

# EVALUATION OF THERMAL STABILITY OF LOW DENSITY POLYETHYLENE FILMS CONTAINING PRO-DEGRADANT AGENTS

Marcelo A. G. Bardi\*, Henrique A. Oliveira, Mara M.L. Munhoz, Luci D. B. Machado

*Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear (IPEN/CNEN-SP), Avenida Professor Lineu Prestes, 2242, Cidade Universitária, São Paulo, SP, Brazil, ZC 05508-000*

Phone: +55 11 31339857

Email: [magbardi@ipen.br](mailto:magbardi@ipen.br)

Abstract

*Plastic materials in general are resistant to oxidation and biological attack after disposal, which is attributed to their high molecular weight, hydrophobicity, and lack of functional groups and/or available sites in a polymer chain for microbial attack. As the consumption of plastic-based short lifetime products are getting very often, society has experienced waste disposal problems from such polymer packaging material, constantly in the centre of public attention. In this context, the development of techniques to obtain plastics capable to be easily degraded on nature is an urge. So, this paper aims to investigate the thermal stability of LDPE films containing different pro-degradant agents by means of oxidative-induction time (OIT). The incorporation of different transition metal stearates in LDPE has been able to cause meaningful reduction on the oxidative-induction time of the polymer. It could be observed that each stearate had a degree of influence on this property, as the following order: CoSt > CeSt > MgSt. Additionally, it can be said that all the studied pro-degradant agents are capable to induce acceleration on the thermal oxidative degradation of LDPE, even in minimal mass proportions.*

**Keywords:** polymer degradation; oxidative-induction time; metal stearates.

## Introduction

The use of low density polyethylene (LDPE) as raw material for innumerable consumable products is really notable, especially when it comes to short lifetime products, such as trash bags, single-use packaging and agricultural mulch films. As described by Madani et al. [1], LDPE contains additives that offer protection against the effects of heat, oxygen, light, high energy radiation and so on. By this way, this material becomes resistant to oxidation and biological attack after disposal, which is attributed to its high molecular weight, hydrophobicity, and lack of functional groups and/or available sites in a polymer chain for microbial attack [2-6]. As a consequence, society has experienced waste disposal problems from such polymer packaging material [7], constantly in the centre of public attention.

Corti et al. [2] elaborated a precise review on the literature about techniques to increase the degradability rate of post-consumable LDPE, highlighting polymer copolymerisation, blending or grafting with functional polymers and compounds, as well as on the use of pro-oxidant additives. In general, all mentioned techniques intend to use the same principle, inducing an abiotic oxidation and then a molecular weight reduction by polymer chain fragmentation, introducing polar groups and increasing hydrophilicity, which is thought to make the material much more vulnerable to microbial attack [7]. Heat and UV-light are good examples of abiotic factors that are able to induce polymer oxidation [6,8].

When it comes to incorporating pro-oxidant additives, Roy et al. [5] explains that these additives can accelerate the oxidative degradation process and thereby decrease the molecular weight of these polymers to a level where biodegradation can take over. Common pro-oxidants being used for the preparation of “oxo-degradable” films are stearates of transition metals, particularly Ce, Co and Mn. In other papers, Roy et al. [9-10] state that it is well known that transition metals can exhibit variable oxidation states which are responsible for their pro-oxidant nature. In the presence of either light or heat, the additives lead to the generation of free radicals on the polymer chain, which further react with oxygen to form carbonyl groups through a series of reactions. These carbonyl groups then undergo photochemical reactions (Norrish Type I, II, and III) to finally lead to chain scission and physical embrittlement of the samples [11-12].

In the study of Roy et al. [11], it was added traces of manganese stearate on LDPE and it was observed a rapid degradation of the polymeric chain when exposed to xenon arc-weathering and air-oven aging. Additionally, by Flynn-Wall-Ozawa kinetics treatment under N<sub>2</sub> atmosphere, predicted lifetime of thermally aged samples was reduced by a magnitude order of 10<sup>n/2</sup>, where *n* represents the magnitude order of samples that do not contain manganese stearate. In other papers, Roy et al. [5-9] and Konduri et al. [13] compare the effects of three different transition metal stearates on the thermo-oxidative degradation of LDPE films. By means of accompanying the variation of carbonyl index, elongation at break and crystallinity degree by DSC, the following order or influence can be established: cobalt stearate > manganese stearate > titanium stearate > iron stearate. The authors state that degradation initiation and accelerating ability can be explained by their ability to switch between two oxidation states, which in turn lead to decomposition of

hydroperoxides. Additionally, these results indicate that biodegradation rate could be enhanced by exposing LDPE to prooxidants (photo inducers) and UV irradiation, and followed by microbial treatment [13].

Other very interesting results were obtained by Magagula et al. [14] when investigating the influence of  $Mn_2Al$  and  $Co_2Al$  stearates as photodegradants for LDPE films. It was observed that thermo-oxidative degradation has occurred right after processing of LDPE film by screw extruder with profile temperature varying from 90°C to 180°C. By this way, it is possible to reach processing stability of the polyethylene despite the presence of such photodegradants by adding a phenolic and an amine-based antioxidant, suggesting that a controlled ratio of antioxidant/pro-oxidant can improve the properties of the material without affecting its degradation properties after discarding.

So, this paper aims to investigate the thermal stability of LDPE films containing different pro-degradant agents by means of oxidative-induction time (OIT).

## Materials and Methods

### Materials

Low-Density Polyethylene (LDPE) – supplied as pellets by Zaraplast S.A. (São Paulo, SP, Brazil), density =  $0.923 \text{ g}\cdot\text{cm}^{-3}$  (ASTM D-1505) and melting flow index =  $22 \text{ g}\cdot(10\text{min})^{-1}$  (ASTM D-1238); Cobalt stearate (CoSt) – supplied as pellets by Strem Chemicals Inc. (Newburyport, MA, USA); Cerium stearate (CeSt) – supplied as powder by Strem Chemicals Inc. (Newburyport, MA, USA); Manganese stearate-based additive (MnSt) – supplied as pellets by RES Brasil (Valinhos, SP, Brazil).

### Methods

#### *Preparation of LDPE films*

In the first part of the process, master-batches containing LDPE and cerium stearate (CaSt), or cobalt stearate (CoSt) or magnesium stearate-based additive (MgSt), in a proportion of 80/20 (wt. LDPE/ wt. stearate), were obtained by extrusion with temperatures in the range of 170-190°C. Later on, a new fraction of raw LDPE was aggregated to the master-batches to obtain the desired modified LDPE containing pro-degradant agents in a final proportion of 0.2%. Films were obtained by a thermostated compression molder model MA-098 (Marconi Equipamentos e Calibração para Laboratórios Ltda., Piracicaba, SP, Brazil) under temperature of  $190^\circ\text{C} \pm 5^\circ\text{C}$  and then cooled to room temperature.

## Thermal characterization

Oxidative-induction time (OIT) tests were performed by Perkin Elmer DSC6000 and applying samples of  $5 \text{ mg} \pm 0.2 \text{ mg}$  into aluminum crucibles. The flow rate of inert ( $\text{N}_2$ ) and oxidative ( $\text{O}_2$ ) gases was set at  $50 \text{ mL min}^{-1}$ . The temperature program was according to the specifications at ASTM D3895-07.

Once the specimen was loaded into the DSC cell, the samples were let to be purged at room temperature in  $\text{N}_2$  for 5 minutes and then heated up to  $200^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ . When the set temperature has been reached, the samples were equilibrated for 5 min. Once the equilibrium time has expired, atmosphere was changed to oxygen and isothermal operation continued until the maximum exotherm has been reached to allow a complete examination of the entire oxidation. The tangent method was used to determine the OIT.

## Results and discussion

Figure 1 to Figure 4 show respectively the DSC curves for pristine LDPE and their variations containing MnSt, CeSt and CoSt.

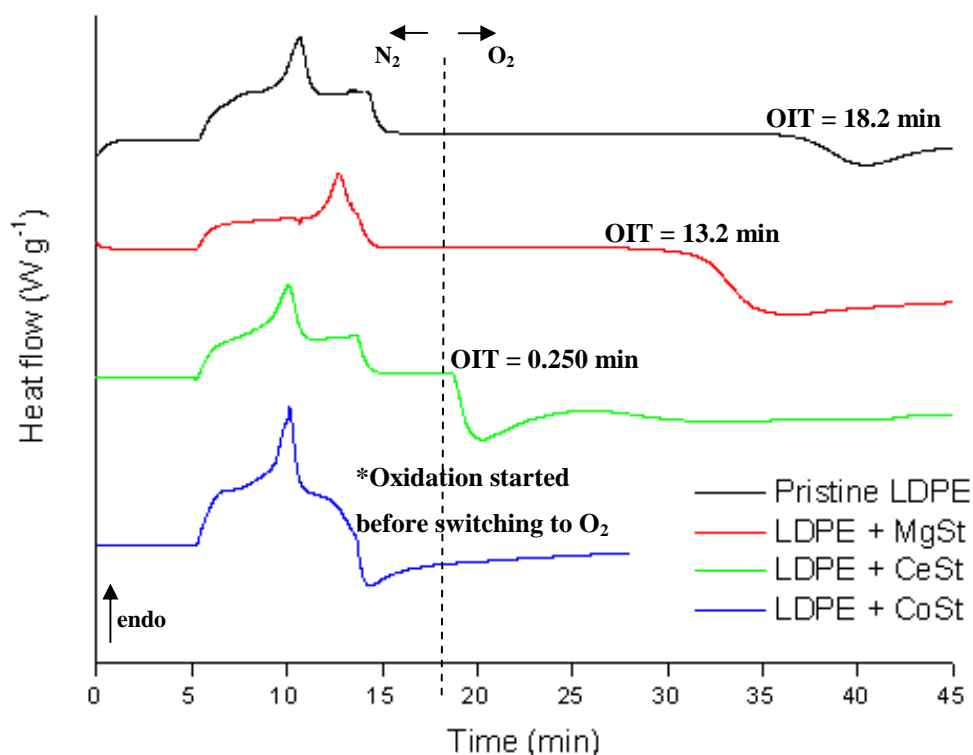


Figure 1 – DSC curve showing OIT calculation for pristine LDPE and LDPE containing manganese stearate, cerium stearate and cobalt stearate.

The first analysis based on Fig. 1 is that the addition of the different metal stearates to LDPE caused a considerable reduction on the oxidative-induction time of the polymer when compared to its pristine composition. Despite all commercial LDPE contains certain level of antioxidant on its composition, the studied transition metal stearates have played their role on accelerating the oxidative degradation in a favorable condition, as suggested by Magagula et al. [14] and Ammala et al. [16].

It is also remarkable that different behaviors have been observed for OIT depending on the stearate added. CoSt has reached the highest impact on LDPE, once it was observed that the polymer had already been degraded just much before the oxidizing atmosphere to be switched into the DSC cell. These observations corroborated the ones published by Roy et al. [15], once cobalt stearate accelerated both pyrolysis as well as thermo-oxidative degradation, which can also be indicated by a reduction on the activation energy values evaluated.

Although not as pronounceable as CoSt, the addition of CeSt also caused a good impact on oxidative degradation of LDPE, presenting a considerable reduction on the OIT. Even if some authors portray CeSt as good oxidative agent for plastics which are sensible to UV light [16-17], these results indicate that it can also be used for compositions that will pass by thermally-induced oxidation process. By another side, the incorporation of MgSt to LDPE did not caused a meaningful alteration on the OIT, although it could be detected and quantified. Despite the fact that Roy et al. [11] observed a great reduction on properties for compositions containing this additive, this was due to a pre-exposition to UV light, indicating that MgSt could be better qualified as photo-sensitizer than as thermo-sensitizer for LDPE, however this do not happen to polypropylene, as described by Rosa et al. [18].

## Conclusions

The incorporation of different transition metal stearates in LDPE has been able to cause meaningful reduction on the oxidative-induction time of the polymer. It could be observed that all studied pro-degradant agents are capable to induce acceleration on the thermal oxidative degradation of LDPE, even in minimal mass proportions. Moreover, each stearate has shown a different degree of influence on this property, as the following order: CoSt > CeSt > MgSt.

## Acknowledgments

The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP by financial support (grant n°. 2010/02631-0), Comissão Nacional de Energia Nuclear – CNEN and Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq for scholarships. In time, the authors acknowledge Universidade São Francisco by offering the twin-screw extrusion, and undergraduate student Gabriel Vieira Toledo Leme for processing the polymer compositions.

## References

- 1 Madani M, El-Bayoumi S, Aly SS, Dayem AM, Hammam M. Modification of low density polyethylene by radiation-induced grafting. I. Grafting procedure, chemical modification of grafted films and electrical properties. *J Phys.* 2012;1:10-5.
- 2 Corti A, Muniyasamy S, Vitali M, Imam SH, Chiellini E. Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. *Polym Degrad Stab.* 2010;95:1106-14.
- 3 Peychès-Bach A, Moutounet M, Peyron S, Chalier P. Factors determining the transport coefficients of aroma compounds through polyethylene films. *J Food Eng.* 2009;95:45-53.
- 4 Zhiyong Y, Mielczarski E, Mielczarski J, Laub D, Buffat P, Klehm U, Albers P, Lee K, Kulik A, Kiwi-Minsker A, Renken A, Kiwi J. Preparation, stabilization and characterization of TiO<sub>2</sub> on thin polyethylene films (LDPE). Photocatalytic applications. *Water Res.* 2007;41:862-74.
- 5 Roy PK, Surekha P, Rajagopal C, Choudhary V. Degradation behavior of linear low-density polyethylene films containing prooxidants under accelerated test conditions. *J Appl Polym Sci* 2008;108:2726-33.
- 6 Liu GL, Zhu DW, Liao SJ, Ren LY, Cui JZ, Zhou WB. Solid-phase photocatalytic degradation of polyethylene-goethite composite film under UV-light irradiation. *J Hazard Mater.* 2009;172:1424-9.
- 7 Fontanella S, Bonhomme S, Koutny M, Husarova L, Brusson J-M, Courdavault J-P, Pitteri S, Samuel G, Pichon G, Lemaire J, Delort A-M. Comparison of the biodegradability of various polyethylene films containing pro-oxidant additives. *Polym Degrad Stab.* 2010;95:1011-21.
- 8 Saccani A, Toselli M, Pilati F. Improvement of the thermo-oxidative stability of low-density polyethylene films by organic-inorganic hybrid coatings. *Polym Degrad Stab* 2011;96:212-9.
- 9 Roy PK, Surekha P, Raman R, Rajagopal C. Investigating the role of metal oxidation state on the degradation behaviour of LDPE. *Polym Degrad Stab.* 2009;94:1033-9.
- 10 Roy PK, Surekha P, Rajagopal C. Surface oxidation of low-density polyethylene films to improve their susceptibility toward environmental degradation. *J Appl Polym Sci.* 2011;122:2765-73.
- 11 Roy PK, Singh P, Kumar D, Rajagopal C. Manganese stearate initiated photo-oxidative and thermo-oxidative degradation of LDPE, LLDPE and their blends. *J Appl Polym Sci.* 2010;117:524-33.
- 12 Roy PK, Titus S, Surekha P, Tulsi E, Deshmukh C, Rajagopal C. Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium. *Polym Degrad Stab.* 2008;93:1917-22.
- 13 Konduri MKR, Koteswarareddy G, Kumar DBR, Reddy BV, Narasu ML. Effect of pro-oxidants on biodegradation of polyethylene (LDPE) by indigenous fungal isolate, *Aspergillus oryzae*. *J Appl Polym Sci* 2011;120:3536-45.
- 14 Magagula B, Nhlapo Nontete, Focke WW. Mn<sub>2</sub>Al-LDH- and Co<sub>2</sub>Al-LDH-stearate as photodegradants for LDPE film. *Polym Degrad Stab* 2009;94:947-54.
- 15 Roy PK, Surekha P, Rajagopal C, Choundhary V. Thermal degradation studies of LDPE containing cobalt stearate as pro-oxidant. *Express Polym Lett.* 2007;1:208-16.
- 16 Ammala A, Bateman S, Dean K, Petinakis E, Sangwan P, Wong S, Yuan Q, Yu L, Patrick C, Leong KH. An overview of degradable and biodegradable polyolefins. *Prog Polym Sci* 2011;36:1015-49.
- 17 Kyrikou I, Briassoulis D. Biodegradation of agricultural plastic films: a critical review. *J Polym Environ.* 2007;15:125-50.
- 18 Rosa DS, Grillo D, Bardi MAG, Calil MR, Guedes CGF, Ramires EC, Frollini E. Mechanical, thermal and morphological characterization of polypropylene/biodegradable polyester blends with additives. *Polym Test.* 2009;28:836-42.