SENSITIVE LUMINESCENCE TECHNIQUES TO ASSESS POLYMER DEGRADATION

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Methods for estimating the progress of oxidative polymer degradation have traditionally involved the measurement of mechanical and macromolecular properties coupled with determination of functional groups, such as carbonyls, ketones and esters in the polymer chain by FTIR spectroscopy. These studies have demonstrated that the useful lifetime of a polymer does not extend much beyond the end of the oxidation induction period, so lifetime determination requires sensitive methods for studying the incipient degradation at short times where the rate of oxidation approaches zero.

The sensitive and complementary techniques we have employed are chemiluminescence (CL) and profluorescent nitroxides (PFN). We have previously demonstrated the sensitivity of these methods for monitoring the induction period of polypropylene oxidation.[1-3] In the PFN method the production of carbon-centred radicals can be measured in the induction period. There are two main methods for switching on fluorescence in PFNs: radical reactions (Figure 1), and redox reactions (Figure 2).
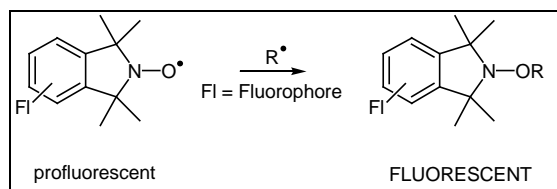

Figure 1: Switching on of PFN fluorescence by trapping an alkyl radical R·

This provides challenges in applications to epoxy resins and polyurethanes where the cure chemistry and catalysis may involve redox reactions. It also limits the use of PFNs where there are transition metal pro-oxidants present in high concentration (as in oxo-degradable polyolefins).
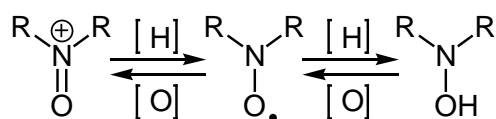
Figure 2: One-electron redox reactions of nitroxides

In that case CL is still the method of choice. An interesting example has been our experience with *cis*-polyisoprene when in contact with a polyolefin containing transition metals. Rapid degradation occurred which was able to spread infectiously through several layers of the polyolefin below where the *cis*-polyisoprene layer had been placed. Figure 3 shows a CL profile from LLDPE alone and then with the addition of cobalt carboxylate and then polyisoprene.
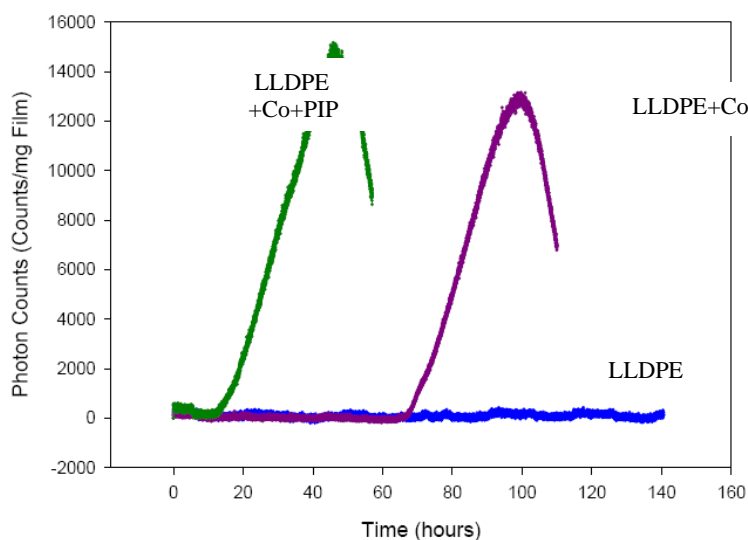
Figure 3: CL profiles from LLDPE in presence of Co^{2+} and polyisoprene (PIP).

One particular feature of both CL and PFN methods is their ready adaptation for imaging of oxidation in space and time so the infectious spreading of oxidation can be mapped.

References:
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