Catalysis of the Crosslinking Reactions of Ethylene Vinyl Silane Copolymers Using Carboxylic Acids and DBTDL

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ABSTRACT: The catalytic effects on the crosslinking behavior of poly(ethylene-*co*-vinyl-trimethoxysilane) were investigated for three different catalysts: the commonly used tin-based compound dibutyltin dilaurate (DBTDL), a low molecular weight carboxylic acid (stearic acid), and a polymer-bound carboxylic acid [ethylene–acrylic acid (EAA) copolymer]. Film samples were prepared and stored in hot water at 90°C and analyses were performed with a decalin extraction method as well as with FTIR techniques. The DBTDL was found to strongly catalyze the first step of the crosslinking reaction, that is, the hydrolysis. Concerning the catalytic activity of the carboxylic acids, the low molecular weight stearic acid has been shown to be a much more effective catalyst than is the polymer-bound carboxylic acid (EAA). Estimations on a molar basis give approximately a factor of five between them in efficiency. The carboxylic acids probably catalyze the hydrolysis as well as the condensation step of the crosslinking. Comparing stearic acid with DBTDL shows that the latter still is the more effective catalyst on a molar basis. Different possible catalytic mechanisms for the DBTDL and acid compounds are proposed based on the Brönsted and Lewis acids' concepts. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 521–528, 1999

Key words: crosslinking; ethylene vinyl silane; polyethylene; catalysis; carboxylic acids

INTRODUCTION

Crosslinking of polyethylene (PE) has been used commercially since the 1950s. Common fields of application are, for example, cable insulation and hot-water pipes. Several technologies have been developed for obtaining crosslinked PE: peroxide crosslinking, irradiation techniques, and silane crosslinking.[1–3] Silane crosslinking is traditionally performed through grafting vinyl silane (VS) onto a PE chain using small amounts of peroxides. Water then acts as a crosslinking agent. In the 1980s, however, an ethylene vinyl silane (EVS) copolymer was introduced to the market,[4] that is, VS was incorporated into the backbone of the polymer chain at the polymerization step.

In the crosslinking of EVS copolymers, two reaction steps are involved: a hydrolysis and a condensation step; see eqs. (1) and (2), respectively. In the hydrolysis, the silane methoxy groups attached to the polymer backbone form silanol groups, and in the second step, two of these condense and a crosslink is formed:

$$—Si—OCH_3 + H_2O \rightarrow —Si—OH + CH_3OH \quad (1)$$

$$—Si—OH + —Si—OH \rightarrow$$

$$—Si—O—Si— + H_2O \quad (2)$$

Table I   Main Characteristics of the Materials

	MFR2 (g/10 min)	$M_w \times 10^{-3}$ [a] (g/mol)	$M_n \times 10^{-3}$ [a] (g/mol)	AA[b] (mol %)	VS (mol %)	T_m[c] (°C)
EVS I	0.7	211	18		0.3	108
EVS II	4.5				0.3	105
EAA	10			4	0	98
St. Acid						70

[a] Determined by GPC.
[b] According to supplier.
[c] Determined by DSC.

These reactions were thoroughly examined in an earlier article[5] and the influence of the temperature and the presence of a catalyst[6] were also investigated. In commercial applications, a crosslinking catalyst has to be used to obtain an acceptable reaction rate. Today, a tin catalyst, dibutyltin dilaurate (DBTDL), is used. It is, however, not suitable for all applications, for example, for film in contact with food or for medical use. Therefore, efforts have been made to find new catalysts for this system. Another reason for finding other catalytic systems are possible restrictions for the use of tin compounds in other applications as well, such as in cable and pipe.

It has been proposed that the tin catalyst acts as a Lewis acid,[7] that is, as a compound that is able to accept electrons. Lewis acids are often inorganic or metal organic compounds which are difficult to mix with EVS. Many publications,[8,9] however, reported on Brönsted acid catalysis of hydrolysis and condensation reactions of silane methoxy and silane hydroxyl groups, respectively, in low molecular weight compounds. Catalysis of polymeric systems has, however, to our knowledge, not been published up to now. Therefore, an investigation of some Brönsted acids as catalysts was performed. Two kinds of Brönsted acids were examined: a low molecular type in the form of stearic acid and a polymeric, poly(ethylene-co-acrylic acid) (EAA). A study of the catalytic effect of the tin catalyst on the crosslinking reaction was also made as a comparison.

The different chemical groups involved in the two-step crosslinking reaction were studied spectroscopically using FTIR and the results of these studies were presented in an earlier article.[5] In that case, DBTDL was used as a catalyst. It was shown that the number of Si—O—Si crosslinks continue to increase also after a maximum gel content had been reached. Mechanical measurements indicate that crosslinks are formed within the already existing gel. In another article,[6] the relatively good crosslinking properties, also in the absence of DBTDL, of an EVS also containing butyl acrylate was discussed. It was shown that butene is released from the polymer at elevated temperatures with a simultaneous formation of acrylic acid groups,[10] giving rise to catalytic activity. In this article, further results from the studies on the EVS material are presented, concentrating on some aspects of catalysis, including catalysis by carboxylic acid groups.

EXPERIMENTAL

Materials

The EVS copolymers used in this investigation were kindly supplied by Borealis AB (Stenungsund, Sweden). The EAA and stearic acid used were both commercially available materials. Some data are presented in Table I. Further data were given elsewhere.[5]

Sample Preparation

Mixing of EAA and EVS was done using a Brabender PLE 651 extruder at 140–160°C with a holdup time of 4 min. Mixtures of EVS and stearic acid were, instead, made via a masterbatch containing 94.5% LDPE, 5% stearic acid, and 0.5% stabilizer. The masterbatch was mixed in different proportions with EVS and this mixture was extruded in the same way as was the EAA + EVS to obtain 0.05–0.5% stearic acid in the final mixture. All extrudates were immediately pressed into 0.2-mm films[5] at 150°C. The films were then stored in water at 90°C for up to 24 h. To avoid undesired crosslinking while waiting for analysis or further treatment, the samples were kept in a freezer at −30°C. To study the catalytic effect of

the tin catalyst, DBTDL and EVS were mixed via a masterbatch based on conventional LDPE in a laboratory extruder (Axon BX 15) to a concentration of 0.05% DBTDL by weight.

Analysis

Transmission spectra were obtained with a Perkin–Elmer 1720 X FTIR spectrophotometer. The following bands originating from different silane bonds were studied: Si—OCH$_3$ at 800 cm^{-1}; Si—O—Si, indicating crosslinks at 1030 cm^{-1}; and Si—OH at 3691 cm^{-1}. See refs. 11 and 12. Absorption indices were calculated using the overtone of CH$_2$ bending at 2020 cm^{-1} as an internal standard. The content of the gel was determined with a decalin extraction method,[13] slightly modified for practical reasons; after crosslinking, the film samples were cut in small pieces instead of being milled and sieved. Finally, the material was put in metal net cushions which were kept in boiling decalin for 7 h. The solvent was replaced after 6 h. After drying, the extracted amount was determined gravimetrically.

RESULTS AND DISCUSSION

First, the results from the examination of the activity of the tin catalyst, DBTDL, in the crosslinking reaction are presented and discussed. Films, of about 0.2-mm thickness, of EVS without a catalyst were stored in water at 90°C up to 124 h. Two slightly different EVS grades were used in this particular case: EVS I and EVS II (see Table I). In Figure 1, the absorption index of the Si—OCH$_3$ groups is given versus the treatment time. No difference in behavior could be seen for the two EVS samples. Therefore, they have been marked in the same way as open squares in the figure. In addition, the corresponding values obtained in our earlier work[5] on EVS containing DBTDL are given in the same figure as closed squares. A drastic difference in the rate of the disappearance of Si—OCH$_3$ groups can be observed. For samples containing DBTDL, a rapid decrease of the amount of silane methoxy groups is obtained, whereas samples without a catalyst show a very slow reaction rate. Even after 124 h, the absorption index has changed less than 3% (linear regression calculation). It seems obvious that DBTDL possesses a strong catalytic effect on the first step of the crosslinking reaction, that is, the hydrolysis.

Figure 1   Absorbtion index of SiOCH$_3$ in EVS versus treatment time in 90°C water: (□) EVS without DBTDL catalyst; (■) EVS with DBTDL catalyst.

Just as expected, no noticeable changes in the absorption index are observed for SiOH groups or can any IR band be observed at 1030 cm^{-1}, indicating the Si—O—Si crosslink, for EVS without a catalyst. These results together with the gel content measurements give further proof for the very slow rate of the crosslinking reaction occurring in EVS material without the presence of a catalyst.

It is a complex and difficult task to study the second reaction step separately due to the need of a catalyst to obtain the SiOH group. If the catalyst, then, cannot fully be removed, step 2 cannot be studied. Considering the mechanisms discussed below, however, it is likely to assume also that the condensation step is catalyzed in the same way as is the hydrolysis step. Much data in the literature[8,9] support the suggestion that steps 1 and 2 are catalyzed by Brönsted acids. These data, however, concern only low molecular weight silane compounds. As no corresponding data for polymers were available, we decided to perform a study on EVS. As a catalyst we chose one low molecular weight carboxylic acid (stearic acid) and one polymer-bound carboxylic acid (EAA) to be mixed with the EVS copolymer:

(a) Mixtures of EVS and stearic acid were pressed to produce films and were treated in water at 90°C and, finally, the crosslinking reaction was evaluated by measuring the gel content and by using FTIR.
(b) Mixtures of EVS and EAA were pressed to produce films and were treated as under (a).

Figure 2   Gel content versus treatment time in 90°C water for EVS containing different amounts of stearic acid; ($\times$) 0.05 wt %; ($\square$) 0.15 wt %; ($\bullet$) 0.30 wt %; ($\blacksquare$) 0.50 wt %.

Stearic acid was chosen due to its suitable physical properties: melting point at 70°C and boiling point at 235°C at a pressure of 20 Torr. The number of carbons is 18, which, in addition, should make it more compatible with PE than with carboxylic acids with a lower number of carbon atoms. Stearic acid is also reported to be catalytically active in similar reactions.[14] In Figure 2, the gel content of EVS containing different amounts of stearic acid is given versus the time of treatment in 90°C water. It is evident that stearic acid has a strong catalytic effect on the crosslinking reaction. The effect of the concentration on the reaction rate is also obvious. Note that the gel content is not equal to zero at $t = 0$ for all samples. This is probably due to precuring during the mixing operation. The effect of the stearic acid content is also clearly demonstrated in Figure 3, where the time needed to obtain 50% gel is presented versus the concentration of stearic acid. FTIR measurements of the Si—OCH$_3$ absorbtion show that the acid has a catalytic effect on the first step, the hydrolysis, as the amount of Si—OCH$_3$ decreases with the treatment time. In addition, a higher concentration of stearic acid seems to result in a stronger decrease of Si—OCH$_3$ groups per time unit, at least initially. An illustration of this is given in Figure 4, where the amount of consumed Si—OCH$_3$ is given versus time. In Figure 5, the resulting gel content is given versus the number of formed SiOH groups, which is assumed to be equal to the amount of consumed Si—OCH$_3$.

At low absorption indices, that is, at low levels of SiOH, there is a clear difference in how much

Figure 3   Time needed to reach 50% gel versus added amount of stearic acid, in weight percent, treatment in 90°C water.

gel is formed for different levels of added stearic acid. The higher the level of stearic acid, the more gel is formed for a certain amount of silanols formed. It is therefore possible to assume that the stearic acid, in fact, catalyzes the second step, the condensation reaction [eq. (2)], as well as the hydrolysis reaction described earlier in this article. This is then in accordance with what has been proposed by other authors[8,9] for low molecular weight compounds. At higher levels of Si—OH, the resulting gel levels are more or less the same for all concentrations of stearic acid. This can probably be explained by the earlier findings[5] using DBTDL as a catalyst, showing that the number of Si—OH groups formed first increases rap-

Figure 4   Consumption of Si—OCH$_3$ versus treatment time in 90°C water in EVS containing different amounts of stearic acid: ($\times$) 0.05 wt %; ($\bullet$) 0.30 wt %; ($\blacksquare$) 0.50 wt %.

Figure 5 Resulting gel content in EVS treated in 90°C water at different conversions of methoxy groups into silanols for different contents of stearic acid; ($\times$) 0.05 wt %; ($\bullet$) 0.30 wt %; ($\blacksquare$) 0.50 wt %.

idly during the first 15–20 h. During this period, the silanols formed are of the free type, nonhydrogen-bonded, and should be easily accessible for the reaction and influence of the available catalyst. Later on, during the course of the reaction, the net increase of silanols is represented by the hydrogen-bonded type instead. Due to the solid state of the polymer giving restricted mobility of the still available free silanol groups and restricted migration possibilities of the catalyst, due to the crystalline areas, this may explain the small differences in the gel content found at higher levels of the formed silanols in Figure 5.

The activity of Brönsted acids was also investigated with a polymer-bound carboxylic acid group. In this case, EAA was mixed with EVS (5 : 95) in a Brabender extruder and the mixture was pressed into films which were stored in water at 90°C. The results were at first somewhat scattered. FTIR measurements indicated that the mixture was not sufficiently homogeneous. A twin-screw extruder (Collin extruder) was therefore used to obtain a better mixture. As shown in Figure 6, which includes two sample series, this seems to be the case. However, the raw data are more scattered than normally experienced with low molecular weight catalysts. However, it has been shown[15] that blends of EAA and LDPE are immiscible at all proportions if the AA content of the EAA copolymer exceeds about 5% on a molar basis. This might be one explanation as to why difficulties in obtaining a homogeneous mixture exists, as the EAA material, within experimental

errors, contains such an amount of AA (see Table I). As discussed in connection to Figure 1, no gel is formed under the conditions used for these experiments, unless a catalyst is present. Figure 6, therefore, shows the important fact that EAA, just as stearic acid, is acting as a crosslinking catalyst for EVS

The results obtained with carboxylic acids as catalyst for the crosslinking of EVS thus seem to be very promising. A final gel content of 70% is reached within 25 h. These results also correspond well to what is obtained when using standard concentrations of DBTDL as a catalyst (0.05 wt %).

Worth noting, however, is that 5% by weight of EAA was used in the EVS/EAA mixtures. This corresponds to 0.18 mol % AA in the total mixture. This molar content would correspond to about 1.8 wt % stearic acid in EVS. Compared to our results from the experiments made with stearic acid, this amount is extremely high. From Figure 2, it can be estimated that far less than this amount of stearic acid is needed to obtain the same reaction rate, that is, a low molecular weight carboxylic acid seems to be much more effective as a catalyst than is polymer-bound carboxylic acid groups. This is probably due to the higher mobility of small molecules compared to larger ones. Two effects are likely to contribute in this case: On a macroscopic level, stearic acid is able to diffuse into the polymer matrix whereas the polymer molecules are fixed by the crystallite structure. Additionally, the carboxylic acid group in stearic acid could be regarded as an end group

Figure 6 Amount of gel formed in a 95:5 mixture of EVS and EAA as a function treatment time in 90°C water; ($\blacksquare$) test series 1; ($\square$) test series 2.

Figure 7 Comparison of catalyst efficiency between stearic acid and DBTDL treatment in a water bath at 90°C; ($\times$) 0.005 mol % stearic acid; ($\square$) 0.015 mol % stearic acid; ($\blacksquare$) 0.01 mol % DBTDL.

Table II Estimated Relative Catalytic Effect of Three Compounds: DBTDL, Stearic Acid, and EAA, with Comparison Made on a Molar Basis

Catalyst	Catalytic Activity (arbitrary units)
DBTDL	20
Stearic acid	5
EAA	1

in a polymer chain, which, in turn, has a higher mobility than has a group attached in the middle of a chain. Also, the efficiency on a molar basis of stearic acid compared to DBTDL is worth noting: DBTDL, 0.05 wt %, corresponds to about 0.01 mol % DBTDL, that is, the tin catalyst still is the most effective on a molar basis. This is illustrated in Figure 7, where the effectiveness of 0.01 mol % of DBTDL and stearic acid, respectively, is shown. As there are no experimental data for 0.01 mol % stearic acid, we have chosen to illustrate it with curves corresponding to two close values: 0.005 and 0.015 mol % stearic acid (corresponding to 0.05 and 0.15 wt %, respectively). It should be mentioned that the tin compounds were reacted into an EAA polymer to obtain the advantage of a polymer-bound catalyst.[16] In this case, the reaction was performed according to what is presented in Scheme 1. In this scheme, "POLYMER" represents a segment of the EAA copolymer. Migration of this compound is reduced compared to conventional DBTDL and will result in less leaching, for example, in the presence of water. On the other hand, the activity of such a compound is most likely reduced in comparison with the corresponding nonpolymer-bound alternatives.

In Table II, we tried to illustrate the difference in the catalytic effect of the three examined com-

pounds in this article, that is, DBTDL, stearic acid, and EAA. As a measure of the catalytic activity, the inverse of the amount of each compound, expressed as mol %, needed to obtain 60% gel after 5 h was conservatively estimated. These figures refer to industrially interesting levels.

Some practical problems during the extrusion of these mixtures occurred in the form of buildup in the die as well as some difficulties in obtaining a smooth surface. This is probably caused by precuring in the material as water is formed due to the formation of anhydrides at elevated temperatures.[6] This is also the most likely explanation of the fact that the gel content (Fig. 2) is not always equal to zero at the onset of the water treatment.

To explain the mechanism of the DBTDL catalyst, one should first consider the results from the tests with acid catalysts; as mentioned before, acids are able to catalyze the crosslinking reaction probably as shown in Scheme 2.[8] A similar mechanism can probably be used also for explaining the condensation step; it was reported[9,17] that the transformation of silanols into Si—O—Si bonds is also catalyzed by protons. Silanols, in general, react in a similar way as do alcohols and alkoxides but are more sensitive to bimolecular nucleophilic substitution reactions.[18] Consequently, the formation of Si—O—Si from silanol could be compared to the formation of ether between two alcohols as proposed in Scheme 3.

Regarding the mechanism of DBTDL, it was proposed by van der Weij[19] that DBTDL itself undergoes a hydrolysis reaction and forms an organotin hydroxide as shown in Scheme 4 and that

Scheme 1

Scheme 2

Scheme 3

Scheme 5

this compound is the actual catalyst. In addition, a carboxylic acid is formed which can act as a catalyst as well (see Schemes 2 and 3). According to ref. 19, the organotin hydroxide further reacts with an alkoxysilane to form an organotin silanolate (Sn—O—Si). It is further proposed[19] that the organotin silanolate is able to react with silanols to form the Si—O—Si crosslink. The proposed reactions are shown in Scheme 5 (see ref. 19). The actual formation of a carboxylic acid after treatment of DBTDL in contact with water was shown by Acima of Switzerland.[20] The fact that DBTDL is a more effective catalyst than is stearic acid might be explained by the double catalytic activity that results from the hydrolysis of DBTDL when an active organotin hydroxide is formed as well as a carboxylic acid.

Another mechanism for the condensation step is proposed in Scheme 6.[7] A thermodynamically stable six-membered ring, as in Scheme 4, is then formed through the hydrogen bonding at the penta-coordinating tin. In principle, still another possibility, a direct reaction between two methoxy groups at a DBTDL site, could be considered.[21]

This means, however, that no hydrolysis step would be needed and no formation of silanol would take place. According to former studies,[5,22] this is not likely to happen, as a very clear change in the concentration of silanol can be detected by infrared spectroscopy during the reaction.

CONCLUSIONS

A strong catalytic effect of Brönsted acids in the crosslinking reactions of EVS copolymers was found. It is probable that the hydrolysis step as well as the condensation step both are catalyzed by the acids. Low molecular weight carboxylic acids as well as polymer-bound ones were evaluated and the study shows a clear difference in activity between them; stearic acid has, in practical terms, been shown to be about four to five times more effective on a molar basis than is the EAA copolymer. Furthermore, it has been shown that a sufficient, but still acceptable, amount of stearic acid is capable of bringing about the crosslinking of EVS as quickly as can DBTDL. However, DBTDL is more effective on a molar basis. Different mechanisms were proposed for the hydrolysis and condensation step and the hy-

Scheme 4

Scheme 6

drolysis was shown to be strongly catalyzed by DBTDL.

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