

Determination of gel content of silane cross-linked polyethylene copolymers using FTIR technique

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ABSTRACT

Silane cross-linking of metallocene-based polyethylene-octene elastomer (POE)/linear low density polyethylene (LLDPE) blend was carried out using two-step Sioplas process in an industrial scale twin-screw extruder. In the study, grafting and cross-linking reactions of vinyl trimethoxy silane (VTMS) were analyzed using FTIR technique. It was found that the cured compound showed absorption peaks at 1078 cm^{-1} and 955 cm^{-1} related to Si-O-Si bonds. A peak was also observed at 3405 cm^{-1} of hydroxyl group produced from hydrolysis of methoxyethylene group during of curing process, reflecting that curing reaction was not completed. The samples were cured at different time intervals (15 min-16 hours). The gel content values determined by solvent extraction and FTIR were in good agreement at curing times more than 4 hours. The efficiency of the silane grafting reaction was determined using the ratio of the absorption peak at 1092 cm^{-1} characteristic of methoxy to the transmittance peak at 1378 cm^{-1} characteristic of methyl group, which is considered as the internal standard. The results showed the highest efficiency of silane grafting reaction at 5 wt.% of VTMS with the least amount of internal standard ratio (0.029), at which the lowest MFI value, and the highest values for gel content, tear strength, compression set and hot set 200°C were obtained. **Polyolefins J (2024) 11: 1-10**

Keywords: Sioplas process; gel content; polyethylene-octene elastomer; FTIR technique; solvent extraction.

INTRODUCTION

Polyolefin elastomers (POEs) are commercial ethylene- α -olefin copolymers produced using metallocene catalysts which are characterized by their narrow molecular weight and compositional distributions. These features result from the catalysts having a single type of polymerization site. POEs with low α -olefin content have a melting point of about 90°C, but those with high percentage of α -olefin (40 wt.%) have a low melting point of about 45°C. The high α -olefin copolymers like elastomers are soft and have low density, while they are

in granular form and can be processed as thermoplastics. The exceptional performance of these copolymers can be attributed to good control of polymer structure, molecular weight distribution, homogeneous monomer composition, and their specific rheology [1-3]. Ethylene-1-octene copolymer is one of these copolymers and a member of polyolefin elastomers which has a wide range of applications due to its excellent compatibility with a large number of other olefins, good processability, excellent elastic properties, high filler acceptance, low

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density, UV resistance, high tensile strength and good elongation [3-8]. Ethylene-1-octene copolymer has recently attracted considerable attention and is commonly used to blend with polyolefins, such as polyethylene and polypropylene [5]. In non-crosslinked state, polyolefin elastomers deform at temperatures above their crystalline melting temperature [3]. When low set is required, the elastomer must be completely cross-linked. Set properties including compression set, tension set and hot set are used to study the properties of vulcanized elastomers. Ethylene-1-octene copolymer with a high percentage of octene is very difficult to be used as a common elastomer in practical applications. However, it can be chemically cross-linked in order to its shape is maintained without any appreciable change at temperatures above its melting temperature, and also to be used in certain applications [9-11].

Improvement of mechanical properties is the primary effect of forming a three-dimensional network of polymer chains. Dimensional stability and increased thermal, chemical and physical stability are other effects of cross-linking process. Another major advantage of cross-linking is that it enables polymers to be used at temperatures above their melting point. As a result, the cross-linking of these polymers has led to their widespread use in different applications [3,4]. Cross-linking allows POEs to exhibit viscoelastic behavior at temperatures above their melting point, so cross-linked POEs are widely used in high-temperature industrial applications [3,6,12]. Therefore, the study of cross-linking of POEs is a topic of great importance in industry. Unlike other polyolefin elastomers such as EPDM, which have double bond in their side chain and can be cross-linked by sulfur systems, POEs do not have double bond in their chemical structure, and cannot be cross-linked by sulfur systems, therefore, they need to be cross-linked through other methods [1]. In a cross-linked network structure, the chemical bonds between the chains may be carbon-carbon bonds or specific bonds, such as siloxanes [13,14].

There are two general methods for cross-linking of POEs: chemical methods including using azo, peroxide and silane compounds, and physical methods involving radiation [1,3,6,10]. Among them, cross-linking by using silane compounds is more common [9,10]. In all cross-linking methods used for polyethylene copolymers with the lack of functional groups in their structure, the degree of cross-linking can be quantitatively measured and controlled by the solvent extraction method according to ASTM D2765 or DIN 16892 standard [13-16]. Gel content measurement is a

direct way to measure the degree of cross-linking [12]. In addition to the extraction method, gel content can be determined using differential scanning calorimetry (DSC) analysis [17]. Silane grafting and cross-linking reactions have been investigated by various methods, including torque [12,18,19], melt flow index (MFI) [12,20], hot set test [12,21] and Fourier transform infrared spectroscopy (FTIR) [12,19,20, 22-26]. FTIR technique is typically used to track the grafting reaction. FTIR characterization is also commonly used to follow the silane grafting and cross-linking reaction. In FTIR spectrum of silane-grafted polyethylene, peaks at 799 cm^{-1} , 1092 cm^{-1} (or sometimes 1090 cm^{-1}), and 1192 cm^{-1} are the characteristic absorptions for Si-alkoxy groups (e.g., $-\text{Si-OCH}_3$) [12,19-23,27-29]. The 1092 cm^{-1} peak typically has the strongest absorption of Si-OCH₃/transmittance of $-\text{CH}_3$ group [19-23,30] and is frequently used as an indication of the silane grafting extension. Peak at 1378 cm^{-1} relates to $-\text{CH}_3$ symmetric deformation [12, 19-23].

In this work, silane cross-linking of POE/LLDPE blend was carried out using the Sioplas process. Silane grafting process was carried out by using an industrial scale twin-screw extruder. The effect of VTMS concentration on the mechanical and thermal properties of the products was investigated. Also, in addition to cross-linking and grafting reactions of silane molecules, efficiency of the silane grafting reaction and gel content measurement by FTIR results were studied. The obtained results were compared with the results obtained from the solvent extraction technique.

EXPERIMENTAL

Materials

Two grades of ethylene-octene copolymer, POE and LLDPE, differing in their octane contents were used. POE was supplied as pellets from SK Global Chemical Co., Ltd, South Korea. It has a nominal melting index of 5 g/10 min at 190°C , a density of 0.868 g/cm^3 and Mooney viscosity (ML 1+4@ 121°C) of 8 Mu. LLDPE was purchased as pellets from Amir Kabir Petrochemical Co., Ltd, Iran. It has a nominal melting index of 0.9 g/10 min at 190°C and 2.16 kg piston force, as well as a density of 0.921 g/cm^3 and Vicat softening point of 100°C . The initiator, benzoyl peroxide (BPO, Arkema, France), vinyl trimethoxy silane (VTMS, RUI Chemical, China) and dibutyltin dilaurate (DBTDL, Merck, South Korea) were reagent grade and used to make silane-grafted POE/LLDPE

blend followed by a subsequent curing. Pentaerythritol tetrakis (3-(3, 5-di-tert-butyl-4-hydroxyphenyl) propionate), Irganox 1010 antioxidant, was purchased from BASF Co., Germany.

Sample preparation

Silane-moisture cross-linking of POE/LLDPE blend was performed in a co-rotating twin-screw extruder with twelve heating/cooling zones (Model CTE 65, Coperion Co., Germany). A screw speed of 30 rev min⁻¹, a constant feed rate (3.5 kg/min) and a temperature profile of 170-210°C from feed zone to die zone were used. A constant peroxide concentration of 0.13 wt.% was used, while, the concentration of the silane was varied in the range of 3-7 wt.%. In this study, a catalyst master batch was used for accelerating the cross-linking reaction. The master batch catalyst consisting of catalyst, antioxidant and fraction of polyolefin elastomer was prepared using a roller. In the next step, a blend of the silane-grafted copolymer (~95 wt.%) and catalyst master batch (~5 wt.%) was readied with an injection molding equipment. All specimens were cross-linked under identical conditions for 4-6 h, per 1 mm in thickness in a water bath system operated at 85°C.

Measurements

Properties of specimens were determined according to the standard methods listed in Table 1.

Hot set test

Hot set test was carried out according to EN 60811-507: 2013 standard. The test was conducted such that the tubular test specimen was kept in a high temperature environment of 200°C for 15 min, under a static load of 20 N/cm².

RESULTS AND DISCUSSION

Investigation of silane grafting and cross-linking reactions using FTIR technique

FTIR characterization is commonly used to follow the silane grafting and crosslinking reaction [12,19-23,27-29]. The transmittance peak positions and their respective assignments for specified groups are given in Table 2. Figures 1 and 2 present the FTIR spectra of the silane cross-linked and grafted POE/LLDPE blend, respectively. In Figure 1, which is related to the silane cross-linked POE/LLDPE blend, the absorption peaks at 1078 cm⁻¹ and 955 cm⁻¹ are related to Si-O-Si bonds which were formed during the silane cross-linking process. Si-C groups showed the peaks at 1196 cm⁻¹ and 850 cm⁻¹. In such samples, two adsorbents (the Si-OCH₃ and Si-O-Si groups) are combined together. For use of FTIR data quantitatively, the peak deconvolution method or a complementary technique should be used [12,22]. The peak observed at 3405 cm⁻¹, which was due to the hydroxyl group produced from the hydrolysis of methoxyethylene group, reflects the fact that curing is not completed. In the FTIR spectrum of the silane-grafted POE/LLDPE blend presented in Figure 2, the peaks at 771 cm⁻¹, 1092 cm⁻¹ (that sometimes appears at 1090 cm⁻¹) and 1187 cm⁻¹ belong to alkoxy silane groups such as Si-OCH₃ [12,19-23,27-29]. As shown in Figure 2, in addition to the appearance of these peaks at 1090 cm⁻¹ and 1187 cm⁻¹, the area under these peaks is smaller than the area under the peak of pure VTMS shown in Figure 3. This observation indicates that a fraction of silane is consumed in the silane grafting reaction. As seen in Figure 3, the absorption peak at 1600 cm⁻¹ which belongs to the vinyl-silane group has disappeared due to the silane grafting.

Table 1. Test method standards used in the project.

Properties	Standard	Test method ^{**}
Hardness, Shore A	ISO 868: 2003	1 s, 15 s
Density	ISO 1183: 2012	-----
Tensile strength-at-break and elongation-at-break	ISO 527: 2012	500 mm.min ⁻¹ , 2-kN load cell, MPa
Hot set test	EN 60811-507: 2013	15 minutes, 200 °C, 20 N/cm ² , %, 8 h cured at 85 °C
Compression set	PSA [*] D45 1132: 2012	22 h at 70 °C, 25 % initial thickness, %
Tension set	PSA D45 1132: 2012	Initial tension was 20 %, %,
Tear strength	PSA D41 5149: 2012	kg/cm
Melt flow index	ISO 1133: 2005	190°C /21.6 kg, g/10 min, uncured
Gel content	ASTM D 2765-95 a: 2016	Refluxing xylene containing 1 % of antioxidant for 6 h, %
Heat aging test at 70°C	ASTM D 573: 2010	168 h,70°C, %

^{*}PSA= peugeot citroen standards

^{**}There are the standard conditions used

Table 2. Peak position assignments [22,31].

Wavenumber, cm ⁻¹	Functional group	Remark
2919	CH ₂	Asymmetric C-H stretch
2850	CH ₂	symmetric C-H stretch
1740	>C=O	>C=O stretching
1445-1465	C-CH ₂	CH ₂ wagging (asymmetric bending vibration)
1367	C-CH ₂	Symmetric bending of C-H bond
1250	C-O	C-O stretching
1192	Si-O-C	O-CH ₃ rocking vibration
1092	Si-O-C	O-C stretching vibration of reacted or unreacted silane
1130/1000	Si-O-Si	Si-O-Si asymmetric stretching
1087/1020	Si-O-Si	Si-O-Si vibration
1023	=C-O-C	=C-O-C stretching
1009/992	CH ₂ =CH-Si	Vinyl chain group
815	Si-O-CH ₃	Si-O-CH ₃ stretching
771-795	Si-O-CH ₃	Si-O-CH ₃ (CH ₃ rocking)
710-730	C-CH ₂	CH ₂ rocking vibration

Gel content measurement using FTIR technique

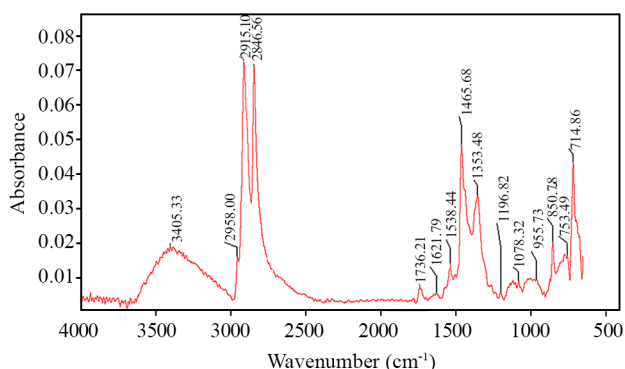
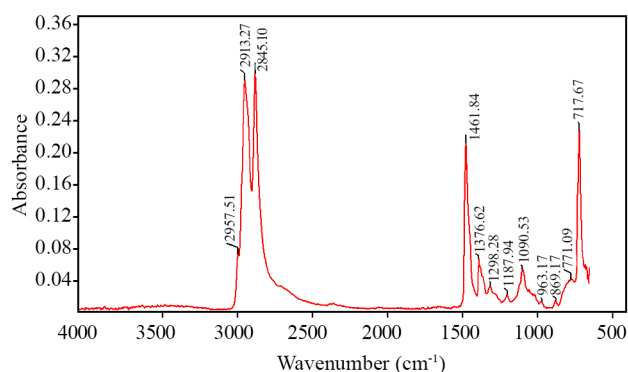
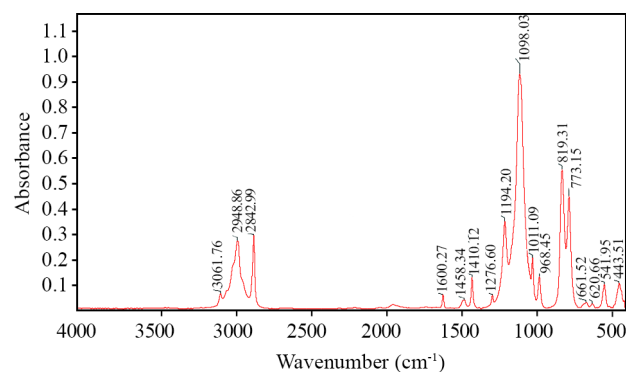
In addition to the solvent extraction method, gel content of the silane cross-linked compound can be calculated using the analysis of the FTIR spectra. For this purpose, the hydroxyl group absorption due to the hydrolysis of the methoxysilane group was calculated, as compared to the total absorbed content of the silane cross-linked compound. The absorption of the hydroxyl group

residue represents the hydrolyzed amount, which, of course, does not participate in cross-linking. Thus, the degree of cross-linking of the cured compound was calculated using the relationships given in Equations 1:

$$\text{Gel content \%} = \{1 - [\text{Absorbance OH group}/\text{Total absorbance of compound}] \} \times 100 \quad (1)$$

The absorption was measured by integrating the peaks through two different methods: first, the use of the region tool option presented in Figure 4, and second, the use of the peak area tool option presented in Figure 5.

In order to compare two methods of solvent extraction and FTIR for determining gel content, samples were cured at different times, between 15 min and 16 h (Figure 6). As Figure 6 shows, the gel contents obtained by using the two methods are in good agreement at curing times greater than 4 h. The discrepancy between the two methods under 4 h of curing times is probably due to the low hydrolysis of methoxy silane groups. According to equation 1, the gel content increases with the decrease in the amount

**Figure 1.** FTIR spectrum of silane cross-linked POE/LLDPE blend.**Figure 2.** FTIR spectrum of silane-grafted POE/LLDPE blend.**Figure 3.** FTIR spectrum of vinyltrimethoxy silane.

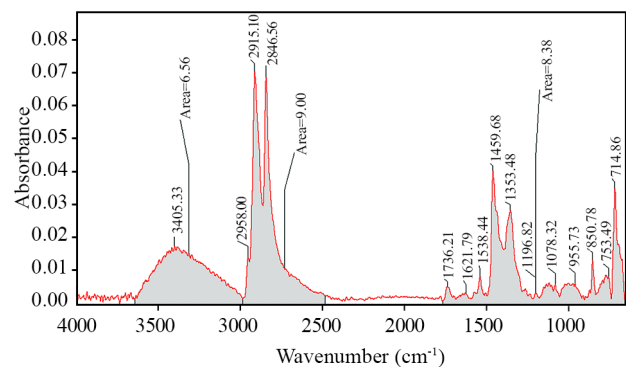


Figure 4. Integration range in the FTIR spectrum of silane-crosslinked compound using region tool option of the device.

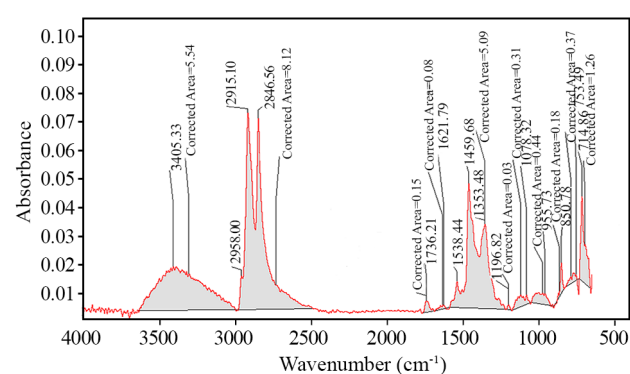


Figure 5. Integration range in the FTIR spectrum of silane-crosslinked compound using peak area tool of the device.

of hydroxyl group absorption.

Effect of silane concentration on grafting reaction

Figure 7 shows the effect of different concentrations of silane on the amount of silane grafting. Quantitative data of FTIR, in particular, the reduction of the absorption density of methoxy groups, may not directly provide the amount of cross-linking. However, FTIR is a non-destructive method that provides meaningful information on the progression of the cross-linking reaction with water [28]. The 1092 cm^{-1} peak has a particularly strong absorption of Si-OCH₃/transmittance of -CH₃ group [12,19-23,27-

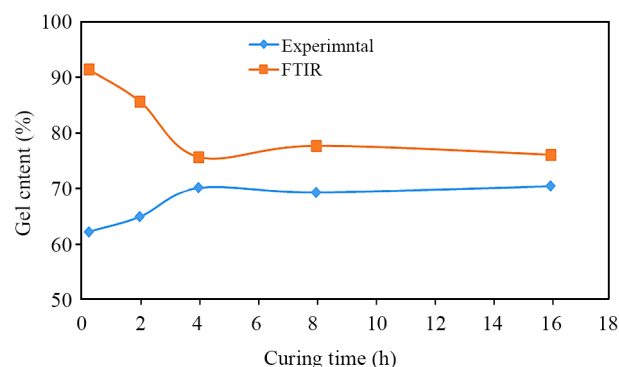


Figure 6. Comparison of gel content obtained using solvent extraction technique (ASTM D 2765-95 a: 2016) and FTIR technique.

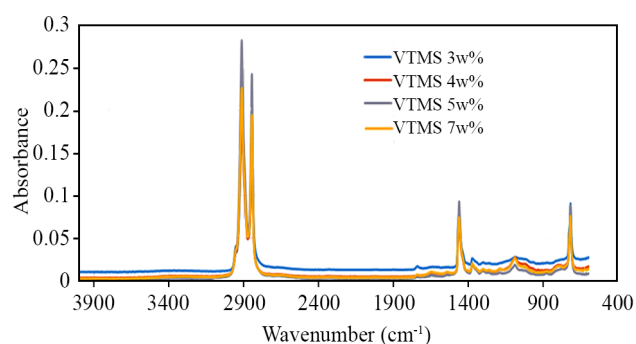


Figure 7. Effect of VTMS concentration on the amount of the silane grafting reaction.

29], and is often used to predict the development of silane grafting. The peak of 1378 cm^{-1} is related to the symmetric strength of CH₃ [12]. In silane grafting reactions, the secondary and tertiary carbons are predominantly involved in comparison with the primary carbon (seen at the end of the chain and lateral branches). Therefore, it is reasonable to use the 1378 cm^{-1} peak as the internal standard available in polyethylene compounds due to low variations absorption of Si-OCH₃/transmittance of -CH₃ group in content during the silane grafting reaction (considered as the internal standard). By choosing the internal standard, the silane grafting efficiency of the silane can be determined by calculating the peak absorption

Table 3. Evaluation of the effect of VTMS concentration on the silane grafting reaction.

	Absorbance 717 cm^{-1} /VTMS wt. %	Absorbance 1090 cm^{-1} / VTMS wt. %	Absorbance 1192 cm^{-1} /VTMS wt. %	Transmittance 1378 cm^{-1} /VTMS wt. %	Absorbance 1090 cm^{-1} / Transmittance 1378 cm^{-1}
Integration range (VTMS wt. %)	684.36-738.20	983.32-1164.69	1164.69-1214.28	1346.05-1423.98	
3	0.588	1.066	0.247	53.249	0.060
4	0.320	0.619	0.114	54.288	0.046
5	0.264	0.312	0.062	54.363	0.029
7	0.183	0.316	0.067	54.216	0.041

ratio of Si-O-CH₃ groups at 1092 cm⁻¹ to the peak absorption of methyl groups at 1378 cm⁻¹ [12,19-23,27-29].

However, as shown in Figure 7 and in Table 3, the intensity of the peaks at 1090 cm⁻¹ and 1192 cm⁻¹ is decreased with increasing concentration of the silane, which can be attributed to the increase in silane grafting. Also, according to the description given above and Table 3, the lowest internal standard value can be observed at the silane concentration of 5 wt.%, indicating the highest silane grafting efficiencies. In addition to the above observations, the absorption in

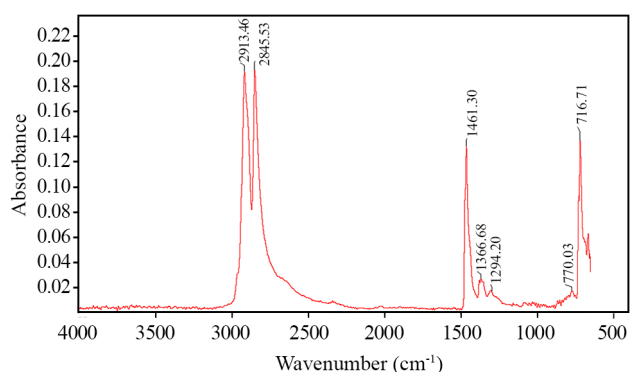


Figure 8. FTIR spectrum of LLDPE LL0209 AA.

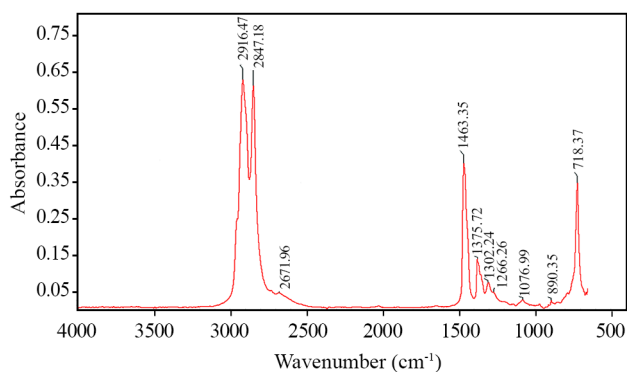


Figure 9. FTIR spectrum of POE Soluter 875L.

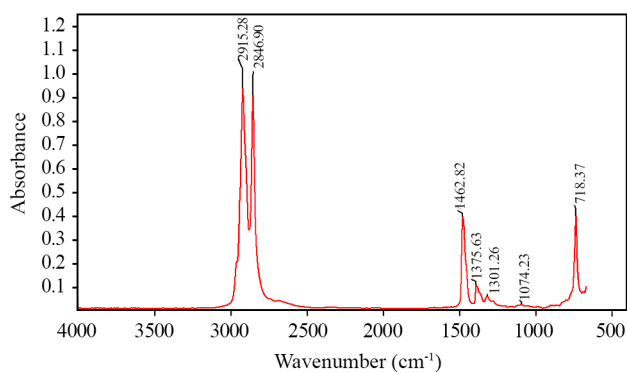


Figure 10. FTIR spectrum of POE Soluter 875L and LL 0209 AA blend.

the region of about 717 cm⁻¹, which is related to the non-saturation of the total polymer, decreases with increasing of the silane concentration. It can be stated that by increasing the amount of silane, the efficiency of the silane grafting reaction is increased (Table 3).

In addition to investigating the silane grafting and cross-linking reactions, the comparison of the absorption peaks at 968 cm⁻¹ and 1011 cm⁻¹ for LLDPE (Figure 8), POE (Figure 9) and the blend of these two polymers (Figure 10) was performed via FTIR analysis. The absorbent peaks at 1076 cm⁻¹ and 890 cm⁻¹ (Figure 9) related to the non-vinyl flexural vibrations can be observed in the spectrum of POE, while they are vanished in the spectrum of LLDPE (Figure 8), and in the spectrum of their blend the intensities of the two peaks (Figure 10) are lower than those observed in the spectrum of POE. The intensity of the absorbed peaks in the VTMS spectrum (as shown in Figure 3) is much higher than the peaks observed in the spectrum of polymers.

Effect of VTMS concentration on properties of the silane cross-linked compound

The various properties of the silane cross-linked compounds prepared with different concentrations of VTMS are presented in Table 4 and Figures 11 to 16. The lowest MFI value (Figure 11) was obtained at 5 wt.% of VTMS, which indicates the highest amount of the silane grafting, and therefore, the highest degree of curing. Obviously, at this concentration of the silane, gel content (Figure 12), tear strength (Figure 13), compression set (Figure 14) and hot set 200°C and tensile strength (Table 4) have the highest values. The further increase in MFI at 7 wt.% of VTMS is probably due to difficulty in accessing reactive centers (tertiary and secondary carbons) for silane grafting compared to the initiation of grafting reaction. Therefore, an

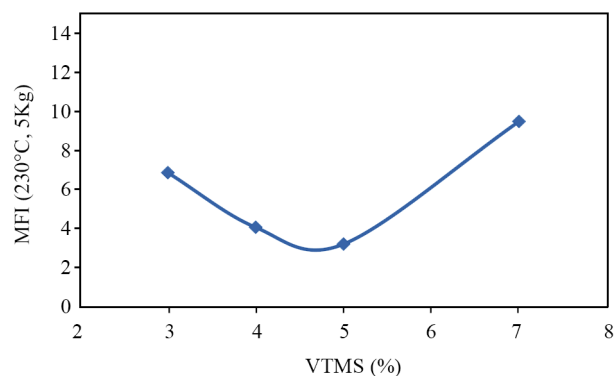
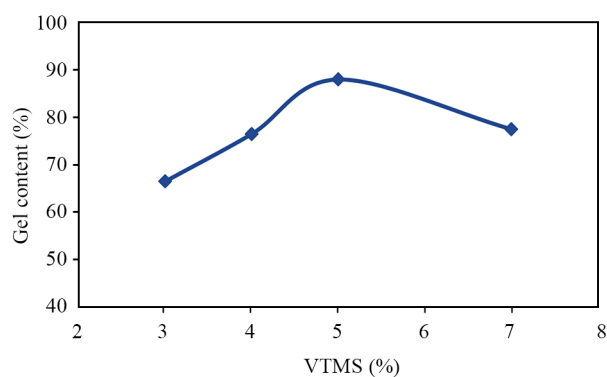
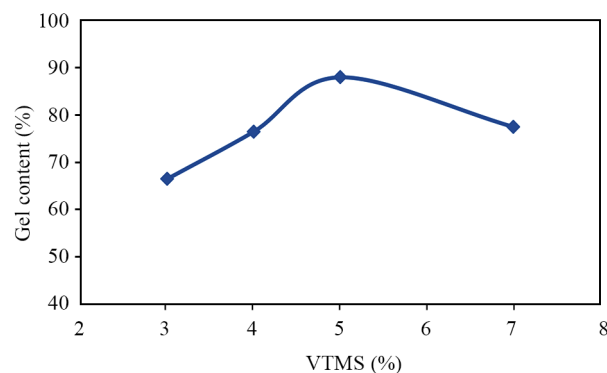


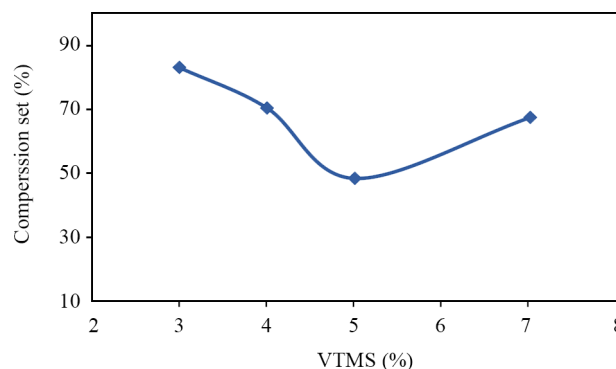
Figure 11. Effect of VTMS concentration on the MFI of the silane grafted compound.

Table 4. Effect of VTMS concentration on the properties of the silane cross-linked compound.

Properties	test method	VTMS 3 wt.%	VTMS 4 wt.%		VTMS 5 wt.%		VTMS 7 wt.%	
			extension >175%	set >15%	extension >175%	set >15%	extension >175%	set >15%
Hot set (8 hr cured at 85°C)	INSO 5525-507	Not passed	23.25	-24.8	7.90	-20.0	13.35	-25.2
Harness(Shore A, 15 S)	ISO 868	81.3	79.8		80.4		81.2	
Tensile strength-at-break	ISO 527, MPa	6.44	6.11		6.65		6.26	
Elongation-at-break	ISO 527, %	426	356		211		376	
Gel content %	ASTM 2765-95a	67	77		88		78	
MFI (230 °C/ 5 kg)	ISO 1133	6.87	4.07		3.21		9.50	
Silane grafted Compound								
Compression set	PSA D45 1132 (22 hr, 70°C)	83.0	70.3		48.3		67.9	
Tension set	PSA D45 1132, 20%, 22 hr, 70°C	68.8	63.5		79.0		66.0	
Tear strength	PSA D41 5149, kgf/cm	20.6	21.7		23.5		22.9	
Aging Δ tensile 	ASTM D 573	2.6	0.4		2.3		4.2	
Aging Δ elongation 	7 day, 70°C,%	28.2	28.2		23.1		6.7	
Aging Δ hardness 		0.5	0.2		2.8		1.3	
Density	ISO 1183	0.896	0.889		0.890		0.888	
Tensile modulus		2.59	2.31		2.82		2.74	
20%		3.11	3.32		4.12		3.39	
50%	ISO 527, MPa	3.53	4.28		5.11		4.34	
100%		4.10	5.06		6.49		5.15	
200%		4.82	5.72			5.76	
300%		5.84	

**Figure 12.** Effect of VTMS concentration on the gel content of the silane cross-linked compound.**Figure 13.** Effect of VTMS concentration on the tear strength of the silane cross-linked compound.

amount of the silane will remain unreacted without participation in the grafting reaction. This excess silane acts as a plasticizer and increases MFI of the silane grafted compound. VTMS significantly affected the density and hardness of the silane cross-linked compound (Table 4). The lowest value of hot set was obtained at 4 wt.% of VTMS. Among the silane cross-linked compounds that hot testing above 4 wt.% of VTMS was approved for them, the highest tensile strength (Table 4) and tensile modulus (Figures 15) were observed in the samples with 5 wt.% of VTMS [32]. Generally, the percentage of elongation (Table

**Figure 14.** Effect of VTMS concentration on the compression set of the silane cross-linked compound.

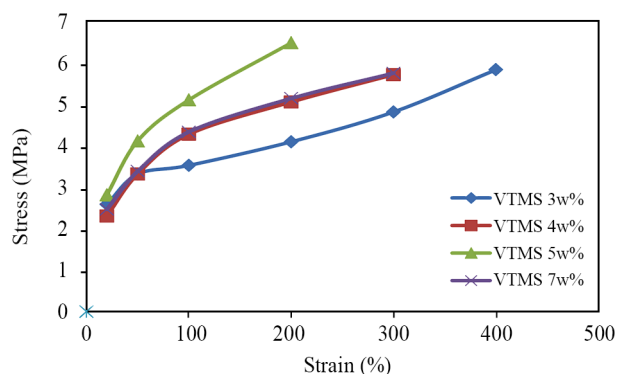


Figure 15. Effect of VTMS concentration on the tensile modulus (ISO 527) of the silane cross-linked compound.

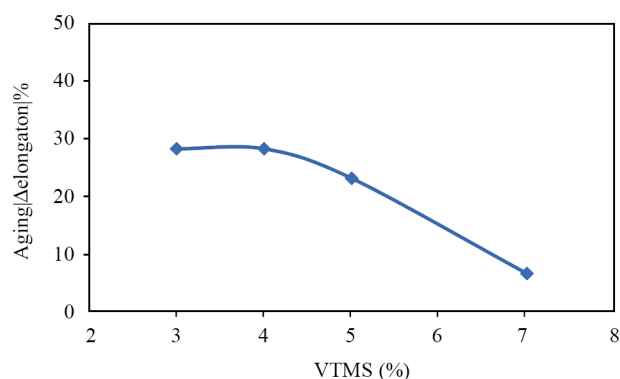


Figure 16. Effect of VTMS concentration on the aging [elongation] % of the silane cross-linked compound.

4) in these silane cross-linked compounds decreases with increasing VTMS concentration. Increasing concentration of VTMS generally does not have much effect on post-aging properties. Based on the obtained results, 5 wt.% of the silane was selected for next studies [20,23,30].

CONCLUSION

Silane-moisture cross-linking of POE/LLDPE blend was carried out using the two-step Sioplas processes in an industrial scale twin-screw extruder. Cross-linking reactions and grafting of the silane were followed by FTIR analysis. It was determined that the Si-O-Si bonds produced during curing process have absorption at 1078 cm^{-1} and 955 cm^{-1} . In the other hand, a peak was also observed at 3405 cm^{-1} which was due to the hydroxyl group produced from the hydrolysis of methoxyethylene group. This peak of absorption is due to incomplete curing that is the basis for measuring gel content using this technique. In order to compare the gel content results obtained from the solvent extraction method (ASTM D 2765-

95 a) and the method presented in this study (FTIR technique), the gel content was measured using each of two methods. At intervals of curing time ranging between 4 and 16 hours, the results obtained from the two methods were in good agreement. The efficiency of the silane grafting was determined by choosing the internal standard (absorption Si-O-CH₃ groups/methyl groups). The results showed that 5 wt.% was the least amount of silane needed for obtaining the highest efficiency of silane grafting reaction. The lowest MFI value was obtained at 5 wt.% of VTMS, indicating the highest amount of the silane grafting, and therefore, the highest degree of curing. At 5 wt.% of VTMS, gel content, tear strength, compression set and hot set 200°C showed their highest values.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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