Kinetics of Silane Grafting and Moisture Crosslinking of Polyethylene and Ethylene Propylene Rubber

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SYNOPSIS

Peroxide initiated graft copolymerization of vinyl trimethoxy silane (VTMO) and vinyl triethoxy silane (VTEO) onto polyethylene (PE) and ethylene propylene copolymer (EPR) was studied. The kinetics of grafting, studied by differential scanning calorimetry, are the same for all the systems and the activation energy for VTMO is 170 ± 4 KJ/mol. Activation energy for VTEO is 185 ± 5 KJ/mol. The VTMO and VTEO graft copolymers of PE and EPR were prepared by reactive processing in a Brabender extruder in the temperature range of 150–200°C. Moisture catalyzed crosslinking of the silane grafted copolymer was also studied. The influence of the structure of the catalyst, its concentration, moisture concentration, temperature, and time on degree and rate of crosslinking has been evaluated. Crosslinking reactions follow first order kinetics with respect to both catalyst and moisture concentration. Activation energy (E_a) of the crosslinking reaction has been determined as 65 KJ mol^{-1}. The mechanism of grafting and crosslinking is discussed.

INTRODUCTION

Recently, the production of functional polymers by the reactive processing of conventional polymers has received attention. This type of functionalization is performed for the modification of properties such as adhesion, dyeability, and so forth, as well as to prepare compatibilizer (interaction promoter) for multicomponent polymer blends and it is sometimes carried out in order to introduce crosslinks into polymers. Vinyl silanes are among the most effective classes of such organofunctional monomers; they can be grafted easily onto the backbone chain of polyolefins through melt processing.

Solution grafting of poly alpha-olefins onto unsaturated silanes for increasing heat resistance and adhesion was first reported in the early 1960s.[1] The technology of making moisture curable polyolefins through silane grafting by bulk processing was also developed and is being used commercially.[2,3] The method of making crosslinkable polyolefins through

silane grafting has gained attention in recent years because of its various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials. Although silane grafted polyethylene has been commercialized, the functionalization of polyolefins by silane grafting through reactive processing, and subsequent crosslinking processes has its problems. To date there is a lack of broad-based knowledge and expertise in this field and very few reports have been published in the literature.

Cartasegna reported on the molecular and structural parameters of ethylene propylene copolymer (EPR) and ethylene propylene diene terpolymer (EPDM) on silane grafting and crosslinking.[4] Dave discussed the peroxide and silane crosslinking process of PE.[5]

For useful commercialization, it is important to know quantitatively the variables and kinetic parameters that affect the grafting as well as the crosslinking processes. Recently, the authors reported on the kinetics and optimization of reaction variables for the preparation of dibutyl maleate (DBM) grafted polyethylene and ethylene propylene diene terpolymer (EPDM) in the bulk,[6] and on its prop-

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erties and applications.[7] The kinetics of peroxide crosslinking of PE and EPDM, and the effect of crosslinking on crystallization and fusion behavior of PE–EPDM blends, have also been studied.[8,9]

The present work demonstrates the kinetics of silane grafting onto PE and EPR. Since the silane grafting reactions are very fast, it is difficult to follow the kinetics directly during reactive processing. Hence, an attempt has been made to use differential scanning calorimetry to monitor the graft copolymerization reactions, because this method potentially allows determination of the rate of polymerization as a function of temperature.[10] Kinetics of crosslinking have also been studied. In addition, the influence of catalyst structure and concentration, and also of moisture concentration, on rate and degree of crosslinking have been evaluated. Finally, the mechanism of grafting and crosslinking is presented.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) (Neste polyethylene DFDS 4445 of Neste Polyeten ab, Sweden), ethylene propylene copolymer (EPR) (VISTALON 808) of Exxon, Belgium, vinyl silanes: vinyl trimethoxy silane (VTMO) (Dynamit Nobel, W. Germany), vinyl triethoxy silane (VTEO) (A 151) and gamma methacryloxy propyl trimethoxy silane (A 174) (Union Carbide, USA), dicumyl peroxide (Dicup of Hercules, Inc.) and stannous octoate (Kosmos 29), dibutyl tin dilaurate (Kosmos 19), and dialkyl tin mercaptide (Kosmos 21) (Goldschmidt A.G., W. Germany) were used directly.

Differential Scanning Calorimetry

Graft copolymerization reactions were studied using Mettler DSC 20 of a TA 3000 system with TC 10A microprocessor. PE and EPR used for DSC study were converted into powder form and antioxidant was removed by dissolving in hot xylene (130°C), followed by precipitation by nonsolvent (acetone) with high speed stirring in icebath. The requisite amount of DCP and silane were made into a solution and were premixed with PE and EPR in a morter. The premixed reactant mixture was encapsulated in hermetically sealed pans and grafting reactions were studied at a heating rate of 20°C per min.

Graft Copolymerization by Melt Processing in a Brabender Extruder

A premix of the PE or EPR, silane, and DCP was continuously fed to a Brabender Extruder (L/D: 25/1, D = 19.1 mm, compression ratio 2:1). Constant reaction temperature was maintained in each of the five successive zones of the extruder with an increasing temperature profile along its length. The temperature range was 150°C to 200°C.

Spectroscopic Analysis

Silane grafted PE (PE_gS) and silane grafted EPR (EPR_gS) were characterized and the degree of grafting was evaluated with the help of the infrared spectra obtained from a Shimadzu IR-420, using thin film (molded at 170°C) of the grafted polymers. Free silane was removed from thin film by acetone extraction. The absorbance of the

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}-O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}- \quad \text{group stretching of the grafted}$$

silane at 1090 cm^{-1} was used for characterization.

Determination of Gel Fraction

Previously weighed samples (cut into a number of small pieces) were allowed to swell and the soluble portions were extracted in Xylene at $120 \pm 2°C$ for 24 h. The samples were then dried to a constant weight in a vacuum oven at $60 \pm 1°C$. The percentage of the weight remaining, with respect to the initial weight, gave the gel fraction.

Determination of Moisture Content

Moisture content was determined by a Mettler DL 18 Karl Fisher Titrator with DL 185 heating oven using pyridine-free Karl Fisher reagent. The concentration of the reagent was standardized by sodium tartarate dihydrate. The result was automatically calculated by the microprocessor.

Theory for Determining the Kinetics of Grafting by DSC

The general scheme for the grafting of vinyl monomer onto polyolefins has been discussed in our earlier reports.[6] As the grafting reactions were studied, using a low concentration of monomer and initiator compared to the polymer content, the occurrence of secondary reactions were assumed to be negligible and they have not been considered for the simpli-

fication of the kinetic model. The possibility of homopolymerization of vinyl silane has been excluded because of its low concentration and low reactivity for propagation, due to steric hindrance. It is assumed that the following mechanisms apply, in the course of graft copolymerization reactions, based on the free radical reactions shown in Figure 1.[4]
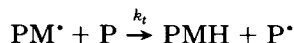
Initiation

Thermal decomposition of initiator:

$$I \xrightarrow{k_d} 2R^\cdot$$
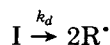
Generation of radical on the backbone of polymer chain:

$$R^\cdot + P \xrightarrow{k_i} P^\cdot + RH$$

Grafting

$$P^\cdot + M \xrightarrow{k_g} PM^\cdot$$
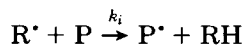
Termination through Chain Transfer to Polymer

$$PM^\cdot + P \xrightarrow{k_t} PMH + P^\cdot$$

Assuming this normal Kinetic scheme, the rate of graft copolymerization may be given by:[11]
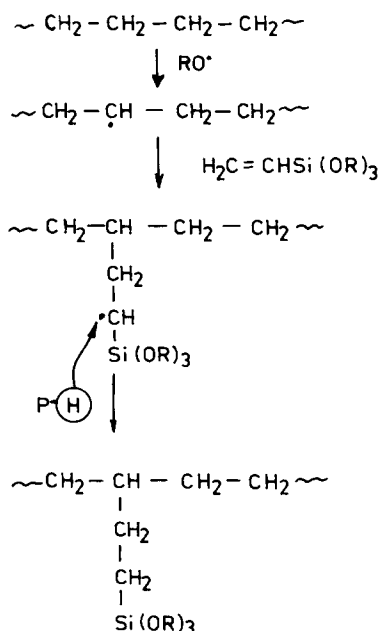

Figure 1 Free radical reactions producing silane grafted PE.

$$r_g = -\frac{d[M]}{dt} = k_g \left(\frac{r_i}{2k_t}\right)^{1/2}[M] \qquad (1)$$

where, r_g is the rate of grafting reaction, r_i is the initiation rate, k_g and k_t are grafting and termination rate constants, respectively, and $[M]$ is the monomer concentration. The rate of initiation

$$r_i = 2fk_d[I]$$
$$\approx 2k_d[I] \qquad (2)$$

At low concentration of initiator f may be assumed to be unity, k_d is the rate constant for the decomposition of the initiator, and $[I]$ is the initiator concentration.

Substituting this rate of initiation, r_i, into eq. (1) gives:

$$r_g = k_g \left(\frac{k_d}{k_t}\right)^{1/2}[I]^{1/2}[M] \qquad (3)$$

Equation (3) reveals that the rate of graft copolymerization is first order with respect to the monomer concentration and half order with respect to initiator concentration. At a fixed concentration of initiator, the rate expression (3) may also be written as

$$r_g = k_{ov}[M] \qquad (4)$$

where,

$$k_{ov} = k_g \left(\frac{k_d[I]}{k_t}\right)^{1/2}.$$

According to Borchardt and Daniels, the heat evolved in a small interval of time is directly proportional to the number of moles reacting during that time.[12] The same assumption is applicable here also. So, the enthalpy change up to a time interval t during a graft copolymerization reaction is directly proportional to the degree of conversion of monomer into the graft copolymer up to that time, and a curve similar to that shown in Figure 2 is obtained. Hence, we may write for the graft copolymerization

$$-\frac{d[M]}{dt} = k_{ov}[M] = \frac{n_o}{AV}\left(\frac{dH}{dt}\right) \qquad (5)$$

or,

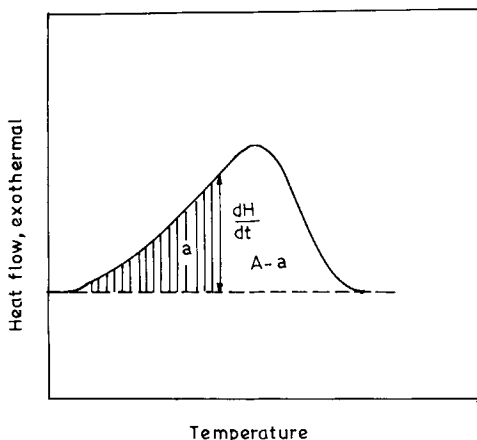$$\left(\frac{dH}{dt}\right) = k_{ov}[M]\left(\frac{AV}{n_o}\right) \qquad (6)$$

Figure 2 Schematic DSC curve showing the exotherm of graft copolymerization reaction.

where,

$\dfrac{d\mathrm{H}}{dt}$ = instantaneous change in enthalpy (heat evolved),

n_o = initial number of moles of monomer,

A = total area under DSC exotherm measuring the total enthalpy change (heat evolved during graft copolymerization reaction), and

V = total volume of the reaction mixture.

The monomer concentration at any instant can be expressed as

$$[\mathrm{M}] = \left(\frac{n_o}{\mathrm{V}} - \frac{n_o \times a/\mathrm{V}}{\mathrm{A}}\right)$$

$$= \left(\frac{n_o}{\mathrm{V}}\right)(\mathrm{A} - a)/\mathrm{A} \qquad (7)$$

where,

a = partial area at any time t.

Substituting eq. (7) into eq. (6), the result is:

$$\frac{d\mathrm{H}}{dt} = k_{ov}\left(\frac{n_o}{\mathrm{V}}\right)(\mathrm{A} - a) \Big/ \mathrm{A} \times \left(\frac{\mathrm{AV}}{n_o}\right)$$

or,

$$\frac{d\mathrm{H}}{dt} = k_{ov}(\mathrm{A} - a)$$

or,

$$k_{ov} = \left(\frac{d\mathrm{H}}{dt}\right)\Big/(\mathrm{A} - a) \qquad (8)$$

Equation (8) is applicable for a first order reaction, as shown here, with respect to monomer concentration. The overall rate constant (k_{ov}) can be readily determined as a function of temperature from the DSC traces.

Again, the change in the rate constant with temperature is given by the Arrhenius equation

$$k_{ov} = k_{o\ ov}\exp(-\mathrm{E}_a/\mathrm{RT}) \qquad (9)$$

where,

$k_{o\ ov}$ is the preexponential (collision frequency) factor,

E_a is energy of activation,

R is molar gas constant, and

T is the Absolute temperature.

Taking the natural logarithm in eq. (9) yields

$$\ln k_{ov} = \ln k_{o\ ov} - \mathrm{E}_a/\mathrm{RT} \qquad (10)$$

Substituting the value of [M] from eq. (7), and k_{ov} from eq. (9) into eq. (5), and converting this into logarithmic form, results in:

$$\ln\left[\frac{n_o}{\mathrm{V}}\frac{(d\mathrm{H}/dt)}{\mathrm{A}}\right] = \ln k_{o\ ov} + \mathrm{E}_\mathrm{A}\left(-\frac{1}{\mathrm{RT}}\right)$$
$$+ \ln \frac{n_o}{\mathrm{V}}(\mathrm{A} - a)\Big/\mathrm{A} \qquad (11)$$

Kinetic analysis of the grafting reaction has been done with the help of multiple linear regression analysis of eq. (11) by employing the partial areas and instantaneous change in enthalpy calculated by inbuilt software.

RESULTS AND DISCUSSION

Typical DSC traces of a few compositions, having the same DCP levels but various quantities of vinyltrimethoxysilane (VTMO), are shown in Figure 3. The plot shows that reaction exotherm, that is, heat evolved during the graft copolymerization reaction, increases with the increase in the quantity of vinyltrimethoxy silane (VTMO). Similar observations have been made for EPR and also for vinyltriethoxysilane (VTEO). However, using the same amount of gamma methacryloxy-propyl trimethoxysilane and DCP, no such sharp exotherm has been obtained, as shown in Figure 4. This reveals that gamma methacryloxy propyl trimethoxy silane
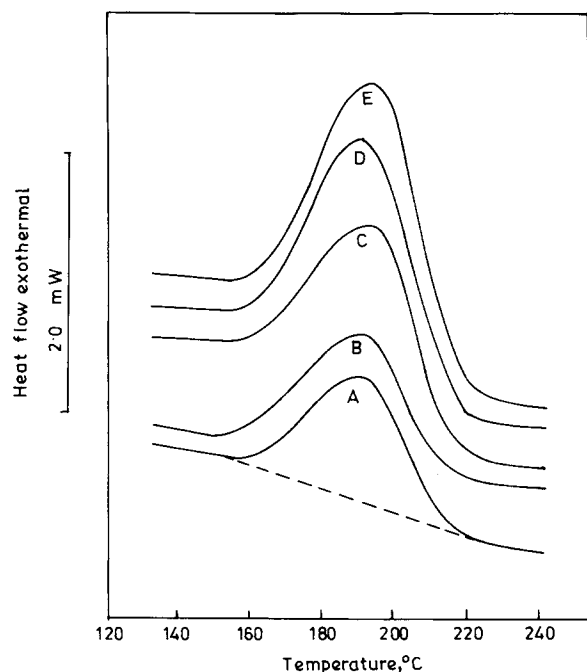
Figure 3 Typical DSC traces of exothermic grafting reactions. Reactant mixtures contain PE 100, DCP 1.6 m mol, and different amounts of VTMO. (A) 37.5, (B) 75, (C) 112.5, (D) 150, and (E) 225 m mol.

concentration of VTMO at which the degree of grafting reaches the steady value is also dependent upon the concentration of DCP. However, it has been found that further increase in DCP concentration, beyond 1.6 m mol per 100 g of PE, does not increase the value of ΔHexo. This finding shows that no significant contribution towards grafting is observed beyond 1.6 m mol of DCP. In the case of a peroxide-initiated grafting process, there is always a possibility of crosslinking reactions due to the similar values of activation energy for grafting and crosslinking reactions.

Activation Energy (E_a) for Grafting Reaction

As shown in Table I, the energy of activation (E_a) for the grafting reaction is 170 ± 4 KJ mol^{-1} for VTMO and for VTEO it is 185 ± 5 KJ mol^{-1}. It has also been observed that E_a values are independent of the concentration of silane and DCP and that the values are similar for PE and EPR. The EPR (Vistalon 808), used for grafting, contains a high percentage (about 75%) of ethylene and the grafting reaction proceeds through the H˙ abstraction from the $-CH_2$ (methylene) unit. Since the grafting reaction proceeds through the same reaction sites

does not undergo the free radical graft copolymerization reaction, probably because of the steric hindrance imparted by the acryloxy group. Similar results have also been obtained during grafting in the Brabender extruder.

In order to assess the importance of parameters affecting the grafting reactions, a systematic study has been made by varying the level of VTMO and DCP. The effect of the concentration of silane on reaction exotherm, reaction order, energy of activation, and preexponential factor has been determined using various levels of DCP; the results for the system containing 1.2 m mol of DCP per 100 g of PE are presented in Table I. The enthalpy change throughout the entire course of the grafting reaction of different systems, containing different levels of DCP, has been plotted against VTMO content in Figure 5. It is observed from Figure 5 that at the same level of DCP, the reaction exotherm increases with the increase in the VTMO content, and ultimately the reaction exotherm levels off at higher concentration. This observation proves that the degree of grafting reaches the saturation limit at this concentration of VTMO. However, for a particular concentration of VTMO, ΔHexo values are higher for the system having a higher amount of DCP. The
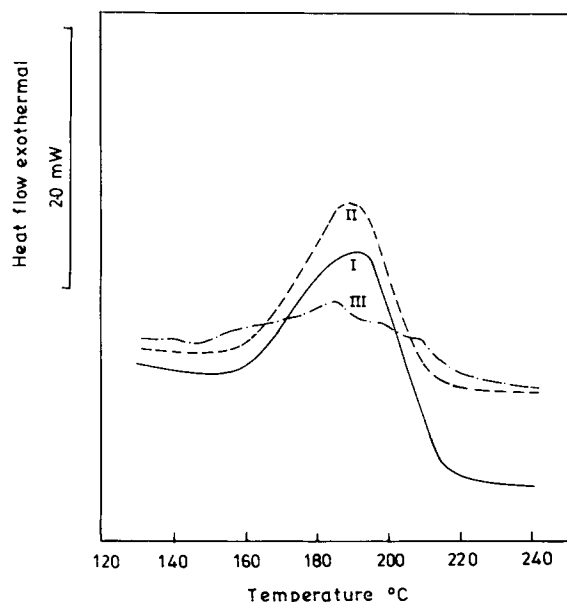

Figure 4 Typical DSC traces showing grafting exotherm of different silanes. Reactant mixtures contain (I) PE 100, DCP 1.6 m mol, VTMO 112.5 m mol; (II) PE 100, DCP 1.6 m mol, VTEO 112.5 m mol; (III) PE 100, DCP 1.6 m mol, gamma–methacryloxy propyl trimethoxy silane (A 174) 112.5 m mol.

Table I   Results of Effect of Variation of VTMO Content on the Grafting Reaction Exotherm, Energy of Activation and lnk_o of the Composition PE 100, DCP 1.2 m mol

Sample No.	VTMO Content m mol	Reaction Exotherm (ΔH_{exo}) (J g^{-1})	Reaction Order	Energy of Activation (KJ mol^{-1})	lnk_o
1	15	6.3	1	170 ± 4	40 ± 2
2	30	8.9	1	170 ± 4	40 ± 2
3	45	10.8	1	170 ± 4	40 ± 2
4	60	12.0	1	170 ± 4	40 ± 2
5	75	15.0	1	170 ± 4	40 ± 2
6	112.5	18.5	1	170 ± 4	40 ± 2
7	150	20.0	1	170 ± 4	40 ± 2
8	225	20.2	1	170 ± 4	40 ± 2

($-CH_2$) unit for both the PE and the EPR, the E_a for grafting is also similar.

The activation energy of a DCP-induced crosslinking reaction is 140 ± 5 KJ mol^{-1} for PE and 130 ± 5 KJ mol^{-1} for EPR, as obtained by DSC at the heating rate of 10°C per min. Because the difference in values of E_a for grafting and the crosslinking reaction is low at low concentration of DCP, the crosslinking reaction is suppressed by vinyl silane and grafting reaction predominates. But, at the concentration of DCP higher than 1.6 m mol per 100 g of PE or EPR, the crosslinking reaction predominates over grafting reactions. Similar observations have been made in the case of DBM grafting.[6]

So, it may be inferred that the degree of grafting increases up to the concentration of 1.6 m mol of DCP and 200 m mol of VTMO per 100 g of PE, beyond which the degree of grafting does not increase significantly. The possible explanations of these facts are (1) the sites for grafting reactions are consumed and (2) the solubility of vinyl silane in PE and EPR may also be a limiting factor for the grafting process.

It is also observed that the grafting reaction follows the first order kinetics regardless of the concentration and types of silane. This observation also proves the validity of the proposed theory. Preexponential factor (ln k_o) has been determined as 40 ± 2 for both VTMO and VTEO.

Isothermal Behavior of Grafting Reaction

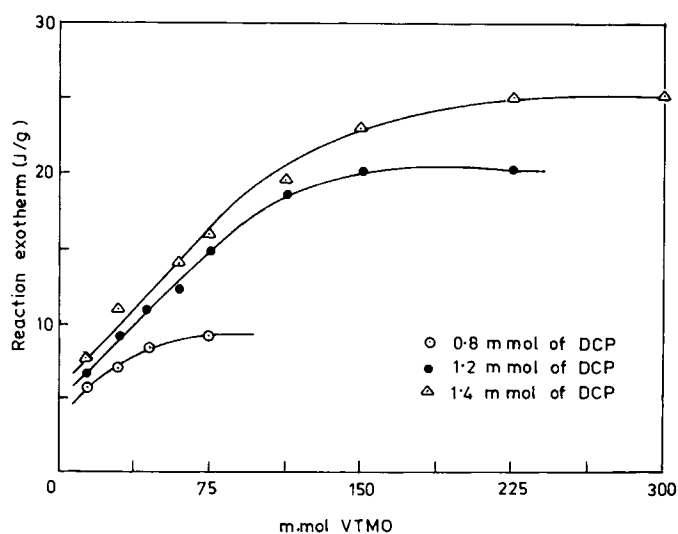The course of grafting reactions, that is, the degree of conversion of the silane to graft copolymer at dif-

Figure 5   Effect of variation of DCP content and concentration of VTMO on grafting reaction exotherm of PE.
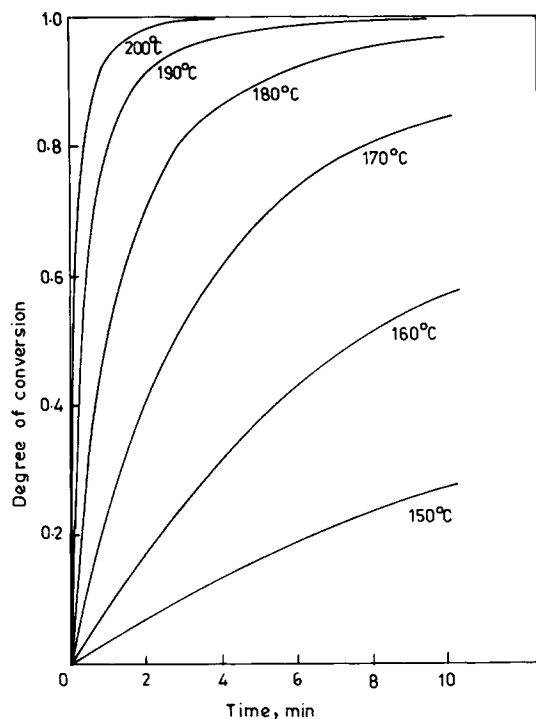
Figure 6 Plot of DSC traces showing degree of conversion of VTMO into the graft copolymer vs. time at different isothermal temperatures. Reactant composition is PE 100, DCP 1.6 m mol, and VT MO 112.5 m mol.

ferent isothermal temperatures, has been calculated through the inbuilt software. The software used the data obtained from nonisothermal (dynamic) DSC.

The results, as a plot of degree of conversion with time at different isothermal temperatures (150, 160, 170, 180, 190, and 200°C), of the system PE 100, DCP 1.6 m mol, and VTMO 112.5 m mol, are presented in Figure 6. The plot shows that the degree of conversion, as well as the rate of conversion, increases with the increase in temperature.

Characterization

For characterization and subsequent studies on crosslinking, silane grafted PE and EPR have been prepared by reactive processing in the Brabender Extruder at a temperature range of 150°C to 200°C, and at screw rpm of 40. The graft copolymers have been characterized by IR methods. The IR spectra of PE and PE$_g$VTMO are shown in Figure 7. Silane grafted PE and EPR with, the degree of grafting of 40 ± 3 m mol per 100 g of grafted copolymer, have been used in the study of crosslinking and its kinetics.

Crosslinking

In the presence of moisture and condensation catalyst, the alkoxy group of the silane derivatives pendant to the grafted copolymer convert to silanol groups and undergo a condensation reaction to form
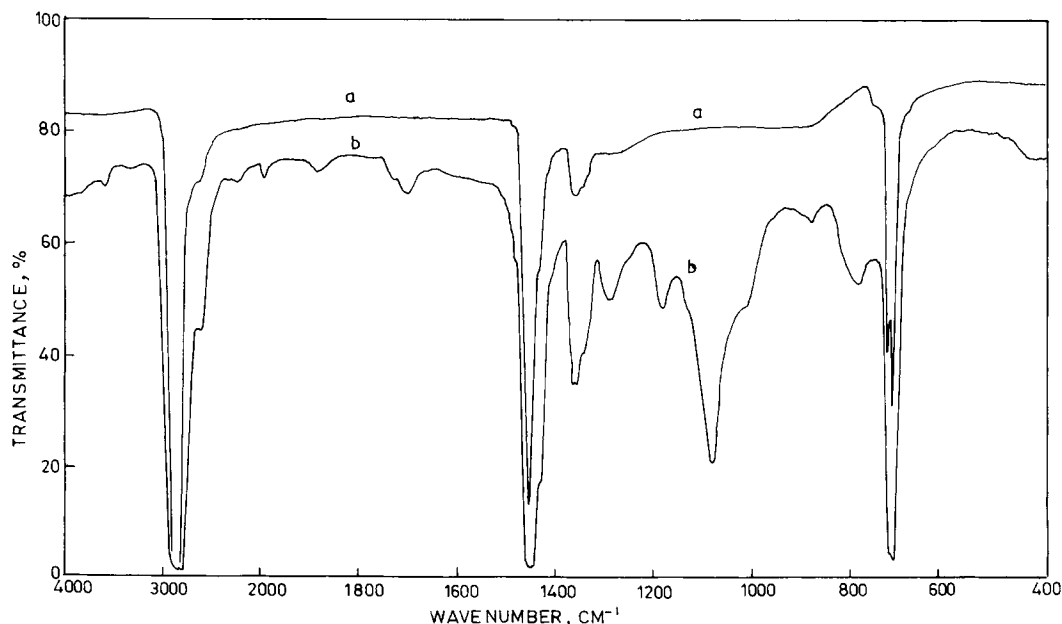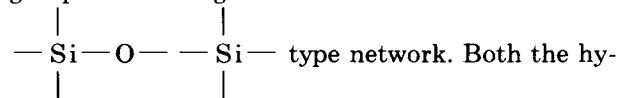
$$
\begin{array}{ccc}
| & & | \\
-\text{Si}-\text{O}- & -\text{Si}- & \text{type network. Both the hy-} \\
| & & |
\end{array}
$$

Figure 7 Infrared spectra of (a) PE and (b) PE$_g$VTMO.

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2  ~ CH₂ – CH – CH₂– CH₂~
              |
             CH₂
              |
             CH₂                    Catalyst ,H₂O          2  ~CH₂ –CH – CH₂– CH₂~
              |            ────────────────────►                    |
       H₃CO – Si – OCH₃              –CH₃OH                         CH₂
              |                                                      |
             OCH₃                                                   CH₂
                                                                     |
                                                            H₃CO – Si – OCH₃
                                                                     |
                                                                    OH

   PEg  VTMO  graft copolymer
                                                            Catalyst │ –H₂O
                                                                     ▼


                          ~ CH₂ –CH – CH₂– CH₂~
                                   |
                                  CH₂
                                   |
                                  CH₂
                                   |
                           H₃CO – Si – OCH₃
                                   |
                                   O
                                   |
                           H₃CO – Si – OCH₃
                                   |
                                  CH₂
                                   |
                                  CH₂
                                   |
                       ~H₂C — CH — CH₂ CH₂~

                          Crosslinked  network
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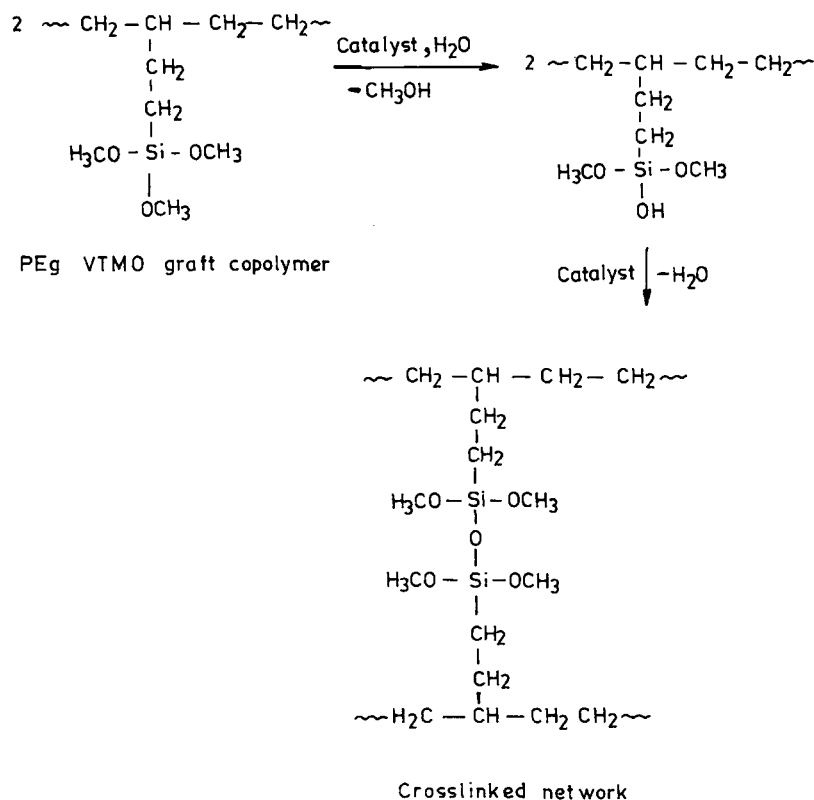
Figure 8   Mechanism of hydrolysis and crosslink formation through the condensation reaction of silanol groups.

drolysis of alkoxy silane to silanol and their condensation reaction occur almost instantaneously.[4] The overall mechanism is depicted in Figure 8.[13]

For studying the influence of catalyst and moisture concentration on the rate and degree of crosslinking, we have studied the kinetics of crosslinking by varying type as well as concentration of catalyst.

Effect of Variation of Catalyst Concentration on the Degree of Crosslinking

Three types of catalysts, stannous octoate, dibutyl tin dilaurate (DBTDL), and dialkyl tin mercaptide, have been studied to discover their efficiency in inducing crosslinking and for the optimization of their concentration. The variation of gel fraction, which is a measure of the degree of crosslinking, has been plotted against a catalyst concentration in Figure 9. It is observed in Figure 9 that the gel fraction increases with the increase in the concentration of catalyst. Although at a higher concentration (above 30×10^{-3} g per 100 g of grafted PE), all three catalysts result in the same degree of crosslinking, at

a lower concentration, the order of their efficiency is stannous octoate < dibutyl tin dilaurate < dialkyl tin mercaptide.
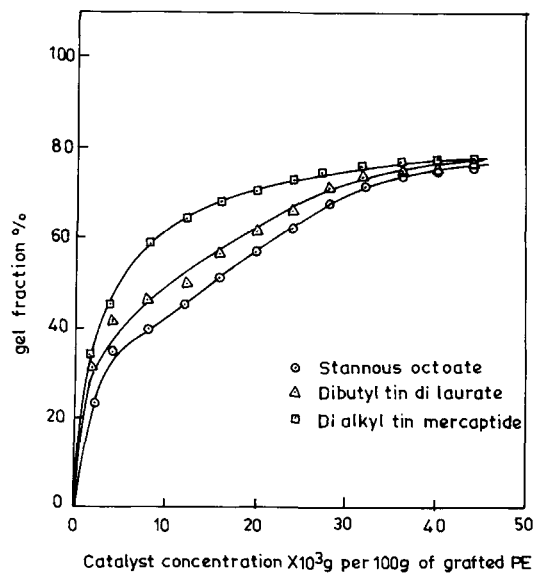

Figure 9   Effect of variation of concentration of different catalysts on gel fraction.
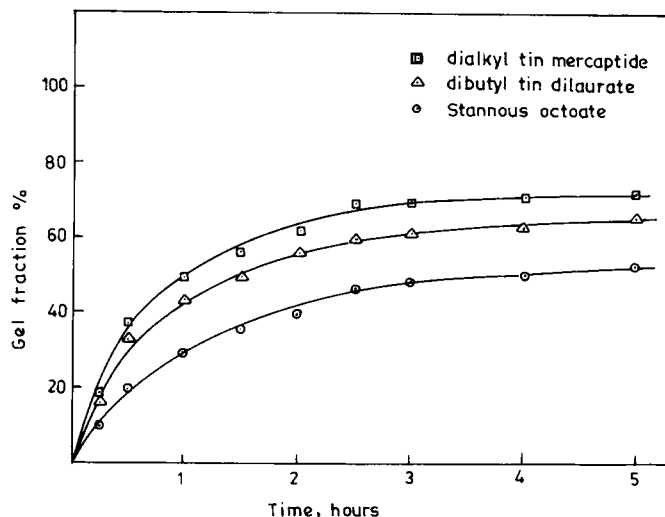
Figure 10   Effect of variation of catalysts on gel fraction.

Effect of Variation of Catalyst on the Rate and Degree of Crosslinking

To observe the effect of variation of the catalyst, all three catalysts with the same concentration (20 $\times$ 10^{-3} g per 100 g of grafted PE) have been used. Crosslinking has been carried out for different extents of time in hot water (90 $\pm$ 1°C). The corresponding gel fraction vs. time is plotted in Figure 10. The plot shows that the rate of crosslinking is similar for dialkyl tin mercaptide and dibutyl tin dilaurate, but a relatively slower rate is observed with stannous octoate. However, the degree of

crosslinking achieved after complete curing at this catalyst concentration follows the order dialkyl tin mercaptide > dibutyl tin dilaurate > stannous octoate, which has also been observed in Figure 9. These tin compounds catalyze the silanol condensation reaction by their Lewis acid behavior. Probably due to stronger Lewis acid character of the mercaptide over carboxylate, di-alkyl tin mercaptide is the most effective catalyst. Similarly, between the two tin carboxylates, dibutyl tin dilaurate shows more pronounced activity than stannous octoate, due to dibutyl tin dilaurate's stronger Lewis acid behavior.
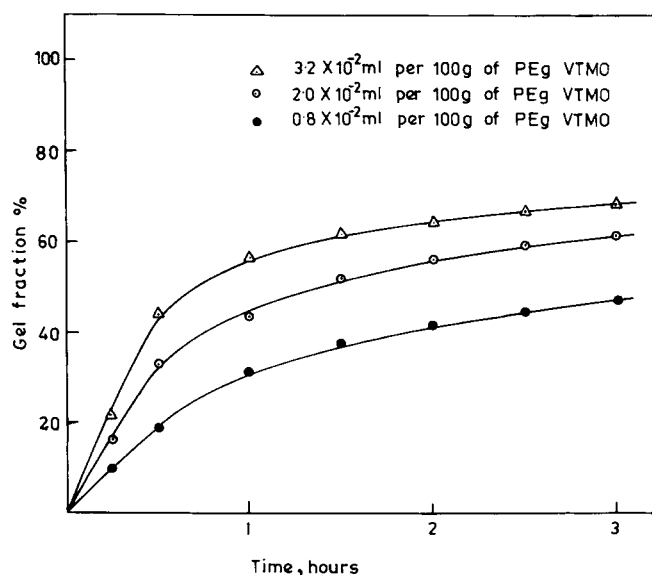

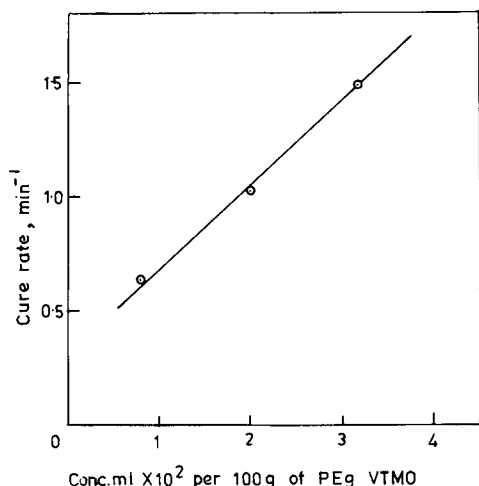**Figure 11**   Plot of gel fraction vs. time of crosslinking.

Figure 12 Plot of cure rate vs. concentration of catalyst (dibutyl tin dilaurate).

Kinetics of Crosslinking

The overall rate of the crosslinking reaction may be expressed as

$$\frac{dx}{dt} = kC_c^a C_m^b \qquad (13)$$

where,

$\frac{dx}{dt}$ = Rate of gel formation,

k = Overall rate constant,

C_c = Concentration of the catalyst,

C_m = Concentration of moisture,

a = Order of crosslinking reaction with respect to catalyst, and

b = Order of crosslinking reaction with respect to moisture.

For discovering the order with respect to the catalyst concentration, PE_gVTMO has been crosslinked to different extents of time in hot water ($90 \pm 1°C$), using three different concentrations of dibutyl tin dilaurate. The plot of gel fraction against time of crosslinking is shown in Figure 11. It is found that, as the catalyst concentration increases, the rate and also the final degree of crosslinking increase. So, both the rate and degree of crosslinking depend on the concentration of catalyst.

From the initial (straight) portion of the curves, the slopes $\left(\frac{dx}{dt}\right)$ have been calculated as a measure of rate of crosslinking and have been plotted against the catalyst (dibutyl tin dilaurate) concentration in Figure 12. As observed in Figure 12, a straight line is generated with a positive slope of unity. This reveals that the rate of crosslinking reaction linearly increases with the catalyst concentration and follows first order kinetics when moisture concentration remains constant. The same observation has been found with two other catalysts also.

Effect of Variation of Moisture Concentration on Rate and Degree of Crosslinking

Similarly, to find out the reaction order with respect to moisture concentration, crosslinking has been
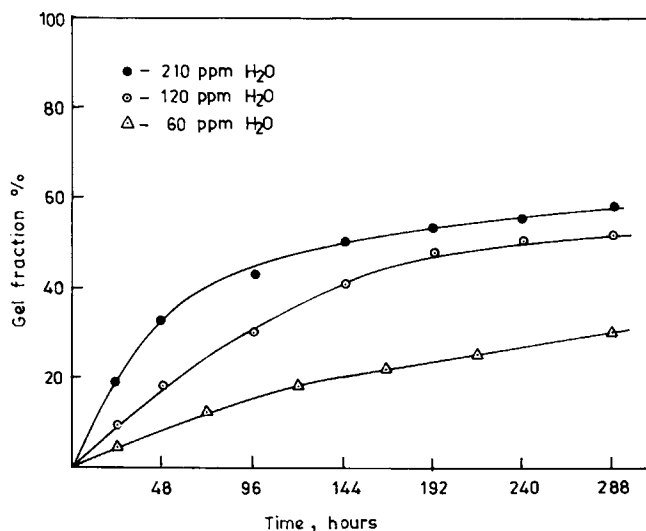

Figure 13 Plot of gel fraction vs. time of crosslinking showing the comparison of cure characteristics that are a result of the difference in moisture content.
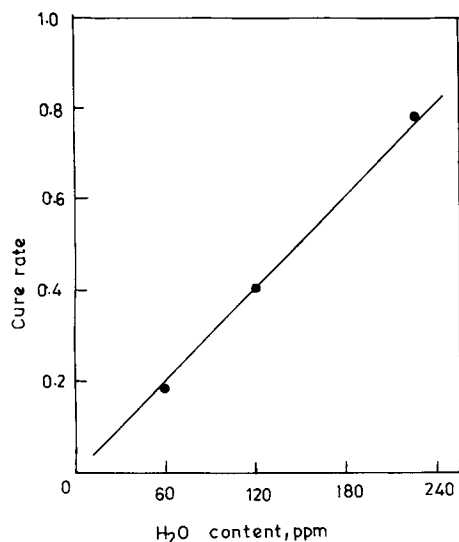
Figure 14   Plot of cure rate vs. moisture content.

carried out by keeping the catalyst concentration and temperature constant (20×10^{-3} g per 100 g of PE_gVTMO and 30°C, respectively). The moisture content has been varied by keeping the samples in water (H_2O content 210 ppm), normal air (H_2O content 120 ppm), and in dessicator (H_2O content 60 ppm). Crosslinking was followed by measuring the gel fraction at different intervals of time (moisture content was measured by Karl Fisher titration). A plot of gel fraction vs. time of crosslinking is shown in Figure 13. It is observed that as the moisture content increases, the rate of crosslinking increases. It is also found that the degree of crosslinking follows a similar trend. The slopes of the initial portion of the curves, when plotted against moisture content, result in a straight line with a slope of almost unity

as shown in Figure 14. This proves that rate of crosslinking also follows first order kinetics with respect to moisture concentration. This has been found true using the other two catalysts as well.

Energy of Activation (E_a) for Crosslinking Reaction

For determining the activation energy (E_a), crosslinking reactions were carried out at different temperatures (30°, 60°, and 90°C) in water using a catalyst concentration of 20×10^{-3} g per 100 g of PE_gVTMO. The corresponding gel fraction has been measured against the time of crosslinking and is plotted in Figure 15, which shows that the rate and degree of crosslinking increase with temperature. From the initial portion of the curves, which provides the rate of crosslinking reaction, Arrhenius plot has been drawn (Fig. 16). The linear temperature dependence of the crosslinking reaction is observed in Figure 16, and the energy of activation (E_a) has been calculated as 65 KJ mol^{-1}. Similar results were obtained with the catalyst stannous octoate and dialkyl tin mercaptide.

CONCLUSIONS

1. Functionalization of PE and EPR can be accomplished by grafting vinyl trimethoxy and vinyl triethoxy silane onto polymer backbone, using free radical initiator by reactive processing.
2. Graft polymerization reactions can be well monitored and grafting kinetics can be determined by differential scanning calorimetry.
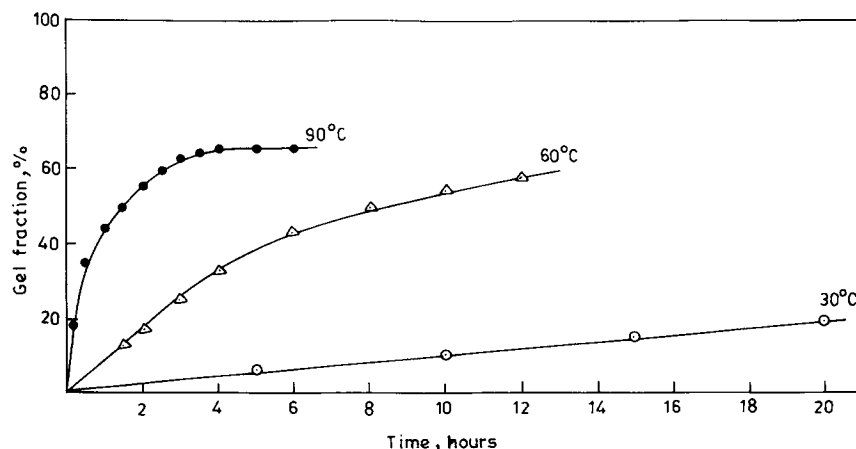

Figure 15   Plot showing gel fraction vs. time of crosslinking at different temperatures.
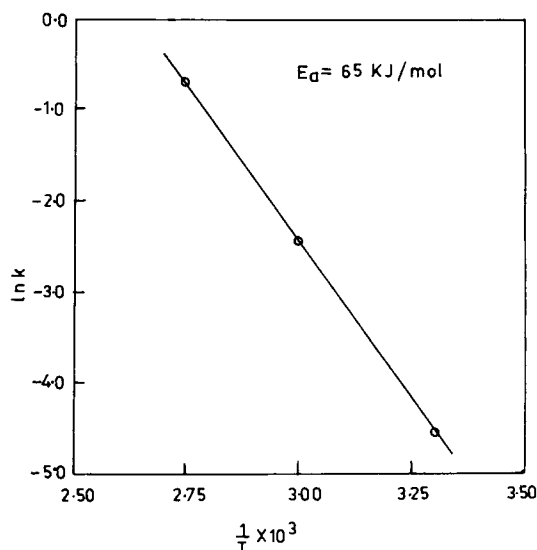
Figure 16 Arrhenius plot of the initial rate of cross-linking reaction.

3. The degree of grafting is regulated both by the monomer (silane) and the DCP concentration. Maximum extent of grafting is obtained with 1.6 m mol DCP and 225 m mol of silane per 100 g of polyolefin.

4. Graft copolymerization reactions follow first order kinetics with an activation energy of 170 ± 4 KJ mol^{-1} for VTMO and 185 ± 5 KJ mol^{-1} for VTEO.

5. Both the degree and rate of crosslinking are guided by the concentration of catalyst and moisture. Crosslinking reactions follow first order kinetics with respect to catalyst as well as moisture concentration.

6. Energy of activation (E_a) for the crosslinking reaction has been obtained as 65 KJ mol^{-1}.

REFERENCES

1. T. R. Santelli, U. S. Patent No. 3,075,948, Jan. 29, 1963.
2. H. G. Scott, U. S. Patent No. 3,646,155, Feb. 29, 1972.
3. P. Swarbrick, W. J. Green, and C. Maillefer, U. S. Patent No. 4,117,195, Sep. 26, 1978.
4. S. Cartasegna, *Rubber Chem. and Technol.*, **59**, 722 (1986).
5. B. Dave, In *Handbook of Elastomers—New Developments and Technology*, A. K. Bhowmick and H. L. Stephen, Eds., Marcel Dekker, New York, 1988, Chap. 12, p. 709.
6. A. K. Sen, B. Mukherjee, A. S. Bhattacharyya, P. P. De, and A. K. Bhowmick, *Die Angewandte Markromolekulare Chemie*, to appear.
7. A. K. Sen, B. Mukherjee, A. S. Bhattacharyys, L. K. Sanghi, P. P. De, and A. K. Bhowmick, *J. Appl. Polym. Sci.*, to appear.
8. A. K. Sen, A. S. Bhattacahryya, P. P. De, and A. K. Bhowmick, *J. Thermal Anal.*, **37**, 19 (1991).
9. A. K. Sen, B. Mukherjee, A. S. Bhattacharyya, L. K. Sanghi, P. P. De, and A. K. Bhowmick, *Thermochimica Acta*, **157**, 45 (1990).
10. P. B. Rim and K. M. O'Connor, *J. Polym. Sci. Part C. Polym. Lett.*, **24**, 95 (1986).
11. M. Okoniewski, J. S. Ledakowicz, and S. Ledakowicz, *J. Appl. Polym. Sci.*, **35**, 1241 (1988).
12. H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).
13. B. Thomas and M. Bowrey, *Wire J.*, 88 (May 1977).