Chemiluminescence and fluorescence for monitoring the photooxidation of an UV-cured aliphatic polyurethane-acrylate based adhesive

Carmen Peinado,*, N.S. Allen, Enrique F. Salvador, Teresa Corrales, Fernando Catalina

*Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

bDepartment of Chemistry and Materials Technology, Centre for Materials Science Research, Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK

Received 8 March 2002; accepted 3 April 2002

Abstract

The photooxidation of an UV-cured polyurethane-acrylate adhesive, has been monitored through the use of chemiluminescence and fluorescence techniques. Chemiluminescence analysis shows early stages of photooxidation in the adhesive when there is neither loss or change in the physical and chemical properties of the material. Moreover, fluorescent probes incorporated into the adhesive formulation have been found to be very useful to detect the first oxidation species. Quenching of fluorescence follows the same kinetics as the chemiluminescence increase during UV-exposure. Two fluorescent probes, p-dimethylamino salicylic acid and 2',7'-difluorofluorescein, were sensitive to the formation of oxidation products. Therefore, good correlations between fluorescence and chemiluminescence were established. We conclude that the fluorescence emission from extrinsic probes can be used as a valuable method to analyse photooxidation from the initial stages. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chemiluminescence; Fluorescence; Fluorescent probes; Photooxidation; Polyurethanes

1. Introduction

The prediction of the useful life of polymer materials is a major challenge for industry. Two approaches have been considered in this regard: (i) the extrapolation of results carried out under accelerated conditions and (ii) the use of highly sensitive techniques which are capable of detecting the initial stages of degradation. Although accelerated ageing has been widely employed to study polymer degradation, some controversies arise from the fact that the material response could vary under extreme conditions compared to those under natural weathering.

It is well-known that the degradation of polymers produces hydroperoxides, which can decompose into alkoxy and hydroxyl radicals accompanied by a weak emission of chemiluminescence (CL). Several authors have found a correlation between CL signals from polymers and the kinetics of their oxidation [1–5]. Although CL emission has concentrated mainly on studies of thermo-oxidation this technique has also been useful to reflect the extent of photo-oxidation in different applications such as automotive coatings [6]. The high sensitivity of CL has been capitalised to evaluate polymer stability to heat [7], UV-light [4], electron beam [8] and γ-irradiation [9].

In the last few years, different mechanisms have been proposed to explain the origin of CL from oxidized polymers, involving several elementary reactions such as fragmentation, rearrangement and electron transfer. The self-recombination of secondary peroxyl radicals is considered to be the main mechanism giving rise to a ketone moiety in an excited triplet state together with singlet oxygen and thus, both can emit light when passing to their ground state [10].

POO· + POO· → POH + ^1O2 + ^3P(C = O)*

Due to the high sensitivity of the chemiluminescence technique, the nature of end groups, residual amounts
of catalyst or other molecular compounds can influence the nature of the emission. For example, volatile compounds released from the polymer can be another potential source of light emission. However, the stability of polymer materials can be evaluated by chemiluminescence even though the exact mechanism of chemiluminescence generation is unknown. Therefore, we have considered this technique appropriate to study the photooxidation behaviour of a polyurethane-acrylate based adhesive which has a complex composition.

This technique offers the advantage of high sensitivity for monitoring the degradation during the earlier stages of the process. Compared to other methods to detect free radicals such as ESR, chemiluminescence is more sensitive by at least two orders of concentration of free radicals. Whilst there are other techniques for evaluating polymer degradation, from an analytical point of view, methodologies such as FTIR, iodometric titrations to determine hydroperoxide concentration, thermal analysis (TG, DSC, ...) often lack sensitivity and this is a major drawback in the detection of the initial stages of degradation.

Fluorescence spectroscopy has also become a powerful technique for studying the physical and chemical behaviour of polymers. The emission of a fluorophore, added to a macromolecular solution, adsorbed in a polymeric film or labelled to polymers, can also report about its microenvironment and this valuable information has been related to polymer structure, interactions, morphology, dynamic changes, rigidity, crystallinity and orientation, etc. Fluorescence analysis has been widely used to study different processes on polymers due to its high selectivity and sensitivity [11–13]. In this sense, fluorescence emission changes from a polymer material due to the appearance of new chromophores (photooxidation species) has been followed during photooxidation [14]. To the best of our knowledge fluorescent probes have not been used to study the complex processes of photooxidation. Among the advantages of using fluorescence, those one of interest for our aims are: (i) high sensitivity which allows the detection of small concentrations of fluorophore probes and (ii) non-touching method, information could be easily collected via optical fibres thus avoiding perturbation of the studied material. In this way, optical remote monitoring is feasible. In this regard, excited-state proton transfer (ESPT) compounds have been employed in technological applications such as in photolithography [15], chemical lasers [16], etc., and as probes of the environment around proteins, micelles and films [17].

The object of the present study was to examine the use of the fluorescence method for monitoring the photooxidation of complex adhesive urethane coatings and to establish a correlation between fluorescence emission changes and those of chemiluminescence.

2. Experimental

2.1. Materials and sample preparation

Two commercial fluorescent probes, p-dimethylamino salicylic acid from Sigma and Oregon Green 488 (2',7'-difluorfluorescein) from Molecular Probes, were selected and their photostability under the conditions used to degrade the adhesive was assessed. Fig. 1 shows their chemical structures.

L350 adhesive was kindly provided by Loctite España. Fractionation and analysis of the components of L350 adhesive showed that it comprises a mixture of 35% polyurethane-acrylate resin (weight average molecular weight=6400) prepared from tolylene 2,4-diisocyanate and poly(oxytetramethylene glycol) with methacrylate groups as chain ends, 15–20% hydroxyl (meth)acrylate, 5–15% lauryl methacrylate, 5–7% acrylic acid, 3–5% tetradecyl methacrylate, 1% of 2,2-dimethoxy-1,2-diphenyl ethanone used as photoinitiator and 2% of an adhesion promoter ([3-(oxyranylmethoxy)propyl]silane.

Homogeneous mixtures of the adhesive formulation and the fluorescent probes (0.05% w/w) were prepared. The adhesive was placed filling an area of 2.5×1.4 cm² between two polyethylene films between two glass plates using a 40 μm spacer then irradiated with polychromatic light using a medium-pressure 400 W mercury lamp (Macam-Flexicure system) until limiting conversion was reached. Full cure of the material was assessed by FT-IR. The samples for chemiluminescence analysis were free of fluorescent probes.

Fig. 1. Structure of fluorescent probes.
2.2. Photoageing

A cylindrical reactor provided with 5 Philips lamps (8 W/lamp) around a central carousel was used for accelerated photoageing. The distribution of the ultraviolet radiation is centred at 365 nm. Under these conditions a temperature of 40–45 °C is reached in the sample holder. From time to time, the samples were removed from the reactor to measure the fluorescence and chemiluminescence spectra.

2.3. Analysis

UV spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Infrared spectra were recorded in a FTIR spectrophotometer Nicolet 520. Fluorescence spectra were recorded on a Perkin-Elmer LS-50B spectrophotometer. Excitation wavelengths were selected at the maximum absorption of the fluorescent probe in the cured adhesive. Emission spectra were corrected using the response curve of the photomultiplier.

Chemiluminescence was measured using a CL400 ChemiLume Analyzer from Atlas Electric Device Co. The adhesive films were held in a small aluminium pan (20 mm diameter) in the sample cell under a continuous flow of dry nitrogen (60 ml/min). The cell is temperature-controlled and was heated up with a pre-test ramp (10 °C/min) to 100 °C. During dynamic experiments, a heating rate of 5 °C/min was used. In order to assure reproducibility of CL signals the dimensions of the specimens were kept constant: discs of 12 mm diameter and 40 μm thickness. The films were covered by a lens focussing the emitted light from the sample to the water-cooled photon-counting photomultiplier, which was previously calibrated using a radioactive standard provided by Atlas. The light emitted was measured as a function of time as the sample was heated isothermally. CL decay rates, \( v_{CL} \), were obtained from the slope of the plot of the inverse of the square root of CL intensity versus time in the linear region [18], \( 1/\sqrt{I_{CL}} = v_{CL} \cdot t \).

3. Results and discussion

3.1. Study of photooxidation of a polyurethane-acrylate based adhesive from chemiluminescence analysis

Fig. 2 shows the CL emission of L350 at different irradiation times, each following a sigmoidal (S-shaped) curve. The signals reach a maximum and then start to decrease to a non-zero intensity and seem to reach a steady state after a certain time. The CL data as a function of UV-irradiation time are summarised in Table 1.

There is an initial induction time \( t_{inh.} \) of 110–140 s in all the measurements which can be related to the induction period of the reaction responsible of chemiluminescence. However, the differences observed for L350 after different UV-exposure times were not significant, demonstrating that the emission is generated from the start of the heat treatment, at 100 °C under nitrogen, by the same type of oxidation species in all the samples. It is known that chemiluminescence can be related to the hydroperoxide content of the polymer [19]. It is interesting to point out that the unexposed sample exhibits a weak CL at 100 °C under nitrogen indicating a low concentration of hydroperoxides (Fig. 2, time = 0). After UV-irradiation the CL integrated intensity and maximum intensity increase with exposure time. This result confirms that CL is related to the history of the photooxidation of the adhesive. Moreover, the CL decay rate, \( v_{CL} \), decreases as the UV-irradiation time increases. This parameter measures the rate of recombination of peroxides and thus, will depend on the molecular mobility [20]. A rapid decrease of the CL-decay rate under UV-exposure is observed in Fig. 3. This feature is in accordance with the suggestion that the CL originates from radical recombination reactions outside the primary cage [19].

<table>
<thead>
<tr>
<th>( t_{irr.} ) (h)</th>
<th>( t_{inh.} ) (s)</th>
<th>( I_{max} ) (mV)</th>
<th>( t_{max} ) (s)</th>
<th>( I_{residual} ) (mV)</th>
<th>Area (V·s)</th>
<th>( v_{CL} ) ((mV)^{-1/2}\cdot s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>125</td>
<td>36</td>
<td>405</td>
<td>0</td>
<td>298</td>
<td>12.3</td>
</tr>
<tr>
<td>1</td>
<td>117</td>
<td>226</td>
<td>400</td>
<td>–</td>
<td>355</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>417</td>
<td>474</td>
<td>222</td>
<td>644</td>
<td>1.6</td>
</tr>
<tr>
<td>6</td>
<td>110</td>
<td>504</td>
<td>522</td>
<td>277</td>
<td>816</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>110</td>
<td>510</td>
<td>565</td>
<td>340</td>
<td>900</td>
<td>0.8</td>
</tr>
<tr>
<td>24</td>
<td>128</td>
<td>728</td>
<td>670</td>
<td>367</td>
<td>1289</td>
<td>0.6</td>
</tr>
<tr>
<td>48</td>
<td>132</td>
<td>779</td>
<td>680</td>
<td>–</td>
<td>1013</td>
<td>0.6</td>
</tr>
<tr>
<td>63</td>
<td>143</td>
<td>791</td>
<td>749</td>
<td>–</td>
<td>1444</td>
<td>0.4</td>
</tr>
</tbody>
</table>
CL maximum intensity was plotted as a function of the exposure time in Fig. 4. These curves show that the photooxidation of the L350 adhesive films starts after only few hours of UV-irradiation and then remains constant for at least the first 70 h. This kind of study is considered to provide a reliable evaluation of the earlier stages of photooxidation. Some scatter in the CL values can be related to a heterogeneous distribution of the photo-oxidation in the films.

The CL-signal is a measure of peroxide concentration and as such could be related to the failure time, detected by the appearance of visual defects such as cracking. In any case, failure of the adhesive L350 was observed during the period of photooxidation. This fact is not surprising because CL reflects bulk degradation while the failure time is determined by a measure of surface degradation. In this regard, since the diffusion rate of oxygen into the substrate plays an important role in the degradation of polymeric materials, it has to be pointed out that L350 showed a relatively high permeability [13] for N₂ and O₂. Therefore, a preferential surface photooxidation is not expected under atmospheric conditions, at least for the thicknesses of the polymer films studied here.

From the temperature-ramped experiments, the activation energy for CL emission from a non-irradiated sample of the polyurethane-acrylate based adhesive was determined. The activation energy was determined to be 85 kJ/mol from the Arrhenius plot of the CL-intensity over the temperature range 60–150 °C. The CL emission may stem from excited carbonyl groups. Of course, other mechanisms are feasible but in this case, explanations of the CL observed and the exact nature of the emitter is difficult to elucidate due to the complexity composition of the UV-cured aliphatic polyurethane-acrylate based adhesive. For example, peroxides from the acrylate is also likely to generate part of CL.

3.2. Study of photooxidation of a polyurethane-acrylate based adhesive by fluorescence

Two commercially available fluorescent probes were used to monitor the photooxidation of L350: Oregon Green (OG) and p-dimethylaminosalicylic acid (p-DASA). Both probes are pH-sensitive [21]. A key property for the suitability of these fluorescent probes was that the photobleaching quantum yield was low. Thus, the photostability of these fluorescent compounds was assessed by UV-absorption monitoring during the period of UV-exposure.

The fluorescence emission of these probes changes as photooxidation of L350 progresses (Fig. 5a–b). The emission spectrum of p-DASA in a non-photooxidised L350 film shows two maxima at 385 and 435 nm. The large Stokes shift of the band at the longest wavelength is a normal feature in those compounds that have an intramolecular hydrogen bond in the ground state and is due to an intramolecular proton transfer in the excited state (ESIPT) [22]. In non polar aprotic solvents the anomalous Stokes shift (ASS) fluorescence appears around 440 nm in addition to the normal band at 330 nm [23]. Moreover, the conjugation of electron donor and acceptor groups through an aromatic system, D–π–A, allows the existence of another emission from a more relaxed state due to intramolecular charge transfer (ICT). Thus, the large Stokes’ shifted emission band becomes broadened as can be observed in Fig. 5(a).

Fig. 3. Plot of CL-decay rate versus UV-irradiation time for L350.

Fig. 4. Plot of CL-intensity at the maximum signal versus UV-irradiation time for L350.

However, it has been observed that the normal and ICT fluorescence emissions are quenched as the p-DASA concentration decreases in protic solvents, followed by the appearance of a new emission from a more relaxed state due to intramolecular charge transfer (ICT). Thus, the large Stokes’ shifted emission band becomes broadened as can be observed in Fig. 5(a). However, it has been observed that the normal and ICT fluorescence emissions are quenched as the p-DASA concentration decreases in protic solvents, followed by the appearance of a new emission at 380 nm. This behaviour has been interpreted as a result of ESIPT coupled charge transfer [23]. During photooxidation a rapid decrease of the emission at 380 nm is observed together with a red shift and also, an intensity decrease of the band initially centred at 440 nm. Different arguments might be put forward for the observed fluorescence intensity decrease such as the formation of...
oxidation products (peroxide, etc.) generated during photooxidation that are able to quench the excited states of emitting fluorophores.

Fig. 5(b) shows that the intensity of the fluorescence emission of OG in L350 decreases during the UV-irradiation of the film, with a slight blue shift of the maximum wavelength.

The ratio between the emission intensity at two different wavelengths and the maximum intensity was used to analyse the behaviour of the probes doped into the adhesive during photooxidation (Fig. 6).

Fig. 7 shows the plots of fluorescence of the two fluorescent probes as a function of the CL-parameters, maximum intensity and decay rate, for the polyurethane-acrylate based adhesive.

In order to analyse the oxidation level of the adhesive by fluorescence, a correlation between fluorescence intensity ratio and chemiluminescence was established. Good correlations can be observed in all the cases indicating that the kinetics of formation of the species which quench the fluorescence and produce chemiluminescence are intimately related. Other properties which correlate with physical or chemical changes occurring during photooxidation were evaluated. However, attempts to correlate fluorescence with FTIR results during photooxidation were unsuccessful mainly due to the lack of sensitivity of FTIR to detect earlier signs of photooxidation.
The photochemical degradation of polyurethanes has been extensively studied in the last three decades [24]. In the case of poly(ether-urethanes) the poor weathering properties are mainly due to the ether component [25]. The abstraction of a hydrogen radical at the α carbon next to the ether moiety, followed by reaction with oxygen gives rise to the formation of a hydroperoxide. As shown in Scheme 1 they can decompose into two radicals: an alkoxy macroradical and a hydroxyl radical, OH·, which can react following three different routes: (i) reaction inside their cage leading to the formation of ester groups and water, further hydrolysis of the ester gives acid groups; (ii) hydrogen atom abstraction by the alkoxy macroradical to give a hemiacetal that converts to an aldehyde which is rapidly oxidized to produce acid groups and (iii) β-scission to produce formates. Moreover, aromatic urethane groups may follow a photo-Fries fragmentation and yellowing of the material was observed under prolonged exposure.

According to the proposed mechanism, FTIR analysis of the L350 adhesive shows a decrease of the absorption of the bands centred at 1110 and at 1224 cm⁻¹, assigned to the stretching of C–O–C and O–CH₂ bonds in ether groups. This behaviour has been associated with the disappearance of poly(tetramethylene glycol) as the main route of photooxidation. Although, no changes in the IR bands corresponding to the carbonyl groups was observed due to the absorption from acrylate groups, the formation of acid groups cannot be disregarded.

The two fluorescent probes used in this work, p-DASA and OG, are pH-sensitive and a decrease of the fluorescence intensity is observed as the pH diminishes, for example, OG has a low pKₐ (4.7). As seen in Scheme 1 acid groups may be obtained as photooxidation products which may be responsible for the fluorescence quenching of p-DASA and OG. However, quenching of the fluorescence emission by other photoproducts can not be excluded.

The CL technique has been efficiently used as a highly sensitive method that gives information on photooxidation of the bulk of the polymer material for adhesive coatings. However, a better understanding of CL-emission should be provided to predict the life time of materials. The same statement is valid for the fluorescence method. Nevertheless, a further improvement of both methods can lead to the development of standard methods to assess the durability of polymer materials. In this regard, we are carrying out comprehensive studies of the photooxidation of different polymeric materials by chemiluminescence/fluorescence and the results will be further reported.

4. Conclusions

These results contribute to the development of a sensitive fluorescence based method in order to assess physical or chemical changes during the early stages of their photooxidation, well before any defects become visible in the adhesive or failure by fracture is observed.

It is noteworthy that there are good correlations between fluorescence and CL measurements during photooxidation of the polyurethane-acrylate adhesive. Therefore, it is possible to assess photostability performance of a material by the fluorescence method after a very short time of exposure due to its sensitivity comparable to that of chemiluminescence. It should be pointed out that intrinsic CL as well as fluorescence from probes sense the photooxidation level in the bulk.

The greater photostability of fluorescent compounds exhibiting an intramolecular proton transfer in the excited state (ESIPT) has stimulated the use of p-dimethylamino salicylic acid as a probe for monitoring photooxidation. Moreover, Oregon Green combines high fluorescence quantum yields together with a great resistance to photobleaching.
Acknowledgements

The authors would like to thank the Union European Commission for funding through the BRITE-Euram Project (BE97–4472). Gratitude is also extended to Plan Nacional I + D + I (Ministerio de Ciencia y Tecnologia) for financial support (MAT 1998–0518-CE and MAT2000–1671). We thank Loctite España for providing the adhesive formulation.

References