

Study of the effect of gamma irradiation on the structure and properties of metallocene linear low density polyethylene containing hindered amines

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Summary

The changes in the carbonyl index, the melt flow rate, the crystalline content and the ultimate tensile properties of metallocene linear low density polyethylene (mLLDPE) films subjected to gamma irradiation from 10 to 800 kGy, were investigated with and without hindered amine stabilizer (HAS). For comparative purposes, unstabilized and HAS stabilized low density polyethylene (LDPE) were also studied. The results indicated that under gamma irradiation, the HAS stabilizer did not have any influence on the oxidative stability of mLLDPE films as compared with unstabilized ones due probably to complexation reactions between the nitroxyl radicals of the stabilizer and the metallocene catalysts leading to inert species. Moreover, higher increases in melt flow index and crystalline content with a fast drop in ultimate tensile properties were observed for higher doses indicating the occurrence of chain scission. It was also found that the metallocene LLDPE structure had no significant effect on the radiation induced oxidative degradation kinetics when compared to LDPE. Whereas, the addition of HAS to LDPE significantly lowered the formation rates of carbonyls and subsequently improved the durability of the material by doubling the half-value-dose.

Introduction

Linear low density polyethylene (LLDPE) is an important commercial class of polymers having different molecular structures and wide range of performance properties which are influenced mainly by the copolymerization process and in particular the type of catalyst system employed, and the type, amount and distribution of chain branches (CB) produced by the α -olefin co-monomer used in the linear polymer [1,2]. Indeed, LLDPE can be synthesized by either Ziegler-Natta or metallocene catalysts [3-6]. The polymers synthesized by Ziegler-Natta catalysts are molecularly heterogeneous due to a very different distribution of co-monomer units along the polymer chains which has strong influence on both their thermal and mechanical properties [7]. Different from the conventional Ziegler-Natta catalysts, metallocene catalysts produce polymers with narrow molecular weight distributions

(MWD) with improved physical and mechanical properties [8]. However, they often have poor processability due to high viscosities. This problem is overcome by introducing in a controlled manner long chain branching (LCB) without broadening the MWD [9]. It has been known that the polymer processing behaviour and many end-use properties are influenced not only by molecular weight (MW) and molecular weight distribution (MWD) but also by long chain branching (LCB) [10]. It is generally accepted that the MW is a major determinant of mechanical properties, while MWD is largely responsible for rheological properties which is an important factor in blowing and extrusion techniques [11]. The excellent properties offered by mLLDPE, i.e. high tensile strength, greater tear strength, higher environmental stress cracking and high clarity film would provide an opportunity for its utilization in many applications such as agriculture, industry and packaging in which it is exposed to various stress factors including natural weathering, thermal oxidation, γ -irradiation, etc. [12,13]. In this respect, Krupa and Luyt [14] studied the influence of γ -irradiation on the thermal and mechanical properties of LLDPE and they concluded that γ -irradiation cross-linking improved the thermal stability of LLDPE, while the mechanical properties depended strongly on the radiation dose. Moreover, the effect of UV light on the thermo-oxidative stability of LLDPE films was investigated by Sen et al. [15]. According to them, films cross-linked by γ -irradiation and containing an antirad agent along with the antioxidants and UV stabilizers attained improved thermooxidative stability. More recently, Basfar et al. [12] reported that LLDPE and LDPE films containing additives, particularly HAS have attained UV stability both in accelerated UV and natural weathering, four times higher than their corresponding pure films. Irradiation of these films with gamma source also showed the progress of cross-linking with reduction of their tensile properties at higher doses.

Although there have been extensive studies on the degradation and stabilization of the conventional polyethylenes, there is however much less published work devoted to the mLLDPE. Only a few papers have so far been published on the effect of ionizing radiation exposure on the oxidation stability of mLLDPE containing hindered amine stabilizers (HAS) [16]. Therefore, the aim of this work was to study the influence of γ -irradiation on the structure and the physico-mechanical properties of mLLDPE films in the absence and in the presence of HAS. In similar experimental conditions, low density polyethylene (LDPE) films were also studied for comparative purposes.

Experimental

Materials

In this study, a commercially available mLLDPE was used. It is based on an ethylene-1-hexene copolymer produced with metallocene single site catalysts using Exxon Mobils proprietary Exxpol technology. The polymer was produced in Saudi Arabia under the trade name *Exceed 1018 CA*. Films made from this resin have been reported to have outstanding tensile, puncture resistance and very good sealing properties. These excellent properties make this polymer proper for mono layer and multi layer blown film applications. The main physical properties of the materials as provided by the manufacturer are as follows: density = 0.918 g.cm^{-3} , melt flow index = 1 g.10min^{-1} , melting temperature = 118°C , $M_w = 107 \text{ kg/mol}$, $M_w/M_n = 2.4$ and content of branched units 1-hexene = $2.61\% \text{ mol}$. The mLLDPE contained a small concentration of commercial antioxidants to provide thermal stability during processing.

The LDPE selected for comparison was produced by *BP Chemicals* from Belgium and it was commercialized under the grade name *Novex LD1407KJ*. The main characteristics are a density = 0.924 g/cm³ and a melt flow index = 0.75 g.10min⁻¹. The hindered amine stabilizer (HAS) used was produced by *Clariant Company* from France under the trade name Sanduvor PR 31. This stabilizer has a single structure that combines hindered amines and a UV absorbing unit detectable at $\lambda_{\max} = 308$ nm in the UV spectrum of the LDPE and $\lambda_{\max} = 314$ nm in the chloroform solvent. The (>C = C<) double bond of Sanduvor PR 31 is able to induce a chemical reaction with the polymer chains [17]. The stabilizer was added to the matrix in a concentration ratio 0.3% w/w. The chemical structure of Sanduvor PR 31 is presented in Figure 1.

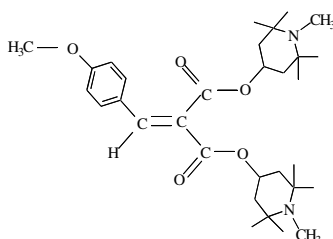


Figure 1. The chemical structure of HAS used (Sanduvor PR 31).

Sample preparation

The HAS powder was compounded into the mLLDPE or the LDPE pellets by extrusion process. Thus, films of 90 ± 10 μm thickness were prepared by using a *Battenfeld R 160 SV* extruder (Germany) with a length/diameter ratio of 24. The temperature profile along the barrel of the extruder increased from 160 to 200°C; while in the die, it decreased from 200 to 180°C. The screw speed was fixed at 35 rpm, while the residence time was approximately 5 min. The film was stretched in the air after leaving the die at a pulling speed of 5 m/min. The films were cooled with a large volume of air upward over the surface of the bubble. Both unstabilized mLLDPE and LDPE films were prepared under the same processing conditions.

Gamma irradiation

Gamma irradiation was carried out directly on both unstabilized and HAS stabilized films, in the form of rectangular bands (30 x 20 cm), in ⁶⁰Co industrial equipment at room temperature in air atmosphere at the Nuclear Research Center of Algiers (Algeria). The samples were exposed to 10, 30, 50, 80, 100, 200, 300, 400, 500, 600, 700, and 800 kGy at a dose rate of 32.44 Gy/min. The dose rate was determined by the Fricke dosimeter [18].

Techniques

The IR spectra were recorded using a Shimadzu FTIR spectrophotometer (model 8400 M) at 4 cm⁻¹ resolutions over 40 scans. All spectra were recorded in absorbance mode in the 4000-600 cm⁻¹ region. The oxidation degree, i.e. carbonyl index (CI) under γ -irradiation was obtained by calculating the carbonyl absorption at 1715 cm⁻¹ from the FTIR spectra at different doses, using the spectrum of the starting unoxidized

materials as reference. All absorbances were normalized by the film thickness according to the following equation [19]: Carbonyl index (CI) = $(A_{1715}/d) \times 100$, where A_{1715} is the measured absorbance at 1715 cm^{-1} from the FTIR spectrum at a certain γ -irradiation dose, and d is the film thickness in microns.

The ultimate mechanical properties, i.e. tensile strength at break (σ_b) and elongation at break (ϵ_b) of all the samples were determined as per ASTM D882 using a tensile machine (Zwick/Roell, Germany) with a gauge length of 2.5 cm at a speed of 100 mm/min. All measurements were performed at room temperature, and an average of 5 tests was applied on the samples. The machine is equipped with a computer using the TestXpert logical for the treatment of the experimental data.

Assessment of polymer degradation during γ -irradiation was accomplished through monitoring its rheological implications. Indeed, the melt flow rate test is a simple and convenient method for characterizing both the type of degradation (chain scission or cross-linking) and the extent of degradation of a polymer since the melt flow index (MFI) is inversely related to the molar mass of the polymer and is indicative of the flow characteristics of the molten polymer [16]. The MFI was calculated according to ASTM D1238/79. The flow rate measurement of the extrudates was performed by MVR/MFR tester machine (model 1267 C5, Germany) at 190°C and 2.160 kg. Five measurements were performed for every sample.

The DSC measurements were carried out by using a Mettler DSC-882 differential scanning calorimeter with nitrogen as the purge gas. Samples of almost 10 mg were analyzed at a constant rate of heat of $10^\circ\text{C}/\text{min}$. The melting peak (T_m) was obtained, and percentages of crystallinity were determined using the enthalpy of melting for polyethylene of 100% crystallinity $\Delta H_c = 290\text{J/g}$ [20].

Results and discussion

Oxidation is one of the major changes induced by irradiation of polymer in air. During the radiolysis of polyolefins, hydroperoxides are formed simultaneously with other organic functions, for example ketones. They are the main final products that are determined by FTIR spectroscopy as an alternative tool of investigation [21]. The changes at molecular levels during the process of γ -irradiation of the different samples were monitored by the measurement of carbonyl index growths. Indeed, figure 2-a shows the carbonyl index evolution in the dose range of 0 to 100 kGy for both unstabilized and HAS stabilized mLLDPE films compared to those of the conventional LDPE. It can be observed that both unstabilized and HAS stabilized mLLDPE samples show induction period in the range of 0 to 30 kGy of irradiation, which seems also the same as that of unstabilized LDPE. However, the stabilized LDPE films is oxidised on much longer period exhibiting the highest level of radiolysis stability for all the irradiated polyethylenes assessed by a margin of 20 kGy. This is not surprising since similar results have already been reported in a previous paper [22].

The characteristic sharp and linear increase reflecting rapid auto-oxidation after induction period is evident with all samples excepted the stabilized LDPE films where the formation rates of carbonyls are lower as illustrated in figure 2-b. It is obvious from this figure that the stabilizing activity of HAS in mLLDPE is annihilated in the γ -irradiated samples since a similar oxidation rate is obtained with unstabilized LLDPE films. This may be a consequence of the ability of HAS to complex strongly

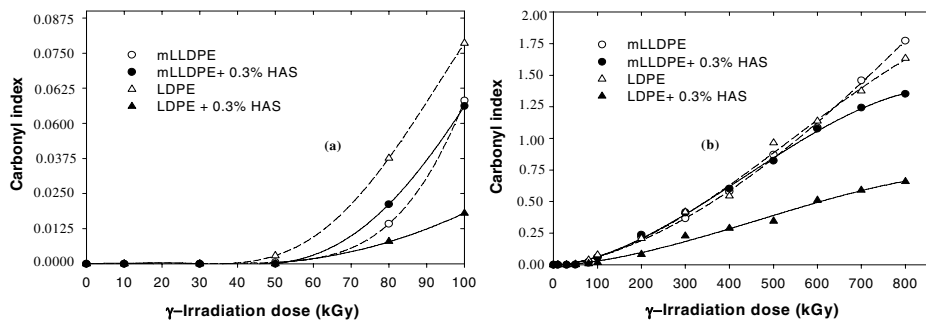


Figure 2. Carbonyl index versus γ -irradiation dose for both unstabilized and HAS stabilized mLLDPE compared to LDPE. (a): 0 – 100 kGy and (b): 0 – 800 kGy.

with transition metal ions of the metallocene catalysts leading to the formation of inert species [23]. The above results indicate also that the metallocene structure of LLDPE does not have any significant influence on the oxidative stability during γ -irradiation process when compared to the conventional LDPE polymer. Figures 3-a and b show the variation of the melt flow index as a function of γ -irradiation dose for both unstabilized and HAS stabilized mLLDPE films at low doses (~ 100 kGy) and high doses (~ 800 kGy), respectively. The results are compared with the conventional LDPE samples. In figure 3-a, it is clearly observed that MFI decreases gradually in the dose range of 0 – 30 kGy for both unstabilized and stabilized mLLDPE passing from almost 1 to 0.15 g/10 min, followed by a steady-state up to 80 kGy, while figure 3-b exhibits the melt flow curves of all irradiated samples at higher doses indicating a fast increase in the MFI values, however less pronounced for the conventional LDPE films. The whole data suggest the occurrence of the two degradation mechanisms, i.e., crosslinking and chain scission, but with higher overall contribution from chain scission at higher doses.

However, at lower doses, the predominance of crosslinking reactions is established as reflected in the decrease of MFI values. The presence of HAS in LDPE significantly lowers the extent of chain scission confirming its capacity to retard the oxidative degradation. These results are in a good agreement with those obtained by FTIR spectroscopy.

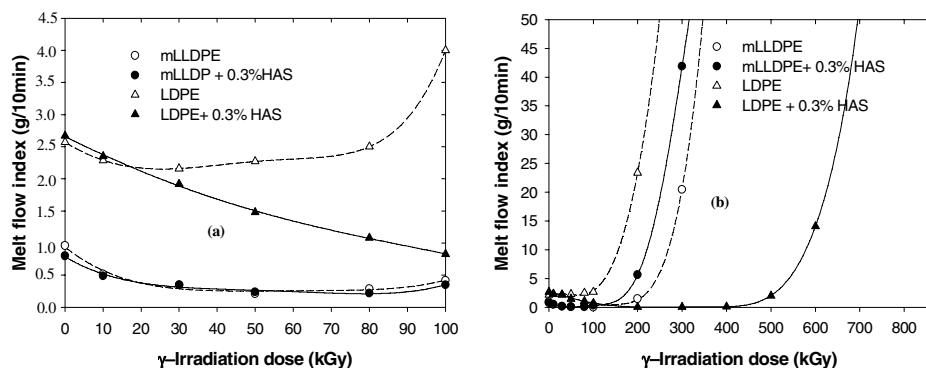


Figure 3. Melt flow index (MFI) change versus γ -irradiation dose for both unstabilized and HAS stabilized mLLDPE compared to LDPE. (a): 0-100 kGy and (b): 0-800 kGy.

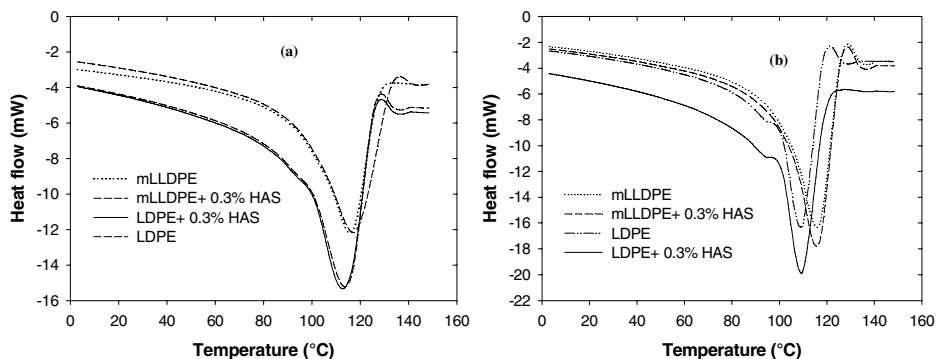


Figure 4. DSC thermograms of unstabilized and HAS stabilized mLLDPE compared to LDPE. (a): before irradiation; (b): after 800 kGy.

Figure 4-a shows DSC thermograms recorded in the first scan in the temperature range 5 – 150°C for all the samples before irradiation, while Figure 4-b referred to those submitted to 800 kGy of exposure. The analysis of the thermograms in figure 4-a indicates the presence of a single peak character around 118°C for the mLLDPE and 114°C for the LDPE and it seems that the melting peak does not undergo any significant changes after irradiation. The high temperature peak observed in the mLLDPE samples is generally attributed to weakly branched molecules, whereas the low temperature endotherms can be associated with more branched molecular species [24]. Moreover, it is clear that the DSC thermograms of our polymers have similar shapes despite significant differences in chain branching, polydispersity and melting temperature. These differences relate probably to the different catalysts systems used for polymerization [25]. Figure 4-a shows that the LDPE has a broader melting point range than the mLLDPE that has a comparatively narrower and higher melting temperature.

The influence of γ -radiation doses on the crystallinity content of both unstabilized and HAS stabilized mLLDPE is shown in Figure 5 and the results are compared with those obtained in similar conditions on LDPE with and without stabilizer. From Figure 5, it can be seen in the early stages of irradiation, almost constancy in the values of the crystallinity content for all the samples. Above 100 kGy, a gradual growth of the crystallinity is observed as the radiation doses increase, however this increase is less pronounced in HAS stabilized LDPE films. According to the literature [14,26], this result is due to some scission of strained macromolecules. Then re-crystallisation of the broken macromolecules follows. Since the irradiation temperature is much higher than the glass transition temperature of polyethylene, sufficient molecular mobility exists for the broken chains to re-organize and re-crystallize.

Attempts have been also made to correlate the changes in the ultimate tensile properties to the variation of structural parameters such as CI and MFI. Figures 6 and 7 show the changes of residual strain and stress at break against γ -irradiation doses for mLLDPE films with and without HAS compared to those of LDPE, respectively. The dimensionless values are calculated by dividing each value at a given dose by the corresponding initial value. In Figure 6, it is observed that the residual strain at break exhibits an initial growth during the first 100 kGy of irradiation for all the studied materials, but, more pronounced for the stabilized LDPE films. Above 100 kGy, this characteristic is however significantly lowered attaining almost a zero value at 600 kGy

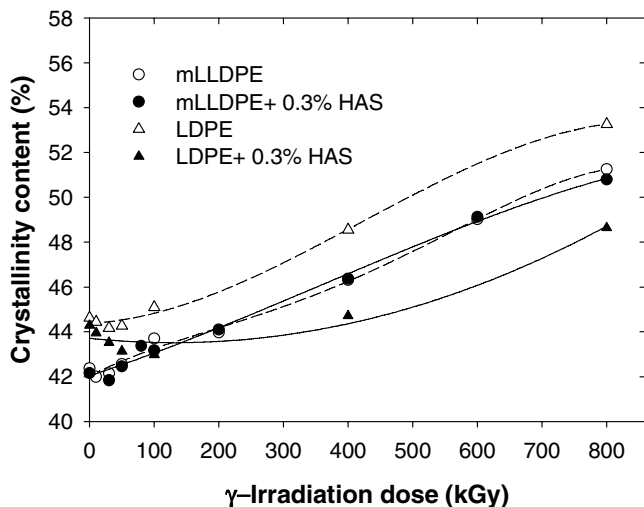


Figure 5. Crystallinity content (%) versus γ -irradiation dose in the range 0 – 800 kGy for both unstabilized and HAS stabilized mLLDPE compared to LDPE.

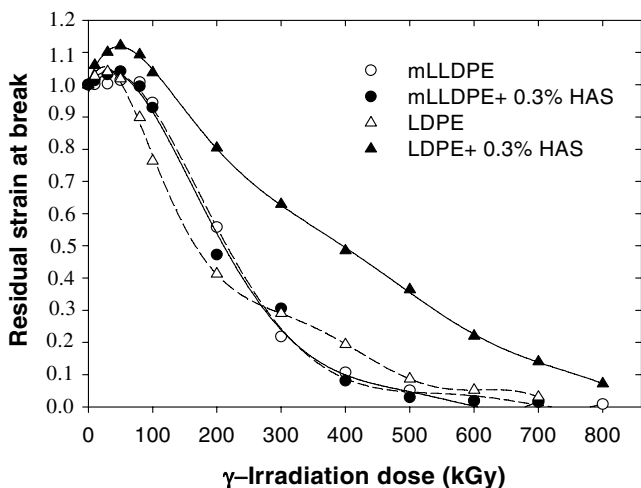


Figure 6. Residual strain at break versus γ -irradiation dose for both unstabilized and HAS stabilized mLLDPE compared to LDPE.

resulting in a very brittle behaviour. According to the literature [26], this behaviour indicates that the crosslinking and the scission of macromolecules in polyethylene take place simultaneously during gamma irradiation, but with different rates on the two ranges of total absorbed doses. The above data show also that the hindered amine stabilizer does not have any influence on the radiation induced oxidative degradation of mLLDPE. On the other hand, the contribution of HAS to the durability of LDPE films is well evidenced through the improvement of the half-life-dose (HLD) reported in table 1. This property, which is the dose that reduces the residual strain at break to 50% of its initial value is related to the radiation resistance of the material [27]. The HLD values reported in table 1 show clearly the contribution of HAS to the durability

of LDPE samples which is almost doubled. The data above are consistent with the FTIR, MFI and DSC measurements. The variation of residual stress at break as a function of γ -irradiation doses is shown in Figure 7. Although elongation at break is more important than stress at break in studying the degradation of polymers because the former can give an early indication of embrittlement [28]. It is observed in Figure 7 that all the samples exhibit a slight increase in the residual stress at break in the initial 30 – 50 kGy, while the next 300 kGy of exposure lowers significantly this property to almost 70% of its initial value, particularly for mLLDPE and LDPE. In the case of stabilized LDPE, the drop of the residual stress at break is less intense (~ 30%). A slight change in this property is observed for the last 500 kGy of irradiation. According to the literature [28], the greater drop in mechanical properties for mLLDPE relative to the conventional LDPE is explained as a result of a greater drop in MFI due to chain scission. This mechanical behaviour is attributed to the easy cleavage of branching chains that result in the reduction of branching in mLLDPE. The ultimate tensile properties (stress and strain at break) of HAS stabilized LDPE samples are superior to those of mLLDPE confirming the previous findings.

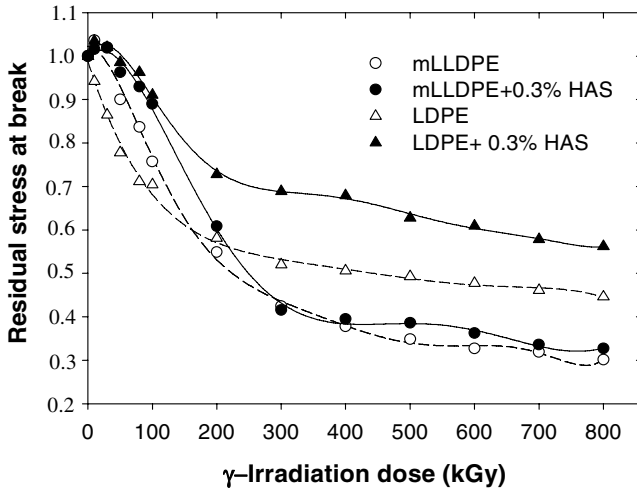


Figure 7. Residual stress at break versus γ -irradiation dose for both unstabilized and HAS stabilized mLLDPE compared to LDPE.

Table 1. Half-value-dose for mLLDPE and LDPE films with and without HAS

Samples	mLLDPE	mLLDPE + 0.3% HAS	LDPE	LDPE + 0.3%HAS
Half-value-dose (kGy)	210	219	200	405

Conclusions

The presented results showed that the presence of HAS in mLLDPE films did not have any stabilizing effect against gamma irradiation induced oxidative degradation. This was supported by the fact that both unstabilized and HAS stabilized mLLDPE

samples exhibited almost the same oxidation rate kinetics. This suggests that this result was due to the occurrence of strong complexing reactions between HAS and the transition metal ions of the metallocene catalysts leading to the formation of inert species. On the other hand, the efficiency of HAS to protect LDPE toward oxidation in gamma irradiation was confirmed by an increase in the value of the half-life-dose (HLD) of the material by almost twice when compared to unstabilized sample. Moreover, it was found that the metallocene LLDPE structure had no significant effect on the radiation induced oxidative degradation kinetics in comparison with the LDPE polymer. All reported data suggest a more balanced competition between crosslinking and chain scission but with higher overall contribution from chain scission at higher doses. At lower doses, the predominance of crosslinking reactions was established as supported by a decrease in the MFI values.

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