Fourier transform infra-red spectroscopic study of thermal degradation in poly(ether ether ketone)–carbon composites*

K. C. Cole†
National Research Council Canada, Industrial Materials Institute, 75 Boulevard de Mortagne, Boucherville, Québec, Canada J4B 6Y4

and I. G. Casella
Dipartimento di Chimica, Università degli Studi della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy

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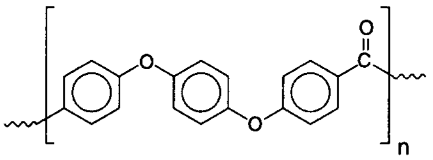
Fourier transform infra-red (*FT*i.r.) spectroscopy was used to study the thermal degradation that occurs in composite materials consisting of poly(ether ether ketone) (PEEK) reinforced with carbon fibres. Spectra were measured by diffuse reflectance for samples of prepreg and moulded laminate exposed to temperatures in the range 400–485°C for different periods of time in both air and nitrogen atmospheres. In spite of some spectral distortion arising from front-surface reflection, useful information can be obtained concerning the reactions that occur and their relative rates under different conditions. The reactions and their activation energies are found to be similar to those observed for neat PEEK film, described in a previous publication. In an inert atmosphere, the degradation involves a pyrolytic-type mechanism which produces a new carbonyl species absorbing at 1711 cm^{-1}, probably a fluorenone-type structure; the activation energy for this process is around 240 kJ mol^{-1}. In an oxidizing atmosphere, the same species is produced but at a faster rate, with an activation energy of around 200 kJ mol^{-1}. In addition there is a second reaction which requires the participation of oxygen and produces a species absorbing at 1739 cm^{-1}, probably ester groups; the activation energy for this reaction is about 130 kJ mol^{-1}. Some samples were also analysed by photoacoustic spectroscopy. Within the limits of the technique, no significant difference could be discerned between the degradation behaviour of PEEK–carbon composites and that of neat PEEK films.

(Keywords: poly(ether ether ketone); PEEK; thermal degradation; diffuse reflectance; *FT*i.r.)

INTRODUCTION

One of the most widely investigated thermoplastic matrices for high-performance composite materials is poly(ether ether ketone) (PEEK), semicrystalline polymer with the chemical structure shown below.



Although this polymer has a high degree of thermal stability, it is important to understand its degradation since the high temperatures required for processing (above 380°C) may produce changes that will affect the ultimate performance. In a recent publication[1], we reviewed the current state of knowledge of thermal degradation in PEEK and extended it by using Fourier transform infra-red (*FT*i.r.) spectroscopy to study the degradation process in films of the commercial product. Both transmission and attenuated total reflection (a.t.r.) methods were used. The degradation mechanism was found to depend on the atmosphere. In an inert atmosphere, a new carbonyl species is produced which absorbs at 1711 cm^{-1}. In an oxidizing atmosphere, the same species is produced but at a faster rate, and in addition a second species is observed which absorbs at 1739 cm^{-1}. By measuring the growth of the different peaks as a function of time at different temperatures, it was possible to estimate relative reaction rates and hence determine activation energies. These were found to be in good agreement with those obtained in earlier thermal analysis studies[2–4].

In this work, we extend the study to composite materials based on a PEEK matrix reinforced with carbon fibres. The strongly absorbing nature of the carbon fibres precludes the use of transmission for these materials. A.t.r. is also difficult, because the rough surface and non-deformable nature of the samples makes it very difficult to achieve good contact between the sample and the prism. Hence it is necessary to turn to other techniques such as diffuse reflectance or photoacoustic spectroscopy, even though these have certain disadvantages which limit their usefulness. In particular,

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† To whom correspondence should be addressed

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diffuse reflectance spectra are subject to distortion arising from front-surface reflection[5]. In this paper, results obtained by diffuse reflectance for thermally degraded samples are analysed and compared with those obtained for neat PEEK. In addition, some photoacoustic spectra are presented and discussed.

EXPERIMENTAL

Three types of PEEK–carbon composite material were studied. The first was APC-2 prepreg as received from ICI (sheets of unidirectional carbon fibres impregnated with PEEK resin, carbon fibre content 61% by volume, thickness 0.125 mm). The second was moulded laminate 2 mm thick made by pressing 16 plies of APC-2 for 5 min at 400°C and 0.7 MPa. The third was moulded laminate 1 mm thick made by pressing four layers of commingled PEEK–carbon fabric (NCS-1057 from BASF, carbon fibre content 61% by volume) for 5 min at 400°C and 2.8 MPa. Samples of PEEK film (Stabar K200 from ICI) were also used. For thermal treatment, specimens about 1 cm square were placed in a Lindberg furnace in an atmosphere of either static air or flowing nitrogen.

*FT*i.r. spectra were measured on a Nicolet 170SX instrument equipped with a mercury cadmium telluride detector. For diffuse reflection, a 'praying mantis' accessory from Harrick Scientific Corporation was used. The sample was mounted in the usual position, with its surface in a horizontal plane; this 'off-axis' configuration reduces the specular component of the reflected radiation. Specimens were oriented with the fibre direction parallel to the beam direction of the instrument. For each spectrum, 512 scans were accumulated at a resolution of 4 cm^{-1}. The reference material was lightly compacted potassium bromide. For quantitative treatment, the spectra were converted to Kubelka–Munk units; this was found to give a better match to the transmission spectrum than a conversion to pseudoabsorbance (log $1/R$). They were then baseline-corrected to remove the underlying carbon absorption. For photoacoustic work, 512 scans were accumulated at a resolution of 8 cm^{-1} with the use of a model 200 cell from MTEC Photoacoustics Inc. The reference material was carbon black (Fisher Scientific No. C-198).

RESULTS AND DISCUSSION

For reference purposes, *Figure 1* shows the spectrum of amorphous PEEK film as measured by a.t.r. with a 45° germanium prism[1]. The original reflectance spectrum has been converted to absorbance and multiplied by $\bar{\nu}/1000$ to correct for the variation of penetration with wavelength. The result is an excellent match for the transmission spectrum of a thin PEEK film, as reported and discussed by Nguyen and Ishida[6].

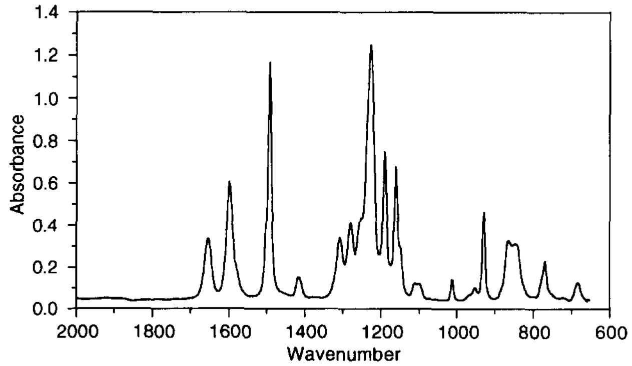
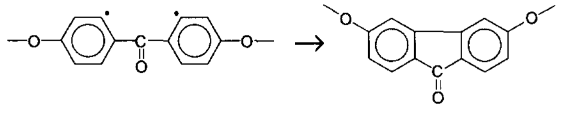


Figure 1 The attenuated total reflectance spectrum of amorphous PEEK film (Stabar K200), measured with a 45° germanium prism, converted to absorbance, and corrected for penetration depth

Samples of APC-2 prepreg, moulded APC-2 laminate, and moulded NCS-1057 laminate were heated in nitrogen or air for different periods of time at four different temperatures. APC-2 prepreg had a rough surface with a thin layer of PEEK resin following the contours of the carbon fibres. The laminates had a smooth surface as moulded, but heat treatment caused the resin to flow enough for the surface to lose its smooth texture. Even though the Harrick accessory was used in the 'off-axis' configuration, in which the specular component is not detected, the rough nature of the surface means that some front-surface reflection is diffusely reflected and therefore seen in the spectrum. *Figure 2* shows some typical spectra recorded for APC-2 prepreg; they have been scaled so that the overall intensity corresponds to that of the reference spectrum (unheated prepreg). The effects of the front-surface reflection can be clearly seen. The greatest effects are observed for the more intense absorptions, where the front-surface reflection causes an apparent inversion of the peaks. Because of this, in most of the spectra the 1491 cm^{-1} aromatic ring absorption appears as a doublet and the 1226 cm^{-1} ether absorption appears as a negative peak. Peaks of intermediate intensity, such as those at 1599, 1190 and 1161 cm^{-1}, tend to appear distorted and with reduced intensity compared to the true spectrum. Weaker peaks, however, such as those at 1653, 1415, 1307, 1278 and 1100–600 cm^{-1}, are the least affected by front-surface reflection and better resemble the true spectrum in terms of shape and relative intensity.

Although the diffuse reflection spectra provide more limited information than a.t.r. spectra, they are nevertheless useful for following the changes that occur on thermal degradation at the surface of the composite. The most important changes occur in the carbonyl region, shown in more detail in *Figures 3* and *4*. These are very similar to those observed for PEEK films[1]. Untreated PEEK has a carbonyl band at 1653 cm^{-1}. When it is heated in a nitrogen atmosphere, a distinct new peak appears at 1711 cm^{-1}, along with a weaker one near 1452 cm^{-1}. The origin of these peaks is uncertain, but as discussed in the earlier paper[1], they are believed to arise from a fluorenone-type structure formed by cyclization of a diradical:



In an air atmosphere, in addition to the above-mentioned peaks, a second carbonyl peak is observed to grow at 1739 cm^{-1}. It is accompanied by a weak but detectable peak at 1065 cm^{-1}. These are attributed to ester groups formed by oxidation of the original carbonyl groups. The lower the treatment temperature, the more prominent is the 1739 cm^{-1} peak with respect to the 1711 cm^{-1} one.

In spite of the complications associated with the diffuse reflection technique, it was felt that quantitative information could be obtained concerning the growth of the

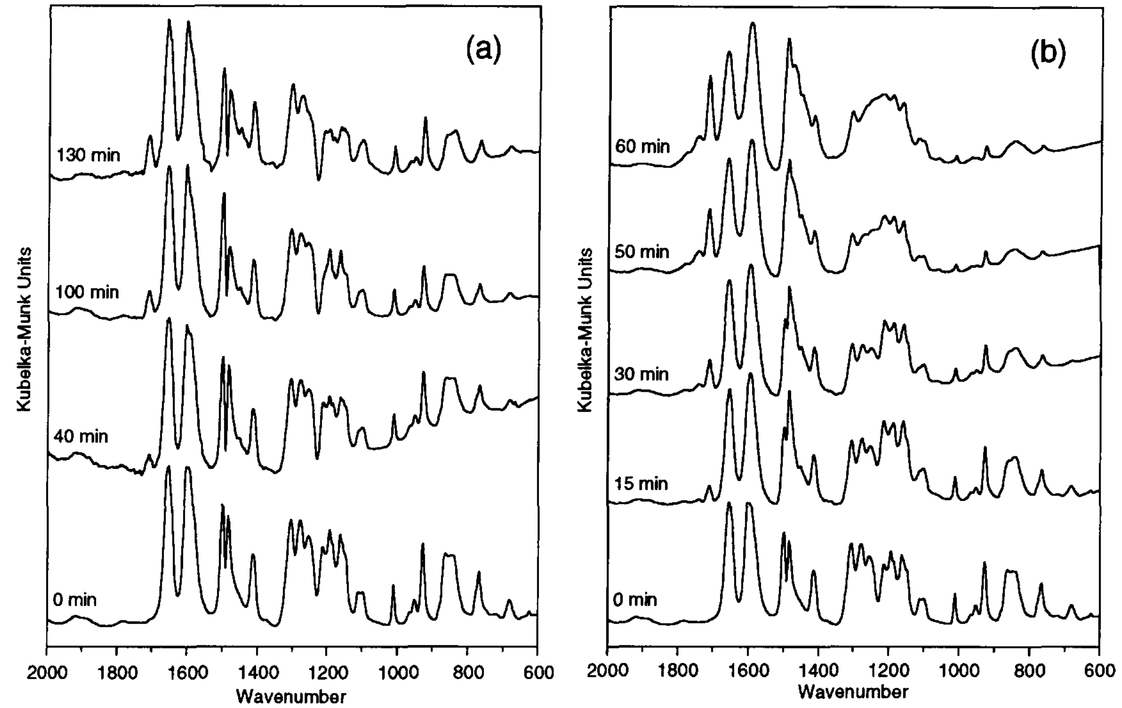


Figure 2 Diffuse reflectance spectra of APC-2 prepreg after heating at 460°C for different times in (a) nitrogen and (b) air

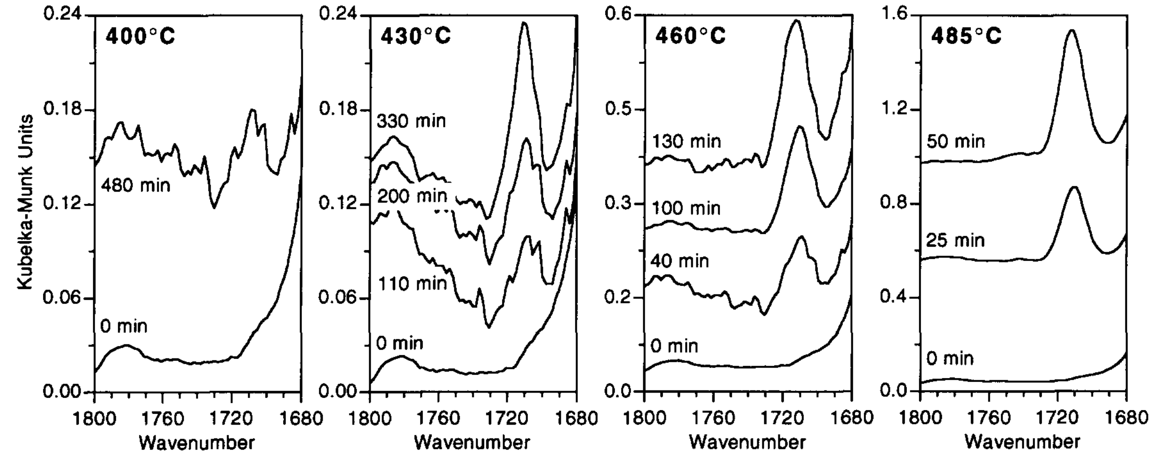


Figure 3 Diffuse reflectance spectra (carbonyl region) for APC-2 prepreg heated in nitrogen under different temperature/time conditions. Curves are displaced in the y-direction for clarity

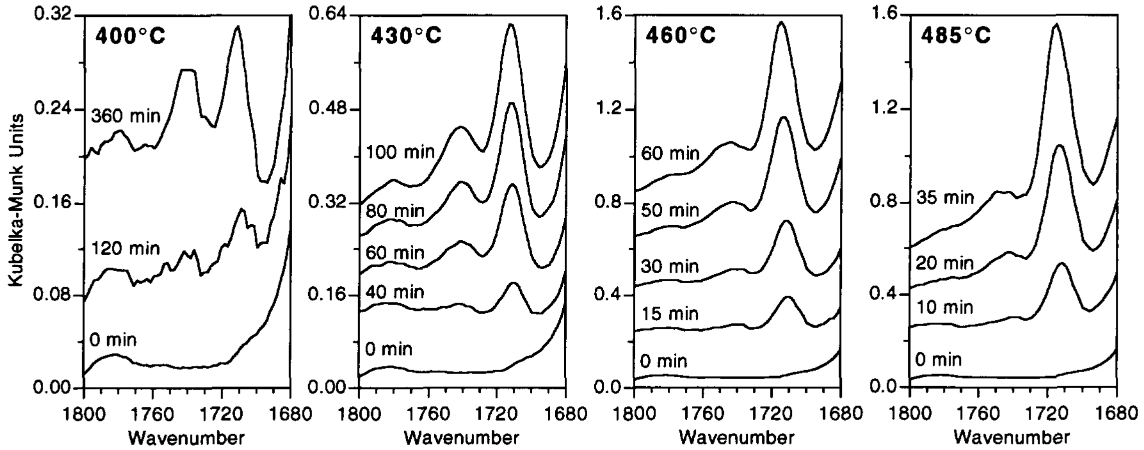


Figure 4 Diffuse reflectance spectra (carbonyl region) for APC-2 prepreg heated in air under different temperature/time conditions. Curves are displaced in the y-direction for clarity

two new carbonyl peaks. This assumes that the complicating factors affect all the spectra in a similar manner, so that relative comparisons may still be valid. As was done for the a.t.r. spectra of PEEK films[1], the ratio of the heights of the new carbonyl peaks with respect to the original peak at 1653 cm^{-1} was plotted as a function of time at different temperatures. The 1653 cm^{-1} peak was chosen as reference because, in addition to the reasons given in the earlier paper[1], it is less intense than the peaks at 1599 and 1491 cm^{-1} and therefore less subject to interference from front-surface reflection. To measure the height of the 1653 cm^{-1} peak, a baseline was drawn between the valleys at about 1820 and 1530 cm^{-1}. To measure the height of the new carbonyl peaks, a spectrum of untreated material was first subtracted in order to obtain a more level baseline between the valleys on either side of the peaks

Experiments were done not only on APC-2 prepreg but also on laminates moulded from APC-2 prepreg and from NCS-1057 commingled PEEK–carbon fabric. Based on the results obtained for the APC-2 prepreg, the amount of degradation occurring during the short 5 min moulding time at 400°C is considered to be negligible.

Figures 5 and *6* show the results obtained for APC-2 prepreg and NCS-1057 laminates. The degree of scatter is somewhat higher than for PEEK films and obviously precludes any detailed analysis of the degradation kinetics. This is not surprising given the complications affecting the diffuse reflection spectra. Nevertheless, the effect of varying the temperature is clearly seen and it is possible, as in the case of the films, to consider the growth of the peak ratios as linear, as a first-order approximation. Thus linear regression with $y = mx$ was applied to obtain slopes corresponding to the rate of degradation. These were then used to make Arrhenius plots, two examples of which are given in *Figure 7*. These show that the growth of the 1711 cm^{-1} peak is significantly faster in air than in nitrogen (three to 10 times within the temperature range studied). The activation energies determined from the Arrhenius plots for the different composites are summarized in *Table 1*, along with those obtained previously for the PEEK films[1]. Within experimental error, the results are the same for all three types of composite as well as for the film surface analysed by a.t.r. This suggests that the basic degradation mechanism is the same in all cases. The knowledge of this mechanism which has been gained from the i.r. spectra may be summarized as follows. In the absence of oxygen, the predominant degradation reaction has an activation energy in the vicinity of 240 kJ mol^{-1} and gives rise to a new carbonyl species absorbing at 1711 cm^{-1}. In the presence of oxygen, the same species is produced but the reaction appears to be significantly accelerated by the oxygen. The apparent activation energy is around 200 kJ mol^{-1}. There is also a second reaction, not observed in the absence of oxygen, which produces a species absorbing at 1739 cm^{-1} and has an apparent activation energy around 130 kJ mol^{-1}. It should be noted that the activation energies determined from the experiments done in an air atmosphere are considered

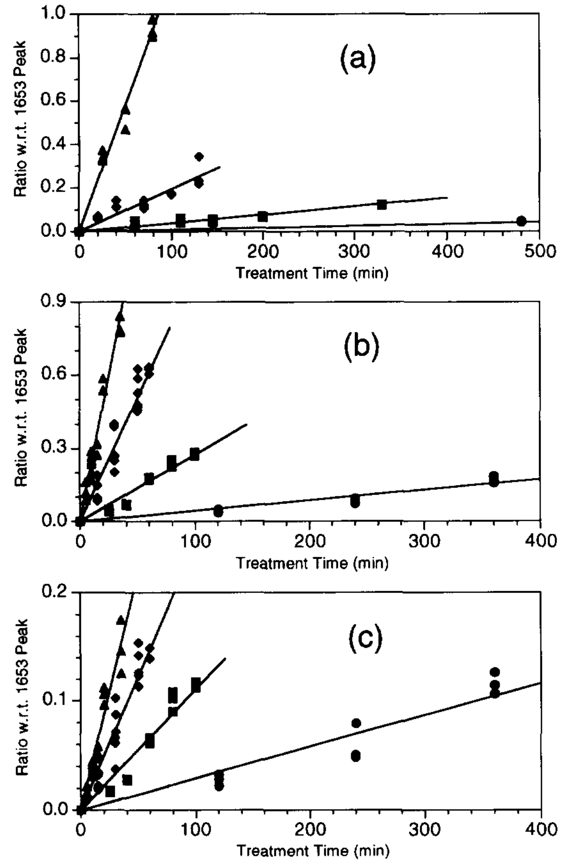


Figure 5 Growth of carbonyl peaks in the diffuse reflectance spectra of APC-2 prepreg as a function of time: ●, 400°C; ■, 430°C; ◆, 460°C; ▲, 485°C. (a) The 1711 cm^{-1} peak in a nitrogen atmosphere; (b) the 1711 cm^{-1} peak in an air atmosphere; (c) the 1739 cm^{-1} peak in an air atmosphere

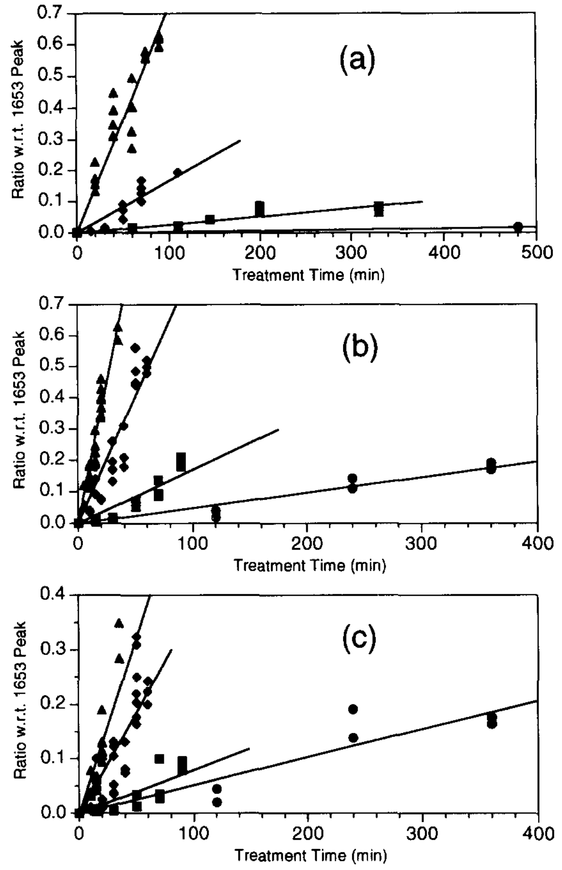


Figure 6 Growth of carbonyl peaks in the diffuse reflectance spectra of NCS-1057 laminate as a function of time: ●, 400°C; ■, 430°C; ◆, 460°C; ▲, 485°C. (a) The 1711 cm^{-1} peak in a nitrogen atmosphere; (b) the 1711 cm^{-1} peak in an air atmosphere; (c) the 1739 cm^{-1} peak in an air atmosphere

Table 1 Calculated activation energies (kJ mol^{-1}) obtained from the Arrhenius plots for the rate of growth of carbonyl peaks in different PEEK materials

	Peak and atmosphere		
Material	1711 cm^{-1} N_2	1711 cm^{-1} air	1739 cm^{-1} air
APC-2 prepreg	239±21	201±15	133±13
APC-2 laminate	224±28	203±10	147±12
NCS-1057 laminate	262±2	184±10	136±23
Film (by a.t.r)	236±10	211±2	116±16
Film (by transmission)	240±11	(153±4)	(52±13)
Average	240	200	133

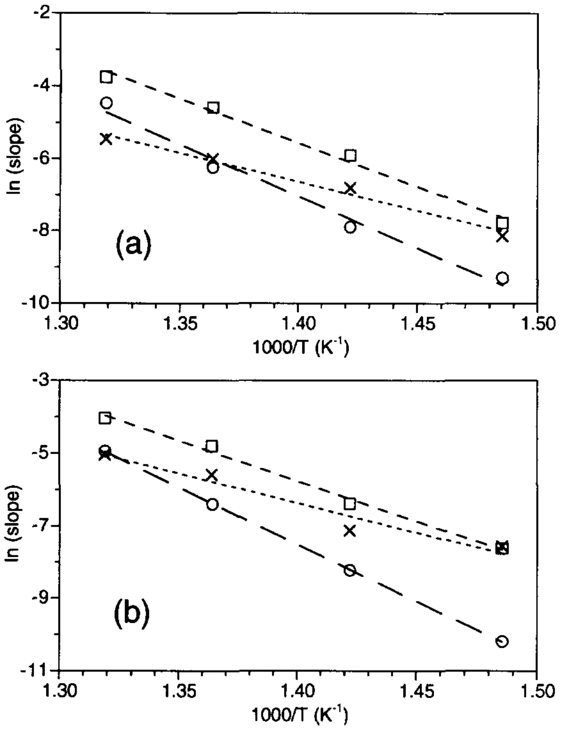


Figure 7 Arrhenius plots for the rate of growth of carbonyl peaks in the diffuse reflectance spectra of (a) APC-2 prepreg and (b) NCS-1057 laminate: ○, the 1711 cm^{-1} peak in a nitrogen atmosphere; □, the 1711 cm^{-1} peak in an air atmosphere; ×, the 1739 cm^{-1} peak in an air atmosphere

'apparent' because they are influenced by the diffusion of oxygen into the samples. This explains why the values obtained for the PEEK film from the transmission experiments (*Table 1*) are so low compared to the others. The transmission spectra provide information on the entire film. Because it takes longer for the oxygen to diffuse to the centre, there will be a gradient in oxygen concentration and extent of degradation from the surface to the centre. The measured reaction rates will incorporate the effects of the diffusion and this will be reflected in the calculated activation energies. The a.t.r. and diffuse reflection techniques measure only the top few micrometres of the samples. While diffusion will still be a factor, it will be less important than in transmission and the calculated activation energies will be closer to the 'true' values. This is why the transmission results for an air atmosphere are enclosed in parentheses in *Table 1* and were not used in calculating the average values reported.

As discussed in the earlier paper[1], the results obtained here by i.r. spectroscopy corroborate and help to clarify the findings of Day *et al.*[2–4], who studied the degradation of PEEK by means of thermogravimetric analysis. For a nitrogen atmosphere[2,3], depending on the method used to analyse the data, they obtained an activation energy in the range 198–237 kJ mol^{-1}. This is similar to the average value of 240 kJ mol^{-1} reported here. For an air atmosphere[4], for experiments done at high temperatures or fast heating rates they obtained values in the range 177–250 kJ mol^{-1}. This is because under these conditions degradation occurs rapidly; there is little time for oxygen diffusion to occur and the dominant reaction is the one producing the peak at 1711 cm^{-1}, for which we obtain an activation energy around 200 kJ mol^{-1}. For experiments done at lower temperatures or slow heating rates, Day *et al.* obtained activation energies in the range 86–133 kJ mol^{-1}. Under these conditions, there is more time for oxygen diffusion to occur and the dominant reaction is the one which produces the peak at 1739 cm^{-1}, for which we obtain an activation energy of 133 kJ mol^{-1}.

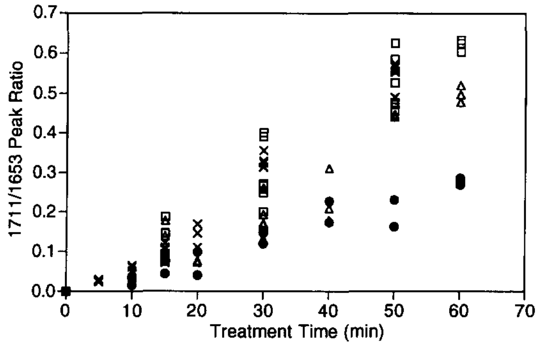


Figure 8 Comparison of the rate of growth of the 1711 cm^{-1} peak in the spectra of samples heated in air at 460°C: ●, PEEK film by a.t.r.; □, APC-2 prepreg by diffuse reflectance; ×, APC-2 laminate by diffuse reflectance; △, NCS-1057 laminate by diffuse reflectance

Although the calculated activation energies are similar for PEEK film and composites, an interesting result is observed when the actual rates of growth of the new carbonyl peaks (as expressed in terms of the peak height ratios 1711 cm^{-1}/1653 cm^{-1} and 1739 cm^{-1}/1653 cm^{-1}) for a given temperature and atmosphere are compared. In general, the points for the PEEK film fall somewhat lower than those for the composites. An example is given in *Figure 8*. The question arises as to whether this means that the degradation is faster in the composites or whether the difference arises from the different techniques used; front-surface reflection effects in the diffuse reflectance spectra could cause the 1653 cm^{-1} peak to appear weaker than it should be. One way to check this is to measure both types of sample with the same technique, so photoacoustic spectroscopy was tried for this purpose.

Like diffuse reflectance, photoacoustic spectroscopy provides information on the surface of a sample. It has the advantage of being much less affected by surface morphology and front-surface reflection, but the disadvantage of being less sensitive (lower signal-to-noise ratio). The photoacoustic spectrum of PEEK–carbon prepreg has been reported[7].

Figure 9a shows the photoacoustic spectra obtained for Stabar K200 PEEK film after exposure in air at 485°C for different times. They have been scale-expanded to have approximately the same overall intensity. They are of reasonably good quality and show the same changes observed in transmission and a.t.r., in particular the growth of peaks at 1711, 1739 and 1452 cm^{-1}. *Figure 9b* shows similar spectra for NCS-1057 moulded laminate.

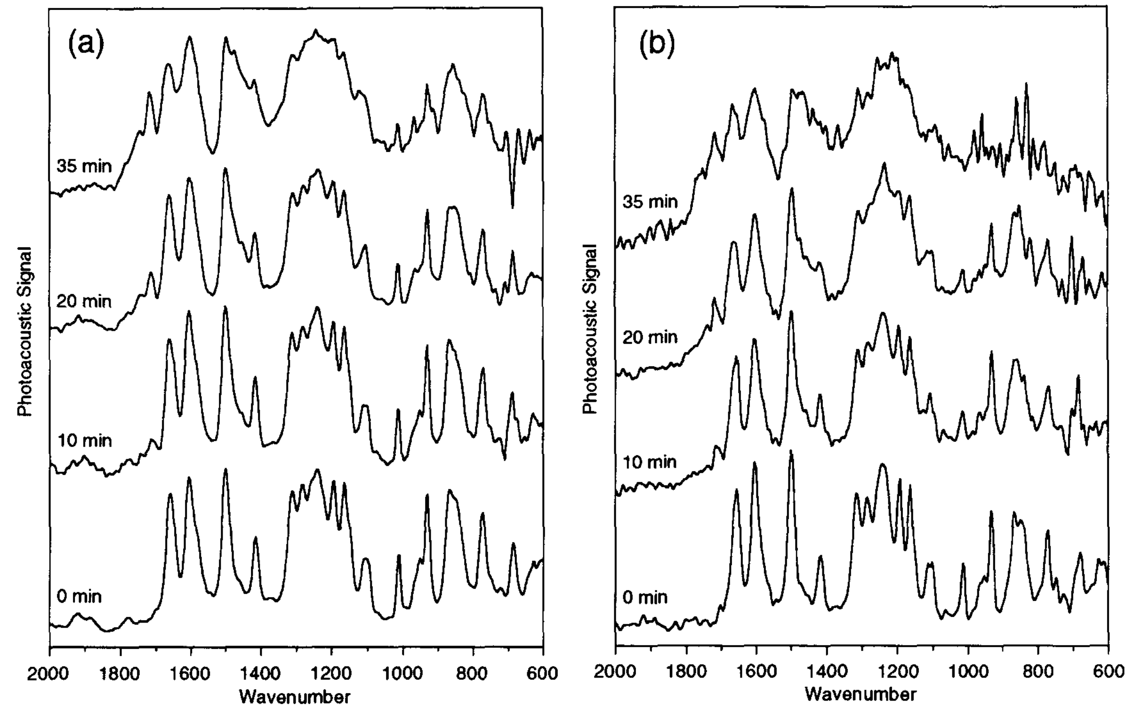


Figure 9 Photoacoustic spectra of (a) Stabar K200 PEEK film and (b) NCS-1057 laminate after heating in air at 485°C for different times

These are generally of poorer quality, because there is also carbon absorption and the surface layer of PEEK is thinner, especially after some is lost during the thermal treatment. The situation is even worse for prepreg. Because of the high noise level, quantitative treatment of these spectra is difficult. However, comparison of *Figures 9a* and *9b* shows that the evolution of the spectrum appears to be the same for both the film and the laminate. The same was true for some samples exposed in a nitrogen atmosphere. These results suggest that the degradation proceeds at a similar rate in the neat film and the composites. This is in contrast to the findings of Day *et al.*[8], who observed that when PEEK is exposed at 400°C the crystallization behaviour is affected to a greater extent if carbon fibres are present. This may be explained by the fact that the samples they studied were in the very early stages of degradation and the crystallization behaviour is very sensitive to the degradation. The samples involved in this work were generally considerably more degraded and were no longer capable of crystallization. While a difference between neat PEEK and PEEK–carbon composites may exist, it is too small to be detected by *FT*i.r. It is concluded that the apparent difference between film and composite seen, for example, in *Figure 8* is due to the different techniques used.

CONCLUSIONS

In spite of the complications caused by front-surface reflection, diffuse reflectance *FT*i.r. spectroscopy can be used to obtain qualitative and quantitative information concerning the nature of thermal degradation in PEEK–carbon composites. Within the limits of the precision of the technique, the mechanism is found to be the same as in PEEK films[1]. It involves two predominant pathways. In an inert atmosphere, it proceeds by a pyrolytic-type mechanism which produces a new carbonyl species absorbing in the i.r. at 1711 cm^{-1}, probably a fluorenone-type structure. The activation energy for this process is about 240 kJ mol^{-1}. In an oxidizing atmosphere, the same species is produced but at a faster rate, and the activation energy is about 200 kJ mol^{-1}. In addition there is a second mechanism which requires the participation of oxygen and produces a species absorbing at 1739 cm^{-1}, probably ester groups. The activation energy for this process is about 130 kJ mol^{-1}.

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