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Use of 9,10-diphenylanthracene as a contrast agent in chemiluminescence imaging: The observation of spreading of oxidative degradation in thin polypropylene films

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Abstract

Thin films of polypropylene were doped with a chemiluminescence (CL) activator, 9,10-diphenylanthracene (DPA), and were thermally oxidised in a CL imaging apparatus to determine whether heterogeneous oxidation processes such as spreading of oxidation could be observed. The presence of DPA resulted in significantly more intense CL images compared with undoped polymer, due to the efficient chemically induced electron exchange luminescence reaction between DPA and hydroperoxides. Hence, the CL images from DPA-doped PP were used to locate the position of hydroperoxides in the oxidising polymer. For thermal oxidation at 150 and 140 °C hydroperoxides were observed to form in localised regions of the films, whilst other areas remained hydroperoxide free. As the oxidation time increased the concentration of hydroperoxides in these areas increased and they were observed to spread to the remainder of the polymer. Time-resolved line maps from the images indicated that zones with high concentration of hydroperoxides travel through the polymer during oxidation. Integrals of CL images from the thermal oxidation of DPA-doped polymers indicated that a significant degree of oxidation had occurred by the end of the "induction period" for a conventional CL-intensity oxidation–time profile. This is a likely reason why spreading of oxidation has not previously been observed for undoped PP films.

Keywords: Chemiluminescence imaging; Chemically induced electron exchange luminescence; Polypropylene oxidation; 9,10-Diphenylanthracene; Heterogeneous oxidation; Oxidative spreading

1. Introduction

Oxidation of thick polymer articles has often been observed to be heterogeneous in the near-surface regions, due to diffusion limitation of oxygen access. The presence of oxidation product gradients from diffusion-limited oxidation has been demonstrated using a variety of techniques including vibrational spectroscopy [1–3] and ESR imaging [4].

The process has also been demonstrated to be more generally heterogeneous due to other factors, including the inhomogeneous distribution of impurities such as catalyst residues. Richters [5] was one of the first to observe localised oxidation during the "induction period" of polypropylene (PP) oxidation. These results were obtained using optical microscopy in combination with SO_2 staining. Later, others [6–8] were also able to observe heterogeneous oxidation of a variety of polyolefins using dinitrophenyl hydrazine staining and UV microscopy. Scheirs et al. [8] demonstrated that ex-reactor particles obtained from the same batch of HDPE have a range of stabilities. More recently, some of the present authors have identified titanium catalyst residues in ex-reactor PP particles

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using Raman microscopy, optical microscopy and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis [9]. It was further demonstrated that photooxidation of the polymer was initiated in localised regions around the catalyst residues. In a subsequent study the appearance of degraded regions around catalyst residues was further demonstrated using graft polymerisation from hydroperoxides formed during photooxidation [10].

Using chemiluminescence (CL) and SEM Celina et al. [11] observed that individual PP particles had a range of stabilities. Furthermore, they demonstrated that oxidation was able to spread through the gas phase from one particle to another. Ahlblad et al. [12] were also able to demonstrate that physical spreading of oxidation between EPDM particles is possible. Using CL imaging Celina et al. [13] demonstrated that oxidation spread from a region of pre-oxidised polymer to the remainder of the sample during oxidation. Dudler et al. [14] showed that an unstabilised film placed on the edge of a thin strip of stabilised PP was able to "infect" the stabilised film. Furthermore, as the antioxidant was consumed the oxidation was observed to spread down the length of the stabilised strip.

In light of the above evidence and that from other studies [15,16], it is evident that polyolefin oxidation is heterogeneous even when oxygen diffusion does not dominate. However, heterogeneous oxidation of unstabilised polyolefins has yet to be observed unequivocally using CL imaging.

To be able to observe heterogeneous oxidation and oxidative spreading in real time, the time available for data acquisition is relatively short and the data points need to be spatially resolved. Imaging techniques (as opposed to point-to-point mapping) are better suited to obtain spatially resolved data relatively quickly. CL imaging has been used to follow the thermal oxidation of a variety of polymers. Due to the lower sensitivity of CCD cameras compared to photomultiplier tubes (PMTs), samples analysed in the form of a film are usually required to be thick ($\sim 100\ \mu m$). Images from thick films tend to show artefacts such as guiding of the emitted light to the edges of the film and to cracks formed during oxidation [17,18]. These artefacts tend to dominate the images, because of their greater brightness. Furthermore, the brightness of the artefacts results in poor contrast for the bulk of CL. Due to light scattering, the spatial resolution of CL imaging is in the order of $10\ \mu m$. Since the domain size has been theorised to be in the submicron region [11,19], the probability of observing heterogeneous oxidation is low, due to the large thickness of the films, because the number of domains that the detector can observe increases with increasing thickness. Although heterogeneous oxidation may be occurring this may be obscured for thicker films, because the probability of observing an unoxidised region from the top down is reduced with increasing film thickness.

In previous publications we proposed that the primary light-emitting reaction during oxidation of unstabilised and undoped PP was the reaction between acyl peroxides and certain carbonyls, and that CL intensity (I_{CL})–time profile of *pure* PP represents the accumulation of secondary oxidation products, such as carbonyls [20,21]. More recently, Jacobson has reported that this is also true for the thermal oxidation of ultra high molecular weight polyethylene which is of high purity and additive-free [22,23]. The implication of this discovery is that CL from undoped PP occurs in regions of the polymer that are highly oxidised. Therefore, when the maximum CL intensity is reached the polymer has reached the maximum carbonyl concentration, at which time the oxidation product distribution has a greater probability of being homogeneous. In the lifetime prediction of polymers, the most important stage of oxidation is the "induction period" where very little CL is observed. With the current generation of charge coupled device (CCD) detectors, little information can be gathered in this region. This situation may only be remedied when more sensitive detectors can be manufactured or other means to intensify light emission are employed.

In a previous publication we demonstrated that a CL signal with a significantly greater intensity was obtained from polymer samples doped with low levels of 9,10-diphenylanthracene (DPA) [21]. Furthermore, it was demonstrated that the luminescence observed followed a different profile compared with CL intensity (I_{CL})–time profiles of undoped, pure PP and that DPA-enhanced CL was directly proportional to the concentration of peroxides in the sample. It was proposed that the trace amounts of DPA doped in the polymer react with peroxides (or their scission products) to generate CL via a chemically induced electron exchange luminescence (CIEEL) mechanism. Therefore, it follows that DPA-enhanced I_{CL}–time profiles provide a method of measuring hydroperoxide concentration rather than the accumulation of secondary oxidation products such as ketones, acids and esters, which is probably the case for I_{CL}–time profiles from unstabilised and undoped PP. In the present work, the oxidation of thin PP films doped with low levels of DPA has been followed in a CL imaging apparatus. Hence, the spatial distribution of hydroperoxide concentration should be observable in real time. From studies of CL emission from PP it has been shown that hydroperoxide concentration vs. time curve is the derivative of carbonyl concentration vs. time curve and thus the maximum hydroperoxide concentration occurs at the point of the inflection of carbonyl concentration vs. time curve [20]. Therefore, the maximum of DPA I_{CL}–time curve will also occur at the inflection of carbonyl curve. Furthermore, the point where the "induction period" ends on a carbonyl concentration vs. time curve corresponds to a higher intensity in DPA I_{CL}–time curve, so that more information on the spatial distribution of oxidation product in the "induction period" should be observable.

2. Experimental

2.1. Materials

Unstabilised PP powder, Hostalen PPK0160 (Hoechst AG), melt flow index (MFI) at 230 °C/2.16 kg of 0.9 g min^{-1}, crystallinity by XRD of 45% [19] was used. The sample was extracted with AR hexane using a Soxhlet apparatus for 6 h.