

Investigations on the Electrochemical Surface Treatment of Carbon Fibers

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Desized polyacrylonitrile (PAN) based carbon fibers (CF) were chemically and electrochemically oxidized and reduced. CF surfaces were activated via cyclic voltammetry studies with anodic and cathodic scans. The changes in CF surfaces were studied by contact angle measurements. Lifshitz-van der Waals and acid-base components of single fibers were determined. In general, oxidation resulted in the formation of an acidic surface energy component and reduction gave rise to no change in the number of basic functionalities at the CF surface.

Key Words: carbon fiber; cyclic voltammetry, contact angle.

Introduction

Carbon fibers are generally surface treated to maximize the degree of intimate molecular contact that is attained between the adhesive and the substrate during the bonding operation. Furthermore, some degree of surface roughening may often assist in attaining good interfacial contact¹. Therefore the fibers are usually given a series of surface treatments to increase their surface reactivity and surface energy and to reduce the number of flaws by gaining new properties that are not found in pure CF materials²⁻⁵. In a previous study⁶ it was observed that electrochemical treatment at high potentials in a concentrated ammonium bicarbonate (AB) solution gave rise to gas (CO₂) evolution and scaling at the CF surface, which resulted in low oxidation levels. They also found that increasing ammonium concentration resulted in nitrogen containing functional groups at the surface. In addition, Nakao et al² found that fibers treated in AB had lower oxygen content compared to electrochemically treated fibers in acidic solutions. They also supplemented their work by cyclic voltammetry studies. Previously, we reported data on the surface properties of sized and unsized CFs and the effect of wet chemical oxidation in HNO₃ and anodic oxidation in H₂SO₄ for unsized graphite fibers. The changes in adhesional properties were tested by single fiber pull-out tests for the unsized fibers.

In this study, cyclic voltammetry of CF and a graphite rod (as the working electrodes) were studied in ammonium bicarbonate (AB) and sulfuric acid as the electrolytes. Carbon fibers that were desized by dichloromethane were later electrochemically surface activated with those electrolytes at rather low

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potentials. In the case of AB, again a rather dilute solution was employed to reduce any fiber damage that might occur. Single fibers were then studied repetitively to calculate the surface energy parameters.

Experimental

Materials

Carbon fibers were obtained from BASF (Celion G40-700) and had a high strength intermediate modulus of about 40 Msi.

Chemicals except acetone and ammonium bicarbonate were of spectroscopic grades. Acetone was distilled in a fractional distillation column and ammonium bicarbonate was dissolved in cold water, filtered with blue band paper. Dichloroethane and sulfuric acid were supplied by Merck. Diiodomethane, ethylene glycol, formamide and n-decane were products of Aldrich Chemical Company.

Equipment

Sartorius Micro Balance, Model M25D, in conjunction with an Oriel Encoder Mike Control Unit Model 18008 as vertical mobile stage was used in contact angle measurements.

Cyclic voltammograms were recorded with a Potentiostat Wenking POS 73 potentiostat on a Lloyd PL3 XY Recorder.

Electrochemical treatments were carried out in electrochemical cells using the same equipment.

Experimental Procedure

Surface Pretreatments for Desizing of Carbon Fibers

In their desizing process Fitzer and Weiss⁸ use extraction in methylethyl ketone. In this study, fibers 10 cm in length were washed with distilled water. Afterwards, they were refluxed in dichloroethane for one day and rinsed with acetone and deionized water in a petri dish. Finally, they were dried at 120°C for one day.

Cyclic Voltammetry (CV)

Cyclic voltammograms were recorded in a potential range 1.5V to -0.3V (vs Ag/Ag⁺ (Saturated Calomel Electrode -0.5 V)) in sulfuric acid (50% by volume). This range was 1.7V to -1.0V for the fibers studied in 0.1M ammonium bicarbonate. Nitrogen gas was bubbled through the cell prior to recording voltammograms. The cell used in CV studies is given in Figure 1.

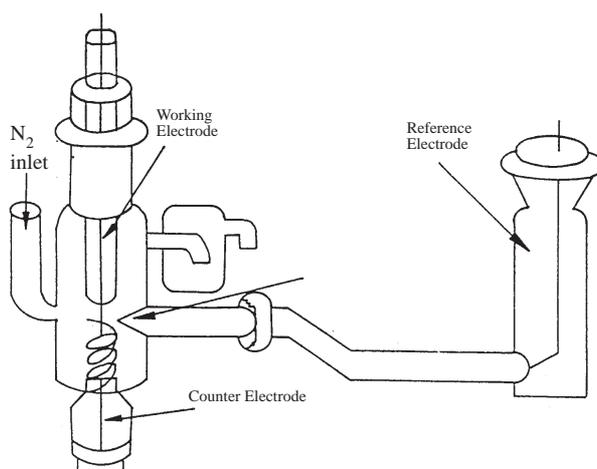


Figure 1. Cyclic Voltammetry Cell

Electrochemical Treatments

Cleaned fibers were inserted into a controlled potential electrolysis cell (Fig. 2). The electrolytic cell was composed of 0.1M ammonium bicarbonate as the electrolyte, a platinum wire as the counter electrode, the silver wire as the reference electrode and carbon fibers as the working electrode. Treatments were applied for 20 min for anodic oxidation, 20 min for cathodic reduction and 20 min oxidation followed by 20 min reduction. 1.1V of potential was adjusted for those treatment types. The second electrolysis was carried out in sulfuric acid (50% by volume) at 0.6V for 1 h. Later, fibers were washed with deionized water and dried at 125°C for one day. Upper tips of fibers were wrapped with platinum wire attached to steel wire. The electrolyte was properly arranged to penetrate through the fibers while nitrogen gas was bubbling into the electrolytic cell.

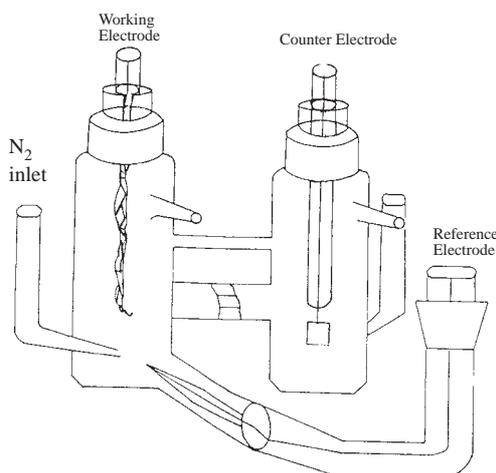


Figure 2. Controlled Potential Electrolysis Cell

Contact Angle Measurements

A single fiber was separated from the bundle and taped between two pieces of adhesive tape. One compartment of weighing twig, by which the fiber was suspended, gradually touched the liquid surface while the

mobile stage velocity was adjusted to 1 $\mu\text{m}/\text{sec}$. Later, the mobile stage was stopped to determine the force on the fiber as the contact angle advanced. The contact angle apparatus is shown in Figure 3.

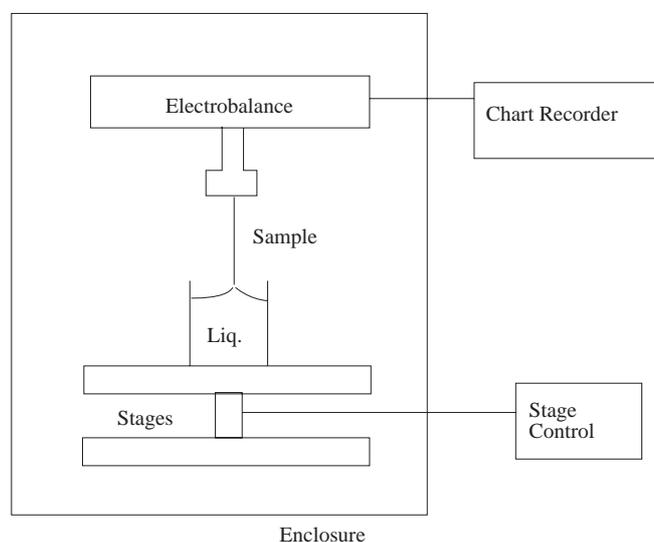


Figure 3. Contact Angle Apparatus

Calculation of Surface Energies

The total surface energy (γ_I) of a given material, I, can be considered as being composed of two additive parts, namely, the Lifshitz-van der Waals (γ_I^{LW}) component and the acid-base (γ_I^{AB}) component. The details of the theoretical background are given elsewhere⁹⁻¹⁰. In summary, the following equation is used to calculate the polar surface component of the CF with a polar liquid (Diiodomethane). The last two terms on the right-hand side of the relationship is omitted in the first step.

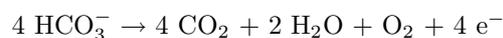
$$(1 + \cos \Theta)\gamma_L = 2[(\gamma_L^{LW}\gamma_S^{LW})^{1/2} + (\gamma_L^+\gamma_S^-)^{1/2} + (\gamma_L^-\gamma_S^+)^{1/2}]$$

where γ_L is the surface energy of the probe liquid, and γ^+ and γ^- are the acid and base components of the designated phases respectively. With the measured and calculated values of γ_L , γ_L^{LW} , γ_S^{LW} , two simultaneous equations, in terms of the parameters γ_S^+ , γ_S^- and two advancing contact angles Θ_1 and Θ_2 measured for two bipolar liquids (ethylene glycol and formamide) are constructed. These two equations can then be solved for γ_S^+ and γ_S^- provided that γ_L^+ , γ_L^- and γ_L^{LW} are known for the probe liquids.

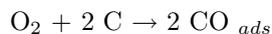
Results and Discussion

Cyclic Voltammetry Studies and Electrochemical Treatment of CF

In previous studies of electrochemical surface activation in NH_4HCO_3 , it was speculated that nitrogen was introduced to the fiber in the form of amine and/or amide groups [6]. This was supported by the absence of acid character in surface energy. In the electrolytic cell, loss of CO_2 might take part through the following reaction:



Some of the oxygen might be adsorbed on the fiber surface,



a. Ammonium Bicarbonate

The studies with 0.1M NH_4HCO_3 were carried out by obtaining the background CV of a system containing platinum wires as the working and counter electrodes with Ag/Ag^+ as the reference electrode. A reversible peak at -0.75V was found during the cathodic scan. The couple at ca. -1.5 V, however, can be attributed to the solvent discharge (Fig. 4).

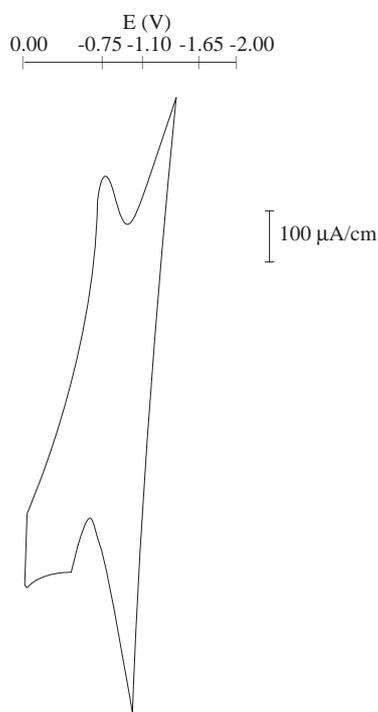


Figure 4. Cyclic Voltammogram of Pt in 0.1 M NH_4CO_3 (cathodic scan)

When CF was used as the working electrode with a Pt counter electrode, two irreversible reduction peaks at -0.5 and -1.0V and an oxidation peak at around 0.0 V were observed (Fig. 5). This is valid for both cathodic and anodic scans, i.e., no matter the direction of the sweep, the three above-mentioned peaks appear without being affected by each other.

CV results were utilized to carry out electrolysis treatments with anodic oxidation and alternating oxidation-reduction processes at 20 min intervals at 1.1V and -1.1V. The oxidation potential was kept at a higher value than the measured potential to increase the rate of oxidation.

Peak (a) is the direct oxidation peak of the system and peak (b) is the direct reduction of the system. Peak (c), which appears only after the appearance of (a), must be the reduction of the oxidation products produced on peak (a).

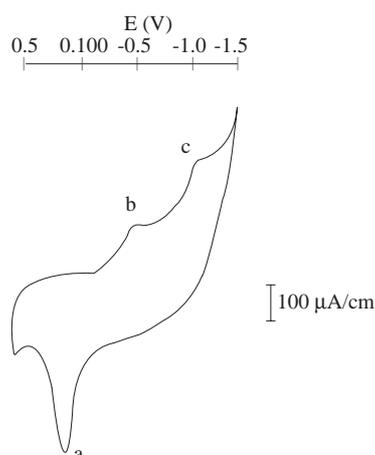


Figure 5. Cyclic Voltammogram of CF in 0.1 M NH_4CO_3 (anodic scan)

b. Sulfuric Acid

In the acidic medium, the graphite rod reveals +0.4 V (oxidation) and +0.3V (reduction) peaks upon the first anodic scan whereas the CF has peaks of +0.6V (oxidation) and +0.2V (reduction). In the case of the carbon fiber working electrode, not only was a rather large difference between the oxidation and reduction peaks observed, but also the charge under the curve was about 10 times greater than that of the voltammogram taken with a graphite electrode of approximately the same size (Fig. 6).

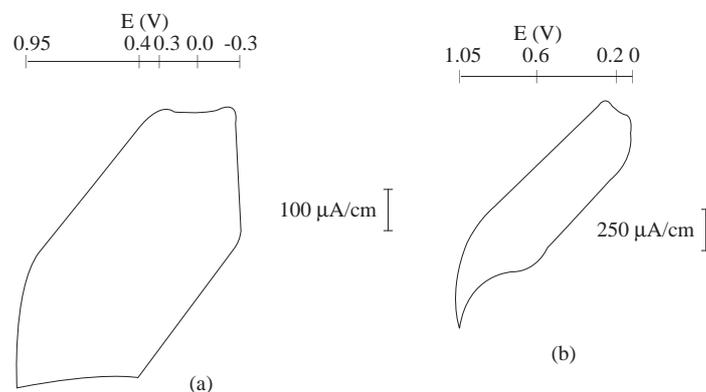


Figure 6. Cyclic Voltammograms of graphite rod and CF in H_2SO_4 (50% by volume). a) Anodic scan for graphite rod, b) Anodic scan for CF.

Surface Energy Determinations of Carbon Fibers

Desized and electrochemically surface activated carbon fibers were investigated with contact angle measurements. Each measurement was repeated several times and surface energy parameters were calculated from the averaged values.

From Table 1, it is observed that desized CF is basic. In a previous study we reported data of the surface free energy parameters of epoxy sized G40-700. The sized fibers exhibited acidic character (31.4, 0, and 31.4 $\text{mJ}\cdot\text{m}^{-2}$ for γ^{LW} , γ^- and γ^+ respectively). It is interesting to note that after sizing, a reversal of the surface polarity of G40-700 occurs. This result may be due to the effectiveness of the desizing process.

After the electrochemical treatment in sulfuric acid, the fiber acquired the same amphoteric character when a certain amount of acidity occurred. The basic component of the surface energy component was also increased. It should be noted that 60 min is a rather long oxidation time, during which a significant amount of surface etching may occur. The contact angle data over such a rough surface may not be reliable due to large hysteresis effects¹¹. The rather high value of the contact angle manifests itself in the low γ^{LW} and total γ_S . In NH_4HCO_3 treatments, amphoterism was also found in the anodically oxidized specimens, while in contrast cathodically reduced sample exhibited a basic character. In contrast to the sulfuric acid treatment, the total surface energy was found to be greater for the ammonium bicarbonate treatment. Furthermore, γ^{AB} , which is $2(\gamma^+\gamma^-)^{1/2}$, showed a maximum for 20 min oxidation in ammonium bicarbonate. It is also interesting to note that reduction in the same solution did not increase the basic component of the CF surface energy. The behavior of the oxidized-reduced samples also supports the preceding observation. The CF surfaces acquired an acidic character, which was unaffected by the reduction process. The Lifshitz van der Waals (LW) component of NH_4HCO_3 treated fiber is 42.7, whereas that of H_2SO_4 treated fiber is 29 $\text{mN}\cdot\text{m}^{-1}$.

Table 1. Surface Energy Parameters of Fibers in mJ/m^2 .

| Substrate | γ^{LW} | γ^+ | γ^- |
|-------------------------------|---------------|------------|------------|
| Unsize ^a | 40.7 | - | 5.1 |
| 60 min oxidized ^b | 29.0 | 1.9 | 8.2 |
| 20 min oxidized ^c | 34.2 | 4.0 | 5.2 |
| 20 min reduced ^d | 42.7 | - | 4.5 |
| Oxidized+reduced ^e | 32.1 | 4.9 | - |

- a) Unsizeing was applied to CFs.
 b) In H_2SO_4 at 0.6V.
 c) In NH_4HCO_3 at +1.1V.
 d) In NH_4HCO_3 at -1.1V.
 e) In NH_4HCO_3 oxidation at 1.1V followed by reduction at -1.1V.

Preliminary single fiber pull-out tests were also carried out on sized and desized G40-700 fibers from model matrices, namely polystyrene (PS) and polymethylmethacrylate (PMMA). Desized fibers gave extremely low ILSS (Interlaminar Shear Stress) values (5.5 MPa (megapascal) with PMMA and 5.9 MPa with PS), whereas the sized CFs exhibited considerably greater ILSS values (15.0 MPa with PMMA and 26.5 with PS⁷). Electrochemical treatment resulted in no change in the low ILSS values of the desized fibers.

Conclusion

The cyclic voltammetry studies indicate that in 50% sulfuric acid, oxidation and reduction of the CF surface are possible at +0.6 V and +0.2 V respectively. Compared to the graphite electrode, a completely different set of potentials and a tenfold increase in electrolytic charge transfer exists at the CF surface. In the case of ammonium bicarbonate, two reduction peaks at negative potentials and an oxidation peak at 0.0 V were observed. Electrochemical treatments of the fiber surfaces produced acidic surface groups in H_2SO_4 and NH_4CO_3 solutions, which were not present at the untreated surfaces. The reduction process does not seem to be effective in creating any basicity (or acidity) at the surface except creating neutral species in 0.1 M NH_4CO_3 . The creation of no basicity after a 20 min oxidation-reduction sequence also supports the above

conclusion. This study shows that under reasonably low potentials, significant amounts of electrochemical activity exist at the CF surfaces, which can activate the fiber surfaces. The effect of these changes on the adhesive properties will be presented in a forthcoming publication.

Acknowledgments

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References

1. A. J. Kinloch, in **Adhesion and Adhesives Science and Technology**, Cambridge University Press, Chapman and Hall (1990).
2. F. Nakao, Y. Takenaka and H. Asai, **Composites**, **23**, 365 (1992).
3. T. R. King, D. F. Adams and D. A. Buttry, **Composites**, **22**, 380 (1991).
4. W. Weisweiler and K. Schlitter, "Surface Modification of Carbon Fibers by Plasma Polymerization", in **Carbon Fibers, Filaments and Composites**, J. L. Figueiredo, Edition (NATO ASI Series, Netherlands, 1990), pp 263-274.
5. I. N. Ermolenko, "Properties of Carbon Fibers", in **Chemically Modified Carbon Fibers**, VCH, Weinheim, 69 (1990).
6. C. Kozlowski and P. M. A. Sherwood, **Carbon**, **24(3)**, 357 (1986).
7. A. R. Akbay and E. Bayramlı, **J. Adhesion**, **50**, 155 (1995)
8. E. Fitzer and R. Weiss, **Carbon**, **25(4)**, 455 (1987).
9. D. Chan, M. A. Hozbor, E. Bayramlı and R. L. Powell, **Carbon**, **29(8)**, 1091 (1991).
10. N. Dilsiz, N. K. Ering, E. Bayramlı and G. Akovalı, **Carbon**, **33(6)**, 853 (1995).
11. R. H. Bradley, Ling and I. Sutherland, **Carbon**, **31(7)**, 1115 (1993).