

Surface Photo-oxidation of Phenoxy Resin and Polyetheretherketone

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(Received 31 July 1987; accepted 11 August 1987)

ABSTRACT

The changes in surface chemistry of phenoxy resin and polyetheretherketone during photo-oxidation were monitored by ESCA. Extensive oxygen uptake was observed for both materials and the data showed that oxidation of the phenyl rings had occurred. Comparison of phenoxy resin with its acetylated derivative indicated that the changes in surface chemistry of the former during the initial stages of exposure were not due to the hydroxyl group.

INTRODUCTION

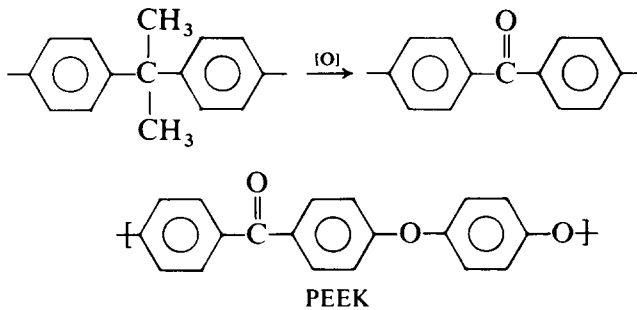
The photo-oxidation behaviours of Bisphenol A polysulphone, polycarbonate and phenoxy resin have previously been compared with respect to changes in bulk chemistry.¹ We have examined the changes in surface

chemistry, by ESCA, or polysulphone² and polycarbonate³⁻⁵ and report here the corresponding changes in phenoxy resin.

The surface photo-oxidation of polyetheretherketone (PEEK) has not been reported previously in the literature. Apart from the intrinsic interest in this polymer, because of its applications as an engineering plastic, its relevance to the present study arises from two areas.

(a) The only carbon atom in the polymer that is not part of a phenyl ring is that of the ketone group. Thus, for extensive oxygen uptake during photo-oxidation to occur, the phenyl rings must be directly involved. This would provide further evidence for the oxidative attack of the aromatic rings in polymers containing phenyl groups during photo-oxidation.²⁻⁵

(b) The heat curing of phenoxy resin in air is believed to oxidise the isopropylidene unit to form aromatic carbonyl groups that can initiate photo-oxidation.⁶ As can be seen from the structures shown below, this structure is similar to the repeat unit of PEEK. Therefore, PEEK provides the opportunity to study the contribution of the aromatic carbonyl group to surface photo-oxidation:



EXPERIMENTAL

Phenoxy resin and PEEK were exposed to the output of a 500W Hanovia medium pressure mercury arc lamp via a Pyrex window ($\lambda > 290$ nm) in a flowing oxygen atmosphere as previously described.³ In order to examine the role of the hydroxy functionality in the ether portion of phenoxy resin, films were exposed to the vapour pressure of acetyl chloride for 15 min prior to irradiation. The wavelength dependence of the surface photo-oxidation of PEEK was also studied. Wavelength selection over the range 270 to 360 nm (with a 10 nm bandpass and 1.5 mW/cm² photon flux) was achieved by using an Applied Photophysics 900W Xenon arc lamp and f3.4 monochromator.

ESCA spectra for each sample were recorded either on an AEI ES200B or a Kratos ES300 electron spectrometer employing Mg $k\alpha_{1,2}$ radiation. All the

results discussed in the next section were recorded at an electron take off angle of 30° . The corresponding data at 70° revealed essentially the same changes as at 30° ; i.e. the changes in surface chemistry are vertically homogeneous over at least the topmost 40 Å. The spectra were peak fitted and integrated using a DuPont 310 curve resolver or the peak fitting routines on a Kratos DS300 data system. Binding energies are referenced to the hydrocarbon component at 285 eV.

RESULTS AND DISCUSSION

The C_{1s} and O_{1s} spectra in Fig. 1 are for phenoxy resin irradiated ($\lambda > 290$ nm) at a photon flux of 5.7 Wm^{-2} . The C_{1s} envelope for the starting material consists of a main photo-ionisation peak at 285 eV due to carbon atoms not bonded to oxygen. The shoulder at 286.6 eV is due to carbon singly bonded to oxygen. A $\pi \rightarrow \pi^*$ shake up satellite centred at 292 eV is also present, indicative of the unsaturation present in the polymer. On exposure the C_{1s} envelope becomes more complex with the appearance of carbonyl and carboxylate functionalities. The O_{1s}/C_{1s} area ratios are displayed in Fig. 2, along with the percentage contributions to the C_{1s} envelope arising from oxidative functionalities. The oxygen uptake is extensive. For example, after 16 h exposure over 50% of the carbon atoms in the surface are bonded to at least one oxygen atom. After 15 min exposure there is a slight decrease in the O_{1s}/C_{1s} area ratio although essentially no change in the number of

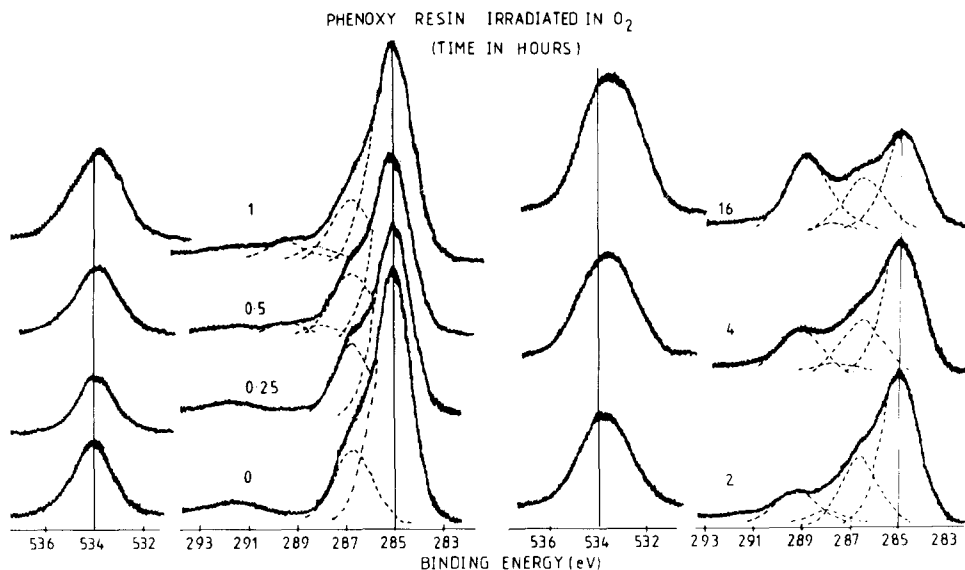


Fig. 1. C_{1s} and O_{1s} core level spectra for phenoxy resin irradiated in oxygen ($\lambda > 290$ nm, $I_0 = 5.7 \text{ Wm}^{-2}$).

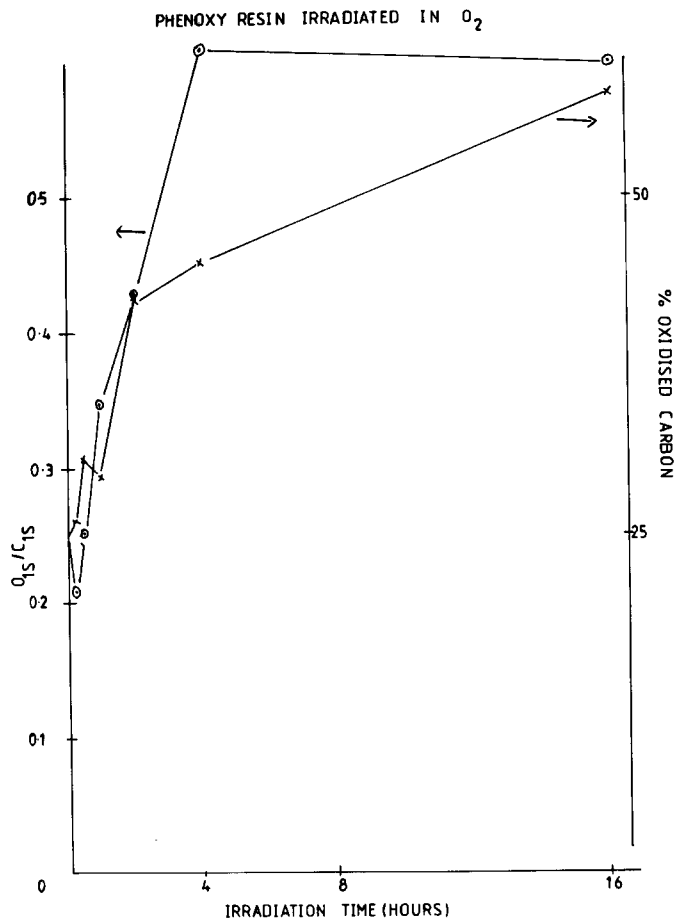


Fig. 2. O_{1s}/C_{1s} area ratios and percentage contribution to the C_{1s} envelope arising from oxidative functionalities for the spectra in Fig. 1.

carbon atoms bonded to oxygen is observed. The origin of this observation is not clear; however, it may be indicative of a crosslinking reaction.

The nature of the oxidised surface is revealed in Fig. 3 where the various C_{1s} components are displayed as a function of time. Irradiation for one hour results in a substantial decrease in the contribution arising from the C—O component which may be indicative of some main chain scission at the ether linkages. A short induction period is evident for the formation of carbonyl and carboxylate functionalities. This was not observed during the surface photo-oxidation of polycarbonate and polysulphone exposed under identical conditions. The carboxylate peak, on extended irradiation, becomes a dominant feature of the surface and after 16h exposure it contributes 30% to the total C_{1s} signal intensity. Further, the carbon singly bonded to oxygen component, at this point, is less than the carboxylate,

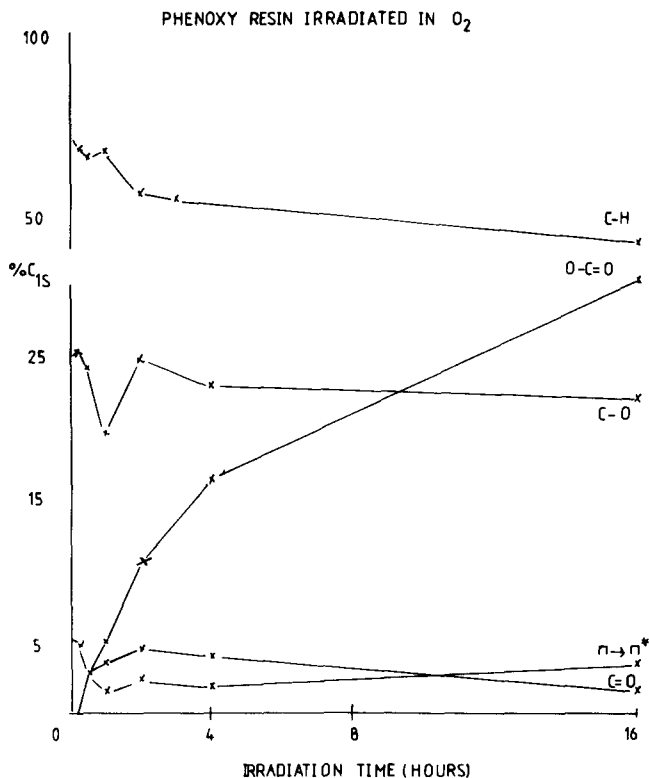


Fig. 3. C_{1s} component analysis for the spectra in Fig. 1.

indicating that some of the latter peak is due to acid functionalities as well as ester. The extent of oxidation and the observed decrease in the $\pi \rightarrow \pi^*$ shake up satellite intensity (Fig. 3) suggest that photo-oxidation involves oxidative attack of the aromatic ring system as well as the dimethyl and hydroxy aliphatic ether portions of the polymer. The binding energy of the $\pi \rightarrow \pi^*$ component moves to lower binding energy on exposure which might be due to carbonate formation as has been suggested for polysulphone.²

The initial decrease in the O_{1s}/C_{1s} area ratio, as noted above, may be indicative of a crosslinking reaction in the surface. Bulk photo-oxidation studies of phenoxy resin revealed a rapid and simultaneous crosslinking reaction occurring with photo-oxidation.¹ By replacing the hydroxyl group of the aliphatic ether portion of the main chain with an ester (by reaction with acetyl chloride) it was found that the crosslinking reaction no longer occurred, i.e. this latter reaction was due to the hydroxyl group.¹ To investigate the role of this functionality in the surface, phenoxy resin films were exposed to the vapour pressure of acetyl chloride. The C_{1s} and O_{1s} core levels in Fig. 4 reveal the changes in phenoxy resin after such treatment. A carboxylate peak at 289.2 eV is readily apparent and contributes 6% to the

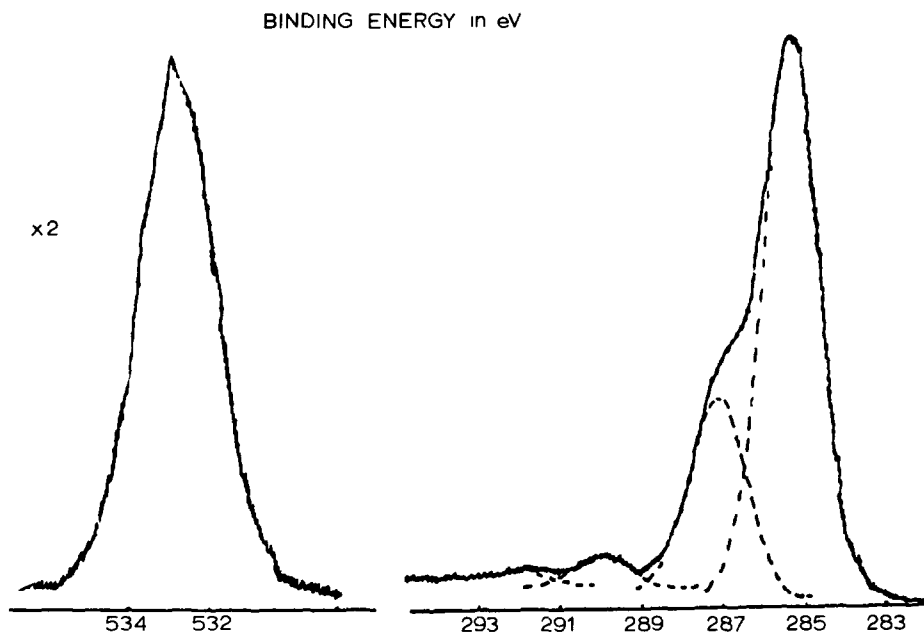


Fig. 4. C_{1s} and O_{1s} core level spectra for acetylated phenoxy resin.

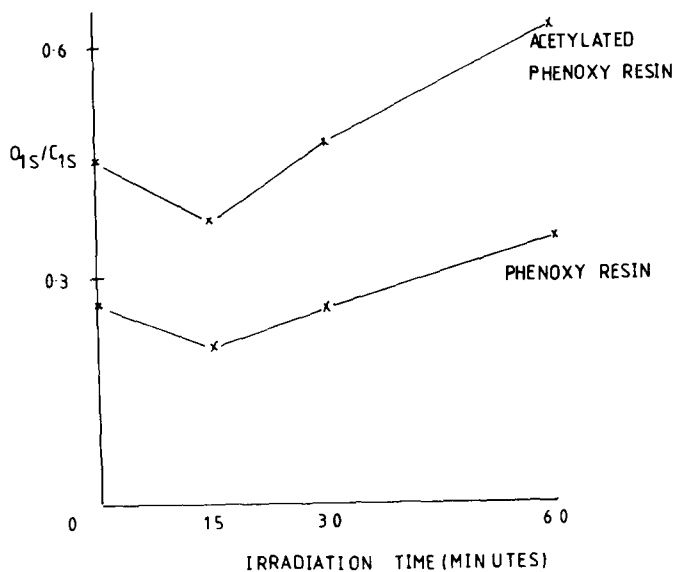


Fig. 5. O_{1s}/C_{1s} area ratios for acetylated phenoxy resin irradiated in oxygen (for comparison, the data for the unacetylated phenoxy resin are included).

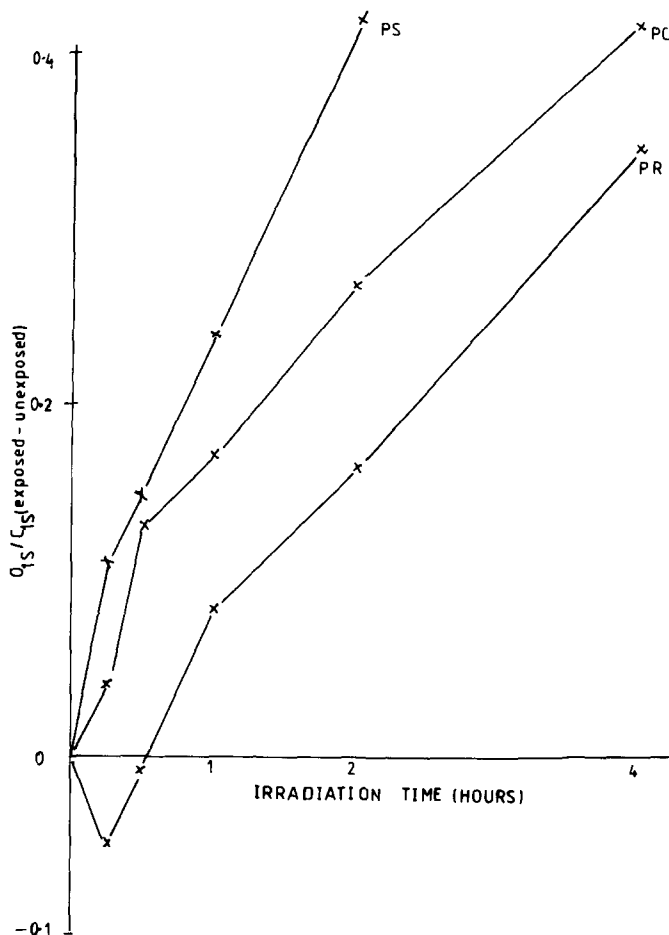


Fig. 6. Comparison of oxygen uptake as a function of irradiation time for polysulphone (PS), polycarbonate (PC) and phenoxy resin (PR). ($\lambda > 290 \text{ nm}$, $I_0 = 5.7 \text{ Wm}^{-2}$).

total C_{1s} intensity. This is in good agreement with the theoretical value of 5%. The higher level may arise from Bisphenol A residues in the surface.

The O_{1s}/C_{1s} area ratios for the acetylated samples after irradiation over 60 min, compared to the unacetylated films in Fig. 5, reveal that the initial decrease in the oxygen level is not due to reactions involving the hydroxy functionality, since the profiles are comparable. The higher oxygen content in the surface arises from the contributions due to the ester group. As the 'crosslinking' reaction is not observed in either polycarbonate or polysulphone, the observed phenomena must still involve the aliphatic ether group.

It is of interest to compare the oxygen uptake in the surface of the three Bisphenol A polymers, polycarbonate, polysulphone and polycarbonate, for which the relevant data are displayed in Fig. 6. From these data the apparent

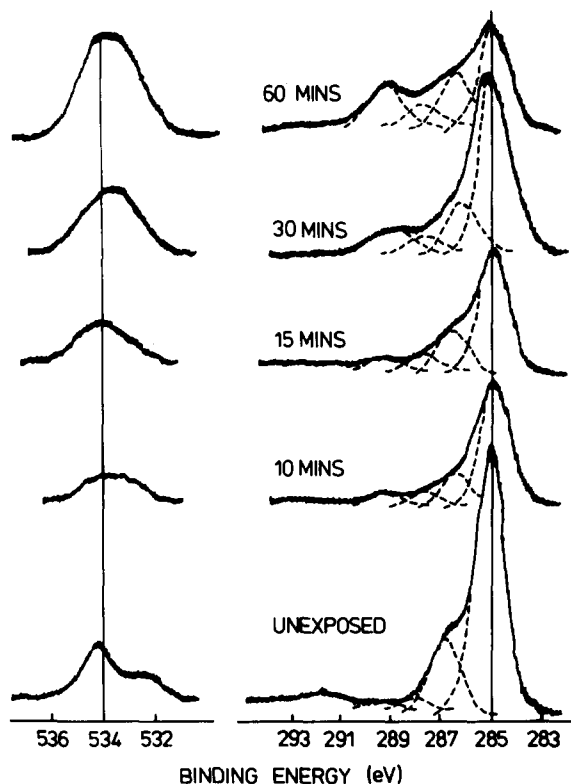


Fig. 7. C_{1s} and O_{1s} core level spectra for PEEK irradiated in oxygen ($\lambda > 290$ nm, $I_0 = 27 \text{ Wm}^{-2}$).

order of reactivity is polysulphone > polycarbonate > phenoxy resin which is in contrast to the bulk data. However, the 'crosslinking' reaction of phenoxy resin probably lowers the apparent oxygen uptake and as such the reactivity of this is higher than of polycarbonate. Further evidence for this reactivity may be taken from the very high levels of carboxylate formed in phenoxy resin.

Polyetheretherketone (PEEK)

It is evident from the structure of this polymer that it contains a benzophenone unit. Consequently, it is not unreasonable to expect PEEK to exhibit considerable reactivity to UV irradiation at wavelengths > 290 nm. The C_{1s} and O_{1s} core levels in Fig. 7 are for the unexposed material and after irradiation at a photon flux of $27.4 \text{ Wm}^{-2} \text{ h}^{-1}$ in an oxygen atmosphere for various periods of time. (Note the 2:1 intensity of the O_{1s} core level, in the unexposed film, indicative of the nature and proportions of the two oxygen

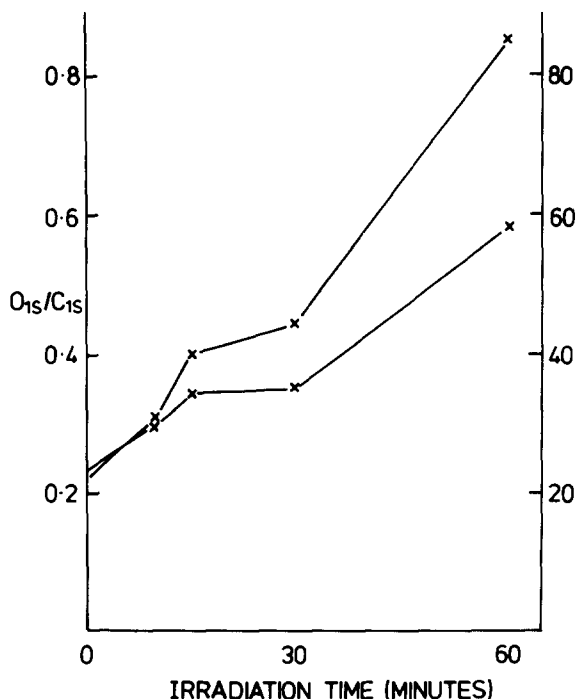


Fig. 8. O_{1s}/C_{1s} area ratios and percentage contribution to the C_{1s} envelope arising from oxidative functionalities for the spectra in Fig. 7.

environments.) The changes in both the C_{1s} and O_{1s} envelopes are indicative of extensive oxygen uptake as is more clearly shown in Fig. 8.

The changes in the C_{1s} envelope are shown in Fig. 9. The component due to carbon not bonded to oxygen decreases, as to be expected. There is an initial decrease in the intensity of the $\underline{C}-O$ component, indicative that the ether linkages in the polymer are being cleaved. On allowing for the initial level of carbonyl in the polymer, it is evident that the rate of carboxylate formation is greater than carbonyl. This appears to be a common feature of most aromatic polymers with in chain phenyl groups when irradiated under the conditions of a pure oxygen atmosphere and a filtered medium pressure mercury arc lamp. The $\pi \rightarrow \pi^*$ component decreases in intensity during exposure. The slight increase in intensity during the later stages of exposure may, as in phenoxy resin, indicate the formation of carbonate groups.

After 1 h exposure nearly 60% of the carbon atoms in the surface are bonded to oxygen. Such a level of oxidation has to involve the carbon atoms in the phenyl rings. It is worth emphasising that the surface that is being examined by ESCA has, by the very nature of the experiment (i.e. analysis chamber pressure is typically 10^{-8} torr), to consist of reasonably high molecular weight material. This would suggest that photo-oxidation results

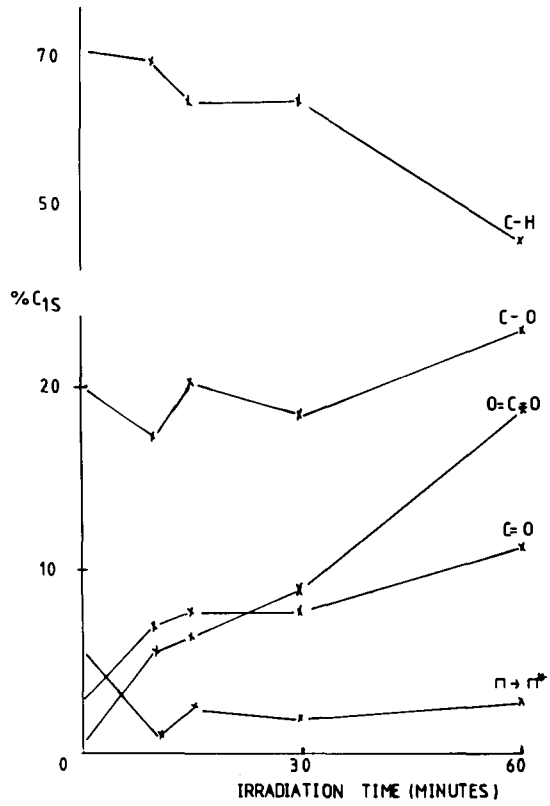


Fig. 9. C_{1s} component analysis for the spectra in Fig. 7.

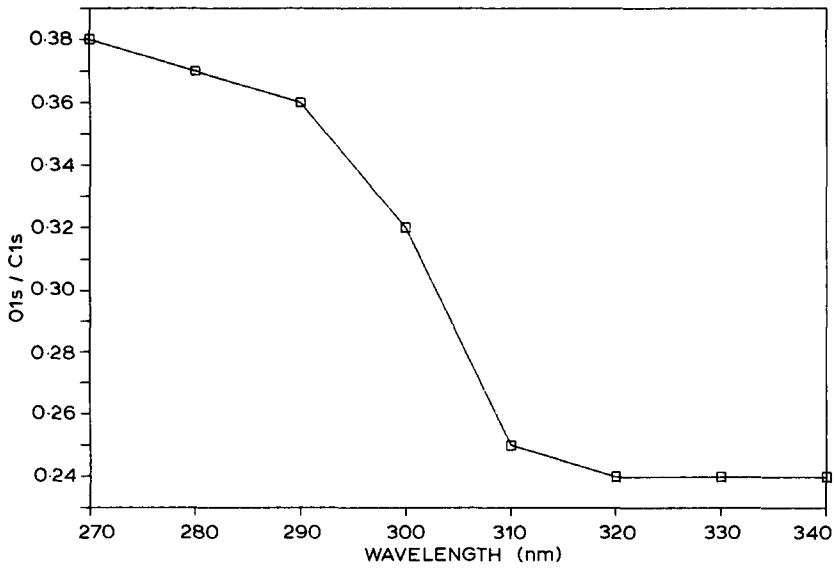


Fig. 10. O_{1s}/C_{1s} area ratio for PEEK irradiated in air as a function of wavelength.

in the oxidative attack of the phenyl moieties, via ring opening reactions as opposed to extensive main chain cleavage. The data for PEEK also indicate that if phenoxy resin, during heat curing, were to form aromatic carbonyls, then the surface at least will be very sensitive to photo-oxidation. However, phenoxy resin itself is very susceptible to photo ageing and in the surface regions it would appear that the presence of aromatic carbonyls is not necessary to initiate photo-oxidation.

The data in Fig. 10 are for the O_{1s}/C_{1s} area ratios for PEEK exposed for 4 days in air as a function of irradiation wavelength (270–360 nm). Between 360 and 310 nm the ratios do not change and are essentially the same as for the unexposed material. At 300 nm, oxygen uptake becomes evident and appears to reach a plateau value at 290 nm. These data suggest that under the broad band of wavelengths used in the mercury arc lamp experiments, the region between 290 and 310 nm is primarily responsible for the initiation of photo-oxidation.

CONCLUSION

The surface photo-oxidation of phenoxy resin involves a reaction of the aliphatic ether portion of the polymer which, in the initial stages, may be due to crosslinking. This does not appear to involve the hydroxy functionality. Extensive carboxylate formation occurs. The level of oxygen uptake and the decrease in the intensity of the $\pi \rightarrow \pi^*$ shake up satellite (indicative of the unsaturation present in the starting material) suggests that oxidative attack of the phenyl groups has occurred. This is supported by the nature of the surface photo-oxidation behaviour of PEEK.

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