An electron spin resonance study of the correlation between the free carbon content and mechanical properties of Nicalon SiC fibres

B. Catoire and M. Sotton
Institut Textile de France, 35 rue des Abondances, 92100 Boulogne, France

and G. Simon and A. R. Bunsell
Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux, BP 87, 91003, Evry, France
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The amount of carbon present in SiC fibres (Nicalon) strongly influences the high-temperature creep behaviour of this ceramic material. Using electron spin resonance (e.s.r.) spectroscopy, data on the variation of the amount of this phase have been obtained. Good correlation between the e.s.r. intensity and mechanical behaviour of samples annealed at high temperature ($T > 1000$°C) has been observed. Moreover, e.s.r. gives evidence of a drop in free carbon content at 1100°C under argon. This drop appears only at 1300°C in air. An explanation of this phenomenon is proposed.

(Keywords: SiC fibres; free carbon content; electron spin resonance spectroscopy; creep behaviour; high-temperature annealing)

INTRODUCTION

The development of an SiC fibre produced by the pyrolysis of an organometallic precursor has excited the interest of researchers and potential users as it offers the possibility of making ceramic matrix composites for use at temperatures above 1000°C.

The process of pyrolysis is an important step in the manufacture of these fibres and the conversion from a polycarbosilane (PCS) precursor fibre accounts for the Nicalon fibre containing products other than SiC[1,2].

Electron microprobe and Auger spectroscopy have shown that industrial Nicalon fibres contain not only SiC but also an important amount of free carbon and oxygen[3]. The free carbon (7 to 15% by weight) strongly influences the high-temperature creep behaviour of this ceramic material. A study of this phase and its evolution when SiC fibres are subjected to high temperatures ($T > 1000$°C) was undertaken with the help of electron spin resonance (e.s.r.).

EQUIPMENT AND PROCEDURES

The silicon carbide fibres used in this study are Nicalon NLM 102 type produced by Nippon Carbon (some tests were done on NLP 101 fibres). The average diameter of the fibres was 15 μm. The pyrolysis temperature of the polycarbosilane was about 1300°C[2]. Auger spectrometry has revealed that about 15% by weight of the NLM 102 fibre is free carbon (7% with the NLP 101 type). E.s.r. spectra were recorded on a Bruker ER 100 D e.s.r. spectrometer (X band) with a sensitivity of 2×10^{11} spins/gauss.

The e.s.r. experiments were on samples of Nicalon NLM 102 fibres annealed between 1000°C and 1500°C in air or in a neutral argon atmosphere. The dwell time at each temperature was fixed at 1 h. After annealing, the fibres were finely crushed and mixed (1/50) with diamagnetic silica gel. The powder was then placed in a quartz tube and observed by e.s.r. at room temperature.

Tensile creep tests were performed on monofilaments from 24°C up to 1300°C. The mechanical testing machine is described elsewhere[4].

RESULTS

Electron spin resonance

A typical narrow ($\simeq 1.5$ G wide) symmetrical singlet with a g value of 2.0028 (characteristic of coal pitch) is observed on Nicalon SiC fibres as shown in *Figure 1*. This spectrum is very similar to that observed for an 'amorphous' carbon deposit obtained by electrical discharge (*Figure 2*). Moreover, these results are in good accordance with those of other workers for coal or fine carbon powders[5,6]. No e.s.r. signal is observed in the same experimental conditions on SiC powder.

Influence of annealing temperature. Irrespective of the annealing conditions, 1000°C to 1500°C under air or argon, and with all the recording parameters being fixed, the shape of the e.s.r. spectra was unchanged and very similar to that observed in *Figure 1*. On the other hand

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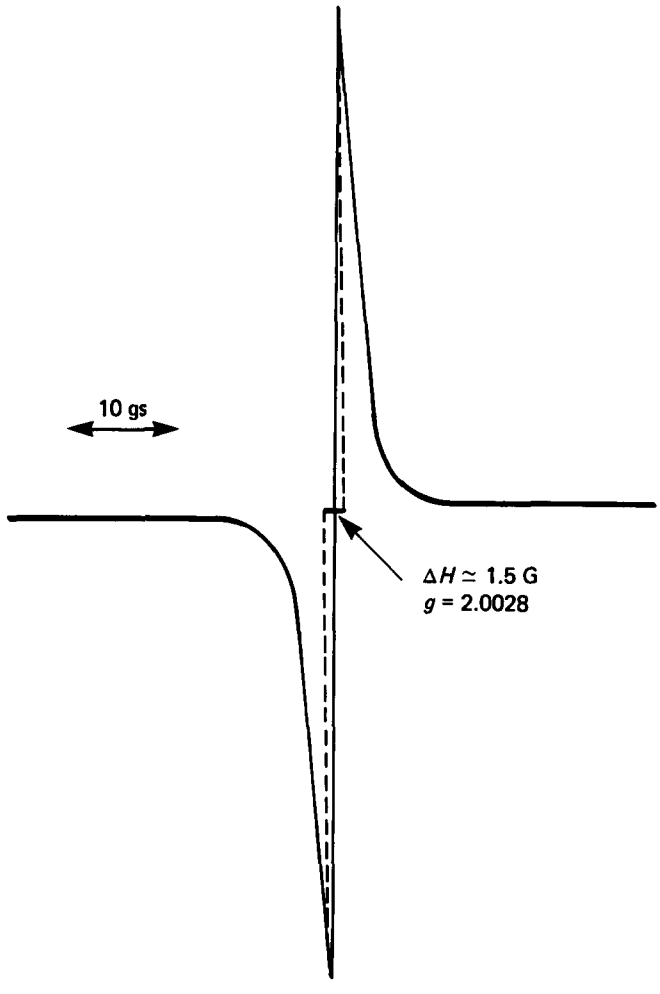

Figure 1 E.s.r. spectrum of Nicalon NLM 102 fibre (1/50 with silica gel)

the intensity of the spectrum varied in large proportions. *Figure 3* shows the variation of the line intensity (arbitrary units) as a function of heat treatment temperature; curve A is for heat treatments in air, curve B is results obtained in an argon atmosphere. It is to be remembered that e.s.r. generally gives the derivative curve of the absorption. The surface under the absorption curve is then proportional to the amplitude of the derivative. If the spectra have the same shape, the intensity allows a relative estimate of the number of spins present in the sample.

We can see from *Figure 3* that there is a strong decrease of the free carbon content when the fibre is subjected to a temperature higher than 1100°C in argon. In air, a similar situation is observed at 1300°C.

Influence of heat treatment duration. Figure 4 shows the e.s.r. line intensity plotted *versus* the dwell time (in the range from 1 to 30 h) at 1300°C in air (these conditions are the limits at which the carbon content of the fibres does not fall abruptly; see *Figure 3*).

During the first 5 h of annealing, an important decrease of the e.s.r. intensity is observed, after which the curve tends towards an asymptote for longer annealing times.

Evolution of content of free carbon. The structure of the segregated free carbon obtained during the PCS pyrolysis process, which occurs at about 1300°C, can be considered not to change[7] in the temperature range 1000–1300°C. This view is supported by the shape of the e.s.r. spectra remaining quite unchanged. The number of spins, that is the free carbon content, is therefore proportional to the e.s.r. intensity.

Figure 5 shows the e.s.r. intensity plotted against the free carbon content of the two types of Nicalon fibres studied (20% molar for NLP 101, 40% for NLM 102). The carbon content was measured by means of Auger

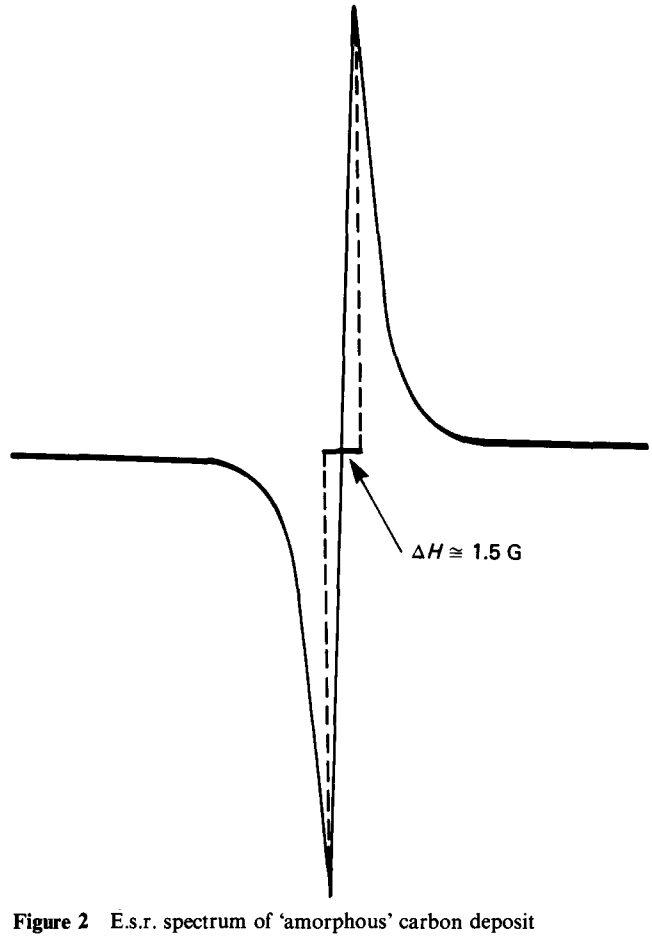

Figure 2 E.s.r. spectrum of 'amorphous' carbon deposit

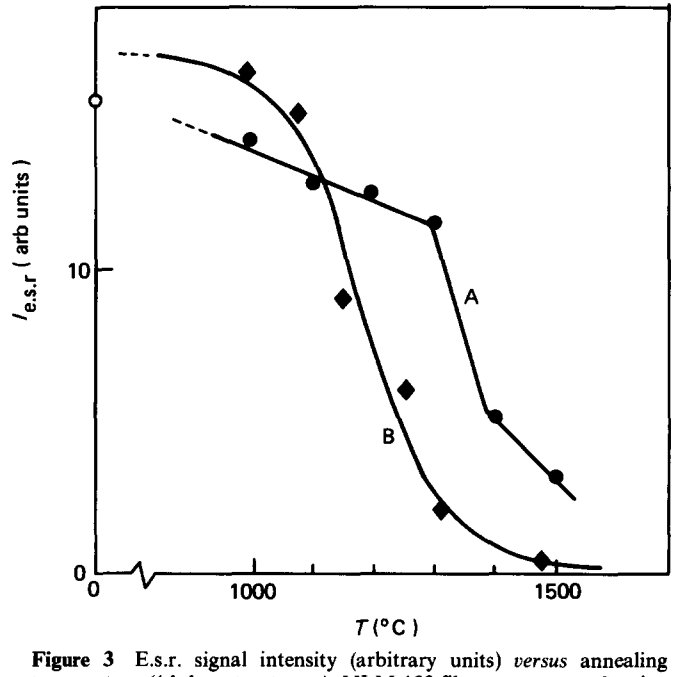

Figure 3 E.s.r. signal intensity (arbitrary units) *versus* annealing temperature (1 h heat treatment): NLM 102 fibre; ◆, argon; ●, air

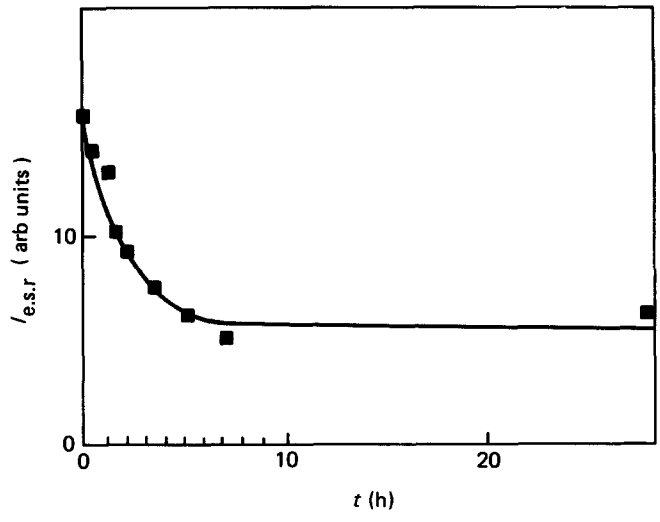

Figure 4 E.s.r. signal intensity (arbitrary units) as a function of dwell time at 1300°C in air: NLM 102 fibre

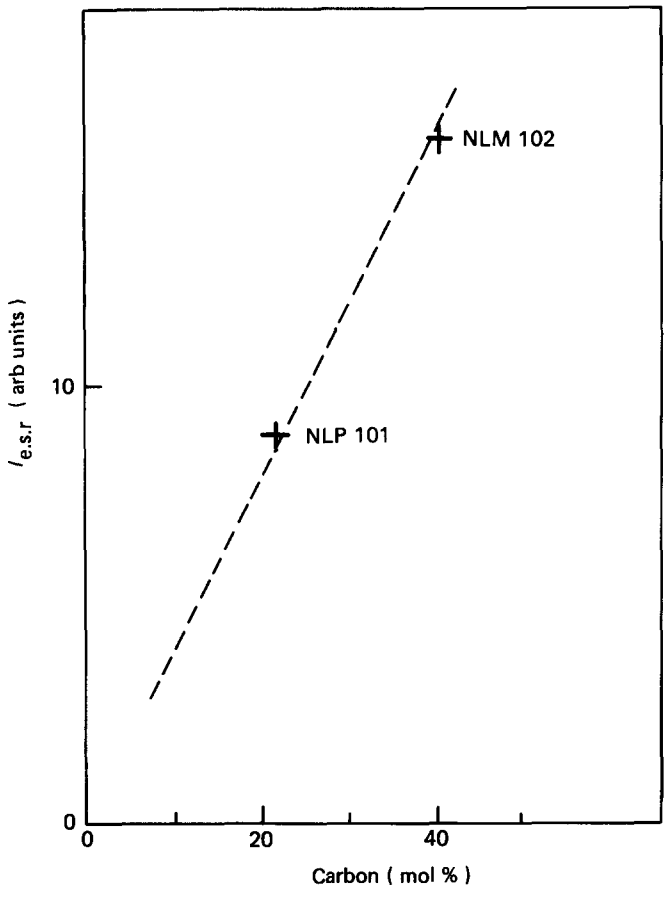

Figure 5 E.s.r. signal intensity (arbitrary units) *versus* carbon content measured by means of Auger spectroscopy

spectroscopy. A tentative correlation between Auger and e.s.r. measurements is plotted in *Figure 5* for the two types of Nicalon fibres we have studied. Although the broken straight line on the graph should not be taken as a calibration curve, the intensity of the e.s.r. signals shows good agreement with the variation of the carbon content in the fibres measured by Auger spectroscopy.

Mechanical experiments

Description of creep phenomenon. Simple tensile and tensile creep tests were conducted at temperatures between 24°C and 1300°C and details are given elsewhere[3,8]. This paper only concerns the results obtained during creep tests. Long-term tests of fibres under steady loading give evidence of a creep phenomenon which occurs above 1000°C. An example of the mean creep curves at 1100°C, 1200°C and 1300°C is shown in *Figure 6*; the applied stress was 0.6 GPa and the tests were conducted in an argon atmosphere.

The important point here is that below 1200°C and in the low-stress region (under 0.3 GPa), the creep deformation is inhibited. The steady-state creep equation can be written:

$$\dot{\varepsilon} = A(\sigma - \sigma_0)^n \exp(-\Delta H/RT)$$

where $\dot{\varepsilon}$ is the strain rate during the steady-state creep, σ the applied stress, σ_0 the threshold stress under which no creep can occur, n the stress exponent and ΔH the activation energy of the phenomenon governing creep. The latter two parameters are linked to the deformation mechanism.

Influence of temperature on threshold stress. The strain rate $\dot{\varepsilon}$ during steady-state creep (second part of the creep curve, 20 to 30 h after loading) is plotted *versus* the stress σ applied to the fibre at 1100°C, 1200°C and 1300°C respectively in *Figures 7, 8* and *9*. The experiments were carried out on NLP 101 fibres. Similar curves were obtained with NLM 102 fibres; although a smaller number of experiments was carried out on the latter.

The points plotted on the graphs of *Figures 7, 8* and *9* represent the slope of the creep curve under different stresses at the temperature mentioned (1100°C, 1200°C and 1300°C). We have expressed these values in a linear plot system. An analytical treatment of the data has allowed the determination of the threshold stress σ_0 and the stress exponent n of the above-mentioned creep equation.

It can be seen that the threshold stress reduces with increasing temperature:

$\sigma_0 = 0.3$ GPa at 1100°C
$\sigma_0 = 0.17$ GPa at 1200°C
no threshold stress at 1300°C

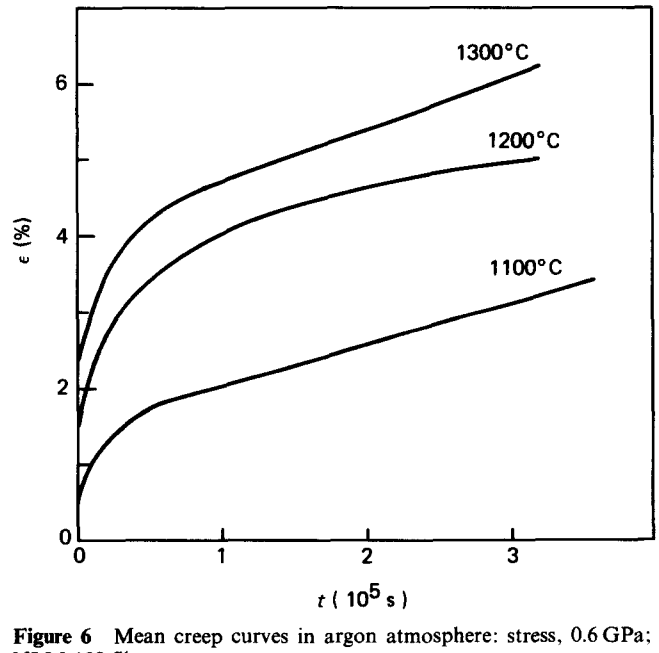

Figure 6 Mean creep curves in argon atmosphere: stress, 0.6 GPa; NLM 102 fibre

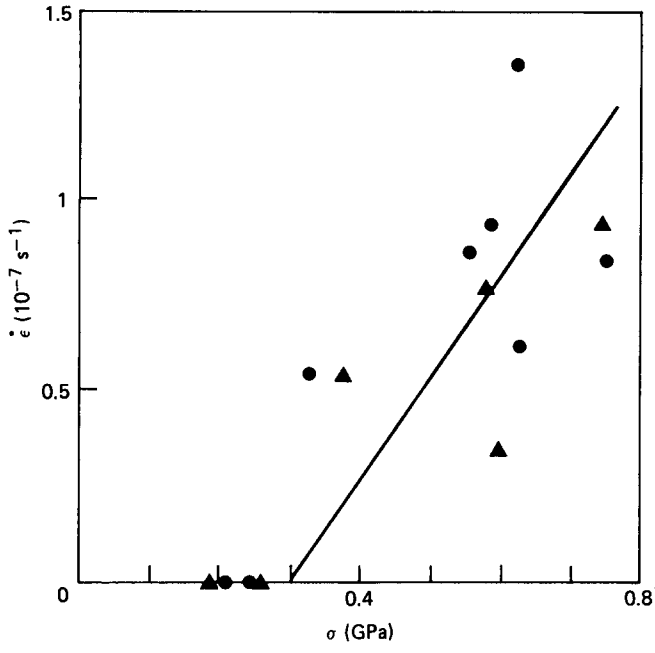

Figure 7 Dependence of the strain rate on stress at 1100°C: NLP 101 fibre; ▲, argon; ●, air

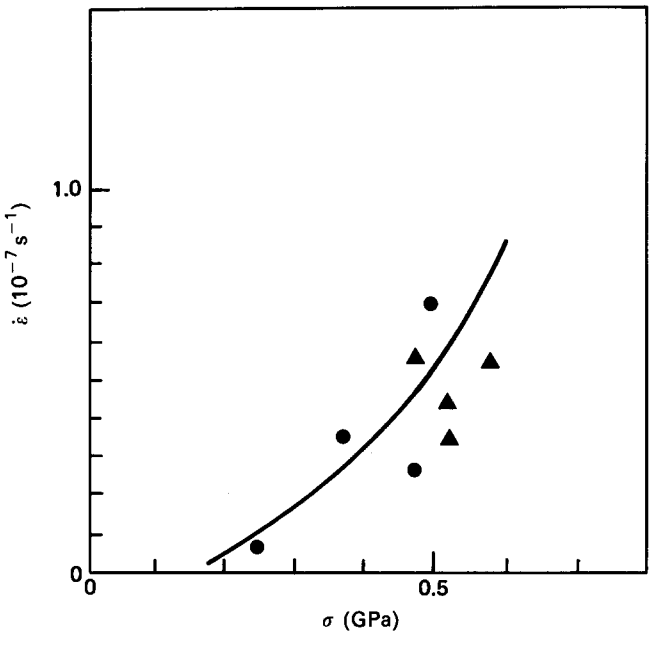

Figure 8 Dependence of the strain rate on stress at 1200°C: $t = 10^5$ s; $\sigma = 0.17$ GPa; NLP 101 fibre; ▲, argon; ●, air

DISCUSSION

The results of the mechanical experiments show that the threshold stress observed in the creep of SiC fibres is temperature-dependent.

In a theoretical study on the behaviour of gold samples containing a variable amount of alumina particles, Ashby[9] showed that a relationship exists between the threshold stress and the alumina content. The presence of these particles inhibits the creep deformation.

In our case, it seems that the free carbon in the Nicalon fibre would have the same effect on its mechanical behaviour.

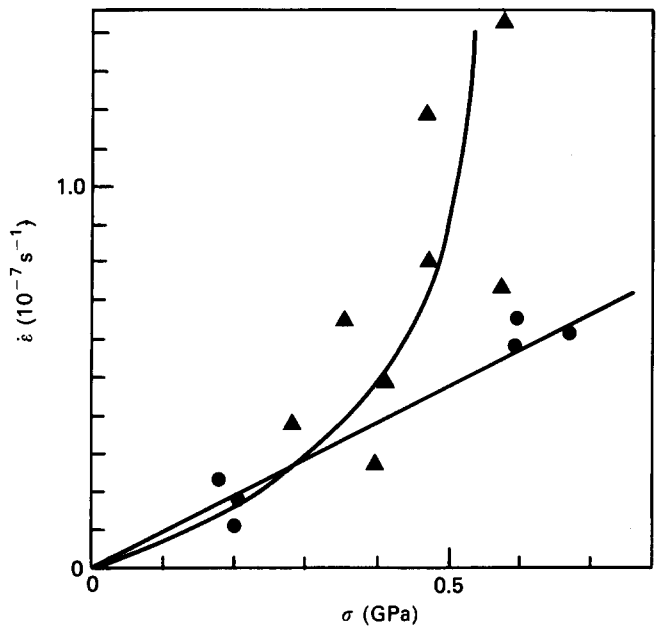

Figure 9 Dependence of the strain rate on stress at 1300°C: NLP 101 fibre; ▲, argon; ●, air

The observed e.s.r. spectrum (a symmetrical line about 2 Gs wide) must be that of clusters of free carbon produced during the pyrolysis of PCS at about 1300°C. The evolution of the e.s.r. intensity allows the variations of the free carbon content, which is responsible for the creep behaviour of the fibres at low stress, to be followed.

Moreover, e.s.r. gives evidence of a drop in the free carbon content at 1100°C under argon; this drop appears only at 1300°C in air for a 1 h heat treatment. This curious behaviour can be understood as the Nicalon fibre contains oxygen which reacts above 1100°C with free carbon to form carbon monoxide CO.

It has been shown elsewhere[8] that when heat treating the fibres in air the silicon carbide is surface-oxidized, creating an SiO_2 tight protective film. This film decreases the kinetics of CO departure from the fibre and inhibits the reaction, which is intrinsic to the fibre, between oxygen and carbon. The e.s.r. results (*Figure 3*) confirm this hypothesis (difference in the carbon behaviour under air and argon).

CONCLUSIONS

We have seen that free carbon plays an important role in the mechanical behaviour of the Nicalon fibres.

E.s.r. has proved to be a straightforward method for following the evolution of this phase, which is responsible for the creep threshold stress.

REFERENCES

1 Hasegawa, Y., Iimura, M. and Yajima, S. *J. Mater. Sci.* 1980, **15**, 720
2 Hasegawa, Y. and Okamura, K. *J. Mater. Sci.* 1983, **18**, 3633
3 Simon, G. and Bunsell, A. R. *J. Mater. Sci.* 1984, **19**, 3649
4 Simon, G. and Bunsell, A. R. in '3eme Journée nationale sur les Composites' (A. Corvino *et al.*), Pluralis, Paris, 1982, p. 195
5 Aronson, S., *et al. Carbon* 1978, **16**, 69–72
6 Ranby, B. and Rabek, J. F., 'ESR Spectroscopy in Polymer Research', Springer-Verlag, Berlin, 1977, pp. 344–65
7 Marchand, A. and Amiell, J. *Carbon* 1970, **8**, 707–26
8 Simon, G. and Bunsell, A. R. *J. Mater. Sci.* 1984, **19**, 3658
9 Ashby, M. F. *Scr. Metall.* 1969, **3**, 837