Thermochimica Acta, 211 (1992) 209–228
Elsevier Science Publishers B.V., Amsterdam

Fourier transform infrared spectroscopic study of thermal degradation in films of poly(etheretherketone)

K.C. Cole [a] and I.G. Casella [b]

[a] *National Research Council of Canada, Industrial Materials Institute, 75 boulevard de Mortagne, Boucherville, Québec J4B 6Y4 (Canada)*
[b] *Università degli Studi della Basilicata, Dipartimento di Chimica, Via N. Sauro 85, 85100 Potenza (Italy)*

(Received 26 March 1992)

Abstract

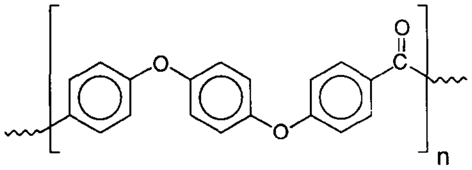
Fourier transform infrared (FT-IR) spectroscopy was used to study the reactions which occur upon thermal degradation of films of poly(etheretherketone), or PEEK. Samples were exposed to temperatures in the range 400–485°C in both air and nitrogen atmospheres, and spectra were measured in both transmission and attenuated total reflection (ATR). The thermal degradation produces new carbonyl species, and the rate of growth of their IR peaks was used to determine activation energies for the reactions which produce them. In an inert atmosphere, the degradation involves a pyrolytic-type mechanism which produces a new carbonyl species absorbing in the IR at 1711 cm^{-1}, possibly a fluorenone-type structure. The activation energy for this process is 236 kJ mol^{-1}. In an oxidizing atmosphere, the same species is produced but at a faster rate, and the apparent activation energy is 211 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}, possibly ester groups. The activation energy for this reaction is 116 kJ mol^{-1}. Because of the time required for oxygen to diffuse into the polymer, oxidative degradation is more pronounced at the surface, especially at higher temperatures. Thus ATR gives a more reliable value of the activation energies than transmission measurements on the bulk film.

INTRODUCTION

There is currently a great deal of interest in the development of thermoplastic polymer matrices for use in high-performance composite materials. The principal advantages of these materials over the widely used thermoset matrices are their shorter processing time, increased toughness, and improved hygrothermal stability. One of the most promising matrices is poly(etheretherketone), or PEEK, which is a semicrystalline polymer with the chemical structure shown in Form. 1. This

---

Correspondence to: K.C. Cole, National Research Council of Canada, Industrial Materials Institute, 75 boulevard de Mortagne, Boucherville, Québec J4B 6Y4, Canada.



Form. 1. PEEK.

structure, consisting entirely of aromatic rings joined by relatively stable connecting groups, confers a high degree of thermal stability [1], but the high processing temperatures required (about 380°C) mean that the possibility of thermal degradation during processing cannot be ignored. Because this can have significant effects on the ultimate performance of the composite product, there has recently been considerable interest in studying the degradation.

It has been shown that even at temperatures as low as 110°C, oxidation of PEEK can be detected by very sensitive chemiluminescence techniques [2], but the effects are extremely small. The degradation becomes much more significant when the temperature approaches the melting point, and several studies have been done in these conditions [3–9]. The main techniques used for detecting changes are melt viscosity measurements and differential scanning calorimetry (DSC). In the latter case, a sample of PEEK is subjected to a thermal treatment and then rapidly quenched to keep it in the amorphous state. Its thermal behaviour is then recorded by DSC and compared with that of an untreated sample. Degradation produces several changes: the glass transition temperature T_g increases; the cold crystallization peak broadens, diminishes in intensity, and moves to higher temperature (T_c); and the melting peak temperature maximum T_m decreases. When PEEK was heated in a nitrogen atmosphere at different temperatures for up to two hours [3], the changes were practically negligible at 380°C, small but measurable at 400°C, and somewhat larger at 420°C. For longer times at 420°C greater changes were observed [4], and after 60 h the DSC thermogram did not exhibit any crystallization or melting peak. The melt viscosity was found to increase with time. In an air atmosphere, the effects of degradation are much more pronounced than in a nitrogen atmosphere [3]. At 400°C, the changes are greater after 30 min in air than after 2 h in nitrogen, and after 2 h in air the crystallization and melting peaks have practically disappeared. Even at 326°C, after 110 h in air PEEK is highly degraded [5]. Others have reported generally similar results [6–9]. It is interesting to note that in PEEK/carbon composites the presence of carbon fibres appears to accelerate the degradation somewhat, whether in air or in nitrogen [10].

When the temperature is well above the melting point, the degradation is much more rapid, and in this case thermogravimetric analysis (TGA) is a good technique for characterization [11–20]. Day et al. have made a detailed study [11–13] in which they used both dynamic and isothermal TGA to study the kinetics of thermal decomposition. In dynamic TGA with a heating rate of 1°C min^{-1}, most of the weight loss occurs between 500 and 580°C. In a nitrogen atmosphere, a carbon char corresponding to about 50–60% of the initial weight is left behind, whereas in an air atmosphere, the weight loss is complete. In isothermal TGA in nitrogen, the weight loss is negligible at 400°C but is measurable in reasonable times at 430°C and above. The decomposition appears to be a one-stage process with an activation energy of around 230 kJ mol^{-1}; the results suggest that it is random chain scission. In air, measurable weight loss occurs at temperatures as low as 375°C. The decomposition is much more complex than in nitrogen and the derivative TGA curve shows two distinct stages. Analysis of the kinetics is complicated, especially because oxygen diffusion into the polymer must also be considered. Depending on the treatment of the data, activation energies as low as 100 kJ mol^{-1} are calculated. Other, less extensive, TGA studies have given similar results [14–20]. In some of these [17–20] the volatile decomposition products have been analysed. The most abundant compounds produced are phenol, benzoquinone, benzophenone, benzene, dibenzofuran and diphenyl ether. An interesting finding [6, 17] is that in the presence of air, copper significantly accelerates the degradation of PEEK, whereas nickel, aluminium, and stainless steel have little effect.

The changes observed in thermally degraded PEEK are generally attributed to chain scission followed by crosslinking. However, there is surprisingly little published information on attempts to understand the chemical changes occurring in the initial stages of degradation. Day et al. [21] have obtained some evidence for the assumed mechanism by analysing samples of PEEK heated at 400°C in nitrogen and air. The percentage of gel (material insoluble in methane sulphonic acid) was found to increase from 0 to 40% as the PEEK was heated in air for up to 6 h. This was taken as evidence for crosslinking. However, the intrinsic viscosity of the soluble fraction was found to decrease, an indication of chain scission. Infrared and nuclear magnetic resonance spectroscopy results provided further support for this mechanism.

In this work, Fourier transform infrared (FT-IR) spectroscopy was used to explore further the reactions occurring on thermal treatment of PEEK. FT-IR has the advantage of being able to provide information on the disappearance and formation of specific chemical groups in the polymer. In terms of sensitivity, it may be considered to be intermediate between DSC, which can detect the effects of degradation in its early stages, and TGA, which is only applicable when the degradation has advanced to the stage of producing volatile molecular fragments. The FT-IR spectrum of undegraded PEEK has been reported and discussed by Chalmers et al. [22] and Nguyen and Ishida [23–25]. We report here the spectra of PEEK film after thermal treatments in nitrogen and air atmospheres in the range 400–485°C. These spectra, obtained by both transmission and attenuated total reflection (ATR), provide both qualitative and quantitative information on the nature of the chemical changes occurring as a result of the degradation and on the kinetics of the reactions. A future publication [26] will deal with degradation in PEEK/carbon composites, as studied by means of diffuse reflection and photoacoustic methods.

EXPERIMENTAL

Materials

The PEEK film used was the commercial product Stabar K200 as obtained from the manufacturer, ICI Films (Wilmington, DE, USA). Heat treatment was done in a Lindberg muffle furnace in either static air or a flowing nitrogen atmosphere.

FT-IR spectroscopy

Spectra were recorded on a Nicolet 170SX instrument equipped with a mercury cadmium telluride detector. The resolution was 4 cm^{-1} and the number of scans accumulated was generally 512. For transmission work, samples were placed on clean glass microscope slides for heat treatment and detached with tweezers before measurement. ATR measurements were done on a Harrick Scientific Corp. twin-parallel mirror attachment with a 45° single-pass-parallelogram germanium prism ($50 \times 10 \times 3$ mm^3). The samples used for ATR work were placed on clean aluminium foil for the heat treatment and the foil was left in place for the measurement. Because curling of the specimen edges occurred in some cases, oversize specimens were used and the edges trimmed before measurement in order to assure good contact between the sample and the prism. Specimens were placed on both sides of the prism with rubber pads behind to distribute the pressure evenly, and the clamps were tightened with finger pressure.

RESULTS AND DISCUSSION

Transmission

A reference spectrum of untreated PEEK film (thickness 50 μm) is shown in Fig. 1(a). To eliminate interference fringes, this was measured with p-polarized radiation and with the sample tilted at the Brewster angle of 58°; the effective path length is thus about 59 μm. This relatively high sample thickness is both an advantage and a disadvantage. The disadvantage is that the strongest bands of the PEEK show complete absorption and hence provide no information. The advantage is that weak bands

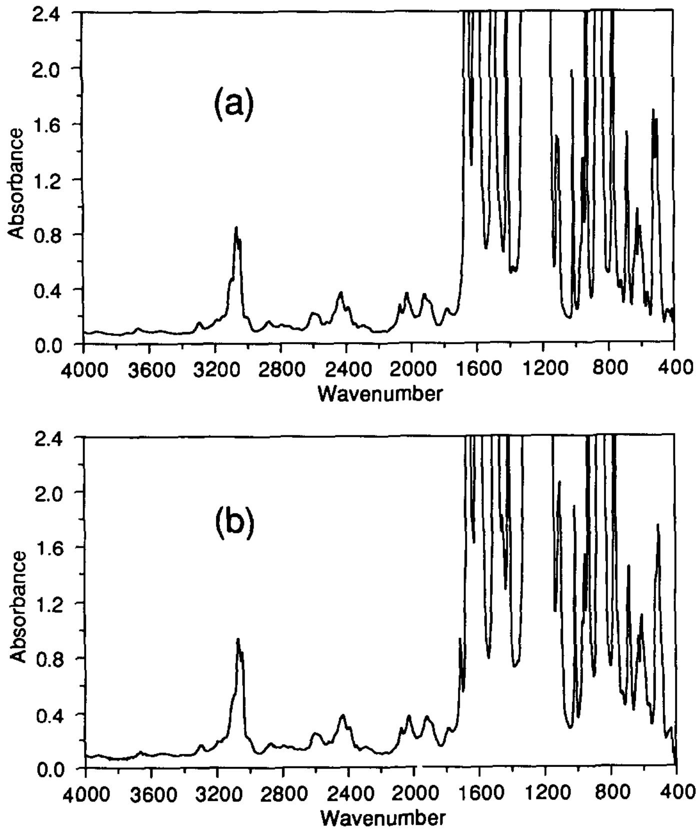


Fig. 1. Transmission FT-IR spectra of PEEK film: (a) as received, and (b) after heating in a nitrogen atmosphere at 460°C for 130 min.

arising from the degradation are more easily detected, provided they lie in the window regions outside the strong absorptions. This is illustrated in Fig. 1(b), which shows a typical spectrum of a heat-treated film. The most obvious change observed is the appearance of a new peak in the carbonyl region at 1711 cm^{-1}, distinct from the original carbonyl peak at 1653 cm^{-1}. There is also a new peak at 1452 cm^{-1}, as well as some slight changes in shape of some of the other peaks.

To better detect the changes which occur on heat treatment, the reference spectrum of Fig. 1(a) was subtracted from the spectra of the heat-treated samples. To take account of any thickness variations, the subtraction factor was adjusted so as to cancel out the bands arising from undegraded PEEK. The subtraction factor was then used to "normalize" the difference spectra so that they all corresponded to the same effective thickness as the reference spectrum. Figure 2 shows the changes in the carbonyl region for samples heated in a nitrogen atmosphere at different temperatures and for different times. The new peak always occurs at the same frequency of 1711 cm^{-1}, regardless of the temperature, and appears

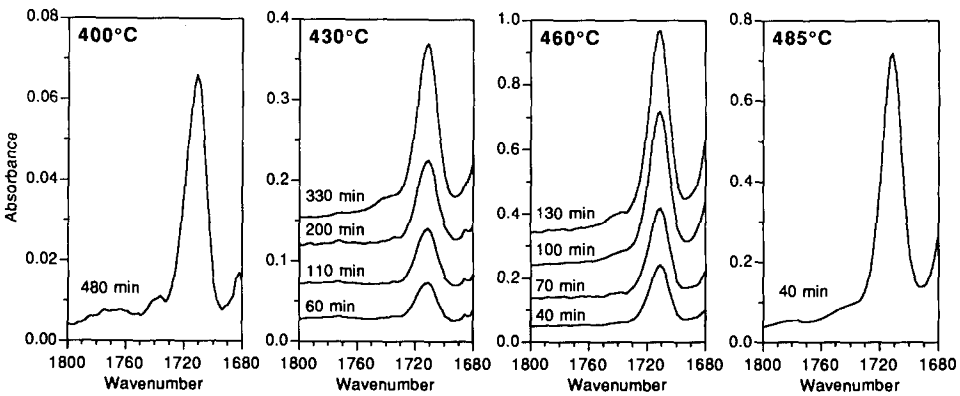


Fig. 2. Transmission difference spectra (carbonyl region) for PEEK film heated in nitrogen under different temperature/time conditions. Curves are displaced in the y direction for clarity.

to grow steadily with time. The rate of growth depends strongly on the temperature; at 400°C the maximum absorbance is only 0.07 after 8 h, whereas at 485°C it is ten times as high as this after only 40 min. When the samples are heated in an air atmosphere, the behaviour is quite different, as shown in Fig. 3. In this case two new carbonyl peaks are observed. The first appears at the same frequency as in nitrogen but grows more quickly. The other appears at 1739 cm^{-1}. At higher levels of degradation, both show a slight shift to higher wavenumber (by about 2 cm^{-1}). The lower the treatment temperature, the more prominent is the peak at 1739 cm^{-1} with respect to the one at 1711 cm^{-1}. This could be due to a difference in the activation energies of the reactions responsible for the two peaks, but oxygen diffusion into the films is undoubtedly an important factor as well. While the growth of the 1711 cm^{-1} peak appears to be accelerated by the

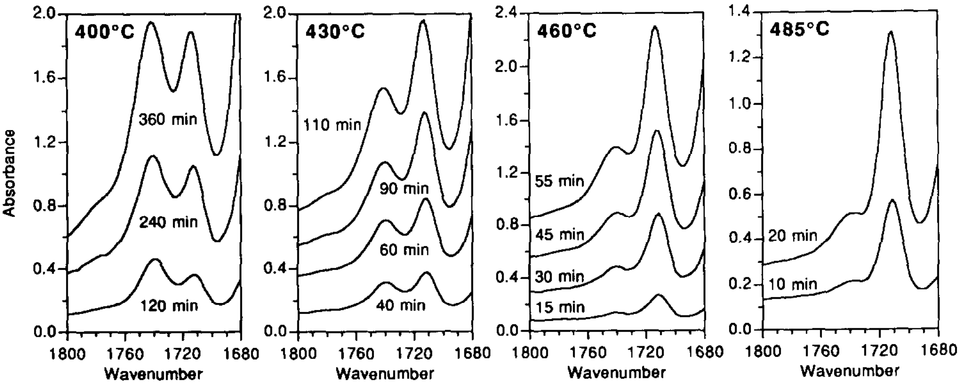


Fig. 3. Transmission difference spectra (carbonyl region) for PEEK film heated in air under different temperature/time conditions. Curves are displaced in the y direction for clarity.

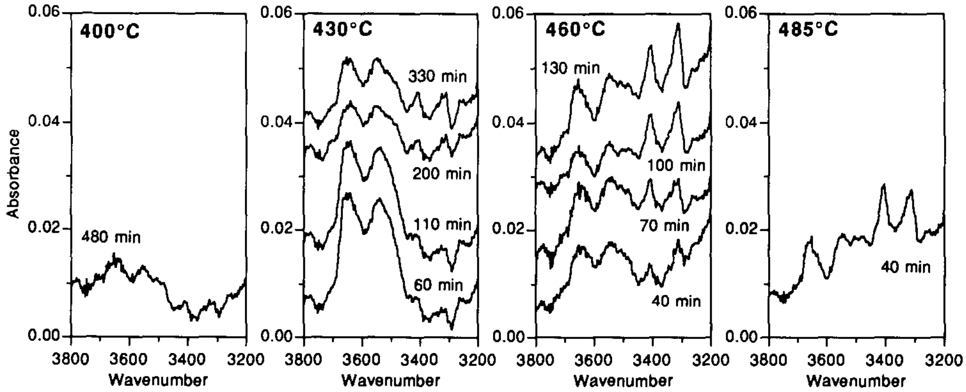


Fig. 4. Transmission difference spectra (hydroxyl region) for PEEK film heated in nitrogen under different temperature/time conditions. Curves are displaced in the *y* direction for clarity.

presence of oxygen, it also grows in nitrogen; therefore, oxygen is not required. The 1739 cm^{-1} peak, however, is not observed in nitrogen, so oxygen is necessary for its formation. At 400°C, both reactions are relatively slow so the oxygen has more time to diffuse into the bulk of the film and the 1739 cm^{-1} peak is dominant. At higher temperatures the reactions are faster, there is less time for the oxygen to diffuse into the film, and the 1711 cm^{-1} peak grows faster than the 1739 cm^{-1} peak. Close examination of the difference spectra also shows that the growth of the 1739 cm^{-1} peak is accompanied by a weaker peak at 1065 cm^{-1}.

Changes are also observed in the hydroxyl region of the transmission spectra, but they are much weaker than those seen in the carbonyl region. In a nitrogen atmosphere (Fig. 4), at low levels of degradation the spectrum is dominated by two peaks at 3645 and 3540 cm^{-1}. At higher

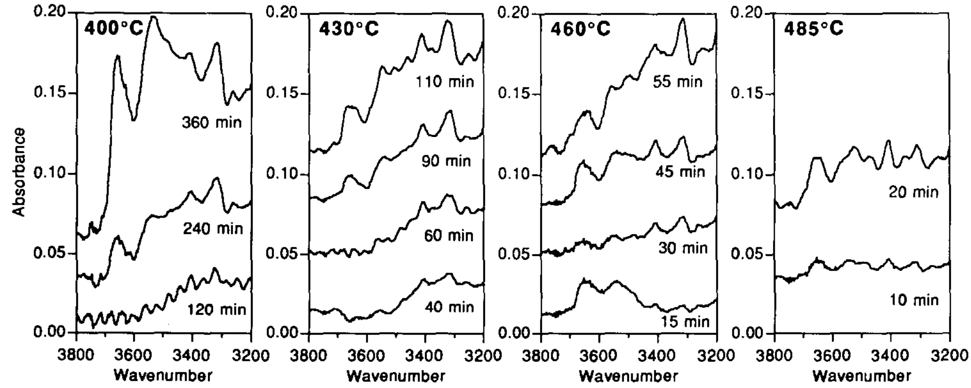


Fig. 5. Transmission difference spectra (hydroxyl region) for PEEK film heated in air under different temperature/time conditions. Curves are displaced in the *y* direction for clarity.

levels of degradation, these become weaker and are replaced by two peaks at 3405 and 3310 cm^{-1}. In an air atmosphere (Fig. 5), the same four peaks are observed but the situation is more complex and others are also present.

Upon degradation, the film changed colour from slightly yellow through various degrees of amber, eventually to become completely black. It is interesting to note that for the films exposed in nitrogen, no significant decrease in thickness was observed, whereas for those exposed in air the thickness showed a measurable decrease (up to 40% in the most extreme cases). This loss of material in air is in keeping with the FT-IR results for thin films reported by Day et al. [21].

Attenuated total reflection

Because the ATR technique [27] measures only the surface of the film, it overcomes to a large extent two problems associated with transmission: that of the excessive absorption caused by the film thickness, and that of

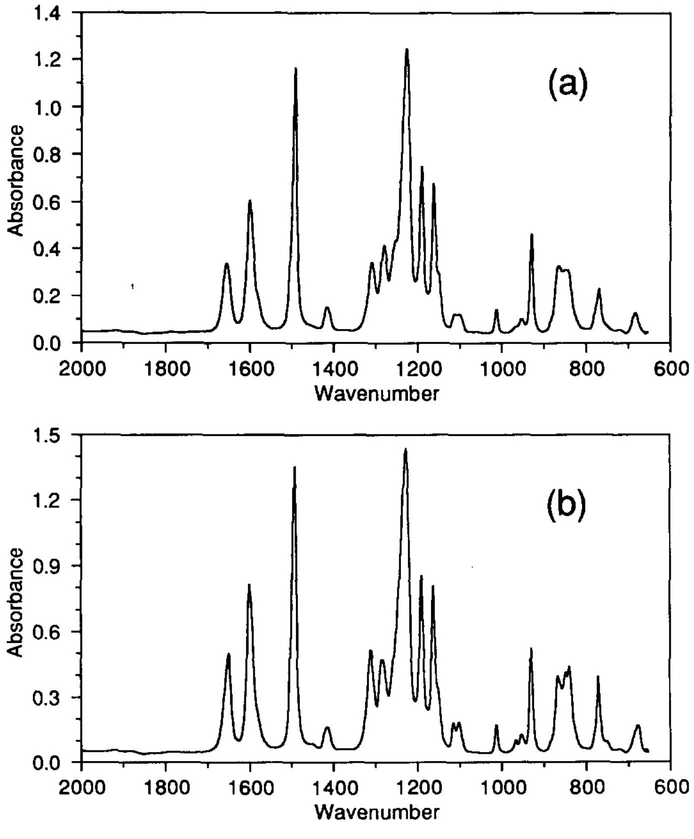


Fig. 6. Wavelength-corrected ATR spectra for (a) amorphous Stabar K200 film, as received, and (b) more highly crystalline film, annealed at 240°C for 1.5 h.

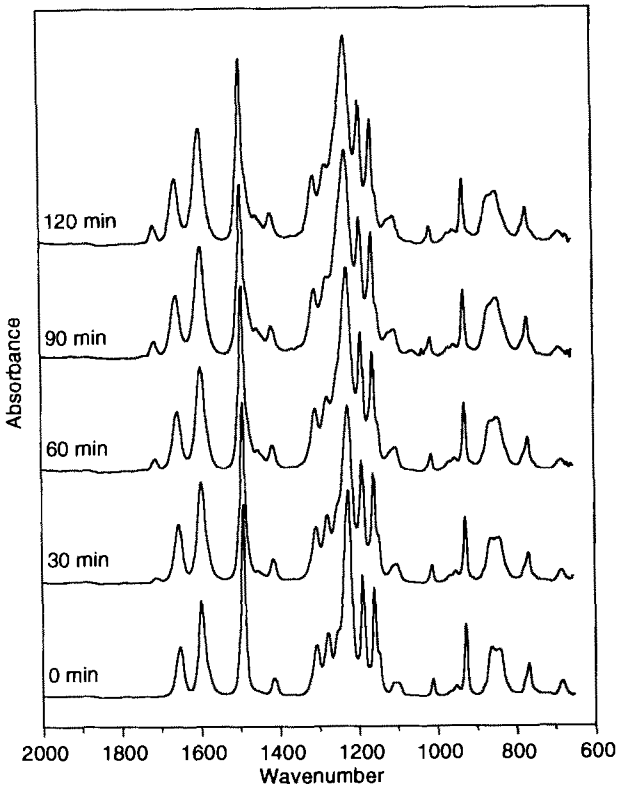


Fig. 7. ATR spectra of Stabar K200 film after heating in nitrogen at 485°C for different times.

oxygen diffusion. With a germanium prism, the effective penetration depth varies from about 0.3 μm at 2000 cm^{-1} to 1 μm at 700 cm^{-1}. To correct for the variation of penetration depth with wavelength, after conversion to absorbance the spectra were multiplied by $\bar{v}/1000$, where $\bar{v}$ is the frequency in wavenumbers. Figure 6 shows the ATR spectra of Stabar film in the amorphous state (as received) and after annealing at 240°C for 1.5 h to increase the degree of crystallinity. The spectra are of very good quality and in excellent agreement with the transmission spectra of very thin films reported by Nguyen and Ishida [23]. In fact, they could be subtracted from each other to give spectra corresponding to pure amorphous and crystalline components, identical to those obtained by Nguyen and Ishida. However, it should be pointed out that when spectra were recorded using a KRS-5 (thallium bromoiodide) prism, substantial peak distortions and even inversions were observed because of the lower refractive index of the KRS-5 compared to germanium. The assignment of peaks in the spectrum of PEEK has been discussed by Nguyen and Ishida [23–25]. The major ones may be attributed to carbonyl stretching (1653 cm^{-1}), phenyl ring vibrations (1599 and 1491 cm^{-1}), ether group

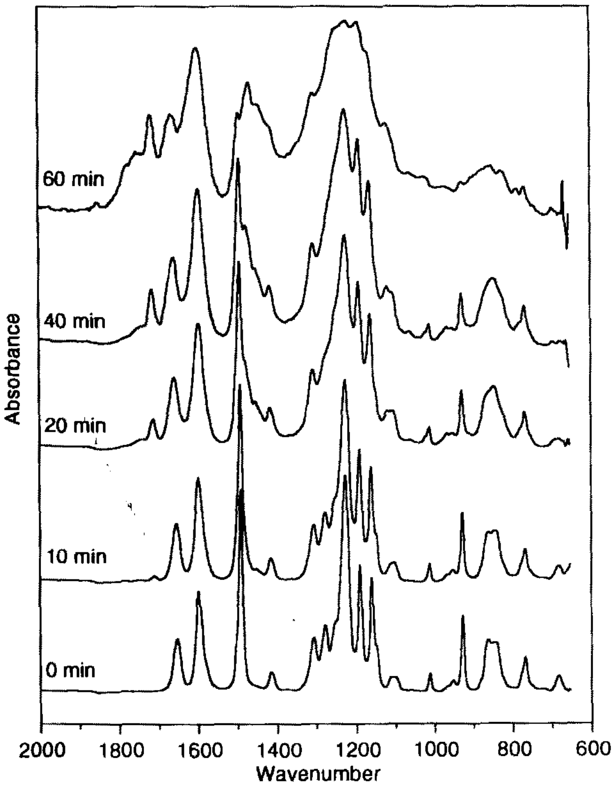


Fig. 8. ATR spectra of Stabar K200 film after heating in air at 485°C for different times.

stretching (1226 cm^{-1}), and phenyl ring C–H deformations (1200–600 cm^{-1}).

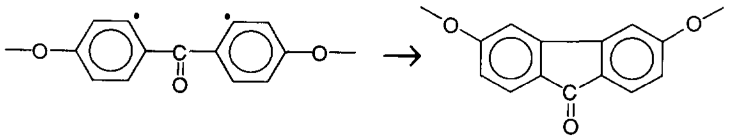
With ATR, it is possible to follow changes in the overall spectrum upon degradation. These are illustrated in Figs. 7 and 8 for the case of 485°C. In a nitrogen atmosphere (Fig. 7), apart from the new peaks already seen in the transmission spectra, it is possible to detect the growth of a shoulder (around 1478 cm^{-1}) on the 1491 cm^{-1} peak and a shoulder on the high frequency side of the ether peak at 1226 cm^{-1}. In an air atmosphere (Fig. 8), the changes are similar but occur much faster. After 20 min, the PEEK is slightly more degraded than after 120 min in nitrogen. After 60 min, severe degradation has occurred and the spectrum has lost most of its features.

Interpretation of the spectra

In spite of the relatively simple chemical structure of PEEK, interpretation of the spectral changes which occur on degradation is not an easy task. Comparison with model compounds is difficult because the vibrational frequencies of carbonyl and hydroxyl groups attached to a phenyl ring can be significantly affected by the nature and position of other substituents on the ring, as well as by hydrogen bonding. The following discussion considers some of the possibilities. Previous work [9, 18, 20, 21] suggests that the first step in the degradation is random chain scission at the ether and carbonyl linkages, with the ether groups apparently being the less stable [1, 18, 20]. The ether and carbonyl free radicals produced can abstract hydrogen from an aromatic ring to form phenol and aldehyde groups respectively. The aryl radicals produced by loss of hydrogen can then combine with each other to form crosslinks between chains, thus bringing about changes in the crystallization behaviour.

The peaks produced in the hydroxyl region upon degradation (Fig. 4) are probably due to phenol groups. Phenol has been identified as a major decomposition product upon pyrolysis of PEEK [17–20]. The presence of several peaks could be explained in terms of different structures and different states of hydrogen bonding. For instance, the peaks at 3405 and 3310 cm^{-1} could correspond to more highly hydrogen-bonded ("polymeric") forms of the species responsible for the peaks at 3645 and 3540 cm^{-1} [28]. However, it is difficult to be more specific. It is interesting to note that when the films were treated with sodium hydroxide solution, the peaks at 3645 and 3540 cm^{-1} decreased in intensity whereas the ones at 3405 and 3310 cm^{-1} did not.

Assignment of the carbonyl peaks is also difficult. One possibility is aldehyde groups formed by hydrogen transfer as mentioned above. The carbonyl frequency of aromatic aldehydes is greatly affected by ring substituents [28]; however, it is generally at 1700 cm^{-1} or below, even with ether groups in the para position [29]. Furthermore, no evidence of aldehyde groups was detected in the C–H stretching region of our spectra (near 2700 cm^{-1}) or in the pyrolysis products of PEEK [18–20]. This would seem to preclude assignment of the peaks at 1711 or 1739 cm^{-1} to aldehyde groups. A second possibility is a fluorenone-type structure formed by cyclization of a diradical as shown in Form 2. The simple compound 9-fluorenone has its carbonyl absorption at 1715 cm^{-1} and also has a strong peak near 1450 cm^{-1} [29, 30]. Thus the peaks which we observe at 1711 and 1452 cm^{-1} could be explained by such a structure. However, no fluorenone was detected in the pyrolysis products, although



Form 2. Cyclization of the diradical.

the analogous product dibenzofuran, with an ether group in place of the carbonyl, was detected [18–20]. A third possibility for the carbonyl species is ester groups. These could be formed even in the absence of air by recombination of carbonyl and ether radicals. In a simple compound comprising an ester group between two phenyl rings (phenyl benzoate), the carbonyl peak occurs at 1730 cm^{-1} [29]. This does not appear to be significantly changed by the presence of ether and carbonyl groups in the para position of the rings, because the polymer poly(*p*-oxybenzoate) consisting of phenyl rings joined by ester groups is reported to absorb at 1735 cm^{-1} [31]. These products also have a moderately strong peak in the 1050–1060 cm^{-1} range. In a comparison of polymers consisting of phenyl rings linked by different groups, ester groups were found to be much more thermally stable than carbonyl or ether groups in an oxidizing atmosphere, but in an inert atmosphere the difference is less pronounced [1]. Thus the peak at 1739 cm^{-1}, which we observe only in an air atmosphere, could arise from such groups, especially because we observe a peak at 1065 cm^{-1} in conjunction with it. Yet another possibility for the carbonyl groups is a quinone-type structure, because benzoquinone is among the pyrolysis products [17, 19, 20]. However, these generally absorb below 1680 cm^{-1} [29], so if they are present their peaks would be hidden by the PEEK carbonyl absorption. Finally, there are other possibilities, such as carboxylic acids, peracids and peresters. Acids are particularly difficult to assign because they can exist in non-hydrogen-bonded, single-bridge hydrogen-bonded, or dimeric hydrogen-bonded forms, all of which absorb at significantly different frequencies [28]. It is impossible to make more precise assignments without doing further work based on derivatization or other techniques. For the present, based on the above discussion, we tentatively assign the 1711 cm^{-1} peak to a fluorenone structure and the 1739 cm^{-1} peak to ester groups.

Quantitative treatment

Even though the origin of the two carbonyl peaks at 1711 and 1739 cm^{-1} is not clear, it is possible to perform a quantitative treatment of the spectra in order to obtain information about the kinetics of the reactions responsible for their formation. In the case of the transmission difference spectra, the heights of the peaks were measured with respect to a baseline drawn between the valleys on either side (usually around 1770 and 1692 cm^{-1}). Because the spectra were all normalized to the same thickness, the peak height is a measure of the concentration of the absorbing species. Figure 9 shows plots of the peak height against time for different atmospheres and temperatures. Within the limits of the experimental scatter, the growth can be considered to be linear with time, so linear regression was used to calculate slopes which can be considered to

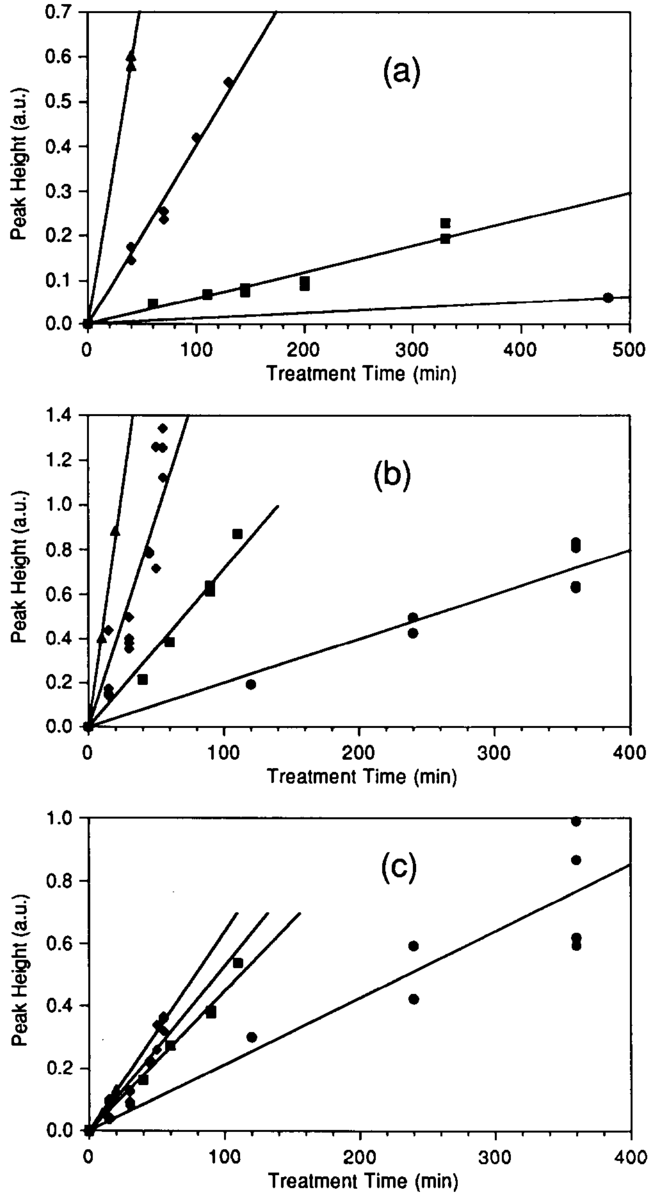


Fig. 9. Growth of carbonyl peaks in the transmission spectra of Stabar K200 film as a function of time at 400°C (●), 430°C (■), 460°C (◆) and 485°C (▲): (a) the 1711 cm^{-1} peak in a nitrogen atmosphere; (b) the 1711 cm^{-1} peak in an air atmosphere; (c) the 1739 cm^{-1} peak in an air atmosphere.

be a measure of reaction rates. These were then used to plot Arrhenius curves as shown in Fig. 10. It is seen that the growth of the 1711 cm^{-1} peak is substantially faster in air than in nitrogen. The activation energies calculated from the data shown in Fig. 10 are given in Table 1. In an inert atmosphere, the reaction which produces the peak at 1711 cm^{-1} has an

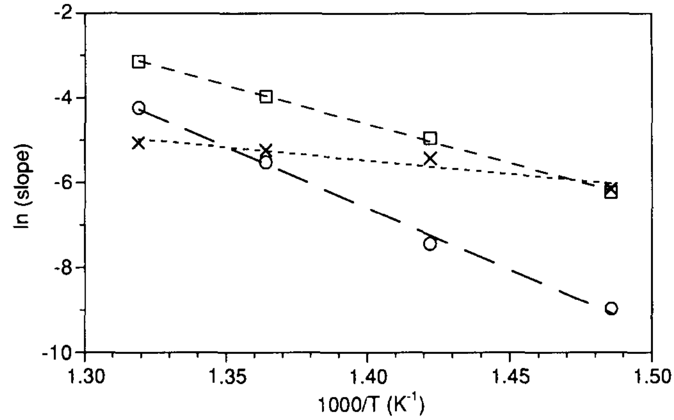


Fig. 10. Arrhenius plots for the rate of growth of carbonyl peaks in the transmission spectra of Stabar K200 film: (○) the 1711 cm^{-1} peak in a nitrogen atmosphere; (□) the 1711 cm^{-1} peak in an air atmosphere; (×) the 1739 cm^{-1} peak in an air atmosphere.

activation energy of 240 kJ mol^{-1}. In an oxidizing atmosphere, the value is substantially lower at 153 kJ mol^{-1}, and the value for the reaction which produces the 1739 cm^{-1} peak is lower still at 52 kJ mol^{-1}. However, the latter two values must be considered "apparent" activation energies because they are affected by the rate of oxygen diffusion into the films, as discussed above.

In the case of the ATR spectra, the overall spectrum intensity is dependent upon the degree of contact between the sample and the prism, which is difficult to control. Hence it is impossible to "normalize" the spectra as was done in the case of transmission. Instead, for quantitative analysis one of the peaks in the spectrum must be used as an internal reference to calculate the ratio of the carbonyl peaks with respect to it. The following were considered: the PEEK carbonyl peak at 1653 cm^{-1}, the phenyl ring stretching bands at 1599 and 1491 cm^{-1}, and the phenyl C–H deformation peak at 1012 cm^{-1}. The most logical choice would be one of the phenyl ring peaks, because the rings are expected to be the

TABLE 1

Calculated activation energies (kJ mol^{-1}) obtained from the Arrhenius plots shown in Figs. 10 and 12

IR peak (cm^{-1})	Atmosphere	Transmission results (Fig. 10)	ATR results (Fig. 12)
1711	Nitrogen	240 ± 11	236 ± 10
1711	Air	153 ± 4	211 ± 2
1739	Air	52 ± 13	116 ± 16

most stable entities in the polymer. However, the intensities of these peaks can be affected by changes in the substituents on the rings. In fact, close examination of various peak ratios in the ATR spectra as a function of treatment time showed that the 1599 cm^{-1} peak decreases in intensity at much the same rate as the 1653 cm^{-1} peak in either nitrogen or air. The 1491 and 1012 cm^{-1} peaks, however, decrease at a rate similar to the 1653 cm^{-1} peak in nitrogen, and even faster in air. Thus, the 1653 cm^{-1} carbonyl peak was chosen as reference, though it is expected to decrease as the carbonyl groups are transformed. A further reason for this choice was to facilitate comparison with diffuse reflection spectra of PEEK/carbon composites, to be reported in a later publication. The height of the 1653 cm^{-1} peak was measured with respect to a baseline drawn between the valleys at about 1750 and 1535 cm^{-1}. For measurement of the peaks at 1711 and 1739 cm^{-1}, the reference spectrum of untreated PEEK was subtracted first in order to draw a baseline between the valleys on either side. For the samples treated at 400°C in nitrogen, these peaks were too weak to measure accurately. The calculated peak ratios are plotted as a function of time in Fig. 11. As in the case of the transmission spectra, the growth can be considered linear with time, and regression was used to calculate slopes which were then used to produce Arrhenius plots (Fig. 12). As before, the 1711 cm^{-1} peak grows faster in air than in nitrogen (six to ten times as fast over the temperature range studied). The apparent activation energies are given in Table 1. For growth of the 1711 cm^{-1} peak in a nitrogen atmosphere, the value is 236 kJ mol^{-1}, which is in excellent agreement with the value of 240 kJ mol^{-1} obtained from the transmission spectra. However, the values obtained for the 1711 and 1739 cm^{-1} peaks in an air atmosphere (211 and 116 kJ mol^{-1} respectively) are much higher than the values obtained in transmission. It is believed that these are a better indicator of the true activation energies. Because ATR measures only the surface of the film, the complicating effects of oxygen diffusion should be smaller, although not necessarily negligible.

To make a more quantitative comparison of the transmission and ATR results, the ratio of the two peaks at 1711 and 1012 cm^{-1} was plotted as a function of treatment time. This is the only ratio which could be calculated for both types of spectrum. The results are shown in Fig. 13. In a nitrogen atmosphere (Fig. 13(a)) at a given temperature, the ATR and transmission results fall on the same curve, showing that there is no difference between the surface and the bulk of the film. In an air atmosphere (Fig. 13(b)), this is true at 430°C, where the degradation is slow with respect to the diffusion of oxygen into the film. However, at higher temperatures, the ATR results tend to be higher than the transmission results, indicating that the surface is more degraded than the bulk because the oxygen has had less time to diffuse into the film. This confirms the hypothesis concerning oxygen diffusion and indicates that the activation energies obtained by ATR are more reliable.

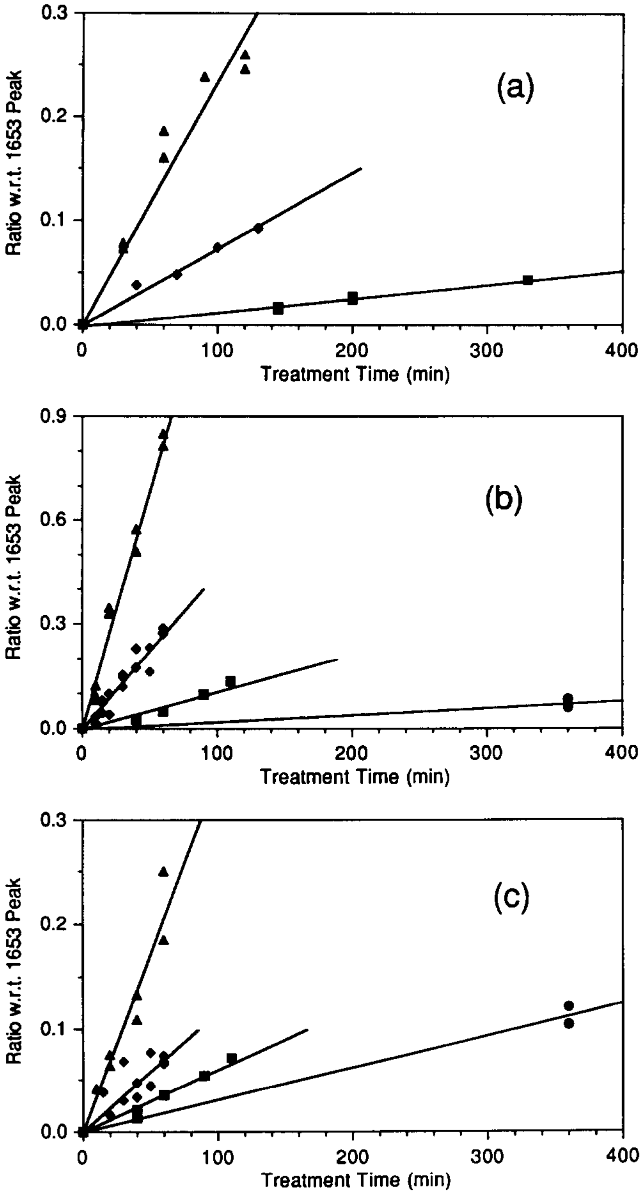


Fig. 11. Growth of carbonyl peaks in the ATR spectra of Stabar K200 film as a function of time at 400°C (●), 430°C (■), 460°C (◆) and 485°C (▲): (a) the 1711 cm^{-1} peak in a nitrogen atmosphere; (b) the 1711 cm^{-1} peak in an air atmosphere; (c) the 1739 cm^{-1} peak in an air atmosphere.

These results both corroborate and help to elucidate those obtained from thermogravimetric analysis work by Day et al. [11–13]. They obtained experimental data under both isothermal and dynamic conditions and analysed them by various methods. For purposes of comparison with our results, we have taken their activation energies which correspond to

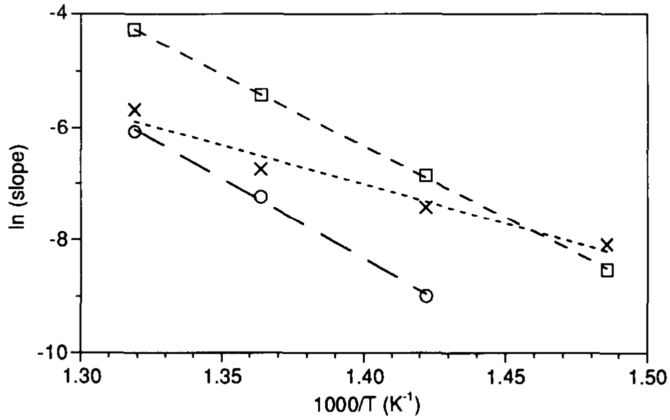


Fig. 12. Arrhenius plots for the rate of growth of carbonyl peaks in the ATR spectra of Stabar K200 film: (○) the 1711 cm^{-1} peak in a nitrogen atmosphere; (□) the 1711 cm^{-1} peak in an air atmosphere; (×) the 1739 cm^{-1} peak in an air atmosphere.

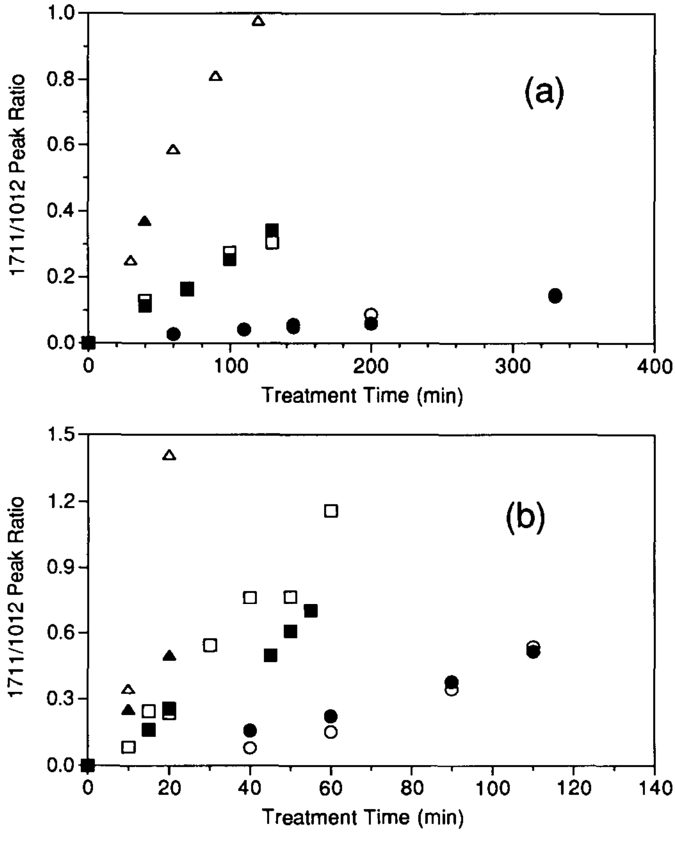


Fig. 13. Comparison of the rate of growth of the 1711/1012 cm^{-1} peak height ratio in transmission and ATR spectra of Stabar K200 film at 430°C (●, ○), 460°C (■, □) and 485°C(▲, △), for samples exposed in a nitrogen atmosphere (a) and in an air atmosphere (b). Solid symbols represent transmission results, open symbols ATR results.

TABLE 2

Activation energies for PEEK degradation obtained by Day et al. from thermogravimetric analysis data [12, 13]

Atmosphere	TGA Conditions	Extent of conversion	E_a (kJ mol^{-1})
Nitrogen	Dynamic	0.05	237
Nitrogen	Isothermal	0.05	221
Air	Dynamic: fast heating (>1°C min^{-1})	0.05	199
Air	Isothermal: high temperature (>440°C)	0.2	200
Air	Dynamic: slow heating (<1°C min^{-1})	0.05	116
Air	Isothermal: low temperature (<440°C)	0.2	115

the early stages of degradation (extent of conversion 0.2 or less) and which were calculated by the methods proposed by Flynn. These are summarised in Table 2. In nitrogen, the results indicated a rather straightforward random chain scission process and the calculated activation energy was not particularly dependent on the method used. Values of 237 and 221 kJ mol^{-1} were obtained from the dynamic and isothermal data respectively [12]. This is in very good agreement with our values of 240 kJ mol^{-1} (transmission) and 236 kJ mol^{-1} (ATR) for a nitrogen atmosphere. In an air atmosphere, the reaction mechanism was found to be much more complex and the results more dependent on the conditions used. For dynamic experiments, the result depends on the heating rate. If this is greater than 1°C min^{-1}, the apparent activation energy E_a is 199 kJ mol^{-1}, but if it is less than 1°C min^{-1}, E_a is 116 kJ mol^{-1} [12]. For isothermal experiments, the result depends on the temperature. If this is greater than 440°C, the activation energy is 200 kJ mol^{-1}, but if it is under 440°C, E_a is 115 kJ mol^{-1} [13]. These results may be explained in terms of oxygen diffusion. At high heating rates or high temperatures, the degradation is rapid compared to oxygen diffusion into the polymer, and the dominant reaction is the one which produces the IR peak at 1711 cm^{-1}. For this we obtain an activation energy of 211 kJ mol^{-1}, which is in good agreement with Day's results of 199 and 200 kJ mol^{-1}. At low heating rates or low temperature, however, there is more time for oxygen diffusion, and the predominant degradation reaction is the one which produces the IR peak at 1739 cm^{-1}. Again, our E_a value of 116 kJ mol^{-1} for this peak is in excellent agreement with Day's results of 116 and 115 kJ mol^{-1}. Thus, although we do not know the details of the reaction mechanisms, there seems to be two dominant pathways. The first is a pyrolytic-type mechanism which produces a species absorbing at 1711 cm^{-1}, possibly a fluorenone-type structure. The second involves the participation of oxygen and produces a species absorbing at 1739 cm^{-1}, possibly ester groups.

CONCLUSIONS

The thermal degradation of PEEK has been shown to involve two predominant pathways. In an inert atmosphere, it proceeds by a pyrolytic-type mechanism which leads to a new carbonyl species absorbing in the IR at 1711 cm^{-1}, possibly a fluorenone-type structure. The activation energy for this process is 236 kJ mol^{-1}. In an oxidizing atmosphere, the same species is produced but at a faster rate, and the activation energy is 211 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}, possibly ester groups. The activation energy is 116 kJ mol^{-1}. Because of the time required for oxygen to diffuse into the polymer, oxidative degradation is more pronounced at the surface, especially at higher temperatures. Confirmation of the nature of the new carbonyl species and a more complete description of the reactions occurring would require further work.

ACKNOWLEDGEMENT

I.G.C. thanks the European Institute for Technology (EIT, Paris, France) for sponsoring his visit to Canada.

REFERENCES

1 W.W. Wright, in G. Geuskens (Ed.), Degradation and Stabilisation of Polymers, Applied Science Publishers Ltd., New York, 1975, Chap. 3, pp. 43–75.
2 S.K. Brauman and J.G. Pronko, J. Polym. Sci. Part B: Polym. Phys., 26 (1988) 1205.
3 M. Day, T. Suprunchuk, J.D. Cooney and D.M. Wiles, J. Appl. Polym. Sci., 36 (1988) 1097.
4 Y. Deslandes, M. Day, N.-F. Sabir and T. Suprunchuk, Polym. Compos., 10 (1989) 360.
5 A. Lustiger, F.S. Uralil and G.M. Newaz, Polym. Compos., 11 (1990) 65.
6 C.N. Velisaris and J.C. Seferis, Proc. SPE Ann. Tech. Conf. (ANTEC), 31 (1985) 401.
7 C.-M. Chan and S. Venkatraman, J. Appl. Polym. Sci., 32 (1986) 5933.
8 C.-C. Ma, H.-C. Hsia, W.-L. Liu and J.-T. Hu, Polym. Compos., 8 (1987) 256.
9 A. Arzak, J. Nazábal and J.I. Eguiazábal, Plastics, Rubber Compos. Proc. Appl., 15 (1991) 119.
10 M. Day, T. Suprunchuk, J.D. Cooney and D.M. Wiles, Proc. Int. SAMPE Tech. Conf., 20 (1988) 132.
11 M. Day, J.D. Cooney and D.M. Wiles, Polym. Eng. Sci., 29 (1989) 19.
12 M. Day, J.D. Cooney and D.M. Wiles, J. Appl. Polym. Sci., 38 (1989) 323.
13 M. Day, J.D. Cooney and D.M. Wiles, Thermochim. Acta, 147 (1989) 189.
14 W.E. Moddeman, W.C. Bowling, E.E. Tibbitts and R.B. Whitaker, Polym. Eng. Sci., 26 (1986) 1469.
15 C.-C.M. Ma, H.-C. Hsia, W.-L. Liu and J.-T. Hu, J. Thermoplastic Compos. Mater., 1 (1988) 39.
16 R. Yokota, T. Sakino and I. Mita, Kobunshi Ronbunshu, 47 (1990) 207.
17 R.B. Prime and J.C. Seferis, J. Polym. Sci. Part C: Polym. Lett., 24 (1986) 641.
18 J.N. Hay and D.J. Kemmish, Polymer, 28 (1987) 2047.
19 Y.-F. Luo, R.-Z. Huo, X.-G. Jin and F.E. Karasz, Huaxue Tongbao, 10 (1989) 43.

20 M. Day, J.D. Cooney and D.M. Wiles, J. Anal. Appl. Pyrolysis, 18 (1990) 163.
21 M. Day, D. Sally and D.M. Wiles, J. Appl. Polym. Sci., 40 (1990) 1615.
22 J.M. Chalmers, W.F. Gaskin and M.W. Mackenzie, Polym. Bull., 11 (1984) 433.
23 H.X. Nguyen and H. Ishida, Polymer, 27 (1986) 1400.
24 H.X. Nguyen and H. Ishida, J. Polym. Sci. Part B: Polym. Phys., 24 (1986) 1079.
25 H.X. Nguyen, Investigation of the Interfacial Structures of High-Performance Composites, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, U.S.A., August 1986.
26 K.C. Cole and I.G. Casella, to be published.
27 N.J. Harrick, Internal Reflection Spectroscopy, Harrick Scientific Corp., Ossining, NY, 1979.
28 L.J. Bellamy, The Infra-red Spectra of Complex Molecules, 3rd edn., Chapman and Hall, London, 1975.
29 C.J. Pouchert, The Aldrich Library of FT-IR Spectra, Edition 1, Vols. 1 and 2, Aldrich Chemical Co. Inc., Milwaukee, 1985.
30 W.W. Simons (Ed.), The Sadtler Handbook of Infrared Spectra, Sadtler Research Laboratories, Philadelphia, 1978.
31 J. Menczel, J.P. Walsh, Jr. and B. Wunderlich, J. Polym. Sci. Polym. Phys. Ed., 19 (1981) 837.