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Surface modification of PBO fiber by electrostatic discharge for composites

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ABSTRACT

Purpose: PBO fibers provide great potential applications as reinforcement fibers for advanced composites due to the excellent thermal resistance and specific stiffness and strength. However, the interfacial adhesion between reinforcing fiber and polymer matrix in a composite system is a primary factor for the stress transfer from matrix to fiber. In this paper, the effects of surface treatment on the modification of PBO fiber and its composite materials have been investigated using electrostatic discharge under atmospheric pressure. The surface treatment process has been designed to improve fiber/matrix interfacial bonding quality while providing minimum alteration to the bulk characteristics of the reinforcement fiber.

Design/methodology/approach: Both as-spun (AS) and high-modulus (HM) PBO fibers were surface treated and characterized in this study. The characterization techniques included scanning electron microscopy, MTS tensile tester, dynamic contact angle analysis system and microbond pull-out tests.

Findings: The results showed that PBO fibers exhibited -10% reduction in tensile strength after the proposed treatment process. The AS fiber surface free energy could be increased from 49.90 mJ/m^2 to 65.42 mJ/m^2 (+31%) and the HM fiber surface free energy could be increased from 46.20 mJ/m^2 to 65.36 mJ/m^2 (+41%). The interfacial shear strength between PBO fiber and the epoxy matrix was improved to 41.6 MPa (+20%) for AS fiber system, and it improved to 40.1 MPa (+23%) for HM fiber system. The composite failure mode also shifted from fiber/matrix interface adhesive failure to partly cohesive failure.

Research limitations/implications: The composite interfacial shear strength was improved through the increased surface free energy of PBO fiber. The more cohesive failure mode allowed more energy to be dissipated during failure.

Originality/value: The proposed electrostatic discharge treatment process could improve the surface characteristics of PBO fiber and the applications in advanced composites.

Keywords: Composites; Surface treatment; Surface free energy; Interfacial shear strength

MATERIALS

1. Introduction

In the continued quest for high performance, high temperature and lightweight materials, the development of poly(1,4-phenylene-cis-benzobisoxazole) or PBO polymeric material has been a significant step [1-5]. The specific tensile stiffness, specific tensile strength, and thermal and environmental stability of PBO fiber surpass those of many other materials.

PBO belongs to the new class of high performance rigid-rod PBZ materials. The rigid rod main chain backbone structure provides excellent chemical resistance and ensures good tensile, impact and tribological properties under a wide range of conditions. The polymer is usually synthesized in strong acids and kept as a highly viscous dope for processing. Fiber spinning is done by a dry-jet wet-spinning technique that warrants a high degree of molecular chain orientation through an elongational flow. After coagulation in a suitable medium, the fiber is dried

and heat-treated to set the structure. Several attempts have been carried out in pushing the mechanical properties towards the theoretical values based on molecular crystal structure [6]. So far, three PBO fiber grades have been available in the literatures, including as-spun (AS), high-modulus (HM), and an experimental grade fiber (HM+) that uses a non-aqueous coagulation method.

PBO fibers provide great potential applications as reinforcement fibers for advanced composites due to the excellent thermal resistance and specific stiffness and strength. However, the interfacial adhesion between reinforcing fiber and polymer matrix in a composite system is a primary factor for the stress transfer from matrix to fiber. Several surface treatment methods have been studied for the modification of fibers or polymers [7-12], including chemical treatment, plasma treatment, electrolytic oxidation, and coupling agents [13-16]. These surface treatment processes might generate chemical wastes that could pollute the environment, or have required a vacuum system that might be expensive to operate. It is therefore required to develop an environment-friendly process that can improve PBO fiber surface characteristics. The lower operation cost can be a plus.

In this paper, the effects of surface treatment on the modification of PBO fiber and its composite materials have been investigated using electrostatic discharge under atmospheric pressure. No chemical discharge was involved. The surface treatment process has been designed to improve fiber/matrix interfacial bonding quality while providing minimum alteration to the bulk characteristics of the reinforcement fiber. Both as-spun (AS) and high-modulus (HM) PBO fibers were surface treated and characterized in this study. The fiber surface morphology was examined by scanning electron microscopy. The corresponding change in fiber tensile strength was measured by MTS tensile testing machine using a cardboard sample frame. The surface free energy was quantified using a dynamic contact angle analysis system. In addition, the interfacial adhesion properties of the PBO fiber reinforced epoxy composites were studied by microbond pull-out tests. In addition, the composite failure mode would be discussed.

2. Experimental

2.1. Materials

The PBO fiber samples were cleaned and dried before being used in the electrostatic discharge treatment study [20]. Both AS and HM PBO fibers were received from Toyobo Co. Ltd, Japan. The basic physical and mechanical properties have been summarized in Table 1. The samples were washed subsequently in tetrahydrofuran, methanol, and distilled water for 12 h at room temperature for each step. The fiber samples were also dried in a vacuum oven at 100˚C for another 12 h.

2.2. Electrostatic discharge treatment

The surface treatment of PBO fiber samples were carried out using SC-PM5 electrostatic discharge system (Sien Chun Electric, Taiwan). Two different operating voltages were studied at room temperature and atmospheric pressure: 5 kV and 10 kV. Much higher voltage would create unstable discharge that resulted sparks and could damage the fiber samples. The distance between the discharge electrode and the samples was about 1.5 cm. The PBO fiber sample was fed through at a linear velocity of 1 m/min while the discharge electrode system was kept stationary.

The actual residence time for the fiber sample in the treatment zone has been estimated in the range of 1-2 sec. The treated sample was then designated as, for example, AS-10kV, indicating that AS PBO fiber has been treated at 10kV in the process. The untreated sample (UT) was also included in the study as control for both the AS or HM fibers.

2.3. Analysis of PBO fibers

The surface morphology of PBO fiber both before and after the electrostatic discharge treatment was examined by scanning electron microscopy. The corresponding tensile strength properties of the fiber samples were analyzed by MTS tensile testing machine at room temperature. Each monofilament sample was mounted across a cardboard sample frame using a room temperature curing adhesive according to ASTM D3379-75 [17]. A gauge length of 10 mm at a crosshead speed of 1 mm/min was used. The tensile strength was then calculated from the ultimate load divided by the cross-sectional area.

The surface free energy of PBO fiber was analyzed from the measured contact angles between each sample and five different liquid contact media, including n-hexadecane, dimethyl sulfoxide (DMSO), ethylene glycol (EG), formamide and water. A Cahn DCA-322 dynamic contact angle analysis system was used at 25˚C. The surface free energy γ was calculated by an extrapolation method [18]. The dispersive component γ^{d} (α^2) was derived from the intercept and the polar component γ^{p} (β^2) was from the slope data.

2.4. Characterization of PBO Composites

The effects of electrostatic discharge modification on the interfacial adhesion properties between PBO fiber and epoxy matrix were studied by microbond pull-out tests [17, 19].

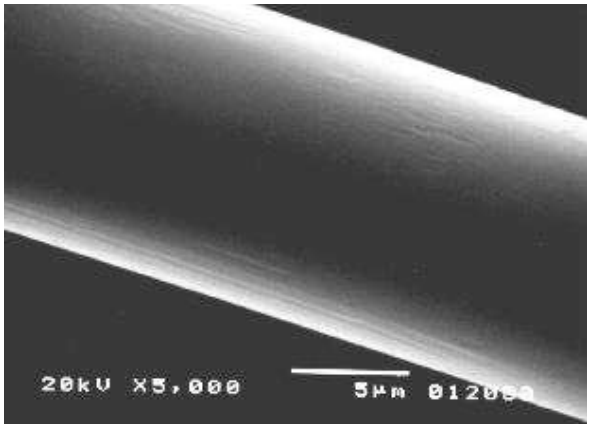


Fig. 1. SEM micrograph of the untreated AS PBO (AS-UT) fiber sample

Table 1.
Physical properties of AS and HM type PBO fibers

Property	PBO - AS	PBO - HM
Filament diameter (μm)	12	12
Filament denier (d)	1.5	1.5
Density (g/cm^3)	1.54	1.56
Tensile strength (GPa)	5.8	5.8
Tensile modulus (GPa)	180	280
Elongation to break (%)	3.5	2.5
Moisture Regain (%)	2.0	0.6
Decomposition temperature (°C)	650	650
Limiting oxygen index (%)	68	68

The Epon 828 type epoxy was premixed with a hardener and delivered to PBO fiber using a syringe. The cured epoxy was then debonded in shear from PBO fiber by the jaws of a microvice. The microbond specimens were pulled by MTS tensile testing machine at room temperature at a crosshead speed of 0.5 mm/min.

The apparent interfacial shear strength (IFSS) was calculated from $\tau = F/\pi$ DL. Here, F is the pull-out load, D is the diameter of the fiber, and L is the embedded length. In addition, some unidirectional PBO fiber reinforced epoxy model composites were prepared from fiber strands. These samples were fractured to reveal the interfacial adhesion bonding quality by the examination using scanning electron microscopy.

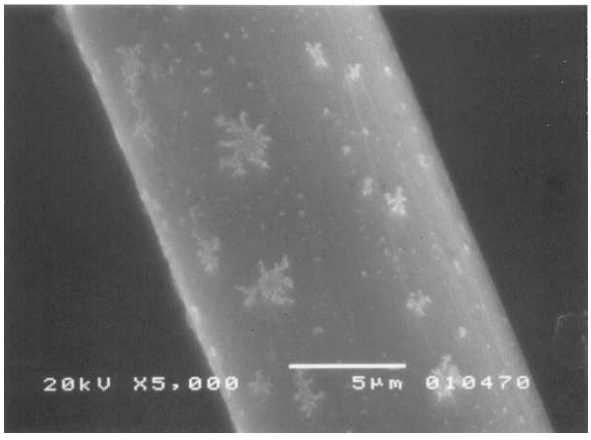
3. Results and discussion

3.1. PBO fibers

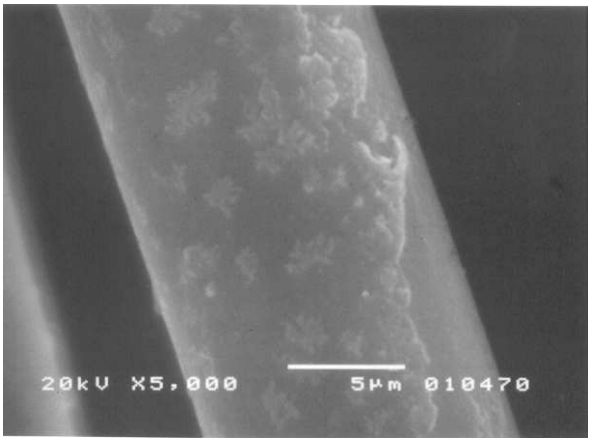
The surface morphology of the untreated and treated PBO fibers has been examined by scanning electron microscopy and the SEM micrographs are shown in Figures 1 and 2, respectively. The untreated fiber has a smooth surface with some streak. The fiber diameter is around 12 μm. The surface of the treated samples displayed some scars from the electrostatic discharge treatment. It seemed that a thin layer of oxidized substance has been deposited on the surface which has gradually driven the original streak less obvious. The surface treatment effects also appeared to be uniform. The degree of surface modification increased with the applied discharge voltage. However, when the applied discharge voltage was above 20 kV, the treatment process could have seriously damaged the fiber structure integrity. Figure 3 shows an example of the damaged area. The treatment operation became unstable and the results were not uniform. High voltage operation should thus be avoided.

The effects of electrostatic discharge treatment process on the tensile strength properties of PBO fibers are shown in Figure 4. Each data entry was the average of more than 50 measurements. There had been some concerns that the electrostatic discharge treatment process introduced surface defects and could seriously reduce the tensile strength. The results showed that the untreated.

AS fiber had a tensile strength of 5.72 GPa while the treated fibers showed an average value of 5.14 GPa. This represented a reduction in strength by -10%. The excellent tensile properties of the PBO fiber was thus pretty much retained. The HM system showed a very much similar level of reduction in its fiber tensile strength. The untreated HM-UT sample had the tensile strength of 5.87 GPa. After the electrostatic discharge treatment, the tensile strength average value became 5.28 GPa for the treated HM systems. Therefore, PBO fibers exhibited limited reduction in their tensile strengths after the suitable electrostatic discharge treatment process.



(a) AS-5kV



(b) AS-10kV

Fig. 2. SEM micrographs of the treated AS PBO samples

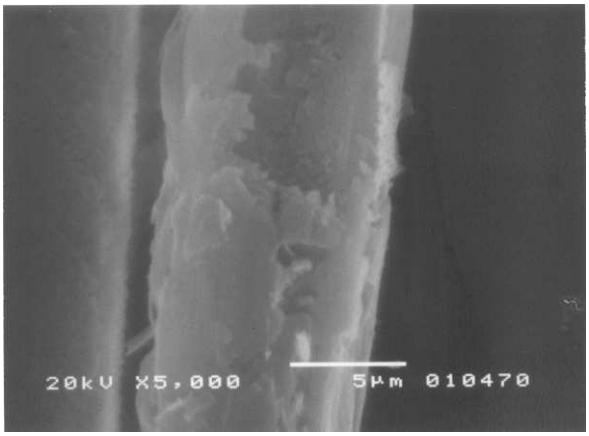


Fig. 3. A damaged area in PBO fiber sample from high discharge voltage

The fiber surface free energy characteristics were also derived using a Cahn dynamic contact angle analysis system. Table 2 shows the measured contact angles of both AS and HM fiber samples with five different contact liquid media under the various treatment conditions. Each data entry was the average of five or more measurements. The untreated AS sample had a higher contact angle of 44.7° with water while the AS-10kV had only 12.8°. In general, the measured contact angles were decreased along the treatment process. This suggested a better wettability for composite processing. In addition, the untreated AH sample showed the highest contact angle of 52.3°, but the AH-10kV had only 13.1°, all with water. The calculated surface free energy components are listed in Table 3. Figure 5 shows the total surface free energy of both AS and HM PBO fibres. The untreated AS-UT sample showed a total surface free energy of 49.9 mJ/m^2 while the value increased with the discharge voltage. The total surface free energy of AS-10kV was improved by +31% to 65.42 mJ/m^2. In addition, the polar components of the surface free energy increased much more than the dispersive components. On the other hand, the untreated HM-UT sample had the lowest total surface free energy of 46.2 mJ/m^2 and would be more difficult to wet. However, after the electrostatic discharge treatment, the total surface free energy of HM-10kV sample was highly increased by +41% to 65.36 mJ/m^2. The improvement was also mainly in the polar component of the surface free energy.

3.2. PBO composites

The effects of electrostatic discharge treatment on PBO fiber reinforced epoxy composites were also studied. The measured apparent interfacial shear strength results of the AS and HM PBO fiber model composites are shown in Figure 6. Each data entry was the average of more than 30 measurements. Shear debonding was observed throughout the examination. The untreated AS-UT PBO system exhibited a lower value of 34.7 MPa. The interfacial shear strength was increased to 39.2 MPa for the AS-5kV sample and 41.6 MPa for the AS-10kV sample. This represented an improvement by +13%~+20%. The trend has been in accordance with the results in fiber surface free energy analysis. For the HM PBO epoxy model composite systems, the interfacial shear strength was the lowest at only 32.5 MPa for the untreated HM-UT sample. After the proposed electrostatic discharge treatment experiment at 5 kV, the HM-5kV sample showed an improvement of +19% in its interfacial shear strength to 38.7 MPa. In addition, the HM-10kV sample showed an improvement of +23% in its interfacial shear strength to 40.1 MPa.

Figure 7 shows SEM micrographs of the fractured surfaces of the untreated AS-UT and treated AS-10kV composites. It was evidenced that the interfacial adhesion bonding quality between the AS PBO fiber and epoxy resin has been significantly improved. Before the treatment, PBO fiber surface was rather clean. There was no or very little epoxy resin adhered to the fiber surface in the fractured composite sample. However, the treated AS fiber system showed significant amount of epoxy resin adhered to PBO fiber surface for the AS-10kV sample.

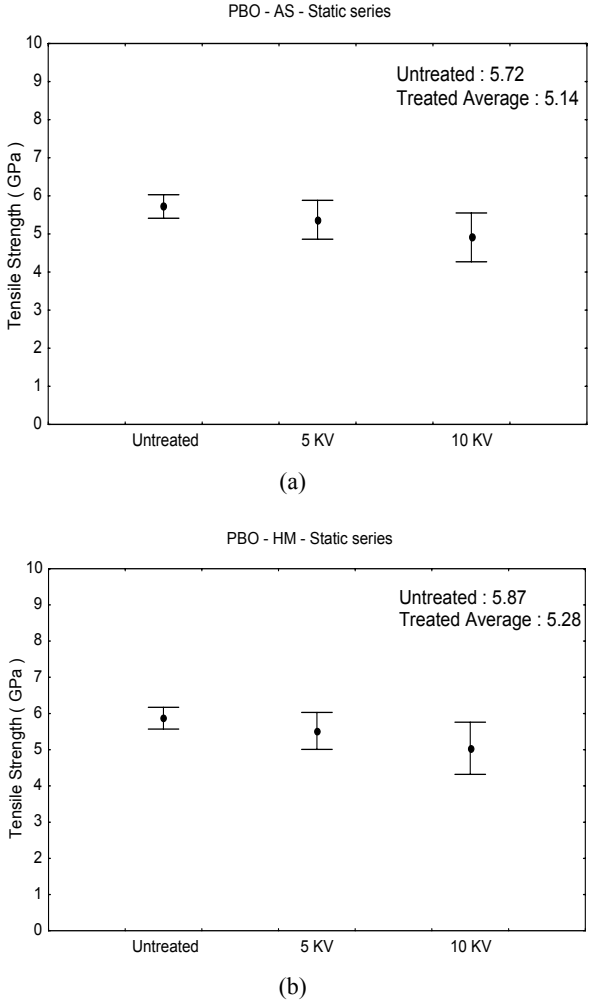


Fig. 4. The effects of electrostatic discharge treatment on the tensile strength of (a) AS and (b) HM PBO fibers

Table 2.
The measured contact angles of PBO fiber samples under the various treatment conditions

Sample	n-Hexadecane	DMSO	EG	Formamide	Water
AS – Untreated	31.5	36.4	37.2	40.6	44.7
AS – 5KV	13.7	15.5	20.8	18.6	23.9
AS – 10KV	9.4	11.2	9.6	10.5	12.8
HM – Untreated	31.3	34.7	36.2	42.8	52.3
HM – 5KV	13.2	19.4	14.9	20.2	28.1
HM – 10KV	9.8	10.7	7.9	12.7	13.1

Table 3.
The calculated surface free energy components for PBO samples

Sample	α	β	γ^d	γ^p	$\gamma=\gamma^d+\gamma^p$
AS-Untreated	4.39	5.53	19.30	30.60	49.90
AS – 5KV	4.61	6.36	21.24	40.41	61.65
AS – 10KV	4.59	6.66	21.09	44.33	65.42
HM - Untreated	4.60	5.00	21.20	25.00	46.20
HM – 5KV	4.66	6.21	21.75	38.60	60.35
HM – 10KV	4.59	6.65	21.07	44.29	65.36

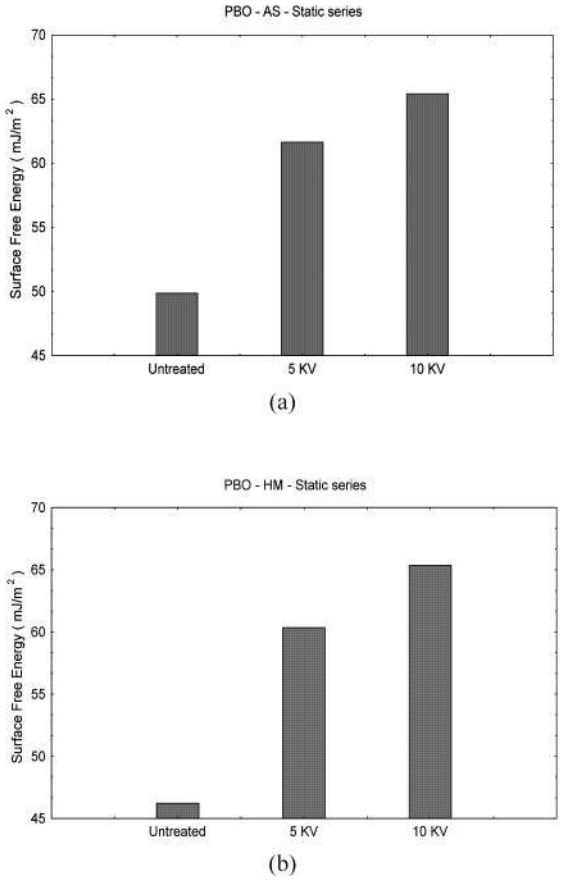


Fig. 5. The surface free energy of (a) AS and (b) HM grade PBO fiber samples

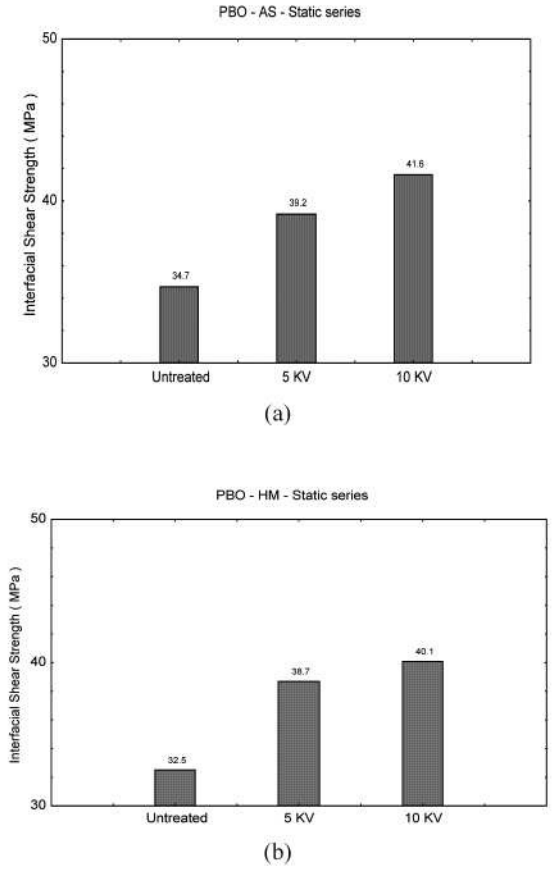
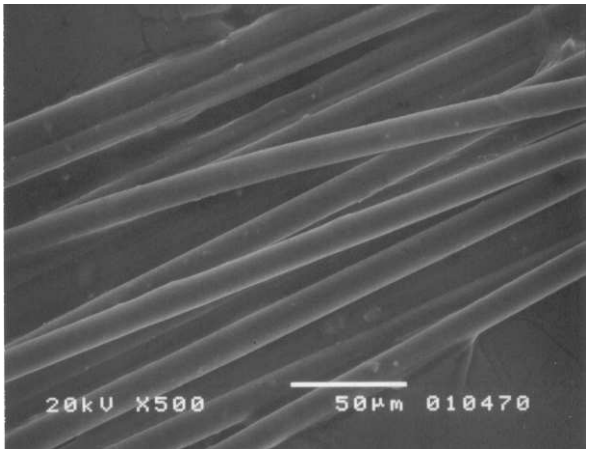
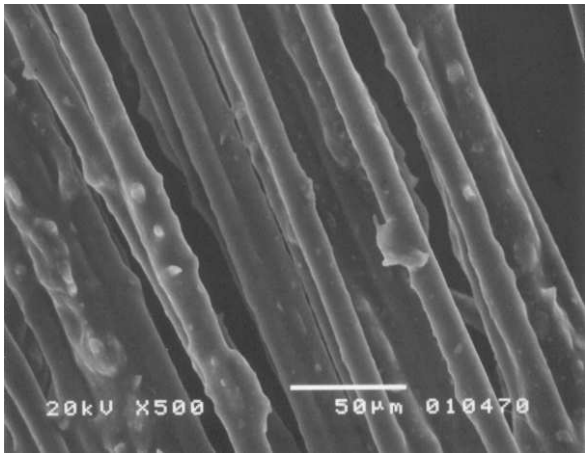


Fig. 6. The apparent interfacial shear strength results of the PBO model composite samples

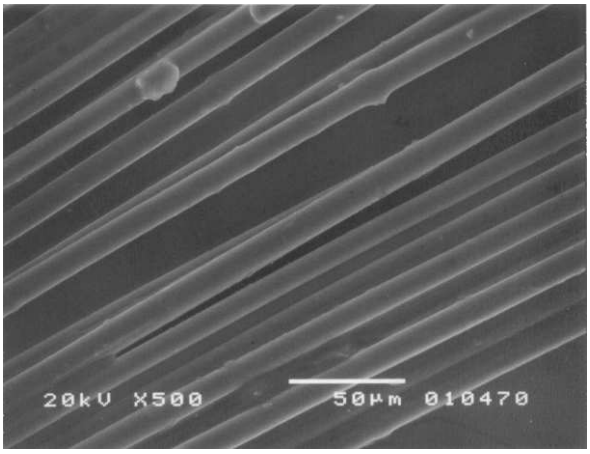


(a) AS-UT

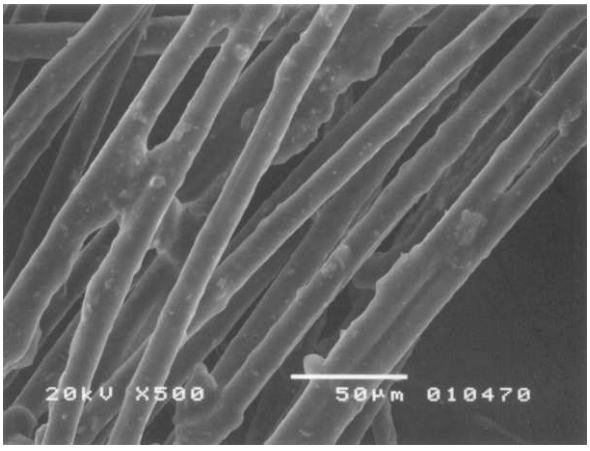


(b) AS-10kV

Fig. 7. SEM micrographs of the fractured surfaces of the (a) untreated AS and (b) treated AS-10kV composites



(a) HM-UT



(b) HM-10kV

Fig. 8. SEM micrographs of the fractured surfaces of the (a) untreated HM and (b) treated HM-10kV composites

Therefore, the failure mode has changed from adhesive failure to partly cohesive failure after the electrostatic discharge treatment.

The HM PBO fiber system exhibited a similar trend. The SEM micrographs of the fractured surfaces of the untreated HM-UT and treated HM-10kV composites are shown in Figure 8.

The failure mode of the composite also changed from adhesive failure to partly cohesive failure after the proposed electrostatic discharge treatment. This explained the modification improvement results in the corresponding apparent interfacial shear strength data in the microbond tests.

4. Conclusions

The effects of electrostatic discharge treatment on PBO fiber and the composites have been investigated. Both AS and HM grade PBO fibers were surface treated and characterized in this study. The SEM results showed that the electrostatic discharge treatment deposited a thin layer of oxidized substance on the fiber surface. The degree of surface modification increased with the applied discharge voltage. However, when the applied discharge voltage was above 20 kV, the treatment process could have seriously damaged the fiber structure integrity.

The treatment operation could become unstable and thus should be avoided. PBO fibers exhibited about 10% reduction in tensile strength after the treatment process. The treated AS fibers still showed an average value of 5.14 GPa and the treated HM showed 5.28 GPa. Therefore, the excellent tensile properties of the PBO fiber was much retained. On the other hand, the decrease in contact angle and the increase in fiber surface free energy could help composite processing and the resulting interfacial shear strength. The untreated AS sample had a higher contact angle of 44.7° with water while the AS-10kV had only 12.8°. This suggested a better wettability for composite processing. In addition, the untreated AH-UT sample showed the highest contact angle of 52.3°, but the AH-10kV had only 13.1° with water.

The AS fiber surface free energy could be increased from 49.90 mJ/m^2 to 65.42 mJ/m^2 and the HM fiber surface free energy could be increased from 46.20 mJ/m^2 to 65.36 mJ/m^2. Shear debonding was observed throughout the examination of the PBO/epoxy model composites.The interfacial shear strength between PBO fiber and the epoxy matrix was improved from 34.7 MPa to 41.6 MPa for the AS fiber system, and it improved from 32.5 MPa to 40.1 MPa for the HM fiber system. In addition, it has been evidenced that the interfacial adhesion bonding quality between the PBO fiber and epoxy resin was significantly improved based on the observation of fractured surface of composites.

The treated fiber system showed significant amount of epoxy resin adhered to PBO fiber surface. The failure mode has thus changed from adhesive failure to partly cohesive failure after the electrostatic discharge treatment. Both PBO fiber systems exhibited the similar trend. This explained the improved results in the corresponding interfacial shear strength in the microbond tests for the model composites.

Acknowledgements

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