

Influence of Boron Treatment on Oxidation of Carbon Fiber in Air

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SYNOPSIS

An investigation is performed to study the influence of boron treatment on carbon fiber: its oxidation behaviors, kinetics, and structure and properties at a high-temperature atmosphere in air. PAN-based carbon fiber is treated with either liquid organoborate or inorganic borate, which elevates the decomposing point above 260°C and doubles the average oxidation activation energy from about 100 kJ/mol of the untreated fiber to above 200 kJ/mol of the treated fiber, with the first order of the fiber oxidation reaction under nonisothermal conditions. The boron coating formed on the fiber surface after the treatment may cap off the specific surface active sites to function as a diffusion barrier that inhibits the oxidation, and its main structure is identified as boron oxide by means of X-ray diffraction and XPS analyses. During the process, the mechanical properties develop slightly; however, the morphology structure observed by SEM changes greatly. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Carbon fiber and its composites have a wide variety of applications in both the aerospace and the utility communities,¹⁻⁵ where common polymers and classical alloys cannot be used, because of their light weight and excellent physicochemical properties, such as high specific strength and modulus, low linear expansion coefficient, relatively high heat conduction, and high corrosion stability in many media, etc. However, the major limitation to their extensive uses is their susceptibility to oxidation at high temperature in air.⁶⁻⁸ Beginning at about 300°C, carbon fiber reacts with oxygen to form carbon dioxide and carbon monoxide gases, which changes the structure and degrades the properties. Therefore, great efforts are being expended on attempting to provide strong oxidation resistance for carbon materials at high temperature in the past decade.^{9-10,19} Many approaches are being considered to protecting carbon materials from oxidizing. These approaches can be divided into oxidation inhibitors, protective coatings, or sealants. It has been suggested that certain oxides, such as B₂O₃¹¹ and P₂O₅,¹² and some other protective coatings, such as CVD silica film,¹³ can

inhibit the oxidation reaction of carbon in air with a certain effect.

However, despite much work, the systematic theory of understanding of oxidation kinetics, inhibition, and protection of carbon fiber still does not exist.^{10,14} This may be the reason that much of the research is not available in the open literature. For complete understanding of the oxidation of carbon fiber in air, the author performed the reaction under nonisothermal conditions in the present investigation, which gave rise to the basic oxidation data of the behaviors, kinetics, and structure and properties before and after boron treatment of carbon fiber at a high-temperature atmosphere.

EXPERIMENTAL

Materials

The carbon fiber examined is one based on polyacrylonitrile (PAN) based fiber and was carbonized at 1250°C and its properties measured (Table I). The fiber was impregnated in liquid alkyl borate B(OC₄H₉)₃, alkylene borate B(OCH₂CH=CH₂)₃, and boric oxide solution B₂O₃. After the impregnation, the fiber was dried and then heated at a nitrogen atmosphere of 873 K, for forming a diffusion

Table I The Physicochemical Properties of 6K Carbon Fiber

Fineness (tex)	Tenacity (GPa)	Modulus (GPa)	Elong. (%)	Density (g cm ⁻³)	Carbon Content (%)
370	2.6	230	1.1	1.74*	97

* Measured with the impregnation method.

barrier or doping boron on the fiber surface to enhance the oxidation resistance.

Thermal Gravimetric Analysis (TGA)

For the kinetic study of the fiber oxidation, the oxidation rates and weight changes were measured and recorded with a Dupont 9900 Thermal Analysis System at an air flow of 200 mL/min. The fiber samples cut prior to the examination were measured with different heating rates. The temperature ranged from room temperature to 1200°C.

Scanning Electron Microscopy (SEM)

For the microstructural observations, a Cam Scan/4 scanning electron microscope was used to examine the surface of all selected fiber samples before and after boron treatment and after partial oxidation to determine the location of preferential oxidation and to examine the oxidation resistant effects of the treatment. The samples were coated with an Au-conducting layer to minimize the edge effects. During the examination, the samples were magnified 200 to 5,000 times.

X-Ray Photoelectron Spectroscopy (XPS)

For structure analysis of the carbon fiber surface, XPS spectra of the treated or untreated fiber samples were collected by PA1550 ESCA/SAM multifunctional spectrometer using AL K_α radiation. The elements present were identified by the characteristic binding energies of their electrons. The susceptibility was 0.8 eV for binding energy and the source was operated at 2.7 kV.

Wide-Angle X-Ray Diffraction (WAXD)

For the crystallite parameter analyses, the treated or untreated fiber samples were examined by means of a Rigaku D/max-rb X-ray diffractometer, using CuK_α monochromatic radiation at 40 kV and 30 mA. Scans of each sample were made between the angular range of 6–60°.

Mechanical Properties

The mechanical properties of the fiber samples before and after treatment were measured at room temperature using a YG-001 Single Fiber Mechanical Tester at a testing gauge of 10 mm and testing speed of 2 mm/min. Each specimen was prepared to adhere to the paper frame with gum.

RESULTS AND DISCUSSIONS

Oxidation Behaviors

Oxidation data for the fibers (untreated or treated with borates) in flowing air as a function of temperature are shown in Figure 1. In the experiments,

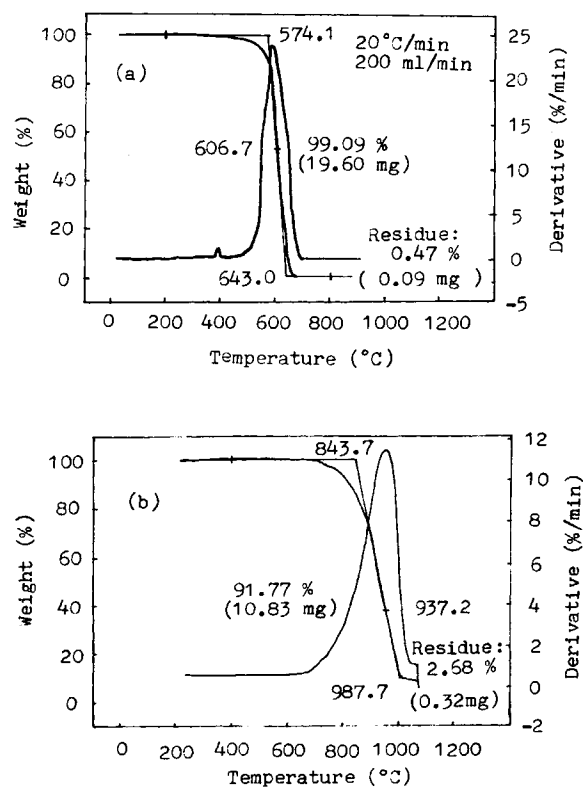


Figure 1 The weight loss of fibers in air. (a) PAN-based carbon fiber, (b) fiber treated with B(OCH₂CH=CH₂)₃.

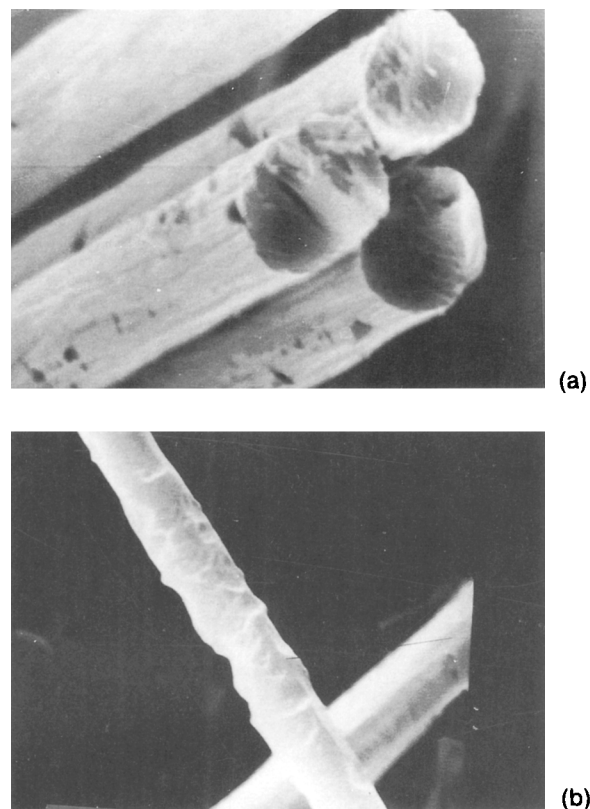
Table II The Effect of Borate Treatments on the Oxidation Resistance of Carbon Fiber

Treatment Method	Decomposing Point (°C)	Temp. at Different Weight Loss (°C)		
		5%	10%	50%
6K PAN-CF	574.1	534.3	568.5	608.8
B ₂ O ₃	835.4	771.3	809.9	920.7
B(OCH ₂ CH=CH ₂) ₃	843.7	768.1	809.3	919.9
B(OC ₄ H ₉) ₃	842.0	756.5	805.6	929.4

the airflow speed was 200 mL/min, the temperature of the system furnace was increasing at a rate of 20°C/min, and the weight change was continuously recorded. As the figure shows, the untreated carbon fiber begins to lose its weight in air at about 300°C and the gasification rate becomes increasingly rapid at higher temperature. At 574°C, the fiber begins to decompose; it oxidizes almost completely when temperature reaches about 643°C. The residual of 0.47% is based on the initial weight of the fiber. By contrast, the fiber treated with alkylene borate B(OCH₂CH=CH₂)₃ shows a very low gasification rate in hot air. The decomposing point is elevated about 269°C, from 574°C to 843°C, while gasification of the treated fiber takes place at about 650°C. A similar effect on inhibiting oxidation of the fibers is achieved by the other boron treatments, as shown in Table II. In spite of the inorganic borate or liquid organo-borate treatment, they have almost the same trends to increase the oxidation resistance, with nearly the same decomposing-point temperature, which is about 45% higher, about +260°C, than that of the untreated carbon fiber. At different weight loss levels, the treated fiber can withstand higher temperature in air than the untreated fiber. Therefore, the treated fibers have obviously higher temperature performance.

The morphology of the fiber changes in air, along with the temperature enhancing and the time durations, are shown in Figures 2 and 3. It is evident from Figure 2 that the untreated fiber shows some pits on its surface after only 10 minute residence in 500°C air. The pits develop and the diameters of the fiber become smaller 50% about than that of raw fiber when the temperature increases to 600°C, which shows that the oxidation first takes place at attacking active sites and then develops along with temperature.¹⁵ However, the difference in the surface morphology of treated fiber from that of untreated fiber is observed clearly in Figure 3. When the fiber treated with borate is oxidized under the same conditions as the untreated fiber (10 min in 500°C air atmosphere), SEM microphotographs reveal that

the surface of the treated fiber remains the same as raw-fiber surface. Even when the temperature is increased to 700°C the treated fiber is still smooth, on the whole, and rare defects could be observed on the surface; this means the treatment for retarding oxidation of the fiber is effective, mainly owing to the boron coatings on the fiber surface capping off the specific surface-active sites.²⁰ But with the higher temperature, the boron coatings on the surface may be melted and gradually volatilized so that they disconnect partially to make some specific active sites appear and carbon gasification become appreciable. When the treated fiber is exposed in a 900°C air

**Figure 2** SEM microphotographs of carbon fiber after oxidation in air. (a) 500°C, 10 min, (b) 600°C, 10 min.

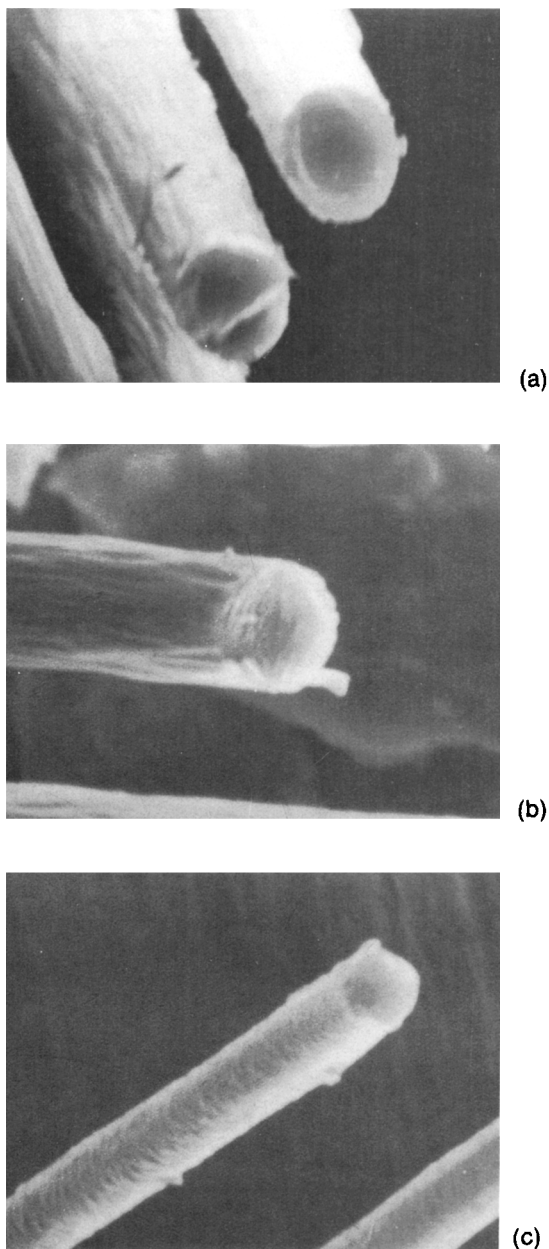


Figure 3 SEM microphotographs of the fiber treated with $B(OCH_2CH=CH_2)_3$. (a) 500°C, 10 min, (b) 700°C, 10 min, (c) 900°C, 10 min.

atmosphere for 10 min, its initial morphology diminishes and its diameter becomes thinner, showing that the oxidation resistance of the boron treatment on carbon fiber has no further function.

Oxidation Kinetics

The oxidation rate of carbon fiber increases with increased temperature and resident time in air, or with decreased activation energy. The correlation

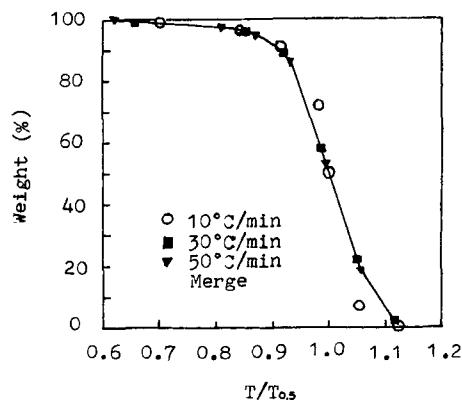


Figure 4 Weight loss of carbon fiber versus $T/T_{0.5}$ at different heating rates.

between reaction rates and fiber properties is sometimes quite complex. To determine the oxidation kinetics of carbon fiber in air, the reaction is performed under nonisothermal conditions¹⁶ with different heating rates, as shown in Figure 4. The curves adjusted with $T/T_{0.5}$ in Figure 4, where $T_{0.5}$ is the temperature of 50% weight loss,¹⁰ exhibit similar tendencies for weight loss under the different oxidation conditions. This shows that the oxidation of carbon fiber has only one rule in air; it meets the following statistical equation:

$$\begin{aligned}
 W(\%) = & -883.25 + 7019.76 \times (T/T_{0.5}) \\
 & - 24888.2 \times (T/T_{0.5})^2 + 43436.2 \\
 & \times (T/T_{0.5})^3 - 35117.4 \times (T/T_{0.5})^4 \\
 & + 10483.9 \times (T/T_{0.5})^5 \quad (1)
 \end{aligned}$$

with the regression of -0.983 .

Arrhenius plots of the oxidation under different heating rates are shown in Figure 5. At the different

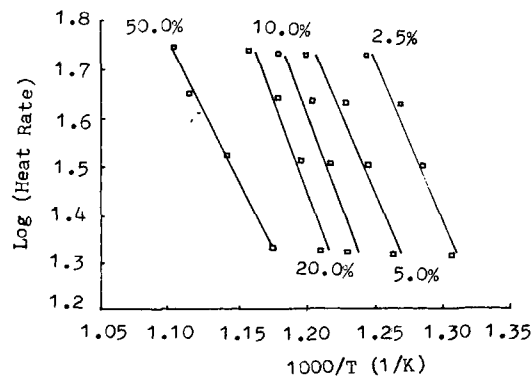


Figure 5 Arrhenius plot of carbon fiber under oxidation in air.

Table III Kinetic Parameters at Different Conversion Levels

Conversion (%)	Untreated Carbon Fiber		Treated Carbon Fiber	
	E_a^* (kJ mol ⁻¹)	60 min Half-life Temp (°C)	E_a (kJ mol ⁻¹)	60 min Half-life Temp. (°C)
2.5	102.3	484.1	192.1	717.6
5.0	98.6	477.9	220.3	717.4
10.0	124.7	470.4	263.3	725.2
20.0	120.1	453.0	265.2	736.1

* E_a : Activation energy.

reaction conversions all curves are straight and parallel, which means that the oxidation also has only one rule, as the results show in Figure 4. It is the first order reaction. The apparent activation energies of oxidation under nonisothermal conditions are listed in Table III. Obviously, the average activation energy of the oxidation of untreated carbon fiber is about 100 kJ/mol, though there are some changes in the actual values at different conversion levels. The estimate lifetimes,¹⁶ using the kinetic parameters at the conversion level of 5%, are listed in Table IV. It is clear that the lifetimes decrease as temperature increases. The lifetime is about 11.4 h at 300°C, while it is only 0.529 h at 400°C, for the untreated fiber. This shows that carbon fiber is not suitable for use in higher temperature (above 300°C) situations if it is not treated with boron or other inhibitors.

To elevate the use temperature of carbon fiber, it is necessary to treat the fiber to retard its oxidation in air. After the boron treatment, the gasification of the fiber at different heating rates and temperatures is shown in Figure 6. The curves are adjusted with

$T/T_{0.5}$ overlap, and they meet the statistical equation:

$$\begin{aligned}
 BO(\%) = & 11180.5 - 74603.3 \times (T/T_{0.5}) \\
 & + 195791 \times (T/T_{0.5})^2 - 252340 \times (T/T_{0.5})^3 \\
 & + 159552 \times (T/T_{0.5})^4 - 39529.1 \\
 & \times (T/T_{0.5})^5 - 39529.1 \times (T/T_{0.5})^5 \\
 = & 1 - W(\%) \quad (2)
 \end{aligned}$$

with the regression of 0.886.

As above, the oxidation activation energies of the fiber treated with borate are listed in Table III. The average activation energy at different conversion levels is about 200 kJ/mol, which is twice that of untreated fiber. Therefore, the lifetime estimated with the kinetic parameters at the conversion level of 5% is longer, as listed in Table IV. It is evident that the lifetime of treated carbon fiber at 500°C is 120 h, which is 2,200 times higher than that of the untreated fiber, 0.541 h. Even when the treated fiber is used in 600°C air, it can last 2.36 h. This is equal to the lifetime of the untreated fiber used at 350°C,

Table IV Lifetime Estimate at Different Temperatures

Temperature (°C)	Life of PAN-CF (h)	Life After Boron Treatment* (h)
300	11.4	
350	2.17	
400	0.529	
450	0.156	
500	0.0541	120
550	0.0335	14.9
600	0.00934	2.36
650		0.456
700		0.104
750		0.0276

* B(OCH₂CH=CH₂)₃ treatment.

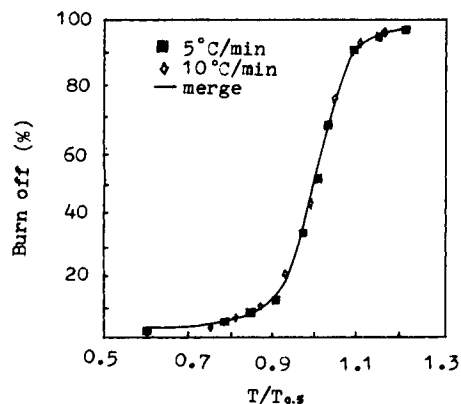


Figure 6 Weight changes of the fiber versus $T/T_{0.5}$ after B(OCH₂CH=CH₂)₃ treatment.

Table V The XPS of the Fibers

Sample	Peak Position (ev)	Half-high Value of Peak (eV)	Structure Character
6K PAN-CF	C1s	284.6	Aromatics C
		286.32	C—O
	O1s	532.9	C=O
		533.9	C—O
B(OCH ₂ CH=CH ₂) ₃	C1s	284.6	Aromatics C
		285.6	C—O, B—C
		287.3	C=O
	O1s	531.8	B—O
		533.2	C—O
		535.0	H ₂ O, BO ₃ coordinate

2.17 h; thus it can be said that boron treatment on carbon fiber elevates its using temperature at least 250°C.

Structure and Properties

Boron treatment of carbon fiber may cause changes in the structure and properties. The XPS data for carbon fiber before and after treatment, given in Table V, were calculated from the XPS spectra using the computerizing procedure. The carbon and oxygen elemental components on the surface of untreated carbon fiber^{17,18} show main binding energies of 284.6 eV and 532.9 eV, respectively. Besides the aromatic C structure, C—O or C=O of carbonyl compounds on the untreated fiber surface are clearly revealed, which may be a result of surface contamination; these, however, may become the specific surface active sites during the oxidation of the fiber at high temperature in air. After boron treatment, the surface structure becomes more complex, as shown in Table V. The boron elemental chemical structure appears in the form of B—O (at a binding energy of 192.8 eV) mainly, and B—C or B—B somewhat (at a binding energy of 188.7 eV, where the difference of binding energy between B—O and B—B is quite small). At the same time, the elemental carbon and oxygen chemical structure of the surface also changes slightly in agreement with the boron structure. As a result, the inhibiting barrier (which may be composed mainly of boron oxide⁶ and less of boron carbide) for the oxidation of the fiber is formed to modify the high-temperature performance of the fiber in air. This is also supported by X-ray diffraction spectra of the fiber, as shown in Figure 7. A small diffraction peak between 27 and

28.3° 2θ appears near the main peak of the fiber after carbon fiber is treated with borates. Although the borates—liquid organoborate or inorganic borate—have different chemical structures, the diffraction peaks of the treated fiber have same positions and similar forms, which indicates that the barriers on the fiber surfaces have one kind of chemical structure.

During the treating process, the inhibiting barrier is formed on the surface while the substrate structure develops, as shown in Table VI. Here, the crystallite structure of the fiber has changed somewhat. The crystallite size L_c tends to become smaller with increased annealing temperature; the interlayer spacing d , however, undulates only slightly. Hence, this change influences the mechanical properties of the fiber, as given in Table VII. From the mechanical

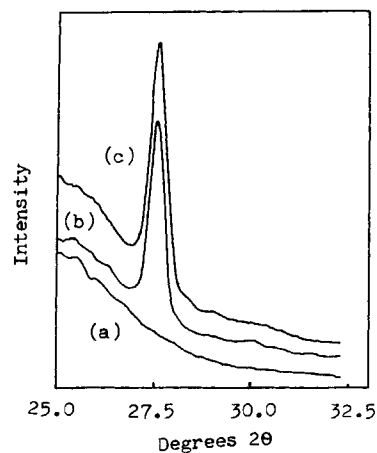


Figure 7 X-ray diffraction patterns of fibers treated with different borates. (a) Raw fiber, (b) B₂O₃ treatment, (c) B(OCH₂CH=CH₂)₃ treatment.

Table VI Effect of Temperature on the Structure

Annealing Temp. (K)	2θ (deg)	d_{002} (nm)	L_{c002} (nm)
PAN-CF	25.00	0.356	1.864
773	25.02	0.356	1.701
873	24.90	0.357	1.688
973	25.00	0.356	1.608

Table VII Effect of Different Treatments on Properties

Treating Method	Tenacity (GPa)	Modulus (GPa)
PAN-CF	2.60	230.0
B(OC ₄ H ₉) ₃	2.48	222.3
B(OCH ₂ CH=CH ₂) ₃	2.68	223.4
B ₂ O ₃	2.39	218.9

data in Table VII, it is clear that different treatments on the fibers degrade their whole modulus to some extent, and fluctuate the strength slightly. None of these changes is strongly significant.

CONCLUSION

Boron treatment, with either inorganic borate or liquid organo-borate, has been found to be very effective at inhibiting the oxidation of carbon fiber in high-temperature atmospheres, mainly because it caps off the specific surface active sites. After treatment, the thermal characteristics of the fiber are greatly elevated and mechanical properties change slightly in comparison with those of the untreated fiber. XPS and X-ray diffraction show that the boron coatings formed on the surface after the treatment have mainly one structure form, boron oxide, which

has a function of retarding the carbon fiber oxidation at high temperature in air.

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REFERENCES

1. E. Fitzer, *Carbon Fibers and Their Composites*, Springer-Verlag, New York, 1985, p. 46.
2. Mukesh K. Jain and A. S. Abhiraman, *J. Mater. Sci.*, **22**, 278 (1987).
3. Graham Dorey, *J. Phys. D: Appl. Phys.*, **20**, 245 (1987).
4. David A. Schulz, *SAMPE J.*, **2**, 27 (1987).
5. A. T. Sherkov, *Fiber Chem.*, **1992**, 137.
6. D. W. Mckee, C. L. Spiro, and E. J. Lanby, *Carbon*, **22**(3), 285 (1984).
7. A. Agrawal and H. Yinnon, *J. Mater. Sci.*, **21**, 3455 (1986).
8. Long-Gui Tang, Ph.D. Thesis, China Textile University, 1993.
9. D. L. Fecko, L. E. Jones, and P. A. Throver, *Carbon*, **31**(4), 637 (1993).
10. Ismail M. K. Ismail and William C. Hurley, *Carbon*, **30**(3), 419 (1992).
11. M. Chesneau, F. Beguin, J. Conard, et al., *Carbon*, **30**(4), 714 (1992).
12. D. W. Mckee, *Carbon*, **24**(3), 331 (1986).
13. T. M. Wu, W. C. Wei, and S. E. Hsu, *Carbon*, **29**(8), 1257 (1991).
14. L. E. Jones and P. A. Throver, *Carbon*, **29**(2), 251 (1991).
15. Krishan L. Luthra, *Carbon*, **26**(2), 217 (1988).
16. E. I. Dupont de Nemours & Co., Inc., Thermal Analysis/Data System, 1985.
17. H. Vincent, C. Vincent, J. P. Scharff, et al., *Carbon*, **30**(3), 495 (1992).
18. P. Densin, F. R. Jones, and D. J. F. Watt, *J. Phys. D: Appl. Phys.*, **20**, 306 (1987).
19. M. L. Yunitskaya, L. L. Kalacheva, T. P. Shchavaleva, et al., *Fiber Chem.*, **1991**, 204.
20. Ismail M. K. Ismail, *Carbon*, **29**(6), 777 (1991).

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