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EFFECT OF IONIZING RADIATION ON MECHANICAL AND THERMAL PROPERTIES OF LOW-DENSITY POLYETHYLENE CONTAINING PRO-DEGRADANT AGENTS

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ABSTRACT

The wide use of plastics on packages of short-lifetime products has presented harmful consequences for the environment due to their low degradation rate. By this way, improved results to the bio-assimilation of polyolefins have been achieved by the incorporation of pro-oxidant components. The aim of this work is to evaluate the mechanical and thermal behavior of low-density polyethylene (LDPE) modified by those agents and submitted to ionizing radiation by gamma rays. LDPE was modified using a masterbatch containing calcium stearate (CaSt), or magnesium stearate (MgSt) or Clariant® commercial metallic complex. The final amount of stearate in modified LDPE was 0.2%. The films were obtained by compression molding. Samples were gamma irradiated at absorbed doses of 15 kGy and 100 kGy. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on samples, as well as mechanical analysis by universal testing machine. Thermal properties of samples presenting pro-degradant agents were affected by the ionizing radiation in the dose range studied, and some of the mechanical properties were clearly modified by reducing their values of tensile strength at break and elongation at break.

1. INTRODUCTION

Plastics have been applied in the large majority of short-life products due to some characteristics of these materials e.g. low specific weight, mechanical resistance, a trouble-free processability and considerable durability [1]. Alariqui and collaborators still consider that resistances to both photo-oxidative degradation and microbiological attack have leaded the polymeric materials to a highlighted position in the transformation industries [1].

By another side, the great number of polyolefinic products has caused harmful consequences to the Nature due to the low degradation rates reached by these products after their inappropriate discharging [2-5].

As described by Strömberg and Karlsson [6], the largest part of the collected plastic municipal solid waste fraction is consisted of packaging materials, specially polypropylene (PP) and polyethylene (PE). In terms of sustainable development, the recovery of plastic waste by means of mechanical recycling has seemed to be a favorable technique [6], but the difficulties on separating the large varieties of plastic found on the waste is largely affecting its economical viability.

By this way, the degradability of polyolefins has been studied [6-12]. In polymer science, the process of degradation is defined as the conversion of macromolecules into products of low molecular weight [6], which can be easily assimilated by microorganisms present in the environment, known as biodegradation [13-14].

Koç and collaborators [15] evaluated the oxidative thermal degradation of low-density polyethylene (LDPE) in a semi-batch reactor system and it was found that this process is not spontaneous even if it requires lower energy than non-oxidative degradation processes.

Hasan and collaborators [16] analyzed the degradability of samples of LDPE after submitted to both photo (exposure to UV light) and chemical (exposure to nitric acid) treatments. By means of Fourier transform infrared spectroscopy (FTIR), it was observed that in case of UV and nitric acid treated LDPE, peaks appeared at 1710 cm^{-1} and 831 cm^{-1}, which were then reduced after microbial treatment, indicating breakdown of polymer chain. It was also verified that UV-nitric acid and microbial treatment induced oxidation reactions which enhanced and accelerated the biodegradability rate of LDPE pieces, showing a synergistic effect.

In this context, the use of ionizing radiation to modify polymeric structures leads to the formation of very reactive intermediates, such as free radicals, ions and excited states. These intermediates can follow several reaction paths, which result in disproportion, hydrogen-abstraction, arrangements and/or the formation of new bonds. The ultimate effect of those reactions can be the formation of oxidized products, scission of main chains or cross-linking. The degree of these effects depends on several factors, such as the structure of the polymer and the conditions of treatment before, during and after irradiation [17].

Fig. 1 presents the main processes that irradiated polyolefins may undergo. Ions created in a given spur quickly recombine with electrons, leading to a second population of electronically excited molecules in addition to those created directly in the same spur as a result of secondary electrons. A fraction of the excited molecules dissociate into free radicals, the reactive species mainly responsible for the degradation occurring when polymers are exposed to gamma radiation. For dissociation events involving main-chain scission, the low mobility of the resulting macromolecular radical pair favor geminated recombination [18].

$$RH \longrightarrow RH^{+}, RH_2^{+}, e^{-}, RH^{*}, R\cdot, H\cdot, H_2, \text{etc}$$
$$RH^{+}, RH_2^{+} \longrightarrow RH^{*}; \quad RH^{*} \longrightarrow R\cdot, H\cdot, H_2$$
$$RH + H\cdot \longrightarrow R\cdot + H_2$$
$$R\cdot + R\cdot' \longrightarrow R - R'$$

Figure 1. The main entities formed in irradiated polyolefins [19].

According to Charlesby [20], many of the changes observed are not completed when irradiation is stopped but continue progressively over periods of weeks. This behavior may arise from the reaction of residual radicals in the system, from oxygen attack on these radicals, from progressive fracture of bonds due to internal stress set up by occluded gases or from the slow rate of diffusion to the surface of the gases. The induction of formation of free radicals by means of radiation is a useful tool to accelerate the polyolefinic degradation.

Oliveira and collaborators [21] analyzed the influence of electron-beam irradiation (EB) on mechanical properties of multilayer packaging materials based on polyolefins (e.g. LDPE, PP, PET) under doses up to 120 kGy, verifying an increasing on tensile strength at break and elongation at break whereas the penetration and sealing resistance decreased.

The usage of substances that catalyze the thermal or photo-oxidative degradation, known as pro-degradant agents, which are generally composed by transition metals (e.g. zinc, copper, cobalt, manganese etc), has been evaluated by some authors [22-26]. Bikiaris and collaborators [22] studied the effect the use of cobalt stearate in LDPE/starch blends whereas Roy [23] evaluated the influence of the latter agent in the degradation of LDPE films.

Li [24] observed that the incorporation of lanthanum oxide on LDPE has increased the latter’s on-set temperature, when submitted to thermogravimetry (TG), although it has not affected the main chain scission of the polymer, which indicates that thermal-oxidative stabilization is more related to oxygen atmosphere than to presence of the oxide.

Chiellini and co-authors [25] evaluated the influence of different proprietary pro-degradant systems in LDPE, and verified that they were effective in inducing the oxidative degradation of the polymer backbone. It was also observed that the rate of degradation directly depends on the temperature where higher mass loss is achieved at higher temperatures. This was accompanied by the production of low molar mass, oxidized fractions, which become vulnerable to microorganisms in biodegradation tests due to their wettability and functionality.

In another study, Magagula and collaborators [26] verified the potentiality of Mn_2Al-LDH-stearate and Co_2Al-LDH-stearate to be applied as a pro-degradant in LDPE samples. These additives were incorporated into blown polyethylene films via a 10% masterbatch and then the films were subjected to accelerated ageing in a QUV weatherometer. It was found that both additives were effective to promote the photodegradation, especially because of 100 h of

QUV exposure was sufficient to cause mechanical embrittlement of films containing as little as 0.1% of either active additive.

By this way, the objective of this paper is to evaluate the presence of pro-oxidant agents on low-density polyethylene (LDPE) and its mechanical and thermal behavior after submission to electron beam (EB) irradiation processing.

2. EXPERIMENTAL

2.1. Materials

Low-Density Polyethylene (LDPE) – supplied as pellets by Zaraplast S.A. (São Paulo, SP, Brazil), with density of 0.923 g/cm^3 (ASTM D-1505) and melting flow index of 22 g/10min (ASTM D-1238).

CESA-BIO PEA0420086-ZN pro-degradant additive (named, in this paper, Clariant) – supplied as pellets by Clariant S.A. (São Paulo, SP, Brazil).

Calcium stearate (CaSt) – in the form of powder, supplied by Dacarto Benvic S.A. (Diadema, São Paulo, Brazil).

Magnesium stearate (MgSt) – in the form of powder, lot 200604295, produced by The Spherd Chemical Company and supplied by AMC do Brasil Ltda. (São Paulo, SP, Brazil).

2.2. Films preparation

In the first part of the process, masterbatches containing LDPE and calcium stearate (CaSt), or magnesium stearate (MgSt) or Clariant commercial metallic compost, in a proportion of 80/20 (wt. LDPE/ wt. stearate), were obtained by extrusion with temperatures in the range of 170-190ºC. Later on, a new fraction of raw LDPE was aggregated to the masterbatches to obtain the desired modified LDPE containing pro-degradant agents in a final proportion of 0.2%. Films were obtained by a thermostatized compression molder model MA-098 (Marconi Equipamentos e Calibração para Laboratórios Ltda., Piracicaba, SP, Brasil) under a temperature of 190ºC ± 5ºC and then cooled to room temperature.

2.3. Irradiation procedure

Samples were irradiated with gamma rays from ^{60}Co source at a dose rate of 10 kGy·h^{-1}, and absorbed doses of 15 kGy and 100 kGy under air atmosphere. These doses were performed after considering that the gamma irradiation is a very effective treatment to promote structural modification in polymers.

2.4. Mechanical analysis

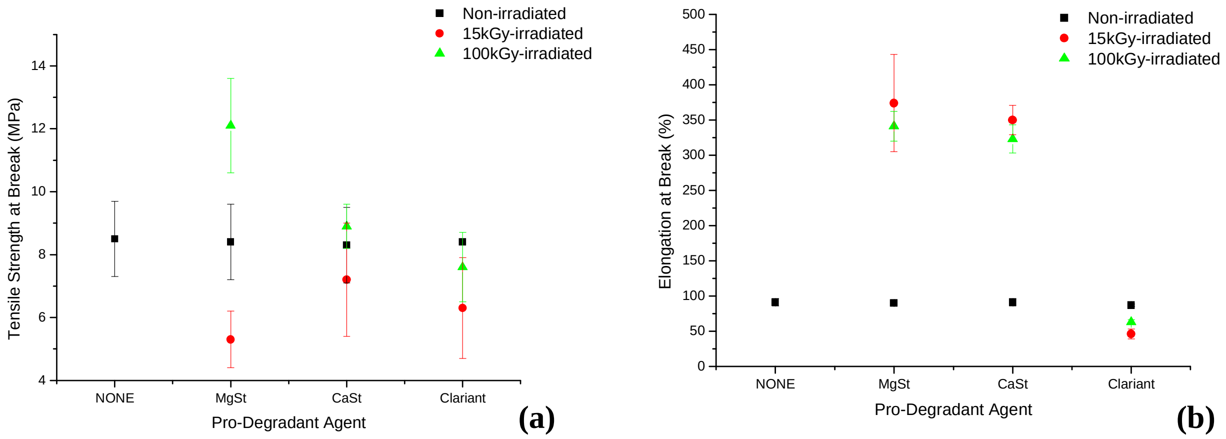
Plates (200 mm × 200 mm × 1.0 mm) were prepared by compression molding and type IV specimens (ASTM D-638/99) were stamped with a cutting tool. The tests were performed using a model DL 2000 NS 5921 universal testing machine (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil). The control program used was Tesc version 3.01 and the load cell had a capacity of 20 kgf. The specimens were 25 mm long and the speed of stretching was 50 mm·min^{-1}. The values are the average results ± standard error of 10 determinations.

2.5. Thermoanalytical investigations

Thermal behavior of samples was studied by thermogravimetry (TGA) and differential scanning calorimetry (DSC). TG curves were obtained using a TGA/SDTA851^{e} thermobalance from Mettler-Toledo. Sample masses of about 10 mg were set in alumina open crucible and then heated from 25^{o}C to 900^{o}C at a heating rate of 10^{o}C·min^{-1} under dynamic air atmosphere (50 mL·min^{-1}). DSC measurements were carried out on a DSC823^{e} from Mettler-Toledo. Sample mass of about 10 mg was set in aluminum crucible with pierced lid and then heated from 25^{o}C to 150^{o}C at a heating rate of 10^{o}C·min^{-1} under dynamic nitrogen atmosphere (50 mL·min^{-1}). For all studied samples, it was recorded a preliminary thermal cycle in order to remove previous thermal history.

3. RESULTS AND DISCUSSION

Fig. 1 presents the average values for tensile strength at break, elongation at break and Young’s modulus for pristine LDPE and its modifications, before and after gamma irradiation.



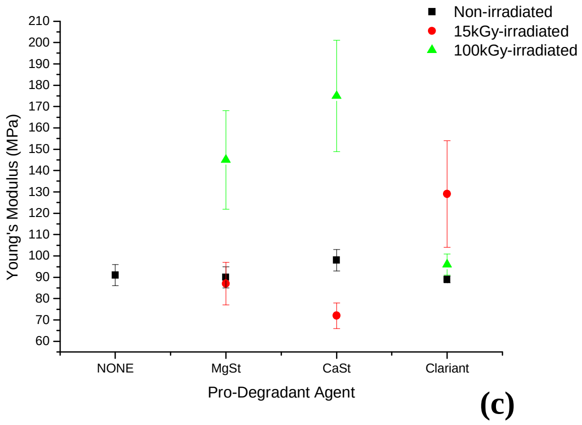


Figure 2. Mechanical properties of pristine LDPE and pro-degradant-modified LDPE, non-irradiated and gamma-irradiated samples: (a) tensile strength at break, (b) elongation at break and (c) Young's modulus.

By Fig. 2, it can be seen that incorporation of different metallic compounds to LDPE has slightly modified the polymer mechanical properties, as supported by Osman et al [27], suggesting that processing of materials (extrusion) has not promoted premature degradation reactions, which might have been induced by these compounds.

By another hand, gamma radiation, in the studied doses, has meaningfully affected these properties due to radiation to be able to randomly promote either cross-linking or chain scission of the main polymer backbone, as reported by some authors. In this case, chain scissions can be observed for samples submitted to 15 kGy whereas cross-linking is observed on the highest dose, indicating that the long exposition time allows the polymeric chains to reorganize and, by this way, to create cross-linkages. This indicates that metallic stearates reduce the susceptibility of LDPE undergo chain scission in higher doses, as described by Suarez et al. [28].

$LDPE_{MgSt}$ has presented the highest reduction on tensile strength at break when 15 kGy-irradiated and the highest increasing when 100 kGy-irradiated (Fig. 2(a)), and the commercial pro-degradant agent has presented the lowest degree of chain reorganization of all evaluated samples when 100 kGy-irradiated (Fig. 2(c)).

Table 1 presents the melting temperature for LDPE and its modifications, with/without gamma irradiation.

Observing Table 1, it is possible to verify that melting temperature (T_m) for LDPE corresponds to the ones mentioned at literature and that this value is greatly dependent on density and branching degree of the polyolefin [29].

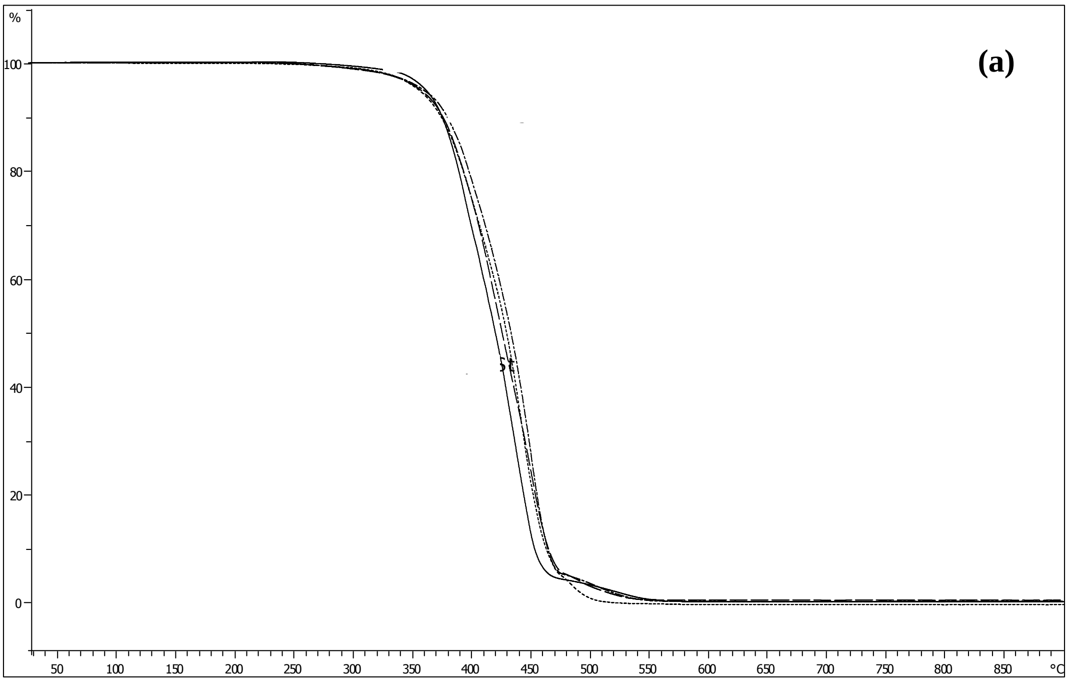
The incorporation of pro-degradant agents has, in general, increased the T_m of LDPE. Roy et al. [30] said that this increasing is due to alterations on the chain length promoted by some cross-linking reactions.

When the samples were submitted to gamma radiation, it was seen a reduction on T_m by increasing the radiation doses, in the studied range, independent of the pro-degradant agent added to polymer. As described by Stojanović et al. [31], the total effect of radiation induced changes depends upon the relation between the cross-linking and chain scission reactions. In other words, cross-linking in the amorphous region causes a decrease in the melt entropy by configurational constraints, thus increasing the melting temperature, whereas the chain scission reactions cause a decrease in the melting temperature by increasing the melt entropy.

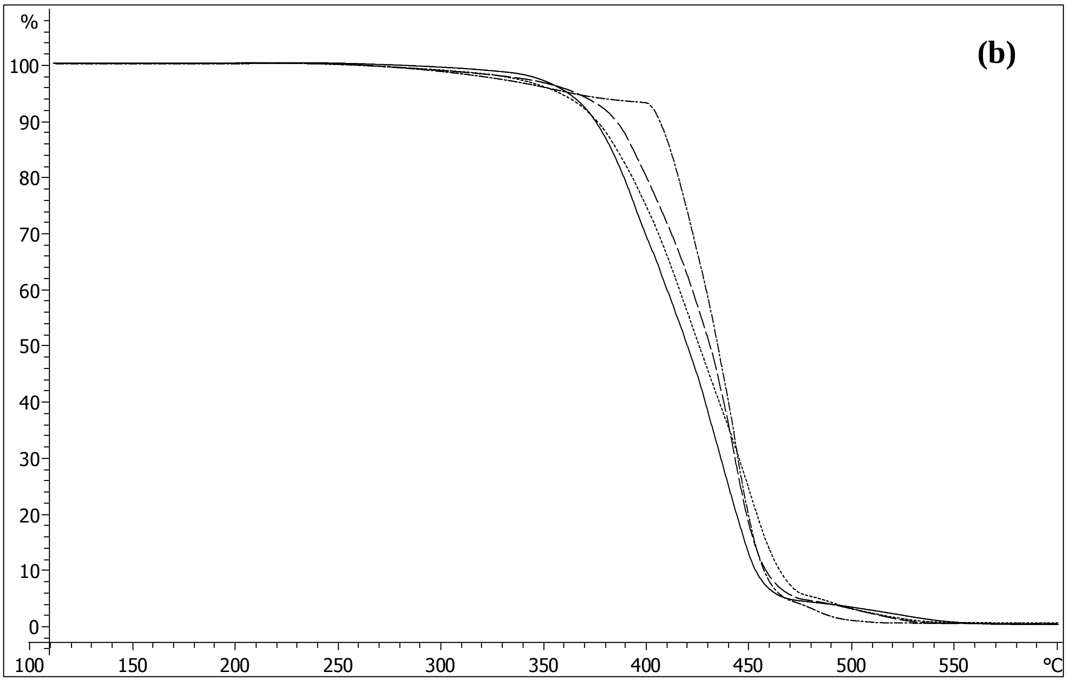
Table 1. Melting temperature for LDPE and modified LDPE samples before and after gamma irradiation

Material	**Melting temperature (^oC)**		
	Non-irradiated	*15kGy-irradiated*	*100kGy-irradiated*
LDPE	105	105	105
$LDPE_{Clariant}$	106	106	105
$LDPE_{CaSt}$	114	113	110
$LDPE_{MgSt}$	113	111	110

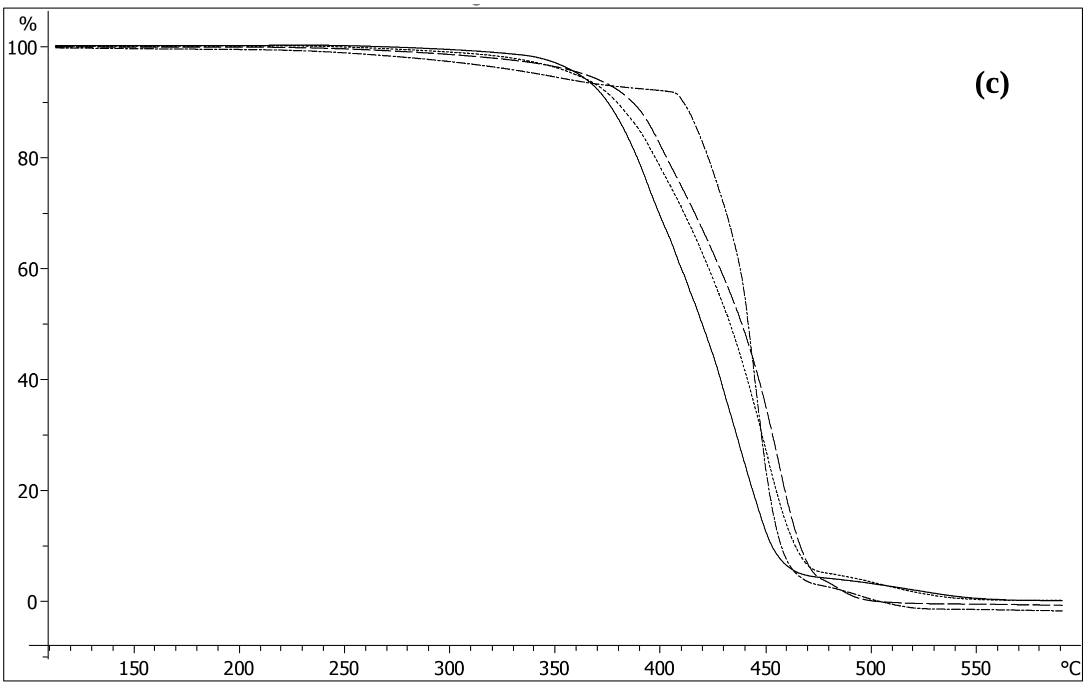
Fig. 3 presents the TG curves for LDPE and its modifications, with/without gamma irradiation.



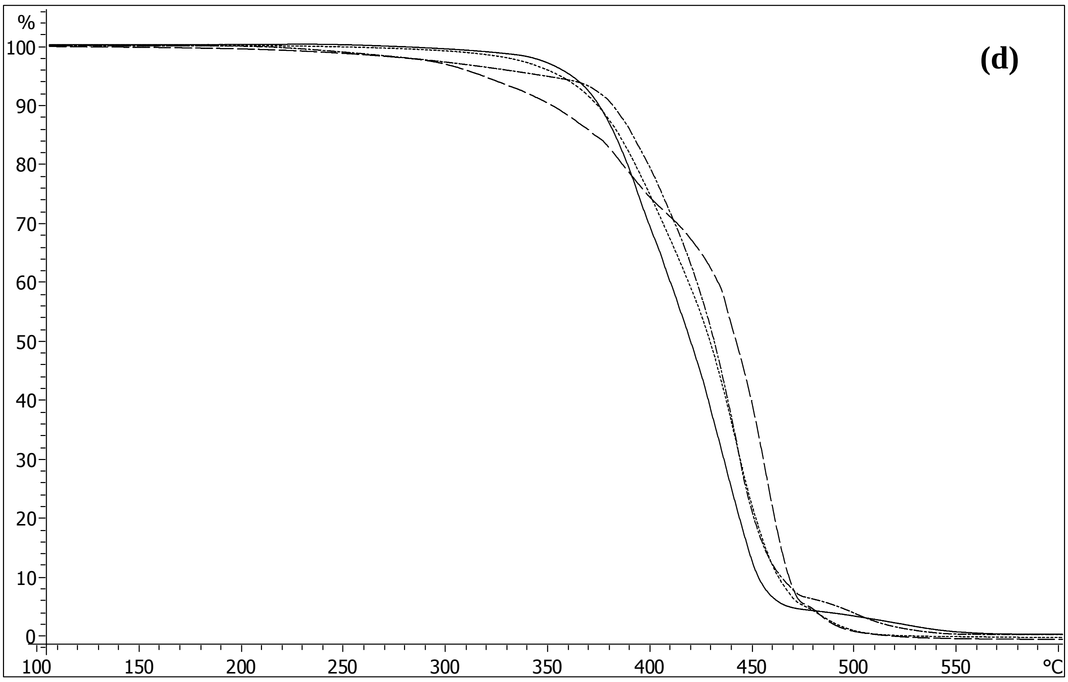
LDPE (—); $LDPE_{Clariant®}$ (··········); $LDPE_{CaSt}$ (– – –); $LDPE_{MgSt}$ (– · –)



LDPE (———); LDPE$_{CaSt}$ (··········); 15kGy-LDPE$_{CaSt}$ (– – –); 100kGy-LDPE$_{CaSt}$ (– · – ·)



LDPE (———); LDPE$_{MgSt}$ (··········); 15kGy-LDPE$_{MgSt}$ (– – –); 100kGy-LDPE$_{MgSt}$ (– · – ·)



LDPE (—); LDPE$_{\text{Clariant}}$ (··········); 15kGy-LDPE$_{\text{Clariant}}$ (– · –); 100kGy-LDPE$_{\text{Clariant}}$ (– – –)

Figure 3. TG curves from (a) non-irradiated LDPE and its modifications, (b) non-irradiated and irradiated LDPE$_{\text{CaSt}}$, (c) non-irradiated and irradiated LDPE$_{\text{MgSt}}$ and (d) non-irradiated and irradiated LDPE$_{\text{Clariant}}$.

By Fig. 3(a), it can be seen a slight reduction on the on-set degradation temperature for LDPE when metallic compounds were incorporated to it, what corresponds to oxidative degradation reactions of LDPE and other polymers [23, 26, 32]. In this context, Magagula et al. [26] said that a free radical may form on the polymer due to the effects of heat. The free radical rapidly combines with available oxygen to form a peroxy radical. This subsequently abstracts labile hydrogen from a nearby polymer chain, regenerating the original chain free radical and resulting in a hydroperoxide. Under the influence of heat the latter cleaves to form two additional free radicals. This chain reaction causes rapid proliferation of free radicals that ultimately results in polymer chain scission taking place that leads to a loss of desirable polymer properties.

Analyzing both Figs. 3(b) and 3(c), it is possible to observe that both LDPE$_{\text{CaSt}}$ and LDPE$_{\text{MgSt}}$ presented a similar thermal behavior, indicating that gamma irradiation caused chain scission and cross-linking in LDPE. It can be also suggested that 15 kGy-irradiated samples mainly suffered chain scission whereas 100 kGy-irradiated has presented both mechanisms, but cross-linking in higher intensity. Curves of Fig. 3(d) show that kinetics of the first step of thermal degradation is highly affected by the increasing of radiation dose.

3. CONCLUSIONS

The incorporation of pro-degradant agents has not meaningfully affected the evaluated mechanical and thermal properties of LDPE. On the other hand, the irradiation process greatly influences these behaviors of the pro-degradant-added samples, thus reducing their thermal stability. Additionally, the higher is the absorbed dose in the studied range, the higher is the temperature of the second step of thermal degradation and its kinetics.

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