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Project Summary

Monitoring Techniques for Carbon Fiber Emissions: Evaluation A

William D. Conner

An investigation was carried out of methods and techniques applicable to the detection and monitoring of carbon fibers as they are emitted in processes involving their manufacture or use. The specific activities of these programs were: (1) to perform a detailed literature search on relevant information about candidate measurement methods, (2) to determine the typical effluent conditions under which carbon fibers are emitted to the atmosphere, (3) to evaluate the various applicable candidate monitoring techniques, (4) to perform a comparison of these methods, and (5) to select a preferred monitoring technique. The following conclusions were reached: (a) routine carbon fiber emissions to the atmosphere are, at present, negligible; (b) no extant instrument is capable of selective detection and measurement of carbon fiber aerosols; and (c) techniques can be developed to provide a practical instrumental solution to carbon fiber monitoring.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Recent years have seen the rapidly growing importance of carbon and graphite composites in their application to high-strength materials in aircraft, automobiles, military hardware and other uses. The promise of drastic reductions in weight, and other significant advantages, as results of the replacement of steel and aluminum by these composites has stimulated their development and optimization at a rapidly accelerating pace. A significant drawback of this material, however, has been recently identified: inadvertent combustion of such a composite can result in large-scale aerosolization of the carbon or graphite fibers embedded in the composite binder The release and airborne transport of these fibers, whose length may reach 20 mm, has been found to cause serious effects on electrical and electronic equipment as a result of the relatively low electrical resistivity of these fibers. Spark-over shorting, degradation of insulation, circuit impedance alteration, and secondary effects accompanying such primary ones have created an understandable concern about potential catastrophic results of any massive release of this type (i.e., aircraft crash, etc.) affecting a wide urban and/or industrial area.

Carbon Fibers - Properties and Release Mechanisms

In the period 1963-1965, it was discovered that very high strength filaments could be obtained by subjecting a precursor fiber to a rigidly controlled tensile stress during high temperature pyroliza-tion. Technically, the term "carbon fiber" applies to fibers which have been pyrolized at temperatures of 1100°C to 1200°C, and the term "graphite fiber" applies to those carbon fibers which have been heat treated at temperatures on the order of 2200°C to 2700°C. In practice, however, *the two terms* are often used interchangeably to describe the high-stiffness carbon-based fibers.

Carbon Fiber Properties

Individual fibers are about 8 μm in diameter and are produced in the form of yarns, each strand containing thousands of individual fibers. The chemical and physical properties that produce strength and stiffness characteristics also result in very high electrical conductivity for the fiber. The very high temperatures at which fibers are formed ensure their virtual indestructibility under most conditions.

The singular properties of carbon/graphite fibers become of practical interest when they are translated into a useful form through consolidation with a matrix (binder), into a composite material. Studies based on experience gained from R&D programs, and from production of advanced composite aerospace structures, indicate that utilization of graphite fiber composites in aircraft can add strength and reduce weight providing significant cost and performance benefits.

The high electrical conductivity of the carbon/graphite fibers is the prime factor in their negative effects on electrical equipment; however, other properties such as small fiber diameter, generally short length and low density are also important contributing factors. These latter fiber characteristics permit any small movement of air to cause free fibers to become airborne and to be transported over relatively long distances by normal atmospheric motion. Because of their high conductivity, carbon/graphite fibers which settle on or across electrical contacts or circuits can cause effects which could damage equipment or cause it to malfunction. They can cause: (1) resistive loading; (2) temporary shorts; or (3) electrical arcing

A summary of the most important properties and their typical values, or range of values, are shown in Table 1.

Table 1. *Typical Properties of Carbon Fibers*

Diamagnetic susceptibility	*5 x 10^{-6}*
Index of refraction:	
Real part	*1.8 to 2.7*
Imaginary part	*0.7 to 1.6*
Tensile strength	*1.4 x 10^{9} pascal*
Tensile modulus	*2.4 x 10^{11} pascal*
amorphous carbon	*1.8 x 10^{3} to 2.1 x 10^{3} kg m^{-3}*
Density	
graphite	*1.9 x 10^{3} to 2.3 x 10^{3} kg m^{-3}*
Electrical resistivity	*1 2 x 10^{5} to 1.4 x 10^{-5} Ωm*
Diameter	*5 to 10 μm*
Typical length range	*100 μm to 20 mm*
Specific heat	*711 joule kg^{-1} $°K^{-1}$*
Melting point	*3823°K (graphite sublimes at 3640°K)*
Boiling point	*5100°K*
Ignition temperature in air	*673°K*
Carbon assay	*92 to 99 percent*
pH	*6*

Emissions from Carbon Fiber Production

Basic Process

Carbon and graphite fibers are manufactured from precursor fibers, most commonly polyacrylionitrile (PAN), but pitch, tar and rayon fibers are also used as precursors. Pitch and tar can be transformed into a suitable fiber by pyrolysis in a nitrogen atmosphere with subsequent extrusion. Bundles or tows of precursor fibers are wound around frames to maintain a tensile stress during the initial heat treatment step. PAN fibers are heated to 220°C in an oxidizing atmosphere with various degrees of stretching to improve Young's modulus

The next step in the process is to carbonize the oxidized fibers in an inert atmosphere at temperatures of up to 1500°C. Rayon fibers are also stretched during this stage (or held in tension to prevent shrinkage) to improve tensile strength and stiffness. A final heat treatment step at temperatures of up to 3000°C may be included.

Technically, carbon fibers pyrolized at temperatures between 1100° and 1500°C, consist of an amorphous carbon network and exhibit a higher electrical resistivity. Graphite fibers are pyrolyzed at temperatures between 2000° and 3000°C, consist of a crystalline fiber structure, and exhibit a very low electrical resistivity.

Uses

There are two major uses for carbon and graphite fibers (1) carbon fiber reinforced plastics (CFRP) and (2) carbon fiber reinforced carbon (CFRC). The reinforced plastic may be produced from either resin impregnated carbon-base molding composites or preimpregnated laminates. In either case the plastic parts are produced in molds at temperatures usually less than 165°C and at pressures of about 21-35 kg/cm² (300-500 psi). The CFRC is produced by heating carbon fibers in a bulk carbon matrix to 2700°C at ambient pressure in nitrogen, argon and other inert atmospheres. Carbon fibers may be found in the exhaust gases of the CFRC process.

Current Emissions

The result of a survey undertaker within this program indicate at this tim that routine emission by manufacturin operations, of significant amounts o carbon fibers into the atmosphere i rather unlikely. It appears quite probabl that the only environmentally detrimen tal releases of such fibers are to b associated with large scale, high tem perature, possibly explosive, open incin eration of carbon fiber composite mate rials, such as those studied by NASA.

Future drastic increases in the vol umes of production of both fibers an their composites may, however, chang this picture, as different methods c production are applied and as economi considerations may affect the degre and effectiveness of emission contr measures At this time and in the vie of manufacturers of these material routine incineration of scrap composite and/or fibers is unusual because of th high cost of these materials whic dictates minimization of waste and r disposal.

Method of Carbon Fiber Detection

A wide variety of potentially applicable methods of carbon fiber detection and assessment can be identified. However, very few methods, if any, are available at present for the unequivocal identification and sizing of such airborne particles, and even less so, for their automated monitoring. Most of the techniques used heretofore are either cumbersome, or nonspecific to carbon fibers, or both. Table 2 is a comprehensive summary of the state-of-the-art in carbon graphite-fiber detection and measurement technology. The detection specificity of each of these techniques is graded by its ability to discriminate carbon particles from those of predominantly noncarbon composition, by its specificity to fibrous shaped aerosols, and its combined selectivity to fibers composed mainly by carbon Table 2 grades each method by its compatability with automated, continuous or continual monitoring, i.e., without requiring intensive human intervention. Those methods that are potentially more compatible with source monitoring applications are so marked Estimates of cost for development and commercialization of the methods are given For the development category, the three categories have the following approximate equivalence

(a) LOW—The technique has already been developed and tested. It may require a relatively small additional effort to finalize a practical design. This additional development cost would be on the order of $50,000 or less

(b) MED—The method has been researched, and applied to other or at best similar types of measurements. It requires additional efforts to evolve a practical system applicable to carbon fiber monitoring. Further development costs are on the order of $50,000 to $150,000.

(c) HIGH—This technique has not been explored sufficiently for this application, or its overall practicability has not been demonstrated empirically. A dedicated development effort is required whose cost equals or exceeds $150,000.

The approximate commercial cost hierarchy is defined as follows:

(a) LOW—The cost of the presently available device or instrument or of an instrument eventually developed, is equal to or less than about $2,000

(b) MED—Instrument cost, as defined in (a), between $2,000 and $10,000.

(c) HIGH—Instrument cost, as defined in (a), exceeding $10,000.

Conclusions

Several important conclusions were reached within this program These conclusions relate to the various areas investigated as part of this project (a) the review of candidate monitoring methods, (b) the determination of the conditions and magnitude of carbon fiber emissions, and (c) the relative merits of the potentially applicable monitoring techniques

One of the central corollaries derived from the information research performed within this program is that routing emission of carbon fibers from manufacturing operations are, in general, of negligible importance; i.e., the emission rate of carbon fibers into the atmosphere resulting from the normal production activities does not warrant, at the present time, an intensive monitoring program. Incidental and uncontrolled carbon fiber releases, however, remain a matter of concern.

Future drastic intensification of the industrial volume of production of carbon fibers and related products may, however, modify this situation sufficiently to warrant a careful reassessment of the above presented conclusions. It appears, at this time, that instrumentation for in-plant monitoring as well as ambient monitoring of carbon fibers may be required in order to reduce or prevent electrical equipment failure within industrial environments, as well as to provide adequate means to assess the potential damaging effects of open and uncontrolled combustion of carbon-fiber containing materials.

The second major conclusion, reached as a result of the study under consideration, is that no airborne carbon fiber detection and monitoring instrument is presently available capable of unambiguous identification and measurement of such fibers, in the concomitant presence of other aerosols.

The third important inference derived from this study is that there are sensing and detection techniques which, if properly developed for the specific objective under consideration, can provide unequivocal and selective methodology for the continuous automated monitoring of airborne carbon fibers, in the presence of other contaminating particles. It appears feasible that such a technique, or combination of techniques, may be applicable to in-plant, emission testing, and ambient monitoring applications. The most promising of these techniques is: a photo-thermal-electric alignment method, combined with light scattering characterization.

Table 2. *Summary Tabulation of Potentially Applicable Techniques to the Detection and Measurement of Carbon Fibers, Including a Qualitative Cost Analysis*

Method	Detection Specificity			Compatibility with	Cost		Observations
	Carbon	Fiber	Carbon-Fiber	Autom Monit.	Develop.	Commercial	
1 High Volt Spark	Med	Med	Med	High[e]	Low[a]	Med	Limited to fibers longer than 1mm.
2 Brass Ball	Low	Med	Low	High[e]	Low[a]	Med	Limited to fibers longer than 2mm
3. Low Volt. Grid	Low	Med	Low	Med	Low[b]	Low	Unpredictable operation, low collection efficiency.
4. Cont Optical Counter	Low	Low	Low	High[e]	Low[b]	Low	Nonspecific to C-fibers, insensitive.
5 Lidar	Low	Low	Low	High	Low[a]	High[d]	Nonspecific to C-fibers.
6. Microwave	Low	Med	Low	High	High[c]	High	
7. Sticky Tape	Low	High	Med	Low	Low[a]	Low[d]	Requires microscopy of collected sample.
8 Filter Screen	Low	High	Med	Low	Low[a]	Low[d]	Requires microscopy.
9. Spectrophone	High	Low	Low	Low[e]	Med[b]	High	See Photo-thermal detection as preferred technique.
10. Micro-Raman	High	Low	Low	Low	High[b]	High	
11 Optical Absorption	High	Low	Low	Med	Med[b]	Med	Required collection of particles.
12. Angular Light Scat	High	High	High	Low	Med[b]	High[d]	Limited usefulness except for LISMEFA (see No. 26).
13. Light Polarization	Low	High	Low	High	Med[c]	Med	Not useful for individual fiber detection
14. Differential Conductivity	Low	Med	Low	Med	High[a]	Med[d]	Coulter-counting may be incompatible with conductive fibers.
15. Differential Elect. Mobility	Low	Med	Low	High[e]	Med[b]	Med	
16. Electr. Alignment	Low	High	Low	High[e]	Low[a]	Med[d]	This technique must be used in combination with other detection methods
17. Magnetic Alignment	Med	High	Med	Med[e]	Med[b]	Med	Same as above.
18 Aerodyn. Alignment	Low	High	Low	High	Med[b]	Med	This technique must be used in combination with other detection methods.
19. Ultrasonic Effects	Low	Med	Low	High	High[c]	Med	Requires fiber alignment.
20. Video-Microscopy	Low	High	Med	Low	Med[a]	High[d]	Requires collection on a medium.
21 Spark Spectrometry	High	Low	Med	High[e]	Med[c]	Med	Requires other techniques for fiber identification.
22. Laser-Spark Spectrometry	High	Low	Low	High[e]	Med[b]	High	Same as above.
23. Scintillation Analysis	High	Low	Low	High	Med[b]	High[d]	Same as above.
24 X-Ray	High	Low	Low	Low	Med[a]	High[d]	Same as above.
25. Differential Light Scat.	High	Low	Low	High[e]	Med[c]	Med	Same as above.
26. LISMEFA	Low	High	Low	High[e]	Med[a]	Med[d]	Applied in GCA-FAM. Useful in combination with carbon-specific techniques.
27. Photo-thermal detection and Electric Alignment	High	High	High	High[e]	High[c]	Med	Highly specific to carbon fibers.

[a]Development largely completed.
[b]Partially developed.
[c]To be developed.
[d]Commercially available.
[e]Potentially adaptable to source monitoring.

} As applicable to the detection of carbon fibers.

This Project Summary was authored by ***William D. Conner****, who is also the EPA Project Officer (see below).*
The complete report, entitled "Monitoring Techniques for Carbon Fiber Emissions: Evaluation A," (Order No. PB 81-205 932; Cost: $9.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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