperatures, up to 200°C, only traces of a band at 1810 cm^{-1} , i.e., anhydrides, can be observed. For the sample treated at 220°C, a significant band can be observed at 1810 cm^{-1} , as well as one band at 1030 cm^{-1} representing both $-\text{Si}-\text{O}-\text{Si}-$ and noncyclic anhydride. In addition, the difference spectrum between the treated and original samples [see Fig. 9(C)], shows increased absorption at 1720, 1765, and 900 cm^{-1} . The two latter bands are related to cyclic anhydride,¹⁷ while the former possibly can be assigned to the ester carbonyl structure shown in Eq. (4).¹⁸ Another possibility would be oxidation products, which normally have an absorption maximum at 1720 cm^{-1} , but this is less likely regarding the conditions used in these experiments, $\text{O}_2 < 5 \text{ ppm}$.¹²

For the sample treated at 250°C the trends discussed are still more pronounced. Furthermore, the consumption of $-\text{SiOCH}_3$ groups, Eq. (2), can clearly be observed by the decreased intensities of the bands at 800 and 1090 cm^{-1} . Finally, after treatment at 300°C, nearly all of these groups seem to have reacted since there is hardly any absorption at these frequencies. The intensities of the bands at 1030 and 1810 cm^{-1} have increased substantially. In the difference spectrum [Fig. 9(D)], significant changes can be noted in the relative intensities of the bands in the carbonyl region in comparison to the 220°C sample [Fig. 9(C)]. The band at 1720 cm^{-1} has decreased in intensity, and it is now possible to observe a resolved band at 1745 cm^{-1} , which can be assigned to noncyclic anhydrides. Although the band at 1765 cm^{-1} due to cyclic anhydride has increased in intensity as well, the absorption at 1810 cm^{-1} is now much stronger.

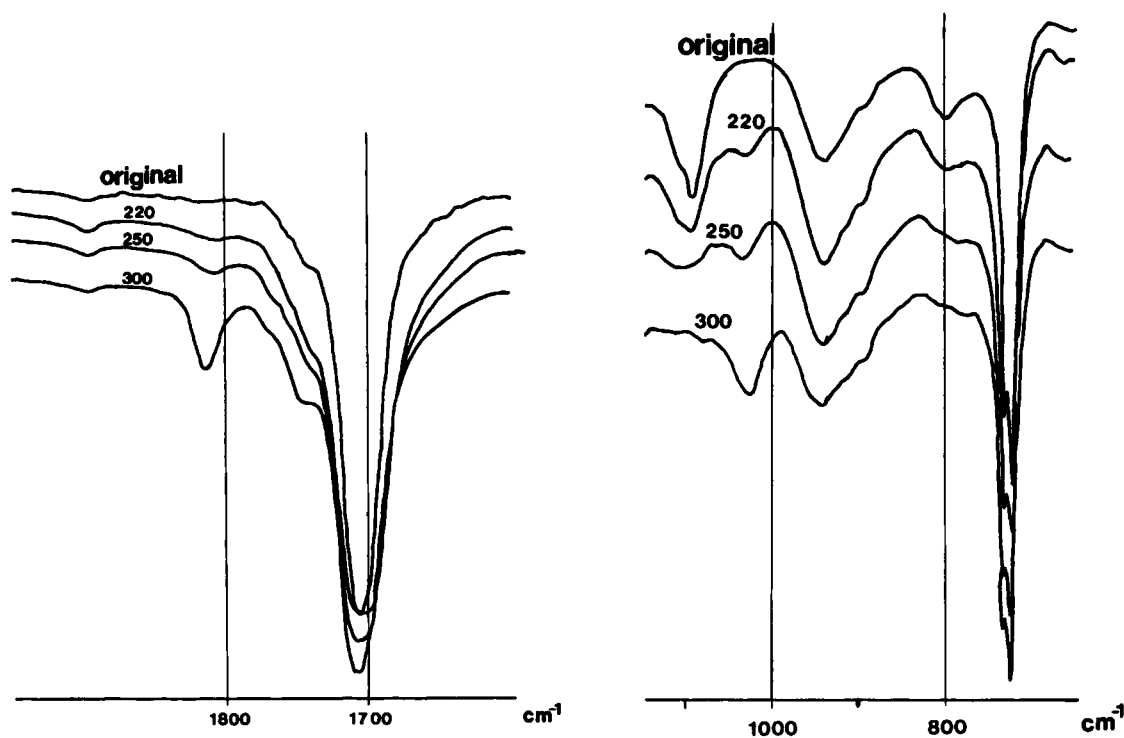


Figure 9 The effect of heat treatment on the FT-IR spectra of a blend of EVS-II and EAA (50 : 50). (A) 1600–1900 cm^{-1} , transmittance spectrum. (B) 650–1100 cm^{-1} , transmittance spectrum. (C) 650–1100 and 1600–1900 cm^{-1} in the difference spectrum obtained by subtracting the spectrum of the original spectrum from that of the 220°C sample, absorbance spectra with positive deflection for bands increasing in intensity. (D) 650–1100 and 1600–1900 cm^{-1} in the difference spectrum obtained by subtracting the spectrum of the original spectrum from that of the 300°C sample, absorbance spectra with positive deflection for bands increasing in intensity.

As discussed earlier the IR spectra show that both cyclic and noncyclic anhydrides have been formed. Both have two stretching bands in the carbonyl region, 1720–1770 and 1810–1870 cm^{-1} . Due to ring strain cyclic anhydrides tend to absorb at a higher wave number, e.g., compare isobutyric anhydride and succinic anhydride in Table V. However, the reported absorption frequencies of glutaric anhydride (1756 and 1802 cm^{-1}) compare well with those observed (1765 and 1810 cm^{-1}). Such a structure is formed if a dyad of two acrylic acid units reacts to form anhydride, which would be favored by the close proximity. The band at 1810 cm^{-1} can therefore be assumed to represent the total content of anhydrides. The absorption index for this band is shown by the solid line in Figure 10. The curve is exponential with a sharp increase between 250 and 300°C. The band at 1765 cm^{-1} can be used as a relative measure of cyclic anhydride. As seen by the broken line in Figure 10, the content of this structure increase initially with temperature but becomes constant at higher temperatures. For lower temper-

atures cyclic anhydrides should therefore be dominating. A lower starting temperature for formation of cyclic anhydrides is plausible as this reaction should be favored by the proximity of the reacting groups. On the other hand, the low concentration of acrylic acid (ca. 3.7 mol % in the EAA copolymer) implies that the amount of cyclic anhydride should be limited in accordance with the behavior of the absorption index of the band at 1765 cm^{-1} . Consequently, the strong increase in the total content of anhydride between 250 and 300°C can be related to noncyclic anhydride.

Table V Absorption Frequencies for Some Anhydrides

Compound	Wave Number (cm^{-1})	Ref.
Succinic anhydride	1865, 1782	24
Isobutyric anhydride	1803, 1743	25
Glutaric anhydride	1802, 1761	24

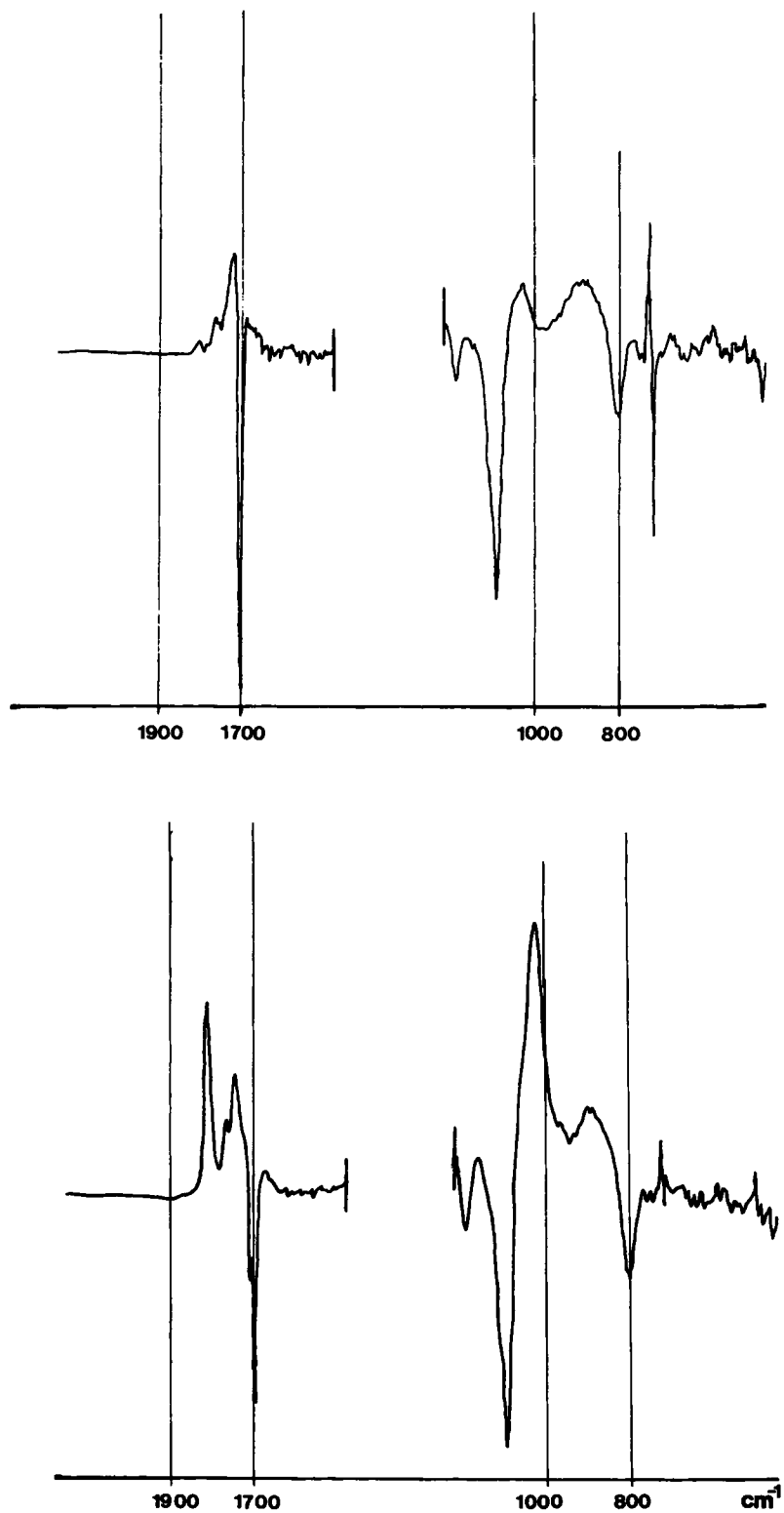


Figure 9 (Continued from the previous page)

The absorption index for the band at 1030 cm^{-1} is given by the broken line in Figure 11. No absorption could be observed after heat treatment at 160°C ,

but for higher temperatures the absorption increases linearly with temperature. This band represents both silane crosslinks and noncyclic anhydride.

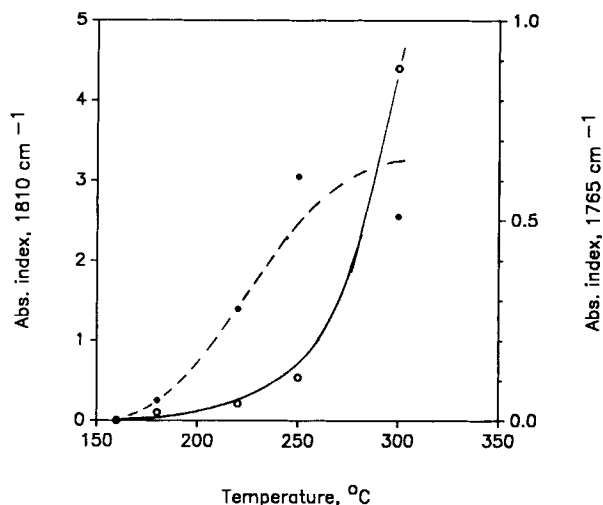


Figure 10 Absorption index for the anhydride band at 1810 cm^{-1} and the band specific for cyclic anhydrides at 1765 cm^{-1} in blends of EVS-II and EAA (50 : 50) treated for 10 min in dry nitrogen at different temperatures: ○, —, 1810 cm^{-1} ; ●, - - - -, 1765 cm^{-1} .

However, with regard to the faster increase between 200 and 250°C compared to the anhydride absorption at 1810 cm^{-1} (cf. solid line), and with reference to the earlier discussion, it can be concluded that the band at 1030 cm^{-1} mainly can be attributed to $-\text{Si}-\text{O}-\text{Si}-$ crosslinks for temperatures below 250°C . It can be mentioned that the maximum absorption index observed for the $\text{Si}-\text{O}-\text{Si}$ band of EVS-I is 2.4.⁷ As the content of silane comonomer is the same in EVS-II, the maximum absorption index at 1030 cm^{-1} due to $\text{Si}-\text{O}-\text{Si}$ can be estimated to 1.2 for the blend with 50% EAA. This and the strong increase in content of anhydrides above 250°C as evidenced by the band at 1810 cm^{-1} shows that the band at 1030 cm^{-1} becomes increasingly dominated by noncyclic anhydride at higher temperatures.

As discussed earlier crosslinking of EVS was facilitated by the addition of 5% EAA. This could be related to internal production of water as a result of anhydride formation. It is therefore tempting to relate the decreased critical temperature for gelation observed in the blend with 50% EAA to earlier formation of water. This is confirmed by the absorption index for the band at 1810 cm^{-1} , which starts to show positive values at 180°C compared to 220°C for the blend with 5% EAA. With respect to the earlier discussion, it can be assumed that the decreased onset temperature is due to formation of cyclic anhydrides. It must be pointed out, however, that no absorption bands due to anhydrides could be observed after heat treatment at 160°C , which

on the other hand caused substantial gel formation for the 50 : 50 blend. It was furthermore not possible to detect any $-\text{Si}-\text{O}-\text{Si}-$ crosslinks in this sample.

Another important observation is that the maximum observed content of gel for the 50 : 50 blend is 57%. Provided that physical effects leading to inclusion of noncrosslinked material are not operative, this should be impossible unless EAA would be incorporated into the gel. This, as well as the low onset temperature for gel formation, indicates that other crosslinking mechanisms may be operative. Contributions from anhydride formed by intermolecular reaction is, of course, an obvious possibility. In that way the high maximum content of gel can be explained but not the low onset temperature. This explanation is, however, invalidated by blank experiments with EAA that did not lead to any gel formation as measured by extraction, although considerable amounts of anhydride could be observed by FT-IR. This indicates that "noncyclic" anhydrides should be macrocycles, i.e., formed by an intramolecular reaction between two carboxylic acid groups in the same chain but well separated.

Reactions between EVS and EAA is another possible explanation. This should lead to $-\text{Si}-\text{O}-\text{CO}-$ crosslinks according to Eq. (4), which would explain the absorption band observed at 1720 cm^{-1} . This band is too close to the much

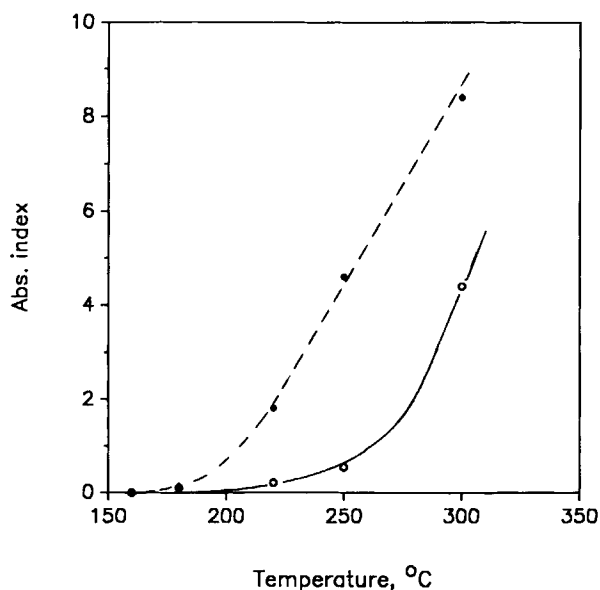


Figure 11 A comparison of the absorption index for the anhydride band at 1810 cm^{-1} and that of the band at 1030 cm^{-1} due to $-\text{Si}-\text{O}-\text{Si}-$ as well as anhydride in blends of EVS-II and EAA (50 : 50) treated for 10 min in dry nitrogen at different temperatures: ○, —, 1810 cm^{-1} ; ●, - - - -, 1030 cm^{-1} .

stronger absorption band of dimeric carboxylic acid at 1705 cm^{-1} to allow a correct subtraction and baseline definition. No absorption index has therefore been calculated for this band. In the difference spectra it can, however, be seen that its intensity is strongest in the sample heated at 220°C [Fig. 9(C)]. In the spectra of the 300°C sample only a small shoulder can be seen at 1720 cm^{-1} . This behavior is quite obvious as the increased formation of water at higher temperatures favors hydrolysis of the silane groups to silanol, Eq. (2). Even if $\text{Si}-\text{O}-\text{CO}$ should be formed, the presence of water should lead to hydrolysis as this bond is very sensitive to humidity.¹⁸ The formation of $-\text{Si}-\text{O}-\text{CO}-$ contributes to the low onset temperature for gel formation. In the difference spectrum between the sample treated at 160°C and the original sample, a small band could be observed at 1720 cm^{-1} . In this case it was possible to estimate an absorption index, ca. 0.01. The presence of $\text{Si}-\text{O}-\text{CO}$ is thus the only detected crosslink structure that could contribute to the relatively high content of gel observed in the 50 : 50 blend after heat treatment at 160°C , ca. 40%. Admittedly, the absorption index is quite low and further work is necessary to confirm this statement.

In conclusion, this investigation has shown that the processing problems, i.e., premature gel formation, that have been observed for ethylene vinyl silane-butyl acrylate copolymers can be related to reactions of the butyl ester groups. At about 250°C degradation to carboxylic acid starts, and these groups form anhydride with simultaneous formation of water. Liberated water subsequently hydrolyzes methoxy silane groups to silanols, which condensate to form $-\text{Si}-\text{O}-\text{Si}-$ crosslinks. These reactions have been confirmed using blends of EVS and EAA. In the latter case anhydride formation and crosslinking starts at considerably lower temperatures. At high loadings of EAA (50%) the presence of another crosslink structure formed by reaction between EVS and EAA, $-\text{Si}-\text{O}-\text{CO}-$, has been observed. This structure might be responsible for the relatively high content of gel, ca. 40%, observed after heating EVS with 50% EAA at 160°C . In our continued investigation on crosslinking of ethylene vinyl silane copolymers we are trying to establish the relative importance of the different crosslinking structures. Work on the catalytic effect of different groups is also in progress.

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