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Chemical cross linking versus high energy electron beam cross linking of HDPE: electrical properties study

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Abstract

Cross linking of high density polyethylene (HDPE) was first performed via high energy 10 Mev electron beam (EB) irradiation. HDPE was also cross linked with Dicumyle peroxide (DCP).The gel content of samples was determined by solvent extraction. Degree of cross linking was evaluated by hot set apparatus; as well .In order to clarify the effect of nature of cross linking, correlation of electrical properties such as volume resistively, dielectric constant, dielectric strength with the type of cross linking system was made. It was found that, in the same amount of gel content, electrical properties of samples cross linked by the two methods, differed.

Keywords: Electron Beam; Cross linking; High density polyethylene; Electrical properties.

1. Introduction

Polyethylene (PE) is one of the most important thermoplastics but its applications are restricted in specified areas due to its low melting point, solubility or swelling in hydrocarbons and tendency to crack when stressed. Cross linking of various types of polyethylenes, improves their toughness flexibility and impact resistance, resistance to solvents and chemicals, and their service temperature. On the other hand, by cross linking, the semi crystalline polymer exhibits the mechanical properties of a thermoplastic below its melting temperature(Tm) and exhibits the mechanical properties of a rubber above Tm [1-4]. Cross linked PE is used in hot water piping installation, wire and cable industry, heat shrinkable products, etc [5-7].

Essentially three cross linking process are used in the wire and cable industry .Two types of chemical cross linking, those employing organic peroxides or silanes, respectively are still frequently used for the improvement of polyethylene and other polymer based insulations for wire and cable [8, 9]. The most common compound for peroxide cross liking of PE in wire and cable industry is Dicumyl peroxide (DCP) which decomposes at 120 to 125 °C ,generating free radicals needed for the process plus byproducts (carbinol, acetophenone and methane). However, the advantages of radiation cross linking over the chemical process have brought about its steady growth of about 10 to 15 % annually since the mid-1970s, when high energy and high current electron accelerators became widely available for radiation processing [10-12]. Moreover;

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energy consumption for the radiation processing is much lower than that for chemical cross linking process. The dose required for the desirable degree of cross linking is determined by the electron current of the accelerator and by the wire or cable speed; therefore, the process control is quite simple.

The effect of cross linking on the properties of various types of PE has been extensively studied [13-16]. Most of the studies were on low density polyethylene and (LDPE) and linear low density polyethylene (LLDPE). On the other hand, there are not documented studies concerning correlation of electrical properties with method of cross linking. In the present study electrical properties of HDPE are investigated with respect to nature of cross linking.

2. Experimental

2.1. Materials

High density polyethylene (HDPE 44005, MFI = 0.55, d=0.944) was obtained from Bandare Imam Petrochemical Co., Iran. Samples of granular shape were compression molded using Dr. Collin warm press instrument between polyester sheets at 165 ^{0}C to prepare sheets with 2 ± 0.1 mm thickness. DCP was supplied from GMBH Germany.

2.2. Sample preparation

High density polyethylene granules were melted in a cam type internal mixer (Plasti-Corder, BBRABENDER, Germany) with speed of 50 rpm at 145 °C for 7min, and then DCP was added and mixed for 3 min. The chemical cross linking process took place during compression molding of sheet samples using Dr. Collin warm press instrument between polyester sheets at 195 ° C to prepare sheets with 2 ± 0.1 mm thickness.

2.3. Gel content measurement

The gel content of the cross linked HDPE was determined gravimetrically, according to ASTM D 2765 using a 16 h soxhlet extraction cycle with p-xylene as the solvent at 150 °C. Irganox 1010 was added at 0.5 wt% to inhibit polymer degradation during the extraction. Approximately 0.3 g of the cross linked polymer sample was cut into small pieces and placed in a pre weighted stainless steel fine wire mesh. After the extraction cycle, the sample was washed with acetone and vacuum dried to a constant weight. The gel fraction was calculated as the percentage ratio of the final weight of the polymer to its initial weight.

2.4. Hot set test

The hot set test was carried out in a hot test oven (UT 6050HS Heraeus Germany)according to DIN 57472 part 602 VDE 0472.The dumbbell shaped samples were placed in hot set oven under a definite static load at 200 °C and the elongation between two marks was measured after 15 min.

2.5. Irradiation

The samples were irradiated with dose of 300kGy and a constant dose rate. The irradiation process was performed using the Rhodotron type electron accelerator machine, TT200 model, using 10 MeV electron beam with a maximum of 8 mA beam current. Details of dose measurements are given in Ref. [17].

2.6. Electrical properties

Variation of the electrical properties was studied dynamically. All samples were placed in a desiccator for Ca. 24 hrs before measurement.

2.7. Volume resistively

Volume resistance was measured at room temperature by TERAOHMMETER CEAST Company made by Italy (ASTM D-257).

2.8. Dielectric loss tangent and dielectric constant

A Dielectric Loss measurement system, model TRS-10T, (ANDO ELECTRIC Company, Japan) was used for determining dielectric constant and dielectric loss tangent of the samples. Frequency was set at 1 MHz in the experiments (ASTM D 150).

2.9. Breakdown voltage and strength

A Dielectric Rigidity system, (P/N 6135.053, CEAST Company; Italy) was used for determining the breakdown voltage of the samples (ASTM D 149).

3. Results and discussion

3.1. Gel content measurements

Cross linkable polymers used for wire and cable insulations are polyolefins, certain fluoropolymers and elastomers. Radiation cross linking processes, differ in two ways with chemical cross linking counterparts. First the fact that radiation cross linking occurs in non molten state but instead; chemical cross linking take place in molten state. On the other hand, in chemical cross linking due to introduction of chemicals such as DCP, cross linked points have polar nature, in spite of the fact that; in radiation cross linking cross linked points are mainly non polar in nature .Indeed, it is expected that these factors affect the ultimate properties of final products especially concerning electrical properties. To investigate such a phenomenon a comparison was made between two systems of cross linking in the same amount of gel content i.e. as a measure of cross linking density. Electrical properties of polymers were conclusively discussed in the related literature [18, 19]. In order to compare the electrical properties from each system five samples, which had almost identical gel content, were, chose to measure the electrical properties. These samples had approximately the same cross link density which was confirmed with hot set test. Gel content results, with respect to dose and DCP percent, are collected in Table 1.

Table 1
Gel content results for radiation cross linked samples.

Sample ID	Dose(kGy)	Gel Content
R_1	25	20
R_2	75	55
R_3	150	65
R_4	200	75
R_5	300	85

Table 2
Gel content results for chemical cross linked samples.

Sample ID	%DCP	Gel Content
C_1	0.2	18
C_2	0.5	56
C_3	0.7	62
C_4	1	74
C_5	1.5	87

3.2. Volume resistance studies

Volume resistance experiments are illustrated in Fig. 1. In radiation cross linking, electrons may produce radiation defects in the material .The higher the absorbed dose, the grater the number of defects. Such defects may introduce conduction mechanisms and reduce volume resistively compared to non irradiated ones.

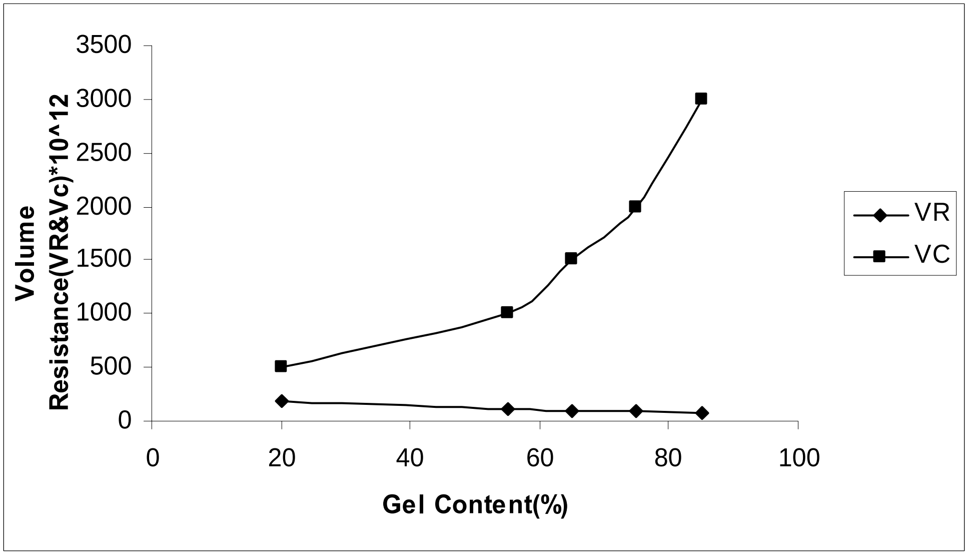

Fig. 1. Volume resistance vs. gel content.

Fig. 1 demonstrates that volume resistance is increased for chemical cross linking against gel content although for radiation cross linking such a trend is not seen. On the other hand, in the radiation cross linking, volume resistance is slightly decreased; which may be due to introduction of some defects in radiation cross linking which introduce conduction mechanisms. Chemical cross linking method seems to be more efficient in this regard, because volume resistance is increased with gel content. It should be noted; the higher the volume resistance of electrical insulating material the lower dissipation of current will be.

3.3. Dielectric constant studies

The dielectric constant indicates the ability of an insulator to store electrical energy, so it is desirable to have the capacitance of the insulating material as minimum as possible. Fig. 2 shows variation of dielectric constant against gel content .From the figure it can be interpreted that for chemical cross linked samples with increasing of DCP content the dielectric constant is increased although in irradiated sampled the value is almost constant. On the other hand; radiation cross liked samples; showed better properties in this regard.

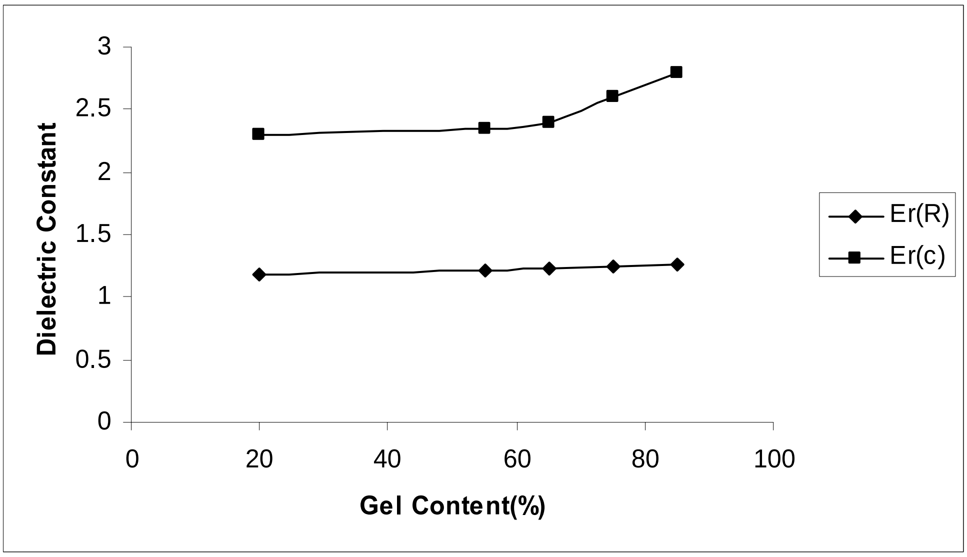

Fig. 2. Dielectric Constant vs. gel content.

3.4. Dissipation factor studies

For most polymers tan δ decreases as the degree of cross linking increase, because reactive polar groups are either neutralized or hindered by cross linking. From the Fig. 3 it can be concluded that dielectric loss tangent tan δ of chemically cross linked samples is decreased a bit as a function of gel content but irradiated samples didn't change significantly.

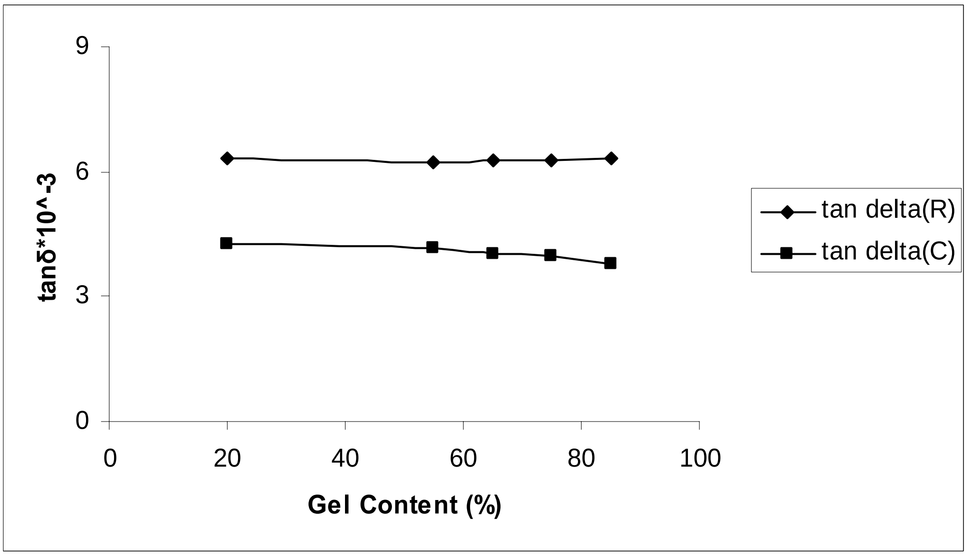

Fig. 3. Dielectric loss tangent vs. gel content.

3.5. Dielectric strength studies

Dielectric breakdown is caused when electrons detached from the molecules acquire sufficient energy in the electric field to yield secondary ionization and avalanche. Fig. 4 shows that dielectric strength of chemical cross linked samples are almost higher than corresponding irradiated ones and didn't show considerable variation against gel content.

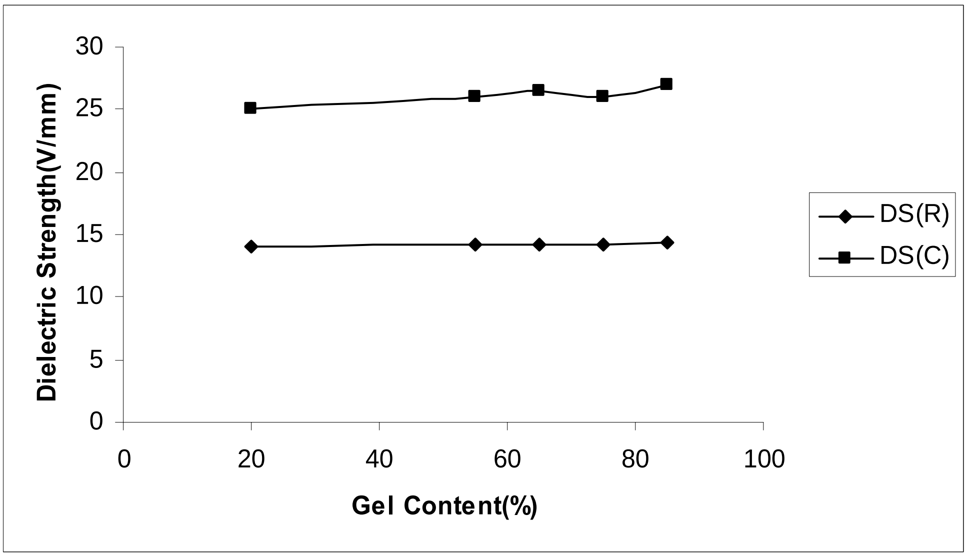

Fig. 4. Dielectric strength vs. gel content.

4. Conclusions

From the results it can be concluded that route of cross linking system have considerable effects on the electrical properties of polymers. On the other hand it was observed with respect to some electrical properties such as volume resistivity, tan delta and dielectric strength chemical crosskicked samples exhibited superior properties. However dielectric constant values of Chemical cross linked samples were higher than radiation cross linked counter parts; which may be considered as disadvantage for chemical cross linking.

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