An e.s.r. study of the thermal degradation of Kevlar 49 aramid

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The thermal degradation of Kevlar 49 aramid in the temperature range 350°–550°C has been investigated by e.s.r. spectroscopy. Accumulation of paramagnetic centres occurs above 470°C in vacuum and above 370°C in air. Above 520°C, the rate of formation of radical centres is approximately the same in air and vacuum. Measurements of g-factors show that the radical centres formed on thermal degradation in air are associated with a greater amount of chemically bound oxygen atoms than those formed in vacuum, indicating that the initial degradative processes in air are associated with oxidation of the fibre.

Keywords Degradation; thermal; electron spin resonance; Kevlar 49 aramid; oxidation

INTRODUCTION

Interest in synthetic aromatic polyamides (aramids) has increased markedly in recent years. This followed the discovery of the nematic anisotropic (liquid crystalline) behaviour of *para*-substituted, extended-chain aramids[1–4] which allowed production of high performance fibres such as Kevlar. It has now been established that the structure of Kevlar aramid is essentially poly(1,4-phenylene terephthalamide)[5–8]. Various mechanistic studies of the thermal and thermo-oxidative degradation[9–14], photodegradation[15,16], as well as studies of other thermal properties of aramids[8,17] have been reported in the literature. However, little has been published on the application of electron spin resonance (e.s.r.) to studies of pryolysis and thermo-oxidative degradation of aramids.

In this paper an e.s.r. study of the paramagnetic centres formed during the thermal degradation of Kevlar 49 fibres in air and vacuum is reported to provide some insight into the importance of oxidation reactions in the initial stages of the degradation process in air.

EXPERIMENTAL

Sample preparation

Kevlar 49 roving (Du Pont type 968, 7100 denier) was used in all experiments and was dehydrated before use. E.s.r. specimens for thermal degradation in air were preheated at 120°C for 2 h and stored over silica gel. Specimens for thermal degradation in vacuum were heated at 150°C for 3 h at 10^{-2} Pa and sealed under vacuum.

Thermal degradation

Thermal degradation of e.s.r. samples was carried out in an electrically heated tubular furnace maintained at constant temperature (±5°C).

E.s.r. spectra

E.s.r. spectra were measured at room temperature using a JEOL 3BS-X e.s.r. spectrometer with dual sample cavity (JES-MCX-1). Peak heights (I_0) were measured relative to manganese(II)-doped magnesium oxide; g-factors were measured relative to DPPH ($g = 2.0037$).

RESULTS AND DISCUSSION

The initial untreated Kevlar 49 roving showed a weak, slightly asymmetric e.s.r. absorption of $g = 2.0048$ and $\Delta H_{\max} = 1.4$ mT (*Figure 1a*), presumably due to paramagnetic impurities or trapped radicals introduced during the manufacturing process. This signal was consistent with the $g = 2$ resonance reported by Clarkson[18]. The weak initial signal did not, however, interfere significantly with measurements of thermally formed paramagnetic centres, which showed a strong symmetrical e.s.r. absorption ($\Delta H_{\max} = 0.6$ mT) of nearly Gaussian lineshape (*Figure 1b*). The signal was stable at room temperature over extended periods and was unaffected by oxygen. The temperature dependence of the e.s.r. signal intensity obeyed the Curie Law indicating that the paramagnetic centres were free radical in nature.

Similar e.s.r. signals have been observed on the thermal degradation of other similar polymeric materials[19]. They are generally considered to be due to highly delocalized free radical structures resulting from secondary homolytic bond scission and crosslinking reactions and the

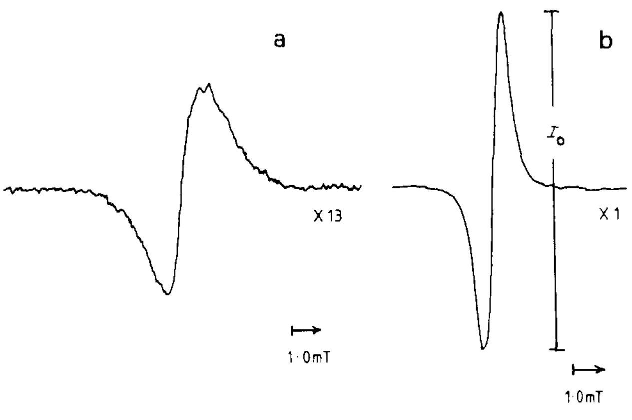

Figure 1 (a) E.s.r. spectrum of untreated Kevlar 49 fibre; (b) e.s.r. spectrum of Kevlar 49 fibre heated in vacuum for 30 min at 500°C

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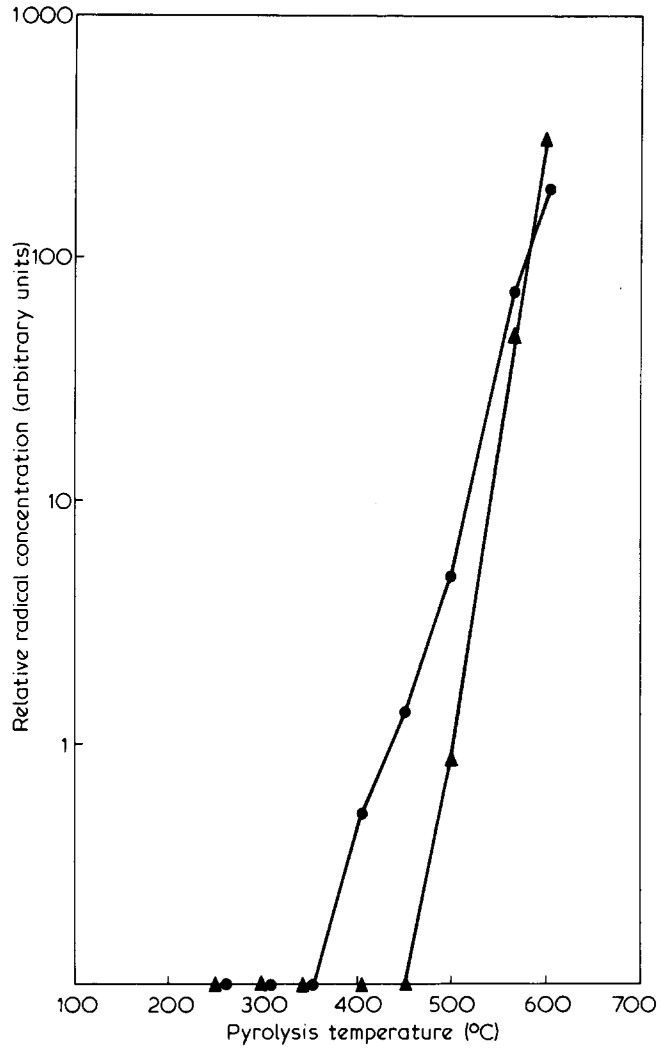


Figure 2 Temperature dependence of the accumulation of free radicals in Kevlar 49 fibre heated in air (●) and in vacuum (▲). (Sample heated for 10 min at each temperature.)

formation of conjugated structures[20]. The absence of any hyperfine splitting indicates that the observed radicals are the result of extensive bond-breaking and bond-forming reactions.

In order to establish the dynamic aspects of free radical formation during the thermal degradation of Kevlar 49 aramid in vacuum and in the presence of oxygen, e.s.r. spectral parameters were measured after pyrolysis in the temperature range 350°–550°C as a function of pyrolysis time and temperature. *Figure 2* shows the accumulation of free radicals (in arbitrary units) in Kevlar 49 heated in air and vacuum as a function of pyrolysis temperature. The radical concentration increases rapidly above 370°C for fibres heated in air. A similar rapid increase occurs above 470°C for material heated in vacuum. The latter is in excellent agreement with observations of Kalashnik *et al.*[10] for poly(1,4-phenylene terephthalamide) fibres of their own manufacture.

The rates of formation of free radicals in Kevlar fibre heated in air and vacuum at several temperatures are shown in *Figure 3*. No significant differences in spectral lineshape were observed under the different conditions and, in particular, no hyperfine splittings which could be attributed to primary degradation radicals were observed, even in the early stages of the low temperature degradation. In addition, no fine structure was resolved on lowering the temperature of e.s.r. measurement to −173°C. *Figure 3* shows that, at temperatures below 520°C, the rate of free radical formation in the fibre is very much greater in the presence of oxygen than in vacuum. *Figure 4* indicates that at 520°C the rate of radical formation is similar under both conditions and approaches a maximum level with increasing pyrolysis time. Approximate activation energies for radical formation in the temperature range 390°–520°C, derived from the initial slopes of the curves in *Figure 3* were 77 and 207 kJ mol^{-1} for Kevlar heated in air and vacuum, respectively.

Figure 5 shows the changes in g-factor of the free radicals with pyrolysis time and temperature for fibre heated in air and vacuum. Overlap with the initial e.s.r. signal present in the original material prevented precise measurements for very low radical concentrations and only those results for the higher concentrations are shown in *Figure 5*. The data in *Figure 5* show that, for Kevlar fibre heated in the presence of oxygen, the g-factor

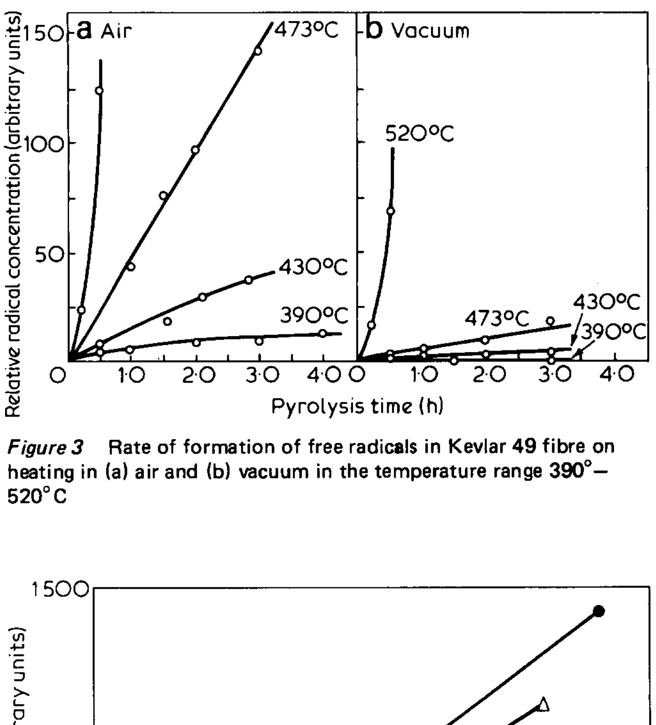


Figure 3 Rate of formation of free radicals in Kevlar 49 fibre on heating in (a) air and (b) vacuum in the temperature range 390°–520°C

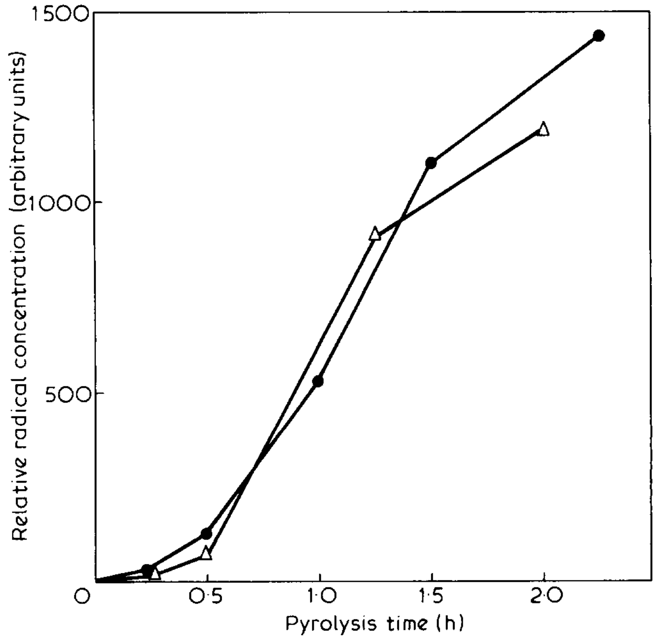


Figure 4 Formation of free radicals in Kevlar 49 fibre on heating in air (●) and vacuum (△) at 520°C

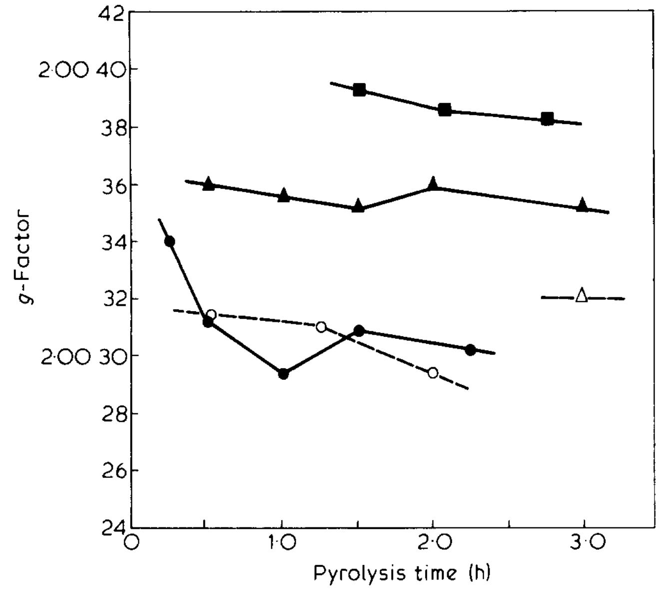
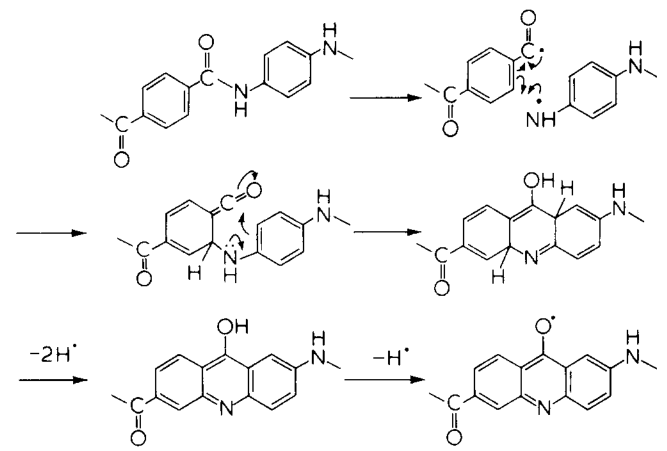


Figure 5 Effect of pyrolysis conditions on the g-factor of free radicals formed in Kevlar 49 fibre heated in: (a) air 520°C (●), 473°C (▲), 420°C (■); (b) vacuum 520°C (○), 473°C (△)



Scheme 1

decreases both with increasing pyrolysis time and with increasing pyrolysis temperature. The sample heated in air at 520°C shows an initial rapid decrease in g-factor levelling off at a value of approximately 2.0030. Fewer accurate points were obtained for fibre heated in vacuum. However, it can be seen that on heating in vacuum at 520°C the g-factor observed is the same as the limiting value obtained on pyrolysis in air. In addition, the g-factor observed on pyrolysis in vacuum at 473°C is considerably lower than that obtained on pyrolysis in air at the same temperature.

Singer[21,22] has shown that high g-factors (relative to the free electron value of 2.0023) for free radicals formed on pyrolysis of polymeric materials are due to orbital overlap with oxygen in oxygen-containing functional groups present in delocalized radical systems. The higher g-factors result from the higher spin-orbit coupling of oxygen (152 cm^{-1}) compared to carbon (28 cm^{-1}). A decrease in g-factor on vacuum pyrolysis of polymeric materials under conditions of increasing pyrolysis temperature and time was attributed to the loss of oxygen-containing functional units by homolytic bond scission reactions.

The higher g-values obtained on heating Kevlar 49 in air (*Figure 5*) are thus consistent with the incorporation of oxygen as functional units into the radical structure. Also, the higher rate of radical formation in the temperature range 370°–470°C in air (*Figure 3*) can be attributed to thermal oxidation reactions. The decrease in the g-factor with pyrolysis time and temperature for fibre heated in both air and vacuum is due to loss of oxygen-containing units. This occurs rapidly for the polymer heated in air above 520°C indicating that the initiating oxidation reactions are complete in the early stages of pyrolysis.

From the data available it is possible only to speculate on the nature of the delocalized radical systems produced on thermal degradation of Kevlar 49 aramid and the reactions leading to their formation. Recent pyrolysis-gas chromatography-mass spectrometry studies[7] of Kevlar 49 showed that initial volatile products—aniline, benzonitrile, p-phenylenediamine, carbon dioxide—are detected above 530°C. Other studies of volatile product formation on pyrolysis of poly(1,4-phenylene terephthalamide) in vacuum[10] also showed that benzonitrile, p-phenylenediamine and aniline were the major volatile degradation products evolved above 510°C. These results show that scission of the aromatic–NH and amide NH–CO linkages are major initial processes in the thermal degradation of Kevlar. *Scheme 1* shows a cyclization reaction initiated by scission of the amide linkage which could be important in the formation of highly delocalized radical systems. In this reaction a phenoxyl radical is produced and further reactions of this type involving adjacent amide linkages can lead to the formation of extensively delocalized linear and angular polycyclic free radical systems. The experimental results do not, however, provide direct confirmation of the occurrence of this reaction. In the presence of oxygen, Kevlar is less thermally stable with the initial degradation, an oxidation process involving the formation and subsequent reactions of peroxidic intermediates. This leads to the incorporation of oxygen as both ring and substituent functions with a corresponding increase in the g-factor of the free radicals observed. Subsequent homolytic scission reactions result in loss of the oxygen-containing structural units resulting in a decrease in g-factor with increasing pyrolysis time.

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