

## Density crosslink study of gamma irradiated LDPE predicted by gel-fraction, swelling and glass transition temperature characterization

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### ABSTRACT

Experimental results showed that the crosslink density of polymeric stocks may be predicted from values of gel content based on the reactive portion of the stocks, that is, exclusive of plasticizers and fillers. Where entanglements may be neglected, the crosslink density is directly proportional to functions of the gel and sol contents. In order to predict the behavior of carbon-chain polymers exposed to ionizing radiation, an empirical rule can be used. According to this rule, polymers containing a hydrogen atom at each carbon atom predominantly undergo crosslinking. During irradiation, chain scission occurs simultaneously and competitively with crosslinking, the end result being determined by the ratio of the yields of the two reactions. The ratio of crosslinking to scission depends basically on factors including total irradiation dose, dose rate and the presence of oxygen. The glass transition temperature ( $T_g$ ), temperature below which the polymer segments do not have sufficient energy to move past one another, marks the onset of segmental mobility for a polymer. Properties such as melt index, melt strength, crystallinity, glass transition, gel fraction, swelling ratio and elasticity modulus were assessed in LDPE (2.6 g.10 min<sup>-1</sup> melt index) gamma irradiated within a 10, 15, 20 and 30 kGy and results obtained were further discussed prior conclusion.

### 1. INTRODUCTION

Polyethylenes are commodity plastics that account for more than 70% of total plastics market. Polyethylene (PE) is easy available at relatively low cost and easily available. It finds applications in household items, packaging, insulation, net ropes, fishing rods or medical applications, etc....[1].

Polyethylene (PE) is one of the most important thermoplastics but its use is restricted in certain applications due to its low melting point, solubility or swelling in hydrocarbons and tendency to crack when stressed. In an effort to tackle these disadvantages there has been considerable work based on the crosslinking of PE. Crosslinking adds a very important feature to the polymer, because it will not melt and flow when heated. On the other hand, by crosslinking, the semi-crystalline polymer exhibits the mechanical properties of a thermoplastic below its melting temperature and exhibits the mechanical properties of a rubber above  $T_m$  [2-5]. Cross-linking is a broadly used method for the modification of polymer properties. This process involves the formation of three-dimensional structures causing substantial changes in material properties. Cross-linked polyolefins, especially polyethylene (PE) are of significant interest as well [6-10]. Crosslinking can be accomplished

either by high-energy irradiation or through the use of chemical cross-linking additives. PE when irradiated with electron-beam (EB),  $\gamma$ -rays, and other forms of high energy radiation predominantly undergoes cross-linking [11]. Crosslinked PE has become widely adapted for a number of industrial applications, which require withstanding high temperature environments. Polymeric materials when subjected to  $\gamma$ -irradiation are known to undergo cross-linking and/or chain-scission accompanied by free radical formation. The former is reflected by an increase in molecular weight and glass transition temperature ( $T_g$ ) of the polymer whereas the latter has an opposite effect.[12].

As the irradiation dose increases, chains in the polymer network will undergo further crosslinkage until high crosslinking density is produced. Ueberreiter and Kanig reported that the change in glass transition temperature was directly proportional to crosslink density. [13] Chain crosslink may enhance melt index, melt strength, crystallinity, glass transition, gel fraction, swelling ratio and elasticity modulus, while chains scission decreases these properties. [14]. The main difference between thermoplastic and crosslinked polymer is that, at temperature above the crystalline melting point crosslinked polymer behaves as a soft rubber while thermoplastic has no significant strength above melting temperatures. The changes in the properties of polyethylene due to crosslinking have been compared and documented in literature [15-16], drastically reducing melt index, but presenting a low gel content (<3%) for gamma radiated PE at doses lower than 30 kGy [17-18]. The swelling ratio decreases with radiation dose, as a reflection of the gel content curve. It is observed that the results are nearly in accordance with those of gel content, supporting the formation of network structure on irradiation [19].

The most significant improvement is made on the rheological properties (e.g., melt strength, that can be simply defined as the ultimate force that the polymer melt can withstand while being stretched.) and hence the processability of the polymers [20-24] Among the many PE grades, low density polyethylenes (LDPEs) have higher melt strength because the polymers inherently contain significant long-chain branching. The degree of polymer crosslinking was assessed by measurement of the glass transition temperature [25]. The glass transition is exhibited by amorphous polymers or the amorphous regions of partially crystalline polymers when a viscous or rubbery state is transformed into a hard, brittle, glass-like state. The glass transition of polymers is observed by DSC as a stepped increase in the heat capacity of the sample during heating due to an enhancement of molecular motion in polymers. The  $T_g$  values of a polymer system are more dependent upon crosslinking, being mechanical properties of polymers sensitive to temperature changes; above  $T_g$  a crystalline polymer has an intermediate modulus depending on the degree of crystallinity present [26]. PE is a partially crystalline polymer; specifically, the glass transition juncture for LDPE is negative 193 degrees Fahrenheit (or negative 125 degrees Celsius). As it warms further, the molecules can wobble even more as they enter the rubbery state. [27].

Elastic modulus increased initially with increasing gamma radiation dose and it is supposed to decay at higher doses, when it will take place chain scission, indicating its dominance over crosslinking [28].

In this article we essentially modify LDPE via gamma radiation, within 10 to 30 kGy range to induce crosslinking. Crosslinked LDPE samples are subsequently evaluated in terms of their physical and mechanical properties and results obtained showed to be an efficient tool to predict density crosslink.

## 2. MATERIALS AND METHODS

### 2.1. Sample preparation

Commercially available polyethylene grade exhibiting 2.6 g/10 min Melt Index and supplied by Quattor was selected as base resin for radiation modification and used in pellets. The base resin was gamma irradiated, at 10, 15, 20 and 30 kGy doses,  $^{60}\text{Co}$ , in air, at a 5 kGy/h rate.

### 2.2. Methods

For the characterization of samples, there were assessed following properties, before and after radiations:

#### 2.2.1. Melt Index

Melt Index analyses were accomplished in a CEAST apparatus, *modular line*. Samples were analysed at 190° C temperature, 2.16 kg load, 240 seconds pre-heating time, according to ASTM D1238-04C [29].

#### 2.2.2. DSC Analysis

The thermal behavior of pure and irradiated polyethylene samples was examined in a DSC Mettler Toledo apparatus, according to ASTM D3418-08 [30], by using 5 – 9 mg of sample, within a 25 to 300 °C program, at a 10°C/min, in a nitrogen flow of 50 ml/min. Crystallinity was calculated according to Eq. 1.

$$X_{DSC}(\%) = \left( \frac{\Delta H_c}{\Delta H_T} \right) 100 \quad (1)$$

Where  $\Delta H_T$  is  $\Delta H_C$  of 100% crystalline PE (68.4 Cal/g or 290 J/g), Heat of fusion ( $\Delta H_c$ ) is the energy involved in the formation and melting of crystalline regions and equal to area under the melting peak [31].

Tg values were determined according a -50 °C to 50 °C program, 10 °C/min rate, 50 ml/min nitrogen flow, for the onset of heat capacity change.

### 2.2.3. Gel-fraction essay

In this test it was used around 0.3 g of sample, wrapped in a 500 mesh steel screen and the entire assembly (120  $\mu\text{m}$ ) was further immersed in xylene P.A. (approximately 250 ml) in a 500ml bottle. The test was accomplished in triplicate and samples were subjected to a reflux system, by solvent ebullition at 135  $^{\circ}\text{C}$ , via a heating mantle, and a ball condenser is used in its condensation, adapted to the bottle mouth. This system was subjected to a 24 hour reflux, in accordance with ASTM D 2765-01 [31]. During the extraction, gel-fraction did not dissolve in the solvent and remained inside the steel screen, while the non-crosslinked fraction was dissolved, migrating to the solvent. Samples drying process was accomplished in an oven at 150  $^{\circ}\text{C}$ , for one hour and afterwards samples were kept at 60  $^{\circ}\text{C}$ , in the oven, for more 15 hours.. Wrappings were weighed and gel-fraction was calculated, by applying the Eq. 2:

$$\text{Fração Gel (\%)} = \left( \frac{M_f}{M_i} \right) 100 \quad (2)$$

Where  $M_f$  is the final mass and  $M_i$  is the initial mass for each sample.

### 2.2.4. Swelling essay

Swelling test, intended for the assessment of material capacity in absorbing solvents, was performed using Xylene P.A.. Irradiated and non-irradiated samples were dipped in xylene and weighings were accomplished each 15 minutes at first hour, each 30 minutes at the second hour and each 1 hour, for a 8 hour period after starting the test. Samples were centrifuged for one minute before the final weighing, for eliminating in a standardized way solvent excess.

The degree of swelling was calculated according to the Eq. 3.

$$Q(\%) = \left( \frac{m - m_o}{m_o} \right) 100 \quad (3)$$

Where  $m_o$  is the mass of the unswelled sample and  $m$  is its mass after swelling in solvent.

### 2.2.5. Melt Strength

Irradiated and non-irradiated samples were previously extruded in a Haake Rheomex 332p, single-screw, 3:1 L/D and 19/33 compression rate, further connected to a Rheotens 71.97, Götffert, that consists of a pair of rollers rotating in opposite directions; the polymer melt strand from a capillary die is drawn by the rotating rollers, whose velocity increases at a constant acceleration rate, registering the tensile force needed for elongation of the extruded filament in function of the draw ratio, while the polymer melt has being stretched underwent uniaxial extension [33]. Test conditions: take-up speed of the Rheotens wheels initially equal

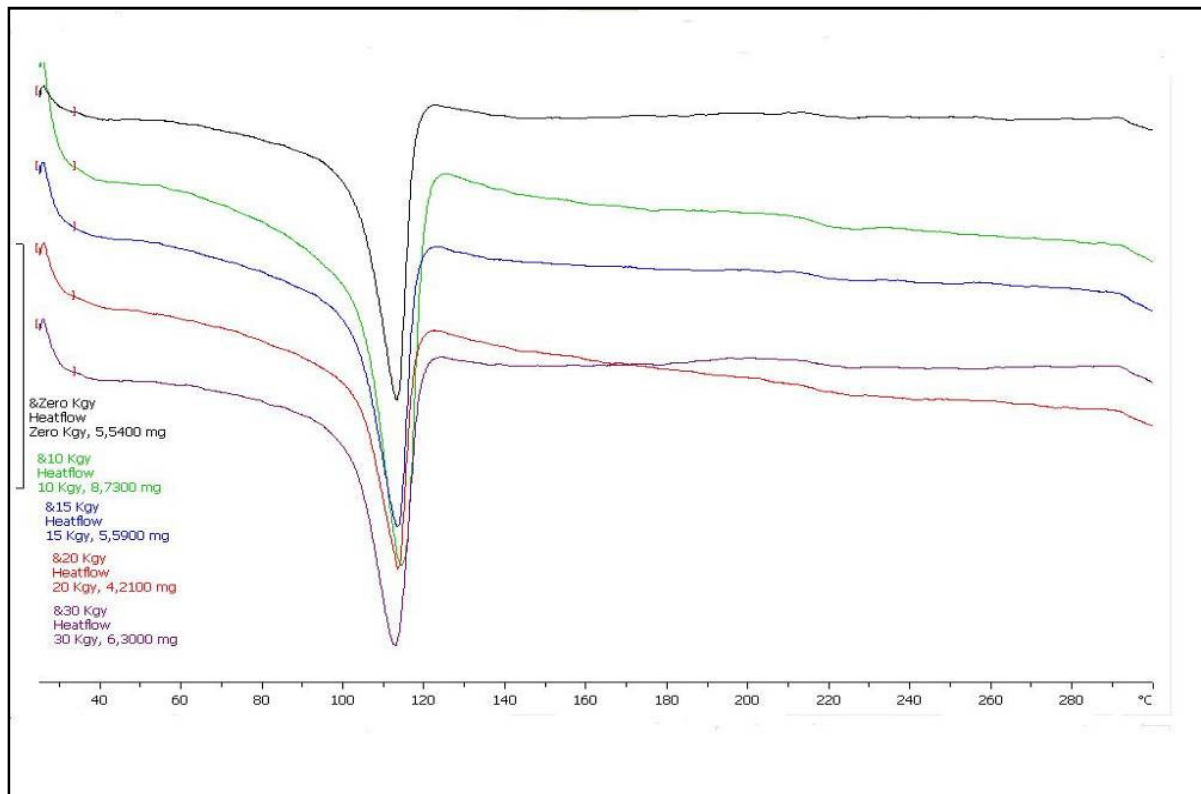
to 14.7 mm/s, 2 mm die and velocity of extruded polymer strand adjusted for a tensile force zero. The experiment is started by slowly increasing the take-up speed of the Rheotens wheels until the polymer filament breaks; each Melt Strength experiment was repeated five times.

### 2.2.6. Elasticity Modulus

Tests were accomplished in accordance with ASTM D 638-08 [34], in an EMIC dinamometer, model DL 300, 300 kN maximum capacity.

## 3. RESULTS AND DISCUSSION

A brief of thermal behavior shown by gamma irradiated 10 to 30 kGy and non-irradiated samples is indicated in Fig.1:



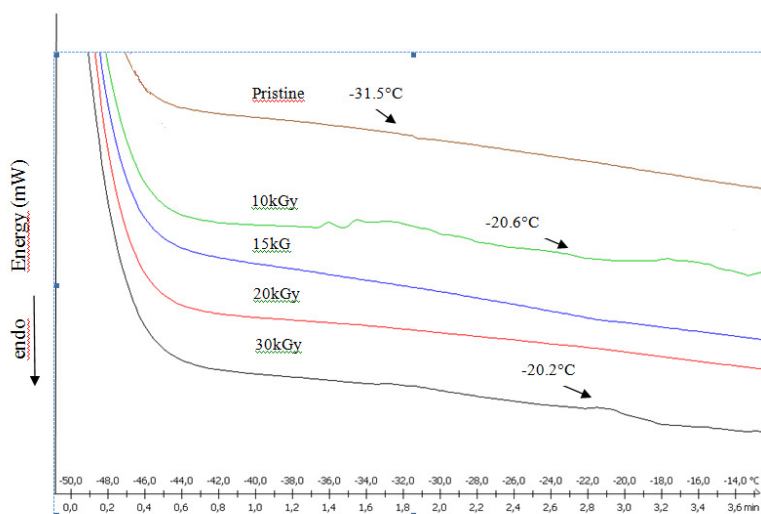
**Figure 1: DSC curves for 0, 10, 15, 20 and 30 kGy samples.**

Using the DSC enthalpy of fusion and taking 290J/g [31] as the value for the 100% crystalline LDPE, results within a 29.4 to 32.0 % range of crystallinity was found. In Table 1 are presented obtained results for each sample:

**Table 1: DSC results for 0, 10, 15, 20 and 30 kGy samples**

Sample	$\Delta H$ (mJ/mg)	$T_m$ (°C)	Crystallinity (%)
0 kGy	91,04	110,47	31,4
10 kGy	92,05	111,34	31,7
15 kGy	92,68	110,57	32,0
20 kGy	87,60	110,65	30,2
30 kGy	85,28	109,92	29,4

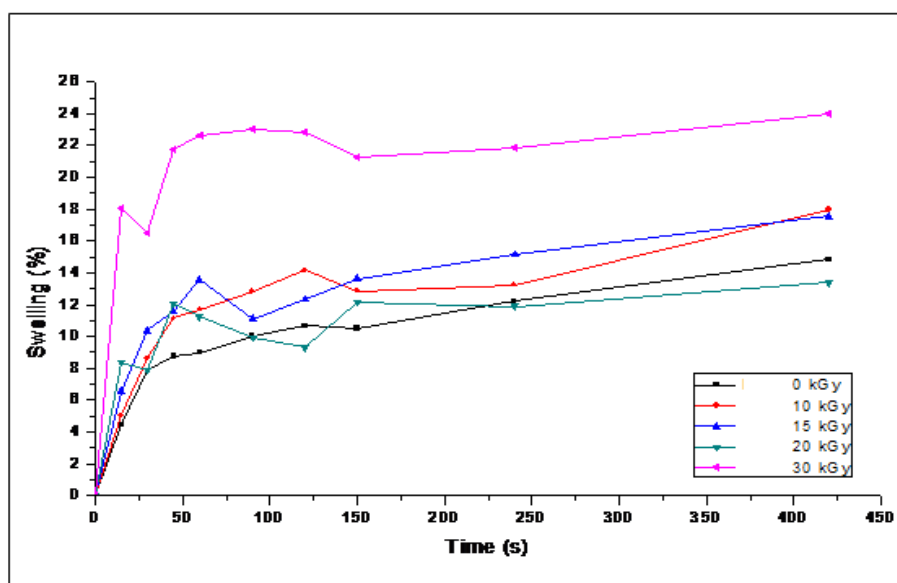
Glass transition ( $T_g$ ) results are shown in Fig. 2:



**Figure 2:  $T_g$  values for 0, 10, 15, 20 and 30 kGy samples.**

$T_g$  values were obtained from triplicate determinations; being a single slope of the baseline, visualization of  $T_g$  is extremely scarce. From Fig.2 just three readings were feasible: Pristine (-31.5°C), 10 kGy (-20.6°C) and 30 kGy (-20.2°C).

Figure 3 indicates swelling for 0, 10, 15, 20 and 30 kGy samples, although theoretically the higher the irradiation dose, the lesser the swelling capacity, this characteristic was not clearly proved. Behavior shown for 30 kGy sample was entirely non-expected; just the 20 kGy one presented an expected lower swelling capacity when taking pristine as reference.



**Figure 3: Swelling kinetics for 0, 10, 15, 20 and 30 kGy samples immersed in xylene.**

The non-flowability of gamma irradiated samples inside the plastometer when performing melt index test, as shown in Table 2, is associated to their high viscosity, proving the efficacy of inserted branching, even at low doses ( $\leq 30$  kGy).

Low results obtained for gel fraction ( $< 3\%$ ), according to Table 2, are the expected ones for modified LDPE resins; even at low radiation doses, it has already occurred the crosslinking, proved by the high viscosity of irradiated samples inside the plastometer, when accomplishing melt index investigations.

Melt strength increases as the molecular weight distribution (MWD) becomes broader and it is well known that not only the increase in the average molecular weight (MW) of a polymer results in higher melt strength [35], but also in lower MFI. The increase in MW is associated with a decrease in MFI and an increase in Melt Strength; consequently, the higher the melt strength, the higher the crosslinking (Table 2).

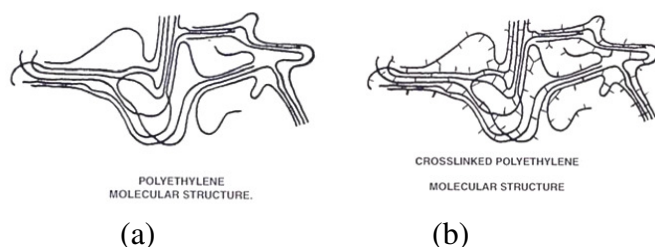
Elastic modulus increased from pristine up to 30 kGy sample indicating the dominance of crosslinking over chain scission (Table 2).

**Tabela 2: Melt Index, Gel-fraction, Melt Strength and Elastic Modulus for 0, 10, 15, 20 and 30 kGy**

Sample	Melt Index ( $\text{g} \cdot 10^{-1} \text{ min}^{-1}$ )	Gel-fraction (%)	Melt Strength, at 190°C (cN)	Elastic Modulus (MPa)
0 kGy	2,62	0.73	2.0	204
10 kGy	None flow	0.62	5.4	244
15 kGy	None flow	1.52	12.0	444
20 kGy	None flow	1.77	25.0	740
30 kGy	None flow	1.83	52.0	810

## 4. CONCLUSIONS

Melt index, melt strength, gel fraction and elastic modulus analyses were capable to predict crosslink and consequently density crosslink, by modifying P.E. molecular structure, as can be shown in Fig.4.



**Fig. 4: Polyethylene molecular structure for non-irradiated Polyethylene (a) and for crosslinked Polyethylene (*Micropol Ltd.*)**

Equilibrium swelling is a feasible and simple experiment to determine the cross-link density. Since cross-linking cannot be seen directly, it must be measured indirectly and the degree of cross-linking should be inversely proportional to the degree of swelling. At the present study, swollen irradiated samples should not present the expected behavior; so, in our future work the swelling technique will be exhaustively used, eventually among other ones, aiming to the determination of density crosslink of crosslinked Polyethylene resins.



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