ELSEVIER

Thermochimica Acta 392–393 (2002) 23–27

thermochimica acta

www.elsevier.com/locate/tca

Use of a CCD imager for simultaneous DSC–chemiluminescence and multiple sample polymer degradation studies

Lecon Woo*, Craig Sandford, Henk Blom, Y. Samuel Ding

Baxter Healthcare, Corporate Research and Technical Services, Round Lake, IL 60073, USA

Received 15 November 2000; accepted 17 April 2001

Abstract

Digital electronic imaging using charge coupled devices (CCD) has become popular due to its mass adoption in the personal computer and photographic applications. The CCD sensors are moderate in resolution, extremely sensitive, offer wide dynamic range, and compared with photo-multipliers, capable of withstanding exposure to bright light without damage. These characteristics made CCD detectors ideal for chemiluminescence (CL) studies for polymer oxidative degradation.

We will present the use of a CCD imager with a DSC for simultaneous oxidative induction time (OIT) and CL studies. In addition, since these CCD imagers are inherently area imagers, making them easily adapted for multiple sample studies.

Keywords: Polymer degradation; CCD imager; Chemiluminescence

1. Introduction

Chemiluminescence (CL) has long been recognized as a powerful tool in polymer degradation and lifetime prediction studies. It is believed the CL signal originated from activated oxygenated species produced from peroxide and hydroperoxide intermediates. Matisova-Rychla and Rychly [1] studied CL induction time as a function of antioxidant concentration and initial hydroperoxide concentrations, and their results in Figs. 1 and 2 clearly show the expected linear dependence on antioxidant content and the inverse exponential dependence on hydroperoxide. These results are similar to findings using the oxidative induction tests by differential scanning calorimeter (DSC) [2].

The intensity of the detected CL signal is in general depending on three factors: the chemical reaction rate, quantum efficiency of the photon generation, and the detector conversion efficiency. Although the quantum efficiency for the reaction is quite low, the visible wavelength of emitted photons is sufficiently short to allow easy detection. Photomultipliers and image intensifiers are frequently used in earlier studies [3–5]. However, despite of the very high gain, they are subjected to damage when exposed to ambient light, in addition to relatively high costs. The recent introduction of charge coupled devices (CCD) makes it feasible to construct moderate cost quantum detectors with relative ease.

Both the OIT and CL data support the general mechanism of degradation where the primary alkyl free radicals are propagated through atmospheric oxygen diffusing into the polymer via the formation of peroxy and hydroperoxy free radicals (Fig. 3). In this

---

* Corresponding author. Fax: +1-847-270-6341.
E-mail address: wool@baxter.com (L. Woo).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00066-7

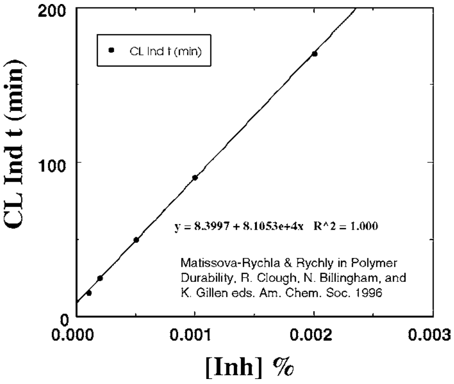


Fig. 1. CL induction times.

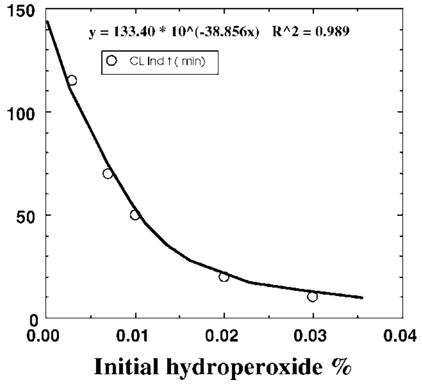


Fig. 2. Hydroperoxide effect.

regard, the action of the phenolic antioxidant is mainly that of a hydrogen donor in eliminating organic free radicals, and becomes sacrificially consumed in the process.

2. Experimental

Although digital consumer cameras of far greater resolutions are available, none offers the very long exposure times and the sensor cooling required for the extremely low-level photo detection for CL. At the mean time, many of the "scientific" grade CCD cameras offers very high sensitivity and sensor cooling at orders of magnitude higher cost. The Meade CCD imager was originally designed for "intermediate" level amateur astronomy, with high sensitivity at moderate resolution and moderate cost, and as such, ideally suited for our purpose.

Characteristics of the Meade 216X CCD imager:

Imaging CCD	Texas Instrument TC255, frame transfer type
Pixels	324 (H) × 242 (V)
Pixel size	(10 μm × 10 μm)/pixel
Well capacity	70000 electrons
CCD conversion	12 μV/electron
Dark current	<1.6 electrons/s at −5 °C
Shutter speed	0.004 s to 120 min
Analog digital conversion	16 bit
Temperature control	Peltier Element to −25 °C from room temperature
Software	Pictor View (PC interfacing and image processing)

A series of machined brass adapters allow the mounting of a 5 mm focal length C-mount lens to the CCD camera. First is a cylindrical coupler to the

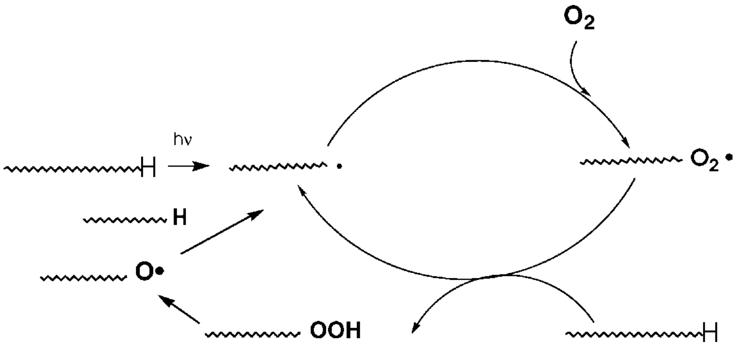


Fig. 3. Oxidative kinetic chain reaction.

mating metric threads on the CCD camera. A 1.5 in. long fine metric spiral threads were machined on the coupler's inner surface. Riding on this set of spiral grooves is a focusing carrier where the C-mount lens is attached. By experimentation, the carrier position for different subject distances were marked. Finally, an absolutely light tight enclosure sitting on top of the Dupont 910 DSC cell was constructed with the CCD camera assembly located approximately 75 mm from the DSC sample disk. To insure proper focusing, a white light LED was mounted on the interior of the enclosure to provide illumination. To allow photo detection, the DSC cell's silver lid and the metal cover were replaced with two circular fused quartz disks. Without the silver lid, the dynamics of the DSC cell response to step temperature command was considerably retarded. However, since most of the experiments required long experimental times, this loss of temperature response was not deemed serious.

The CCD camera interfaces to a personal computer via the serial port, and powered by a separate 12 V power source. The Meade Pictor View^{TM} camera driver software provides control functions including Peltier cooling to set points up to 25 °C below ambient, exposure times from 4 ms to 120 min, as well as automatic consecutive exposures of up to 50 frames. A separate image processing software MaxIM DL^{TM} was used for further processing and convenient photometric measurements.

Typically, a raw image frame needs to go through a calibration process: subtraction of a "dark frame" taken at the identical CCD temperature and exposures, subtraction of a "bias" frame—taken with zero exposure time (location specific readout noise), and normalizing against a "flat field"—a frame taken on an even illumination field for element to element sensitivity variations. In this way, signals nearly two decades below the dark noise level became detectable, and the CCD, although of very modest cost, came within about a factor of two to become a "single photon" detector, as determined from the dark current specifications of the camera chip.

Measured performance of the completed CCD-DSC system is as follows:

Dark current at 0 °C	2.3 counts/pixel/s
Luminous watch dial	520 counts/pixel/s
PP at 160 °C	<0.1 counts/pixel/s
PP at 125 °C	0.075 counts/pixel/s
PVC at 230 °C	0.2 counts/pixel/s
PVC at 190 °C	0.22 counts/pixel/s

It can be seen that detection at nearly two orders of magnitude below the dark current was possible through digital subtraction and image enhancements. It is also interesting to note that compared to OIT, the CL intensity does not heavily depend on temperature. This factor would make CL ideally suited for long term, low temperature polymer durability studies.

3. Results and discussion

3.1. Simultaneous DSC–CL experiment

The measured CCD dark current and the temperature dependence was found to be clearly Arrhenius in functional dependence with an activation energy approximately 67 kJ/mol. This indicates to achieve the best signal to noise (S/N) ratios, especially for long exposures in CL detection, cooling to at least 0 °C is a necessity.

To test the chemoluminescence detection, an electron beam irradiated polypropylene film about 1 cm × 2 cm in size was placed on a semicircular aluminum foil on the DSC sample detector platform, DSC temperature was held isothermal at 160 °C, purge gas was switched from nitrogen to air at 100 ml/min and 30 min successive exposures were taken. From the calibrated frames in Fig. 4, it is clearly seen that at about 120 min into the experiment, a faint chemiluminescent image became detectable. Photometric data by subtracting the signal intensity from the sample side from the reference side resulted in a clear CL onset of about 100 min. This onset coincided with the DSC detected OIT of about 105 min(Figs. 5 and 6). One should note, however, when very long integrating exposures are used, an apparent delay in the onset time can be expected. Another observation on this simultaneous DSC–CL experiment is after the onset, the DSC signal rises rapidly to a maximum and followed with a pronounced decay, while the CL signal remained strong long after the DSC maximum and decay. This observation clearly indicates that

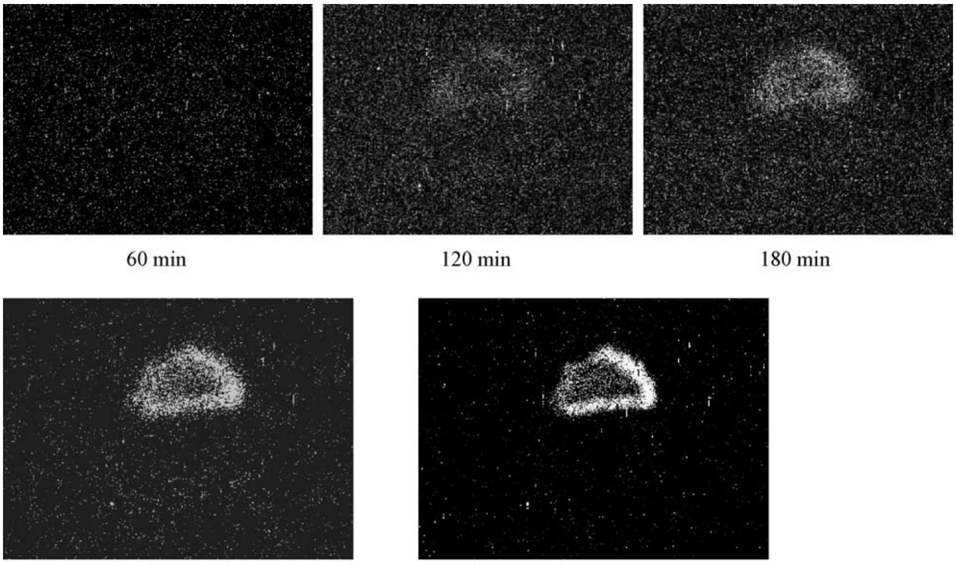

60 min
120 min
180 min
750 min
1900 min

Fig. 4. Irradiated PP CL signal.

although DSC and CL both detected the same onset, CL signal persists much beyond the exothermic maximum. It is very possible during the decay phase for the DSC, the reaction is dominated by steadily declining concentration of the intact hydrocarbon polymer, while concentration of degradation products remains high. From the exothermic oxidative heat generation point of view, intact polymer possesses far more caloric value compared to highly oxygenated reaction products.

3.2. Multiple sample experiment

Since the DSC cell can accommodate more than one samples held in the standard sized aluminum pans, it is interesting to see if more than one samples can be run in the same chamber. Fig. 7 illustrates the placement of six PP samples of two types arranged in a triangular placement. Of course, samples placed outside the DSC detector platform are not expected to be detected calorimetrically. A frame captured at the 1000 min

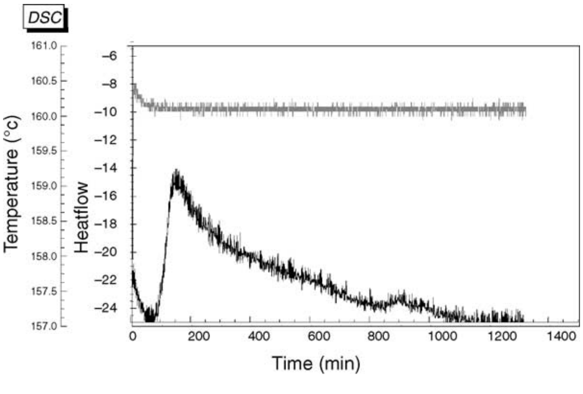


Fig. 5. PP 100 kGy eB 160C OIT.

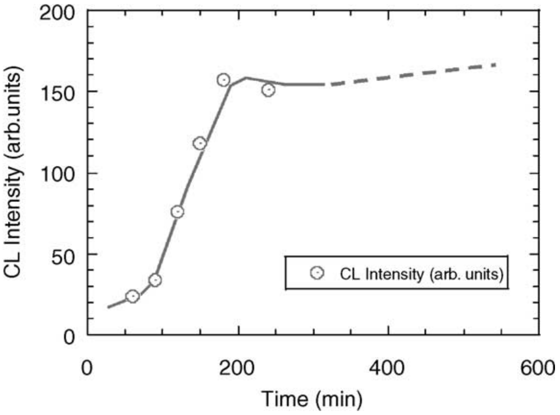
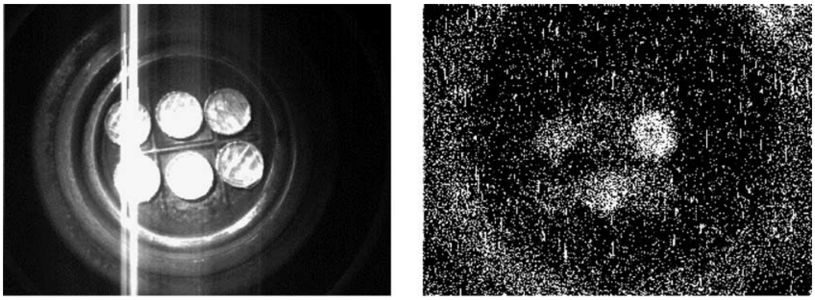


Fig. 6. Simultaneous CL signal.



Time Zero

Time = 1000 min
@ 145 C

Fig. 7. Six sample DSC 100 kGy, eB 145C.

illustrated the much more prominent CL signals from samples on the sample platform compared with the cluster associated with the reference side.

4. Summary

We have successfully adapted a moderate cost CCD imager to a heat flow DSC. The imager has demonstrated near single photon detection capability for chemiluminescent measurements while the DSC providing simultaneous calorimetric data. It was found that the CL onset corresponded closely to DSC OIT data measured in air. However, the CL signal appeared to persist far beyond the DSC OIT signal maximum. In addition, under the same image frame captured on the DSC cell, multiple samples can be studied together. This particular aspect could lead to greater instrument pro ductivities. Another advantage for the image detection is that spatial events specific to sample's heterogeneous structure can be studied in addition to a calorimetric composite signal.

References

[1] L. Matisova-Rychla, J. Rychly, Polymer Durability, in: R. Clough, N. Billingham, K. Gillen (Eds.), American Chemical Society, Washington, DC, 1996.
[2] ASTM Standard Test Method D-3895-92.
[3] R. H. Fleming, A. Y. Craig, Polymer Degradaton and Stability, Vol. 37, 1992, pp. 173–180.
[4] L. Zlatkevich, ACS Symp. Ser. #280, 1985, p. 387.
[5] L. Zlatkevich, in: G. A. George (Ed.), Luminescence Techniques in Solid State Polymer Research, Marcel Dekker, New York, 1989, pp. 93–134.