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Rapid measurement of polymer photo-degradation by FTIR spectrometry of evolved carbon dioxide

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Abstract

A novel method, allowing simultaneous UV exposure of a polymer sample and IR interrogation of the vapour in a specially constructed cell, has been applied to polyethylene (PE) samples containing TiO_2 pigments with different photoactivities. Measurements of the CO_2 generated by films exposed to ultraviolet irradiation (UV) were completed in 5 h − very much less than conventional accelerated tests. The TiO_2 pigments used included anatase and rutiles with different surface treatments. Anatase pigmented material gave significantly higher CO_2 emission than unpigmented PE whilst rutile-pigmented PEs either gave reduced CO_2 emission or enhanced emission, according to the surface treatment. The ranking of the pigments as protectants or pro-degradants correlated well with the carbonyl index measured after more than 300 h exposure to UVA fluorescent tubes in a QUV machine.

The method was then used to probe mechanistic aspects of the photo-oxidation of pigmented polyethylene (PE) film. For unpigmented polymer the photo-degradation was sensitive to changes in the small fraction of incident UV below 300 nm, but for pigmented films this was much less important. This is because unpigmented film degrades by direct photochemical attack whereas, for pigmented film, photocatalysis by TiO_2, which absorbs in the 300–400 nm region, is important. For films whose photo-oxidation was dominated by photocatalysis by the TiO_2 the rate of oxidation was shown to vary as the square root of the UV intensity. By contrast, for unpigmented films the rate of direct photochemical oxidation was linearly proportional to UV intensity. The difference is a consequence of the controlling role of electron–hole recombination in photocatalytic processes. For both unpigmented and pigmented films the rate of oxidation was shown to increase with increasing humidity and oxygen content of the atmosphere.

Keywords: Titanium dioxide; Photo-degradation; Photocatalysis; Polyethylene film

1. Introduction

Most polymers degrade under solar ultraviolet (UV) irradiation and various stabilizers are used to improve their UV resistance [1–3]. Both carbon black and TiO_2 are effective UV absorbers and confer significant protection from UV because of rapid attenuation produced by absorption and scattering. Despite this, some forms of TiO_2 increase degradation of polymers [4–6] because UV absorption leads to heterogeneous initiation of photocatalytic oxidation at the surface of the TiO_2 particles. In this paper, direct UV initiated degradation of the polymer will be referred to as photochemical degradation, whereas breakdown initiated by UV generation of active intermediates at the surface of the TiO_2 will be designated photocatalytic oxidation. Because of the complexity of these processes ab initio prediction of polymer stability is not possible. Rapid test methods are required to accelerate development of improved stabilizers, to assess the effect of pigments and fillers in polymer composites, and to assist prediction of the service lifetime of polymers.

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We have recently developed an early measure of paint photo-degradation [5–7] by using a specially designed FTIR cell to measure photo-generation of CO_2. A related infrared (IR) assay of evolved CO_2 has been developed by Worsley, Searles and co-workers and applied to PVC plastisols [8,9]. This paper describes the extension of our in situ method to measure photo-degradation of unpigmented and pigmented polyethylene films. A primary focus of the work was to determine whether the FTIR method could be used to discriminate between the activities of different TiO_2 pigments and for this purpose the CO_2 measurements have been compared with the results of a conventional test of polymer stability – carbonyl group development.

As well as differentiating between pigments, the earlier work on paint photoactivity made it possible to probe details of the photo-degradation mechanism by allowing measurement of the effect of oxygen partial pressure, humidity, and of UV intensity (I) and wavelength on breakdown of both acrylic and alkyd films. It was, for example, possible to demonstrate that the breakdown depends on $I^{1/2}$ [6,11], as predicted from model experiments over 20 years ago [10] but never previously demonstrated for real paints. Therefore, a further aim of the work reported in this paper was to measure the effects of changes in atmosphere and irradiation on polymer-degradation, and thus demonstrate the usefulness of the FTIR/CO_2 method for mechanistic studies.

2. Experimental

2.1. Materials

Low density polyethylene samples made from LDPE Riblène MR10 (Polimeri Europa) were provided by Huntsman-Tioxide, (Billingham, Cleveland, UK and Calais, France) pigmented films were made with a selected range of either commercially available or experimental TiO_2 pigment (Table 1) at a loading of 5 parts per hundred parts of resin (phr).

2.2. Reaction cell and UV exposure conditions

An IR cell in which the sample was mounted and exposed to UV from a xenon lamp via a flexible light guide and a calcium fluoride window was central to these experiments (Fig. 1). The evolution of carbon dioxide, generated by UV irradiation of the sample, was monitored by an interrogating IR beam that passes through the cell parallel to the sample surface (and perpendicular to the UV illumination) via calcium fluoride windows. The 8 mm i.d. samples (typical weight 11 mg) were held against a magnetic disc by a shaped metal ring and fixed to it by magnetisable wires ~0.5 mm in diameter and 1 mm long. Within the cell, the sample could be located either at the rear, position A, or – as shown in Fig. 1 – at the front. In the latter case the sample-holder was mounted on two microscope slides positioned with the plane of the slides at right angles to the infrared windows. In this way the forward extension of the sample-holder did not block the infrared beam. The cell had ports to admit gas and before measurements began it was flushed, for at least an hour, with the gas in which the reaction was to take place. At the start of the run the taps were closed and the cell contents isolated. Measurements were made with the cell placed in a Bio-Rad FTS-60 spectrometer fitted with a liquid nitrogen cooled narrow-band MCT detector.

Table 1
Description of the polyethylene film samples used in this study

Sample	Crystal	Production process	Uncoated or coated	Coating level
U1	Unpigmented	Not applicable		Not relevant
A2	Anatase	Sulphate process	Coated	Low
R3	Rutile	Sulphate process	Coated: Al_2O_3	Low
R4	Rutile	Sulphate process	Coated: Al_2O_3	Low
R5	Rutile	Chloride process	Coated: Al_2O_3/SiO_2	Medium
R6	Rutile	Chloride process	Coated: Al_2O_3/SiO_2	Medium

The broad band, ~280–800 nm, output from a 150-W high-pressure Xenon arc lamp (Oriel) was filtered by a 100-mm water filter, to reduce IR heating, and selected solar filters (AM0 and AM1.5 either singly or in combination) were used to remove short wavelength radiation. The spectral distribution shown in Fig. 3 was measured

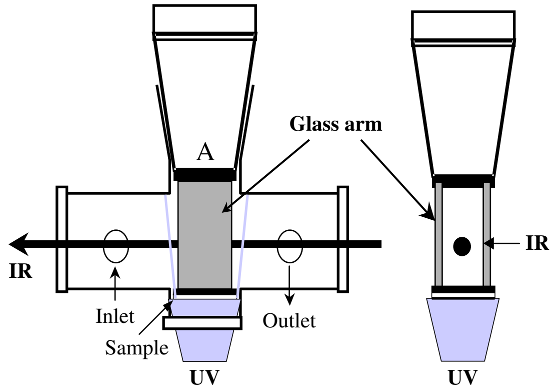

Fig. 1. The IR cell in which the polymer film is exposed to UV. The film can be placed close to the UV window (as shown here) or directly on the ground glass cone at A, at the side of the cell far from the UV window and behind the interrogating IR beam.