

Surface Acid-Base Characteristics of Fiber Materials by Contact Angle Measurements

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SYNOPSIS

Contact angle measurements were used to study the surface acid-base characteristics of treated and untreated carbon fibers, and of treated and untreated silicon carbide fibers. It has been shown that, when untreated, the surfaces of these two fibers exhibits "amphoteric," but the base character is dominant. After oxidization in a liquid phase, the surface acid character of the carbon fibers changes little, whereas the base character becomes much stronger. The treatment, with boiling-concentrated HNO₃ for three hours and the sintering treatment in air at 500°C for eight hours, has little effect on the surface acid-base characteristics of the silicon carbide fibers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Carbon fiber is a reinforcing material with excellent properties. The interface adhesion between carbon fiber and a resin matrix, however, is unsatisfactory because of the inert nature of the fiber surface. Thus, it is commonly necessary to treat the surface of carbon fibers. Surface oxidization is one of the treatment methods.

Silicon carbide fibers are extensively used in ceramic-matrix composites, and are also used in metal- and polymer-matrix composites. The advantages of SiC fibers have been demonstrated in many industrial applications.

The mechanical performance of a composite material strongly depends on the properties of fiber-matrix interface and, in particular, on the level of adhesion between the reinforcing fiber and the matrix. In a system of polymeric composites, the acid-base interaction mechanism on adhesion interface has been proved by many experimental phenomena.¹ The characterization technique for surface acid-base character, however, has not been developed sufficiently.

van Oss et al.² suggested that the acid-base characteristics on a polymer surface can be characterized

in the related parameters of surface energy (γ). In this theory, γ^- is used to indicate the parameter of surface energy, due to proton acceptor and/or electron donor functionality, which can be called the basicity parameter, and γ^+ is used to indicate the parameter of surface energy, due to proton donor and/or electron acceptor functionality, called the acidity parameter. Both γ^- and γ^+ can be related with the acid-base component of surface energy (γ^{AB}) by $\gamma^{AB} = 2(\gamma^- \gamma^+)^{1/2}$. The apolar component of surface energy (γ^{LW}) includes dispersive interaction, dipole-dipole interaction, and dipole-induced dipole interaction, which is overwhelmingly dominated by the dispersion.

From this theory, Young's equation, and Dupre's adhesion equation, the following equation can be obtained:

$$(1 + \cos \theta) \gamma_L^T / 2 = (\gamma_L^{LW} \gamma_S^{LW})^{1/2} + (\gamma_L^+ \gamma_S^-)^{1/2} + (\gamma_L^- \gamma_S^+)^{1/2} \quad (1)$$

where θ is the equilibrium contact angle of liquid L on solid S and γ_L^T is the surface tension of liquid L .

According to eq. (1), all three surface energy parameters (γ_S^{LW} , γ_S^- , and γ_S^+) of a given solid material can be determined by means of contact angle measurements with three liquids of different polarities if the γ_L^{LW} , γ_L^- , and γ_L^+ values for all three liquids

are known. Thus, the surface acid-base characteristics of the material can be evaluated. However, the absolute values of γ^- and γ^+ are unavailable for any known compound (even for water). An arbitrary assumption is that, for water, $\gamma^- = \gamma^+$. Based on the assumption, the relative values of γ^- and γ^+ of other liquids can be measured. Therefore, the γ_s^- and γ_s^+ values, determined by the above method for a solid material, are also relative. This, however, does not affect the quantitative characterization of surface acid-base character.

In this article, attempts have been made to characterize the surface acid-base character of carbon fibers and silicon carbide fibers in the related parameters of surface energy by measurements of the contact angles between some liquids and the fibers, and to examine the effect of surface treatment on the surface acid-base character.

EXPERIMENTAL

Materials

Medium-strength carbon fibers (Shanghai Carbon Factory) were used in this work. The surface of the carbon fibers was oxidized with a mixture solution of potassium chlorate (15 wt %) and concentrated H_2SO_4 (40 wt %) for 1, 2, 5, 10, 20, and 40 min, respectively. The specimens were then washed several times with distilled water and dried in a vacuum oven at 120°C for 15 h. They were then stored in a vacuum desiccator until measurements were performed.

Silicon carbide fibers, used in this work, were NLM-102 Nicalon fibers (Nippon Carbon Co.). Under nitrogen atmosphere, the Nicalon fibers were heated to 500°C and were maintained at that temperature for 30 min to remove the resin film on the fiber surface. An SiC fiber specimen was obtained. The specimen was added to a boiling, concentrated HNO_3 solution for corrosion treatment for 3 h. The specimen was then washed with distilled water and was dried in a vacuum oven at 120°C. The specimen obtained was referred to as SiC(HNO_3). In another treatment, the SiC fiber specimen was sintered in air at 500°C for 8 h and an SiC(air) specimen was

Table I Parameters ($mJ \times m^{-2}$) of Surface Tension of Testing Liquids

Liquid	γ_L^T	γ_L^{LW}	γ_L^-	γ_L^+	Reference
Diiodomethane	50.8	50.8			2
Water	72.8	21.8	25.5	25.5	2
Glycerol	64	34	57.4	3.92	3

Table II Contact Angles (Degree) Measured with Three Liquids on Carbon Fibers

Oxidization Time (min)	0	1	2	5	10	20	40
Diiodomethane	24.7	20.5	19.3	18.0	16.1	15.3	15.6
Water	56.2	35.4	28.0	27.0	24.8	23.5	21.5
Glycerol	45.5	32.0	27.4	22.4	20.3	21.5	23.0

obtained. The three types of specimens were also stored in a vacuum desiccator before measurement.

Measurement

The JY-82 Contact Angle Measurement Meter (Chengde Testing Machinery Factory) was employed.

Contact angles between a fiber monofilament and liquids were measured by the tilting method, using a microscope having a magnification of 150. During the measurements, the ambient temperature was 23° ± 1°C and the relative humidity was not more than 50%.

Testing liquids included diiodomethane, glycerol, and deionized water. Table I shows the values of γ_L^{LW} , γ_L^- , and γ_L^+ of these three liquids. Before measurement, diiodomethane and glycerol in analytical reagent grade were dried with 4A molecular sieve for 24 h and no further purification was performed.

Each contact angle was measured five times and the results were averaged. The error was not more than ±2 degree.

RESULTS AND DISCUSSION

Carbon Fibers

Table II shows the measured results of the contact angles for three liquids on those carbon fibers that had been oxidized for different times.

Table II shows that the contact angles between three liquids and carbon fibers all becomes smaller when the oxidization time increases. Moreover, the contact angles between the apolar liquid (diiodomethane) and carbon fibers decrease less and the contact angles between the polar liquids (water and glycerol) and carbon fibers decrease more. This means that the oxidization treatment enables the polarity on the carbon fiber surface to become stronger.

According to eq. (1), the γ_s^{LW} , γ_s^- , and γ_s^+ values of the surface energy for untreated and treated carbon fibers can be calculated from the data in Tables I and II. The results obtained are presented in Table III.

Table III shows that the oxidization treatment has no effect on the apolar component (γ_s^{LW}) of the

Table III Parameters ($\text{mJ} \times \text{m}^{-2}$) of Surface Energy for Untreated and Treated Carbon Fibers

Oxidization Time (min)	0	1	2	5	10	20	40
γ_S^{LW}	47.1	48.2	48.5	48.8	49.2	49.4	49.3
γ_S^+	0.92	1.10	1.16	1.48	1.50	1.25	1.19
γ_S^-	20.1	34.4	38.6	37.2	38.0	39.9	41.3

surface energy for carbon fibers. The γ_S^{LW} is ascribed primarily to dispersive force, which is independent of the chemical composition at the material's surface. Thus, γ_S^{LW} is not affected by oxidization. The γ_S^{LW} value for carbon fibers is about $48.5 \text{ mJ} \times \text{m}^{-2}$, which is in agreement with the referenced values.^{4,5}

It is also shown in Table III that the surface of untreated carbon fibers exhibits "amphoteric," but the base character is stronger ($\gamma_S^- = 20.1 \text{ mJ} \times \text{m}^{-2}$) and the acid character is weak ($\gamma_S^+ = 0.92 \text{ mJ} \times \text{m}^{-2}$). After oxidization, the γ_S^+ value changes little, and the value of γ_S^- increases greatly.

It is well known that after carbon fibers have been oxidized, oxygen-containing groups, such as carboxyl, phenolic hydroxyl, carbonyl, nitroso, etheric, lactone, and quinoid structures, are produced on the fiber surface. The occurrence of carbonyl, nitroso, etheric, lactone, and quinoid structures would enhance the electron-donating ability of the fiber surface. On the other hand, carboxyl and hydroxyl would enhance the proton-donating ability of the fiber surface. At the same time, these two kinds of groups also possess electron-donating ability. Therefore, oxidization treatment causes the base character on the surface of carbon fibers to become stronger. Based on the acid-base interaction mechanism on the adhesion interface, oxidization-treated carbon fibers will be more suitable for strong interaction with acidic resins (e.g., phenolic resin).

Table III shows that after the oxidization time surpasses two minutes, the increasing extent of the γ_S^- value becomes gradually smaller. The longer the oxidization time, the more seriously the mechanical strength of carbon fibers is affected. Thus, oxidization time should optimally be within two minutes, according to the results presented in this article.

Table IV Contact Angles (Degree) Obtained with Three Liquids on SiC Fiber Specimens

Fiber Specimen	SiC	SiC(HNO ₃)	SiC(Air)
Diiodomethane	34.0	24.9	19.0
Water	57.2	55.0	49.1
Glycerol	48.0	43.1	37.0

Table V Surface Energy Parameters ($\text{mJ} \times \text{m}^{-2}$) for SiC Fibers

Fiber Specimen	SiC	SiC(HNO ₃)	SiC(Air)
γ_S^{LW}	44.0	47.0	48.6
γ_S^+	1.02	1.14	1.29
γ_S^-	20.8	20.1	23.0

Silicon Carbide Fibers

The measured contact angles between three liquids and three SiC fiber specimens are presented in Table IV. The γ_S^{LW} , γ_S^+ , and γ_S^- values of different SiC fiber specimen surfaces can be calculated (see Table V).

It is evident from Table V that the surface of untreated SiC fibers also exhibits amphoteric. Moreover, the acid character is weaker and the base character is stronger. This may be because there is a thin (several hundred angstroms) SiO₂ layer on the Nicalon fiber surface.⁶ Oxygen atoms in this SiO₂ layer would possess electron-donating ability.

Table V also shows that the treatment, with boiling-concentrated HNO₃ for three hours, and the sintering treatment in air, at 500°C for eight hours, have little effect on the γ_S^{LW} value and the acid-base character of the surface for SiC fibers. This is easily understood because the abovementioned SiO₂ layer could suppress the oxidization of the SiC fibers. The work of Rubio et al.⁷ shows that SiC fibers (Nicalon type) are resistant to the corrosion attack of HNO₃. This is in agreement with the experimental result of this article.

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