

Evaluation of the Initial Stages of Polymer Degradation using Chemiluminescence

1. Introduction

Methods to determine the extent of polymer degradation are increasingly being demanded by the polymer and plastic processors. These are required to pin down the causes of defects, improve product quality, evaluate raw material supplies, and to optimize the recycling process. Evaluations needed in the pelletization and moulding process are shown in Fig. 1. Assessment of polymer degradation at each processing stage is desirable as each can result in degradation. Recycling stages such as repelletization of spool runner can also benefit from tests for oxidative polymer degradation. However it is difficult, and often impossible, to detect degradation differences using conventional methods which are frequently too insensitive. This paper introduces chemiluminescence (CL) as the ideal tool for use by industrial polymer and plastic processors to detect the early stages of oxidation.

2. Auto-Oxidation Mechanism and CL Method

The auto-oxidation mechanism is illustrated in Fig. 2. Initially, non-oxidized polymer (RH) generates radicals under stimulation by heat and light. Peroxyl radicals (ROO•) result from the reaction with oxygen. ROO• converts to peroxide (ROOH) which reverts to ROO• on decomposition. ROO• combine to produce excited carbonyls and active oxygen such as singlet oxygen. When the excited compounds are released to the ground state, energy is released as heat and light. The amount of peroxide which correlates to the degree of oxidation is determined by measuring the amount of light. This is the so-called CL method. ROOH resulting from auto-mechanism and the amount of surface ROOH are both recorded using this method.

Classical techniques for evaluating polymer degradation frequently lack sufficient sensitivity. E.g. Fourier-transform infrared spectroscopy (FT-IR) cannot detect generated carbonyl or differences in molecular weight at the early stages of degradation. The CL method, conversely, has the ability to sensitively detect the intermediate product of oxidation ROOH, and thus identify slight differences in degradation and oxidation at the very early stages.

3. CL Analyzer (CLA) System

Tohoku Electronic Industrial's CLA illustrated in Fig. 3 uses a photomultiplier (PMT) from Hamamatsu Photonics K.K. The PMT temperature is controlled below -25°C by use of electronic cooling which suppresses thermal noise and yields a superior signal to noise ratio (S/N). The sample chamber temperature can be adjusted from room temperature to 168°C in a choice of oxygen, air or nitrogen

atmospheres. Responding to the needs of high-thermal resistant plastics, a chamber capable of operating at 350°C has been recently developed. A variety of chamber types are available including an integrated mixing stirrer for analyzing liquid reactions, a flow type for connection to high-performance liquid chromatography, special types for living organisms, built-in laser irradiation type, etc.

4. CLA Operation

CLA is simple to use: all that's required is to insert the chamber containing the sample into the CLA and press the start button. Samples can be solid, liquid or gaseous. There are only four measurement parameters viz. Measurement Mode, Temperature, Time, and Chamber Atmosphere. The Measurement Mode has both Intensity and Spectrum CL measurement functions.

Taking account of CLA's high sensitivity, care is needed to ensure that the chamber, samples and sample dish are clean and contaminant-free. As CLA is a comparative procedure, reference samples are necessary.

5. Analysis

Typical time-course CL behaviour is shown in Fig. 4. On heating the samples in the sample chamber, surface oxidized products such as peroxides decompose and emit light (1). Subsequently, with the antioxidants inhibiting oxidation, the amount of CL is reduced (2). When the antioxidants are consumed, auto-oxidation starts (3). The starting point is the oxidation induction time (OIT) as indicated (4). OIT provides an efficient way to assess a material's oxidation stability without there being any need to oxidise prior to measurement.

6. Evaluation Examples

6-1. Surface oxidation measurement of Polypropylene (PP)

Details of the PP pellets used are shown in Tables 1 and 2. The following were assessed:

- a) Relationship of CL with extrusion temperature and number of recycles
- b) OIT
- c) Comparison of CLA with conventional methods

The results of (a) are shown in Figs. 5-1 and 5-2. The left chart in Fig. 5-1 shows the total CL counts for 5-times recycled pellets at 230, 260, and 300°C (Runs 1,2, and 5). Alongside are shown the total CL count results for pellets recycled 1, 3, and 5-times (Runs 3, 4, and 5) at 300 °C. A strong correlation is

observed between the amount of CL generated at the early stages of oxidation and temperature/number of extrusions.

Fig. 5-2 shows the effect of a range of antioxidants on the CL count (Runs 1, 6, 7, and 8). The varying CL counts are a measure of the relative effectiveness of the antioxidants on retarding oxidation.

The OIT (b) results are shown in Fig. 6. The ascending order of OIT's reflects the decreasing propensity to oxidation.

The comparative test results from (c) are shown in Fig. 7. On the left side is the correlation between oxidation onset temperature from differential scanning calorimetry (DSC) and CL counts and, to the right, the correlation between fluidity from melt flow rate (MFR) and CL counts. Good correlation is seen in each case. The early stages of oxidations are impossible to observe with physical methods such as tensile, flexure, and Charpy impact tests.

CL has a number of advantages over DSC:

- Directly measures ROOH from the CL generated on decomposition of ROOH
- Ease of operation
- Low temperatures measurement (< polymer melting point) ensuring minimal sample damage

The above advantages for PP equally apply to polycarbonates and polyamides.

6-2. CL Image Recording

Use of a highly sensitive CCD camera mounted on a CLA (CLA-IMG) yields clear CL images of the samples in the chamber. CL images of 0, 0.5, and 1.0 wt % Irganox1010 and additive-free PP plates at 160°C in an oxygen environment are shown in Fig. 8. The additive-free sample strongly emits photons arising from oxidation. In contrast, the additive-content samples emit no emissions due to the effect of the antioxidant Irganox1010. The time-course CL changes for virgin and recycled PC plates in an oxygen environment at 220°C are shown to the left in Fig. 9. To the right is the CL image after 30 min. Emissions from recycled PC plate are higher than virgin – not only at the early peak stage but also after the peak.

6-3. Inspection of Raw Material Supplies

The CL results from Japan-produced virgin and 50hr-aged PP compared with an imported PP are shown in Fig. 10. Excessive CL emission is only observed in the aged imported PP. This result well

demonstrates the potential for predicting oxidative degradation by subjecting raw material supplies to CL analysis.

7. Future of CLA

CLA was originally developed to detect the oxidation of food oils and later used for foodstuffs, cosmetics, medicines and polymers. Application in the field of polymers has surged in the last few years. The ability to carry out highly-sensitive detection of the oxidation of polymers has resulted in CLA being used for quality management, quality improvement, shortened development times, reduction of defective products, etc. CL is increasingly being used to commercial advantage throughout processing from raw material supplies inspection, through development and commercialization, to recycling and final product defect analysis.

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• Figures

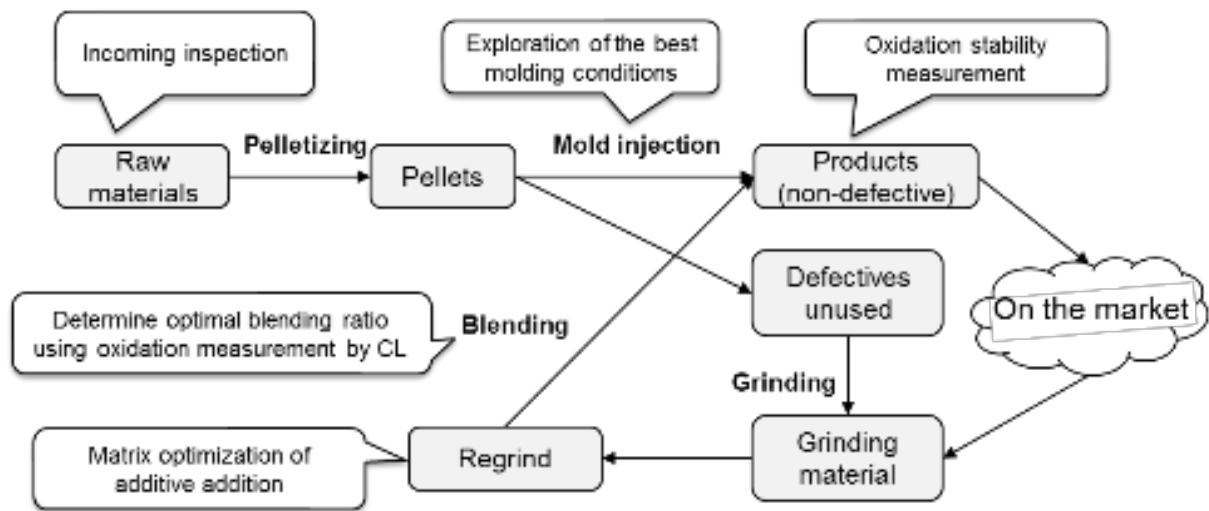


Fig. 1. Optimization of polymer & plastic processing by use of oxidation measurements

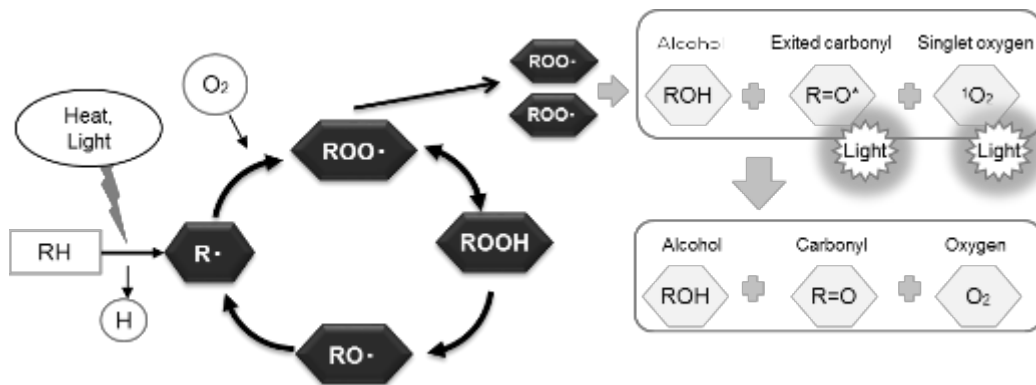


Fig. 2. Auto-oxidation mechanism

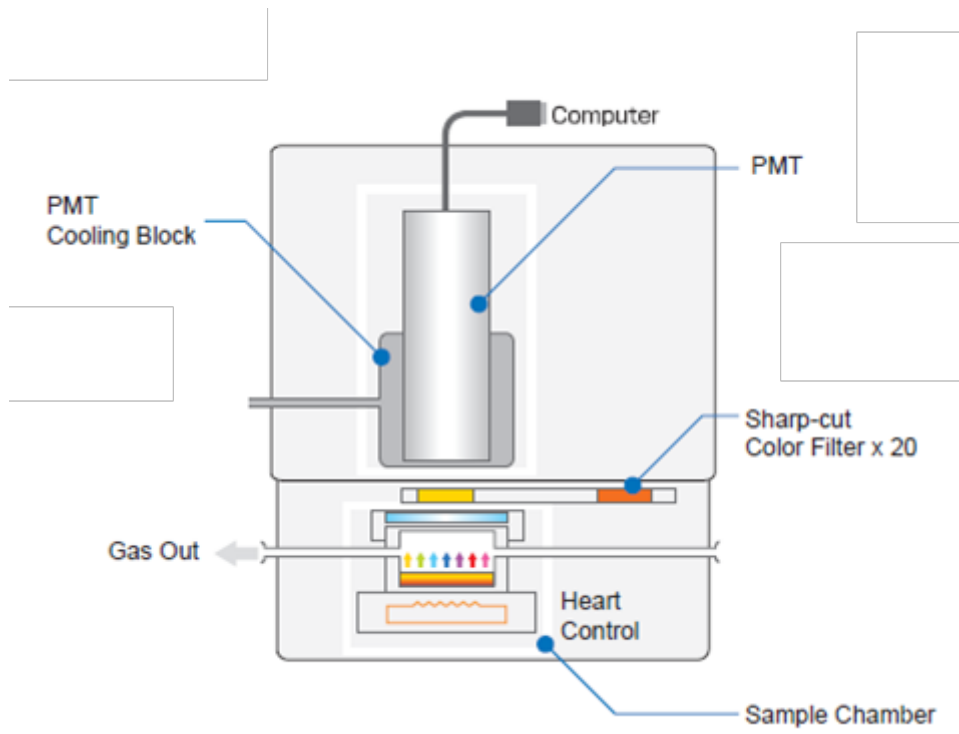


Fig. 3. CLA System

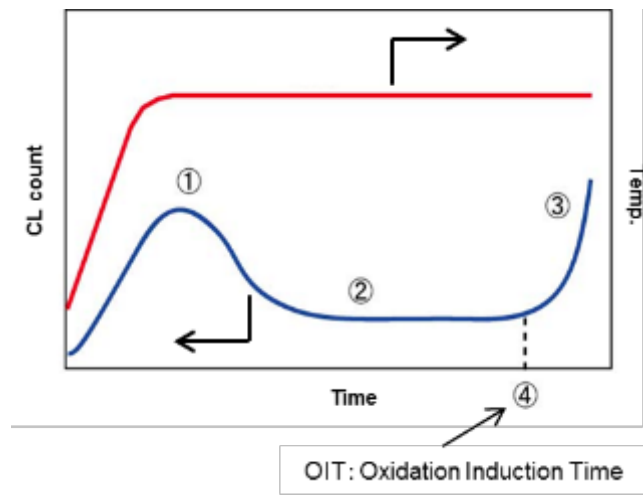


Fig. 4. Typical CL behaviour

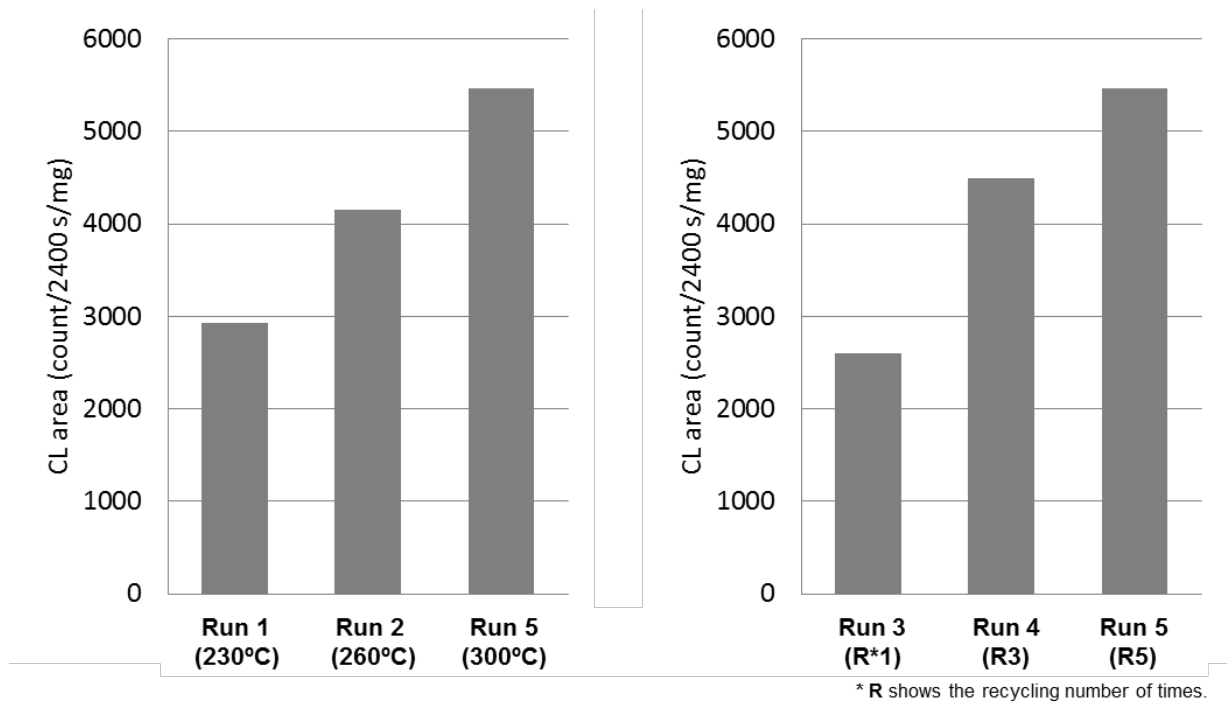


Fig. 5-1. CL counts related to extrusion temperatures and number of cycles

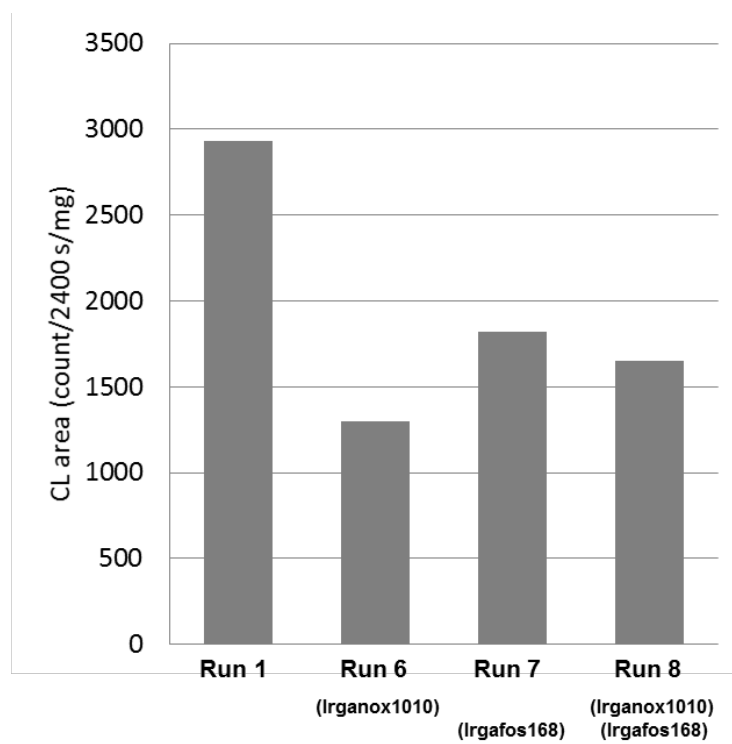


Fig. 5-2. Effect of stabilizer variation on CL

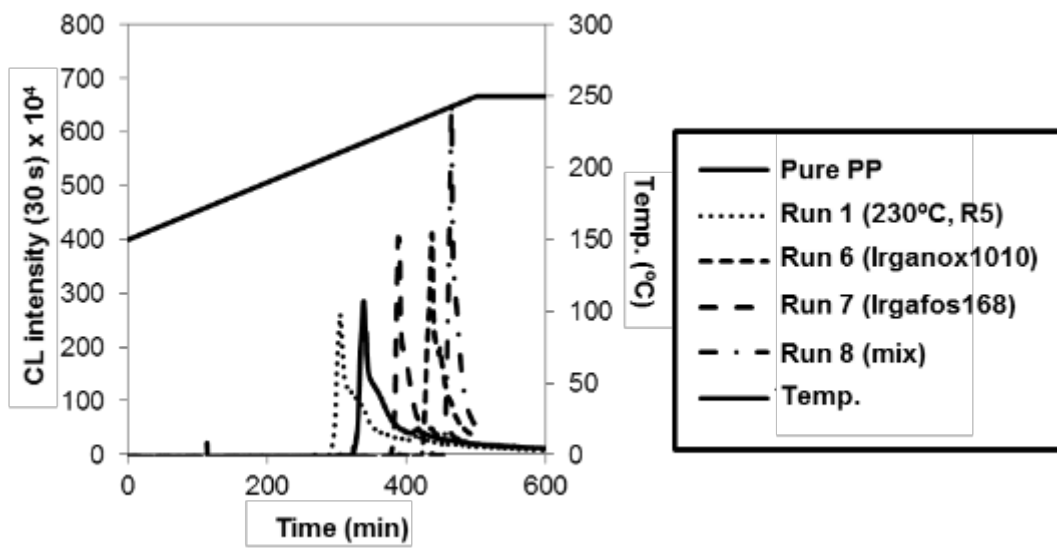


Fig. 6. Effect of stabilizer variation on OIT

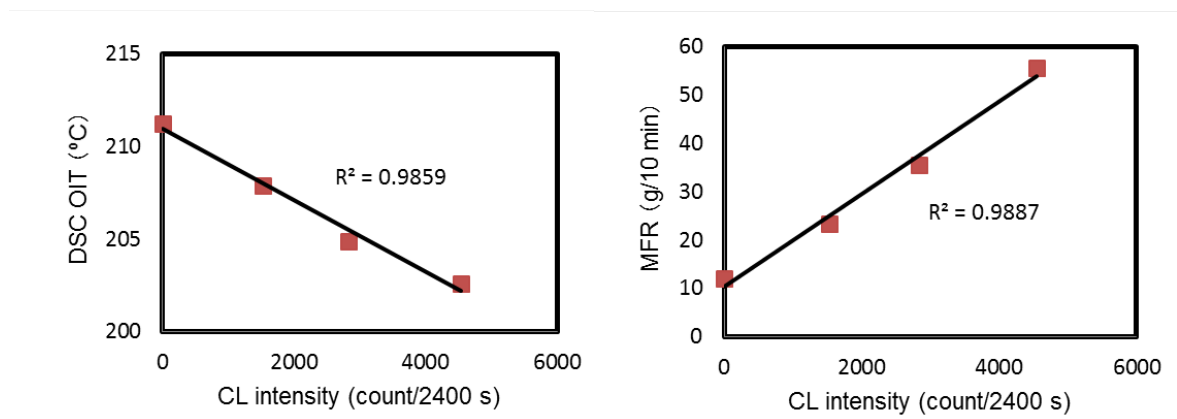


Fig. 7. Correlation of CL with DSC and MFR behaviour

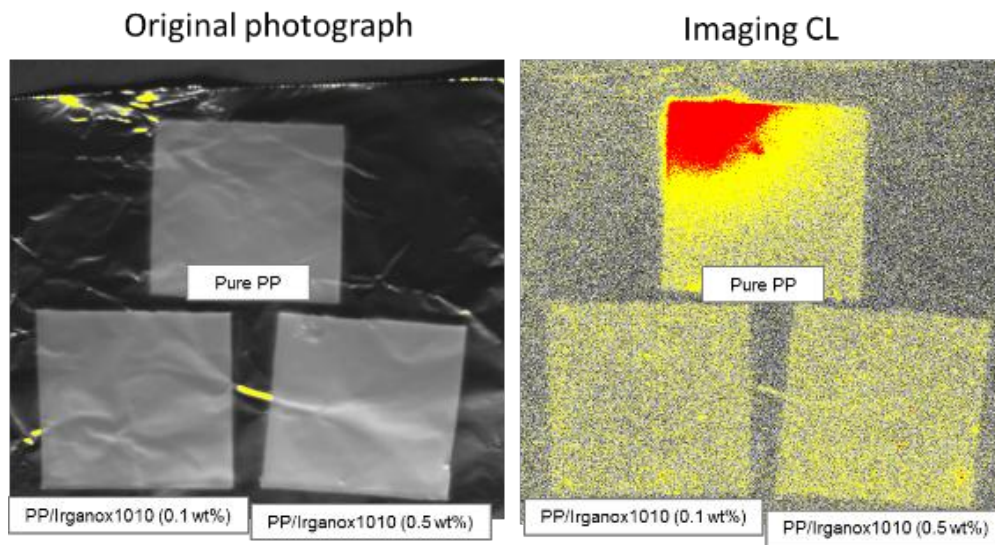


Fig. 8. CL imaging of PP

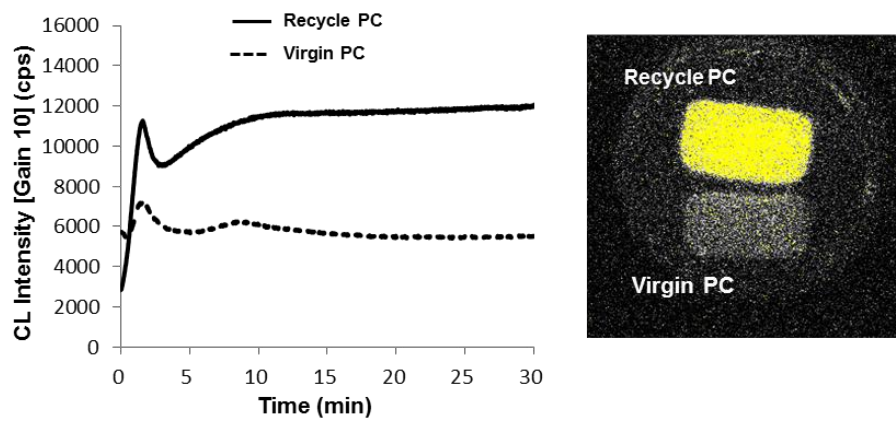


Fig. 9. CL behaviour of PC

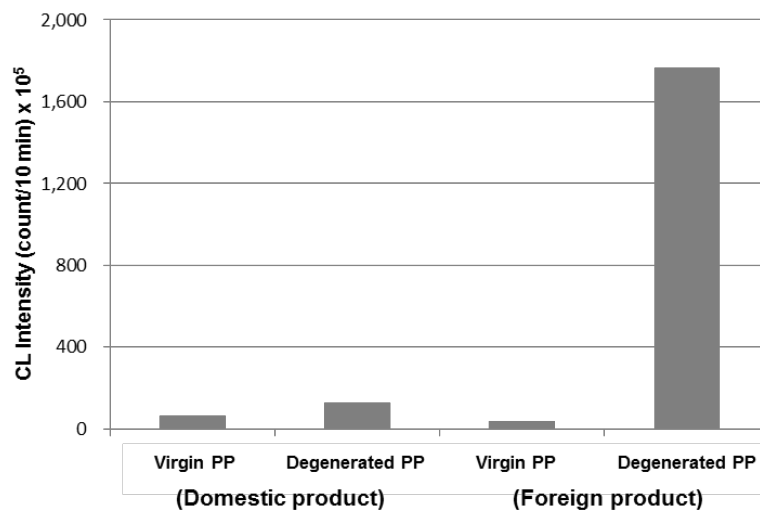


Fig. 10. Comparison of domestic and imported PP's at 180°C in N₂

• **Tables**

Table 1. Materials

Material ^a	Manufacturer
PP ^a	Japan Polypropylene Co., Ltd.
Irganox1010 ^b	BASF Co., Ltd.
Irgafos168 ^c	BASF Co., Ltd.

a: PP pellet grade is Ziegler-Natta catalyst-based isotactic PP of NOVATEC PP MA3.

b: Irganox1010 is phenolic primary antioxidant.

c: Irgafos168 is phosphate processing stabilizer.

Table 2. Preparation conditions of PP-based samples

Run ^a	Irganox1010 (ppm)	Irgafos168 (ppm)	Extrusion Temp. (°C)	Recycle Number
1	0	0	230	5
2	0	0	260	5
3	0	0	300	1
4	0	0	300	3
5	0	0	300	5
6	2000	0	230	5
7	0	4000	230	5
8	2000	4000	230	5

a: PP (Run 1-5), PP/Irganox1010 (Run 6), PP/Irgafos168 (Run 7), and PP/Irganox1010/Irgafos168 (Run 8)