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Characterization and quantification of the cross-linking of linear low density polyethylene with silane grafting by Fourier transform infrared (FTIR) spectroscopy

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The way of making cross-linkable polyethylene through silane grafting has gained much 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. This work deals with silane grafting and moisture cross-linking of linear low density polyethylene (LLDPE). The grafting reaction was performed in an internal mixer using di-cumyl peroxide (DCP) as initiator and vinyl-trimethoxy silane (VTMOS) as grafting agent. Characterization and quantification of the grafting was performed by Fourier transform infrared (FTIR) spectroscopy. The cross-linking was done by subsequent immersion of grafted samples in hot water**.** The effect of silane and peroxide concentration was more considerable than time. The order of degradation temperature was: cross-linked LLDPE then grafted LLDPE and at last LLDPE.

Keywords: LLDPE; Silane grafting; Cross-linking; FTIR.

1. INTRODUCTION

Polyethylen is the most important in terms of commercial applications employed to produce wire, cables, plastic pipes, etc. [1]. The cross-linking of polyethylene drastically improves the material properties such as creep behavior, thermal performance and higher impact and chemical resistance [2-3]. Grafting of vinylsilanes to polyolefin substrates in the present of peroxide is the most common example of graft reactions [4]. The three main cross-linking methods that are of commercial interest involve radiation cross-linking, peroxide cross-linking and silane cross-linking [5]. The latter technique that involved cross-linking with organofunctional silane developed through the processes has been used successfully since the 1970s, and has gained great attention in recent years because of its advantages compared with radiation and peroxide cross-linking [6-9].

The advantages of using the silane grafted polymer are easy processing, low coast and capital investment and also better properties of the cross-linked materials. The most commonly used silane for manufacturing cross-linkable PE is the vinyltrimethoxysilane (VTMOS) [10-11]. This silane conventionally has been introduced into PE by melt grafting using peroxide [12]. Initially the peroxide decomposes to form free radicals. These radicals then abstract hydrogen atoms from the polyethylene backbone to generate radical sites onto which the VTMOS is attached. In the second stage the graft copolymers are hydrolysed and cross-linked by forming Si-O-Si linkages under treatment with water in the presence of a suitable catalyst. Un-cross-linked polyethylene has the melting point of 100-130°C, however, after cross-linking no flow would be noticed even at 150°C, where elastic behavior prevails [13-14]. Hjertberg and coworkers studied the kinetics of silane grafting reactions of VTMOS graft copolymer [15]. Ahmed and coworker’s studied FTIR analysis of silane grafted high density polyethylene [16]. Fourier transform infrared spectroscopy is the most widely used technique for determining degree of grafting and cross-linking both quantitatively and quantitatively [17-22]. Other methods such as gel content or solvent uptake are not as accurate as FTIR and they used solvent and are not environmental friendly.

The main focus in this paper is to produce a grafted linear low density PE and then qualitatively and quantitatively analyse the graft copolymer in the first stage of the grafting reaction by FTIR spectroscopy. This will also include investigating the effect the concentration of additives (PE and peroxide) has on the grafting level.

2. EXPERIMENTAL

2.1. Methods

Linear low density polyethylene (LLDPE) was supplied by NCP (Iran), under trade name of LL220 with a melt index of 2g/10 min. The silane used was vinyl trimetoxysilane (VTMOS) which was in liquid form and boiling temperature of 123°C by Evonik (Germany). The peroxide used as initiator was dicumyl peroxide in powder form by Hercules with 98% purity.

2.2. Sample preparation

Grafting reaction of silane onto LLDPE was performed in an internal mixer (Brabender, Plasticorder, Germany). The roller type rotors were selected. The mixing bowl capacity was 55 ml. The temperature profile of grafting process was as follows: 125° C for 3 min then increasing the temperature to 180° C with 2 min and at last 180° C for different periods of time (2, 5, 10, 15, 18 min) to investigate the effect of time in grafting level. At first the polyethylene was fed into the extruder at 125° C. After melting the polymer the silane/DCP mixture was added and the temperature was increased. This procedure was selected to minimize the evaporation of silane at high temperatures. The torque and temperature of mixer was monitored to evaluate the state of grafting process and changing in viscosity during grafting. The silane concentration was in the range of 0.64-7.5 phr while for DCP it was 0.01- 0.35 phr. Cross-linking was carried out in hot water for 24 hr. In this research the catalyst has not been used to avoid the premature cross-linking of samples.

2.3. Analysis

The melt flow index of virgin polyethylene was measured according to ASTM D 1238 in a Zwick machine. The extent of grafting reaction was analyzed by FTIR (Equinox 55, Bruker Company) using thin film samples. Film samples were prepared by hot pressing (Mini test press, Toyoseiki, Japan). Samples were placed into hot press under a load of 25 MPa at a temperature of 190°c for 3 min. They were then cooled in a cold press for 1 min. The films were held on a sample holder. The FTIR spectrums were scanned over a range of 600-4000 cm^{1}. Thermal Gravimetric Analysis (TGA) was done to evaluate the thermal resistant of different samples using a TGA (PL-1500, Polymer laboratories) with the rate of 10 °C/min in nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Monitoring of grafting

Fig. 1 shows the variation of torque of mixer versus time for a sample containing 6 phr and 0.28 phr silane and DCP, respectively, for 12 min. The first peak is related to the melting of polyethylene. With incorporation of grafting additives and increasing the temperature the second peak was observed at about 6 min of mixing. This peak is corresponded to the grafting of silane to polyethylene. By grafting the viscosity of sample was increased. Similar curves were obtained for different samples. Fig. 2 shows FTIR spectra of LLDPE homopolymer (A) and the modified LLDPE) with various amount of silane (B – F). Three new bands are observed at 1192 cm^{-1}, 1096 cm^{-1} and 812 cm^{-1}. The 1192 cm^{-1}, 1096 cm^{-1} bands were assigned to the methoxy groups (Si-O-CH_3) and and 815 cm^{-1} silane carbon bonds (Si-OCH_3), respectively.

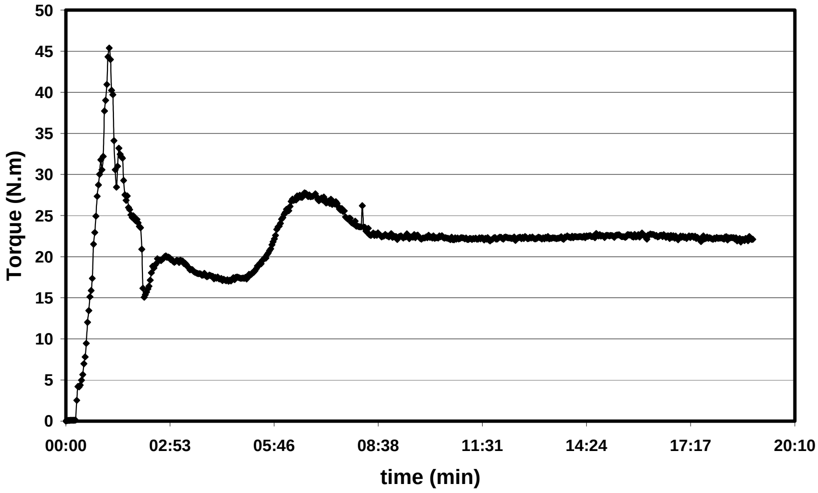

Fig. 1. Variation of torque with mixing time for a sample containing 6 phr and 0.28 phr, silane and DCP, respectively, for 12 min.

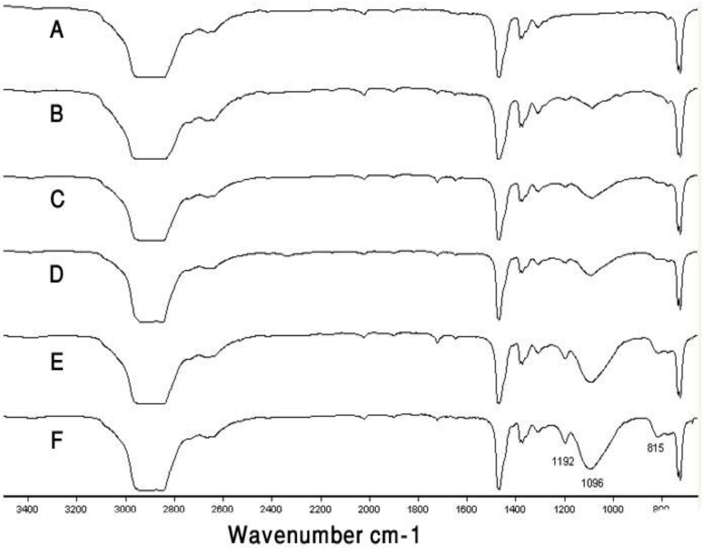

Fig. 2. FTIR spectra of LLDPE (A), grafted LLDPE with (B) 0.64 phr, (C) 2phr, (D) 4phr, (E) 6 phr, (F) 7.5 phr of silane with 0.18 phr peroxide for 2 min.

Table 1 shows the main bands assignments. Fig. 3 displays that the extent of silane grafting reaction increased as the amount of silane used increased. In the (B – F) curves, the band intensities at 1096 cm^{-1}and 1192 cm^{-1} start to increase because more VTMOS is presented than quantity of Si-O-C bonds were increased. We can use the ratio intensity of absorption bands of Si-OCH_3 in 1096 cm^{-1} to the absorption band of C-CH_2 in 1367 cm^{-1}, as R. The 1367 cm^{-1} bond was chosen as an internal reference, that doesn't change during the grafting reaction. That is relative amount of silane grafting.

$$R=A_{1096}/A_{1367} \qquad (1)$$

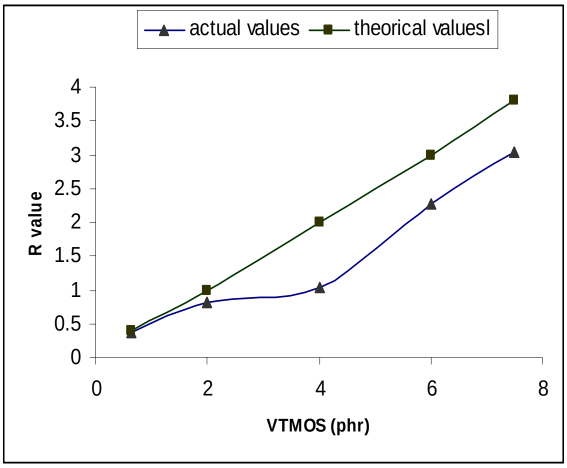

Fig. 3. Effect of VTMOS concentration on grafting level.

According to the beer Lambert law A=εbc, A is the absorbance intensity, ε is the absorption coefficient, b is the path length of light (here is thickness of the films and c is concentration of vibrating group. In relationship R, A_{1096} is correspond to silane and A_{1367} for polyethylene, so

$$R=A_{1096}/A_{1367}=A_{silane}/A_{polyethylene}=\varepsilon\, b\, C_{silane}/\varepsilon\, b\, C_{polyethylene} \qquad (2)$$

If ε b = k, then, k and $C_{polyethylene}$ is constant for all samples, therefore $R = KC_{silane}$ and by this equation we can calculate the theoretical absorption ratio. In Fig. 3 shows the difference between actual and theoretical of R values. Because during the grafting process some of silane is lost, therefore, C_{silane} and R ratio were decreased.

Table 1. Main peaks assignments.

Wave number (cm^{-1})	Functional group	Interpretation
1192	Si-O-C	O- CH_3 rocking vibration
1092(1096)	Si-O-C	stretching vibration of reacted silane
1087/1020	Si-O-Si	siloxan vibration
1130/1000	Si-O-Si	silaxan asymmetric stretching
815	Si-O-CH_3	Si-O-CH_3 Stretching
795	Si-O-CH_3	CH_3 Rocking
1367	C-CH_2	CH_2 Rocking vibration

3.2. Effect of peroxide concentration

Fig. 4 shows FTIR spectra of modified LLDPE with various amount of peroxide with the VTMOS concentration kept constant at 6 phr for 2 min. There is a relative increases in extent of silane grafting when the amount of peroxide increases. As peroxide is an initiator and when its amount increases, radicals increase, but these radicals can react with each other and produce the molecules that can't participate in grafting reaction. On the other hand, with increasing the peroxide concentration, the risk of peroxide cross-linking which leads to formation of C-C bond increases. These premature cross-linking decreases the flow ability of samples in other processes such as compression molding selected for making films for FTIR analysis. It should be noted that we repeat the test for sample containing 6 phr silane and 0.18 phr peroxide at 2 min to check the results. Although a little difference was observed between the final results for R values (2.0 vs. 1.96) in general, the results were comparable. The comparison between silane and peroxide effect on grafting efficiency, it can be said that the effect of peroxide is more pronounced them of silane. In the Fig. 4 it is clear that very low amount of DCP (for example 0.01 phr) causes a significant amount of silane grafting. However, increasing the DCP value did not change the silane grafting efficiency, considerably (Table 2). Table 3 summarizes the R value for different DCP at constant silane content.

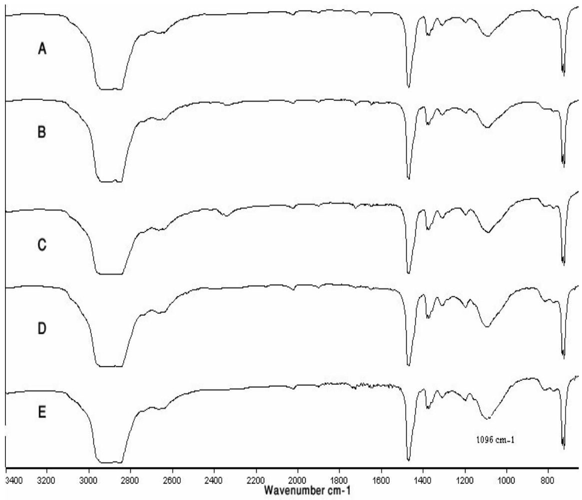

Fig. 4. FTIR spectra of LLDPE samples that have reacted with (A) 0.01 phr (B) 0.08 phr (C) 0.18 phr (D) 0.28 phr (E) 0.35 phr of peroxide with 6 phr silane for 2 min.

Table 2. Actual R values for samples (B-F) with various amounts of VTMOS**.**

Sample	VTMOS concentration (phr)	R values (actual)
B	0.64	0.372
C	2.00	0.825
D	4.00	1.025
E	6.00	2.028
F	7.50	3.041

Table 3. R values for (A-E) samples with various amounts of DCP

Sample	peroxide concentration (phr)	R values
A	0.01	1.72
B	0.08	1.88
C	0.18	1.96
D	0.28	2.28
E	0.35	2.50

3.3 Effect of time

Fig. 5 shows the modified LLDPE with 6 phr silane and 0.18 phr peroxide for various mixing time. This figure clearly displays that with increasing in reaction time the extent of grafting and the R value do not increase, significantly. The half life of peroxide at 180° C is less than 1 min. It can be expected that at the selected times in the current research causes the peroxide degraded to free radicals that can attack to polymer chains to form macro radicals. However, in fact more time is needed to complete the reaction and the differences between grafting values with time will reflect his.

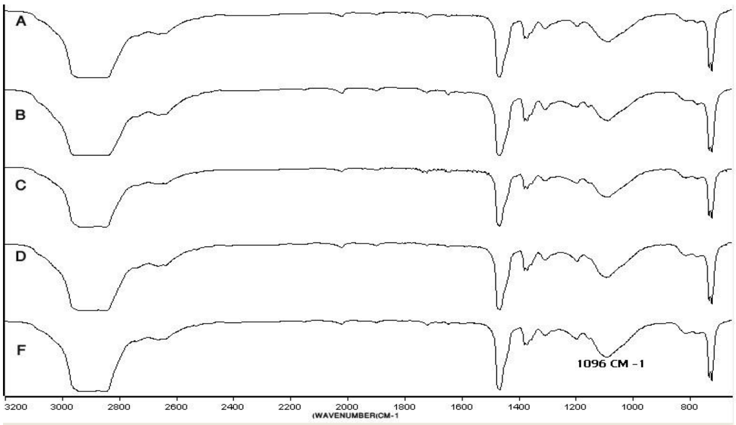

Fig. 5. FTIR spectra of LLDPE samples that have reacted with 6 phr silane and 0.18 phr peroxide for (A) 2 min (B) 5 min (C) 10 min (D) 15 min.

3.4.Cross-linking

Fig. 6 shows FTIR spectra of LLDPE before and after cross-linking with hot water for 24 h. Variation of FTIR characteristic bands with cross-linking has been depicted in Figure 6. From this figure, peak at 1087 cm^{-1} and shoulder in 1018 cm^{-1} are assigned to Si-O-Si group and the extent of peaks at 1192 cm^{-1} and 815 cm^{-1}assigned to Si-O-CH_3 were decreased. The cross-linking reaction takes place through condensation and hydrolysis of methoxy groups in presence of water molecules. The cross-linked sample is a network which is not flow able (Table 4).

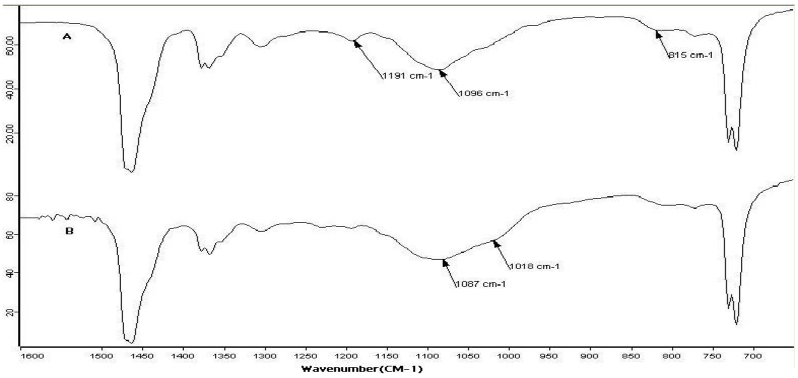

Fig. 6. FTIR spectra of LLDPE samples that have grafted with silane (A) before cross-linking with boiled water and (B) after cross-linking for 24 h.

Table 4. R values for samples (A-E) with different time of mixing.

Sample	Time of mixing (min)	R values
A	2	1.96
B	5	1.92
C	10	1.96
D	15	2.00
E	18	2.08

3.5. TGA diagram

Fig. 7 Shows TGA(thermal gravimetric analysis) of LLDPE (A) LLDPE after silane grafting with 6 phr silane, 0.18 phr peroxide and (C) sample B after cross-linking with hot water for 24h. The degradation temperatures of cross-linked LLDPE, are higher than that of grafting LLDPE and for the grafting sample are higher than the LLDPE without grafting. Generally, one of the main limitations of polyethylene is its low service temperature.

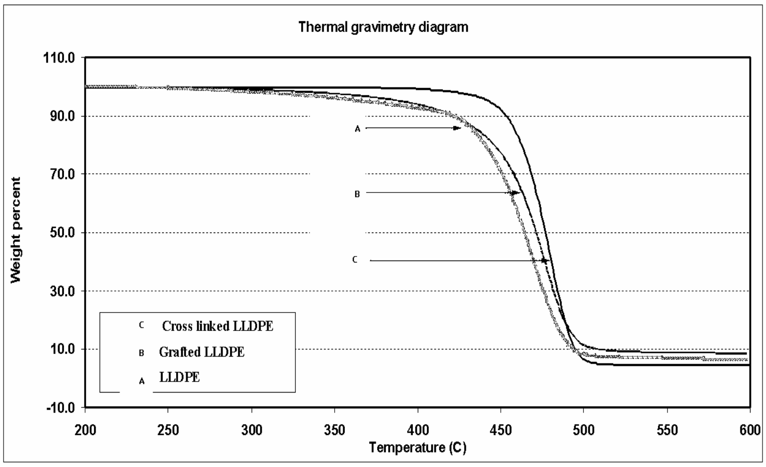

Fig. 7. TGA diagram (A) LLDPE (B) grafted LLDPE (C) cross-linked LLDPE.

Cross-linking is a way to increase the service temperature of polyethylene. With cross-linking strong chemical bonds form among polyethylene chains. These bonds have more resistance to thermal degradation. Therefore, cross-linked polyethylene is a suitable material for applications such as hot water piping systems and insulation of medium to high voltage power cables. For grafted polyethylene, although the chemical bonds have not formed, it leads to increase of physical entanglements between polyethylene chains which finally increase the resistance of grafted LLDPE at higher temperature compared to virgin LLDPE.

4. CONCLUSION

Silane cross-linking of polyethylene in melt processing was carried out in an internal mixer. The effect of formulation ingredients such as initiator and grafting agent was studied. Results showed that grafting can take place under suitable condition, successfully. Grafting level increased with increase of peroxide and silane concentration. It can be concluded that very low amount of peroxide is enough for achieving a reasonable amount of grafting. Thermal resistance of LLDPE increased with both grafting and cross-linking.

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