Aspects of the Crosslinking of Polyethylene with Vinyl Silane

Gul Bali Shah,[1] Mohammad Fuzail,[1] Jamil Anwar[2]

[1]*Applied Chemistry Laboratories, Pakistan Institute of Nuclear Science and Technology, P. O. Nilore, Islamabad, Pakistan*
[2]*Chemistry Department, University of Punjab, Lahore, Pakistan*

ABSTRACT: The crosslinking reaction of low-density polyethylene with vinyl triethoxysilane was studied in great detail. The effects of a wide range of concentrations (0–27.33 phr silane and 0–1.25 phr benzoyl peroxide) on the mechanical properties, hot-set testing, gel contents, and burning behaviors of the resulting crosslinked polyethylene were studied. The effect of variations in the concentration of silane was found to be a dictating parameter for all these properties. Moreover, at or above a certain threshold concentration of silane (4.56 phr), samples not only qualified for hot-set testing but also showed other properties at an optimum level. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3796–3803, 2004

Key words: crosslinking; flame retardance; mechanical properties

INTRODUCTION

Polyethylene (PE) can be extruded into three types of products: cables, pipes, and sheets/films. All these applications are important, but the fact that PE is a thermoplastic with low melt viscosity limits its service temperature to a lower level. Continuous use under stress at up to 100°C for hot-water pipes, occasional increases in the temperature above a certain limit during extrusion, and temporary electrical overloads on cables unfortunately make ordinary PE unsuitable for these applications. There is a need to modify PE in such a way that its thermal stability is increased to endure high service temperatures. For this purpose, PE is crosslinked; that is, its chains are bound together to form a network. Presently, there are three commercial methods[1,2] used for the crosslinking of low-density polyethylene (LDPE): (1) peroxide crosslinking,[3] (2) radiation crosslinking,[4] and (3) crosslinking through the grafting of silane followed by moisture crosslinking.[5] Each method has its own applications according to its particular advantages.

PEs crosslinked by peroxide in the presence of silane are based on LDPE and high-density PE. LDPE is used for the insulation of high- and medium-voltage power cables. The chemistry of PE crosslinking with peroxide is well known.[6–9] Crosslinking via silane is a thermochemical reaction in which the peroxide first decomposes at an elevated temperature; this results in the formation of oxy radicals. These oxy radicals have the potential to abstract hydrogen from the PE molecule and can attack the vinyl group of a molecule and convert it into free radicals. These free radicals either combine with one another or attack another molecule in a similar fashion to propagate the free-radical reaction. This process results in the grafting of vinyl silane onto PE chains, and this is the prerequisite for the crosslinked material. Crosslinked PE has unique properties that noncrosslinked PE does not. In this manner, a molecular network is formed. There are a number of peroxides available that can be used for the crosslinking of polymers in which free-radical formation is involved. These peroxides behave differently and, therefore, can affect vulcanization differently. These peroxides have been reported to exhibit different decomposition times for silicone rubber formulations at 140°C.[10]

The effects of various parameters on the molecular structure of a polymer have an impact on the development of new polymeric products, which can be tailored according to the requirements. Some researchers have investigated the efficiency of peroxide in terms of the number of crosslinks formed for each molecule of peroxide.[11–13] The facile hydrolysis and condensation reaction of the alkoxy group of the grafted silane are then exploited in homogeneous polymeric systems for the crosslinking of PE chains, and this results in a polymer network.

It has been shown by IR and ^{13}C NMR that for low-density and high-pressure types crosslinked with peroxide or silane, the degree of chain branching is the same in the soluble part of the crosslinked sample as

TABLE I
Properties of Crosslinked PE with Various Silane Concentrations, Cured at 105°C

Sample	Silane (phr)	Gel contents	Elongation at room temperature (%)	Tensile strength (kg/mm^2) at room temperature	Hot-set temperature at break (°C)
Control	0.000	0	250	1.3	120
1	1.14	43	170	1.61	128
2	2.28	50	150	1.64	160
3	4.56	63	148	1.74	250
4	6.83	67	127	1.6	248
5	11.38	68	118	1.45	250
6	18.22	70	100	1.3	255
7	27.33	75	100	1.25	261

in the polymer before crosslinking.[14] Gel permeation chromatography analysis has shown that the soluble portions of samples are in all cases lower molecular weight materials than the corresponding starting materials. The molecular weight distribution in the materials before crosslinking is bimodal, in contrast to the materials after the crosslinking if samples, for which it is unimodal.

In this work, a sequential series of experiments was performed to monitor the effects of variations of basic parameters, such as the concentrations of silane and benzoyl peroxide (BPO), on the crosslinking of PE and its subsequent mechanical and flame-retardant properties. This basic study was designed to determine how to optimize the properties of crosslinked PE and to tailor the properties of a polymer network according to its requirements.

EXPERIMENTAL

Materials

Vinyl triethoxysilane (VTES; formula weight = 190.32, assay > 98%) was supplied by Fluka (Buchs, Switzerland). Analytical-grade dibutyl tin dilaurate (DBDTL; formula weight = 631.56) was purchased from Merck–Schuchardt. LDPE (commercially known as Lotrene) granules were supplied by Qapco, Ltd. (Qatar). BPO was purchased from Fluka. These chemicals were used without further purification.

Crosslinking of PE

In the first step, vinyl silane was grafted onto PE chains by a free-radical reaction initiated by a peroxide catalyst, which in our case was BPO. To ensure the homogeneity of the materials for grafting, LDPE was crushed with a Thomas–Wiley 3383-L1O series intermediate mill (New Jersey) into a powder form, and then the weighed amounts of the materials were mixed.

The LDPE powder (40 g) was placed in a 250-mL beaker, a weighed amount of BPO was added, and

they were mixed with a glass rod. Precise amounts of silane and the catalyst dioctyl tin dilaurate were added separately to the mixture dropwise from the respective syringes. During the addition of silane, the LDPE powder was continuously stirred with a glass rod to homogeneously distribute the ingredients. Once this process was complete, the material was charged to a Rheodrive 5000 closed Brabender mixer (Haake, Germany) set at 140°C, and mixing was continued for 5 min. The grafting process was completed in the Brabender mixer, and then the materials were pressed into a sheet of the required thickness in a heat press set at 190°C. In the second step, the prepared sheets were treated for curing in an autoclave at 105°C for 4 h.

Characterization of crosslinking

Tensile strength measurements

An Instron 4301 from High Wycombe (Buckinghamshire, England) was used for the measurement of the tensile properties at a strain rate of 50 mm/min with dumbbell specimens cut according to BS 903 Part A2 1956 Die C. The tensile strength and elongation-at-break percentage were calculated from an isothermal stress–strain curve. An average of three modal values of the tensile strength of the five samples tested was quoted.

Gel content

The gel content, that is, the insoluble material, was determined by the refluxing of the true solvent (toluene) onto weighed crosslinked PE samples in a Soxhlet apparatus for more than 24 h. After this, the samples were taken out and were dried in an oven at 80°C to a constant weight. The percentage of insoluble contents in each sample was recorded (Table I) as the gel content.

Hot-set testing

Hot-set testing was carried out on a dumbbell-shaped sample. The sample was attached on one side with a

Sample	Silane (phr)	LOI	Time taken to burn (s)	Observation of the burning of the sample
1	0.000	20	110	Smooth flame; the sample melted and flowed downward along with the flame; the sample rolled down on itself.
2	1.14	20	150	See previous.
3	2.28	20	159	See previous.
4	4.56	20	189	Flame not smooth, but the sample burned with sparks, and the sample could withstand its standing position.
5	6.83	20	190	See previous.
6	11.38	20	246	See previous. In addition, a small amount of char formation took place.
7	18.22	20	295	See previous.
8	27.33	20	300	See previous.

PE = 91; BPO = 0.78.

hook attached to a vertical stand, and a load of 20 N/cm^2 was attached to the lower end. The stand had a fixed ruler for recording the increase in the length of the sample due to the load and high temperature. This setup was placed in an oven with see-through glass in front, and it was preheated to a fixed and constant temperature of 200°C under normal air conditions. The behavior of the sample was watched, and the elongation between two marks on the sample after 15 min was recorded. These specifications fitted the requirements of hot-set testing (i.e., sustaining a load of 20 N/cm^2 at 200°C for 15 min) according to standards such as BS 6746 F, IEC 540, ISO 6427, DIN 16892, and ASTM D 2765-90. For comparison, the temperature was increased and the breaking temperature was recorded (Table I) for each composition.

Burning characteristics of crosslinked samples

The burning properties of the samples were measured with a model D candle-type flammability tester (Toyo Seiki Seisaku-Sho, Ltd., Tokyo, Japan). A minimum limited oxygen index (LOI = 20) for the burning of the sample, measured by a hit-and-trial method, was set for all the sample tests. The pressure of nitrogen and oxygen was adjusted by the regulation of values to 1.5 kg/cm^2. The mixture of these gases was fed into the combustion section; there, it was further uniformly mixed by means of glass beads at the bottom of the combustion section and then was fed into the combustion column. After the flow of this mixture of gases for 30 s, the upper portion of the specimen, which had constant dimensions of 1 mm × 6.5 mm × 140 mm, was ignited. The combustion time and visual observations about the burning properties for the whole sample are recorded in Table II.
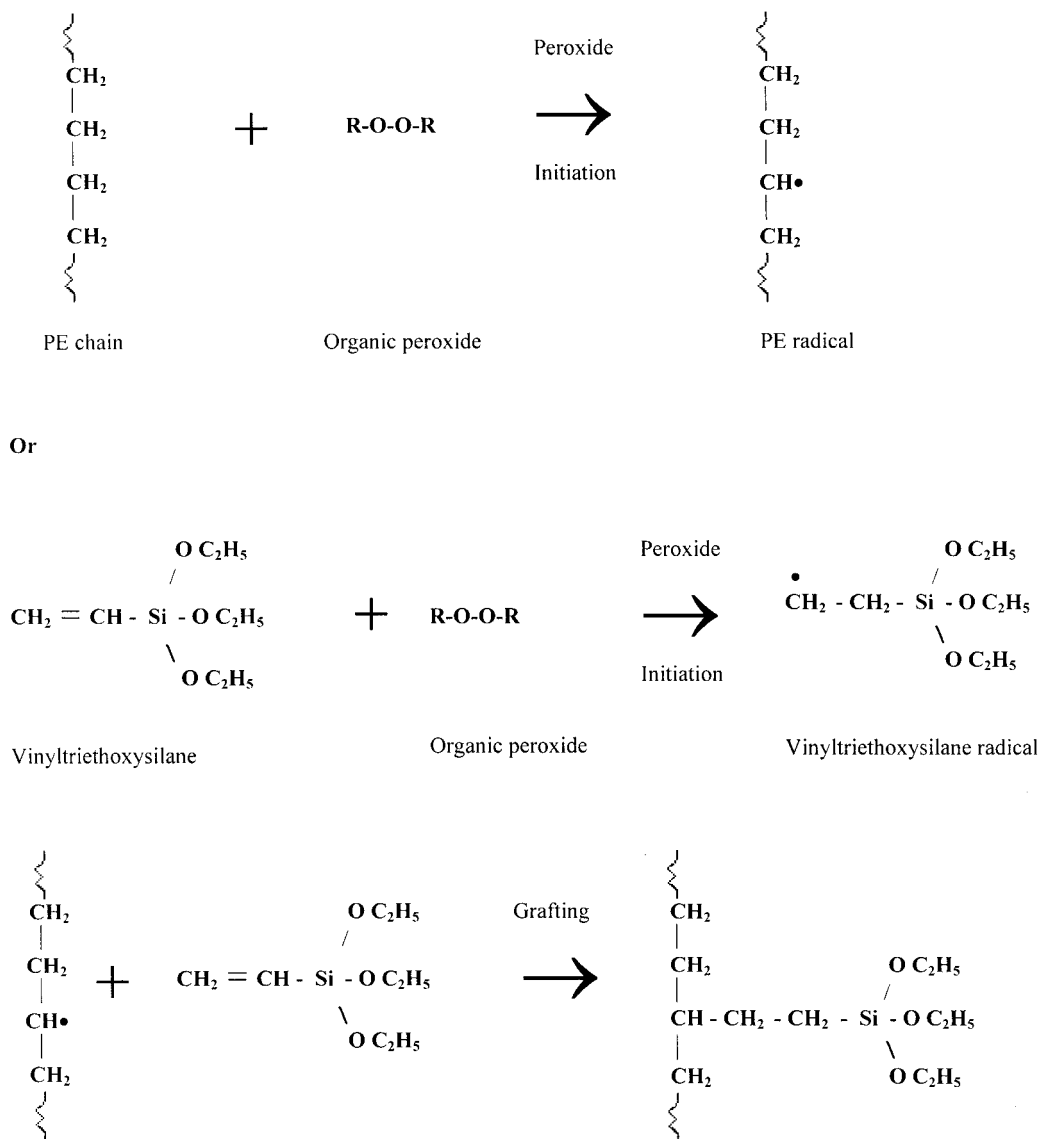
RESULTS AND DISCUSSION

LDPE, in the form of a mixture with an initiator, silane, and a catalyst, when charged to a closed Bra-

bender mixer, melts, and a higher temperature initiates a free-radical reaction. The enclosed chamber of the mixer prevents the volatility of VTES. Peroxide radical formation takes place in the chamber at 140°C, abstracting hydrogen from the PE chain or attaching to vinyl groups of silane, thus forming a free radical on PE or silane. It is due to this free-radical formation that the silane molecules are ultimately grafted onto PE chains. The grafting of silane to PE chains is shown in Scheme 1.

In the second stage, sheets are treated in an autoclave; the catalyst DBDTL, which is known to reduce the activation energy[15–17] for the hydrolysis and condensation of silanes, facilitates the hydrolysis of the ethoxy groups of the silane molecules and subsequently causes the condensation of the resulting OH groups of the grafted silanes. This results in polymer molecular network formation, that is, the crosslinking of PE chains. The crosslinking is completed in about 4 h. The hydrolysis and polycondensation of grafted silane (crosslinking) are depicted in Scheme 2.

The chemistry of the two steps of crosslinking of PE is not new and has already been reported.[2] The curing of PE has been carried out in an autoclave at 105°C for 4 h. The curing time of the silane-grafted material depends on the conditions used for curing. In this respect, different researchers have used different conditions. However, it is obvious from a literature survey that the time needed for curing is not constant. For example, Narkis et al.[18] observed 10 h for the crosslinking of silane-grafted PE when it was exposed to water at 80°C; this was two orders of magnitude less than at 23°C.[19] In another case,[20] the maximum gel content was achieved in water at 90°C after 20 h of exposure. However, even after that, further siloxane bond formation took place up to 100 h of exposure. Although postcuring (crosslinking after the proper time) may have some effect on the properties, for comparison under identical conditions, this debate has

$$\text{PE chain} + \text{R-O-O-R} \xrightarrow[\text{Initiation}]{\text{Peroxide}} \text{PE radical}$$

PE chain   Organic peroxide   PE radical

Or

$$\underset{\text{Vinyltriethoxysilane}}{CH_2 = CH - \overset{\displaystyle O\,C_2H_5}{\underset{\displaystyle O\,C_2H_5}{Si}} - O\,C_2H_5} + R\text{-}O\text{-}O\text{-}R \xrightarrow[\text{Initiation}]{\text{Peroxide}} \underset{\text{Vinyltriethoxysilane radical}}{\overset{\bullet}{CH_2} - CH_2 - \overset{\displaystyle O\,C_2H_5}{\underset{\displaystyle O\,C_2H_5}{Si}} - O\,C_2H_5}$$

Vinyltriethoxysilane   Organic peroxide   Vinyltriethoxysilane radical

$$\text{(PE radical)} + CH_2 = CH - \overset{\displaystyle O\,C_2H_5}{\underset{\displaystyle O\,C_2H_5}{Si}} - O\,C_2H_5 \xrightarrow{\text{Grafting}} \text{(PE grafted silane)}$$

Scheme 1

been set aside. It has been assumed that most of the curing is completed within the 4-h period during which samples are treated in an autoclave for 4 h at 105°C. The characterization results are presented in Tables I–III.

As shown in Table I, an increase in the concentration of silane in the first part (up to 4.56 phr) generally results in an improvement in the mechanical properties, which is a result of the increase in the crosslinking of PE via silane. In the third column of the table, the gel content increases as the concentration of silane increases. This property is an established characteristic of PE crosslinking, and its proportional variations with the concentration of silane agree with the expectations. As the concentration of silane increases, crosslinking increases, and so the gel content (insoluble materials) increases. The elongation-at-break percentage decreases (Fig. 1) as the concentration of silane increases because the increase in silane results in the introduction of crosslinking nodes, which constrain the molecular mobility of the system, and so a reduction in the elongation-at-break percentage is observed according to the theory of rubber elasticity.[21,22]

The tensile strength of the material, as depicted in Figure 1, also shows first an increase and then a decrease in its properties. This type of trend observed for PE is not new but has already been observed and reported for silicone networks for both the tensile strength[22] and tear strength.[23] The initial increase in the tensile strength, as explained previously,[22,23] can be attributed to an increase in the crosslinking density. As a result, hidden imperfections in the polymer networks and polymer chain that otherwise are more exposed in the noncrosslinked polymer networks occur, and consequently, the applied external stress is
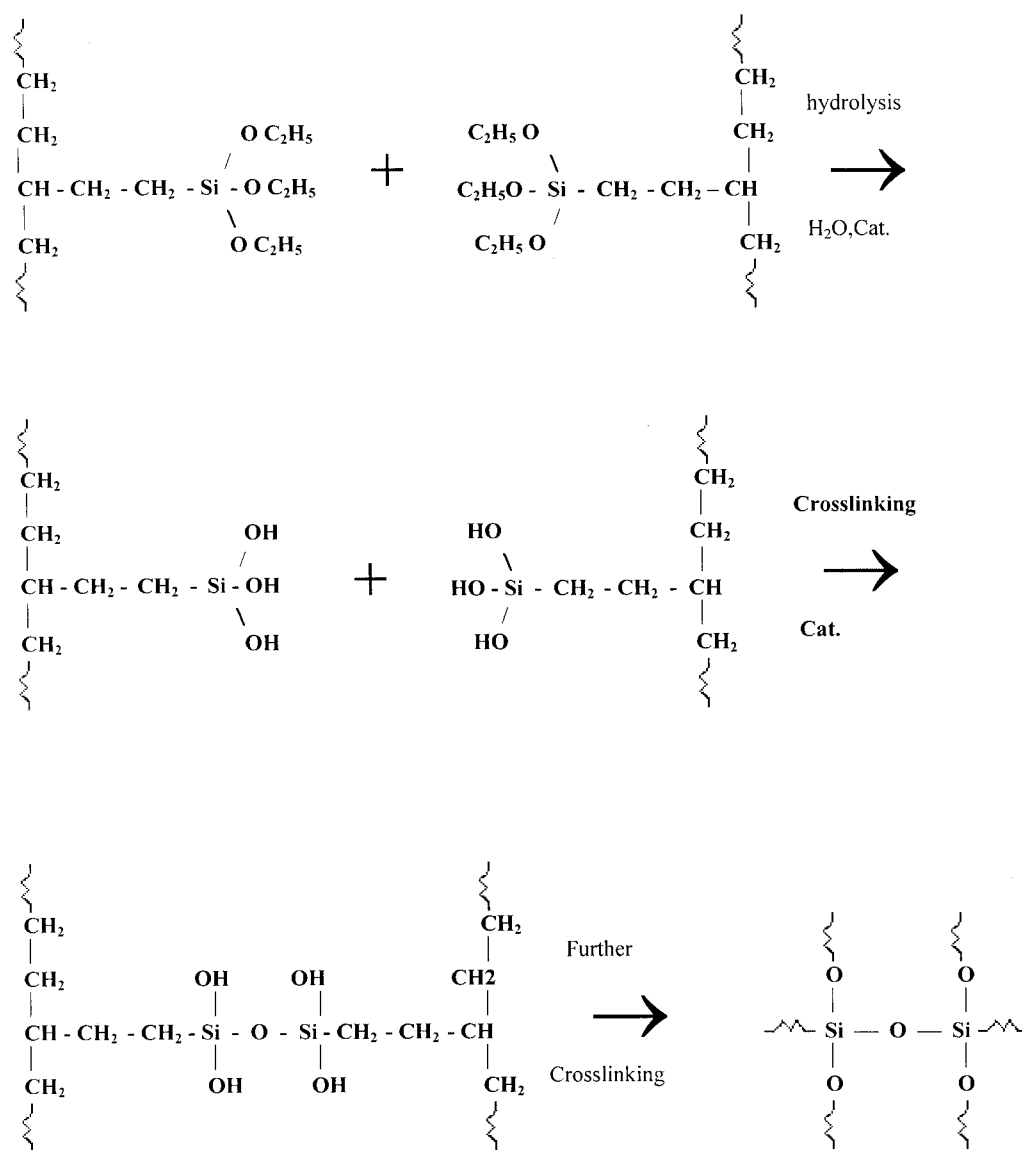
Scheme 2

supported in a very effective manner and an increase in the tensile strength is observed. As for the decrease in the tensile strength with a further increase in the

concentration of silane above 4.56 phr, the silane causes further crosslinking, which reduces the average length segment between the crosslinking nodes to such an extent that these chains do not have enough capacity for orientation during extension and hence the ability to sustain external stress; therefore, failure occurs.

Similarly, the breaking of a sample at the hot-set temperature shows an improvement in the temperature with the concentration of silane. The relevant data are plotted in Figure 2. The crosslinking of PE with silane performs a dual function. First, it ties the chains to one another by covalent bonding; this imparts tightness to the polymer network, and so the performance at high temperature increases. Second, the incorporation of silane, which after crosslinking results in the formation of Si—O—Si bonds, imparts flame retardancy to the polymer network. This property of the

TABLE III
Effect of the Concentration of BPO on the Mechanical Properties of PE

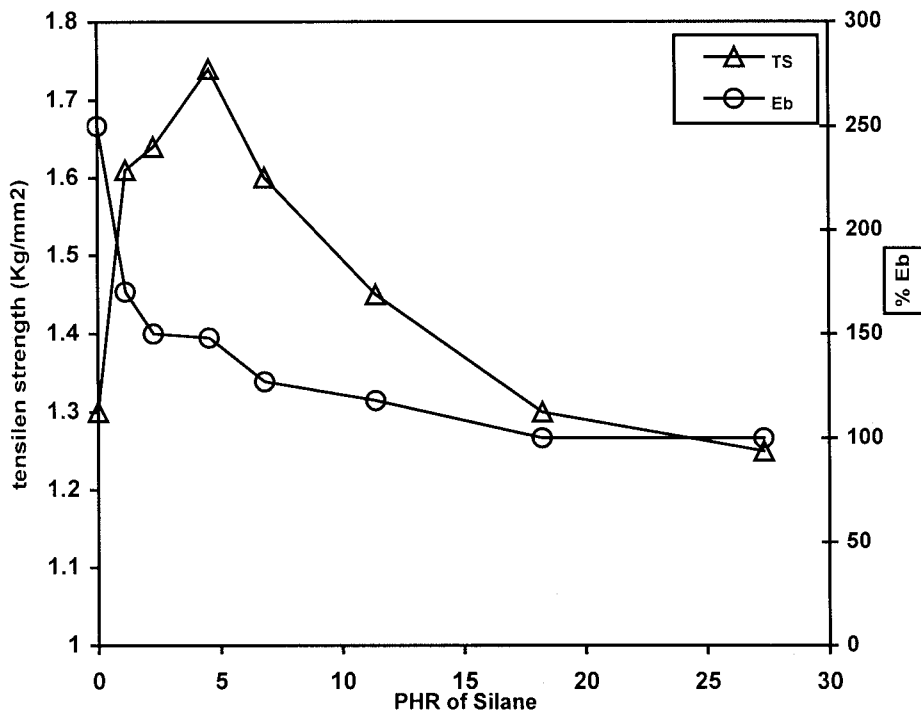| Sample	BPO	Elongation at break (%)	Tensile strength
1	0.0	720	1.4
2	0.25	180	1.63
3	0.5	153	1.6
4	0.75	120	1.55
5	1.0	112	1.49
6	1.25	76	1.43

PE = 91; silane = 7.42.

Figure 1 Effect of the silane concentration (phr) on the tensile strength (TS) and elongation-at-break percentage (% EB) of crosslinked PE.

material shows that at a higher temperature, the dictating parameter in the formulation of the material is silane.

Table II summarizes the burning properties of the materials with the variations in the silane concentra-tion. The improvement in the flame retardancy of the material observed with an increase in the concentration of silane at such a lower level is interesting. However, the variation in the flame retardancy observed with the variation of the concentration of silane
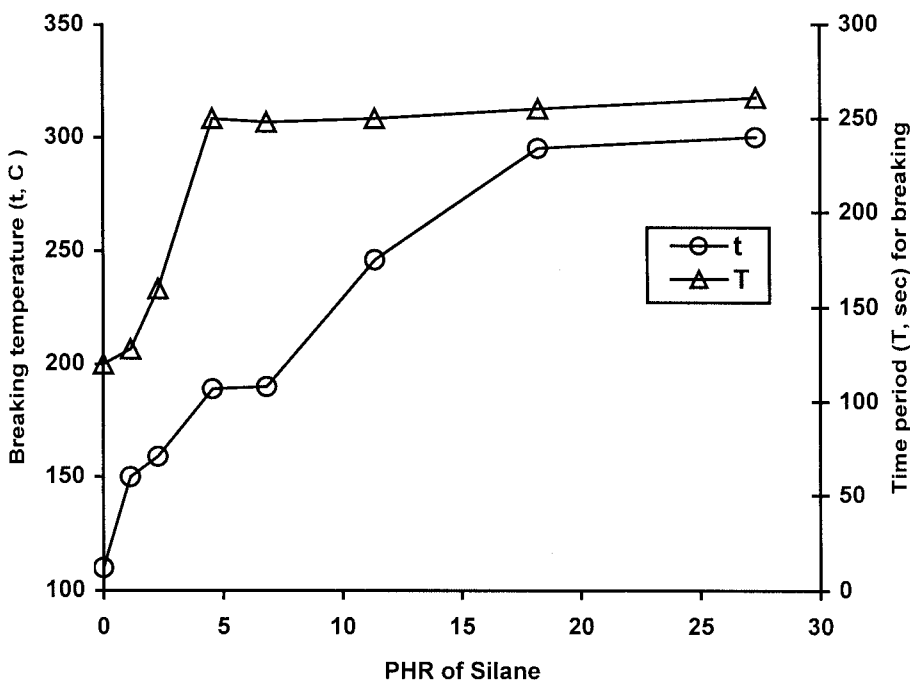

Figure 2 Effect the silane concentration (phr) on the breaking temperature and time period for breaking of crosslinked PE.
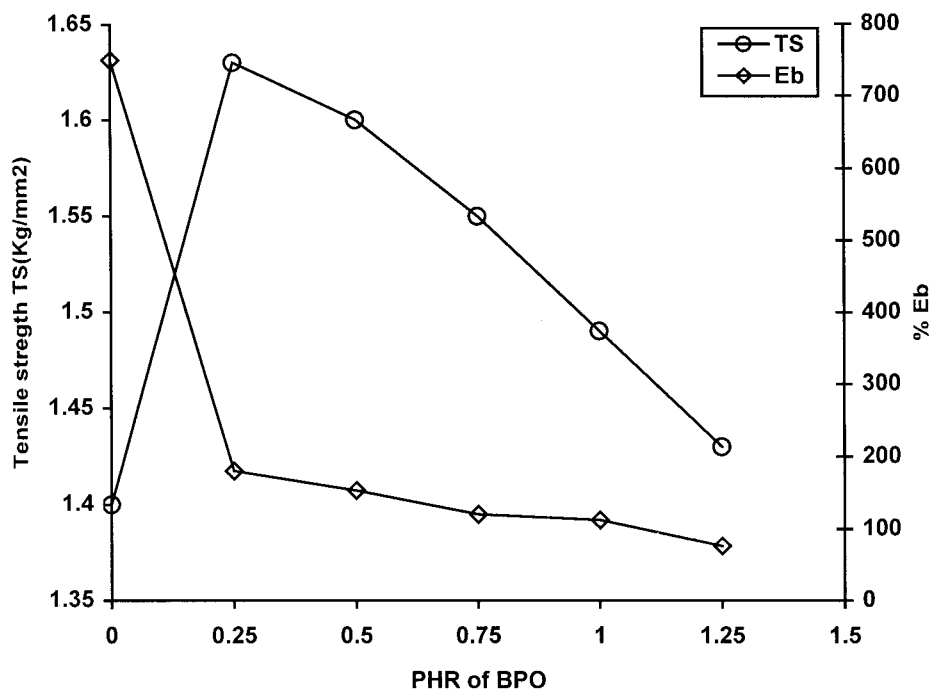
Figure 3 Effect of the concentration of BPO on the tensile strength (TS) and elongation-at-break percentage (% EB) of crosslinked PE.

is too small to be detected by LOI measurements. The exact burning times required for samples of the same dimensions (1 mm × 140 mm × 6.5 mm) but with different compositions were measured under identical conditions with an LOI instrument. As shown in the table, there is a gradual increase in the time period required for the burning of a sample with an increase in the concentration of silane. The control sample, which contains no silane, burns in 110 s, whereas the last sample (sample 8) under identical conditions burns in 300 s. There is a threefold increase in the time period for the burning of a sample with the maximum concentration of silane. A graphical representation of these characteristics is given in Figure 2.

Apart from this difference in the period of time for burning, there is a clear-cut difference in the visual observations recorded in Table II during the burning of samples of different compositions. The control sample burns with a smooth flame propagating easily downward along the sides that is associated with a drip phenomenon. The melt flow thus results in the rolling down of the sample on itself, and the sample cannot withstand its standing position during burning. This type of property is observed up to 2.8 phr silane. After this, there is a drastic change observed in the burning behavior, such as a nonsmooth flame (burning with sparks), and the sample gradually acquires the ability to withstand its standing position while burning. The flame does not propagate along the sides, but burning continues from the top to the bottom of the sample only. As the concentration of

silane reaches 11.38 phr, flame retardancy improves, and a small amount of char formation takes place. This property increases up to the last composition, which contains 27.33 phr silane. This means that silane does impart flame retardancy to the materials.

Table III records the effects of variations of BPO on the properties of crosslinked PE. The elongation-at-break percentage gradually decreases with the concentration of BPO. As the concentration of BPO is increased, the same amount of silane can effectively be grafted onto PE. With an increase in the 0concentration of BPO, the hydrogen abstraction from PE increases in a random way, and as a result, the chains are bonded to one another at short intervals. This is reflected (Fig. 3) in the reduction of the elongation-at-break percentage of the material with an increase in the concentration of BPO. This increase in the abstraction of hydrogen from the PE chains, which results in the formation of free radicals, also increases the possibility of side reactions. During side reactions, these free radicals, because of an increase in their number, combine with one another and form covalent bonds between the PE chains or between vinyl silane. As for the trend associated with the tensile strength, there is a decrease as the concentration of BPO increases.

As for the burning properties of samples of different compositions and various amounts of BPO, not much of a difference is observed. The burning characteristics are nearly the same as those of sample 4 in Table I. The variation of the BPO concentration does not appreciably affect the burning behavior. This is logical because BPO,

after the grafting of silane onto PE chains, is converted into another form, and its concentration is too low to affect the burning properties of the materials.

CONCLUSIONS

The crosslinking of PE with vinyl silane results in improved mechanical and flame-retardant properties for the materials. The concentration of silane is a dictating parameter that controls these properties. The crosslinking of PE with vinyl silane has for the first time been studied in a detailed manner, and the composition corresponding to the optimum properties has been established. This study thus provides detailed guidelines to researchers for tailoring the properties of crosslinked PE through variations in the basic parameters according to their own requirements. Improvements in properties such as the tensile behavior and elongation-at-break percentage, a reduction in the tendency toward brittle rupture, a reduction in the drip phenomenon during burning, improved thermal dimensional stability, and improved rupture performance for polymers can effectively be tailored by an established and important technique known as crosslinking.

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