



## Development of high-throughput chemiluminescence imaging instrument for parallel evaluation of polymer lifetime



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### ABSTRACT

A high-throughput chemiluminescence imaging instrument is developed to realize facile and systematic data accumulation in degradation and stabilization of polymer. The instrument works based on imaging chemiluminescence of 100 oxidatively degrading polymer samples that are placed in a multi-cell with arrayed wells being flushed with atmospheric gas, and thereby enables simultaneous acquisition of 100 chemiluminescence curves. The present study reports validation and demonstrative application of the instrument for the oxidative degradation of stabilized polypropylene with a variety of hindered phenol anti-oxidants. Based on quantitatively accurate and large-volume data on oxidative induction time, not only the feasibility of the new instrument but also a number of useful aspects of stabilizers are demonstrated.

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### 1. Introduction

With the continuing expansion of the polymer industry, growing attention has been paid not only on developments of renewable feedstock-based polymer [1–3] but also on reuse/recycle of fossil-based polymer with a dominant share [4–6]. One of major concerns for the latter is to maximize the stability of polymer so as to minimize degradation during its processing and service [5,7–11], in which stabilizers (such as anti-oxidants, light stabilizers, anti-hydrolysis agents, and etc.) play a pivotal role.

A variety of stabilizers have been developed and more or less commercially available for each type of polymer and its application. However, if one aims at enormous stabilization beyond average, only the way is to explore stabilizers and their combination specific to the polymer and application of interests, otherwise, it is inevitable to merely increase the amount of the addition in cost of concomitant drawbacks [12–14]. The problem lies in the difficulty to accumulate systematic knowledge on detailed structure–activity relationships of stabilizers [15–19] and their combination [20–23], whose main causes are summarized below:

- i) The practical activity of a stabilizer is not solely determined by its intrinsic activity, but by many other factors such as mixing uniformity, solubility, migration, extraction/volatilization resistance in polymer, and so on [24–29]. Consequently, the activity of a stabilizer largely depends on the choice of polymer, and the processing and degradation methods [22,30,31], which makes it difficult to accumulate literature data in a systematic way.
- ii) In general, the degradation of polymer initiates and spreads in a spatially heterogeneous manner [32–38]. For example, the degradation of polypropylene (PP) initiates at the proximity of metal catalyst residues [33,36], and subsequently spreads along physicochemically weaker regions such as spherulite interfaces [38] and regions that contain lower concentrations of stabilizers due to incomplete mixing [37]. Therefore, the lifetime of polymer greatly relies on the weakest region present in a sample piece [34]. This fact suggests that measures for the polymer lifetime (such as oxidative induction time) are greatly distributed, since the lifetime is determined by accidental inclusion of the weakest regions in a sample piece. Consequently, the number of sample pieces must be large enough for acquiring quantitative trends.

Thus, it can be concluded that knowledge accumulation on stabilizers is not realized without systematic lifetime measurements for each of stabilizers and their combination under constant

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preparation and degradation protocols. Nonetheless, such systematic lifetime measurements are not practically easy, facing multi-dimensional and time-consuming aspects of experiments: A variety of stabilizers or an enormous number of their combination need to be tested, for each of which repetitive measurements are essential. Lifetime measurements can be greatly shortened through accelerated aging, but the extent of the acceleration is limited for reasonable extrapolation to the reality [39,40]. Likewise, in polymer stabilization, the major bottleneck has been definitely at poor throughput in lifetime measurements in contrast to the required number of the measurements.

Since the last two decades, high-throughput screening (HTS) is becoming increasingly popular as a powerful tool to attain quick screening and combination optimization in materials science [41–43]. The lifetime of polymer can be measured by various methods such as the carbonyl index by IR spectroscopy, the molecular weight measurement using size-exclusion chromatography, the oxidative induction time (OIT) by differential scanning calorimetry (DSC), and so on. However, their extension to high-throughput evaluation of polymer lifetime has been scarcely attempted. Though Wroczynski et al. reported the first application of the HTS concept to the polymer degradation based on facile measurements of the melt flow index (as a measure of chain scission), the method is limited to the degradation in melt processing [44].

The chemiluminescence (CL) method is recognized as one of the most sensitive methods for *in-situ* detection of auto-oxidative degradation of polymer. Due to its mechanical simplicity and high sensitivity, high-throughput evaluation of polymer lifetimes would be realized by applying CL imaging to arrayed polymer samples under oxidation degradation. To date, most of previous efforts relevant to CL imaging have focused on studying space-resolved degradation within a single polymer sample. As was stated by Ahlblad, Gijssman, and their coworkers (who have firstly applied CL imaging to simultaneous acquisition of CL curves for 11 polymer pieces) [45–47], the following major technical issues must be resolved:

- iii) It is well established that oxidative polymer degradation propagates in an infectious manner, in which a degrading sample promotes the degradation of neighboring samples through emission and migration of volatile organic compounds [48,49]. Therefore, arrayed samples under a degradation test need to be physically and atmospherically isolated among each other.
- iv) As the polymer oxidation follows an Arrhenius behavior in terms of temperature, high temperature uniformity is required among arrayed polymer samples [50].

In this contribution, we report a home-made high-throughput CL imaging instrument (HTP-CLI) for realizing lifetime determination of 100 polymer samples in a single measurement. Quantitative accuracy and mutual independence of 100 parallel degradation tests were successfully proven using thermooxidative degradation of stabilized polypropylene (PP) samples. In addition, the efficacy of 10 different hindered phenols was systematically compared based on results of 300 degradation tests, which were acquired within 1 month using HTP-CLI in contrast to *ca.* 3 years for conventional methods.

## 2. Experimental

### 2.1. Materials

Additive-free powder of isotactic polypropylene (iPP,  $M_n = 4.6$

$\times 10^4$ , *mmmm* = 98 mol%) was obtained by bulk polymerization of propylene using a 4th-generation Ziegler–Natta catalyst. Hindered phenol anti-oxidants of AO and IRGANOX series were supplied from ADEKA Corporation and Toyotsu Chemiplas Corporation, respectively (Fig. 1).

### 2.2. Sample preparation

Test samples for the developed instrument were prepared as follows: The pristine polypropylene powder was first melt mixed with 1.0 wt% of AO-50 using a two-roll mixer at 20 rpm and at 185 °C for 15 min. Thus obtained masterbatches were further melt mixed with additional pristine powder at 185 °C for 15 min to adjust the content of AO-50 at either 0.07 or 0.10 wt%. The products were hot-pressed into 100- $\mu$ m-thick films at 230 °C and 10 MPa, and then quenched at 100 °C. Thus obtained sample films were termed as PP-0.07 and PP-0.10 according to the anti-oxidant content. Sample films that contained 0.07 wt% of different anti-oxidants were prepared in a similar manner.

### 2.3. Instrumental

The developed HTP-CLI instrument is illustrated in Fig. 2. As was mentioned, infectious spreading of degradation through volatile degradation products is a technical bottleneck for making parallel degradation tests in a small area. We have successfully eliminated the problem by designing a multi-cell that consists of three layers [51]: A well plate with equally-spaced 10  $\times$  10 columnar wells ( $D = 6.0$  mm,  $H = 3.0$  mm), a flow plate to distribute the air flow into each well, and a chimney plate with open cylinders to eject volatile degradation products with the distributed air flow, thus prohibiting the infectious spreading. The multi-cell is placed in a constant-temperature oven which equips cartridge heaters and a circulating fan. Two glass plates are placed at the top of the oven for heat insulation as well as for chemiluminescence detection. A tricolor CCD camera (BU-51C, BITRAN) is loaded at the top of the system. Dry air is supplied at a controlled flow volume to the gas inlets of the multi-cell after heated to a target temperature using an external heater. At the set temperature of 150 °C and the flow volume of 8.0 L/min, the temperature distribution over the multi-cell was measured to be sufficiently within  $\pm 0.5$  °C.

Chemiluminescence was acquired by continuously capturing images with appropriate exposure time (Fig. 2b). These continuous images are analyzed by ImageJ software, where the intensity of the chemiluminescence was calculated based on  $(R + G + B)/3$  for each cell. Likewise, chemiluminescence curves for 10  $\times$  10 samples are simultaneously acquired (Fig. 2c), which are used to determine the oxidation induction time (OIT).

Thermo-oxidative degradation using the developed instrument was performed as follows: 100 sample pieces of 5.0  $\phi$  were cut out from the above-mentioned films and were placed in the multi-cell at room temperature. The multi-cell was heated by the oven to the specific temperature under the fixed flow volume of dry air that was pre-heated at the target temperature. Once the target temperature was attained, the images were continuously acquired and stored with the acquisition time of 20 min until all the pieces finished the chemiluminescence emission.

## 3. Results and discussion

In order to evaluate the feasibility of the instrument, parallel degradation tests were implemented: 100 sample pieces that were cut out from PP-0.07 and PP-0.10 films were subjected to thermo-oxidative degradation at 150 °C under the dry air flow of 8.0 L/

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