Simple Modification Measurement of Photodegradability of Polymers by using Photo-induced Chemiluminescence Technique

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ABSTRACT

Polymers and organic materials that are exposed to sunlight undergo photooxidation, which leads to deterioration of their physical properties. To allow adequate performance under outdoor conditions, synthetic polymers require additives such as antioxidants and UV absorbers. A major problem with optimising polymer formulations to maximise their working life span is that accelerated weathering tests are empirical. The conditions differ significantly from real weathering situations, and samples require lengthy irradiation period. Degradation may not be apparent in the early stages of exposure, although this is when products such as hydroperoxides are formed which later cause acceleration of oxidation. A simple way of quantifying the number of free radicals presents in organic materials following exposure to light or heat is by measuring chemiluminescence (CL) emission. Most polymers emit CL when they undergo oxidative degradation, and it originates from the bimolecular reaction of macroperoxy radicals which creates an excited carbonyl.

Keywords: *chemiluminescence, free radical, photooxidation, oxidation*

INTRODUCTION

Degradation of both natural and synthetic polymers occurs under the influence of environmental factors, such as light, temperature, moisture and pollutants and therefore limits their service life span. It is well known that light exposure leads to the degradation of polymeric materials, and damage is usually more pronounced following exposure to ultraviolet regions than the visible range. Photochemical reactions involving light radiation and atmospheric oxygen cause changes in chemical structure and loss of mechanical properties and lead to changes in physical properties of materials [1]. Common effects are discoloration, embrittlement, tackiness, loss of surface gloss and chalking of the surface [2]. These changes are usually undesirable. However, in the case of one-time-use polymers such as plastic packaging, accelerated degradation is required to reduce environmental pollution.

The oxidative degradation of polymeric materials can be viewed at the molecular level as triggered by chemically reactive molecules such as free radicals (R•, RO• and ROO•), and hydroperoxides (ROOH) [3]. The modification of the polymer properties due to exposure to sunlight or heat in the presence of atmospheric oxygen changes the chemical structure, leading to oxidation, double bond formation, chain scission, and cross linking.

The photooxidation of most polymers proceeds by a radical chain mechanism similar to that proposed by Bolland-Gee for rubbers and lipids [4] and widely applied to all types of polymeric materials. The mechanism of autoxidation involves initiation (formation of free radicals), propagation (reaction of free radicals with oxygen), branching (production of polymer oxy- and peroxy radicals and secondary polymer radicals, resulting in chain scission) and termination (reaction of different free radicals with each other, resulting cross linking) [3]. The photooxidation degradation of most polymers is shown below:

Initiation

$$\text{Polymer} \rightarrow P\bullet + P\bullet$$

Propagation

$$P\bullet + O2 \rightarrow POO\bullet$$

$$POO\bullet + PH \rightarrow POOH + P\bullet$$

Chain Branching

POOH → PO• + •OH
POOH + POOH → PO• + POO• + H2O
PH + •OH → P• + H2O
PH + PO• → P• + POH

Termination

P• + P• → Non radical products
P• + POO• → Non radical products
POO• + POO• → Non radical products + O2

where

PH = Polymer
P• = Polymer alkyl radical
PO• = Polymer alkoxy radical
POO• = Polymer alkylperoxy radical
POOH = Polymer hydroperoxide
HO• = hydroxy radical

The Mechanism of Autoxidation of Polymer [5]

This result in degradation of the mechanical properties and usually significant colour changes. Crucial to the study of free radicals in polymer degradation is the ability to be able to measure free radical species and the products of free radical reactions. Electron spin resonance (ESR) is one technique which can be used for the detection and identification of free radicals formed in chemical reactions. It has been widely used in the examination of free radicals in chemistry and in well-defined biochemical systems [6].

One of the constraints for using ESR is that most polymers have a glass transition (Tg) below or above room temperature and melting (Tm) temperature higher than room temperature and free radicals produced by exposure to UV generally have very short lifetimes at room temperature due to molecular mobility of the polymer, and hence are not directly observable by ESR [7]. Gerlock [8] doped polymer films with a nitroxide spin trap which resulted in formation of more stable, long- lived radicals when the film was exposed to UV light. By varying the concentration of nitroxide in the film, the photoinitiation rate for undoped polymer was obtained via extrapolation. Binns *et al.* [9] developed a low-temperature ESR technique to study free radical generated in polymer films during photolysis by UV light under nitrogen. Samples were cooled at 120 K in flowing nitrogen and exposed to a high pressure Hg/Xe lamp with 300 nm cut-off filter for 2 hours. Results predicting the service life of polymers were obtained within 2 hours.

A simpler method for studying free radical reactions in synthetic and biological organic materials is by using chemiluminescence (CL). It was first observed in 1961 by Ashby [10]. Oxidation of polymer and organic materials involving atmospheric oxygen is often accompanied by a low level of visible light known as CL [10,11]. It originates from the bimolecular reaction of macroperoxy radicals which creates an excited carbonyl. The reaction has a very low quantum yield (10-8 – 10-5) but highly sensitive photon counters make CL detection from most polymers straightforward [12]. The principle of the CL method is the measurement of light emitted from samples during decomposition of peroxides and this has been developed to study polymer oxidation [13-15]. However, its application to the study of the photodegradation of materials has been very limited.

A new technique, photo-induced chemiluminescence (PICL), to study the generation and decay of free radicals formed in materials following exposure to light and oxygen was developed by Millington [16]. This technique has been used in studies on fibrous polymers and proteins [16], photo-degradation of protein fibres [17], photostability of wool keratin doped with photocatalytic TiO2 pigment [18] and the effect of dyes on PICL emission [19]. The advantage of PICL is that it is a very simple and quick technique that can be used to study the effectiveness of additive treatments in reducing the free radical population. Results of the effectiveness of additive performance on fabrics can be obtained within fifteen minutes per sample [7]. Figure 1 shows a typical polymer luminescence against time plot, where a strong burst of PICL emission occurs when the irradiated sample is exposed to oxygen.

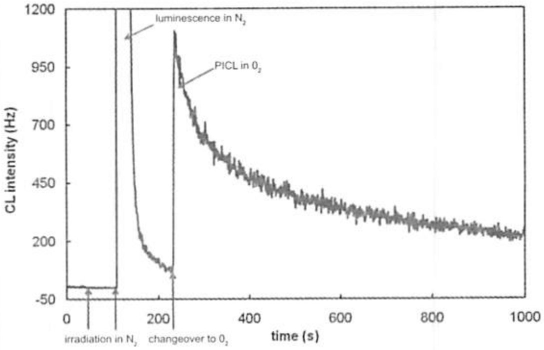

Figure 1: Luminescence from Polyacrylonitrile Fabric at 313K Exposed to UVA Radiation for 60s in N_2. Atmosphere Changed to O_2 2 Minutes After End of Irradiation Period

EXPERIMENTAL PROCEDURES

For PICL studies a Lumipol 3 thermal CL instrument (Polymer Institute of the Slovak Academy of Sciences, Bratislava) was reversibly modified to allow *in situ* irradiation with selected wavelengths from a medium-pressure mercury arc (Lumatec SUV-DC, Lumatech GmbH, Germany) via a liquid light pipe, as shown in Figure 2.

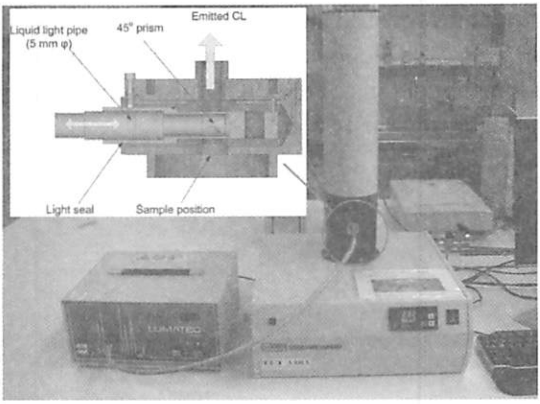

Figure 2: Lumipol Instrument Linked to Lumatec Light Source for PICL Studies. Inset Shows the Adaptor which Allows Samples to be Irradiated *in Situ* with Wavelengths Above 320 nm

Selected wavelengths in the range 320–700 nm enters the Lumipol instrument via a flexible liquid pipe (Lumatec Series 250, 5 mm diameter) and irradiates the sample via a 45° quartz prism built into the light pipe and positioned directly above the sample cavity. The wavelength setting can be varied using a series of filters: filter 1 (400–700 nm), filter 2 (320–500 nm), filter 3 (400–500 nm), filter 4 (320–400 nm), filter 5 (415 nm) or filter 6 (440 nm).

This technique requires a very small sample (8 mm in diameter), cut using a circular cutter. The sample is placed in a small aluminium pan located directly above the heating element. To obtain a PICL signal on a sample, the sample is equilibrated in the instrument in nitrogen atmosphere at constant temperature until a steady baseline is obtained. The sample is then exposed to light for a set period. A large luminescence emission is observed immediately after irradiation, which in most cases decayed very rapidly, usually in less than 30 s. One minute after cessation of irradiation, the atmosphere is switched from nitrogen to oxygen, resulting in a burst of PICL that generally decayed far more slowly than the peak observed in nitrogen. These protocols are applicable to all samples.

Figure 3 shows typical luminescence intensity against time plot for silk fabric using protocol mentioned above. The silk fabric was irradiated under UVA light for 30s and PICL peak was observed when the atmosphere changed to Nitrogen. A spectral analysis of the Lumatec source was carried out using a Solatell Sola-Scope 2000 spectroradiometer (Sola tell Ltd., Croydon, UK). Further details of the PICL instrument and the modification have been described previously [16].

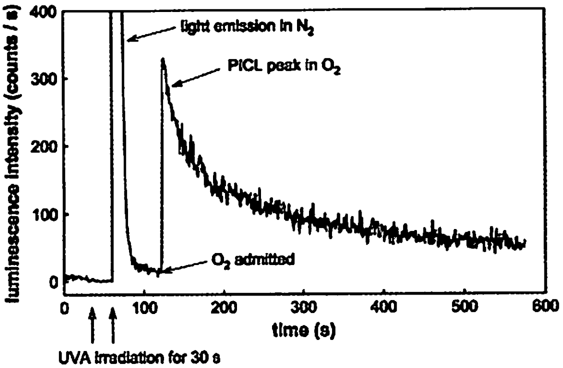

Figure 3: Luminescence from Silk Fibroin at 40 °C Exposed to UVA Radiation for 30 s in N_2. One Minute After Conclusion of Irradiation, the Atmosphere was Changed from N_2 to O_2 to Generate PICL [13]

DISCUSSION

This new technique has been used to study wool photodegradation [17], the photostability of wool keratin doped with TiO2 pigment [18] and the influence of dyes on free radical populations [19]. The PICL technique is also used to monitor the effectiveness of additive formulations. This includes the ability of additives to promote or prevent free radical oxidation [12, 20]. This sensitive technique can also be used as an early indicator of material degradation [7].

The effects of different additives in reducing or increasing free radical population using PICL technique has been studied [12]. Irgacure 2959 (photoinitiator) has produced higher free radical populations than a control sample as shown in Figure 4. The result indicates that Irgacure 2959 has the ability to generate free radical populations and accelerate the oxidation process in EC polymer films. Irgacure 2959 could potentially be used in the natural environment as a degrading agent, which would contribute to the reduction of environmental waste load. In the case of Tinuvin 400 (UV absorbers) it significantly reduced free radical populations when irradiated with UVA light.

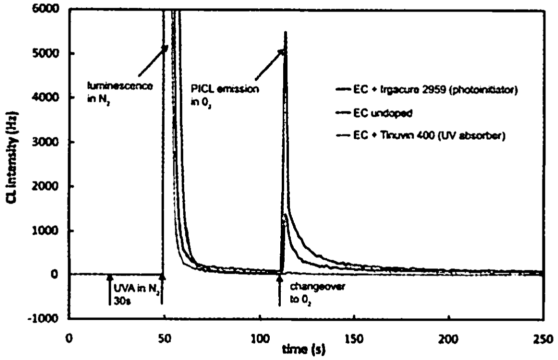

Figure 4: PICL from Ethyl Cellulose Films Doped with Photoinitiator or UV Absorber and Exposed to UVA Radiation at 40°C for 30s in N2 [9]

This study revealed that highly cross linked polymers (eg. polyurethane) and polymers with strong hydrogen bonding networks (gelatin and PVA) have very low PICL intensities at 40°C [17]. Recently we have been studying the effects of UV absorbers, antioxidants and metal chelators doped into polymer films and have found that these reduce PICL intensity [21]. We believe that PICL can be used to optimise additive treatments in polymers to prolong their active life during sunlight exposure. In the case of short-lived packaging materials PICL may be also used to monitor the effectiveness of additives that can promote free radical oxidation, to enable rapid photooxidation of waste polymers in the environment.

SUMMARY

PICL is a promising rapid evaluation technique that can be used to monitor photodegradation of materials by the measurement of chemiluminescence emitted from irradiated samples. The PICL intensity is proportional to the free radical population available to react with oxygen in irradiated materials. Results demonstrate the effectiveness of the PICL technique for the investigation of polymer degradation, particularly in the induction period where most analytical techniques are unable to detect any change in the polymer. PICL, combined with spectrophotometry, which determines the degree of chromatic alteration, may provide new insights into oxidative degradation processes. The PICL technique is an important tool for use in conservation, as it detects the early stages of material deterioration and therefore enables preservation programs to be put in place.

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