The Nucleus **48**, No. 1 (2011) 1-9

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

IDENTIFICATION OF DIFFERENT STRUCTURES FORMED DURING CROSSLINKING OF POLYETHYLENE WITH VINYL TRIETHOXYSILANE FTIR, Si^{29} NMR AND XPS STUDY

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(Received October 20, 2010 and accepted in revised form December 31, 2010)

To bring about improvement in service temperature, mechanical and thermal properties of low density polyethylene, it was crosslinked with vinyltriethoxysilane in the presence of benzoyl peroxide. Identification of different structures which were formed as a result of crosslinking, was carried out by ATR/FTIR, Si^{29} NMR and x-ray photoelectron spectroscopy (XPS). In this article, the effect of silane and peroxide concentrations on the types of different structures or grafts formed during crosslinking has been discussed. FTIR spectra show that Si-O-Si asymmetric stretching and Si-C stretching was observed in the general range 1000-1130 and 735-800 cm^{-1} respectively. Theoretical and experimental band assignments for Si^{29} NMR spectra exhibit the presence of various fragments based on T^0, T^1, T^2 and T^3 structures. It has been found that for the maximum silane concentration, predominate form of crosslink is T^3 i.e trioxygented silane with three silane bridges. XPS analysis further confirms the presence of variety of C, O and Si bonding in the silane crosslinked polyethylene which exhibit varied elemental ratios.

Keywords: *Polyethylene, Silane crosslinking,* Si^{29} *NMR, ATR/FTIR, X-ray photoelectron spectroscopy*

1. Introduction

The crosslinked polyethylene (XLPE) is becoming the material of choice in various applications such as fuel tanks, cable insulation, new buildings and replacement systems. Modification of polyethylene by crosslinking, brings about increase in mechanical properties and service temperature. Another advantage of XLPE over metallic materials (for example steel and copper) is in the speed of installation with push fittings instead of using mechanical joints. There are several techniques for crosslinking, for example by free radicals, radiation or/and by chemical means. Among these techniques; each one has its own inherent advantages and disadvantages. For example radiation crosslinking has advantages such as high extrusion speed, lower raw material cost and cleanliness of the process. However, this process has disadvantages like high installation cost, potential non-uniformity of the crosslinked density and taking consideration into the additional safety precautions for irradiation. On the other hand, the silane crosslinking technique is being preferred due to lower capital investment and increased productivity.

There have been several previous reports about crosslinking of polyethylene with silane and its reaction mechanism [1-5]. After the introduction of two techniques, Sioplas and Monosil during the last three decades; crosslinking of PE has been an expanding field. Researchers used different characterization methods to identify the nature of bond formation during crosslinking. Hjertberg et al. [6] and Palmlof et al. [7] studied the kinetics of crosslinking of the copolymer when reacted with water by measuring the gel contents. The identification and then concentration of different groups (-$SiOOCH_3$, -OSiOOH, and -SiOOOSiO) was performed by using fourier transform infrared (FTIR) spectroscopy. Compared to the gel measurement, FTIR can be carried out in much shorter time. For example in silane-water crosslinking reaction, the methoxy silane groups (Si–OCH3) are hydrolyzed and condensed to form siloxane (Si–O–Si) linkages. If the crosslinking degree increases, the intensity of the Si–O–Si peaks would increase whereas the intensity of the Si–OCH_3 bands would decrease. By examining the changes in intensity of these peaks, the crosslinking degree can be determined [8] in a few minutes.

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The identification and analysis of silica derivative is an important step in understanding the process which is responsible for enhancing the mechanical, thermal and burning properties. Solid state silicon nuclear magnetic resonance Si^{29} NMR has been a very valuable tool for the study of chemical structure of copolymers involving silane units. Qualitative as well as quantitative information about the resulting structures can best be extracted by this technique. Some researchers [9] reported that silicon atoms of mono-, bi-, and tri-substituted alkenyltriethoxysilanes have chemical shifts approximately at -49, -58, and -66 ppm, respectively. They assigned the signal at -55 ppm to silanol group (Si-OH) if its presence is confirmed [10]. However, the formation of Si-OH groups is favored in concentrated acidic conditions. Similarly, all hydrolysable Si-OEt groups show the peaks at about -44.7 ppm in Si^{29} NMR spectrum [11]. After condensation reaction, the structural fragments thus formed can be classified into D (where two Si-O bonds are available for condensation); and T and Q when three and four Si-O bonds may result into the formation of Si-O-Si bridges respectively. Abe and Gunji [12] studied the formation of ladder like (T^3) structure formation in polyphenylsilsesquioxane and reported that this type of structure results in the enhancement of thermal stability and mechanical properties.

In this work, silane crosslinked PE was produced by mixing PE powder, benzoyl peroxide (BPO), vinyltriethoxysilane (VTES) and a catalyst by melt process in Brabendar mixer. In the melt mixer, silane was grafted on to the backbone of PE, via free radicals mechanism. The silane grafted PE was then hydrolysed with steam and crosslinked to form Si-O-Si linkages. Si^{29} NMR and ATR/FTIR were used to find the nature and relative abundance of different silane grafts; while XPS was used to see the types of bonding with respect to silicon, carbon and oxygen.

2. Experimental

2.1 Materials and Method

Low density polyethylene (LDPE) granules were supplied by Qapco, Ltd. (Qatar), VTES (Mol. Wt.190.32 and purity 98 %) and BPO was supplied by Fluka, the catalyst dibutyl tin dilaurate (DBTDL) was purchased from Merck. These chemicals were used without further purification.

2.2. Crosslinking Technique

Silane-grafting of the polymers was performed in the melt by the use of vinyltriethoxysilane and benzoylperoxide. The detail about crosslinking is reported some where in literature [2, 13]. In the first step, vinyltriethoxysilane was grafted on to LDPE by free radical reaction in the presence of BPO at 140 ˚C. LDPE (40 g), the weighed amount of BPO and silane were physically mixed and then material was charged to brebender mixer at 140 ^{o}C. On melting, catalyst was added dropwise and mixing was continued for further 5 minutes. The blend thus formed was pressed into sheets of required thickness in the heat press at 170 ^{o}C. In the second step, the sheets were cured in the autoclave at 105 ^{o}C for 4 hours.

3. Characterization of Crosslinked Structures

3.1. ATR / FTIR

Samples sheets of (~ 1 mm thick) were used for ATR/FTIR analysis. A universal attenuated total reflectance (UATR) attachment on a Spectrum One FTIR spectrometer Perkin Elmer was used. ATR spectra were measured with a resolution of 4 cm^{-1} in the range of 4000 to 650 cm^{-1}. Each spectrum was the result of 16 co-added scans. The UATR uses a diamond coated zinc selenide internal reflection element with a refractive index of 2.4. ATR/FTIR spectroscopy was used to analyze the grafting of silane to polymer backbone and extent of crosslinking with respect to various concentrations of silane and benzoylperoxide. Prior to ATR measurement, the sheets were washed with an excess volume of acetone to remove unreacted silane and any contamination present on the surface. To analyze the structure of the bulk polymer, vertically cut inner cross-section of heat pressed sheet was used for FTIR and XPS study.

3.2. Si^{29} NMR

Cross-polarization NMR technique was used in Si^{29} NMR experimental study. In this technique, NMR signals were transferred from the protons to the silicon-29 nuclei. Moreover, in this method, signal-to-noise ratio is better than the other single pulse excitation technique. A repetition time of 3 seconds and a CP time of 2 ms were used.

3.3. X-ray Photoelectron Spectroscopy (XPS)

XPS data was acquired using a Kratos Axis Ultra X-ray Photoelectron Spectrometer incorpo-

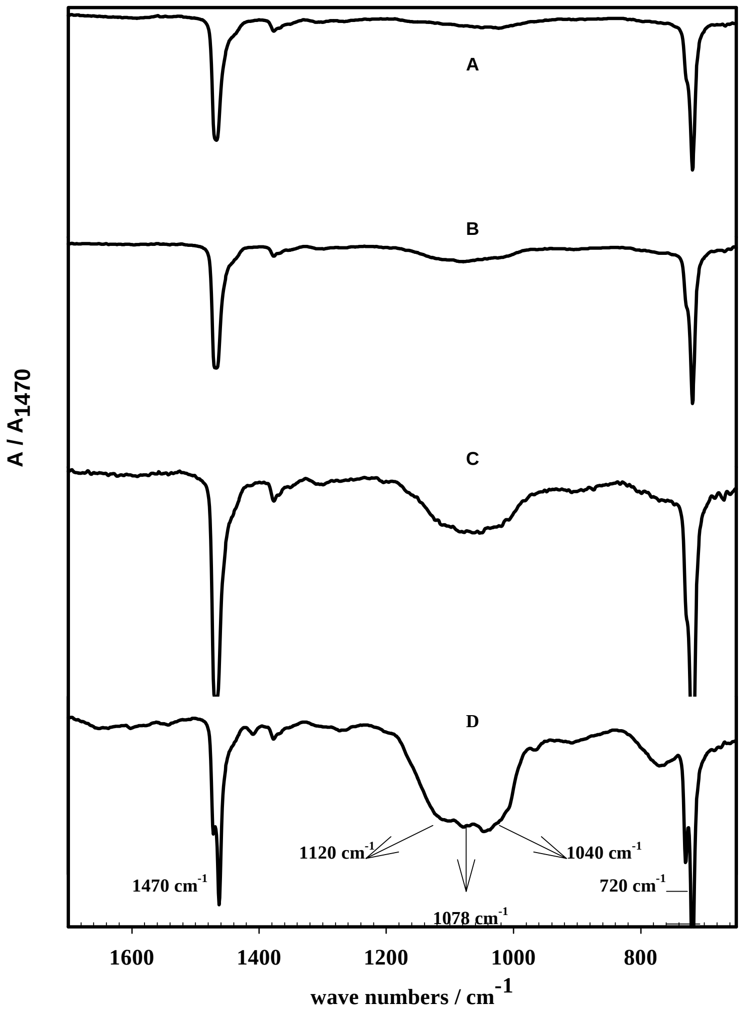


Figure 1. FTIR spectra with respect to silane variation for the bulk of Sil-crosslinked PE (1700-650 cm $^{-1}$) A) Silane 2.28 phr B) 6.83 phr C) 11.38 phr and D) 27.33 phr.

rating a 165mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al X-rays (1486.6 eV) at 150 W (15 kV, 10 mA). Survey (wide) scans were taken at analyzer pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. The base pressure in the analysis chamber was 1.0x10^{-9} torr and during sample analysis 1.0x10^{-8} torr.

4. Results and Discussion

4.1. FTIR Results

FTIR spectra were used to observe the crosslinking of PE with vinyltriethoxysilane (VTES). The spectra were all normalized with respect to the PE band at 1470 cm^{-1}. In polyethylene, the important IR peaks were found at 2940 cm^{-1} (–C–H aliphatic stretching), 1470 cm^{-1} (–CH_2 rocking), and 720 cm^{-1} (–$(CH_2)_2$– wagging) due to the presence of polyethylene chain (Fig. 1). The important absorption peaks for VTES were found at: 2975 cm^{-1} (–C–H aliphatic stretching), 1443 cm^{-1} (–CH_2 rocking), 1391 cm^{-1} (–CH_3 symmetric bending), 2974 cm^{-1} (–C–H vinyl stretching), 1600 cm^{-1} (–C=C stretching), 1070 cm^{-1} (–Si–O stretching) and 957 cm^{-1} (–CH_2 wagging of –Si–CH=CH_2) which is already reported in the literature [14].

In the crosslinked sample, a broad band at 1000-1130 cm^{-1} shows the evidence of grafting of silane on to PE matrix (Fig. 1). The intensity for that particular region is found to increase with the increase in silane concentration in the matrix. The broad peak is rather complex, which simultaneously shows the presence of absorption

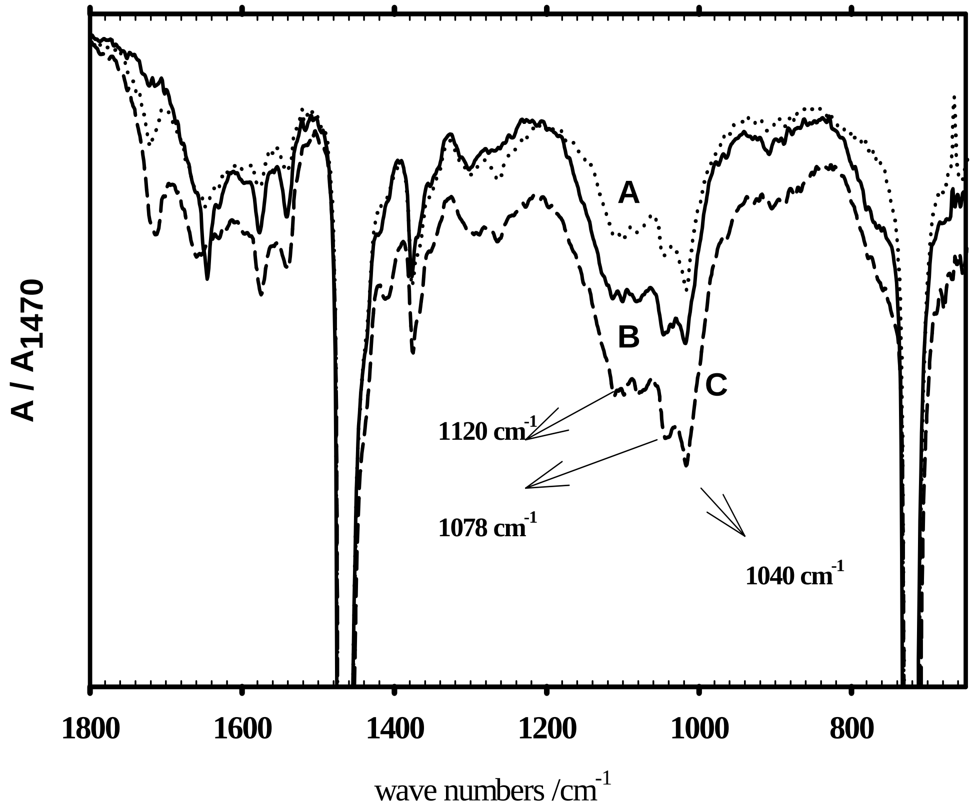
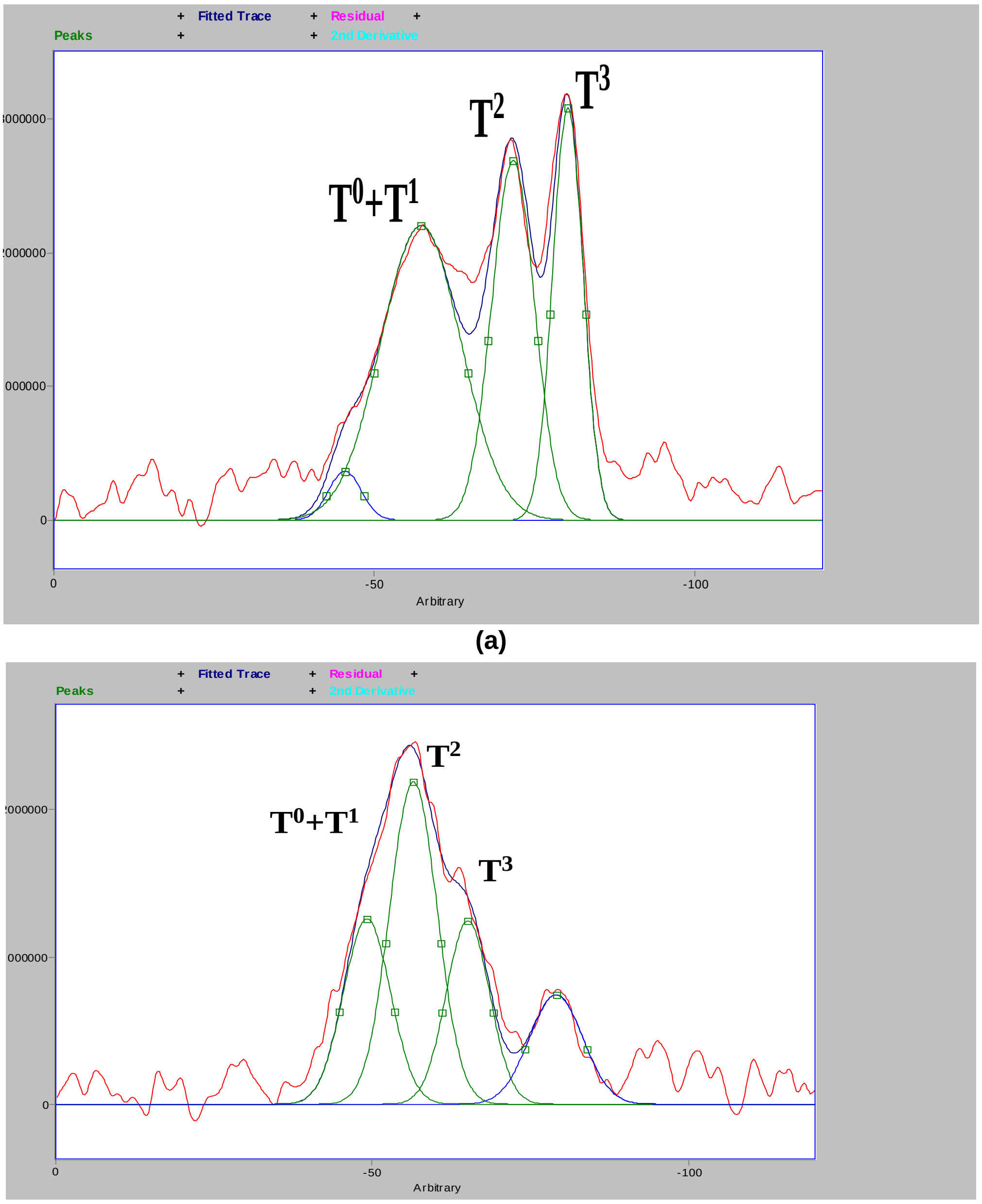


Figure 2. FTIR spectra of the silane crosslinked PE having varied concentration of benzoylperoxide (BPO) (A) BPO= 0.1 % (B) BPO= 0.5 % and (C) BPO= 1.0 %.

at about 1120, 1078 and 1040 cm^{-1}. During crosslinking reaction, ethoxysilane (Si-OC$_2$H$_5$) groups hydrolyze and condense to form siloxane (Si–O–Si) linkages. After crosslinking reaction, the evidence of crosslinking can be seen from the characteristic peaks of siloxane bond (Si–O–Si) at 1040 cm^{-1}. Unfortunately, in the given FTIR spectra, the (Si–O–Si) band at 1040 cm^{-1} appears as a shoulder on the larger band of (Si-OC$_2$H$_5$) at 1078 cm^{-1}, which makes it difficult to quantitatively measure the intensity of Si–O–Si band. Some researchers [14] however, reported the crosslinking reaction in polypropylene by following the decrease in absorption band (of Si-OC$_2$H$_5$) at 1092 cm^{-1} and then in terms of absorption index, which was calculated from the relative absorption peak intensity of the (Si-OC$_2$H$_5$) groups at 1192 cm^{-1} to that of the methyl group at 1377 cm^{-1} as an internal reference. Chen et al. [15] dictated that in case of trimethoxysilane, the decrease in peak at 1117 cm^{-1} and the increase in shoulder peak at 1077 cm^{-1}, provided the evidence that Si-O-CH$_3$ groups were hydrolyzed and condensed to form the Si-O-Si bridge, or network. However, our studies based on mechanical properties [2], show that most of the crosslinking reactions are completed in approximately 4 hours for the used concentration of silane and benzoylperoxide. There is no indication of silanols (~ 3418 cm^{-1}) or unreacted vinyl groups (~1600 cm^{-1}) in the spectra because they are either absent or at very low concentration. Moreover, ATR analyzes only the first 1-2 µm of the sample, and silanol and unreacted vinyls would have to be at a fairly high concentration to be detected.

To see the effect of peroxide on crosslinking by FTIR, three different concentrations (0.1, 0.5 and 1.0 phr) of benzoyl peroxide were used. Fig. 2 shows that increasing peroxide concentration, the intensity of the absorption bands at 1000-1130 cm^{-1} increases and more of silane seems to anchor the polymer matrix in addition to some random crosslinking of PE chains. In contrast to silane variation series, slightly higher crosslinking with respect to BPO variation, particularly for one phr of BPO can be seen from the enlargement of peak at 1040 cm^{-1}.



(b)

Figure 3. Si^{29} NMR spectra of SXLPE with varied concentration of silane and peroxide. a) Silane = 27 phr, b) BPO = 1 phr.

4.2. Si^{29} NMR

Theoretical and experimental band assignments for Si^{29} NMR spectra of silane crosslinked polyethylene have been made on the basis of number of ethoxy groups condensed and crosslinked in the material. Si^{29} NMR spectra with varied concentration of silane and benzoylperoxide are shown in Fig. 3 (a) and 3 (b) respectively. The Si^{29} NMR assignments are difficult to make particularly, when there are different atoms attached to same Si atom. From the FTIR spectra (Figs. 1 & 2), there was no evidence of Si-OH and un-reacted vinyl groups; therefore, presence of silanols and vinyls was ignored while making Si^{29} NMR assignments. It was done because to simplify the assignments of the Si^{29} spectra. According to Alam and Henry [16], Douskey et al. [17] and Yan et al. [18], assignments were made as follow :

Table 1. Effect of silane concentration on the formation of different structures shown by Si^{29} NMR in SXLPE.

Nos.	Sample ID (Silane conc.)	Fitted Region	T^0 or T^1 (%)	T^2 (%)	T^3 (%)	Others
1	Sil-1 (silane= 1.14 phr)	-46.81 -57.90 -71.94	18.66	72.42	8.92	-
2	Sil-3 (silane= 4.56 phr)	-49.18 -56.50 -65.12 -79.08	22.95	40.50	21.06	15.49
3	Sil-5 (silane= 11.38 phr)	-51.32 -57.50 -65.08 -72.67	45.32	19.01	26.53	7.13
4	Sil-7 (silane= 27.33 phr)	-48.15 -56.38 -63.99 -76.22	29.84	20.94	34.14	6.922

Table 2. Effect of peroxide concentration on the formation of different structures shown by Si^{29} NMR in SXLPE.

Nos.	Sample ID (BPO conc.)	Fitted Region	T^0 or T^1 (%)	T^2 (%)	T^3 (%)	Others
1	BPO-1 (BPO=0.1 phr)	-46.81 -57.90 -71.94	18.66	72.42	8.92	-
2	BPO-3 (BPO=0.5 phr)	-49.18 -56.50 -65.12	22.95	40.50	21.06	15.49
3	BPO-5 (BPO=1.0 phr)	-51.32 -57.50 -65.08 -72.67	45.32	19.01	26.53	7.13

The NMR spectral results obtained for Si^{29} showed that, four distinct groups of silicon atoms with different degrees of condensation shown by T^0, T^1, T^2, and T^3 were found to be present in the samples. The concentration of these structures varies with the increase of concentration of VTES (Table 1) and BPO (Table 2). Assignment of Si^{29} peaks show that in T^0, the possibility of attachment of three hydroxyl (or alkoxyl) substituents to silicon atoms, which means that grafting, has occurred from the vinyl end of VTES; however, no condensation or crosslinking occurred. T^1 and T^2 show silicon atom with one and two siloxane bonds leaving behind other ethoxyl groups unreacted. In T^1 and T^2 structures, grafting occurred but partial condensation took place. T^3 suggests grafting and then complete condensation of Si-OC_2H_5 groups with the formation of three siloxane bonds. The peak at about -80 ppm is difficult to assign. From our ATR/FTIR results (Figs. 1 & 2), it was not possible to identify the traces of -OH or vinyl groups if present at 1-2 µm depth. However if some traces of unreacted silane were present, then the peak around -80, could be attributed to T^3+vinyl. Similarly, all hydrolysable Si-OEt groups show the peaks at about -44.7 ppm in Si^{29} NMR spectrum [11].

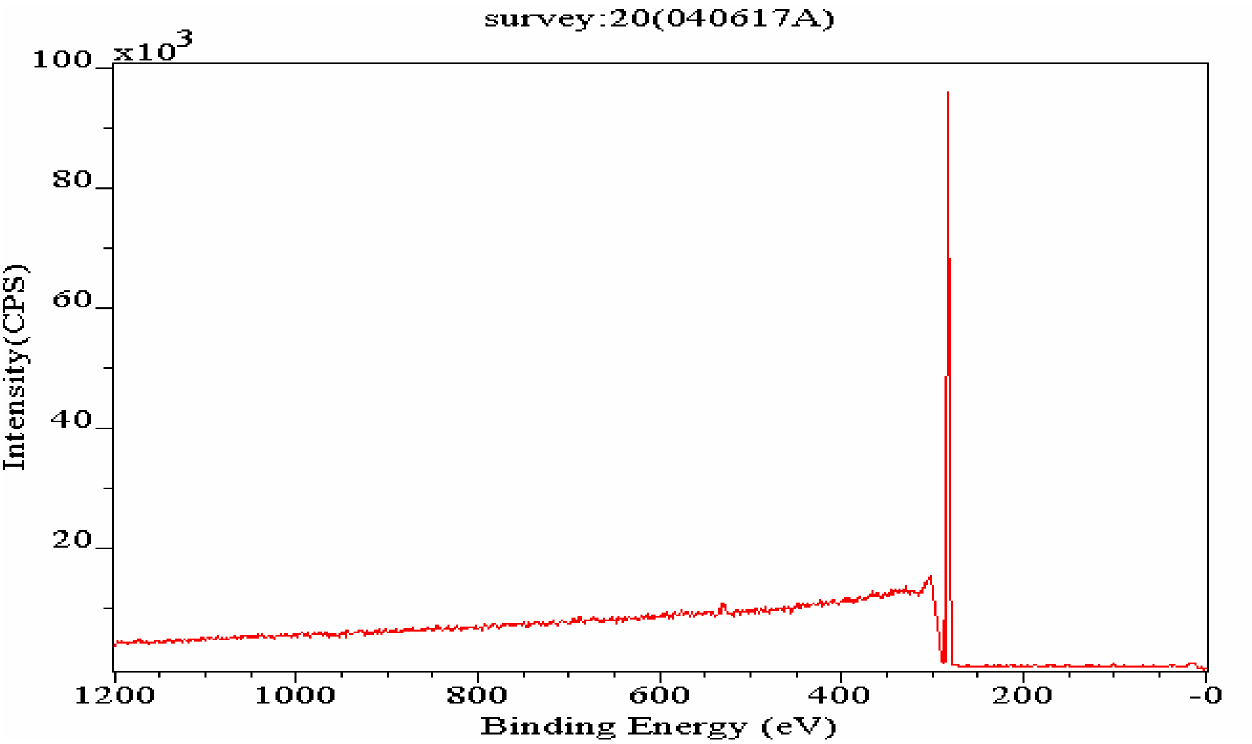


Figure 4. XPS survey scan of SXLPE showing atom % of C, O and Si.

The T^3 structures are predominantly formed at the higher VTES contents in the blend. However, T^0, T^1 and T^2 structures are also practically present for all of the VTES concentrations. It shows that when more amount of silane is present for grafting, then curing reaction also favors the formation of T^3 structure. The increase in number of T^3 structure (Table 2) with the increase in peroxide can be attributed to the large number of free radicals generation during grafting process, which provides more grafting sites for silane. The grafted silane thus attracts more access to water for curing, and hence in the formation of Si-O-Si bonds which gives T^3 proportion.

It is clear, that using higher concentration of silane, the predominant species is T^3. As the T^0 and T^1 peaks are not easy to differentiate, because they are buried in each other, therefore, mixed region was proposed in Tables 1 and 2 for these two peaks. It is also noticed that by increasing concentration of silane, T^3 increases with the decrease of T^2. When grafted Si-OH groups come closer, chances of condensation are enhanced and hence the probability of three dimensional structure formation increases.

4.3. XPS Study

In XPS analysis, a low-resolution scan of the inner cross-section of 1 mm thick sheet was taken to determine the percentage of elements present in the bulk polymer. The relative elemental composition of the sample is presented in Table 3.

Table 3. XPS data showing elemental abundance and distribution in SXLPE.

O1	531.514	0.64 %
O2	532.767	11.11 %
O3	534.070	1.06 %
C-C	285.353	71.16 %
C-O-Si	286.032	9.89 %
C-O-C	287.090	2.99 %
C = O	287.921	0.86 %
Si2p	102-104	0.78 %

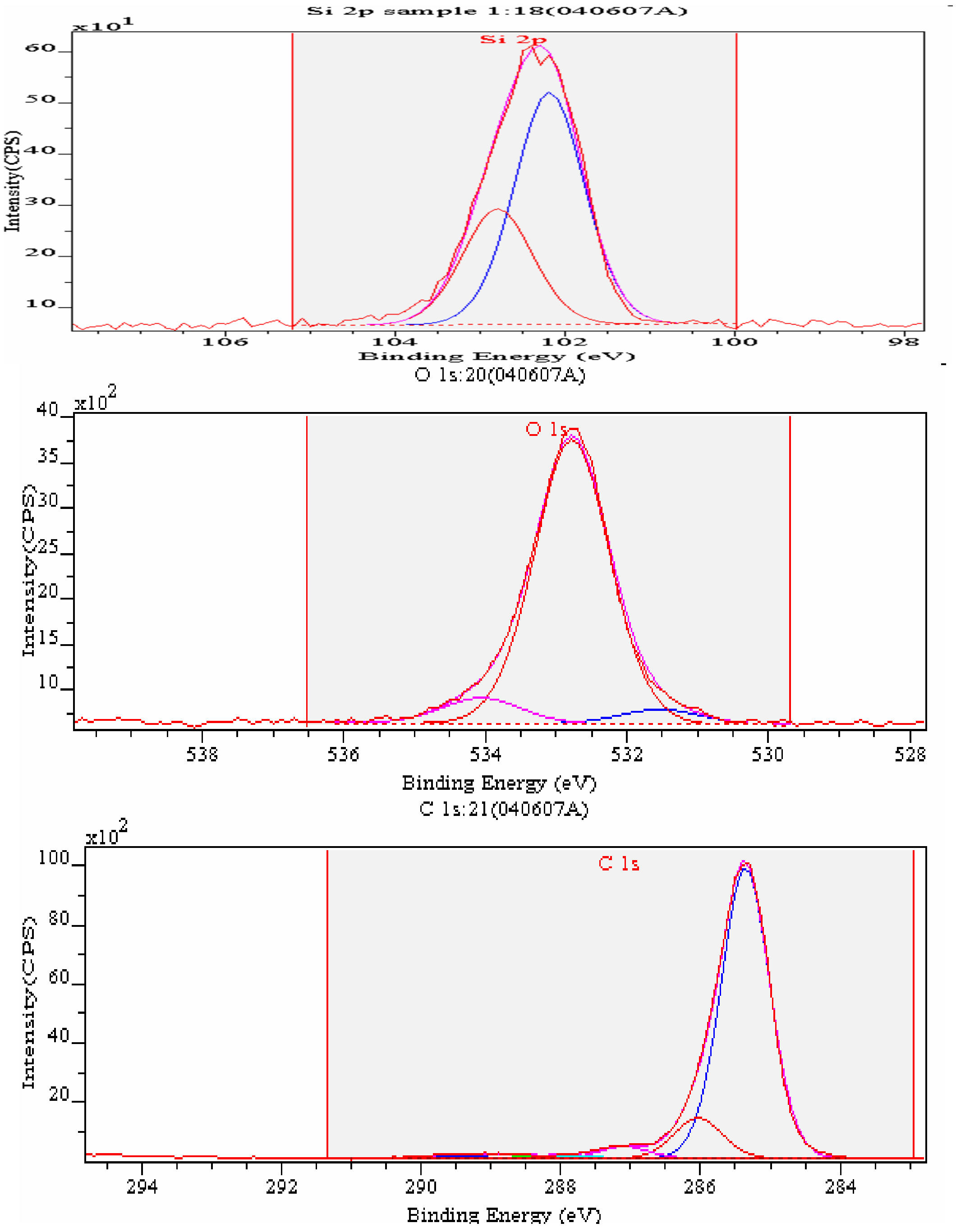


Figure 5. XPS high energy scans showing different types of elemental abundance a) Si2p, b) O1s, c) C1s.

The main elemental peak detected was of carbon, however traces of oxygen and silicon were observed in the spectrum but with low intensity. The elemental ratio for O/C and O/Si was calculated as an indication of bond formation among PE carbon and VTES carbon as a result of grafting as well as O/Si due to condensation of ethoxy groups. For survey scan, range from 0-1200 eV was covered; while a high resolution scans was taken from 530-536 eV, 284-290 eV and 100-106 eV for oxygen, carbon and silicon respectively. To determine the types of Oxygen-Carbon and

Oxygen-Silicon bond present, chemical bond analysis of carbon was carried out by curve fitting. C_{1s} peak from the high resolution spectrum and deconvoluting it in to four sub-peaks corresponding to an un-oxidized carbon C_1, and various oxidized carbons, C_2, C_3 and C_4.

The C1s peak observed at an uncorrected binding energy of about 283 eV, was the major peak present in the survey scan which is in excess of ~ 97 atom percent (Fig. 5). However, smaller peaks for O1s at 530 eV and very small peaks of Si2p at 100 eV were observed as well. In SXLPE survey scan, Si peak was smaller but elemental data shows its presence in all of the scans showing comparatively better dispersion.

Multiplex spectrum of the C 1s components having respective binding energies in SXLPE (Fig. 4) shows that there is an indication of polymer surface oxidation, since some C=O and C-O-C were observed Then there are two usual Si peaks, which do not mean two different Si's but these are O-Si-O, showing silane crosslinks. There is also evidence for the presence of C-O-Si due to some surface contamination, on the O 1s multiplex spectrum.

5. Conclusions

- ATR/FTIR spectra confirm the presence of Si-O-Si bond (crosslinking) at 1040 cm^{-1}.
- The XPS study reveals that major component in the bulk polymer is indeed PE (C & H). However, presence of variety of O1s at about 530 eV and Si2p at 102 eV has been observed in high resolution scans.
- Si^{29} NMR shows that the predominant structure was T^3 for maximum concentration of silane used in this study.
- An increase in silane and peroxide concentration favours the crosslinking process towards completion. However, partially crosslinked structures were found to be present for all of the silane concentrations in the polymer.
- The concentration of silane do affects not only the nature and number of crosslinks but also mechanical and flame retardant properties of the materials.

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