

Correlation Between Onset Oxidation Temperature (OOT) and Fourier Transform Infrared Spectroscopy (FTIR) for Monitoring the Restabilization of Recycled Low-density Polyethylene (LDPE)

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Abstract: In this work a new method was developed for monitoring the oxidative stability of restabilized and non-restabilized low-density polyethylene (LDPE) during multiple extrusion cycles. The method is based on correlations between Fourier Transform Infrared spectroscopy (FTIR) and Onset Oxidation Temperature (OOT). Non-linear calibration curves correlating the concentration of primary or secondary antioxidants and the OOT values were obtained.

Keywords: Recycling of LDPE, thermogravimetry, FTIR, restabilization, primary antioxidants, secondary antioxidants.

Introduction

In relation to plastics, the term recycling is generally taken to mean a series of processing operations performed to produce secondary materials for manufacturing of various types of articles. Post-consumer plastics recycling is not only a high priority item in terms of current public opinion, it has also become an urgent necessity. It is obvious that simple recycling to produce secondary materials cannot by itself solve the environmental problems caused by discarded plastics, not only because of the large quantities involved, but also because of the many types of polymers that are difficult to separate or process together. In the latter case, particularly the articles produced with the recycled materials would have poor mechanical properties and few possibilities for use^[1].

Polyolefins and polyesters are two of the most widely consumed plastics available in large amounts from post-consumer wastes. Polyolefins such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP) are mainly used in pipes, films, blown bottles, agricultural sacks, greenhouses and other packaging. Polyesters such as polyethylene terephthalate (PET) are widely used in carbonated soft drink bottles, textile fibers and films^[2-5].

Some driving forces are accelerating and expanding the demand for these recycled materials, particularly the activities of packagers who wish to use recycled plastic to achieve more environmentally friendly packaging. The properties of recycled plastics are generally poor and strongly dependent on the degradation that occurs in these materials during their lifetime and during reprocessing^[6]. The extent of the chemical changes during reprocessing and subsequent service greatly depends on the chemical reactivity and particularly on the oxidative stability of the polymer. The latter depends in turn on the presence

of antioxidants and stabilizers that are either added or remain from the initial use.

Particularly in the case of LDPE film used in greenhouses, the oxidation is severe because of the intense exposure to the environment. Consequently, the amount of restabilization agent added during reprocessing becomes a significant factor for both cost and upgrading the post-use material.

Statheropoulos et al.^[7] used the oxidative induction time (OIT) method based on thermogravimetry for monitoring the restabilization of post-use LDPE samples subjected to multiple extrusion cycles. A linear relationship between the amount of restabilization agent and OIT appeared to exist even though post-use LDPE for greenhouses contained traces of primary and light stabilizers from its first life. Nevertheless, these authors highlighted that the relationship obtained can only be used for calculating the amount of remaining antioxidant in samples subjected to one remelting cycle because the behavior of the restabilization agent changes after each remelting cycle. Therefore, it is important to consider that some research^[8-10] has stated that OIT is not only a function of the primary antioxidant concentration but that secondary antioxidant addition may play an important role too. This interaction may create difficulties in quantitative determinations, especially in the case of restabilization.

The purpose of this work was to develop a new method for monitoring the oxidative stability of restabilized and non-restabilized LDPE during multiple extrusion cycles. The method is based on correlations between Fourier Transform Infrared spectroscopy (FTIR) and Onset Oxidation Temperature (OOT) based on thermogravimetry. The possibility of using the measurements from this new methodology for quantitative determination of the restabilization system was investigated.

Experimental

Raw materials

LDPE (MFI = 30 g/10 min, $\rho = 0.92 \text{ g/cm}^3$) without additives was very kindly supplied by UNION CARBIDE. The primary and secondary antioxidants were Irganox 1010 (phenolic based material, see Figure 1a) and Irgafos 168 (organophosphite based material, see Figure 1b), respectively. These are CIBA commercial products

Sample preparation

Films for FTIR measurements

The samples examined were virgin LDPE pellets and virgin LDPE additivated with Irganox 1010 and Irgafos 168. The following methodology was used for preparing the latter samples: virgin LDPE (1 g) and the primary and secondary antioxidants were melt mixed. Different samples were prepared at a constant ratio of 1/2 w/w between the Irganox 1010 and Irgafos 168, respectively. As a percentage, this relationship was changed from 0.01%/0.02% to 1%/2% with respect to the total mass of virgin LDPE. The homogenization stage was done by melt mixing of the LDPE and the antioxidants at 170°C for 4 minutes inside an aluminum tube put in a micro oven. After this, the mixture was cooled at room temperature and then film samples were obtained by hot pressing the mixture at 170°C between steel plates with cellulose acetate commercial film as the substrate. This process was conducted for 2 min without applying pressure, followed by 30 sec under pressure at 0.5, 1.0 and 2.0 metric tons, respectively, and then quenched in a water bath at 25 °C. The mean thicknesses of the films were 60 μm .

Multiple extrusion samples

A mixture of virgin LDPE (500 g) and the primary and secondary antioxidants with a fixed proportion of Irganox 1010/Irgafos168 equal to 1%/2% was extruded four times by using a B & P Process Equipment and System twin screw co-rotation extruder, model MT 14TC-25:1, $\Phi=14 \text{ mm}$ and $L/D = 25$. The temperatures of the zones were set at 170, 180, 190, 190, and 200 °C (maximum) throughout all the extrusion cycles. The screw rotation speed was kept at 50 rpm. The mixture output was quenched in a water bath and then palletized. Between each extrusion cycle, the palletized sample was

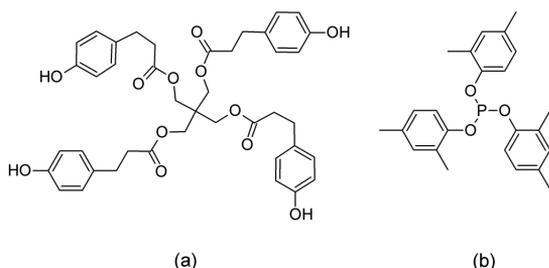


Figure 1. Representation of the chemical structure of the antioxidants: (a) Irganox 1010 and (b) Irgafos 168.

dried at 70 °C for 12 hours before the new extrusion. After this, films of the extruded samples were made following the same methodology described above for the FTIR measurements.

Sample characterization

FTIR measurements

The FTIR spectra in absorbance for the virgin LDPE and mixtures of LDPE and antioxidants before and after the extrusion cycles were done on sample films, recorded with a Hartmann & Braun MB SERIES spectrometer in the region of 400 to 4000 cm^{-1} with 2 cm^{-1} resolution after 64 scans.

To characterize only the antioxidants, the FTIR spectra were obtained on KBr pastilles that contained 0.001 g antioxidant/0.1 g KBr that had been previously dried at 100 °C for 4 hours.

Thermogravimetric analysis measurements

The thermogravimetric analysis of the virgin LDPE and the mixtures of LDPE and antioxidants, before and after the extrusion cycles, were performed with a TG-DTA model Q600 TA instrument. Weight changes were recorded as a function of temperature with heating at 10 °C min^{-1} from room temperature to 500 °C with a sample weighing about 40 mg in a platinum crucible under an oxygen flux of 90 $\text{cm}^3 \text{min}^{-1}$.

When the polymer undergoes thermal degradation, the beginning is defined as the onset oxidation temperature (Thermo gravimetric-OOT).

Results and Discussions

In Figure 2, the FTIR absorbance spectra for the LDPE, Irganox 1010, and Irgafos 168 raw materials are presented.

In the antioxidants' spectra shown in Figure 2, two specific bands with an arrow are seen. The 1740 cm^{-1} band in the Irganox 1010 spectra is attributed to the carbonyl ester group and the 1080 cm^{-1} band in the Irgafos 168 spectra is attributed to the P-O-C₆H₅ group. It is important to remember that these two bands do not overlap some bands of the LDPE spectra and this can be used to quantify the antioxidant content. For this reason,

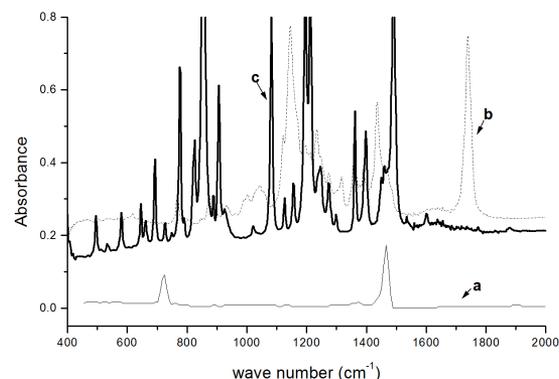


Figure 2. FTIR absorbance spectra for the raw materials: a) LDPE, b) Irganox 1010, and c) Irgafos 168.

the areas related to these bands were obtained for each studied sample by using deconvolution mathematical methods from the Lorentzian function. Figures 3 and 4 show typical results, obtained for Irgafos 168 and Irganox 1010, respectively.

In the determination of the antioxidant content all obtained areas (A, arbitrary units) are normalized by the specific sample thickness (L, μm) in order to prevent influence of the thickness sample. In Figure 4, the representation of the parameter A/L (mean values) is shown as a function of the antioxidant concentration for all LDPE samples studied. The error bars in the A/L parameter indicate that its value is determined in quadruplicate by considering four different regions of the film sample analyzed.

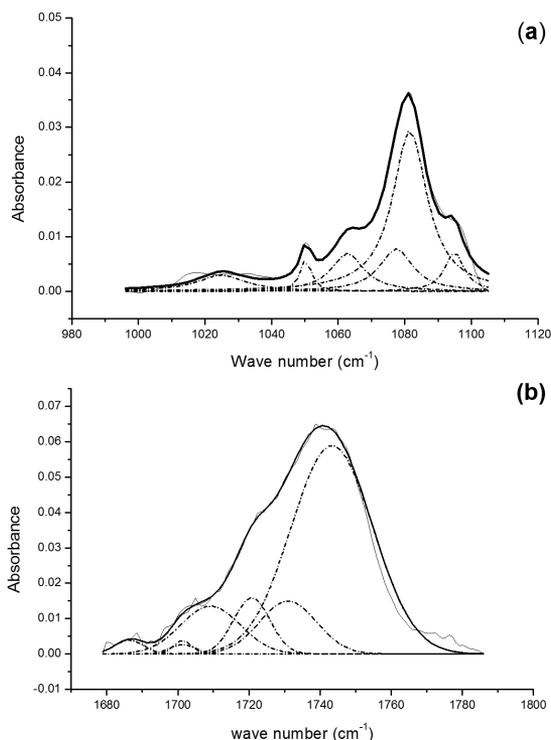


Figure 3. Typical deconvolution result for the FTIR absorbance spectra : (a) region around 1080 cm^{-1} for Irgafos 168; (b) region around 1740 cm^{-1} for Irganox 1010.

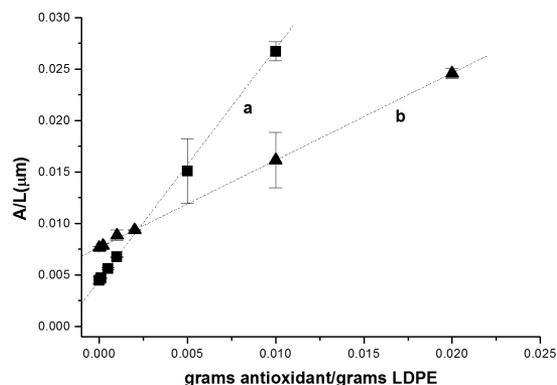


Figure 4. Parameter A/L as a function of antioxidant concentration in LDPE samples: a) Irganox 1010 and b) Irgafos 168.

The results obtained for both antioxidants showed good linear correlation, which corroborates with the Lambert-Beer law.

From the linear fit applied in the curves of Figure 4, the following equations were obtained relating the parameter A/L with the antioxidant concentration in the LDPE samples studied:

$$\text{Irganox 1010: } A/L(\mu\text{m}) = 0.0049 + 2.25 \times C(\text{g/g de LDPE}) \quad (1)$$

$$\text{Irgafos 168: } A/L(\mu\text{m}) = 0.0076 + 0.84 \times C(\text{g/g de LDPE}) \quad (2)$$

In Figure 5, considering the sample LDPE that was prepared with the addition of the primary and secondary antioxidants in the proportion of 1%/2%, the representation of the parameter A/L (for each antioxidant) is shown as a function of the various remelting cycles (extrusions).

From Equations 1 and 2 it is possible to calculate the primary and secondary antioxidant concentration for each remelting cycle. The results obtained are shown in Figure 6 as a function of the various remelting cycles.

For both antioxidants, as expected, their concentrations decrease after each remelting cycle, but it is very interesting to note that when allowing for the error

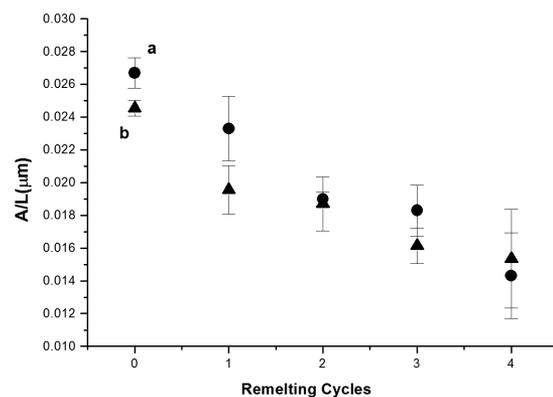


Figure 5. Parameter A/L for the primary and secondary antioxidants present in the LDPE sample for various remelting cycles: a) Irganox 1010 and b) Irgafos 168.

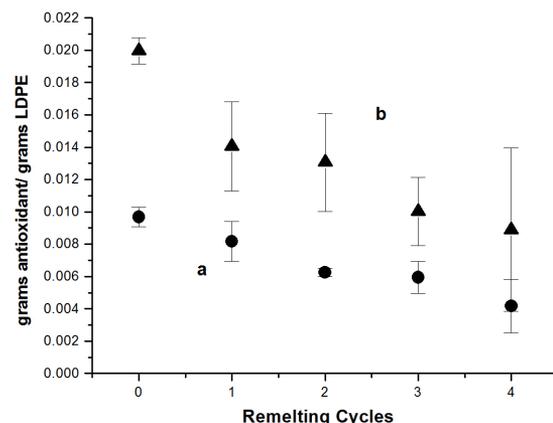


Figure 6. Antioxidant concentration in the LDPE sample for various remelting cycles: a) Irganox 1010 and b) Irgafos 168.

bars, the initial relationship of 1/2 w/w between the Irganox 1010 and Irgafos 168 remained practically constant.

In order to study the effect of primary and secondary antioxidants after each remelting cycle, the onset oxidation temperature (Thermo gravimetric-OOT) was monitored and the results obtained are shown in Figure 7. The presence or effectiveness of antioxidants may be determined by this test method.

As can be seen in Figure 7, the OOT values decrease after each remelting cycle due to antioxidant consumption. It is interesting to note that the slope of the curve decreases in the region between the first and third remelting cycle and then in the region between the third and fourth remelting it abruptly increases. This fact may indicate that a minimum value for both the primary and secondary antioxidant is necessary to prevent LDPE oxidation during the melting process, and if the residual concentration of these antioxidants is lower than this minimum value LDPE oxidation will occur.

It is obvious that the post-consumer polyolefins cannot be safely processed without proper restabilization. Model experiments indicate that even addition of an aromatic phosphite alone enhances the stability during

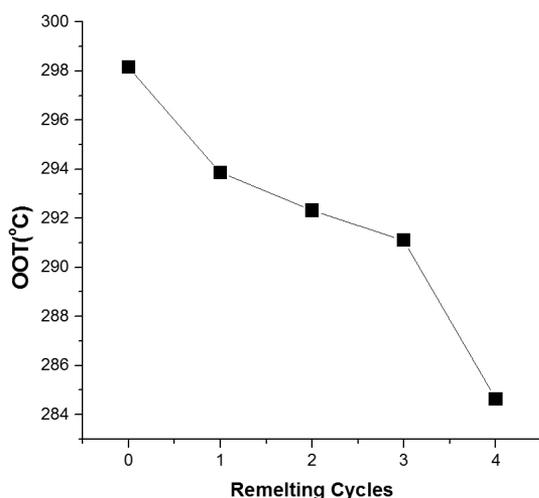


Figure 7. OOT at various remelting cycles.

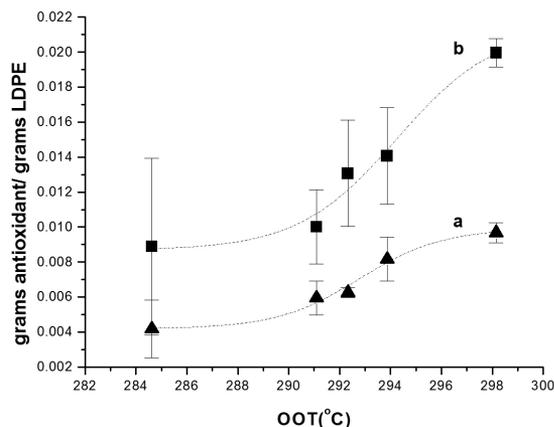


Figure 8. Oxidant concentration as a function of OOT: (a) Irganox 1010 and (b) Irgafos 168.

subsequent processing and heat aging. The restabilization does not 'rejuvenate' the aged polyolefin by removing the sensitizing carbonyl groups; however, their influence is effectively reduced and hydroperoxides that form during aging are deactivated.

Since the oxidant concentration and the OOT values are related to the effect of the various remelting cycles from Figures 6 and 7, these two parameters can also be related to each other. The result of this is shown in Figure 8.

From the non-linear fit applied to the curves of Figure 8, the following equations can be stated:

$$\text{Irganox 1010: } C(\text{g/g}) = [-0,0058] / \left[1 + \exp\left(\text{OOT}(\text{°C}) - 292,78\right) 1,62 \right] + 0,0099 \quad (3)$$

$$\text{Irgafos 168: } C(\text{g/g}) = [-0,124] / \left[1 + \exp\left(\text{OOT}(\text{°C}) - 294,25\right) 1,94 \right] + 0,021 \quad (4)$$

From these equations it is possible to determine the OOT value of a specific recycled LDPE sample and to estimate the concentration of primary and secondary antioxidants for its restabilization, which has become a significant factor for both the cost and upgrading of post-use material.

The residual content of stabilizers in aged recycled polymers is often insufficient for effective protection during reprocessing and subsequent new application. Restabilization enables the re-use of recycled plastics for high-value products.

The use of recycled plastics in new and demanding applications will continue. In addition to technological developments (e.g. separation techniques), compatibilizers, additives, and especially restabilization will contribute to the growth of recyclates.

Conclusions

Infrared spectroscopy and thermogravimetry proved to be simple and accurate techniques for monitoring the restabilization of LDPE samples subjected to multiple extrusion cycles and also for obtaining non-linear calibration curves that correlate the concentration of primary or secondary antioxidants with OOT values. Furthermore, the method can be used to test the sensitivity to structural differences for LDPE from various manufacturers and for different samples of recycled LDPE.

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References

1. La Mantia, F. P. - "Basic concepts in plastics recycling", in: Recycling of PVC and mixed plastics, La Mantia FP ed., Chem. Tec., Toronto (1996).
2. Chen, C. & Lai, F. S. - Polym. Eng. Sci., **34**, p.472 (1994). <http://dx.doi.org/10.1002/pen.760340603>

3. Dimitrova, T. L.; La Mantia, F. P.; Pilati, F.; Toselli, M.; Valenza, A. & Visco, A. - *Polymer*, **41**, p.4817 (2000). [http://dx.doi.org/10.1016/S0032-3861\(99\)00709-0](http://dx.doi.org/10.1016/S0032-3861(99)00709-0)
4. Pluta, M.; Bartczak, Z.; Pawlak, A.; Galeski, A. & Pracella, M. - *J. Appl. Polym. Sci.*, **82**, p.1423 (2001). <http://dx.doi.org/10.1002/app.1980>
5. Ruvolo-Filho, A. & Marconcini, J. M. - *Mat. Res.*, **10**, p.341 (2007). <http://dx.doi.org/10.1590/S1516-14392007000400004>
6. Sadrmohaghegh, C. & Scott, G. - *Eur. Polym. J.*, **16**, p.1037 (1980). [http://dx.doi.org/10.1016/0014-3057\(80\)90220-7](http://dx.doi.org/10.1016/0014-3057(80)90220-7)
7. Kyriakou, S. A.; Statheropoulos, M.; Parissakis, G. K.; Papaspyrides, C. D. & Kartalis, C. N. - *Polym. Degrad. Stabil.*, **66**, p.49 (1999). [http://dx.doi.org/10.1016/S0141-3910\(99\)00051-8](http://dx.doi.org/10.1016/S0141-3910(99)00051-8)
8. Moss, S. & Zweifel, H. - *Polym. Degrad. Stabil.*, **25**, p.217 (1989). [http://dx.doi.org/10.1016/S0141-3910\(89\)81009-2](http://dx.doi.org/10.1016/S0141-3910(89)81009-2)
9. Chen, Y. L. & Ranby, B. - *J. P. Sci.*, part A, **28**, p.1847 (1990). <http://dx.doi.org/10.1002/pola.1990.080280717>
10. Uhnat, M. & Latocha, C. - *Polym. Degrad. Stabil.*, **35**, p.163 (1992). [http://dx.doi.org/10.1016/0141-3910\(92\)90108-H](http://dx.doi.org/10.1016/0141-3910(92)90108-H)

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