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Carbon Fiber Production at Low Temperatures from Polyacryonitrile

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ABSTRACT

Recent safety considerations have sought to lower the electrical conductivity of carbon fibers. Carbon fibers produced from polyacryonitrile at low carbonization temperatures (600°–900°C) possess low electrical conductivity but do not possess adequate strength. Low-temperature processes are described which improve fiber strength but do not increase electrical conductivity substantially. The processes result in a carbon fiber with nearly twice the tensile strength compared to the old process. Process development and its effect on fiber properties are reported.

Background

Carbon fibers are finding wide use in resin composite systems, which are strong, stiff, lightweight construction materials. A major source of carbon fibers is based on a polyacrylonitrile (PAN) fiber precursor. Typically, the PAN is oxidized at 200°–300°C and carbonized in an inert gas at 1200°–1600°C to produce fibers with tensile strengths of 1379 MPa to 3447.5 MPa (200,000–500,000 psi) and modulii of 137.9–206.9 GPa (20—40 $\times$ 10^6 psi). Graphitization, which occurs at heat-treatment at temperatures higher than 2000°C, can also be used to increase the modulus, but it often decreases the tensile strength. There have been recent concerns about product safety during manufacture, application, and disposal because of the fibers' high electrical conductivity. Therefore, using the PAN/carbon-fiber technology as a base, an attempt was made to produce a fiber with good strength and lower electrical conductivity. Fiber-processing parameters were examined to determine if suitable properties could be obtained by varying parameters in the normal fiber-production system or, if no such properties could be thus obtained, to introduce other methods to achieve this goal.

It was known from previous work in the field that the electrical conductivity of carbonized fibers, polymers, and cokes increased as a function of higher heat-treatment temperature (in the range 400°–1500°C) [8, 12, 13, 15, 18]. Various theories for this dependence have been proposed [15]. In addition, there are theories—supported by some experimental evidence—that attempt to explain variation of strength [4, 16, 24]. Some of these theories and some experimental evidence suggest that strength is a strong function of physical properties, such as internal flows or surface flaws, or both, and that electrical properties are more a function of molecular or chemical structure. Thus, the two properties need not vary directly. This suggests the possibility of developing process modifications that increase strength without necessarily affecting, in a significant way, the electrical conductivity.

Although fibers of suitable electrical conductivity are obtained with the usual processing system at lower carbonization temperatures, they do not possess suitable strength. As a result, emphasis was placed on developing a process whose modifications could increase the strength of the fibers. The modifications thus evolved to increase fiber strength were a chemical pretreatment of the PAN fiber at low temperature and addition of an active carbon-containing gas during carbonization. Treatment consisted of reaction in a molten benzoic-acid bath, subsequent oxidation, then carbonization in the active carbon-gas mixture. In the case discussed here, a PAN homopolymer fiber and an acetylene-nitrogen-gas carbonization mixture were used. Other fibers and gases were also used, but the results of that work are reported elsewhere [4]. The modifications discussed here were evolved based on the following four assumptions:

1. Benzoic-acid treatment—intramolecular effects: Benzoic-acid treatment could react with the PAN so that stable, conjugated structures are formed at lower temperatures. These structures would preserve the highly-ordered form of the precursor PAN and reduce the amount of defects created by loss of material on degradation during later processing stages. More nitro-

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gen of the original PAN could also be retained at higher temperatures and act as a scattering site for electrons to decrease conductivity [7, 9, 10, 15, 21].

2. Benzoic-acid treatment—intermolecular effects: Benzoic acid could catalyze the auto-oxidation of PAN by forming and decomposing peroxidic intermediates to crosslink the PAN at lower temperatures, thus preserving more order of the original-oriented PAN in stable structures. Thus, this could lower the number of defects, using the same reasoning as that in assumption 1 [7, 9, 22].

3. Benzoic-acid treatment—interaction effects: Benzoic acid might affect the nature of the fiber substrate produced later in carbonization by introducing free-radical sites, edge groups, or simply through increased porosity and surface area, all of which could affect surface defects or promote interactions, such as surface polymerization or acetylene decomposition, or both [5, 11, 20 23].

4. Acetylene treatment—interaction effects: The acetylene or decomposition products, or both, could react with or deposit on the fiber to produce new stronger compounds or coatings to heal over defects [2, 5, 6, 17, 19, 20, 26].

The processing modifications and their effects on some of the fiber properties will be discussed.

Experimental Procedures

Standard Process to Produce Fibers

A tow of 96 filaments of 0.25-mg/m PAN was oxidized at 260°C over a contact time of ~3 h under a load of 15 g in a tubular reactor of ~2.54-cm diameter to produce a fiber that shrank or extended less than 5% during oxidation. The sample was then heated at a rate of 20°C/min to temperatures within a range of 450°–1100°C in a 20 cm^3/min nitrogen atmosphere under a load of ~50 g in a tubular reactor of ~1.9-cm diameter. This process subsequently will be called the *standard process*.

Modified Process to Produce Fibers

The same PAN tow was first passed through a molten benzoic-acid bath at 175°C with 1-g loading over a contact time of ~3 h to produce fibers that shrank or extended less than 10% in this process. The samples were then oxidized at the control conditions under a load of 50 g to produce fibers that shrank or extended less than 5% in this process. The oxidized fibers were then carbonized at the control conditions, except for the presence of a mixture of acetylene-nitrogen as the atmosphere. This process will be referred to as a *modified process*. This modified process was developed after studying effects of contact time and temperature in the benzoic acid, oxidation, and carbonization steps.

Analytical Tests

Samples of fibers produced by the two processes were also analyzed in an effort to understand the effects of the process steps. Samples of both processes were submitted for infrared (ir) analysis and elemental analysis for carbon, hydrogen, oxygen, and nitrogen. Samples were submitted for x-ray diffraction analysis for crystallinity. Tensile strength and elongation of fiber samples (2.54-cm long) of the final carbonized product were measured. The electrical resistance of carbonized fibers was also measured. Thermogravimetric analyses (TGA) were made using programmed heating rates to simulate furnace conditions. These provided a history of weight change as a function of process conditions. Differential scanning calorimetery (DSC) was used to study heat evolution for the various samples. A series of fiber-weight and shrinkage measurements was also made for fibers treated in the carbonization furnace. Electron microscopy was used to study the surfaces of the fibers produced. Fiber areas were measured microscopically.

Results

Table I shows the tensile strength of samples produced by the standard process (A) and by modification of the fiber process (B–F). Each tensile test was made on 18–20 filaments, and the standard deviation was ~20% (the electrical resistances reported have a standard deviation of ~10%). Benzoic acid treatment, air oxidation, and subsequent carbonization in N_2 produces a sample (B) with average tensile strength similar to that achieved in the standard process. A sample (C) that was air-oxidized and carbonized in C_2H_2 shows about a 40% increase in average tensile strength. A sample (D) heated in benzoic acid, air-oxidized, and carbonized in C_2H_2 shows an even greater increase, ~70%.

A sample (F) first treated in benzoic acid, air oxidized, carbonized in N_2, and then recarbonized in C_2H_2 gives a sample with nearly the same average tensile strength compared with air-oxidized samples carbonized in C_2H_2.

These results suggest that there is an interaction between the fiber and the acetylene as it degrades, and that this interaction is affected by the benzoic-acid treatment.

Table II shows average tensile strength as a function of final carbonization temperature and acetylene concentration for the modified process. Average tensile strength increases with carbonization temperature, then decreases. The maximum occurs at lower temperatures for higher acetylene concentrations. This trend is not unlike that which occurs during deposition of forms of carbon black [2, 19]. Oriented and crosslinked carbon-black structures depend both on concentration and temperature in a similar fashion. Oriented and crosslinked structures are stronger and are desired as a surface layer [19].

TABLE I. Effect of processes on tensile strength of final carbon fiber product.

Sample treatment	Carbonization in: Benzoic acid, 175°C/h	Air oxidation at 260°C, h	100% N_2, at °C	5.34% C_2H_2/N_2, at °C	Tensile strength, MPa	(psi)	% change from (A)
(A) Oxidized and carbonized in N_2 (standard process)	—	~3	700	—	62.46	(90 590)	0.0
(B) Treated with benzoic acid, oxidized and carbonized in N_2	~3	~3	700	—	65.61	(95 160)	+5.04
(C) Oxidized and carbonized in C_2H_2	—	~3	—	700	85.08	(123 400)	+37.3
(D) Treated with benzoic acid, oxidized and carbonized in C_2H_2	~3	~3	—	700	106.3	(154 170)	+70.2
(E) Treated with benzoic acid, oxidized and carbonized in N_2, cooled and carbonized in C_2H_2	~3	~3	700	700	89.62	(129 980)	+43.5
(F) Treated in benzoic acid and carbonized in C_2H_2	~3	—	—	700	71.02	(103 100)	+13.7

TABLE II. Effect of acetylene concentration and temperature on tensile strength during carbonization of a PAN sample treated in benzoic acid at 175°C for 3 h and air-oxidized at 260°C for 3 h.

Sample	Acetylene Concentration, %	Temperature, °C	Tensile strength, MPa	(psi)	Resistance, ohm-cm
1	5.34	647	84.62	(122 730)	44.1
2	5.34	705	106.3	(154 170)	3.18
3	5.34	800	131.8	(191 180)	.058
4	5.34	845	116.9	(169 550)	.019
1	11.3	610	50.74	(73 590)	254.7
2	11.3	705	85.80	(124 345)	1.54
3	11.3	750	93.93	(136 320)	.212
4	11.3	805	80.57	(116 860)	.054
1	14.02	500	47.14	(68 370)	18 300
2	14.02	590	80.62	(116 930)	675.6
3	14.02	655	99.91	(144 900)	9.52
4	14.02	703	91.90	(133 280)	n.a.
Standard process	0.00	705	62.46	(90 590)	4.18

Difficulties can arise, however, with this particular experimental procedure (1) at higher acetylene concentrations and lower temperatures, and (2) at higher temperatures and moderate acetylene concentrations. At lower temperatures and high concentrations, the fibers became coated with a viscous liquid; at higher temperatures the fibers became encased in a solid. In either case the fibers are difficult to separate from the tows during preparation for further testing. Separation of the fibers under these conditions can produce defects and reduce strength. Variations in procedure were made both to study the acetylene-fiber interactions and to prevent the fibers from sticking together. Not all of these variations will be discussed here. The effect of a recent variation in the carbonization procedure is shown in Table III. Here the normal procedure of heating the fiber in the acetylene mixture to set temperature and holding it there for 5 min was changed. The fiber instead was heated to 500°C in 20 cc/min flow of pure N_2, held for 10 min while the acetylene mixture replaced the N_2, heated to the set temperature, the gas flow decreased to 0.5–1.0 cm^3/min during the 5-min hold period, and the system purged with 90 cm^3/min pure N_2 on cool-down. This variation resulted in fibers with improved strength and the same electrical conductivity, and it prevented their sticking together. The procedure not only limits the amount of acetylene available for deposition, but it can also affect the nature of the interactions of acetylene with the fiber itself.

TABLE III. The effect of variation of carbonization procedure on tensile strength.

Procedure	Temperature, °C	Acetylene concentration, %	Tensile strength, MPa	(psi)	Resistance, ohm-cm
Straight heat-up at 20°C/min in C_2H_2	845	5.34	118.2	(171 500)	0.0191
Modified (See text)	840	5.34	162.2	(235 200)	0.0199
		2.0	176.8	(256 433)	—
		1.0	155.4	(225 400)	—
		0.0	72.34	(104 920)	—

Acetylene has been observed to decompose at 500°C to give compounds such as vinylacetylene and others [5, 6, 19]. The fiber may also undergo transformations at these temperatures, such as cyclization of nitrile groups, evolution of gases, and others [3, 5, 14, 20]. Such processes can disturb the order of the deposition or provide new reactant species. This emphasizes the dynamic property and complexity of the system and the importance of correlating mechanism and carbonization procedures. These are presently being investigated to try to improve fiber properties further.

Differential scanning calorimetry measurements were made in N_2 of the PAN and the various pretreated samples up to 600°C. The PAN samples show a sharp exotherm followed by an endotherm in the temperature range of 280°–330°C; minor heat effects also occur at about 400°–500°C. Similarly, the benzoic-acid-treated sample also shows these effects, but they are substantially reduced (about 1% of the PAN). The oxidized PAN and the oxidized benzoic-acid-treated samples are virtually thermally neutral up to 600°C.

The endotherm at about 340°C may be due either to a reaction or to volatilization of material. Based on thermogravimetry analyses (discussed next), substantial loss of material occurs for PAN in this temperature range. Less material is lost for the benzoic acid/oxidized samples.

Thermogravimetric analyses (TGA) were made simulating the furnace treatments of both types of fibers by programming the heating rate. The carbonization atmosphere was pure N_2 and 25% acetylene. The results for the carbonization are shown in Figures 1 and 2.

In Figure 1 it can be seen that the benzoic-acid-treated sample retains more weight at high temperatures and is therefore considered more stable. The TGA for the benzoic-acid-treated sample in the acetylene atmosphere is shown in Figure 2. At 450°C the fiber begins to gain weight; the weight gain levels off at about 600°C. The TGA could not be extended past 650°C because difficulties were encountered with the TGA equipment and this system. In order to study these properties further, a series of runs was made in the fiber reactor instead of with the TGA equipment. The fibers were heated in acetylene atmospheres, held for 5 min, then cooled. The final weight of the sample and

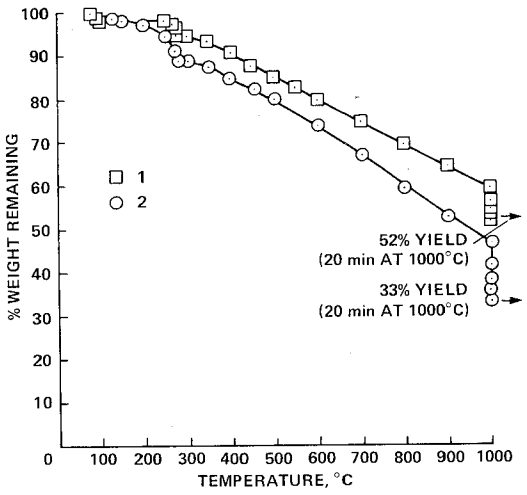

FIG. 1. Effect of benzoic acid pretreatment on char yield in N_2.

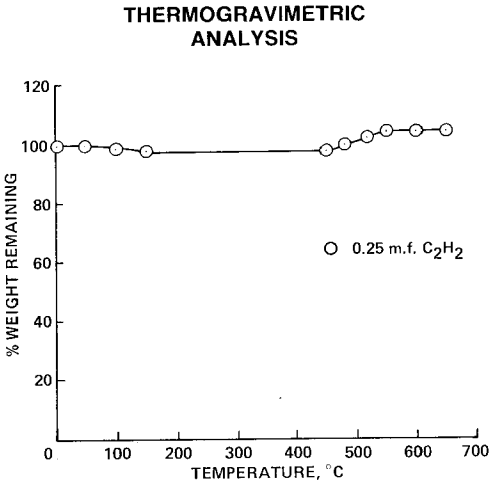

FIG. 2. Effect of acetylene on weight *vs.* temperature of benzoic acid/oxidized fiber.

the amount of shrinkage that occurred under a 50-g load were recorded. Fibers at the high levels of acetylene used in the TGA again showed weight gains at about 500°C.

The results for lower acetylene concentration are shown in Figures 3 and 4. The fibers obtained in the acetylene appeared to have a black coating. The fibers are a few percentage points heavier and shrink less when they are exposed to the 5.34% acetylene atmosphere, compared with the pure N_2 atmosphere. A thermocouple at the center near the fiber did not show any appreciable temperature change between runs with the dilute acetylene and pure N_2 atmospheres. Radiation effects were minimal [1]. Therefore, thermal effects were discounted, and we have additional evidence that the acetylene products deposit on the fiber and can limit shrinkage, which is one possible source of defects. Elemental analysis of the fibers also confirms the benzoic acid, and acetylene treatments affect the elemental composition of the fiber.

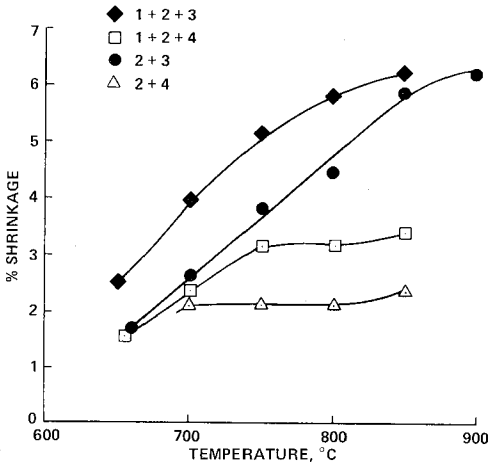

FIG. 4. Effect of acetylene on fiber shrinkage.

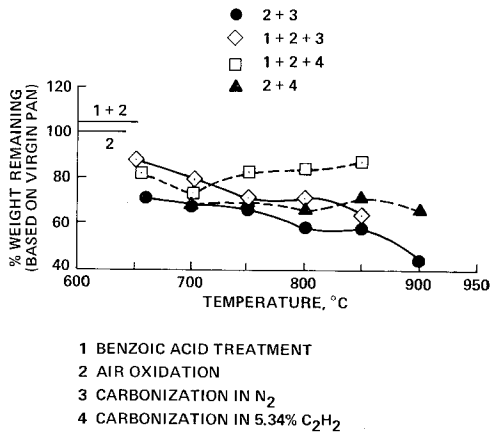

FIG. 3. Effect of acetylene on fiber weight.

TABLE IV. Effect of precarbonization processes on elemental analyses.

	Sample treatment	Wt,%[a] C	H	O	N	Molecular ratio
1	None, theoretical PAN	67.9	5.66	—	26.4	C_3H_3N
2	PAN fiber received (dried to const. wt. at 50°C)	66.93	5.93	1.07[b]	25.40	$C_3H_{3.19}N_{.973}O_{.036}$
3	PAN treated with 175°C benzoic acid 3 h	62.06	4.29	9.78	20.38	$C_3H_{2.49}N_{.847}O_{.36}$
4,2	Oxidized at 260°C for 3 h	59.63	3.16	9.74	20.54	$C_3H_{1.9}N_{.886}O_{.37}$
5,3	Oxidized at 260°C	57.69	2.60	11.64	18.89	$C_3H_{1.62}N_{.84}O_{.45}$

[a] Accuracy of analyses for duplicates better than 3%.
[b] PAN fibers contain anatase (TiO_2) as a delustrant, usually as a few %; if all of this oxygen is in anatase, anatase content is 2.67 wt%.

Table IV shows the carbon, hydrogen, oxygen, and nitrogen contents of the fibers subjected to precarbonization treatments. The effect of carbonization treatments on these as a function of temperature is shown in Figures 5 and 6. Benzoic-acid-treatment at 175°C increases the oxygen content to nearly the value present when the PAN sample is oxidized in air at higher temperatures. There is also a small loss of N_2 and H_2. Thus, it appears that substantial oxygen addition occurs before a major loss of hydrogen in the benzoic-acid treatment stage. Further hydrogen loss occurs during air oxidation at 260°C.

During carbonization the carbon content is increased by the presence of acetylene compared to fibers carbonized in N_2. Oxygen content is decreased for carbonization in acetylene compared to N_2. At higher temperatures the TiO_2 may influence this analysis because the organic char yield decreases while the inorganic content remains constant. In addition, these samples may also contain free radicals that can absorb O_2 from the air. Hydrogen and nitrogen are also decreased; however, at higher temperatures the nitrogen content appears greater in the benzoic-acid-treated sample relative to

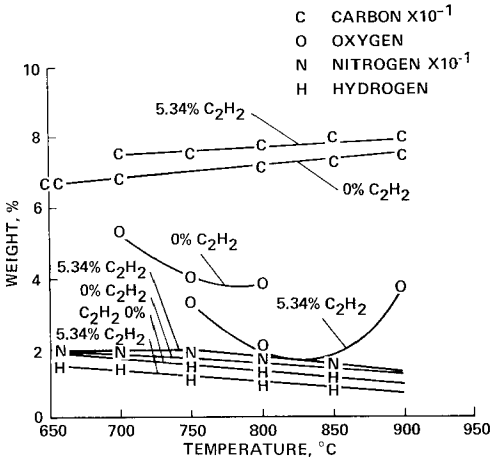

FIG. 5. Elemental analysis for air-only oxidized sample.

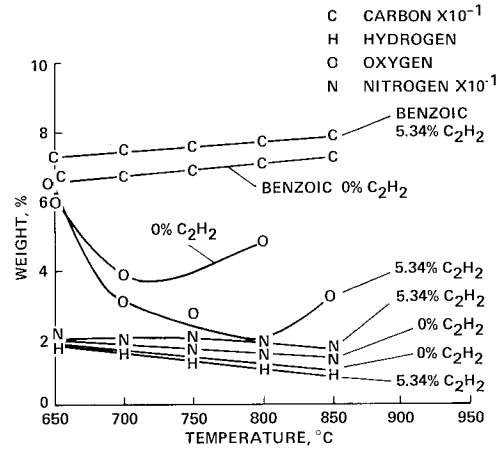

FIG. 6. Elemental analysis for benzoic-acid-treated sample.

the air-oxidized sample. The elemental analyses show more variation in oxygen, however, suggesting that the acetylene interaction may be dependent on the oxygen content and subsequent reduction of the fiber.

Infrared spectra of the benzoic-acid-treated sample and the air-oxidized sample show a marked similarity to those given for conjugated structures such as polycyanoacetylene with additional absorption, possibly due to oxygen-containing functional groups, such as hydroxyl, vinylketonic, and other groups. The ir analysis is ambiguous used by itself. Other supportive analyses must be made to understand the structure. X-ray diffraction studies of the carbonized fibers produced by both methods show that the materials are not crystalline but contain amorphous carbon and anatase. (The anatase is stabilized in the mixture even at high temperatures.) Electron microscopic analysis indicates that the fibers produced without acetylene show some defects with sharp boundaries, such as cracks, whereas the acetylene-treated fibers do not show such sharp boundaries, even though the surface appears not perfectly smooth. Microscopy of cross sections was only partially successful, and microscopy techniques are being improved.

Conclusion

Fibers produced at lower temperatures than the standard carbon fibers, although possessing lower electrical conductivities, did not possess adequate strength. As a result, the standard process was modified in efforts to increase fiber strength. This process included a pretreatment of the fiber in benzoic acid at 175°C, oxidation at 260°C, and subsequent carbonization of the fiber in an acetylene-N_2 mixture at temperatures up to 1100°C. The new process results in a carbon fiber that has nearly twice the tensile strength than the normally-treated fibers at similar carbonization temperatures. The benzoic-acid treatment stabilizes the highly-oriented PAN at lower temperature and results in a fiber that contains substantial amounts of oxygen compared with an air-oxidized fiber at higher temperatures. Both types of fibers give spectra possibly attributable to cyanoacetylene and various oxygen groups. The benzoic-acid treatment, however, gives as ample that contains large amounts of hydrogen. Major loss of hydrogen appears to occur later on during oxidation at higher temperatures and can represent increased conjugation and crosslinking. The benzoic-acid treatment also effects the interaction with acetylene. Acetylene or acetylene decomposition products, or both, deposit on the fiber during carbonization. Further research is in progress to elucidate the mechanisms involved.

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