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OXIDATIVE BEHAVIOR OF IRRADIATED POLYPROPYLENE, PREDICTED AS TEMPERATURE-OXIDATIVE INDUCTION TIME (TOIT)

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ABSTRACT

Organic materials undergo degradation reactions in the presence of oxygen. Most of known polymers have structural elements that are prone to oxidative degradation reactions: inadequate antioxidant content can contribute to this failure. Associated to it, radiation can impart to thermoplastic polymers, at a given level, non desirable effects, compromising, this way, "end-use" of final product.

A new Temperature-Oxidative Induction Time – TOIT (once conventional ASTM-D-3895-95 method showed itself useless for this purpose), is being developed, in order to evaluate radiation effects in PP, under controlled oxygen atmosphere. Basically, it deals exclusively with a special temperature program, involving dynamic and isothermal techniques, comprising too final TOIT determinations in molten state samples. In resume, the whole test is carried out under nitrogen environment; at approximately 150^{o}C, oxygen is introduced, causing initial breakdown of antioxidant protection, accompanied by energy releasing and an upward deflection of the curve above baseline. The changeover point to oxygen flow is considered the zero time of analysis.

Both Polypropylene (PP), stabilized and non-stabilized (irradiated and non-irradiated) ones were assessed; TOIT within a range from 11 to 35 minutes were achieved, as per well defined thermograms.

Keywords: OIT, PP, irradiation, non-stabilized, stabilized

I. INTRODUCTION

Oxidative Stability is an important in-use property for a wide range of materials, including plastics, oils and lubricants and foods. Although other factors such as temperature and exposure to ultraviolet light can adversely affect a material over a long period of time. Attack by oxygen in the atmosphere is usually the key factor in determining the material's lifetime. Special compounds, called antioxidants are often added to a base material to improve its resistance to attack by oxygen (its oxidative stability). Suppliers of base materials are interested in comparing effects of different antioxidants, as well as different levels of the same antioxidant, so that they can achieve the best compromise between increased lifetime of base material and its cost. Since oxidative stability is an exothermic process, DSC provides a convenient way to determine when significant oxidative degradation and material failure begins. Under OIT standard conditions, the initial breakdown of antioxidant protection is accompanied by a release of energy causing an upward deflection of the curve above the baseline. The period of time during which there is no oxidation is commonly referred to as the induction time. This induction time is either a measure of the amount of antioxidant present in the polymer or the effectiveness of a particular antioxidant used. The long-term stability of polymers protected by antioxidant can be quickly evaluated in this high reaction rate environment. If the amount of antioxidant in the polymer is known, then using the induction time one can calculate the linear rate of antioxidant consumption, considering that a calibration curve has been previously plotted.

In our study, TOIT can be defined as the time to the onset of oxidation of a test specimen, exposed to an oxidizing gas (oxygen). In addition, TOIT will provide qualitative/quantitative results of unknown PP samples, besides its capability of identify them.

II. METHODOLOGY

OIT classical methodology, when applied to pure polyolefins samples, irradiated and non-irradiated ones, yield fractional results, always showing very poor response to the polymer sample history and without any repeatability and reproducibility. This oxidation condition is very harsh for pure and irradiated polymers, particularly PP. Polymers

with tertiary carbon atoms in the repeating units, as PP [3], react with peroxides by intramolecular hydrogen abstraction particularly easily. As a result, PP undergoes pronounced molecular weight degradation in the course of processing and is prone to very fast oxidation and consequently very fast degradation, especially on samples submitted to previous aging and irradiation.

In order to cope with the limitations from traditional OIT method, we decided to develop a more useful method applicable by a much broader set of resins. A new procedure to determine OIT, in non-stabilized and stabilized, irradiated and non-irradiated polypropylene has been recently introduced by our group.[1].

This procedure is really useful to compare stabilization systems of polyolefins due to the simplicity, reliability and low operational cost when associated to very fast results. Formerly, several trials were accomplished, by using standard test methods like ASTM D 3895 – 95 [2] for polyolefins. The new procedure was based on two main features: 1- starting the oxidation on melted samples, at temperatures as low as possible; 2- oxidation under slow heating conditions. So, each sample has a set of two values for both time and temperature, as the new method is not isothermal any longer; consequently, we better call it TOIT standing for oxidative-induction time and temperature. This paper aims to show the results of TOIT and its significance for very similar systems [4 -11].

III. EXPERIMENTAL

Differential Scanning Calorimeter. For the thermal analysis of non-stabilized and stabilized PP resins, irradiated and non-irradiated, a Mettler Toledo Model DSC-822 was used. Samples within a 5-10 mg were placed in standard Al pan, with a pierce in the lid in order to obtain a self-generated atmosphere, i.e., a free access to the surroundings (oxygen flow).

Materials. PP samples, stabilized and non-stabilized ones, were kindly supplied by OPP Petroquimica and comprising different stabilizers and molar mass, accordingly: - PP melt index 1.6 (dg/min), pure, thermal and UV/thermal stabilized; - Pure PPs, melt index 1.6, 0.4 and 3.5.
All samples were gamma irradiated in EMBRARAD (Co 60), within a range from 12.5 kGy to 1,000 kGy, under atmospheres of air, acetylene and butadiene.

IV. METHODOLOGY AND RESULTS

Previous determinations were accomplished in accordance with Table 1:

TABLE 1. Previous determinations accomplished by following Programming Temperature.

Rate (^oC/min)	Hold temp. (^oC)	Hold time (min)	Purpose
20.0	190.0	5.0	Heating under N_2 to melt and to erase previous history
-10.0	150.0	10.0	Cooling below melting point, with the sample still not crystallized
2.0	200.0	-	Slow heating under N_2/O_2 atmosphere

Basically, above procedure established for Temperature-Oxidative Induction Time – TOIT allowed the comparison among all kind of PP resins and the results were reported according to: **time, in minutes/ temperature, in degrees Celsius**. For example, a TOIT equal to **26.4/199.1** means that occurred resin degradation after 26.4 elapsed time of oxygen injection, at a 199.1^{o}C temperature.

As per the selection of the heating rate it is possible to facilitate or complicate the interpretation of the measurement. As the temperature sensor does not measure the temperature directly in the sample, but only in vicinity of the sample, a temperature difference between sample and temperature sensor appears with every thermal analysis measuring cell. This depends on the heating rate and the temperature.

Final slopes detected for each individual TOIT determination were capable of providing resins behavior in terms of resistance to oxidation, in spite of their nature:

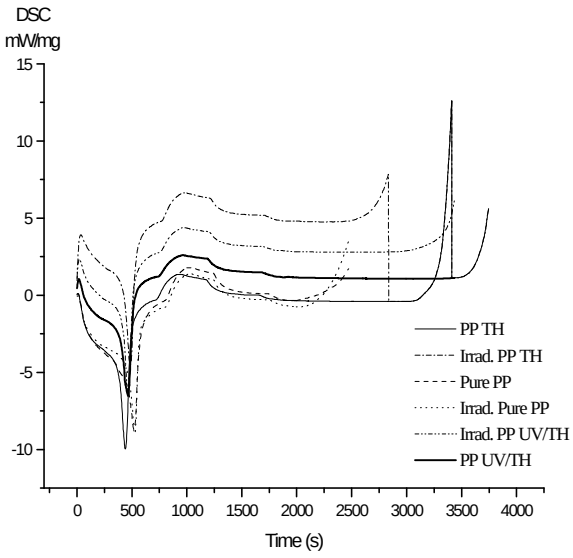

Figure 1. A snapshot of all PP resins tested, stabilized and non-stabilized, irradiated and non-irradiated.

Figure 1 is a miscellaneous of TOIT results, for a given set of tested resins. Proposed method was capable to yield consistent results in regard to molar mass, stabilization and irradiation under acetylene.

Further modifications were accomplished in temperature program, in order to provide more accurate and reliable results for non-stabilized and stabilized PP resins, respectively, (irradiated and non-irradiated ones), as per shown in TABLES 2 and 3:

TABLE 2. Temperature Program for Non-Stabilized PP Resins, irradiated and non-irradiated (initial temperature = 40°C).

Rate (°C/min)	Hold temp. (°C)	Hold time (min)	Purpose
10.0	200.0	10.0	Heating under N_2 to melt and to erase previous history
-10.0	135.0	5.0	Cooling below melting point, with the sample still not crystallized
2.0	200.0	-	Slow heating under N_2/O_2 atmosphere

TABLE 3. Temperature Program for Stabilized PP Resins, irradiated and non-irradiated (initial temperature = 40°C)

Rate (C/min)	Hold temp. (C)	Hold time (min)	Purpose
10.0	200.0	10.0	Heating under N_2 to melt and to erase previous history (1st melting)
-10.0	80.0	2.0	Cooling below melting point, with the sample crystallized (1st crystallization)
10.0	200.0	5.0	Heating under N_2 to melt and to improve molecules reorganization (2nd melting)
-10.0	135.0	2.0	Cooling below melting point, with the sample still not crystallized
-2.0	220.0	-	Slow heating under N_2/O_2 atmosphere

TOIT determinations, as per above methods comprising new temperature programs showed for PP resins assessed expected good and accurate results, according to results shown in Figures 2, 3 and 4 and Tables 4 and 5:

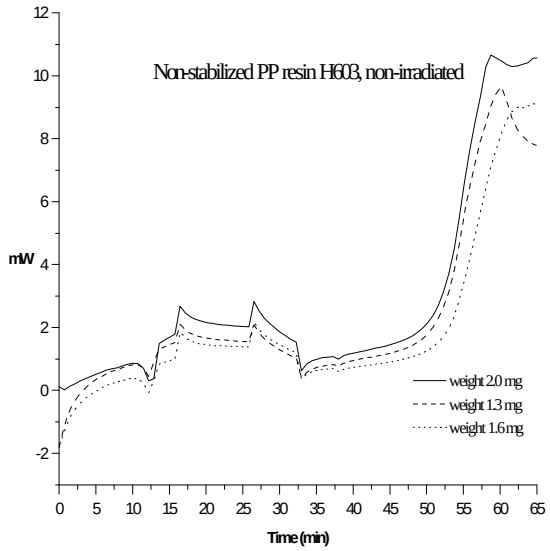

Figure 2. Non-Stabilized PP H603 non-irradiated, in function of weight.

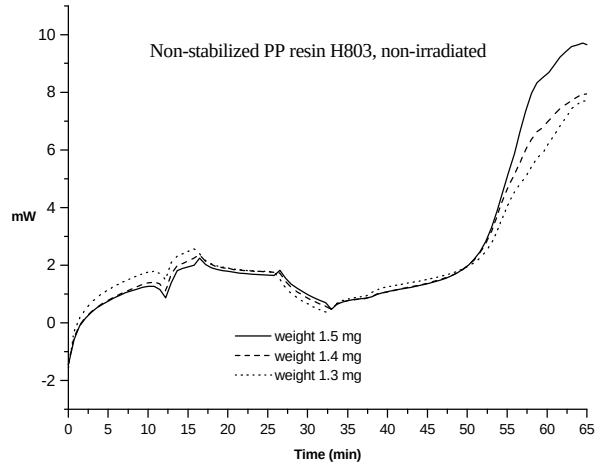

Figure 3. Non-Stabilized PP H803 non-irradiated, in function of weight.

TABLE 4. TOIT for Non-Stabilized H301, H503, H603 and H803 PP Resins (non-irradiated) assessed, at different weights.

Resin	Weight (mg)			
	1.2	1.3	1.5	2.0
H301	-	14.7 /168[a]	15.5/166	14.7/165
H503	15.0/165	14.7/165	14.3/164	-
H603	14.7/164	15.2/165	-	14.7/165
H803	13.8/163	14.3/164	14.0/163	-

a. Degradation time (minutes)/degradation temperature (°C)

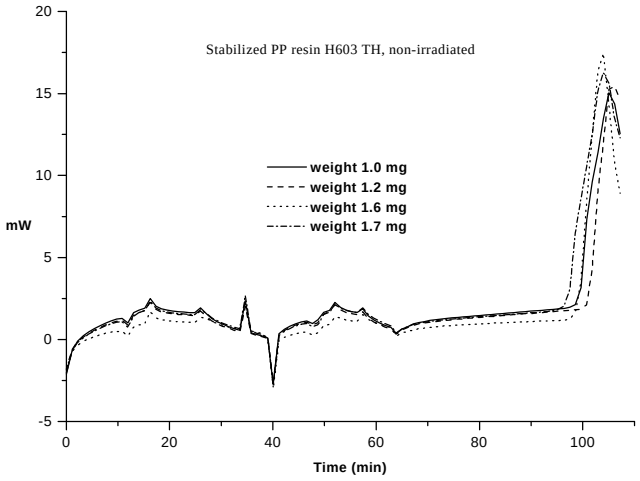

Figure 4. Stabilized H603 non-irradiated, in function of weight.

TABLE 5. TOIT for assessed stabilized H503, H603 TH and UV/TH PP resins (non-irradiated), at different weights.

Resin	Weight (mg)			
	1.0	1.1	1.2	1.7
H503	-	34.4/204	34.8/204	23.5/197
H603-TH	31.7/198	-	31.3/198	31.5/198
H603-UV/TH	14.7/164	15.2/165	-	14.7/165

In order to check the feasibility of proposed method in terms of detecting different characteristics among samples exhibiting diverse nature, oxidative behavior for irradiated PP resins was too evaluated.

PP resins samples – non stabilized H603 and stabilized H603-TH - were previously kept in well tightly and thick wall metal boxes, under air, acetylene and butadiene environment. Next step comprised gamma irradiation (Co 60) within a 12.5 to 1,000 kGy dose, at a 4.00 kGy/hour rate.

At 12.5 kGy dose, just non-stabilized H603 was TOIT analyzed, under acetylene and butadiene environment, as shown in Table 6:

TABLE 6. Evaluated TOIT for non-stabilized H 603, irradiated under acetylene and butadiene, at 12.5 kGy dose.

Environment	Weight (mg)			
	1.4	1.7	1.8	2.0
Acetylene	14.2/163	16.3/168	-	-
Butadiene	-	-	11.9/174	12.5/175-

At 100, 200 and 1,000 kGy doses, both non-stabilized and stabilized H603 were only air-irradiated, according to data presented in Tables 7 and 8:

TABLE 7. Evaluated TOIT for non-stabilized H 603, irradiated under air, at 100, 200 and 1,000 kGy.

Weight (mg)	Doses (kGy)		
	100	200	1,000
1.0	-	-	10.5/156
1.1	-	-	12.4/160
1.3	-	13.4/162	-
1.4	-	12.4/160	-
1.5	12.6/160	-	-
1.6	-	-	11.9/159
1.7	12.1/159	-	-
1.9	-	13.6/162	-
2.1	13.3/162	-	-

TABLE 8. Evaluated TOIT for stabilized H 603-TH, irradiated under air, at 100, 200 and 1000 kGy.

Weight (mg)	Doses (kGy)		
	100	200	1,000
0.9	-	15.8/167	-
1.1	18.6/172	-	-
1.2	16.9/169	-	-
1.4	-	-	17.8/171
1.6	18.6/172	-	-
2.0	-	16.1/167	-
2.4	-	-	16.9/169
2.5	-	18.3/172	-

Aiming to a better view from data obtained as per Tables 7 and 8, plotted graphs for non-stabilized and stabilized oxidative behavior are shown in figures 5 and 6.

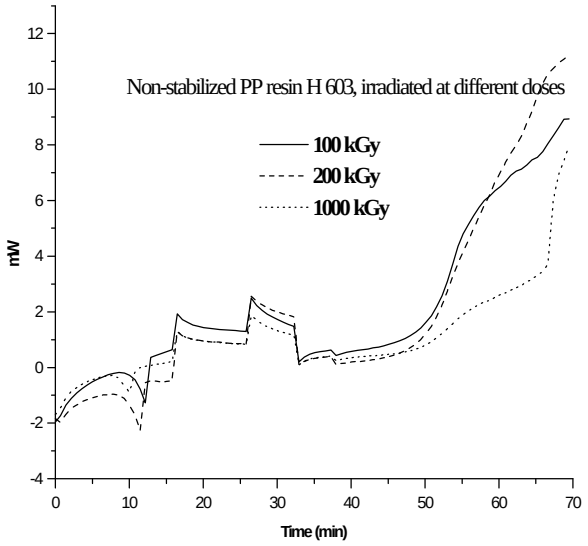

Figure 5. Non-stabilized H603, irradiated under air, at 100, 200 and 1,000 kGy.

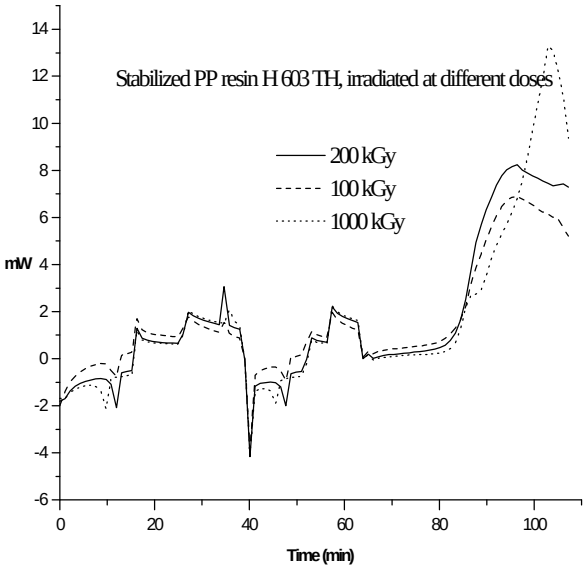

Figure 6. Stabilized H603 irradiated under air, at 100, 200 and 1000 kGy.

V. SUMMARY AND ADVANTAGES OF THE METHOD

- The content of antioxidant in PP resins are able to be evaluated, according to a calibration curve previously plotted;
- Small samples amounts within a 5 to 10 mg, are necessary to perform the test;
- Brief analysis of time: approximately 60 minutes;
- High accuracy of analysis;
- Automatic evaluation of TOIT from an antioxidant curve previously plotted;
- Routine and research analyses made possible by modern TOIT measuring and evaluation systems;
- TOIT measurements possible for non-stabilized and stabilized PP resins.

VI - CONCLUSIONS

Pure, non-stabilized PP resins, showed a medium value for TOIT of 14.6/165, independent of their different molecular weight. After subjected to gamma irradiation, under different atmospheres and doses, just a slight reduction was observed, according to:

- irradiated at 12.5 kGy, under acetylene: none significant variation was detected; therefore, more tests will have to be performed in order to prove it;
- irradiated at 12.5 kGy, under butadiene: a new trend was observed: 12,0/175. So, further tests will have to be performed, before ratifying this as a general rule;
- irradiated under air, at 100, 200 and 1000 kGy: TOIT medium value decreased to 12.5/160, with no significant evidences among irradiation high doses

PP stabilized resins showed to be greatly affected to gamma irradiation, according to results found; from a previous TOIT result around 31.3/190, H 603-TH, when subjected to 100, 200 and 1000 kGy presented TOIT results around 12.7/160. The thermal stabilizer is supposed to be partially consumed during irradiation.

Therefore, as shown by non-stabilized resins, no significant differences were observed among three gamma irradiation doses 100, 200 and 1,000 kGy.

New methodology proved to be effective and sensitive in pointing differences among samples from different characteristics and treatment.

Presently are being provided data consolidation as per developed TOIT method, in order to successfully predict the oxidative behavior of Polypropylene, in general.

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