The Effect of Structural Parameters on the Cross-Linking of Various Grades of LLDPE

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ABSTRACT: *Polyethylene's application for insulating is highly advanced but due to thermoplastic properties, its application confronts constraints such as the limited 70°C temperature of the conductor. Polyethylene thermosetting procedure in which molecules are knotted and a 3D-molecular-network formed is developed to conquer the mentioned problem and to raise the applicable temperature of the insulation. This paper reports the cross-linking of two cable grades of LLDPE by using DCP (Dicumyl Peroxide). DCP was chosen for its prevalence among various cross-linking agents. Structural parameters like molecular weight, melt flow index, viscosity and number of branches were obtained using relative tests as Gel Permeation Chromatography (GPC), Rheometry and Fourier Transform-InfraRed (FT-IR) spectrometer. After calculating the percentage of gel content, properties of the pure and cross-linked samples were compared by thermal and mechanical analysis with DSC, TGA, and DMTA. The effects of cross-linking like melting and decomposition temperatures, crystal formation, viscous and elastic modulus were discussed by using various structural parameters such as MFI, molecular weight, short chain branches. Studies declared that cross-linked polymer, unlike the pure one, had a solid state with thermal mechanical properties in the range of 110 to 120°C, so this assist overcomes the problem of using polyethylene in temperatures around the melting point.*

KEYWORDS: *LLDPE; Cross-link; Structural parameters; DCP; DSC; DMTA.*

INTRODUCTION

POLYETHYLENE (PE) has very good electrical properties (low dielectric loss, low dielectric coefficient, and high insulation solidity) which leads to its wide usage in wire and cable industries as insulation, shield and

jacket in all types of cables. Using PE in communication or low voltage cables is not a problem; however, the problem will rise when facing medium to high voltage cables. In higher voltages, if the temperature of the conductor – insulation interface approaches 70°C, the insulation material will be deformed. This would be a bad situation but the solution is easy. The movement of the chains can be restricted by cross-linking them, so that they will not deform in 70°C and 90°C is the new limit for continuous conditions and a 120°C peak will be available. Several procedures for cross-linking exist but using chemical cross-linking with peroxide which is the prevailing procedure in medium to high voltage cables is more common. Dicumyl peroxide (DCP) is known as famous peroxides, which is commonly used for this purpose.

Some researchers accomplished related studies in this field. Smedberg et al found the optimized amount of the peroxide by testing the various amounts of peroxide with LDPE and LLDPE [1]. Afterward, they developed their researches on the cross-linking and scrutinized the results by IR Spectroscopy [2]. Abbasi also has done the cross-linking with peroxide and studied the results with DSC and DMA. He mentioned that, at room temperature, the cross-linked bonds and crystallinity are optimized and the best mechanical performances are achieved with 2.5% DCP. Also, this number changed to 1.5% for temperatures higher than room temperature, so in this paper, 2% DCP was chosen for cross-linking the polymer chains [3]. *Yu Seunggun et al.* studied on cross-linking of HDPE with different concentrations of DCP and analyzed its effect on crystals.[4] *Nilsson* did the electrical studies after cross-linking the samples with peroxide [5], while the effect of the polymerization degree and of Long *Chain Branches* on the cross-linked samples have been studied by *Andersson* [6, 7]. Some related researches have also been done on SEBS (styrene-ethylene/butylene-styrene) and on EVA (ethylene vinyl acetate) by *Zhisen* [8] and *Morshedian* [9], respectively. *Wang et al.* studied the investigation of the electrical properties of XLPE/SiC nanocomposites[10]. *Khonakdar et al.* used 0.5 to 3% BCUP peroxide on HDPE and compared the properties [11], where Morshedian et al, also performed the same procedure on LDPE and found that between 1.5 to 2.5 was the optimum percentage for DCP [9]. Cross-linking, without peroxide with use of silanes has been done by

Yu Wenwen et al. [12], also the study of the effect of silane cross-linking on the flame retardant property has been done by *Azizi* [13] while cross-linking with Irradiation has been done by Singh [14].

This paper didn't care about the analogy of peroxide percentages and the focus is about the comparison of the thermal analysis properties in a constant percentage of peroxide, so the project has been done in a constant 2% DCP. The test has been done for cross-linking two cable grades of LLDPE by adding 2% DCP (Dicumyl peroxide). The mentioned percent was chosen as a good example from literature surveys. After cross-linking and finding the best procedure to perform the cross-linking, a comparison of the results from thermal and mechanical analyses with DSC, TGA and DMTA is presented and the effects of cross-linking on melting and decomposition temperatures, crystal formation, viscous and elastic modulus has been discussed by using various structural parameters such as MFI, molecular weight, and short chain branches. Thereupon, results will declare cross-linking can overcome the thermal restriction of polyethylene.

EXPERIMENTAL SECTION
Materials
Two Wire and Cable grades of LLDPE have been used for the tests as follows:

1-Sample LL4004E (Density=0.924 g/cm^3) from ExxonMobil

2-Sample LL0220 (Density=0.920 g/cm^3) from Tabriz Petrochemical Complex, Iran.

In the following pages of the report, pure samples will be identified as "4004 Pure" and "0220 Pure" and cross-linked samples as "4004 XLPE" and "0220 XLPE".

Sample Preparation
For cross-linking, 2% DCP was dissolved in methanol and LLDPE, which was powdered to create a better mixture, was added and it formed a homogeneous mixture. The methanol evaporated at 80°C after 3 hours in a vacuum oven at 200 mbar (Absolute). Enough amount of LLDPE+DCP was measured and put in the Specac film maker apparatus model GS15011. In order to form the press mold without activating the peroxide the sample was melted at 130°C and weighed 2 tons. So as to have a bubble-free film a few minutes pause was done
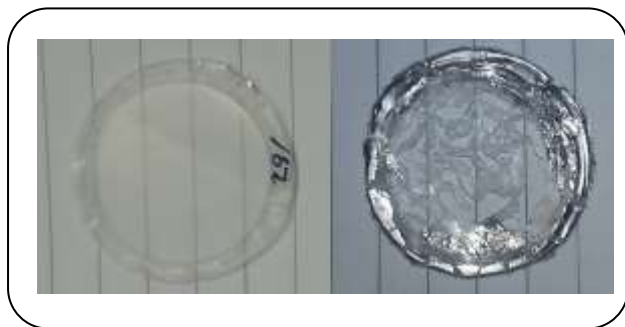
Fig. 1: Good film (Left) and Bad film (Right).

to ensure if any traces of methanol remained in the sample so a uniform sample was shaped, then the temperature was risen up to 170°C to activate DCP and was held for 15 minutes to complete the cross-link[1, 2, 6].

Tests
Gel Content
Gel content measurement was done based on ASTM D-2765. About 0.3gr of cross-linked LLPDE was weighed, put in a little cage (mesh 120) and extracted in boiling xylene for 12 hours (small amounts of Irgonnax1010 as an antioxidant were used). Then the residue was weighed to calculate the percentage of cross-linking. Calculations were based on the mentioned standard [11, 15].

Melt Flow Index (MFI)
MFI was measured by CEAST MODULAR MELT FLOW 7028 machine based on the ASTM D-1238 under the standard condition of 190°C and 2.16 kg [16].

Gel Permeation Chromatography (GPC)
GPC test was done to determine the molecular weight by an Agilent PL-GPC 220 high-temperature machine based on the ASTMD-6474 standard procedure. The test was conducted at 145°C with 1 mL TCB (1,4 trichlorobenzene) solvent for 1 mg sample [6, 17, 18].

Rheometry
Rheometry was obtained by a Gottfert rheograph 25 machine based on the ASTM D-3835 standard procedure[19].

Differential Scanning Calorimetry (DSC)
DSC was done with a Mettler DSC822e machine. First, samples were heated up to 190°C with the rate of 10 °C/min to clear the thermal history, then cooled down to 50°C and finally heated up again to 190°C to achieve

the final result (In the following figures, the first step is not shown). In order to prevent oxidation, N_2 gas was blown at the flow rate of 50ml/min [3, 6, 9, 20-23].

ThermoGravimetric Analyzer (TGA)
TGA was done with a Mettler TGA/DSC machine. Samples were heated up to 600°C with the rate of 10°C/min. In order to prevent oxidation, N_2 gas was blown at the flow rate of 50 mL/min [9, 24].

Fourier Transform Infra-Red spectrometer (FT-IR)
FT-IR was done by Bruker Tensor 27 FT-IR in the range of 400 to 4000 cm^{-1} wave number with the resolution of 4 cm^{-1} [25-28]. Also, the 1-butene comonomer concentration was calculated using the wave number 1378cm^{-1} through the use of ASTM D6645 [2, 9, 29-33].

Dynamic Mechanical Thermal Analysis (DMTA)
DMTA was done by Mettler DMA/SDTA861e with a heating rate of 2 °C/min on 1 Hz frequency [3, 6, 34-36].

RESULTS AND DISCUSSION
GPC
Polymer molecular weight is important because it determines many physical properties. If the molecular weight is too low, the mechanical properties will generally be too low for the polymer material to have any useful commercial applications. In order to be advantageous, the mechanical properties sufficient to bear design loads. Fig. 2 shows the result of GPC test. In these figures, molecular weight has been shown.

MFI
For good processing conditions of the extrusion of the insulation on the conductor of the wire, a comparatively high MFI is usually required. The data for these values are presented in Table 2. Results verified by GPC data and the lower Mw number for 4004, showed a higher MFI and vice versa.

Rheometery
The extrusion rate of polymer melts is limited by the onset of an elastic surface instability known as sharkskin. The appearance of these surface distortions is generally unacceptable for commercial applications. The desire to forestall the onset of sharkskin to higher output rates

Table 1: Molecular Weights, Polydispersity Index (PDI).

Sample #	Mw(g/mol)	Mn(g/mol)	PDI
4004 Pure	96530	17219	5.6
0220 Pure	143225	16313	8.7

Table 2: MFI of the Samples.

Sample #	MFI (Kg/10min)
4004	3.53
0220	2.45
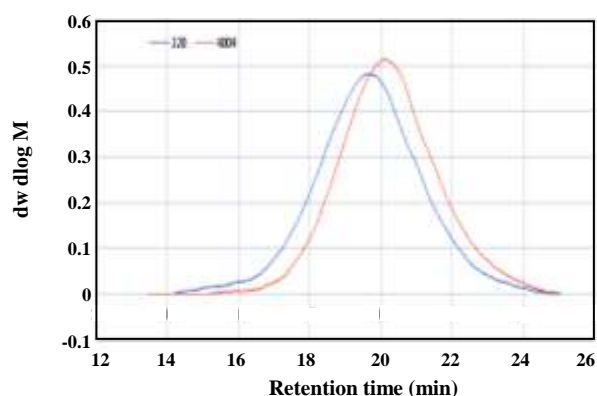
Fig. 2: GPC result for samples.

has brought about a considerable amount of research into the characterization of the nature of the instability. One of the important parameters to reduce sharkskin is to have a wide molecular weight distribution and in the rheometry test, no sharkskin was seen for both samples, and it showed that there would not be any misbehavior in the processing.

Gel Content

Gel content was measured with the procedure mentioned in the last section and the results are as described in Table 3. The results were what we expected because of the study of *Abbasi* [3].

Gel content percent are average of at least five similar tests. Results had a maximum 1% diversity from each other.

DSC

Differential scanning calorimetry is a thermos analytical technique, in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed in such a way that the sample holder temperature increases linearly as a function of time.

Crystallinity percentage is measured in both pure and cross-link by DSC and the results are as reported in Table 4. In pure samples, sample 0220 has less comonomer content and certainly fewer branches. This approved by DCS results which 0220 pure sample has higher crystallinity. In a polymer chain with higher branches, main polymer bone has prevention to lie next to each other in a uniform manner or as the other word, form crystal region. In cross-linked samples, a reduction in the absorbed energy of melting was has been measured. This demonstrated that lower crystallinity is formed. The reason is that of crosslinks' chemical bonds between the chains which did not let the chains to from crystal regions or disfeatured regions. Melt temperatures had a decrease due to the crosslinking process, it might be the result of disfeature the polymer chain and also the crystal regions.

TGA

Thermo gravimetric analysis is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).

The first result of this test was that there is no volatile matter in the sample so it does not face any weight loss until about 460°C, rather the destruction occurred at about 460°C. The exact results are reported in Table 5. So the major result of the test indicated that working under normal operating conditions will be safe for the polymer and there will not be any destruction in normal operation. The amounts of the residues are mentioned in Table 5 and about 10% of the residue remained after the test which was probably due to the presence of some mineral additives.

FT-IR

An FTIR spectrometer collects spectral data in a wide spectral range. This offers a significant advantage over

Table 3: Gel content.

Sample #	Gel %
4004XLPE	87
0220XLPE	84

Table 4: Crystallinity percentage, Energy of fusion and Melt Temperatures.

Sample #	Melt Temp (°C)	Crystallinity %
4004 Pure	121.42	46.18
4004 XLPE	111.01	38.43
0220 Pure	123.36	52.29
0220 XLPE	113.52	38.15
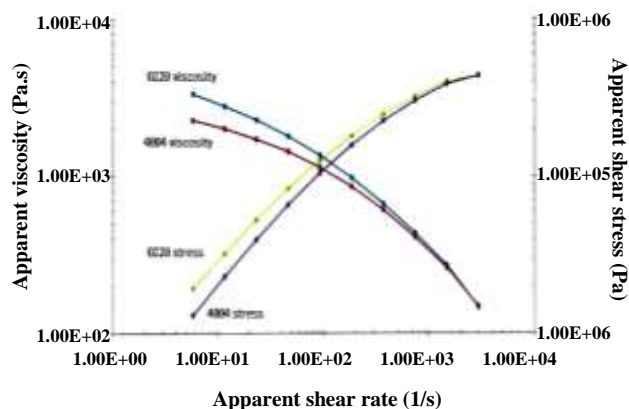
Fig. 3: Capillary Rheometer results in comparison.
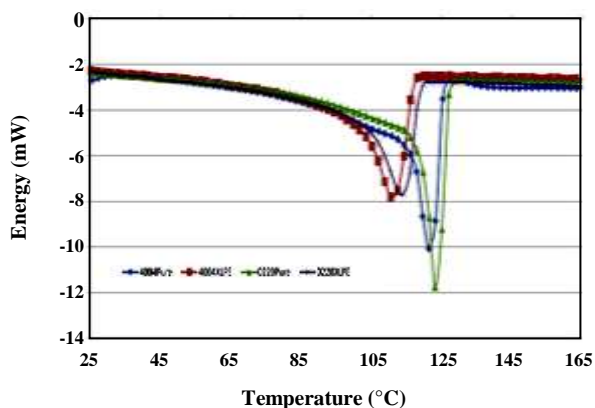
Fig. 4: DSC results comparison.

a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The most important wave numbers from this test can be described as follows:

● 910 cm^{-1}: This wave number represented the carbon double bond (C=C). Test from the pure samples showed this specific wave number, but after cross-linking, there was no sign of this wave number. So it is obvious that all the double bonds reacted in the cross-linking and vanished in that step[28].

● 1740 cm^{-1}: This wave number showed the carbonyl bond (C=O). This wave number was not in the pure samples yet was produced in the cross-linked samples [31] which was due to the cross-linking in the atmosphere and also because of the DCP reactions [33].

● 1378 cm^{-1}: This wave number was the most important wave number in this test. The result of this wave number with the following equations led to 1-butene comonomer percentage and the number of branches in 1000 carbon. These results showed the reason for the greater cross-link in sample 4004 regardless of it's lower molecular weight.

$$\frac{\text{Area}\left(1378\text{cm}^{-1}\right)}{\text{Area}\left(2019\text{cm}^{-1}\right)} = a \cdot N + b$$

$$Wt\% = 100 \cdot \frac{N \cdot M_{com}}{N \cdot M_{com} + \frac{1000 - 2.N}{2} \cdot 28}$$

where N= the number of branches in 1000 carbon, Mcom= molecular weight of 1-butene comonomer (56.11g/mol), a= the slope of the regression line (for 1-butene=0.009), b=ordinate intercept and wt%= comonomer weight percentage [2, 9, 29-33].

DMTA

The dynamic mechanical thermal analysis is a technique used to study and characterize materials. It is the most useful test to study the viscoelastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress is often varied, leading to variations in the complex modulus; this approach can be used to locate the glass transition temperature of the material, as well as identifying transitions corresponding to other molecular motions.

Table 5: Decomposition Temperatures.

Sample #	Decompositiom Peak (°C)	Residue %
4004 Pure	459.41	9.95
4004 XLPE	455.83	10.08
0220 Pure	463.49	10.81
0220 XLPE	457.76	10.47

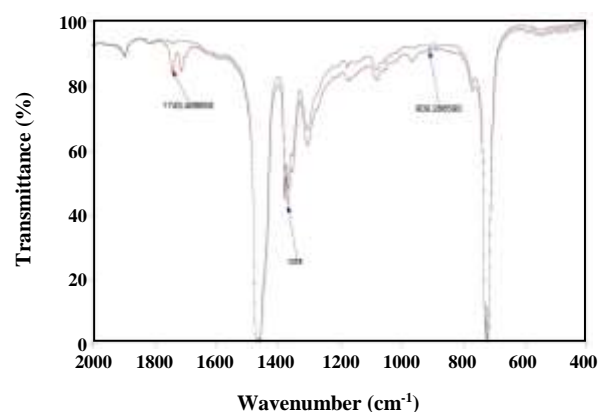*Table 6: Percent of butene-1 comonomer and the number of branches in 1000 carbons.*

Sample #	% Butene-1	No. of branches
4004 Pure	8.3	21.61
0220 Pure	6.8	17.56
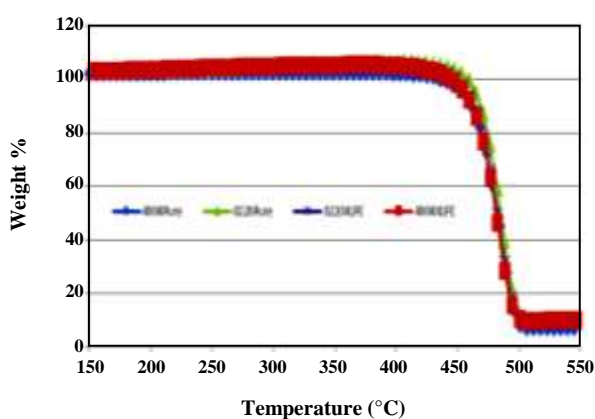
Fig. 5: TGA results comparison.

Fig. 6: FT-IR results comparison for sample 4004 (Upper: Pure, Lower: XLPE).

In DSC results, a decrease in melt point occurred because of lower crystallization and lower crystallization was, in turn, the effect of cross-linking the sample. Apparently it seems that a 10°C decrease in melt point was not according to the project target; however, DMTA results showed that at temperatures around 115°C or higher where the pure sample deformed and lost its stabilities, the cross-linked samples acted like rigid materials, indicating that the target was supplied by cross-linking the polymer.

CONCLUSIONS

As expected, due to cross-linking, a decrease in crystallinity occurred. As a matter of fact, when the cross-linking between the chains is done, it is obvious that the chains cannot act as freely as the pure sample to form a crystal region. This would decrease the crystallinity percentage and due to this decline in crystallinity, a reduction in the melting point was also seen.

Reduction in the melting point is one of the effects of cross-linking and reduced crystallinity percentage and it might not be good for the purpose of the project which is to improve the thermal characterization of the polymer but, as could be seen in DMTA results, the XLPE polymers did not respond to heating like the pure ones did and at higher temperatures where the pure samples deformed and the modulus tended towards zero, not the same behavior was seen in XLPE as it responded like a rigid sample.

Higher cross-link in LLDPE polymers with lower Mw is probably due to the absence of Long Chain Branches (LCB) which prepare a foil of entanglements with a higher
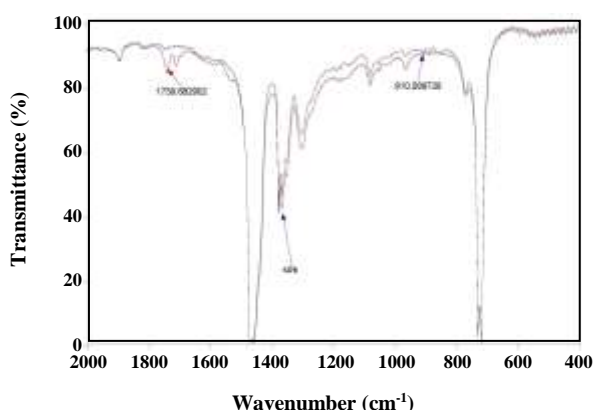
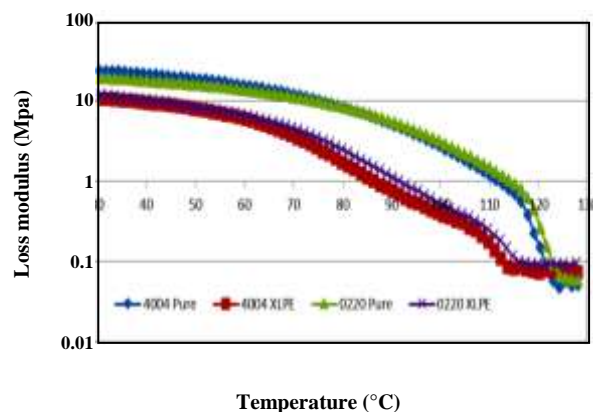*Fig. 7: FT-IR results comparison for sample 0220 (Upper:Pure , Lower:XLPE).*

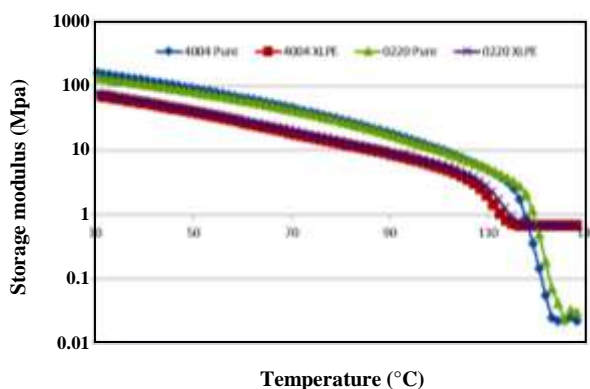*Fig. 9: DMTA M" modulus results comparison.*

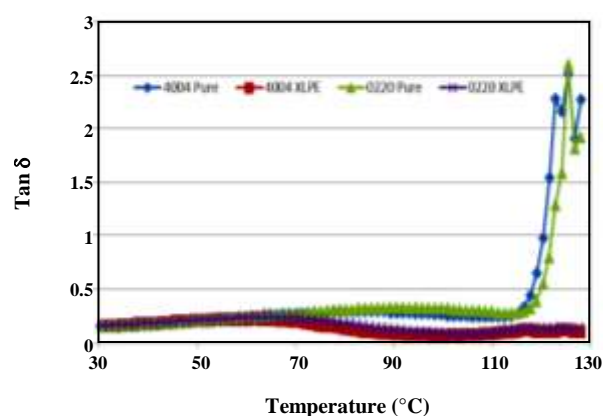*Fig. 8: DMTA Storage modulus results comparison.*

Fig. 10: DMTA Tan δ results comparison.

a number of molecules in it in the same volume and this is what led to higher cross-linked molecules in sample 4004.

The percentage of butene-1 comonomer has been reported and it is expected that polymer 4004 has a higher number of short chain branches (SCB) and contrary to LDPE polymers, in a lower Mw polymer, a higher percentage of cross-linking would be done, because of the higher SCBs.

This fact would prove the data obtained from related tables. In polymer 4004, which has the higher number of cross-linking, reduction of crystallinity and energy of fusion is more than polymer 0220 which has a higher M_w but a lower cross-linking.

Acknowledgments

REFERENCES

[1] Smedberg A., Hjertberg T., Gustafsson B., Effect of Molecular Structure and Topology on Network Formation in Peroxide Crosslinked Polyethylene, *Polymer (Guildf).*, **44**: 3395–3405 (2003).

[2] Smedberg A., Crosslinking Reactions Density Polyethylene in an Unsaturated Low, *Polymer (Guildf).*, **38**(16): 4127-4138 (1997).

[3]   Abbasi F., Morshedian J., On the Improvement of Physical and Mechanical Properties of PE by Crosslinking, *Iran. J. Polym. Sci. Technol.*, (2001).

[4]   Yu S., Park C., Hong S.M., Koo C.M., Thermal Conduction Behaviors of Chemically Cross-Linked High-Density Polyethylenes, *Thermochim. Acta*, **583**, no. Supplement C, pp. 67–71, (2014).

[5]   Nilsson S., Hjertberg T., Smedberg A., Sonerud B., "Influence of Morphology Effects on Electrical Properties in XLPE," Wiley Online Library, (2011).

[6]   Andersson L.H.U., Gustafsson B., Hjertberg T., Crosslinking of Bimodal Polyethylene, *Polymer (Guildf).*, **45**: 2577–2585 (2004).

[7]   Andersson L.H.U., Hjertberg T., The Effect of Different Structure Parameters on the Crosslinking Behaviour and Network Performance of LDPE, *Polymer (Guildf).*, **47**: 200-210 (2006).

[8]   Ma Z., Wang G., Liu F., Jiang P., Effect of Sample Preparation on Water Tree Resistance of XLPE/SEBS Blends, *Iran. Polym. J.*, **19**(5): 353-362 (2010).

[9]   Morshedian J., Azizi H., Salehi Mobarake H., Sioplas Crosslinking of PE: The Effect of EVA on Properties of XLPE, *Iran. J. Polym. Sci. Technol.*, **14**: 281-286(2001).

[10] Wang Y., Wang C., Xiao K., Investigation of the Electrical Properties of XLPE/SiC Nanocomposites, *Polym. Test.*, **50**: 145-151 (2016).

[11] Khonakdar H.A., Morshedian J., Wagenknecht U., Jafari S.H., An Investigation of Chemical Crosslinking Effect on Properties of High-Density Polyethylene, *Polymer (Guildf).*, **44**: 4301-4309 (2003).

[12] Yu W., Shi J., Wang L., Chen X., Min M., Wang L., Liu Y., The Structure and Mechanical Property of Silane-Grafted-Polyethylene/SiO$_2$ Nanocomposite Fiber Rope, *Aquac. Fish.*, **2**(1): 34–38 (2017).

[13] Azizi H., Morshedian J., Mobarake S., Sioplas Crosslinking of PE: Study the Effect of Alumina Trihydrate and Antimony Trioxide on Properties of XLPE, *Iran. J. Polym. Sci. Technol.*, **6**: 381–388 (2001).

[14] Singh A., Irradiation of Polyethylene : Some Aspects of Crosslinking and Oxidative Degradation, *Radiat. Phys. Chem.*, **56**: 375–380 (1999).

[15] ASTM-D2765, "Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics 1," ASTM, vol. i, no. Reapproved, pp. 1–8, (2006).

[16] ASTM-D1238, "Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion," ASTM, pp. 1–15.

[17] Yau W.W., Fleming S.W., GPC Data Interpretation, *J. Appl. Polym. Sci.*, **12**: 2111–2116 (1968).

[18] ASTM-D6474, "Standard Test Method for Determining Molecular Weight Distribution and Molecular Weight Averages of Polyolefins by High Temperature Gel," ASTM, vol. i, no. Reapproved, pp. 1–6, (2006).

[19] ASTM-D3835, "Standard Test Method for Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer 1," ASTM, pp. 1–11, (2008).

[20] Kong Y., Hay J.N., The Measurement of the Crystallinity of Polymers by DSC, *Polymer (Guildf).*, **43**(14): 3873–3878 (2002).

[21] Hatakeyama T., Quinn F.X., "Thermal Analysis: Fundamentals and Applications to Polymer Science", John Wiley & Sons Inc., Chichester, U.K. (1994).

[22] Chen J., Sun Q., Zou Y., Xue G., DSC Studies on the Melting Crystallization of Polyethylenes Prepared from Alkanes of Varying Molecular Size, *Polymer (Guildf).*, **43**: 6887–6891 (2002).

[23] ASTM-E794, "Standard Test Method for Melting And Crystallization Temperatures By Thermal," ASTM, vol. i, pp. 1–4 (2006).

[24] ASTM-E1131, "Compositional Analysis by Thermogravimetry 1," ASTM, pp. 1–5, (2003).

[25] Abdel Moez A., Aly S.S., Elshaerc Y.H., Effect of Gamma Radiation on Low Density Polyethylene (LDPE) Films: Optical, Dielectric and FT-IR Studies, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **93**: 203-207 (2012).

[26] Holland-Moritz K., Holland-Moritz I., Werden K., Application of FT-IR-Spectroscopy on Orientation Processes in Polyethylene Films, *Colloid Polym. Sci.*, **259**(2): 156–162 (1981).

[27] Gulmine J.V., Akcelrud L., FTIR Characterization of Aged XLPE, *Polym. Test.*, **25**(7): 932–942, (2006).

[28] Gulmine J., Janissek P., Heise H., Akcelrud L., Polyethylene Characterization by FT-IR, *Polym. Test.*, **21**(5): 557–563 (2002).

[29] DesLauriers P.J., Rohlfing D.C., Hsieh E.T., Quantifying Short Chain Branching Microstructures in Ethylene 1-olefin Copolymers Using Size Exclusion Chromatography and Fourier Transform Infrared Spectroscopy (SEC–FT-IR), *Polymer (Guildf).*, **43**(1): 159–170 (2002).

[30] Blitz J.P., McFaddin D.C., The Characterization of Short Chain Branching in Polyethylene Using Fourier Transform Infrared Spectroscopy, *J. Appl. Polym. Sci.*, **51**: 13-20 (1994).

[31] ASTM-D6645, "Standard Test Method for Methyl (Comonomer) Content in Polyethylene by Infrared," ASTM, vol. 8, pp. 8–11, (2001).

[32] ASTM D2238, "Standard Test Methods for Absorbance of Polyethylene Due to Methyl Groups 1 at 1378," *Astm*, vol. 14, no. Reapproved, pp. 2–8, (2015).

[33] ASTM-D5576, "Standard Practice for Determination of Structural Features in Polyolefins and Polyolefin Copolymers by Infrared Spectrophotometry," ASTM, vol. 8, pp. 8–10.

[34] Woo L., Ling M.T.K., Westphal S.P., Dynamic Mechanical Analysis (DMA) and Low Temperature Impact Properties of Metallocene Polyethylenes, *Thermochim. Acta*, **272**: 171–179 (1996).

[35] Gulmine J.V., Akcelrud L., Correlations Between Structure and Accelerated Artificial Ageing of XLPE, *Eur. Polym. J.*, **42**(3): 553–562 (2006).

[36] Sha H., Zhang X., Harrison I.R., A Dynamic Mechanical Thermal Analysis (DMTA) Study of Polyethylenes, *Thermochim. Acta*, **192**: 233–242 (1991).