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DSC COMBINED WITH CHEMILUMINESCENCE FOR STUDYING POLYMER OXIDATION

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Abstract

A DSC instrument modified to incorporate a chemiluminescence (CL) detector has been used to make simultaneous measurements of heat flow and light emission for oxidising polymer samples. Comparison of heat flow and light emission from unstabilised polypropylene shows a linear relation between heat flow and square root of intensity, giving indirect confirmation of the Russell mechanism for CL emission. Measurements of oxidation induction times (*OIT*) for stabilised samples show excellent correlation of the two techniques. The advantage of the CL method in being insensitive to thermal transitions in the sample is illustrated by a study of poly(ethylene terephthalate), whilst the very high sensitivity of CL detection is illustrated by its ability to detect peroxides at levels which are not detected by DSC. Finally, the limitations of the *OIT* approach in lifetime prediction by Arrhenius extrapolation are emphasised.

Keywords:, chemiluminescence, DSC, *OIT*, polymer oxidation

Introduction

The importance of oxidative degradation and its effect on the lifetime of polymers is reflected in the long history of published work in this area [1–5] and the successful application of most commercial polymers has been possible only through the development of effective antioxidant additives. The best modern stabilisers can give very long lifetimes to polymers both indoors and outdoors. Indeed without stabilisation most high-tonnage thermoplastics would be unusable in most current applications [6]. This benefit also brings challenges, in that real-life testing is not possible and accelerated methods are the only way of testing additives because tests that approach real-life conditions are time-consuming and expensive. The problem is made worse by the need to optimise synergistic mixtures of stabilisers, which means many test samples.

The most common method of accelerated testing is to raise the temperature to the point where the lifetime is short enough to be measured in a reasonable time. Oxidation can then be assessed by many analytical methods, typically measurement of

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oxygen uptake or carbonyl index (CI), or by measurement of mechanical failure in e.g. embrittlement.

A popular approach to study of stabilised samples has been the use of DTA or DSC methods to measure the so-called oxidation induction time (*OIT*) of a polymer. Typically, isothermal DSC is used, between 190–220°C and the *OIT* is taken as the time to reach the onset of oxidation, detected as the start of an exotherm. The application of high-temperature DSC has been rightly criticised [7]. Since commodity thermoplastics have properties which preclude high-temperature applications [8], the most apparent drawback of the *OIT* method is the need to test at high temperatures. At such high temperatures polyolefins are molten and this raises serious doubts as to the applicability of the results to real-life situations since both the degradation kinetics and the distribution of additives in the molten polymer are completely different from those of the solid material [3, 9]. In addition, some classes of stabiliser, notably the hindered amines, are very effective at low temperatures yet ineffective at high temperatures. Despite these obvious problems, the *OIT* method remains popular for rapid screening of antioxidants and especially for quality control purposes.

More recently, the study of the weak chemiluminescence (CL) emission accompanying the oxidation of polymers has become a popular approach [10, 11]. In a recent inter-laboratory study of *OIT* measurements, carried out by EMPA in Switzerland [12], it was shown that *OIT* data on standard polyethylene samples obtained from a commercial CL instrument were comparable with those from DSC on the same materials.

Since CL and DSC are complementary methods, it is relatively easy to combine both measurements into the same instrument. In this paper we describe some studies of polymer oxidation using simultaneous DSC and CL measurements. By using a commercial DSC instrument modified to incorporate a CL detector, we are able to make direct comparisons of the two methods without any of the complications which arise when using two different instruments and/or samples.

Experimental

Unstabilised polypropylene (PP) powder (density of 0.898 g cm^{-3}, *MFI* 4.6 g/10 min at 260°C, 2.16 kg) was supplied as a ‘Statoil™’ product by Ciba Specialty Chemicals and used as received. A PP sample containing a phenolic antioxidant (Profax 6501, density of 0.897 g cm^{-3}, *MFI* 4.2 g/10 min at 230°C, 2.16 kg, containing 0.005 mass% of Irganox 1010™ and 0.025 mass% calcium stearate) was supplied as pellets by Ciba Specialty Chemicals and used as received. A commercial peroxide crosslinked rubber designed for high-temperature, high-specification applications was also tested. Its additive formulation has not been disclosed.

Simultaneous DSC/CL experiments were performed on a Mettler DSC820 instrument, calibrated for temperature and heat flow by using indium and tin samples in the usual way. The DSC is modified for single photon counting, using a conventional bialkali cathode photomultiplier tube as the detector, coupled to the DSC through a glass window placed immediately above the sample chamber. Photon counting uses a Stanford Instruments Model SR400 gated photon counter.

Results and discussion

Direct comparison of Isothermal DSC and CL

Figure 1 shows the CL emission curve typical of the oxidation of a polyolefin. This curve was obtained from PP in an isothermal experiment carried out at a temperature well below its melting point. The polymer was stabilised by a standard commercial antioxidant package.

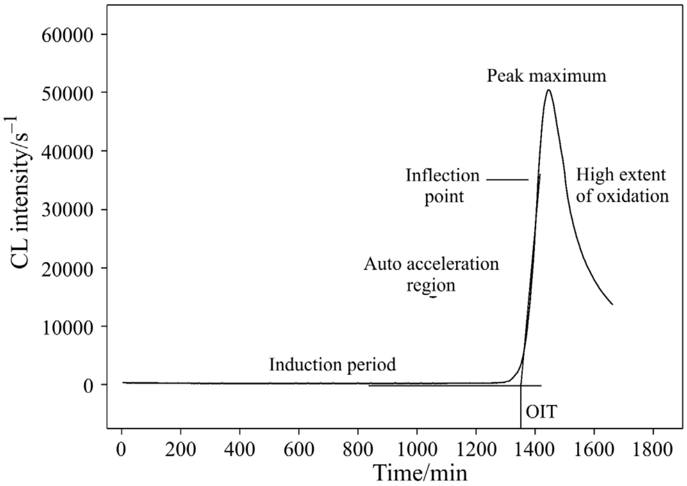

Fig. 1 Typical CL profile: Stabilised PP in O_2 at 150°C

The first region of importance, the induction period, extends from the beginning of the experiment to the point of departure from linearity, the *OIT*. In this period, the AO has successfully suppressed the build up of radical concentrations. This continues until all the AO has been used up, upon which immediate catalytic oxidation occurs and a rapid growth in CL emission shows the beginning of auto-oxidation. During this period the oxidation is auto-catalytic and the polymer swiftly degrades.

A point of inflection on this line marks the end of the auto-catalytic region and signals the slowdown of the oxidation as it approaches the maximum rate from where the rate of oxidation, and therefore the CL intensity, rapidly reduces. It is important to note that past the maximum the sample has been severely degraded and is no longer representative of the parent polymer.

When studying fundamental processes in polymer oxidation it is often better to restrict the study to simpler formulations such as unstabilised polymer thus mitigating any contributions to an already complex system from the additives.

In a DSC instrument the measurement is of the rate of heat flow into or from the sample. As a first approximation, it should thus be proportional to the rate of propagation of the oxidation, since this is the dominant reaction. In its turn, the propagation rate should be directly proportional to the concentration of peroxy radicals, $[RO_2]$, since these radicals are the main carriers of oxidation.

The mechanism of the light emission reaction is more contentious, but it is most commonly attributed to the formation of carbonyl groups in excited states by the recombination of two $[RO_2]$ radicals via an intermediate tetroxide, which rearranges to give excited triplet ketone, an alcohol and molecular oxygen in the so-called Russell mechanism [13]. The light emission is attributed to the relaxation of the excited ketone to its ground state.

If this is true, then we would expect the CL intensity, I, to be proportional to $[RO_2]^2$, since radical termination is second-order. Figure 2 shows the results obtained for unstabilised PP when $I^{1/2}$ is plotted *vs.* the DSC heat flow rate (expressed in mW) for oxidation at three temperatures (120, 130 and 135°C), chosen to give reasonable experimental times while still being well below the melting point of the polymer. The comparison includes all data up to the inflection point of the CL curve (below the peak maximum). The point of analysis termination is illustrated in the inset graph. The lateral curve shift of the curves is a function of the DSC response since the amount of heat required to maintain thermal equilibrium between the reference and sample pans is temperature dependent.

The most important result from Fig. 2 is that the relationship between heat flow and $I^{1/2}$ is linear at all of the temperatures studied, which gives indirect support to the proposal that the CL emission arises from the Russell mechanism. The gradients of the plots are not the same at all temperatures (they decrease slightly with increasing T). This presumably reflects the fact that the DSC is effectively measuring chain propagation, whilst the CL is measuring termination, and the kinetic chain length (the ratio of propagation and termination rates) varies with temperature.

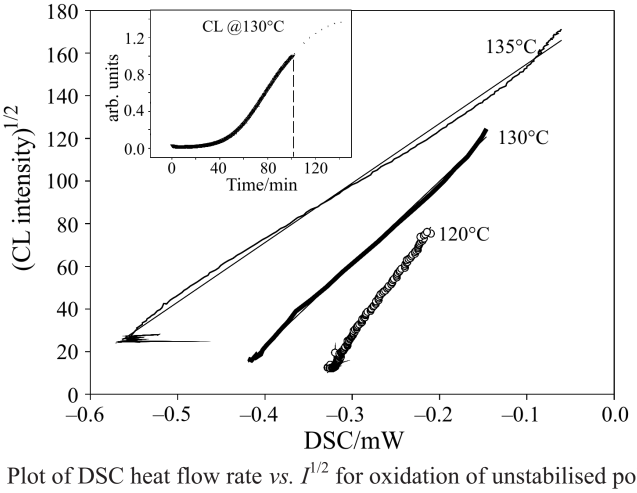

Fig. 2 Plot of DSC heat flow rate *vs.* $I^{1/2}$ for oxidation of unstabilised polypropylene

Isothermal DSC/CL measurements of OIT in stabilised samples

Polymer antioxidants function either by reacting with RO_2 radicals in competition with propagation, or by preventing the formation of RO_2 radicals by removing peroxides from the sample. In either case, they are removing the main source of CL emission as well as stopping the oxidation. Thus we might expect that antioxidants which are effective in delaying the onset of oxidation will also inhibit the CL emission.

Figure 3 shows a typical simultaneous DSC and CL experiment on a stabilised PP sample; the agreement between the two techniques is excellent and an *OIT* can be derived equally well from either method. This experiment was repeated at a series of temperatures chosen to give *OIT* values ranging from a few min up to 20 h. Figure 4 shows that there is good agreement between the two techniques even for the longest

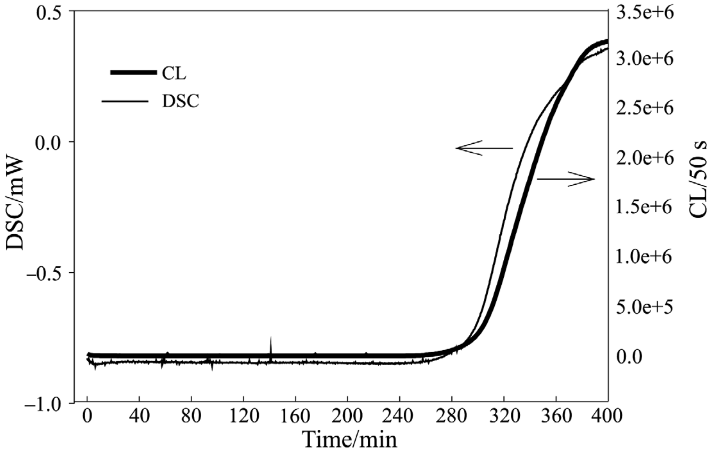

Fig. 3 DSC and CL curves obtained from stabilised PP at 150°C in O_2

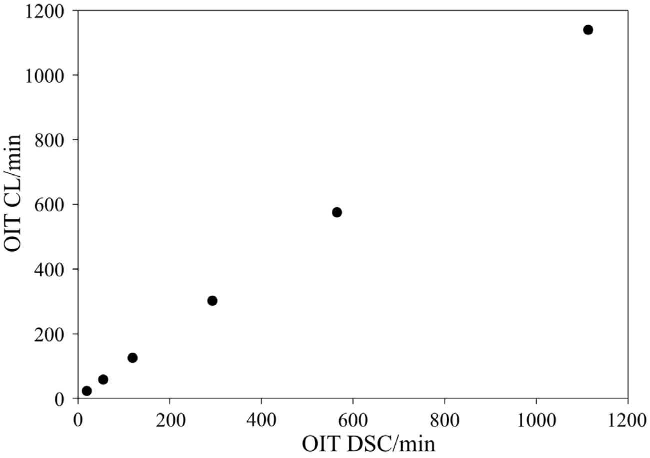

Fig. 4 DSC and CL *OIT*'s obtained from stabilised PP at a range of temperatures

*OIT*s. Compared with DSC, CL thus gives the same *OIT* data. However, it can be more convenient for lower temperature testing of polymer stability [3, 14, 15].

Simultaneous DSC/CL measurements in temperature ramped mode

Unlike the DSC response, the CL signal from an oxidising sample is not directly affected by the other endothermic or exothermic processes that occur during the experiment (although changes in the sample geometry due to melting may have secondary effects). As an example, Fig. 5 shows the simultaneous DSC/CL profile obtained for a sample of a bottle grade poly(ethylene terephthalate) (PET) measured in oxygen atmosphere with a temperature programme rate of 10°C min^{-1}. As the temperature increases, the glass transition, crystallisation and subsequent re-melting of the polymer are clearly seen in the DSC trace but do not directly affect the CL curve. However the oxidation of the polymer, which accelerates rapidly around the crystal melting point cannot be distinguished from the melting or from baseline curvature. In contrast, the CL sees only the oxidation and gives a sharp, unambiguous onset.

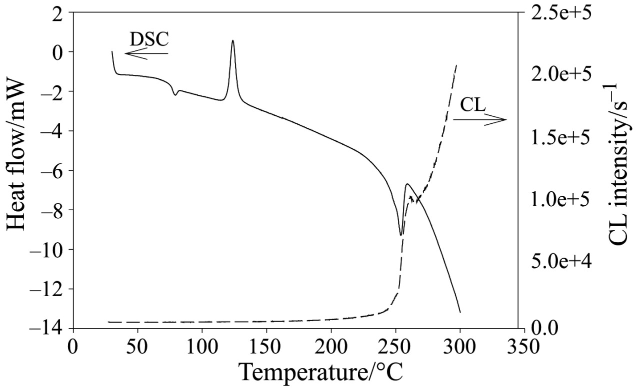

Fig. 5 Simultaneous DSC and CL of PET in oxygen atmosphere at 10°C min^{-1}

Another advantage of CL analysis is that the high sensitivity of single photon detection allows recording of CL from the decomposition of hydroperoxides in inert atmospheres. Although it has been claimed that peroxide decomposition in photo-oxidised polymers can be detected by DSC [16], that work was performed with highly oxidised amorphous polymers; DSC study of peroxides in semi-crystalline polymers is invariably complicated by overlapping peaks from peroxide decomposition and melting.

As an example of the very high sensitivity of CL to peroxides, Fig. 6 shows the CL profile obtained from a peroxide cross-linked rubber when heated at 10°C min^{-1} under nitrogen. Often when such polymers are crosslinked by use of organic peroxides some residual peroxides remain. The DSC trace shows no peaks, but there are two clear peaks in the CL profile. These are present on the first heating run only; they vanish if the polymer is cooled then reheated. The larger peak has its maximum at 220°C suggesting that it may be due to decomposition of the peroxide curing agent [17]. There is a smaller

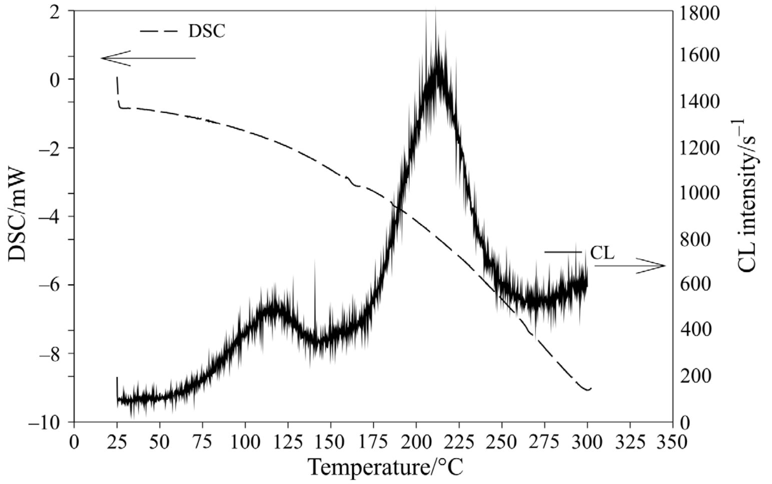

Fig. 6 Simultaneous DSC and CL from a crosslinked rubber sample heated in nitrogen at 10°C min^{-1}

peak occurring at 120°C which we believe represents polymer hydroperoxides formed during processing.

Arrhenius treatment of OIT data

Although the DSC method has been widely used for studying stabilised polymers, and is the basis of an ASTM standard, a major source of contention in prediction of oxidative lifetimes from *OIT* testing is the simple Arrhenius approach which uses classical rate theory to determine the activation energy for the reaction and was first reported for degrading polymers by Sebasta and Rase [18]. Although the consensus appears to be that the *OIT* method is a useful test for establishing the degree of oxidation [19] stabiliser effectiveness [3] and the effects of metal residues [20] on oxidation, most authors have cautioned *vs.* use of the Arrhenius extrapolation to predict *OIT*'s at lower temperatures [3, 9, 20, 21].

Gijsman [22] has studied the oxidation of polypropylene from 70 to 140°C and found that the Arrhenius plots are curved. This curvature was attributed to the effects of residual impurities in the polymer, a consequence of the polymerisation method. Whatever the reason, extrapolation from higher to end-use temperatures produces erroneous predictions for oxidative lifetime. Gillen and Clough have continued this theme by presenting theoretical lifetimes for EPDM material, based on Arrhenius extrapolations, in excess of 55.000 yrs. Billingham *et al*. [3] had already cautioned *vs*. the extrapolation of DTA data through the melting point to make lifetime predictions for polyolefins which have end uses at ambient temperatures. They argued that a number of influences need to be considered including the effects of oxygen starvation at higher temperatures, and also changes in crystallinity and supersaturation of the antioxidant at lower temperatures.

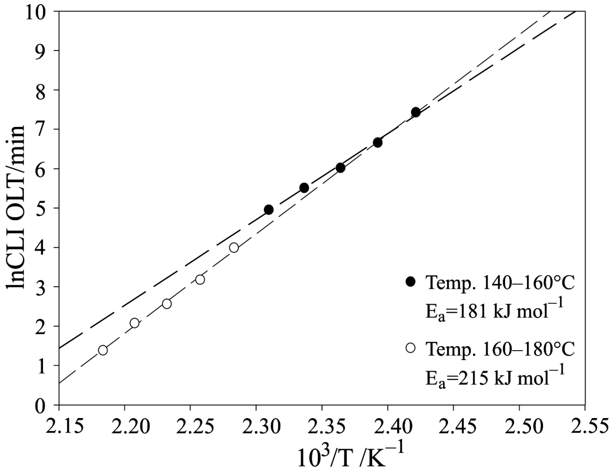

Fig. 7 Arrhenius plot of *OIT* values for a stabilised polypropylene sample measured by CL, over the range 140–180°C in oxygen

As an example of the difficulties, Fig. 7 shows an Arrhenius plot of *OIT*s that were obtained in this work by DSC/CL from a single sample of stabilised PP across a range of temperatures. The activation energy, E_a, can be derived from a regression line drawn through the data. However, it is clear that there are two distinct gradients. A regression line drawn through the values in the temperature range 140–160°C yields an activation energy of 180 kJ mol^{-1}. This value is in agreement with those reported in [3]. However a regression line drawn through the values in the temperature range 160–185°C, yields a much higher activation energy (215 kJ mol^{-1}) and therefore will extrapolate to yield a much higher stability at ambient temperature. It is also of interest that the plots diverge around 165°C, so that the maximum deviation occurs in the melting range of the polymer.

Conclusions

The combination of DSC with CL analysis offers new dimensions in the study of oxidising polymer systems because of the CL emission associated with oxidation of the polymer or decomposition of peroxide impurities.

Simultaneous DSC and CL of unstabilised PP shows that the heat-flow rate determined by DSC is linearly related to the square root of CL intensity, giving indirect confirmation that the CL emission probably arises from bimolecular combination of peroxy radicals.

Since typical stabilising additives interrupt both the oxidation reaction and the CL process, oxidation induction times measured by both methods give very good correlation over a wide range of temperatures. An Arrhenius plot of *OIT vs*. temperature for a stabilised polypropylene across a temperature range chosen to include the melting range is non-linear, with the deviation from linearity occurring in the melting range of the polymer. These data confirm the need for great caution in extrapolating typical *OIT* data to lower temperatures.

In addition to its use for *OIT* measurement it is shown that the CL method can help to distinguish oxidation from other thermal events detected by DSC. The very high sensitivity of the CL measurement can also detect signals from decomposition of traces of peroxides, under conditions where the DSC is too insensitive.

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