Use of Polymer–Metal Ion Complexes To Improve Carbon Fiber–Metal Matrix Compatibility

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Polycyanogen (PCN) and polyazomethine (PAZ) polymer complexes with aluminum or titanium chloride were used to coat carbon fibers. The goal was to improve compatibility to metal while sustaining the mechanical strength of the carbon fiber. The PCN and PAZ polymer complexes were dip coated onto the graphite fiber and then were carbonized by a series of heat treatments. The mechanical properties of the polymer-coated fibers before and after further coating with aluminum were evaluated. Scanning electron microscopy and wetting measurements using a Wilhelmy balance were performed to assist in characterization of the coated fibers. It was found that this new method of coating provides enhanced wettability by metal without any deterioration of the mechanical properties of the carbon fiber.

Introduction

Considerable research has been performed on metal matrix composites (MMCs) in recent years.[1-5] A system of high priority involves carbon fiber reinforced aluminum (CFRAl),[6-9] since it offers an attractive combination of properties: low density, high strength, and potentially easy manufacture. However, carbon fibers are both reactive to and not properly wet by an aluminum matrix, thus introducing many difficulties in the fabrication and high-temperature application of these composites. The nature of the interface is obviously of great importance to the mechanical properties of the composite. The interface is quite complicated, frequently containing an aluminum oxide layer which is unavoidable when aluminum is processed in air. The carbon fiber has a very low surface energy and therefore is incompatible with molten aluminum. The fabrication temperatures of C/Al composites are usually near or above the melting point of the aluminum. Several investigations[6,8,10,11] have established that a reaction can occur at the C/Al interface at temperatures as low as 500 °C, with the reaction product being Al_4C_3, and it is known that such carbide formation reduces the strength of the C/Al composite.

A solution to these problems is to apply a suitable protective coating or diffusion barrier to the carbon fiber. This coating should have a higher surface energy than the carbon fiber to allow for higher wettability with the matrix and also provide for a lower diffusivity of carbon into the metal.

A wide variety of coating methods and materials have been studied, such as chemical vapor deposition (CVD) of a Ti–B coating from BCl_3 and $TiCl_4$;[10] CVD of SiC, TiC, and TiN ceramic coatings;[12] solution coating by organometallic compounds followed by a pyrolysis step;[13] solution coating of K_2ZrF_6;[14,15] applying a liquid metal transfer agent technique for metal carbide coatings;[16,17] and metal deposition of Ni or Cu metal coatings.[18-20] Most of these methods give priority to improving the wettability of the carbon fibers by the metal matrix. While the experimental results do show better compatibility of the coated fibers to the metal matrix, unfortunately the tensile strength of these coated fibers decrease by 30–60%. This decrease is thought to be caused by chemical reaction at the fiber surface during the coating process. The reaction products act like stress concentration points resulting in premature tensile failure. Two methods of coating have sustained the mechanical properties: an electroless Ni-coating process[20] and an organometallic solution coating process.[13]

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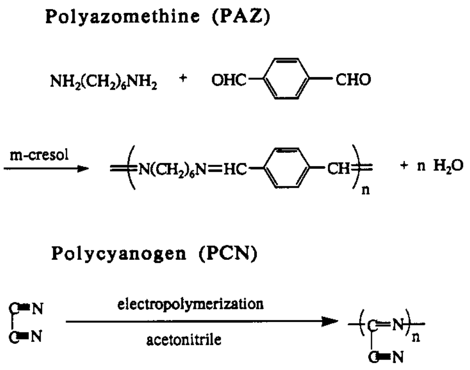

Figure 1. PCN and PAZ polymers.

Both methods showed virtually no degradation of the tensile properties of the coated fibers. Graphite fibers coated using organometallic solutions retained about 80–95% of their tensile strength after consolidation into MMCs.

It was evident that a further modification of the interface between a carbon fiber and a metal matrix might be obtained by the application of metal to the surface in a *disordered carbon layer.* Work in this laboratory has established that polymers containing an imino nitrogen in their backbone can bond to a wide variety of metal ions.[21a] Further, these polymer–metal complexes decompose on heating to yield metal in a disordered carbon matrix. When heated to very high temperatures, ordered graphites are formed containing dispersed metal, metal carbides in certain cases, and oxidized metal at the surface in the case of such metals as aluminum. Polycyanogen[21] (PCN) and polyazomethine (PAZ) complexes with aluminum chloride and titanium chloride were used in this work to provide such a coating technique.

In this paper, we wish to report a study of the mechanical properties of coated carbon fibers as a function of different polymer–metal complex coating solutions and postpreparation heat-treatment protocols. We elected to study four different polymer–metal solutions involving combinations of PCN or PAZ with $AlCl_3$ or $TiCl_3$. In all cases we obtained uniformly coated carbon fibers with a coating thickness of about 0.1 μm. These coated fibers were subsequently infiltrated with aluminum metal by either a vacuum deposition process or by dipping into a melt. The coated-carbon fiber–aluminum filaments were then reheated to 700 °C to simulate MMCs processing conditions. The mechanical properties of the coated fibers at each fiber treatment step were evaluated. Scanning electron microscopy (SEM) and wetting measurements using a Wilhelmy balance were performed to assist in the characterization of the coated fibers.

Experimental Section

Preparation. PCN polymer was synthesized by the electropolymerization of cyanogen gas in acetonitrile.[21b] PAZ polymer was synthesized by polycondensation of hexamethylenediamine with terephthalaldehyde in *m*-cresol.[22,23] Polymers (PCN, PAZ; Figure 1) which have CN linkages in the main chain tend to the rigid and are therefore very difficult to dissolve in any common solvent. However, Jenekhe and Joheson[24] have reported that an aprotic solvent such as nitromethane in the presence of a metal halide such as aluminum chloride can function as a solvent for PAZ. Aluminum chloride is a Lewis acid which can interact with lone-pair electrons on the nitrogen atoms in the imino linkages of both PCN and PAZ polymers. The interaction produces a reduction in intermolecular attraction between chains and a reduction of chain stiffness, allowing solvation of the polymer chain by the aprotic solvent. The advantage of utilizing such a solution in coating the interface between carbon fibers and metal matrix is that this method would enable the solution to deliver the metal ions to the surface of the carbon fibers homogeneously.

Table I. Contact Angles with Water of Carbon Fibers and Reference Materials

fiber	coating	heat treatment temp, °C	contact angle, deg
AS-4[a]			~80
AS-4	PCN/$AlCl_3$	500	48.6
AS-4	PCN/$AlCl_3$[b]	500	47.5
AS-4	PAZ/$AlCl_3$	500	41.9
nylon 6,6			80.7
Pt (wire)			42.7

[a] Donnet, J.; Bansal, R. C. *Carbon Fibers*; Marcel Dekker: New York, 1984; p 148. [b] Double coating of PCN/$AlCl_3$.

Four different polymer–metal chloride solutions (PAZ/$AlCl_3$, PAZ/$TiCl_3$, PCN/$AlCl_3$, PCN/$TiCl_3$) were prepared. The metal chloride (2 wt %) was dissolved in nitromethane, and the polymer was gradually added. The amount of polymer to metal chloride in the complex solution is a ratio of 1:2 for each polymer repeat unit to the $AlCl_3$ or $TiCl_3$ concentration. From the experimental results, a 1:2 ratio of each polymer unit to two metal chloride is the minumum requirement for PAZ to be totally dissolved in the metal chloride solution. PCN requires less metal halide for dissolution, but for consistency a 1:2 ratio was employed in this case.

Hercules AS-4 unsized carbon fibers were chosen as the starting material for the solution-coating process. AS-4 carbon fibers with an average diameter of 7.3 μg/filament were provided in bundles of 3000 filaments and cut into 1.5-in. lengths. Each cut bundle was mounted on an aluminum frame by two aluminum clips. The samples mounted on their frames were placed in a quartz tube furnace and heated to 500 °C for 10 min in a nitrogen atmosphere (step 1) to vaporize and remove any surface impurity.[10–13] After cooling down, the samples were then dipped into a polymer–metal salt solution for 10 min. The samples were then taken out and dried by hanging them in a nitrogen atmosphere overnight. Finally, the coated samples were transferred back to the quartz furnace and heated in two temperature stages: at 200 °C for 2 h, followed by heating, in some cases, at 500 °C for 2 h (step 2). The above heat treatment stabilizes and partially carbonizes the coating layer, as well as reducing the metal ions to metal atoms in the polymer–metal coating layer. Four different coating solutions and two heating profiles were employed in step 2, giving carbon fiber samples prepared under eight different treatment conditions.

The samples prepared under these eight treatment conditions were then subjected to two different aluminum-coating procedures. In the first procedure, molten aluminum was coated directly onto the fibers to examine the improvement in the wettability of the graphite fibers introduced by the new coating layer. Coated carbon fibers were separated into single filaments and mounted one by one on a graphite frame. The frame was dipped into molten aluminum at 690 °C for 10 s (under nitrogen) (step 3).

In an alternate procedure, a vacuum deposition method[25] was employed to deposit aluminum metal on the surface of carbon fibers at a relatively low temperature (step 4). An Al_2O_3-coated tungsten boat containing aluminum metal was used as the evaporation source. The bell jar was evacuated below 10^{-6} Torr, and the boat heated electrically to produce a 1-μm coating on the

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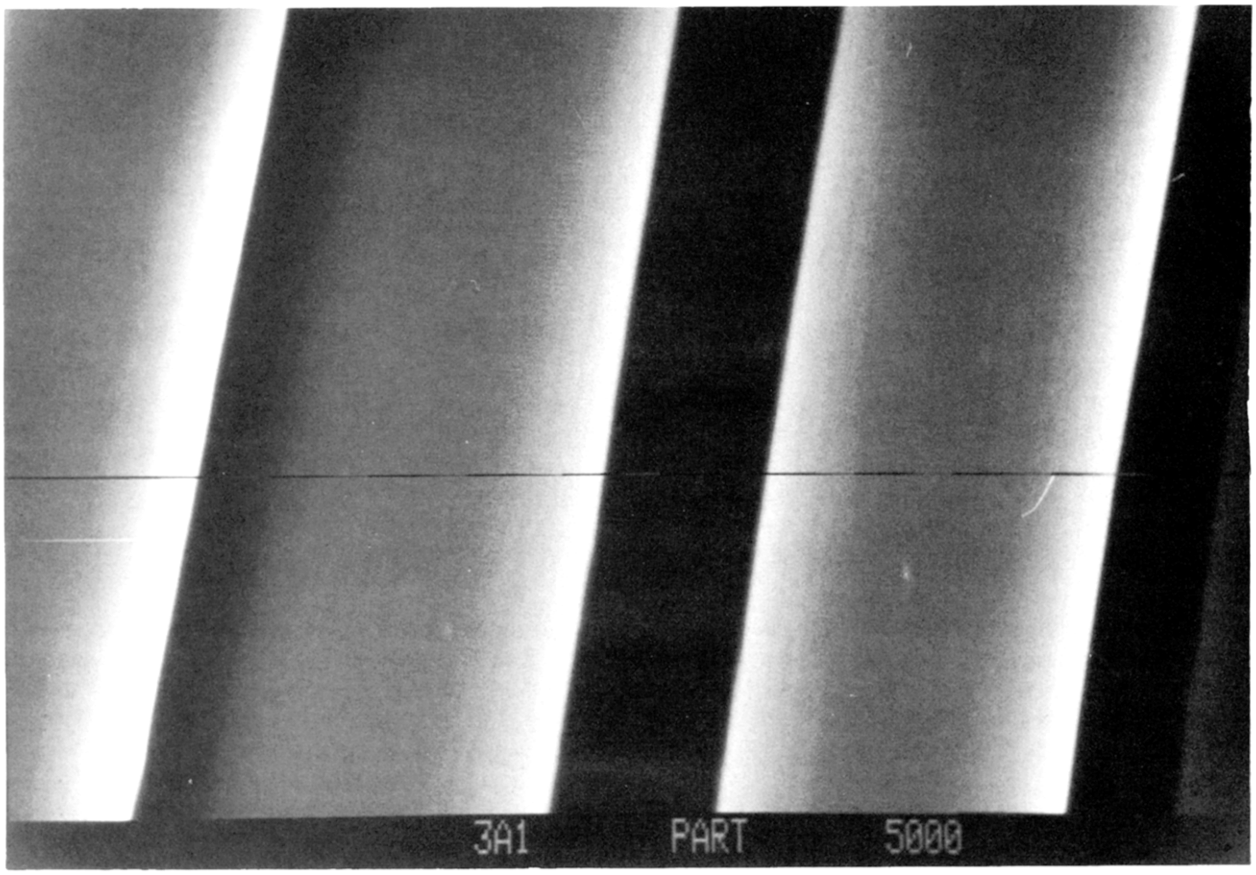

Figure 2. SEM photograph of AS-4 carbon fibers (×5000).

fibers at the target in ~10 min. After deposition, the coated filaments were mounted on a graphite frame, placed into a furnace and reheated to 700 °C for 10 min under a nitrogen atmosphere (step 5). A brief schematic including each processing step follows for processing AS-4 carbon fibers:

Step 1: Clean surface of fiber by heat treatment at 500 °C for 10 min in nitrogen.

Step 2: Dip coat with polymer–metal complex solution. Stabilize and partially carbonize at 200 °C for 2 h and, in some cases, at 500 °C for an additional 2 h.

Step 3: Coat step 1 and step 2 fibers with molten aluminum by dipping at 690 °C for 10 s under nitrogen.

Step 4: Vacuum deposit aluminum (1-μm coating) on uncoated and coated carbon fibers.

Step 5: Reheat step 4 filaments at 700 °C for 10 min.

Measurement. An Instron tester (Model 1122) was employed to evaluate the mechanical properties of the AS-4 carbon fibers, polymer-coated AS-4 carbon fibers, and aluminum-coated fibers. Monofilaments were mounted on a paper frame with vertical sides that are pieces of plastic tape. These tapes were burned off with a hot wire after mounting and prior to loading the specimen. The tensile test was performed at a constant rate of 0.5 mm/min, using a half-inch gauge length. Between 10 and 20 samples were evaluated for each preparation condition. The dimensions of the samples were measured using both optical microscopy and scanning electron microscopy (SEM). The surface morphology of the samples was also studied using SEM.

The surface energy of the polymer–metal coated carbon fibers and the same carbon fibers before coating were measured using a Wilhelmy balance. This technique was developed for the determination of the vertical attractive force across the interface between a liquid and a partially immersed filament.[26] The filament (carbon fiber) is suspended from one arm of a microbalance (Cahn 2000). The container filled with distilled water is raised by means of a very accurate elevating device to immerse the filament. The travel distance is adjusted between 4 and 22 mm. Travel speed is varied between 0.025 and 1.000 mm/min. A recorder produces a graph of the force experienced by the sample as a function of the immersed length of the fiber.

Results and Discussion

Surface Energy Measurements. The wetting force exerted on a fiber by the liquid is

$$F = \gamma_{\text{liquid}} P \cos\theta$$

where F is the wetting force in dyne; γ_{liquid} is the liquid surface tension in dyn/cm; and P is the perimeter of the filament in centimeters. Thus the contact angle between the fiber and liquid is

$$\theta = \cos^{-1}(F/\gamma_{\text{liquid}}P)$$

Data are presented in Table I. The AS-4 carbon fiber has a contact angle of ~80°, whereas the coated carbon fibers have a contact angle of ~48° when a PCN/$AlCl_3$ coating is applied, and a contact angle of ~42° when fibers are coated with PAZ/$AlCl_3$. Under the same conditions, the contact angle for platinum is 43°. The results above indicate that the surface energy of carbon fibers coated with polymer–metal solutions increases markedly and is comparable to a pure metal.

After these treated fibers are coated with molten aluminum, SEM photographs indicate that the surface is homogeneously coated. Figure 2 shows the smooth surface of AS-4 carbon fibers before any coating process. Figure 3 is a photograph of untreated carbon fibers coated with aluminum. There is virtually no trace of aluminum on the surface due to the poor wettability of the carbon fibers. However, in Figure 4 the polymer–metal coating process has been completed placing a coating of ~1 μm on the surface. It is expected that an Al_2O_3 layer will be formed

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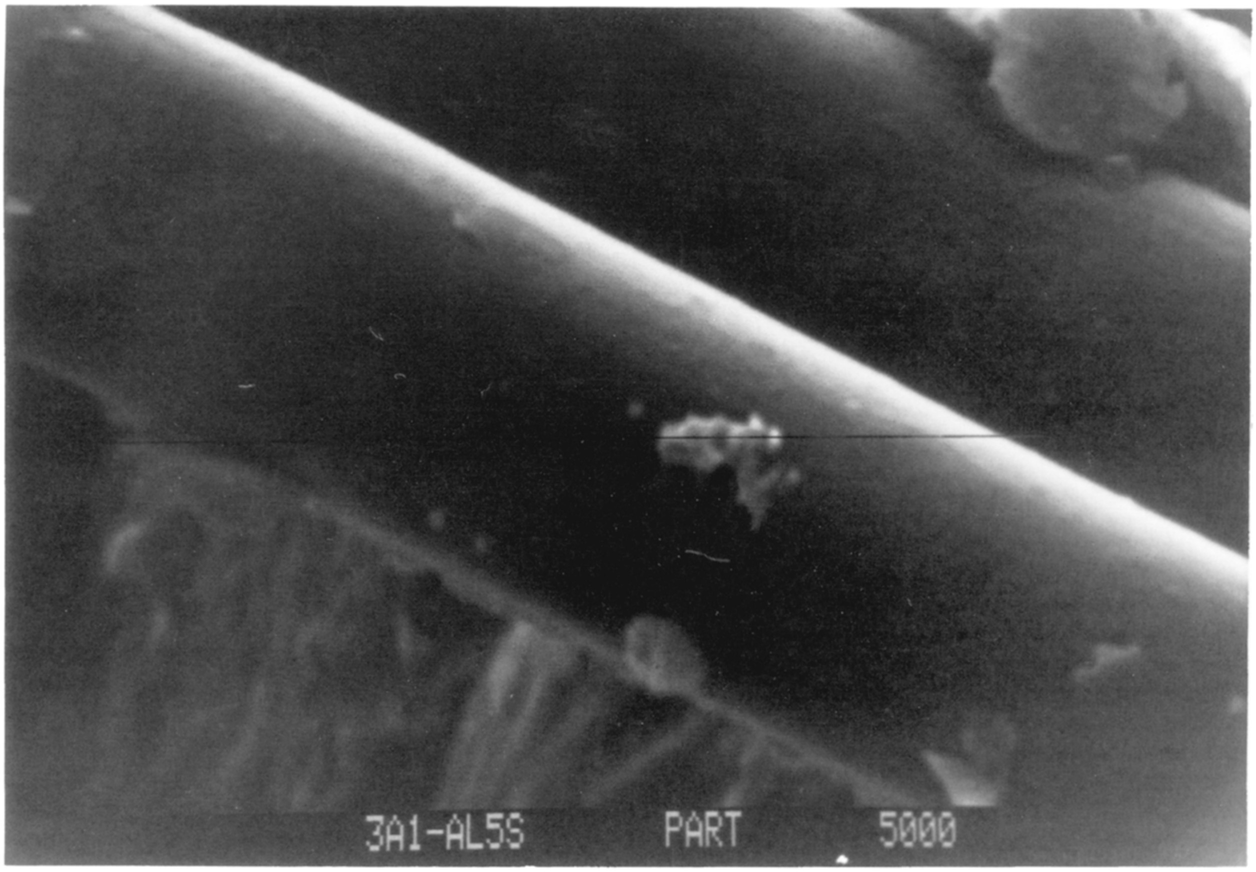

Figure 3. SEM photograph of AS-4 carbon fibers after coating with molten aluminum (×5000).

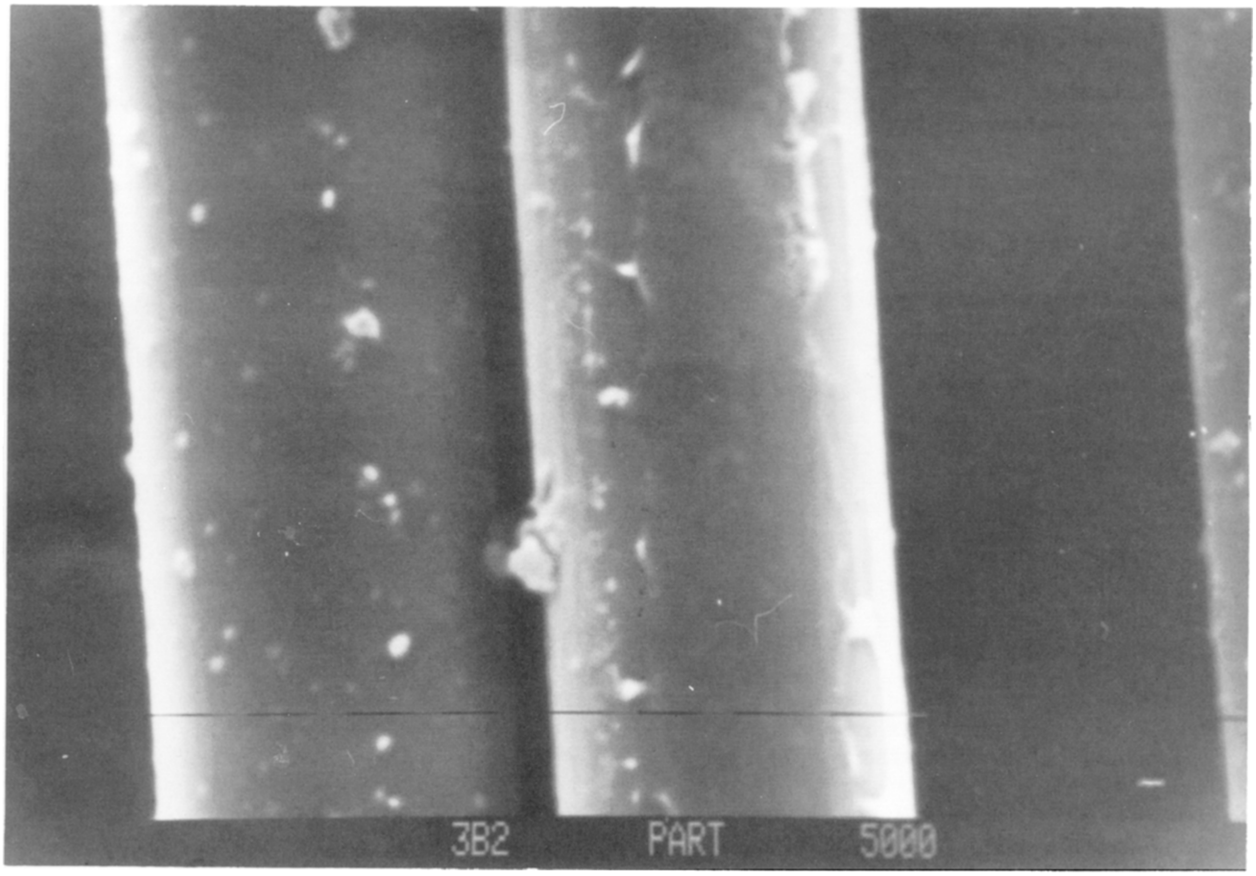

Figure 4. SEM photograph of AS-4 carbon fibers after coating and heating (step 2) processes (×5000).

by thermal treatment of the polymer–metal complex at the interface. In Figure 5 the polymer–metal ion precoated carbon fiber now allows a smooth layer of aluminum coating (~1 μm) on the surface of the carbon fibers.

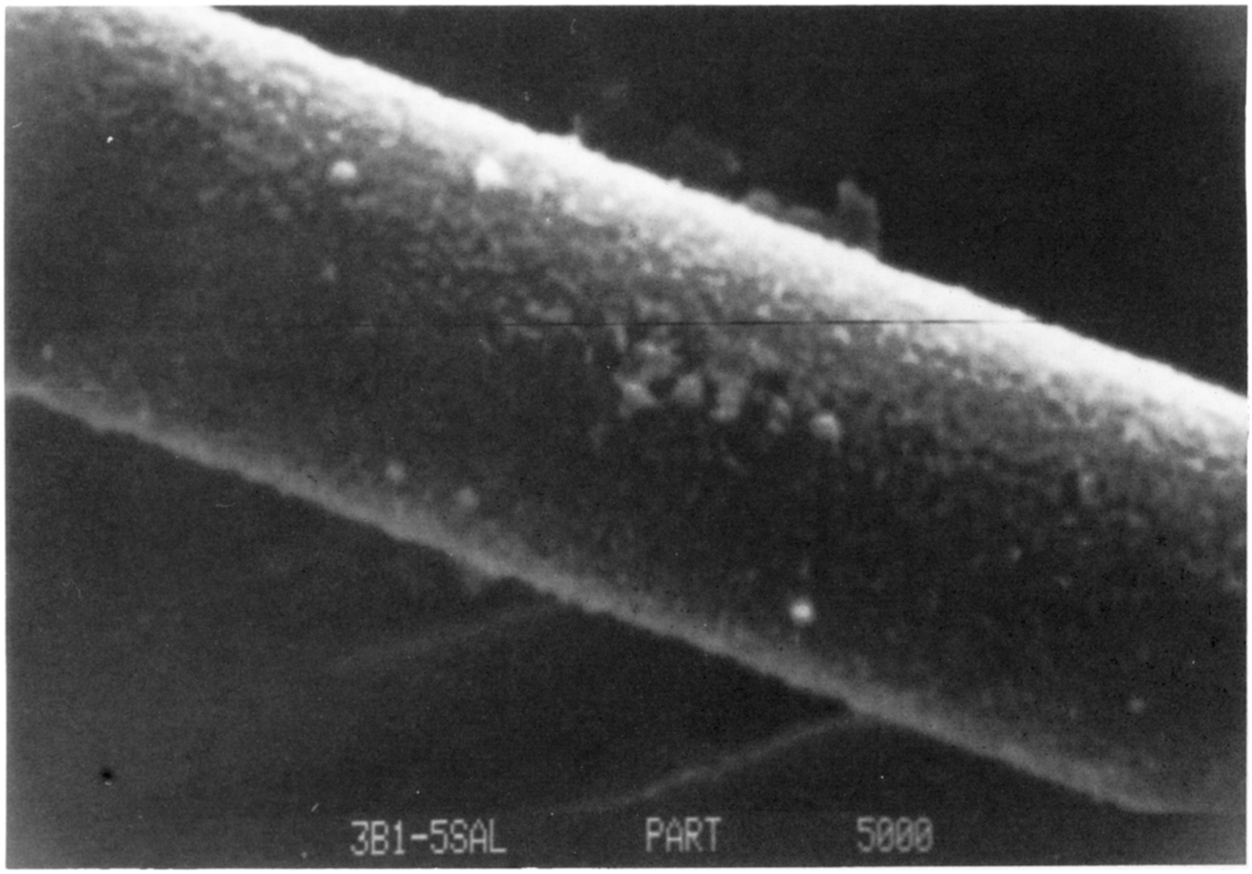

Figure 5. SEM photograph of aluminum coated carbon fibers after processing steps 2 and 3 (×5000).

Table II. Tensile Strength of Treated AS-4 Carbon Fibers after Processing Step 2

sample code[a]	tensile strength, psi × 10^{-5}	strength retention, %
3A2	4.9 ± 0.5	100
3B1	5.0 ± 1.1	101
3B2	4.7 ± 1.3	96
3C1	5.2 ± 0.6	105
3C2	4.7 ± 1.2	96
3E1	5.1 ± 1.2	104
3E2	4.2 ± 0.5	85
3F1	4.9 ± 0.6	99
3F2	4.4 ± 0.6	90

[a] The code 3A2 represents an AS-4 carbon fiber that is preheated to 500 °C to clean its surface. 3B is the 3A2 fiber coated with PCN/$AlCl_3$ solution. 3C is the 3A2 fiber coated with PAZ/$AlCl_3$ solution. 3E is the 3A2 fiber coated with PCN/$TiCl_3$ solution. 3F is the 3A2 fiber coated with PAZ/$TiCl_3$ solution. 1 indicates that the polymer–metal coated fibers are heated to 200 °C for 2 h in processing step 2. 2 indicates that the fibers, after heat treatment in step 1, are reheated to 500 °C for 2 h in step 2.

Table III. Tensile Strength of Filaments after Processing Steps 4 and 5

sample code[a]	tensile strength step 4, psi × 10^{-5}	strength retention, %	tensile strength step 5, psi × 10^{-5}	strength retention, %
3A2	4.2 ± 0.6	108	1.9 ± 0.2	48
3B1	5.0 ± 0.5	128	2.2 ± 0.4	56
3B2	4.0 ± 0.6	102	1.2 ± 0.3	31
3C1	4.4 ± 0.9	112	3.1 ± 0.8	80
3C2	3.6 ± 0.2	91	3.8 [illegible] 0.3	96
3E1	4.6 ± 0.4	117	3.2 ± 0.3	82
3E2	3.3 ± 0.5	84	3.6 ± 0.6	93
3F1	4.2 ± 0.4	106	1.2 ± 0.2	31
3F2	3.7 ± 0.6	94	1.8 ± 0.2	45

[a] Sample codes are defined in Table II. The rule of mixture tensile strength for the carbon-aluminum filament is 3.9 × 10^5 psi (see text for explanation).

Mechanical Properties Measurement. Table II presents the tensile strength of treated AS-4 carbon fibers after processing step 2. The results indicate that the polymer–metal solution coating followed by the heating processes in step 2 does not lead to degradation of the tensile strength of carbon fibers. Many of the literature methods that have been evaluated lead to substantial degradation of mechanical properties.[10–20]

Table III presents the dependence of the tensile strength of the coated carbon fibers produced in step 2 after the further procedures of processing steps 4 and 5, that is, after depositing aluminum on the surface of carbon fibers by vacuum deposition followed by 700 °C heating. The vacuum deposition process in step 4 consists of applying current to evaporate aluminum under vacuum and depositing it on the surface on the carbon fibers (~1-μm thickness of aluminum coating for 10 min of deposition). The tensile strengths in the second column of Table III indicate that this metal coating process does not degrade the strenth of the samples.

The reason for employing processing step 5 (a 700 °C, 10-min heating process) is to simulate MMCs processing conditions and to study their influence on the mechanical properties of the fibers. The results of processing step 5 are presented in the fourth and fifth columns of Table III. A ~52% drop occurs in tensile strength for the fibers in the 3A2 series (without polymer–metal coating applied) as compared to a rule of mixture value. The average tensile strength for the AS-4 carbon fiber is 4.9 × 10^5 psi. The rule of mixture value is simply obtained by averaging these values with the appropriate volume ratio, in this case 23:77 (aluminum:fiber). The cause for this severe tensile strength drop is purportedly aluminum carbide formation

Table IV. Percent Strain of Carbon Fibers

sample code[a]	polymer–metal coating (step 2), % strain	aluminum vacuum deposition (step 4), % strain	reheating (700 °C) (step 5), % strain
3A2	1.8 ± 0.2	2.1 ± 0.2	0.9 ± 0.2
3B1	1.6 ± 0.3	2.3 ± 0.1	1.0 ± 0.4
3B2	1.5 ± 0.3	2.1 ± 0.3	0.6 ± 0.2
3C1	1.8 ± 0.2	1.9 ± 0.3	1.5 ± 0.4
3C2	1.6 ± 0.3	1.5 ± 0.2	2.0 ± 0.3
3E1	1.7 ± 0.3	2.0 ± 0.1	1.6 ± 0.3
3E2	1.3 ± 0.2	1.4 ± 0.2	1.8 ± 0.2
3F1	1.8 ± 0.2	2.2 ± 0.2	0.6 ± 0.2
3F2	1.6 ± 0.2	1.5 ± 0.2	0.7 ± 0.2

[a] See Table II for sample codes.

on the interface.[6,10,11,27-29] The temperature of 700 °C employed in step 5 is way over the 500 °C threshold for the reaction of carbon with aluminum. The combination of consuming carbon atoms from the carbon fibers and aluminum carbide formation on the interface can cause the sample to show premature tensile failure.

The 3E (3E1, 3E2) series gives data for carbon fibers that have a PCN/$TiCl_3$ polymer–metal coating. As shown in Tables II and III, these samples show good tensile strength retention after processing steps 2 and 4 and also an excellent strength retention after processing step 5. These results clearly demonstrate that a PCN/$TiCl_3$ polymer–metal coating process preserves the tensile strength of the carbon fibers.

Similar results are obtained for the coated carbon fibers from the 3C (3C1, 3C2) series, which have a PAZ/$AlCl_3$ polymer–metal coating. Besides good tensile strength retention after processing steps 2 and 4, there is also ~80% strength retention after step 5 for samples in the 3C1 series, and a ~96% strength retention for samples in the 3C2 series. Both the PCN/$AlCl_3$ and the PAZ/$TiCl_3$ coating solution treatment lead to good tensile strength retention for coated carbon fibers after both steps 2 and 4. However after step 5 there is a massive drop in the strength retention (~44–69%).

Table IV gives the percent strain for coated carbon fibers under different treatment conditions. The strain results show similar trends to the corresponding tensile strengths. The Young's modulus of these coated fibers, which is given by their ultimate tensile strength divided by the corresponding strain, should be consistent and show little variation, and the experimental results are in agreement with this prediction.

Conclusions

The results from the surface energy measurements and the molten aluminum dipping experiments both show an impressive wettability improvement for polymer–metal complex coated carbon fibers. The mechanical properties do not degrade after the polymer-metal coating process (step 2), and filaments prepared from them show no degradation as a consequence of the vacuum deposition process (step 4). After heating these filaments to 700 °C for 10 min (step 5), some samples still preserve their tensile strengths to an excellent degree (~80–96%).

The method of applying a polymer–metal coating following by heating causes the carbon fibers to be wet by aluminum and be protected from carbide formation by the highly disordered carbon film on its surface, as well as by some aluminum oxidation. The results suggest that, with a proper choice of polymer and metal compounds, the polymer–metal complex coating process shows high promise as compared to other methods.

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