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A new technique for the study of reactive species generated during the initial stages of polymer photodegradation

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Summary

A low temperature ESR technique has been developed for the observation of free radical intermediates generated in clear polymer films during photolysis by UV light under nitrogen. The technique is simple and reproducible, and can be used for polymers having glass transition temperatures at or about room temperature without the need to employ spin traps. The generation of free radicals can be monitored and quantified during exposure, and the radical yields obtained can then be correlated with the chemical structure of the polymer to provide a rapid predictive evaluation of the exterior durability of the polymer.

Introduction

The exposure of polymers to UV light can lead to excitation of the electron pair in a bond, leading to scission of that bond (photolysis) and the generation of free radicals. Photolysis of a polymer is widely regarded as the first step in the photodegradation process (1,2,3). Scavenging of the free radicals so produced by atmospheric oxygen leads to the formation of hydroperoxides, which eventually leads to embrittlement, degradation of physical properties and eventual failure. Thus the observation and quantification of free radicals produced during the initial stages of photodegradation may form the basis of a rapid predictive test for exterior weatherability.

If the glass transition of a polymer occurs at close to room temperature, 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. Gerlock and co-authors (3,4) have described an ESR technique for the study of photoinitiation of polymer degradation in air which involves doping the polymer film with a stable nitroxide "spin trap". The doped polymer is exposed to UV (either artificially generated or natural sunlight) and the radicals produced are scavenged and stabilised by the nitroxide. By monitoring the change in nitroxide radical concentration for several samples of the same film containing different concentrations of nitroxide, the photoinitiation rate for the undoped polymer film can be estimated by extrapolation. This technique has been applied mainly to hydroxy-functional acrylics crosslinked with melamine formaldehydes or urethanes, which are typical of the formulations used in clear automotive topcoats.

The spin trap technique, however, suffers from a number of disadvantages. Spin traps are typically bulky organic nitroxides which would tend to be rather immobile in a polymer film. Also, due to steric and other considerations, spin traps do not react with all types of free radicals at the same rate. Hence not all free radicals produced upon photolysis of a polymer film will be scavenged and prevented from reacting further. In addition to this, the trap molecules must compete with atmospheric oxygen for the available radicals, and are themselves somewhat photolytically unstable, hence the need for the extrapolation technique. Under ideal conditions, however, the major advantage is that the technique can be used with exposure to natural sunlight.

Sommer and co-workers (5) recently described a low temperature ESR method for evaluating the weather resistance of polymers. Earlier work by the same group (6) showed a positive correlation between

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outdoor weather resistance, using cracking and discoloration as the main criteria for evaluation, and ESR results. Experimental details, especially sample preparation, were not extensive, and the results presented were not quantitative.

We have developed a low temperature ESR technique to quantitatively study free radicals generated in polymers by exposure to UV light, and applied the technique to the study of melamine-crosslinked polyesters similar to those used in paint formulations for coil-coated steel.

Experimental

A Bruker ER200D X-band ESR spectrometer was used in this investigation, operating at 9.3GHz using 2mW microwave power, with a nominal magnet centrefield of 0.33T. Field modulation used throughout was 10G. The films were mounted on a flat plate of Specrosil-grade quartz, as described below, placed in the spectrometer and cooled to 120K in flowing nitrogen using a standard quartz variable temperature insert. The generation of free radicals was accomplished by exposure in the ESR cavity to the filtered output of a high pressure Hg/Xe lamp, focussed through the front wall of a standard rectangular cavity. Using this method the free radical concentration could be monitored with exposure time, and an initial photolysis rate measured. Also, photolysis rates were measured under conditions essentially free of competing reactions such as scavenging by oxygen. The lamp output was filtered using a water filter to remove the infrared component, and a 300nm cut-off filter to remove unwanted short wavelength UV. It is thought that the lamp filtered in this way produced an output with a UV component similar to natural sunlight, but at much higher intensity. Samples were typically exposed for 2 hours, with periodic measurement of radical concentration during exposure.

The spectrometer was calibrated by use of a strong pitch spin standard (Varian, 3x10^{15} spins/cm), and small variations in lamp intensity were corrected by daily exposing a film of known photolytic behaviour to the lamp output.

A hydroxy-functional polyester (M_n ~ 1200) was mixed with hexamethylmethylolmelamine (HMMM, Cyanamid Cymel 303) at 10, 20 and 30 wt%, using p-toluenesulfonic acid (Cyanamid Cycat 4040) as the catalyst. Clear free film samples of 20μm thickness were prepared by coating aluminium panels previously treated with a silicone release coating (Dow Corning Q1-2531). After baking at 232°C PMT, the films were thus easily removed from the aluminium substrate.

Results and Discussion

A common method for observing free radicals is to load the sample into a quartz ESR tube, then generate the radicals if necessary by any of several means and observe them in the spectrometer. This method is useful for liquids and powdered samples, and for polymer films if the radicals are generated uniformly throughout the film (for example by γ-radiolysis). However, for photolysis of film samples by UV light, because the film may contain high extinction coefficient components, radical generation is often confined to the first few Angstroms at the surface. Hence lack of reproducibility of sampling can lead to variable radical yields for different samples of the same film prepared and exposed under ostensibly identical conditions. Thus a valid comparison of different formulations becomes impossible.

In this study, the first sampling method used involved rolling a piece of film approximately 40mm square into a cylinder, loading into a 4mm O.D. quartz ESR tube and flame-sealing under vacuum. Using this method, sample to sample variations occurred in the area of film exposed to UV, leading to the differences in radical yields referred to above. Thus a method involving photolysis of a flat film sample of reproducible area in the spectrometer at a reproducible angle to the light path was developed.

A flat plate of Spectrosil-grade quartz, 1mm thick and 30mm long and attached to a quartz locating rod, was designed to fit into a standard Bruker variable temperature insert (nominally 5mm wide). A registration pin at the top of the rod allowed the orientation of the plate in the spectrometer to be reproducibly set. The total length of the plate was determined such that a length of 2-3mm at the top and bottom of the plate was outside the sensitive region of the spectrometer. A piece of polymer film was cut to size and attached to the plate at the top and bottom using a suitable adhesive, such as a smear of high-vacuum grease, which was found to be sufficiently adhesive at the low temperatures used, and the sample was easily removed at the conclusion of the experiment.

The low temperature method is considered to be valid if it is assumed that the radical-generating reactions are not affected by temperature, and cooling the sample simply stabilises the radicals formed, preventing them from reacting further.

A technique using several layers of film fused together was investigated, but was not further developed since, even though radical yields were found to be higher than for single films, the presence of high extinction coefficient components resulted in less absorption in lower layers of film not directly exposed to the UV light, thus leading to erroneous results.

The reproducibility of the single film technique was checked by separately photolysing three samples of one film formulation under the same conditions. At a given exposure time, all three samples gabe the same radical yield to within 5%.

The technique was used to examine the effect of melamine formaldehyde crosslinker levels on the rate of photolysis. Figure 1 shows the results of photolysis of films containing 10, 20 and 30 wt% HMMM. From this data, initial photolysis rates were calculated, as shown in Figure 2 as a function of HMMM content.

It can be seen from the Figures that increasing the level of crosslinker led to an increase in the initial photolysis rate. The theoretical composition at which all polyester hydroxyls and all crosslinker methoxys are reacted occurs at 12% crosslinker, thus for formulations containing 20 and 30% HMMM there is an excess of crosslinker present and the films will therefore contan unreacted crosslinker methoxy groups. The actual concentration of crosslinks is similar in all formulations, so the large increase in photolysis rate with increased crosslinker concentration can be correlated with excess crosslinker methoxy groups.

It has been shown (7) that the photolysis of methoxylated melamine formaldehyde crosslinkers at low temperature gives rise to methyl radicals, which have been observed at 77K. Indeed, all radical species observed on photolysis at 77K can be rationalised in terms of initial formation of methyl radicals, followed by abstraction and rearrangement reactions.

The results of photolysis of films presented here clearly demonstrate that the presence of excess HMMM crosslinker leads to high photolysis rates, even though the crosslinker itself has only one major chromophore exhibiting a broad absorption peak at λ_{max}= 238nm (7), tailing into the near UV. Some

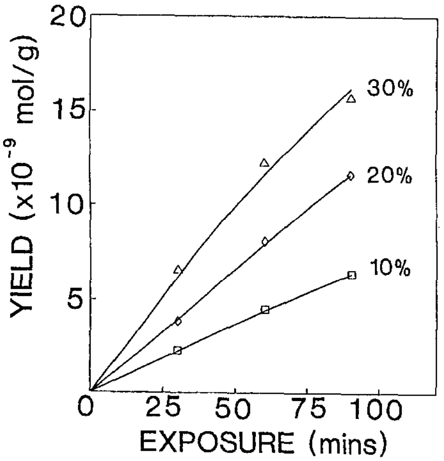

Figure 1
Photolysis of Crosslinked Polyester Films

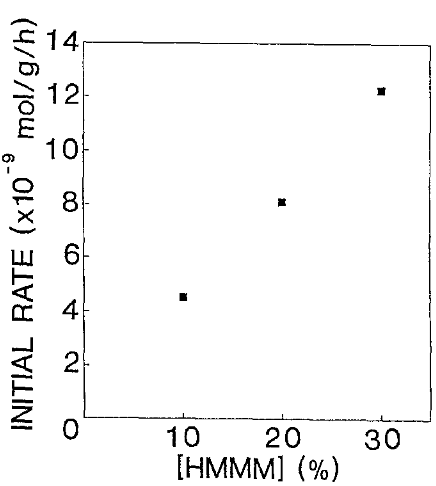

Figure 2
Initial Photolysis Rates

absorption of energy by the crosslinker would thus be expected to occur at >300nm, leading to the generation of very mobile, reactive methyl radicals which can permeate the film, abstract a hydrogen (forming methane) from another polymer site and hence damage the film. Thus in film formulations with high levels of methoxylated crosslinker (such as HMMM), a major degradation mechanism may involve dissociation of the crosslinker at the unreacted methoxy groups, analogous to the degradation of the crosslinker itself.

Conclusions

A low temperature ESR technique has been developed for the observation of free radicals produced in polymers during exposure to UV light. The technique has been shown to be reproducible to within 5%.

It was shown that, for polyester films crosslinked with HMMM, increased levels of crosslinker led to increased initial photolysis rates, indicating that a major photodegradation mechanism may involve dissociation of the crosslinker, particularly if unreacted crosslinker methoxy groups are present.

We are currently evaluating the ESR technique as described as a potentially very fast method to predict differences in the service life of polymers used in outdoor applications (such as in paints for coil-coated steel). Results are obtained within 2 hours, obviating the need for extended outdoor and artificial weathering trials.

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