PERGAMON

Radiation Physics and Chemistry 63 (2002) 489–492

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Temperature dependent oxidative-induction time (TOIT) of irradiated and non-irradiated polypropylene—a new method

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Abstract

OIT's oxidation condition is very harsh for pure and irradiated polymers, particularly PP. 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.

We developed a more useful method applicable by a much broader set of resins. Our group has recently introduced a new procedure to determine OIT, in non-stabilized and stabilized, irradiated and non-irradiated polypropylene. 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 of time and temperature, as the new method is not isothermal any longer, so we better call it "Temperature dependent oxidative induction-time". The new method showed itself as reproducible, sensitive to small changes in additive compositions and simple and inexpensive. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyolefins; Oxidation; Irradiated polypropylene; DSC; OIT

1. Introduction

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 the 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.

OIT classical methodology, when applied to pure polyolefin 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, 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 of the 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 (Lugão et al., 2000a, b). This procedure is really useful to compare

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PII: S0969-806X(01)00544-8

stabilization systems of polyolefins due to the simplicity, reliability and low operational cost associated with very fast results. Formerly, several trials were accomplished, by using standard test methods like ASTM D 3895–95 (ASTM, 1995) 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 temperature oxidative-induction time (TOIT). This paper aims to show the results of TOIT and its significance for very similar systems.

2. Materials

The PP samples were kindly supplied by OPP Petroquimica and had different stabilizers and molar mass (PP melt index 1.6 (dg/min), pure (PP pure), thermally stabilized (PP TH) and UV/thermal stabilized (PP TH/UV)) the irradiations were performed at EMBRARAD, an industrial gamma facility, at 12.5 kGy dose, in an atmosphere of acetylene. PPI stands for irradiated PP.

DSC programming is showed in Table 1. It is important to note that after the first heating to the melt and cooling to 150°C cycle, the resin even below its melting point is still melted, as it did not reach the crystallization temperature. So, the sample can be considered homogeneous with regard to surface quality and oxygen diffusion.

3. Results

Table 2 shows the results of TOIT for a variety of samples. TOIT results will be reported according to a pair of values of *temperature* (°C) and *time* (min). For example:—a TOIT pair of values of *199.07/26.37* means that a resin oxidative degradation occurred at 199.07°C after an elapsed time of 26.37 min, from oxygen injection.

Table 2
TOIT pair of results of selected samples

PP type	Weight (mg)	Temp. (°C)	OIT (min)
PP UV/TH	7.62	197.14	25.86
PP TH	7.84	196.48	25.35
PP pure H603	8.09	163.74	8.36
PPI UV/TH	6.18	200.10	27.22
PPI TH	6.28	179.17	16.59
PPI pure H603	8.04	160.29	6.58

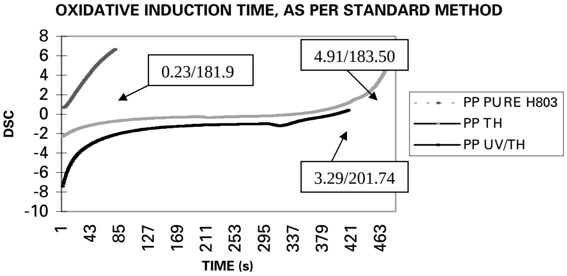

Fig. 1. OIT values for stabilized and non-stabilized PP resins, from 181.9°C, temperature corresponding to “zero time”.

Results shown in Table 2 can be better visualized when compared as pair of resins in a graphic representation as shown in Figs. 2–4.

By formerly using Standard Test Method ASTM D 3895–95, it was impossible to obtain repeatable and reproducible results in all PP samples; the graph corresponding to Fig. 1 was extracted from complete PP graphs

Non-stabilized resins were not capable of providing readable results; they suffered a sudden degradation, as soon as they were submitted to induced oxygen environment. Stabilized resins, in spite of presenting detectable values, were short of repeatability in all trials accomplished.

Fig. 2 shows the comparison of PP stabilized irradiated versus non-irradiated. The TOIT procedure provided a set of meaningful, reproducible values, where it is possible to confirm the consumptions of stabilizers by irradiation.

Table 1
DSC TOIT programming

Rate (°C/min)	Hold temp. (°C)	Hold time (min)	Comments
20.0	190.0	5.0	Heating in 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 in N_2/O_2 atmosphere

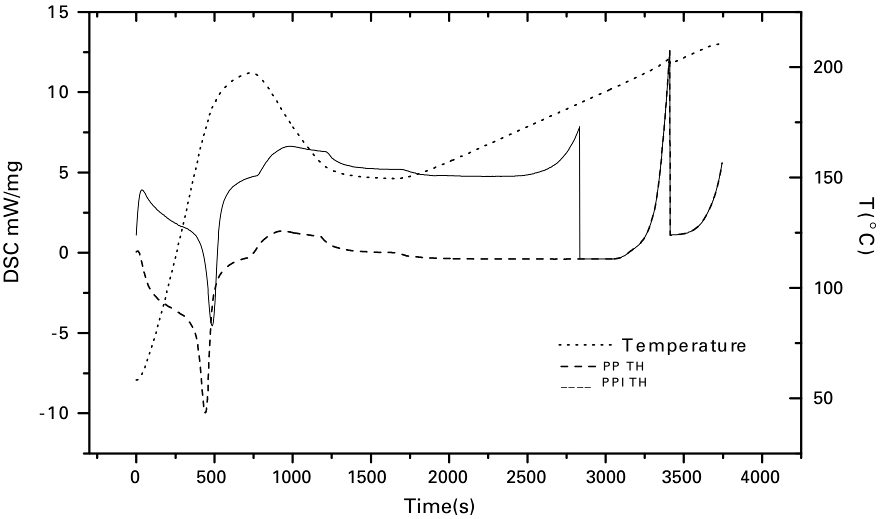

Fig. 2. TOIT values for PP TH, irradiated and non-irradiated, respectively: 16.03/178.18 and 26.37/199.07.

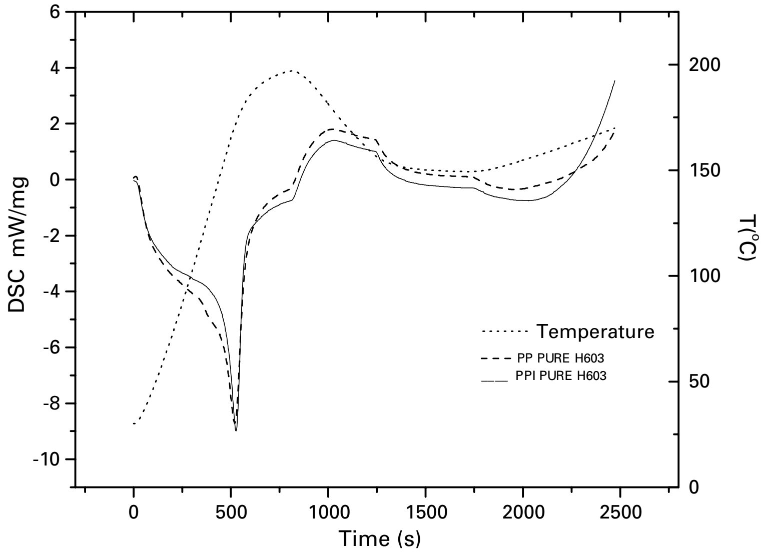

Fig. 3. TOIT values for non-stabilized pure PP, irradiated and non-irradiated, respectively: 6.69/162.26 and 8.37/163.45.

Fig. 3 shows the TOIT comparison between pure PP and PPI. These are non-stabilized samples; so, this is a very important result, which clearly demonstrates the efficacy of the method, as the conventional OIT would provide fractional results, i.e., below 1 min, without any repeatability, reproducibility and significance. It was shown that, even in acetylene, a crosslinking promoter and in an atmosphere oxygen-free, the irradiated resin was more fragile to oxidation. These results confirm previous studies on the irradiation of PP in various atmospheres (Lugão et al., 2000a, b; Black and Lyons, 1957; Dole and Schnabel, 1963). It was shown that PP undergoes sensible degradation at very low doses, even in the absence of O_2.

Fig. 4 shows the TOIT applied to irradiated and non-irradiated UV and thermally stabilized PPs. Again the method provides a clear result showing the consumption of stabilizers.

4. Conclusion

As is well known all the pure resins appear very fragile to oxidation. The stabilized samples showed very

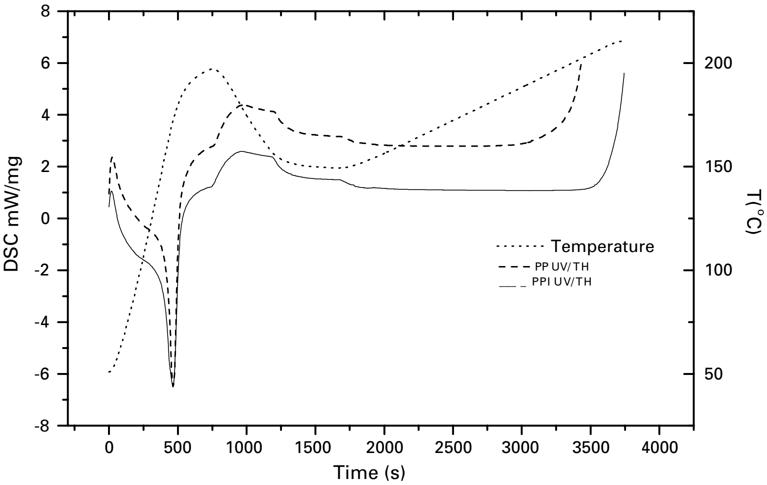

Fig. 4. TOIT values for PP TH-UV, irradiated and non-irradiated, respectively: 25.80/198.58 and 32.24/208.76.

interesting results proving the sensitivity of the new methodology. The irradiated PP UV/TH showed better resistance to oxidation than PP TH. The thermal stabilizer is supposed to be partially consumed during irradiation. Another interesting result was the TOIT of pure PP versus irradiated in acetylene pure PP. Approximately the same result in terms of temperature and time suggests that degradation was not an important reaction in the process. This result was also consistent as acetylene is proved to promote crosslinking in polyolefins samples. So PP irradiated with acetylene at 12.5 kGy is known to have a much broader molecular mass, but approximately the same numerical molecular mass.

Acknowledgements

The authors aclnowledge FAPESP Grant PITE 97/023960 and thank OPP Petroquimica for providing the samples.

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