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The effects of thermal exposure on the structural and mechanical integrity of carbon fibres*

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The chemical composition and the structural parameters and mechanisms that control the oxidative and thermal stabilities of PAN-based C6000, IM6 and T300 carbon fibres used in high performance composites are reported. The fibres contain significant quantities (2.7 to 7.0 wt%) of chemically bound nitrogen. The higher nitrogen containing fibres tend to be more susceptible to oxidation. In the 1200 to 2500° C temperature exposure region, in an inert atmosphere, simultaneous graphitization and nitrogen loss occurs. The nitrogen loss process is predominantly diffusion controlled by the fibre molecular level porosity. The higher nitrogen containing fibre, T300, readily loses its structural integrity at 2500° C, because the high nitrogen evolution paths result in a network of poorly interconnected graphitic crystals.

1. Introduction

Carbon and graphite fibres in polymer–, metal– and carbon–matrix composites are used extensively in aerospace applications as primary structures in tactical aircraft, helicopters, space systems and rockets. The latest fibres exhibit excellent strength and stiffness as a function of temperature. In both present and future applications, however, these fibres in composites will be exposed to increasingly extreme thermal environments as a result of aerodynamic heating, laser exposure and, in the case of carbon–carbon composites, fabrication conditions. Often, thermal exposure will occur in the absence of significant oxygen. It is, therefore, important to understand the structural parameters that influence the oxidative and thermal induced loss of fibre structural integrity.

In this paper we report the chemical composition of typical carbon fibres used in high performance composites. The oxidative stability of these fibres in the 400 to 800° C temperature range are investigated. The affects of thermal exposure time–temperature conditions, in an inert atmosphere, in the 1200 to 2500° C temperature range, on the fibre chemical and physical structure and mechanical integrity are also reported. The mechanisms and associated structural parameters that control the oxidative and thermal-induced structural and mechanical integrity modifications of these carbon fibres are then discussed.

2. Experimental details

2.1. Materials

The carbon fibres studied in this investigation were all formed from the carbonization of polyacrylonitrile, PAN. Two of the carbon fibres were high strain (1.7 to 1.8% ultimate elongation) fibres, namely C6000, Celanese and IM6, Hercules; whereas a third fibre was a lower ultimate strain carbon fibre, T300, Union Carbide, that has been widely used in composites for many years. The manufacturers' reported mechanical properties of these fibres are shown in Table I. The C6000, IM6 and T300 fibres were in the form of tows that contained 6000, 12 000 and 6000 filaments, respectively, with average filament diameters of 5.0, 6.2 and 7.0 μm, respectively. All filaments contained a proprietary sizing surface layer. In some, but not all, of our experiments, two special PAN-based carbon fibres, namely Thornel Special, Union Carbide, and ASX 12, Hercules, were also investigated.

2.2. Experimental procedures

CNH analyses were performed on the carbon fibres with a Perkin–Elmer Elemental Analyser, Model 240. Prior to analyses, the fibre samples were treated with methylene chloride to remove the sizing that would influence the fibre CNH values.

TABLE I Mechanical properties of carbon fibres*

Fibre	Young's modulus (GPa)	Ultimate tensile strength (GPa)	Ultimate elongation
C6000	227	4.2	1.8
IM6	276	4.7	1.7
T300	229	2.7	1.2

*Manufacturer's data from composite strand tests.

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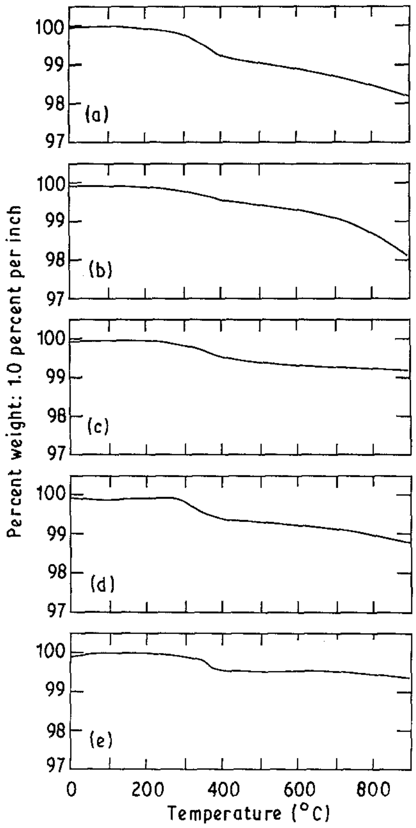


Figure 1 TGA of carbon fibres in a nitrogen atmosphere at a heating rate of 10° C min^{-1}. (a) ASX 12, (b) Thornel Special, (c) IM6, (d) T-300, (e) Celion 6000. Note: sizing on fibre.

Minor impurities in the fibres were determined by inductively coupled plasma atomic emission (ISA, Model JY38) and optical emission (3.4M Jarrel-Ashe Ebert Spectrograph) spectrometry.

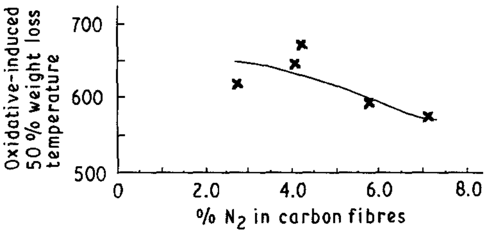
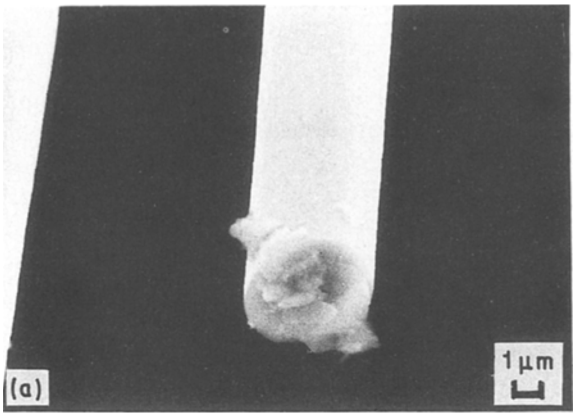


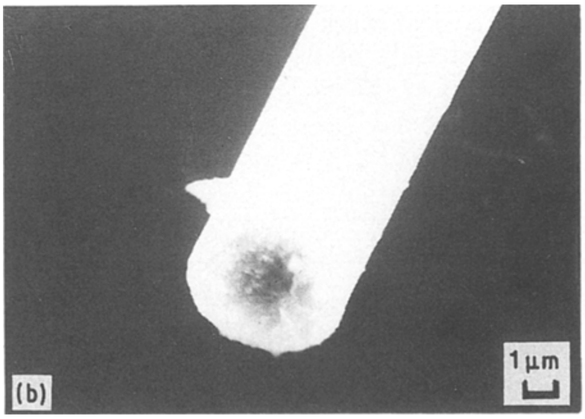
Figure 2 Oxidative-induced 50 wt % loss temperature (heating rate 10° C min^{-1}) plotted against % N content in carbon fibres.

To ascertain the presence of a sizing on the fibres, weight loss measurements were performed by thermal gravimetric analyses, TGA (DuPont 990 Thermal Analyser) at a heating rate of 10° C min^{-1} in a nitrogen atmosphere. The oxidative stability of the fibres were monitored by TGA analyses in air.

For thermal treatment studies of the carbon fibres a radiofrequency furnace capable of attaining temperatures up to 3000° C was designed and built. The power supply was a Tocco unit with a maximum power output of 50 W. The temperature was measured using a pyrometer that had been calibrated for temperature losses. For the thermal treatment, strands of the carbon fibres were placed in graphite crucibles. (A set of crucibles were designated for each type of carbon fibre to minimize cross contamination.) The fibres were then isothermally exposed to temperatures of 1200, 1500, 2000 and 2500° C under an argon atmosphere for periods of either 10, 20 or 30 min. The heating rates were ~ 150° C min^{-1}, whereas the cool-down rates were slower and ~ 10° C min^{-1}.

The characteristics of the graphitic crystal structure present in the fibres were determined from transmission electron diffraction patterns (JEOL 200 CX) of microtomed or ion-milled fibre cross-sections. The effects of the thermal treatment on the overall fibre structural integrity were monitored by scanning electron microscopy, SEM, (Coates and Welter). To ascertain the effects of thermal treatment on the fibre mechanical properties, single filaments of carbon fibres were tested in tension in an Instron testing machine (TTDM) at a gauge length of 5 cm, and strain-rate of 0.1 cm min^{-1}. CNH analyses was also





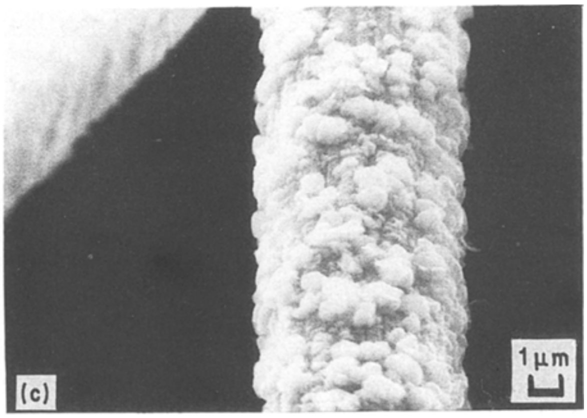


Figure 3 Scanning electron micrographs of the surface structural integrity of (a) C6000, (b) IM6 and (c) T300 carbon fibres after 2500° C thermal exposure.

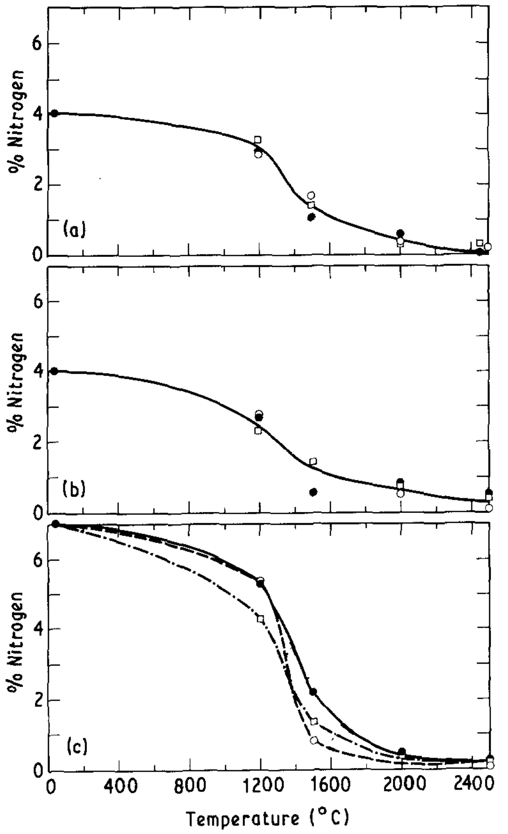


Figure 4 The N%s in (a) C6000, (b) IM6 and (c) T300 carbon fibres as a function of temperature and time thermal exposure conditions. (● 10 min, □ 20 min, ○ 30 min).

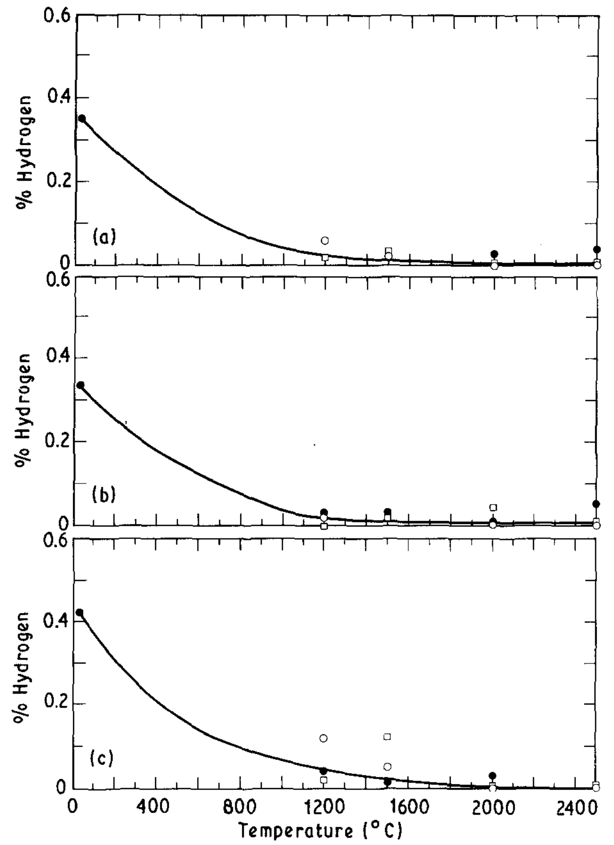


Figure 5 The H%s in (a) C6000, (b) IM6 and (c) T300 carbon fibres as a function of temperature and time thermal exposure conditions. (Symbols as in Fig. 4).

performed on the heat treated fibres. (Sizing was not present on the fibres after thermal treatment and, therefore, the fibres were not treated with methylene chloride prior to analyses.)

3. Results and discussion

3.1. Chemical analyses

In Table II, from C, N, H analyses, the wt % C, N and H and ash content in each carbon fibre is documented. The total nitrogen content in the carbon fibres were in the 2.7 to 7.0 wt % range. For a carbon fibre that contains 7 wt % N, 40% of all the six-membered rings within the fibre would have a pyridine-ring structure that consist of five carbon atoms and one nitrogen atom.

In Table III, the minor impurities in the carbon fibres, in parts per million (p.p.m.), as determined by spectrochemical analyses are tabulated. The totals of these minor impurities are in the 300 to 500 p.p.m. range. The sodium content in the three fibres studied is less than 100 p.p.m., unlike earlier carbon fibres that contained considerably larger sodium concentrations and were, therefore, susceptible to sodium catalysed oxidative degradation [1].

Each of the carbon fibres that were studied contained a proprietary sizing on their surface, which is generally an epoxide. In Fig. 1, a 0.5 to 1.0 wt % loss is observed by TGA in a nitrogen atmosphere in the 300 to 400° C temperature range for all fibres as a result of sizing degradation and volatilization.

3.2. Oxidative stability

The oxidative stability of each carbon fibre was monitored by TGA measurements in air at a heating rate of 10° C min^{-1}. The onset of wt loss for the various carbon fibres occurs in the 430 to 600° C temperature range and 100% weight loss is achieved in the 620 to 760° C temperature range. The variability in oxidative susceptibility of the carbon fibres appears to be related to the residual fibre nitrogen content. In Fig. 2, we plot the temperature at which each type of fibre exhibits a 50 wt % loss against inherent nitrogen content in the fibre. This plot indicates a trend towards lower oxidative degradation temperatures with higher fibre nitrogen content which is associated with the lower oxidative stability of the nitrogen containing six-membered rings relative to the all carbon graphitic rings.

TABLE II Weight per cent C, N, H and ash in carbon fibres from CNH analyses

Fibre	Total N (%)	Total C (%)	Total H (%)	Total ash (%)	Total (%)
Thornel 300	7.03	91.93	0.42	0.08	99.46
Hercules ASX12	4.05	95.42	0.34	0.15	99.96
Hercules IM6	2.72	96.52	0.27	0.12	99.63
Thornel Special	5.71	89.05	0.23	0.02	95.01
Celion 6000	4.08	95.17	0.35	0.22	99.82

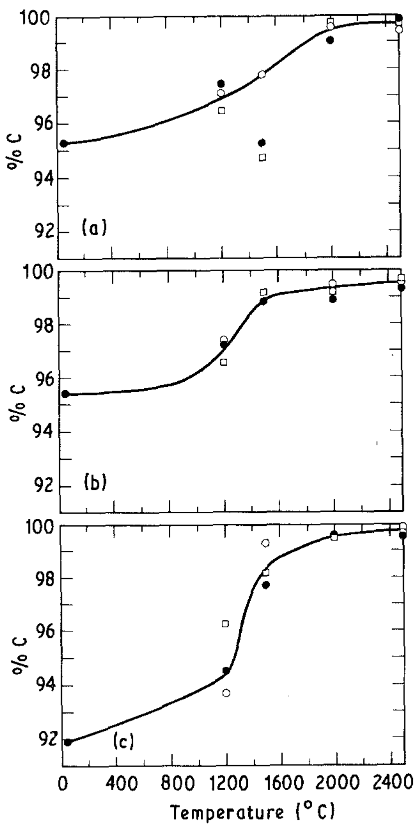


Figure 6 The C%s in (a) C6000, (b) IM6 and (c) T300 carbon fibres as a function of temperature and time thermal exposure conditions. (Symbols as in Fig. 4).

3.3. Thermal treatment

The carbon fibres that were exposed to the 1200 to 2500° C temperature range in an inert atmosphere, for time periods in the 10 to 30 min range were monitored for thermal-induced (i) physical structural changes by transmission and scanning electron microscopy, (ii) mechanical strength deterioration and (iii) chemical structural changes by CNH analyses.

From transmission electron diffraction patterns, the interplanar spacing of the basal planes in the carbon fibres decreased upon heat treatment to ultimately, after 2500° C exposure, that spacing of 0.334 nm associated with the graphite structure, as shown in Table IV. The corresponding increase in crystallite size parallel, L_c, and transverse, L_a, to the fibre axis upon heat treatment at 2500° C is illustrated in Table V. The crystallite parameters were calculated from the Scherrer and Warren, and Bodenstein formulae [2]. Both these observations indicate the growth and perfection of the graphitic structure with heat treatment.

TABLE III Minor impurities in carbon fibres from spectrochemical analyses in p.p.m.

Element	Fibre		
	C6000	IM6	T300
Ca	200	80	30
Na	*	100	*
P	100	*	*
Si	100	200	200
Mg	60	20	20
Cu	30	30	20
Fe	‡	20	10
Al	‡	20	‡
Ni	‡	‡	10
Sr	3	§	§
Total impurities	493	470	290

*Less than 100 p.p.m.
‡Less than 10 p.p.m.
§Less than 3 p.p.m.

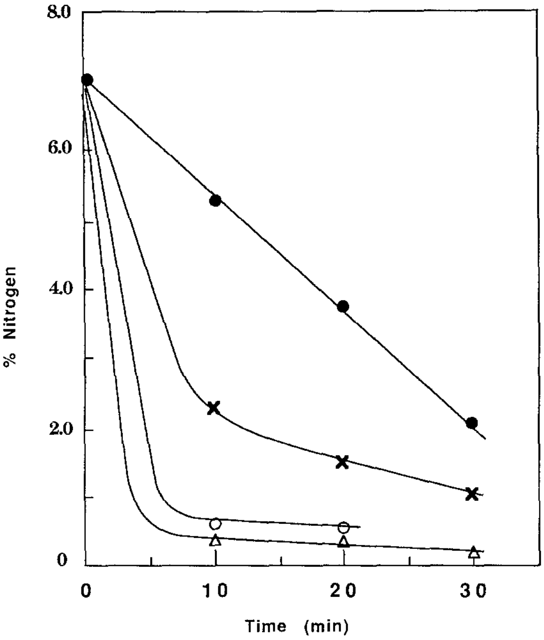


Figure 7 Isothermal nitrogen losses of T300 fibre as a function of exposure time. (● 1200° C, x 1500° C, o 2000° C, △ 2500° C).

The macroscopic fibre structural integrity of a high nitrogen content fibre, such as T300 fibre, is severely deteriorated by the higher temperature thermal treatments. In Fig. 3, SEMs illustrate the rough surface of T300 fibre compared to the lower nitrogen containing C6000 and IM6 fibres, after 2500° C thermal exposure. The surface roughness of the T300 fibres is a result of well developed, plate-shaped graphite crystals that exhibit distinct spots in electron diffraction patterns. The simultaneous graphitization and creation of diffusion paths from the significant nitrogen evolution in T300 fibres results in a network of poorly interconnected graphitic crystals. The aggregated graphitic crystals and their associated surface roughness cause a significant loss in the T300 fibre strength after thermal treatment at 2500° C. The residual strengths of the lower nitrogen content C6000 and IM6 fibres were unaffected by such thermal exposure, as illustrated in Table VI.

The thermal-induced chemical modifications for the percentages of nitrogen, hydrogen and carbon in the carbon fibres as a function of temperature and time exposure conditions are illustrated in Figs 4, 5 and 6, respectively. The carbon fibres lose nitrogen and hydrogen with increasing temperature and time of

TABLE IV Modification of the basal plane spacing in carbon fibres after thermal exposure

Fibre	23° C (nm)	2500° C (nm)
C6000	0.363	0.334
IM6	0.379	0.334
T300	0.379	0.334

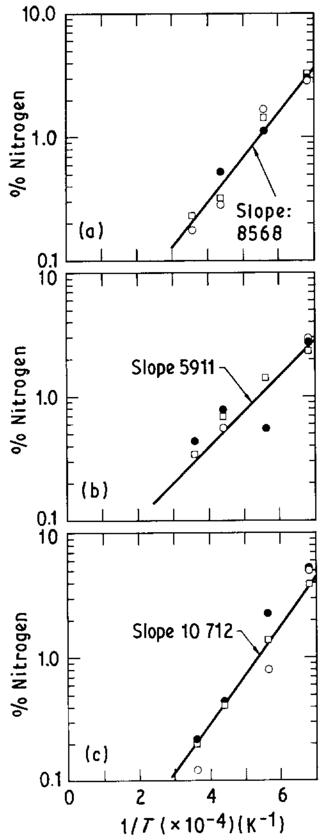


Figure 8 Log of wt % N, in (a) C6000, (b) IM6, and (c) T300 carbon fibres plotted against 1/T. (Symbols as in Fig. 4). Temperature range 1200 to 2500° C.

TABLE VI Modification of tensile strength of carbon fibres after thermal exposure

Fibre	Tensile strength (GN M^{-2})		
	(23° C)		(2500° C)
	Manufacturer's data	Directly measured	
T300	2.7	2.70	*
IM6	4.7	1.95	1.92
C6000	4.2	4.26	4.27

*Degraded, unable to measure.

thermal exposure. The isothermal losses of nitrogen in T300 fibre as a function of time for temperatures in the 1200 to 2500° C range are plotted in Fig. 7. The nitrogen loss is linear as a function of time at 1200° C but becomes non-linear and exponential at higher temperatures.

Three processes are involved in the loss of nitrogen from the carbon fibres, namely, (i) the dissociation of the C–N bonds within the fibre, (ii) the combination of nitrogen atoms to form nitrogen gas and (iii) the diffusion of nitrogen gas out of the fibre. The evolution of nitrogen from a carbon fibre as a function of temperature can be represented to a first approximation by the simple exponential relationship, Equation 1, (recognizing that there exists a complex isothermal time dependence)

$$k = k_0 \exp(-Q/RT) \qquad (1)$$

where k_0 and k are the nitrogen concentrations inherent in the fibre and at temperature T, respectively, R is the gas constant and Q the activation energy of the nitrogen loss whose magnitude is determined by the rate determining step or steps of the three processes involved in loss of nitrogen from the fibre. Linear plots of the logarithm of k against $1/T$ for the loss of nitrogen from the carbon fibres are shown in Fig. 8, which are consistent with Equation 1. From the slopes of these plots the activation energy, Q, for nitrogen loss from each fibre was determined and is documented in Table VII. There is a large spread of 80% in the values of Q for the three fibres, as a result of the complex phenomena that affect the nitrogen loss processes. The C–N dissociation process will be T dependent; the nitrogen atom combination reaction will be nitrogen concentration, t, T and fibre physical structure dependent; whereas nitrogen diffusion through the fibre will be t, T and fibre physical structure dependent. The packing of the fibre physical structure on the molecular level will determine the mobility of N and N_2 species within the fibre. The magnitudes of the values of Q are closer to those energies associated with molecular diffusion processes than those of bond dissociation and recombination. This, therefore, suggests that the large range in the magnitude of Q for the carbon fibres is a result of differences in physical packing of the fibres.

4. Conclusions

The conclusions are as follows.

(1) C6000, IM6 and T300 carbon fibres contain chemically bound nitrogen of 4.1, 2.7 and 7.0 wt % N, respectively. Other minor elemental impurities are in the 300 to 500 p.p.m. range.

(2) Each of the fibres contain a proprietary sizing on their surfaces, which degrades and volatilizes in a nitrogen atmosphere in the 300 to 400° C range with a corresponding 0.5 to 1.0 wt % loss.

(3) The fibres oxidatively degrade in air in the 430 to 760° C range at a heating rate of 10° C min^{-1}, with the higher nitrogen containing fibres tending to oxidize at lower temperatures.

(4) Thermal exposure in an inert atmosphere in the 1200 to 2500° C temperature range for periods of 10 to 30 min causes graphitization and simultaneous

TABLE V Modification in crystallite size, parallel (L_c) and perpendicular (L_a) to the fibre axis in carbon fibres after thermal exposure

Fibre	L_c (nm)		L_a (nm)	
	23° C	2500° C	23° C	2500° C
C6000	24.2	26.6	6.48	7.15
IM6	24.8	37.3	6.66	10.00

TABLE VII Activation energies for nitrogen loss process from carbon fibres

Fibre	Activation energy, Q, (kcal deg^{-1})
C6000	17.03
IM6	11.75
T300	21.29

nitrogen loss. The nitrogen loss process is predominantly a process that is diffusion controlled by the fibre molecular level porosity.

(5) The higher nitrogen evolution during graphitization in T300 fibres compared to the lower nitrogen containing fibres results in a network of poorly interconnected graphitic crystals and complete loss of fibre structural integrity after exposure to 2500° C. The strengths and structural integrity of the lower nitrogen content C6000 and IM6 fibres are unaffected by such thermal exposure.

References

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